

**EFFECTS OF ENCHAINED ESTER
GROUPS ON THE LIVING
CARBOCATIONIC POLYMERIZATION OF
VINYL ETHERS**

WALTER BEAM SHEPHERD Jr.

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ABSTRACT

A series of chloro - substituted 4-(ethenyloxy)butyl benzoate and acetate monomers were polymerized in toluene at -20 and 4° C using an HCl etherate / ethylaluminum dichloride (EtAlCl₂) initiator system in the presence and absence of an externally added esters. The systems were evaluated in accordance with established criteria to determine the degree of “livingness” of each system in the presence and absence of the added ester. The effects of the enchainment of the ester moiety was studied by comparison with the polymerization characteristics of 4-(ethenyloxy)butane in the presence and absence of the externally added ester corresponding to the enchainment of the ester moiety. The effect of the “intramolecular” ester on the living nature of the system was studied and it was determined that the enchainment of the ester moiety is less effective in inducing a living system than the equivalent ester added externally. Further, it was determined that the degree to which an enchainment or externally added ester is able to induce “livingness” in a system is directly proportional to the pK_a of the conjugate carboxylic acid of the ester.

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DECLARATION

I declare that the work contained in this thesis has not been submitted for any other award and that it is all my own work. I also confirm that this work fully acknowledges opinions, ideas and contribution from the work of others.

I declare that the Word Count of this Thesis is 30,355 words.

Name: Walter Beam Shepherd Jr.

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ABBREVIATIONS

BP	Boiling Point
°C	Degrees Centigrade
d	Density
ER	Evaporation Rate
FW	Formula Weight
GC	Gas Chromatography
HPLC	High Pressure Liquid Chromatography
I / [I]	Initiator / Initiator Concentration
IR	Infrared
LPM	Liters Per Minute
M / [M]	Monomer / Monomer Concentration
M _n	Number Average Molecular Weight
M _w	Weight Average Molecular Weight
M _w / M _n	Molecular Weight Distribution
MWD	Molecular Weight Distribution
N _d ²⁰	Refractive Index
NL	Nonlinear
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity Index
pK _a	Ionization Constant
PZN	Polymerization
R _r	Relative Evaporation Rate
RI	Refractive Index
%RSD	Per Cent Relative Standard Deviation
SEC	Size Exclusion Chromatography
STDEV	Standard Deviation
T	Temperature
T _(0.05)	Tailing Factor at 0.05% Peak Height
t	Time
UV	Ultraviolet
VD	Vapor Density
VP	Vapor Pressure

(MONOMERS)

CEVE	2-(ethenyloxy) 2-chloroethane
VOB	4-(ethenyloxy)butane
VOBOAC	4-(ethenyloxy)butyl Acetate
VOBCOAC	4-(ethenyloxy)butyl Chloroacetate
VOBDCOAC	4-(ethenyloxy)butyl Dichloroacetate
VOBTCOAC	4-(ethenyloxy)butyl Trichloroacetate
VOBBZ	4-(ethenyloxy)butyl Benzoate
VOB2CBZ	4-(ethenyloxy)butyl 2-Chlorobenzoate
VOB3CBZ	4-(ethenyloxy)butyl 3-Chlorobenzoate
VOB4CBZ	4-(ethenyloxy)butyl 4-Chlorobenzoate

(ESTERS)

BA	Butyl Acetate
BBZ	Butyl Benzoate
B2CBZ	Butyl 2-Chlorbenzoate
B3CBZ	Butyl 3-Chlorobenzoate
B4CBZ	Butyl 4-Chlorobenzoate
EA	Ethyl Acetate
ECA	Ethyl Chloroacetate
EDCA	Ethyl Dichloroacetate
ETCA	Ethyl Trichloroacetate

(SOLVENTS & REACTANTS)

DCM	Dichloromethane
EADC or EtAlCl ₂	Ethylaluminum Dichloride
DEE or ET ₂ O	Diethyl Ether
HCl	Hydrogen Chloride
HCl-Et ₂ O	Hydrogen Chlorate Etherate
HEX	Hexane

IBVE	iso-Butyl Vinyl ether
THF	Tetrahydrofuran
Tol	Toluene

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CHAPTER 1

INTRODUCTION

1.1. MACROMOLECULAR ENGINEERING

Macromolecular engineering may be defined as the design and synthesis of well defined complex macromolecular architectures (Henderson and Szwarc, 1968). More precisely, macromolecular engineering is the total synthesis of macromolecules, down to their smallest constituents: it embraces the design and control of all molecular parameters including macro- and microarchitecture, molecular weight and molecular weight distribution (Sugihara, et. al., 2010).

The molecular engineer's goal may be oligomers, telechelics, macromonomers, copolymers (of all types) – in short, any and all macromolecular systems and assemblages. The understanding of the structure - properties relationship is critical to the successful application of these engineered structures.

Of particular interest is the application of living carbocationic processes to the synthesis of macromolecular structures with functional groups in the main or pendant chains. The term “functional” in this context refers to any structural moiety capable of reacting chemically or physically to internal or external substances or stimuli.

Chemically reactive functional groups may serve as cross – linking sites or as attachment sites for other functional groups. Some functional groups may also be polymerizable thereby creating macromonomers or telechelic polymers or oligomers if the groups are simply chemically reactive and present on both ends of the polymer chain. Polymeric

materials with functional groups exhibiting electro – optical and / or electro – mechanical properties are of great utility in the development of nonlinear optical fibers, claddings, photonic controls and many other optoelectronic applications.

Living polymerization processes are the key to the synthesis of well defined and complex macromolecular architectures and macromolecular engineering is the key to understanding the relationship between structure and properties. The understanding of the structure – property interrelationship is critical to the successful development of new and novel polymeric materials for new and novel applications.

1.2. LIVING POLYMERIZATION

1.2.1. HISTORICAL

Living polymerizations are generally defined as chain reaction polymerizations which proceed in the absence of the kinetic steps of termination or chain transfer (Quirk and Lee, 1992). Anionic polymerizations in the absence of “chain breaking” reactions were first described by Ziegler and Abkin, et. al.(1936) and Swarc (1956b). Swarc first referred to macromolecules formed in these processes as “living polymers” and anionic polymerizations in the absence of elementary chain breaking reactions such as termination and chain transfer were living polymerizations.

Higashimura and Kishirio (1975) investigated the iodine initiated polymerization of p – methoxystyrene in carbon tetrachloride and dichloromethane, respectively. Higashimura describes the system as “possibly forming living polymers” and in support cited increasing

molecular weight with conversion and continued polymerization with the addition of monomer after the initial monomer charge had been exhausted.

In 1984 Higashimura and Sawamoto described the first living cationic system with the polymerization of isobutyl vinyl ether using an HI / I₂ initiating system (Higashimura, et. al., 1984). Shortly thereafter Faust and Kennedy described a second living system with the polymerization of isobutylene (a monomer that can be polymerized only by a cationic mechanism) by a variety of ester – “Friedel – Crafts acid” combinations (Higashimura, et. al., 1985).

Within the context of the above investigations a Friedel – Crafts acid was defined as a metal halide, organometallic halide or organometal of Lewis acidic nature that in conjunction with cationogens coinstantiate carbocationic polymerizations (Kennedy and Marechal, 1991). Another broader definition (more applicable to polymer oriented systems) is based on the ability of Friedel – Crafts acids, MX_n to coordinate with various conjugate bases, B⁻, such as anions, conjugated bases of Bronsted acids, halogens and metal halides (B⁻ + MX_n ↔ BMX_n⁻). In short, Friedel – Crafts acids are metal halides, organometal halides and organometals capable of coordinatively stabilizing conjugated bases by complexation and thereby increasing the lifetime of associated electrophiles.

Expanding on their original work Higashimura and Aoshima (1986) disclosed the living carbocationic polymerization of vinyl ethers with an organoaluminum halide / ester initiating system. The investigators reported the successful living carbocationic polymerization of vinyl ethers at temperatures as high as + 40° C with M_w / M_n < 1.2 and a linear increase in M_n with monomer conversion.

The field has grown rapidly building on these and other milestones and at the present time there are numerous validated, living anionic, cationic and radical systems (Leasure, J. G., et. al., 2010: Kanazawa, A., Kanaoka, S. and Aoshima, S, 2009: Yonezumi, M., et. al., 2008: Lee, Q, et. al., 2008: Namikoshi, T, Hashimoto, T. and Urushisaki, M., 2007: Il Kim, Yun s., Ha and Chang – Sik Ha, 2004: Bo Jiang, et. al., 2002: Penczek and Kubisa, 1989: Matyjaszewski and Sigwalt, 1987: Kennedy and Ivan, 1991: Matyjaszewski, et. al., 2007: Hsien and Quirk, 1996: Jagur and Grodzinski, 2005).

1.2.2. LIVING CARBOCATIONIC POLYMERIZATION

In the strictest sense a living polymerization is a chain growth polymerization in which propagation proceeds with the total consumption of the monomer in the absence of irreversible chain transfer, termination, isomerization or other chain stopping reactions. Obviously, living carbocationic polymerizations are living polymerizations in which the propagating species is a carbocation, i. e., a carbenium ion (an sp^2 hybridized carbon with a formal positive charge on the trivalent carbon).

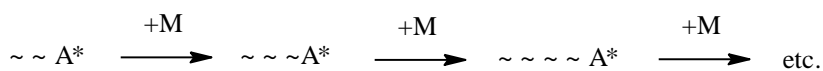
By this definition two types of living carbocationic polymerizations have been defined (Henderson and Szwarc, 1968, Sugihara, et. al., 2010, Kennedy and Ivan, 1991, Matyjaszewski, et. al. 2007, Quirk and Lee, 1992, Flory, 1953, Hsien aand Quirk, 1996,Jagur and Grodzinski, 2005a, Szwarc and Beylen, 1993):

1. Ideal living polymerizations in which chain transfer and termination are absent; the rates of chain transfer and termination reactions are zero, i.e., $R_{tr} = R_t = 0$

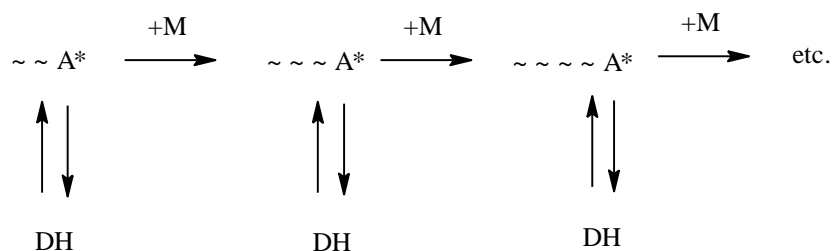
2. Controlled (Matyjaszewski, 2007) or quasi – living (Kennedy and Ivan, 1991) polymerizations in which rapidly reversible chain transfer and / or termination are present and the rate of these processes is faster than that of propagation (see section 1.2.3).

These two cases are depicted graphically in scheme 1-1 where A* is an active growing (living) species, DH is a dormant species arising from chain transfer or termination and M is the monomer.

Ideal Living Polymerizations



Systems with Reversible Transfer and / or Termination

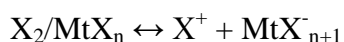
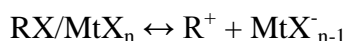
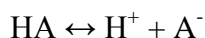


Scheme 1-1 - Ideal versus controlled / quasi living systems

In the above representation the equilibrium rate between A* (active) and DH (dormant) is rapid (or competitive) relative to that of propagation.

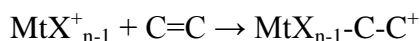
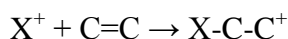
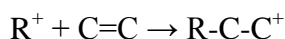
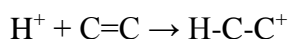
In living or controlled / quasi – living carbocationic polymerizations, the judicious selection of the initiating system is arguably the prime factor (Kennedy and Ivan, 1991). The initiation process may be broken down into two fundamentally distinct events, i.e., ion generation and cationation (formation of the carbocation).

Ion generation is by far the more involved of the two events and is favored by a polar system due to the fact that it generally involves the creation of a charged species from a neutral species. There are a number of mechanisms identified in the ionization process which include the ionization of a simple protonic acid to a proton and counteranion in a polar nonnucleophilic media, ionization and dissociation of a Bronsted acid / Friedel – Crafts acid combination or halogen / Friedel – Crafts acid or self - ionization of a Friedel – Crafts acid all of which may be represented schematically as follows (Kennedy and Marechal, 1991):



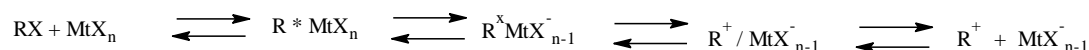
The polar constituent, in most systems, is the solvent or in some instances a polar monomer (self salvation). There are also a number of systems where polar materials such as salts ($ZnCl_2$, ZnI_2 , etc.) are added to increase the polarity of the reaction mixture. Solvation is clearly the driving force in the formation of the initiating ion pair (Higashimura, et. al., 1998).

Following ion generation, the initiation process is completed by the formation of an active species capable of adding monomer, i.e., cationation forming the reactive carbocation. Depending on the nature of the initiator used cationation may involve a proton, carbenium ion, halonium ion or electrophilic Friedel – Crafts acid fragments and may be represented schematically as follows (Kennedy and Marechal, 1991):



Unlike ion generation, cationation and subsequently propagation, are favored by a nonpolar media. Desolvation is the driving force in cationation and depending on whether ion generation or cationation is the rate determining event, the polarity of the media in a specific system may accelerate or decelerate initiation. Scheme 1-2 is a graphic representation of the initiation process the graphic summation of which has been referred to as the Weinstein spectrum of ionicities (Takeuchi, et. al., 1989).

ION GENERATION



CATIONATION

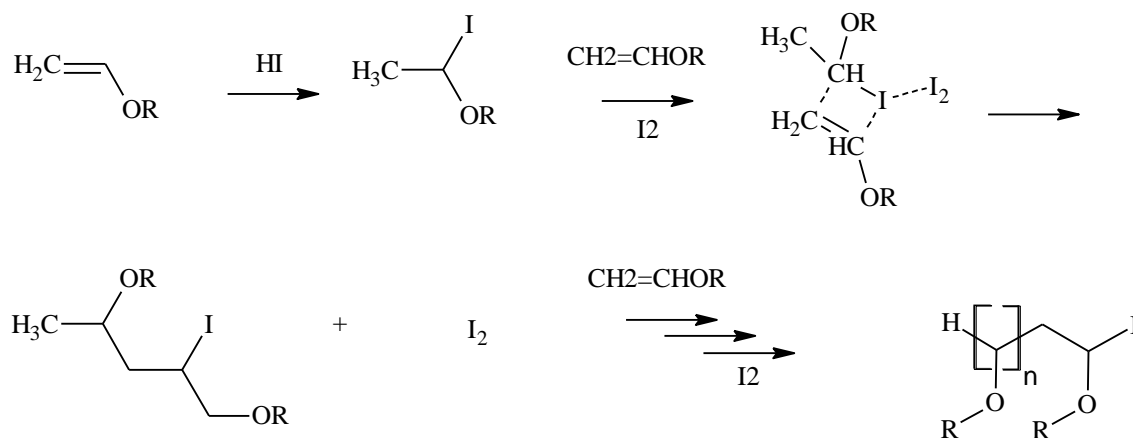


Scheme 1.2 - Schematic representation of initiation process

The entire spectrum of ionicities may be involved in ion generation. In scheme 1.2, RX^*MtX_n is a largely covalent complex, $\text{R}^+\text{MtX}_{n-1}^-$ a contact (tight) ion pair, $\text{R}^+ / \text{MtX}_{n-1}^-$ a solvent separated ion pair and $\text{R}^+ + \text{MtX}_{n-1}^-$ are solvated free ions.

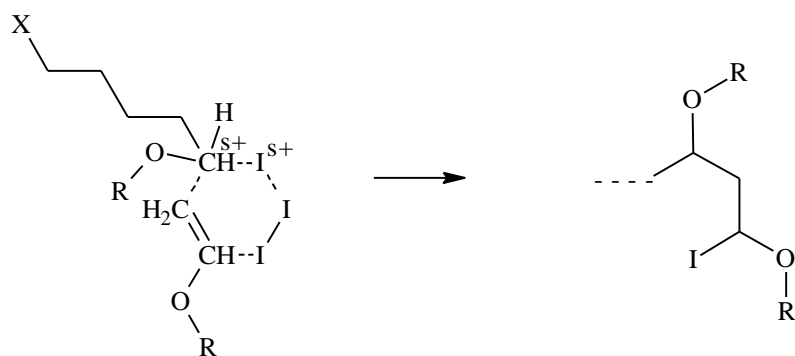
Both the carbocation and the propagating species generated by the reaction of the carbocation with the monomer are inherently unstable in the required acidic system and readily undergo chain transfer, termination, isomerization and other undesirable chain stopping reactions. It is therefore a necessary requirement of living carbocationic systems that the propagating carbocation be stabilized.

Two generalized methods for the stabilization of propagating carbocations in living systems have been proposed (Collins, et. al., 1973, Goethals, et. al., 1990) both of which are based on the concept of nucleophilic stabilization of the propagating carbocation. The stabilization may be achieved “internally” with strongly nucleophilic counter – ions and weak Lewis bases or “externally” with a weakly nucleophilic counter – anion and strong Lewis acid in the presence of a weak Lewis base (typically an ether, ester or amine). The polymerization of vinyl ethers by the HI / I₂ initiator system is an example of the internal system. It was proposed (Heroguez, et. al., 1990, Kennedy and Ivan, 1991, Cho and McGrath, 1988, Szwarc and Beylen, 1993) that the addition of the iodine actually “activates” the C-I bond of the covalent iodine adduct forming a “stretched polarized covalent bond” which facilitates the insertion of monomer into the C-I bond as depicted in scheme 1-3.



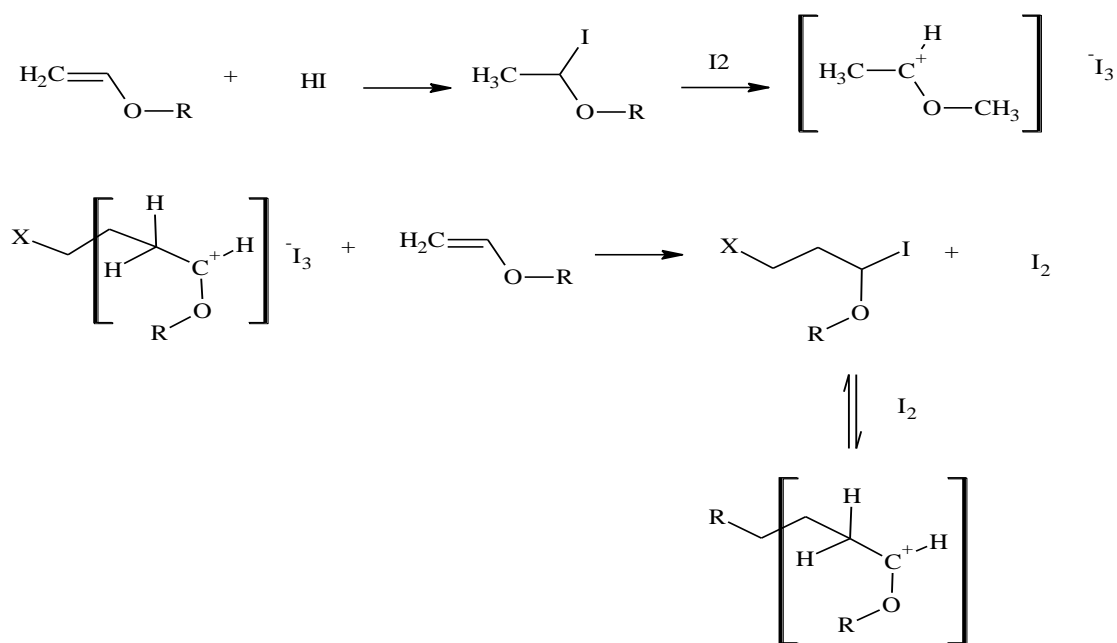
Scheme 1-3. Activation of C-I bond by iodine (I₂)

Matyjaszewski (1996) has suggested that the propagating species proposed by Collins (1973) and Goethals (1990) is better represented by a six membered ring / transition state (scheme 1-4). Higashimura, et. al. (1988) later proposed that in the HI / I₂ initiated polymerization of vinyl ethers the “livingness” of the polymerization is attributable to the stabilization of the carbocation by the I ---- δ⁻I₂ counter anion.



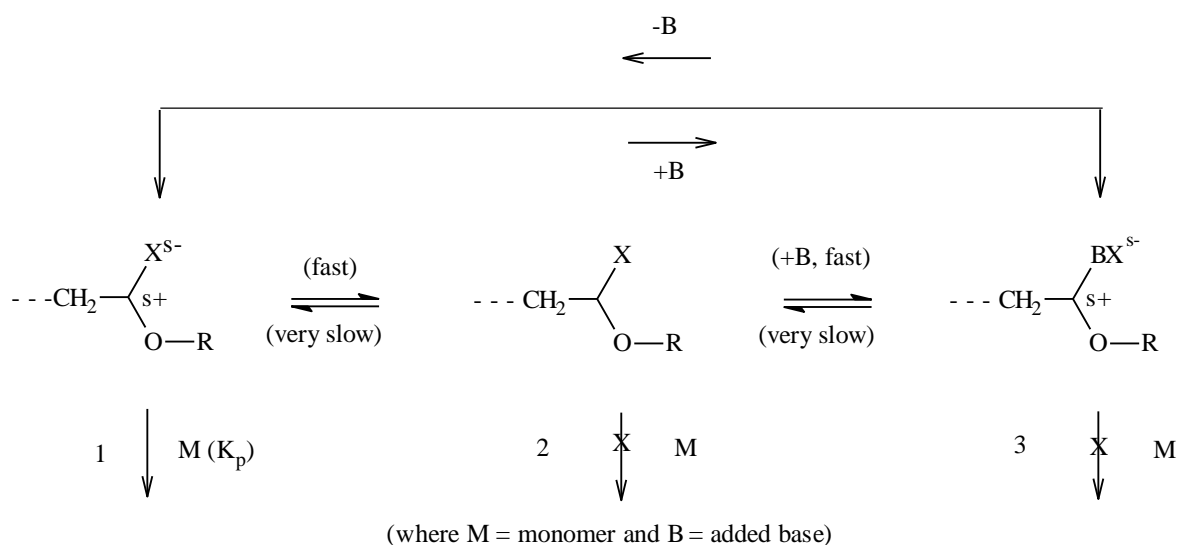
Scheme 1-4. Proposed six membered transition state of - propagating species

Current research suggests that the initiation is a two step process in which the HI rapidly adds to the vinyl ether forming a covalent iodine adduct, $\text{CH}_3 - \text{CH}(\text{OR}) - \text{I}$, which by itself is incapable of initiating polymerization, but in combination with I_2 forms an ion pair which actually initiates polymerization. The propagating species in this case is a carbenium ion which is stabilized by the equilibrium established between the active ionic species and the covalent iodine adduct. This is graphically depicted in scheme 1-5 where the equilibrium between the covalent iodine adduct and the ion pair is rapid and reversible.



Scheme 1-5. Stabilization of propagating carbocation

In the external system the coinitiator is a strong Lewis acid such as ethylaluminum dichloride (EtAlCl_2) which generates a weakly nucleophilic counter anion in combination with the initiator. Reaction of the initiator with the monomer generates the propagating carbenium ion which is inherently unstable forming an inactive covalent species by collapse of the ion pair or abstraction of a β – hydrogen. The addition of a weak base (usually an ester, ether or amine) stabilizes the propagating carbocation by the fast conversion of the covalent species into onium ions which, in turn are rapidly converted into carbenium ions as depicted in scheme 1-6.



Scheme 1-6. Equilibrium between carbenium and onium ions

In the above schematic representation (1) is the actual growing species, (2) is the inactive covalent species and (3) is the non – propagating onium ion.

The equilibrium between the carbenium and onium ions and the covalently species and onium ionions are responsible for the stabilization of the propagating species. The conversion of the inactive covalent species into the active carbenium ion in effect reinitiates or reactivates the propagating carbenium ion.

1.2.3. LIVING VERSUS CONTROLLED SYSTEMS

As stated earlier (section 1.2.1) living polymerizations are chain reaction polymerizations which proceed in the absence of the kinetic steps of termination or chain transfer (Szwarc, et. al., 1956a & b). In such an “ideal system” only growing chains add monomer and these “active species” do not participate in transfer or termination reactions. Further, in such systems the growing chain must remain active indefinitely, i.e., remain reactive over the time interval spanning the laboratory experiment (Quirk and Lee, 1992). The classification of a polymerization as a living system is based on the experimental analysis of the system in accordance with a set of diagnostic criteria (see section 1.2.4).

In a truly living system, transfer and termination do not occur or cannot be detected under specified reaction conditions using currently available instrumentation. In real systems transfer and termination reactions may occur but their contribution is sufficiently reduced by the proper choice of reaction conditions that it is possible to synthesize polymers with predetermined molecular weights, narrow molecular weight distributions, controlled functionality and to prepare block copolymers by sequential monomer addition. Systems of this nature are defined as controlled (Matyjaszewski and Sigwalt, 1987) or quasiliving (Kennedy and Ivan, 1991) and for the purpose of this discussion systems of this nature will be referred to as controlled. The characteristics and properties of living versus controlled polymerization has been investigated by Kennedy and Ivan (1991) and Matyjaszewski, et. al. (2007) and are briefly compared / summarized in table 1-1 and 1-2, respectively.

Table 1-1. Classification of living (L), quasi - living (QL), and non - living (TR & T) carbocationic polymerization systems.

Mechanism symbol	Decisive mechanistic step		[R*]	DP versus [M]	M _w / M _n
	Termination	Transfer			
Living & quasi - living systems					
L(OO)	O	O	Constant	Linear increase	~ 1
Q(RO)	R	O	Constant	Linear increase	~ 1 or > 1
Q(OR)	R	O	Constant	~X / 2 increase	> 1
Q(RR)	R	R	Constant	~X / 2 increase	> 1
Non - living systems					
TR(OI)	O	1	Increases	Approaches a limit	> 1
TR(RI)	R	1	Increases	Approaches a limit	> 1
T(IO)	1	O	Decreases	Approaches a limit	2
T(IR)	1	R	Decreases	Approaches a limit	> 2
T(II)	1	1	Decreases	Approaches a limit	> 2

O = absent, R = reversible, 1 = present / irreversible

Both living and controlled systems will produce well defined polymers only if:

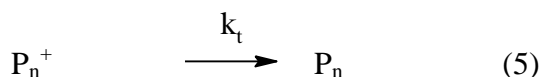
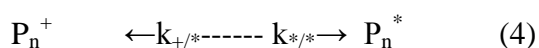
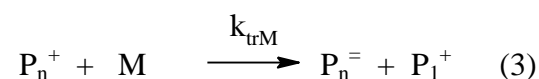
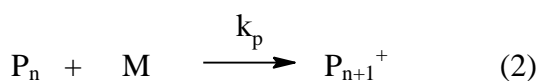
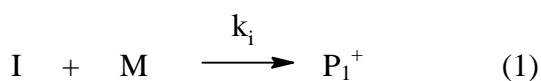
1. Initiation is faster than propagation.
2. The exchange between species of different reactivities is faster than propagation.
3. The rate of depropagation is substantially lower than propagation.
4. The system is homogeneous and mixing is sufficiently fast (Matyjaszewski and Sigwalt, 1987).

	RATE	MW	MWD
Slow initiation	slower than ILS (but with acceleration)	initially higher (but approaches ILS)	< 1.35
termination	slower than ILS (with deceleration)	no effect (limited conversion)	broader than ILS
transfer	no effect	lower than ILS	broader than ILS
slow exchange	no effect	may be lower than ILS	may be very broad or bimodal

Table 1.2: Effect of initiation, termination, transfer and exchange constants on kinetics, molecular weights and polydispersities compared to an ideal Living system (ILS)

A generalized kinetic scheme for both living and controlled polymerization is shown below (scheme 1-7). The initiator I, reacts with monomer M to produce the active / growing species P_1^+ in the initiation reaction (1). The active / growing species propagates as shown in reaction (2) and may also react with monomer to form a new active / growing species constituting a transfer to monomer reaction (3). Spontaneous transfer, often induced by the counterion may also take place and if the new species has a reactivity greater than or equal to the growing species then no kinetic effect will be observed. In some cases the growing species P^+ may be in equilibrium with an active / growing species P^* having a different reactivity (4). The growing species may be terminated through spontaneous uni- or bimolecular reaction or by reaction with a terminating species (5).

The simplest system that produces both living and controlled polymerization consists of only reactions (1) and (2) but well defined polymers can be obtained if the contribution of reactions (3) and (5) are small and the degree of polymerization is limited.



Scheme 1-7
Kinetic scheme for chain polymerization

Slow initiation may take place in a living system in which case the polydispersity will increase and the observed molecular weight, M_n will be higher than the theoretical M_n

(calculated as $DP = [M]/[I]$). The presence of multiple growing species of differing reactivities and lifetimes may also occur resulting in polymers with broad or even bimodal molecular weight distributions. In this case, if the exchange rate of reaction (4) is sufficiently fast a Poisson distribution may still be observed.

1.2.4. DIAGNOSTIC CRITERIA

A number of investigators have proposed diagnostic criteria for the classification of polymeric system as living, controlled or quasi – living and conventional in nature (Swarc, M. and Van Beylen, M., 1987, Kennedy, J., P. and Ivan, B., 1991 Quirk, R. and Lee, B. 1992, Matyjaszewski, K. and Sawamoto, M., 1996). The experimental criteria proposed by Quirk and Lee, 1992 are arguably the most rigid and to some degree discredit the concept of controlled or quasi – living systems in favor of “living polymerizations with reversible termination” and “living polymerizations with reversible chain transfer” to describe polymerizations which proceed in the absence of the kinetic steps of irreversible termination and irreversible chain transfer, respectively. For other systems which exhibit some of the characteristics of living systems Quirk and Lee suggest describing them as “systems possessing characteristics of living polymerizations”.

Arguments for and against the various descriptive terminology notwithstanding, the term “living” will be used to describe ideal living systems and “controlled” will be used to describe non – ideal living systems (Kennedy, J., P. and Ivan, B., 1991, Matyjaszewski, K. and Sawamoto, M., 1996). The terms “controlled and quasi – living” are adequately defined by the respective investigators and will be used for this study (with controlled being used for both controlled and quasi – living).

The following diagnostic criteria are a compilation of the criteria proposed by the above investigators and were, in part, be used to evaluate and classify the polymerization systems of the this study.

Criterion 1.

Polymerization proceeds until all the monomer has been consumed. Further addition of monomer results in continued polymerization.

This criterion is in fact the basis of the description / definition of a living polymerization (Szwarc, 1956a & b, Penczek and Kubisa, 1989). If a system is indeed a living system, then all of the propagating chains must remain active during the time scale of the laboratory experiment (Quirk and Lee, 1992). Even though the complete consumption of the monomer alone is not a useful diagnostic criterion, the continuation of polymerization with the addition of monomer is an important characteristic of a living system. The practical experimental verification of this criterion requires that the molecular weight and molecular weight distribution be determined before and after the second monomer addition. Further, the second addition of monomer should be sufficient to increase the molecular weight, M_n of the final polymer above that of the original or initial polymer. If the system is truly living then the M_n of all the polymer chains will increase and a single SEC peak at the higher M_n should be observed. Also, in an ideal living system the M_w / M_n should not increase with monomer addition. This is a useful and rigorous criterion if used correctly.

Criterion 2.

The number average molecular weight, M_n (or X_n , the number average degree of polymerization), is a linear function of conversion.

The expected number average molecular weight can be calculated as shown in (1):

$$DP_n = [M_{con}] / [R^*] = (W_p / [M_n]) / [I_0] \quad (1)$$

where $[M_{con}]$ is the concentration of monomer consumed, $[I_0]$ is the initiator concentration, $[R^*]$ is the number of propagating sites, W_p is the weight of polymer formed and M_n is the number average molecular weight. Equation (1) predicts a linear increase in M_n (or X_n , the number average degree of polymerization) for a living system. Quirk (1991), Szwarc and Beylen (1993), Penczek, et al (1991) and Sawamoto, et. al. (1987) maintain that this is not a rigorous criterion since it is not sensitive to termination reactions. If termination occurs in the absence of transfer, the number of chains will remain constant and equation (1) will still apply.

The limitations of this criterion have been demonstrate by a number of investigators (Quirk, R and Lee, B. 1991, Penczek et. al, 1991) in experiments where known amounts (5%) of the growing chains were deliberately terminated prior to each of a series of incremental monomer additions. A plot of the resulting M_n versus conversion did show small peaks for the terminated chains with each monomer addition and the observed M_n was slightly above the theoretical or calculated value but the plot remained linear even when 15 – 20% of the growing chains had been terminated prior to the incremental monomer additions. This type of plot will detect chain transfer reactions but it is not sensitive to termination reactions and is therefore not a rigorous criterion for the identification of living systems. Even in the presence of significant termination a linear plot will always be obtained as long as there is no chain transfer.

Criterion 3.

The number of polymer molecules (and active centers) is a constant and is independent of conversion.

Criterion 3 again, is not a rigorous criterion since it is not sensitive to chain transfer reactions as is criterion 2 with respect to chain termination. In this case the plot of M_n versus conversion will remain linear in the absence of termination and the observed increase in the M_n will be below the theoretical or calculated value. Both criteria 2 and 3 may be regarded as necessary but not sufficient unless used in conjunction with more definitive criteria.

Criterion 4.

The molecular weight can be controlled by the stoichiometry of the reaction.

In living systems M_n is a function of the degree of conversion and the stoichiometry of the reaction as described in equation (1):

$$DP_n = [M_{con}] / [I_o] = ([W_p] / M_n) / [I_o]$$

where DP_n is the number average degree of polymerization, $[M_{con}]$ is the concentration of monomer consumed, $[I_o]$ is the initiator concentration, $[W_p]$ is the weight of polymer formed and M_n is the number average molecular weight.

Obviously, this criterion depends on the quantitative utilization of the initiator before all of the monomer has been consumed. This criterion is therefore sensitive to impurities in the system which would change the effective number of moles of initiator and, subsequently the number of active chain ends and polymer molecules.

Quirk and Lee (1992) demonstrated the lack of sensitivity of criterion 3 and 4 to termination and chain transfer, respectively and it was noted that the observed M_n values

compare well with the theoretical or calculated value even when there is significant termination and chain transfer. This being the case it is again obvious that a system in which there is significant termination and chain transfer, i. e., a conventional system may exhibit a M_n close to the theoretical or calculated value based on equation (1) and may also show a linear increase in M_n with conversion. Further, the utilization of the experimentally observed M_n as a rigorous criterion is limited by the error limits of this value.

Criterion 5.

Narrow molecular weight distribution polymers are produced.

The requirements for the formation of a polymer with a Poisson molecular weight distribution ($M_w / M_n \leq 1.1$) in living systems as delineated by Flory (1953) and Szwarc (1993) are as follows:

1. Each polymer molecule must proceed exclusively by consecutive monomer addition to an active terminal group.
2. All active termini must be equally reactive to monomer addition over the entire “life” of the polymerization reaction.
3. All active centers must be introduced at the onset of the polymerization (simultaneous initiation).
4. Termination, transfer and / or interchange reactions must be absent.
5. Propagation must be irreversible.

Matyjaszewski and Sawamoto (1996) have postulated that living polymerizations may lead to well defined polymers with narrow molecular weight distributions and predetermined molecular weights only if:

1. Initiation is faster than propagation.
2. The exchange between species of different reactivities is faster than propagation.
3. The rate of depropagation is substantially lower than propagation.
4. The system is homogeneous and mixing is sufficiently fast.

The authors further state that if these criteria are not met a living polymerization may produce polymers with very broad polydispersities and degrees of polymerization much higher than the $\Delta[M]/[I]_0$ ratio and that these prerequisites must be fulfilled controlled polymerizations as well.

In general it is possible to produce polymers with a narrow molecular weight distribution if the rate of initiation is competitive with propagation rate (requirement 3) which insures that all chains will have the same total reaction time (requirement 1). If initiation is slow relative to propagation the polydispersity of the polymer will broaden.

The presence of more than one type of active center in the polymerization will also broaden the polydispersity due to the fact that the propagation rates of the respective reactive termini may differ (requirement 2). Living polymerizations involving more than one type of active center are commonly encountered in ionic polymerizations where covalent species, contact ion pairs, solvent separated ion pairs and free ions can all be

involved, i. e., the Winstein spectrum of ionicities (Weinstein and Robinson, 1958) (scheme 1-2).

Narrow molecular weight distributions in a living polymerization are not attainable if propagation is not irreversible (requirement 5). This is often encountered in living polymerizations where the monomer has a ceiling temperature at or below the polymerization reaction temperature. In such cases the polydispersity of the polymer increases with time.

The relationship between the polydispersity and the degree of polymerization (X_n) is shown is given in equation (3):

$$X_w / X_n = 1 + [X_w / (X_n + 1)]^2 \approx 1 + [1 / X_n] \quad (3)$$

From the above it is seen that as the molecular weight increase, the polydispersity normally decreases for a given polymerization system (Flory, 1953, Henderson and Szwarc, 1968).

Care must also be taken in evaluating the relevance the polydispersity of a polymer sample. In many cases it is possible to prepare bimodal or even trimodal polymers with narrow molecular weight distributions. For example, a 50 /50 (wt. / wt.) mixture of two monodisperse polymers of molecular weights of 50,000 and 100,000, respectively, would have a polydispersity of 1.13 (which would normally be considered narrow). Further, a narrow molecular weight distribution should not *per se* be used as a criterion for living polymerizations.

Criterion 6.

Block copolymers can be prepared by sequential monomer addition.

In living systems and in the absence of termination and chain transfer this criterion is useful as one of several criteria required for the verification of the living nature of a polymerization system and is subject to the same caveats as requirement 1. Following the polymerization of the base monomer the comonomer should be added at a concentration suitable to separate the copolymer (second) peak from the base (first) peak. The absence of a peak corresponding to the base peak is an indication of the absence of termination or chain transfer. This criterion is sensitive to these reactions and it is useful as one of several criteria required for the verification of the living nature of a polymerization system.

Criterion 7.

Chain – end functionalized polymers can be produced quantitatively.

As a diagnostic test this criterion is severely limited due to the fact that most functionalization reactions are not quantitative. Further, analytical methods for the analysis of the functional groups are subject to experimental error and the sensitivity of the analytical methods decreases with increasing molecular weight.

CHAPTER 2

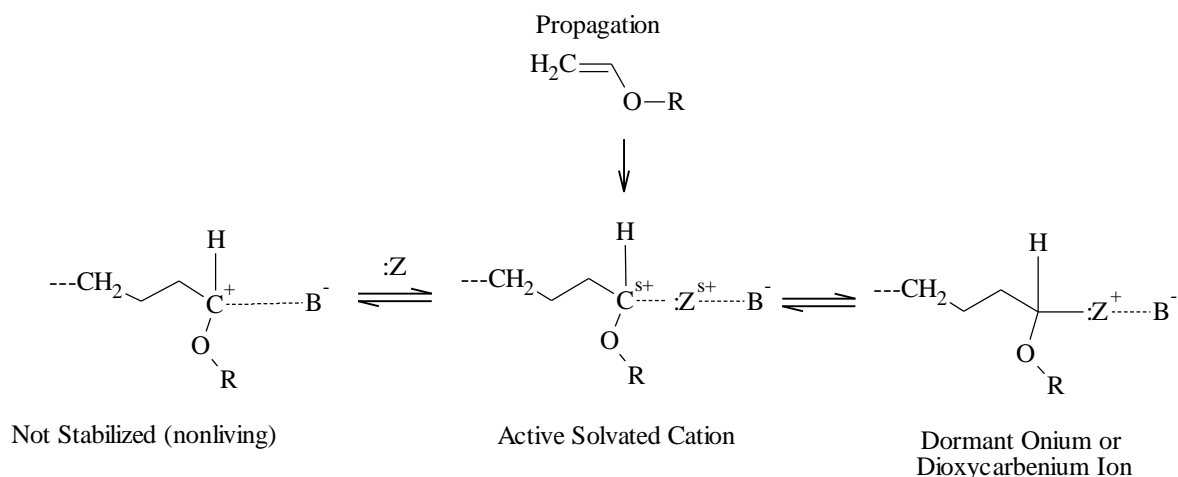
PROJECT AIMS and OBJECTIVES

2.1 PROJECT BACKGROUND

A review of a number of papers (Sugihara et al., 2010; Aoshima and Higashimura, 1986 and 1989; Aoshima et al., 1991a and 1991b; Shohi et al., 1989) on the living carbocationic polymerization of vinyl ethers in the presence of an added ester (Lewis base) prompted the current investigation.

The basic question derived from the first of these papers (Aoshima and Higashimura, 1986) and the subject of the current investigation was whether or not an ester (Lewis base) group enchain in the pendant chain of the vinyl ether (monomer) functions in the same capacity and to the same extent as the same ester group added externally to the polymerization system.

The role of the added ester in moderating or controlling carbocationic polymerizations is not fully understood (Sawamoto and Higashimura, 1990; Kojima et al., 1990; Kaszas et al., 1991). It has been proposed that the ester may stabilize the growing carbocation by a weakly solvating action (Higashimura et al., 1988). It has also been proposed that the added base forms a reversible onium ion with the growing carbocation which acts as a dormant species (scheme 2.1 - 1). Yet another proposal suggests that the ester destabilizes complex counteranions to promote the conversion of the growing carbocation to a covalent species more rapidly (Sawamoto and Higashimura, 1990).



Scheme 2.1.1: Proposed mechanism of formation of active and dormant species by interaction of carbocation and counteranion with added base.

Aoshima & Higashimura (1986) first polymerized 2-(ethenyloxy)ethyl benzoate (a vinyl ether with an ester group in the pendant chain) in a controlled system with EtAlCl_2 at -20°C in toluene (with adventitious water as the initiator). The investigators classified the system as quasi –living (controlled) based solely on the fact that the molecular weight distribution (MWD) was $< \sim 1.2$ and that the molecular weight seemed to increased linearly with conversion. The molecular weight of the polymer was considerably higher than the value predicted from the ratio of the monomer to initiator ($[\text{M}]_0 / [\text{I}]_0$). Due to the fact that no cationogen was employed the precise $[\text{M}]_0 / [\text{I}]_0$ was unknown. Further, no monomer addition experiments were conducted to confirm whether or not the system was actually living, controlled or conventional in nature.

In a later, related paper Aoshima, Kobayashi, et. al. (1991b), studied the effects of ‘externally’ added esters (benzoates and p – substituted benzoates) on the living polymerization of isobutyl vinyl ether (IBVE) with an IBVE acetate / EtAlCl_2 initiator system at $+40^\circ\text{C}$ in hexane. The p – substituted benzoates were used to study the effects of the ester basicity and a second series of experiments using aliphatic carboxylic acid methyl ester were used to study the effects of ‘steric environment’ surrounding the

carbonyl group. It was found that the polymerization rate increases with decreasing ester basicity and it was noted that the polymerization rate increased with increasing bulkiness (steric hinderance) of the carbonyl group.

Although there has been a considerable amount of research on the effects of externally added esters (and other Lewis bases) on living polymerizations with various metal halides the basic question posed above remains unanswered. This project will attempt to provide a definitive answer to this question.

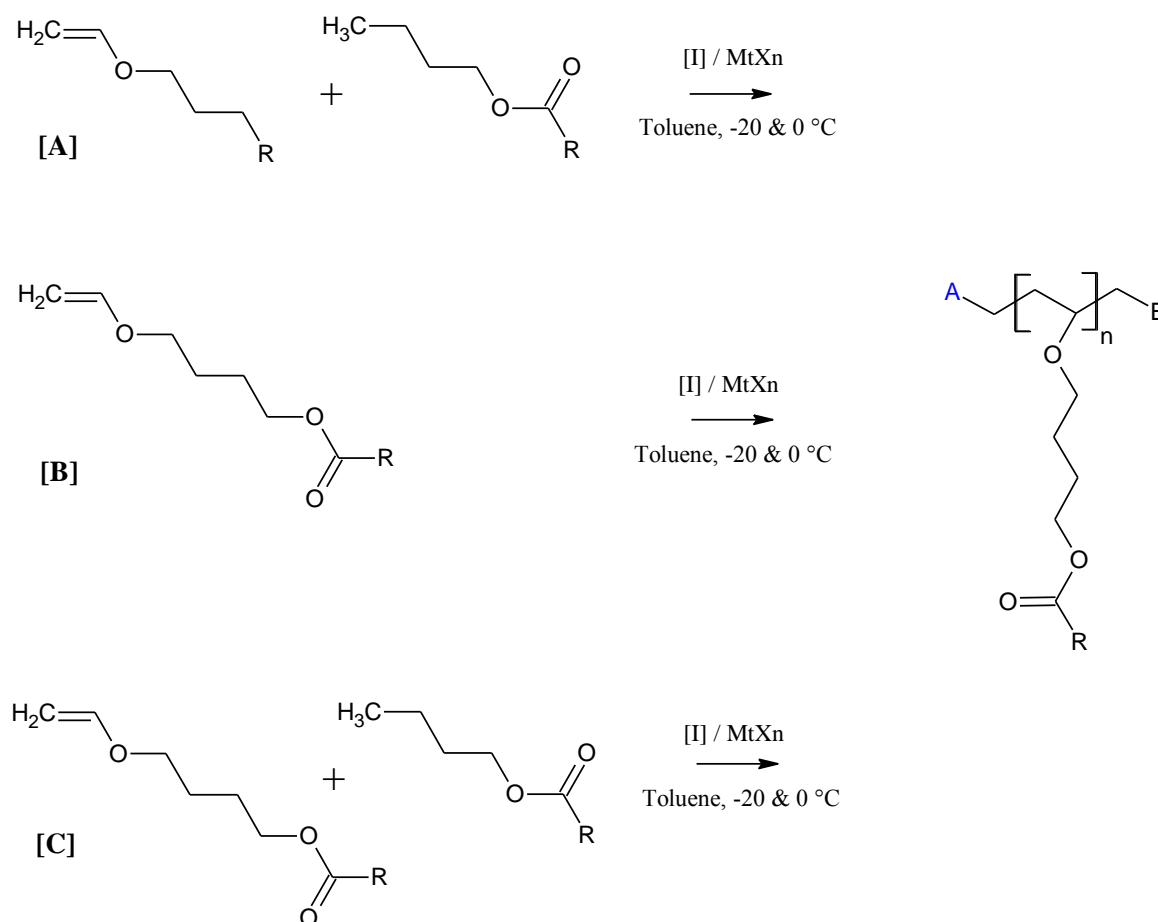
2.2 PROJECT DESCRIPTION

4-(ethenyloxy)butane was polymerized in toluene at -20 and 4° C using a cationogen / metal halide initiating system in the absence of an externally added ester (Lewis base) and then in the presence of a series of butyl acetate and benzoate esters (scheme 2.2.1, A). The data from the polymerizations was used to classify the systems as living, controlled / quasi – living or conventional based on the established diagnostic criteria (section 1.2.4).

4-(ethenyloxy)butyl monomers with acetate and benzoate moieties in the C1 position of the butyl side chain (scheme 2.2.1, B) were then polymerized in toluene at -20 and 4° C in the absence of an externally added ester using the same initiator system. The data from the polymerizations was again used to classify the systems as living, controlled / quasi – living or conventional based on the established diagnostic criteria.

The 4-(ethenyloxy)butyl monomers with acetate and benzoate moieties in the C1 position of the butyl side chain were then polymerized under the same conditions in the presence of an externally added ester corresponding to the enchaind ester moiety (scheme 2.2.1, C) .

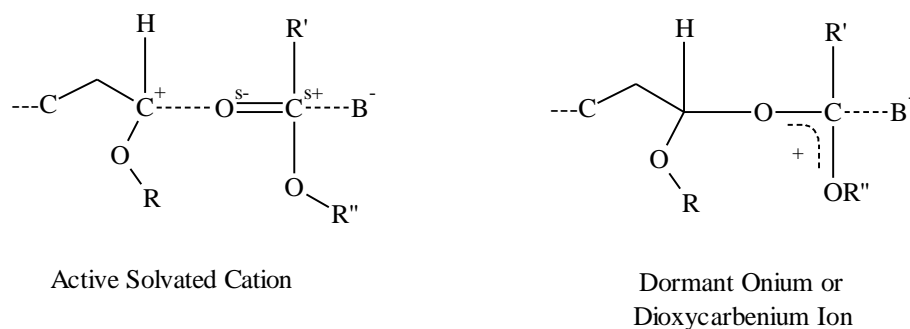
The data from the polymerizations, as before was used to classify the systems as living, controlled / quasi – living or conventional based on the established diagnostic criteria.



Scheme 2.2:1

The initiating system selected for this project was HCl (etherate) / ethylaluminum dichloride (EADC) where the HCL serves as the initiator (I) and the EADC as the coinitiator (CoI). In the seminal paper (Aoshima and Higashimura, 1986) the actual initiator was “adventitious” water in which case the cationogen is H^+ and the counteranion or “gegenion” is OH^- or more precisely the $[\text{EADC}]^+ [\text{OH}]^-$ complex. In the HCl / EADC

initiating system it would then follow that the active and dormant species generated would have the following structure (figure 2.2.1)



where $B^- = Cl^-$, $R = n-C_4H_9$, $R' = CH_3, CH_2Cl, n-C_4H_9$ and $R'' = C_2H_5, 3ClC_6H_4, 4ClC_6H_4$.

Figure 2.2.1

4-(ethenyloxy)butane was select as the subject or base monomer due to a number of factors. From the practical standpoint 4-(ethenyloxy)butane, 4-(ethenyloxy)butan – 1 – ol and 4-(ethenyloxy)butyl benzoate are commercially available and relatively inexpensive. Also, the use of the 4-(ethenyloxy)butyl – 1 – ol and the appropriate acyl halide is an effect method for the synthesis of the subject monomers in high yields. The acylation method also simplifies the isolation and purification due to the fact that the reaction solvents, dichloromethane or diethyl ether, are easily removed at reduced pressure without the application of heat. Further, the only reaction by product of the acylation reaction is the triethylamine hydrochloride which is readily removed by aqueous extraction.

The vinyl ethers and esters selected for this study are shown in table 6.3.2 and 6.4.2 , respectively, and were selected to provide subject systems in which the relative strengths or basicity of the ester or pendant ester moieties could be used as a basis of comparison. The subject monomers are divided into two basic groups, i.e., alkyl and aryl ester pendant moieties.

2.3 OBJECTIVES

- To determine how the basicity or strength of an added ester (Lewis base) affects the degree of livingness of a polymerization system.
- To determine whether or not an ester group enchainned in the pendant chain of a vinyl ether (monomer) functions in the same manner and to the same extent as the same ester group added externally to the polymerization system.
- To develop a method for the determination of monomer conversion in systems where the boiling point of the monomer and / or other components of the polymerization system are sufficiently high that it is not possible to isolate and quantify the monomer and / or polymer concentration.

2.4 FUTURE WORK AND PUBLICATIONS

- Expanded studies on relationship between evaporation rate and the vapor pressure /vapor density product, (VP)(VD) at atmospheric pressure.
- Expanded studies on more precise criteria for the estimation and comparison of the relative strength of bases as applied to polymerization processes.
- Poster presentation at 2011 Eastern Analytical Symposium (Spring Lake, New Jersey, USA) – September, 2011, Title: THE EFFECTS OF VAPOR PRESSURE AND VAPOR DENSITY ON THE ATMOSPHERIC EVAPORATION RATE OF SOLVENTS.

- Oral presentation of paper at Eastern Analytical Symposium (Spring Lake, New Jersey, USA) – November, 2012, Title: DEVELOPMENT AND EVALUATION OF AN SEC METHOD FOR THE DETERMINATION OF MONOMER CONVERSION IN POLYMERIZATION SYSTEMS CONTAINING NON – VOLATILE REACTANTS AND ADDITIVES.
- Oral presentation of paper at PITTCON Conference & Expo (Philadelphia, PA, USA) – March, 2013, Title: COMPARATIVE ERROR ANALYSIS OF VARIOUS METHODS IN THE DETERMINATION OF MONOMER CONVERSION IN POLYMERIZATION SYSTEMS CONTAINING NON – VOLATILE MONOMERS, REACTANTS AND ADDITIVES;
- PREPARATION OF BLOCK COPOLYMERS BY LIVING CARBOCATIONIC POLYMERIZATION OF VINYL ETHERS WITH ENCHAINED ESTER, ETHER AND AMINE GROUPS IN THE ABSENCE OF EXTERNALLY ADDED BASES - submission date to be determined
- DIRECT LIVING CARBOCATIONIC POLYMERIZATION OF VINYL ETHERS WITH NLO ACTIVE SIDE CHAINS – submission date to be determined.

CHAPTER 3

POLYMERIZATION OF ALKYL VINYL ETHERS

3.1. POLYMERIZATION OF 4-(ETHENYLOXY)BUTANE

To establish a basis of comparison 4-(ethenyloxy)butane (VOB) was polymerized at -20 and 4° C in toluene with and without the addition of an added alkyl ester (Lewis base). The esters used for this series of polymerizations were ethyl acetate (EA), ethyl chloroacetate (ECA), ethyl dichloroacetate (EDCA), butyl benzoate (BBZ), butyl 4-chlorobenzoate (B4CBZ) and butyl 3-chlorobenzoate (B3CBZ), respectively. The initiator system used for each of the polymerizations at both temperatures was HCl / ethylaluminum dichloride (EADC) with the coinitorator / initiator ratios ($[CoI] / [I]$) = 4.5 and 9.0, respectively.

At -20° C and with a coinitorator / initiator ratio of 4.5 the polymerization systems with no externally added ester, ECA, EDCA, B4CBZ and B3CBZ developed a deep purple – brown color within 90 minutes following the addition of the EADC. The systems containing EA and BBZ (stronger bases based on the pK_a of the corresponding carboxylic acid) remained colorless initially but also developed the same colored complex after approximately 15 hours. In general, the time required for the formation of the colored complex increased with the increasing basicity of the added ester. The formation of the colored complex has been noted in the literature and attributed to the formation of conjugated double bonds as a result of chain transfer and termination (Aoshima, S. and Higashimura, T., 1983).

The systems containing no ester and EDCA were conventional in nature with broad MWD's > 2.0 , with the MWD increasing with conversion and M_n 's below the theoretical or calculated value based on the initiator to monomer ratio and assuming that one active chain is formed for each initiator unit. Further, the polymerizations did not achieve complete conversion and the increase in the M_n was not linear with respect to conversion (Table 3.1-1).

ESTER	[CoI] / [I]	M_n	MWD	LINEARITY
NONE	4.50	15,200	2.00	NL (IC)
	9.00	14,500	2.00	NL (IC)
EA	4.50	15,200	1.50	L (up to $\approx 70\%$)
	9.00	18,500	1.36	L
ECA	4.50	18,000	1.80	NL
	9.00	15,250	1.72	NL
EDCA	4.50	15,500	2.75	NL (IC)
	9.00	15,000	2.60	NL (IC)
BBZ	4.50	15,800	1.50	L (up to $\approx 70\%$)
	9.00	17,400	1.45	L
B4CBZ	4.50	15,300	1.52	L (up to $\approx 50\%$)
	9.00	15,700	1.45	L (up to $\approx 60\%$)
B3CBZ	4.50	15,650	1.55	L (up to $\approx 50\%$)
	9.00	15,000	1.66	L (up to $\approx 50\%$)

L = linear, NL=nonlinear IC= conv.<1

Table 3.1-1: Polymerization characteristics of 4-(ethenyloxy)butane in toluene at -20 C in the presence of various esters: [VOB] = 40.0 mM, [HCL] = 0.25 mM, calculated M_n = 16,055

In the presence of EA, BBZ, B4CBZ and B3CBZ (stronger bases) the MWD was lower at $\approx 1.50 - 1.55$ and increased with conversion. The M_n increased linearly with conversion up to approximately 70% but deviated at higher conversion in the systems containing EA

and BBZ, respectively, and in each case the M_n was below the theoretical or calculated value. In the systems containing B4CBBZ and B3CBBZ the M_n increased steadily with conversion but was nonlinear above approximately 50% conversion.

Increasing the coinitiator / initiator ratio to 9.0 lowered the MWD of all of the subject systems with the MWD of all of the systems increasing with conversion although the increase in the presence of EA and BBZ was very slight. The increase in the M_n with conversion was linear in the presence of EA and BBZ and linear up to approximately 50% in the presence of B4CBZ and B3CBZ. In all other systems the increase in M_n was nonlinear with respect to conversion. In the absence of added ester as well as in the presence of EDCA conversion was less than 100 % (figure 3.1-1A & B).

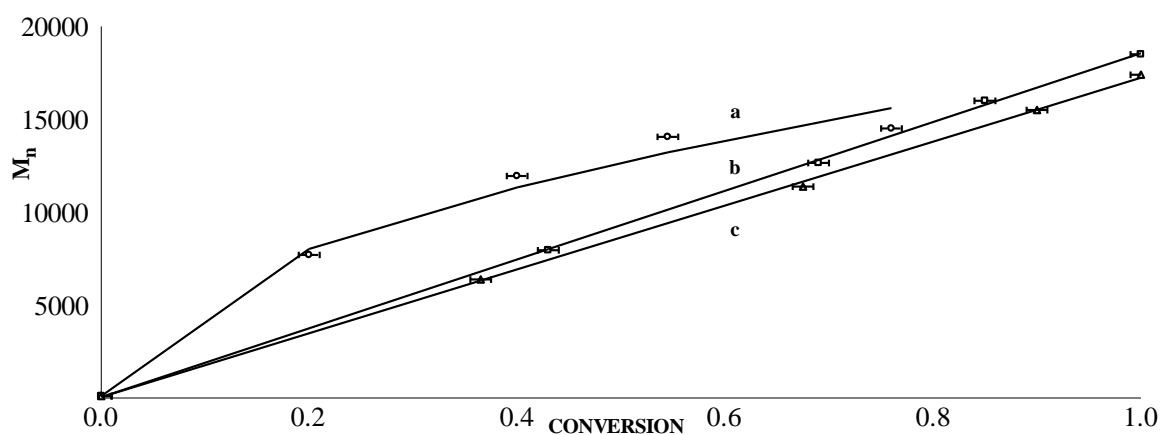


Figure 3.1 -1A: Effect of addition of EA (b) and BBZ (c) on the polymerization of 4-(ethenyloxy)butane at -20°C in toluene versus polymerization in the absence of an ester (a): $[M] = 40.0\text{ mM}$, $[\text{ESTER}] = 10\% \text{ vol.}$, $[\text{HCl}] = 0.25\text{ mM}$, $[\text{EADC}] = 2.25\text{ mM}$

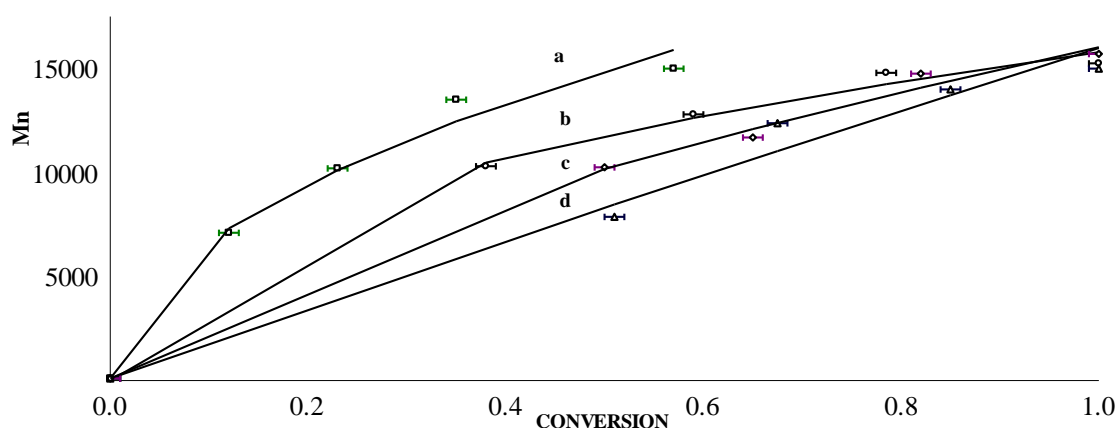


Figure 3.1 -1B: Nonlinear increase in the M_n with conversion in the polymerization of 4-(ethenyloxy)butane at -20°C in toluene in the presence of added esters of varying basicity: (a) EDCA (b) ECA (c) B4CBZ (d) B3CBZ: $[M] = 40.0\text{ mM}$, $[\text{ESTER}] = 10\% \text{ vol.}$, $[\text{HCl}] = 0.25\text{ mM}$, $[\text{EADC}] = 1.25\text{ mM}$,

The addition of monomer to the systems containing EA and BBZ at complete conversion resulted in continued polymerization at the same rate with a linear increase in the M_n with conversion. The M_n remained above the theoretical or calculated value of 16,055 and the MWD continued to increase very slightly with conversion to 1.44 and 1.47, respectively (figure 3.1-2 A & B).

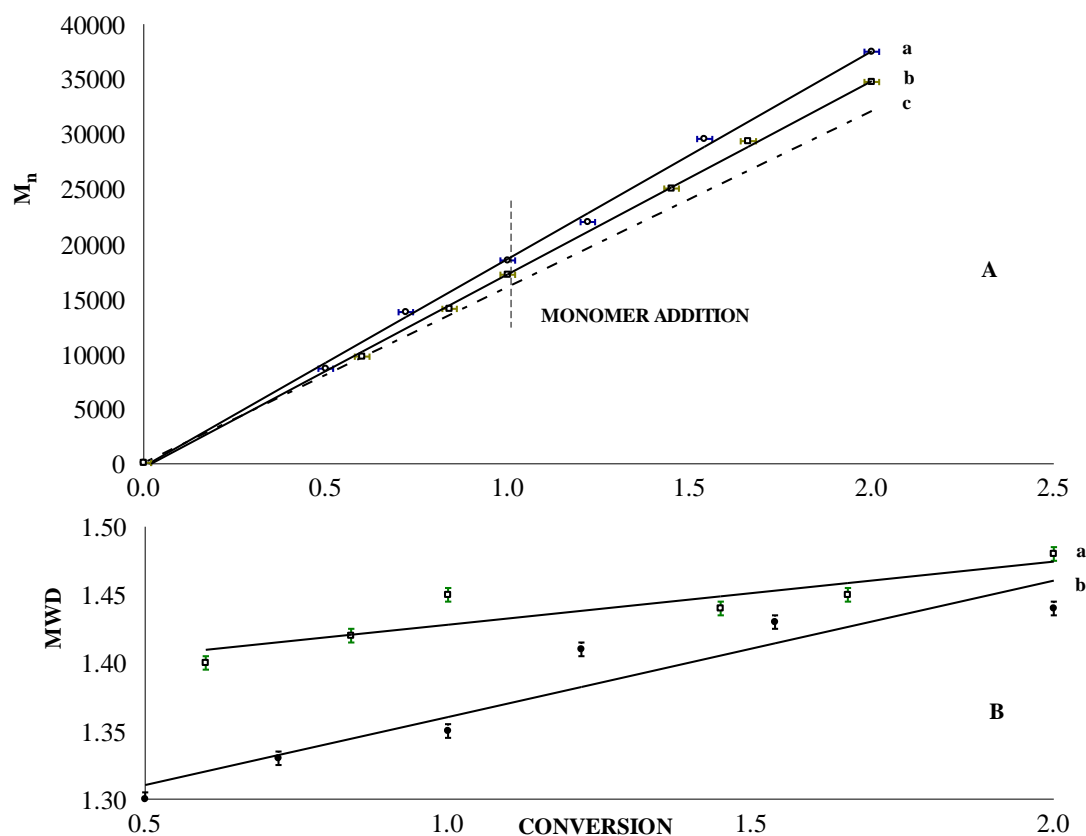


Figure 3.1 - 2: (A) Linear increase in M_n with conversion in the polymerization of 4-(ethenyl)butane in toluene at -20°C in the presence of an added ester (a = EA, b = BBZ, c = none) with continued polymerization at the same rate following the addition of additional monomer (B) Change in MWD with conversion (a = EA, b = BBZ) : $[M] = 40.0\text{ mM}$, $[\text{ESTER}] = 10\%$ vol., $[\text{HCl}] = 0.25\text{ mM}$, $[\text{EADC}] = 2.25\text{ mM}$.

At 4°C the polymerizations were initiated with the addition of the EADC and in the systems containing no added ester a deep purple – brown color developed within 90 minutes. In systems containing weaker bases, i. e., ECA and EDCA the color developed within 30 to 60 minutes and in the system containing EA the color was noted after approximately 9 hours.

At the lower coinitiator / initiator ratio none of the systems exhibited a significant degree of living character and the results from this series of polymerizations are summarized in table 3.1-2. In general the systems all appear to be conventional in nature with broad MWD's and M_n 's above the theoretical or calculated value based on the initiator concentration and assuming that one active chain is formed for each initiator unit.

ESTER	[CoI] / [I]	M_n	MWD	LINEARITY
NONE	4.50	25,700	2.34	NL (IC)
	9.00	20,000	2.25	NL (IC)
EA	4.50	40,000	1.55	NL
	9.00	23,690	1.49	L (to \approx 70%)
ECA	4.50	35,000	1.80	NL
	9.00	27,500	1.72	NL
EDCA	4.50	14,400	2.40	NL (IC)
	9.00	15,000	2.33	NL (IC)
BBZ	4.50	23,350	1.60	NL
	9.00	19,200	1.54	L (to \approx 70%)
B4CBZ	4.50	17,350	1.75	NL
	9.00	16,650	1.68	NL
B3CBZ	4.50	17,225	1.77	NL
	9.00	16,700	1.79	NL

NL =
L = linear, nonlinear IC= conv.<1.0

Table 3.1-2: Polymerization characteristics of 4-(ethenyloxy)butane in toluene at 4° C in the presence of various esters: [VOB] = 40.0 mM, [HCl] = 0.25 mM, calculated M_n = 16,055

The M_n decreased as the strength of the added base decreased due primarily to incomplete conversion while the MWD increased steadily with conversion although complete

conversion was not achieved. The conversion was surprisingly high with all systems achieving $\approx 90\%$ conversion. Polymerization rates appear to be roughly equal with the exception of the systems containing EA and BBZ which proceeded at slightly less than half that of the other systems.

The M_n of all of the systems were above the theoretical or calculated value of $\approx 16,055$ based on the initiator concentration and none of the observed M_n 's increased linearly with conversion. The EA and BBZ systems had the highest M_n and the narrowest MWD (figure 3.1-3).

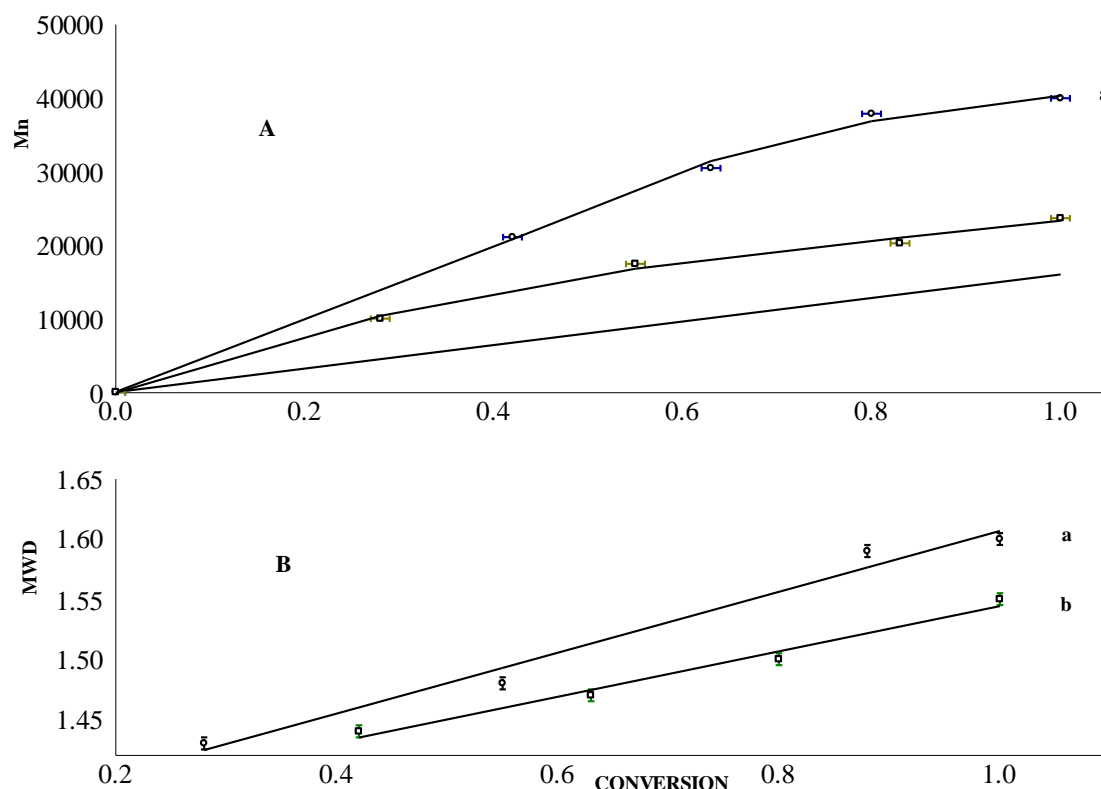


Figure 3.1 - 3: (A) Increase in the M_n with conversion in the polymerization of 4-(ethenyloxy)butane in toluene at 4 °C in the presence of an added ester (a = EA, b = BBZ, c = calculated); (B) Increase in MWD with conversion in the presence of an added ester (a = EA, b = BBZ).

The SEC chromatograph of the polymer obtained in the presence of EA at complete conversion clearly shows a bimodal MWD. The bimodal distribution was observed at low

conversion and became less pronounced with increased conversion (figure 3.1-4).

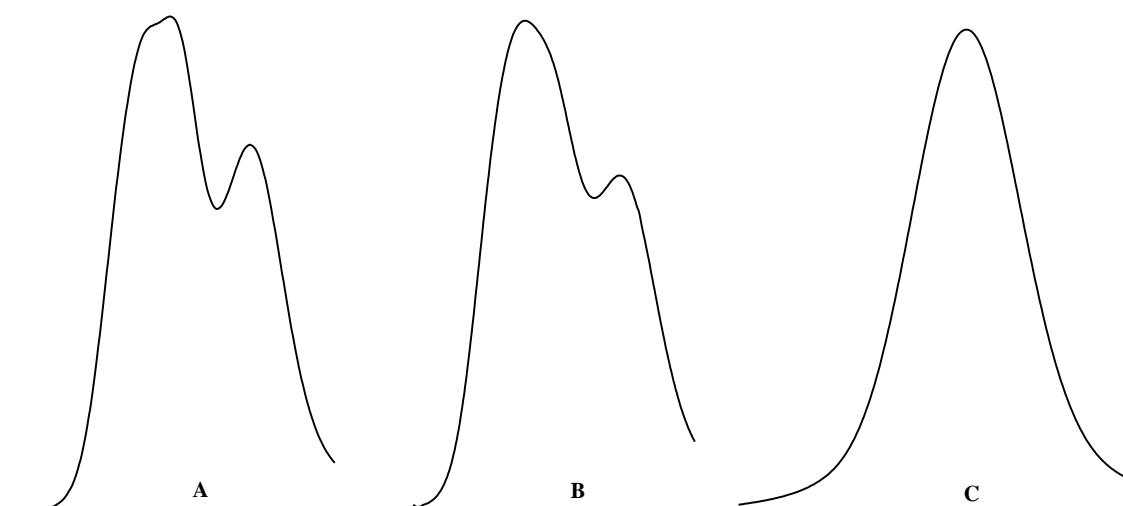


Figure 3.1 - 4: Progressive decrease in bimodal character of poly 4-(ethenyloxy)butane with conversion at 4° C in toluene: A = 20%, B = 40%, C = 85%; [CoI] / [I] = 4.0, [EA] = 10 vol. %

At a coinitiator / initiator ratio of 9.0 the MWD continued to increase with conversion and at 1.42 was equal to the MWD at a 4.0 ratio. The MWD was bimodal at low conversion and again became less pronounced with conversion (figure 3.1-5). The increase in M_n with conversion was linear to approximately 70% conversion but deviated at higher conversion and was above the calculated

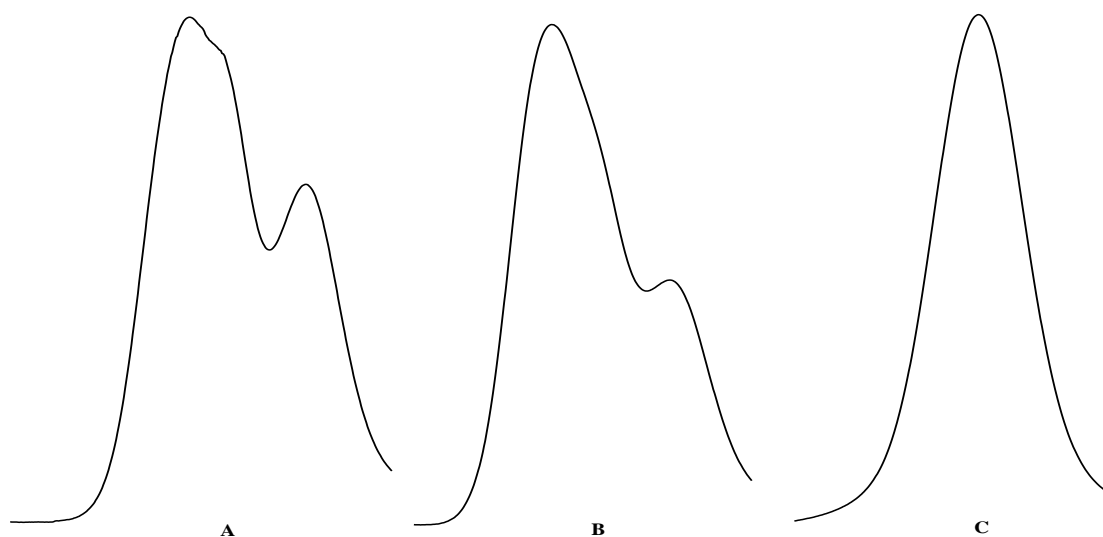


Figure 3.1 - 5: Progressive decrease in bimodal character of poly 4-(ethenyloxy)butane with conversion at 4° C in toluene: A = 15%, B = 60%, C = 90%; [CoI] / [I] = 4.0, [EA] = 10 vol. %

The R_p was higher at a coinitiator / initiator ratio of 9.0 and complete conversion was achieved in 15 hours as compared with 192 hours at a 4.5 coinitiator / initiator ratio.

3.2. POLYMERIZATION OF 4- (ETHENYLOXY)BUTYL ACETATES

3.2.1. 4-(ethenyloxy)butyl acetate

In toluene at -20°C and a coinitiator / initiator ratio of 4.5, 4-(ethenyloxy)butyl acetate (VOBOAC) polymerized to complete conversion with the MWD increasing to ≈ 1.57 with conversion (figure 3.2.1 – 1B - a). The M_n increased linearly up to approximately 55% conversion but was above the theoretical or calculated value (figure 3.2.1- 1A - a). As noted in the polymerization of VOB a purple – brown color complex formed within 12 hours of initiation by the addition of the EADC.

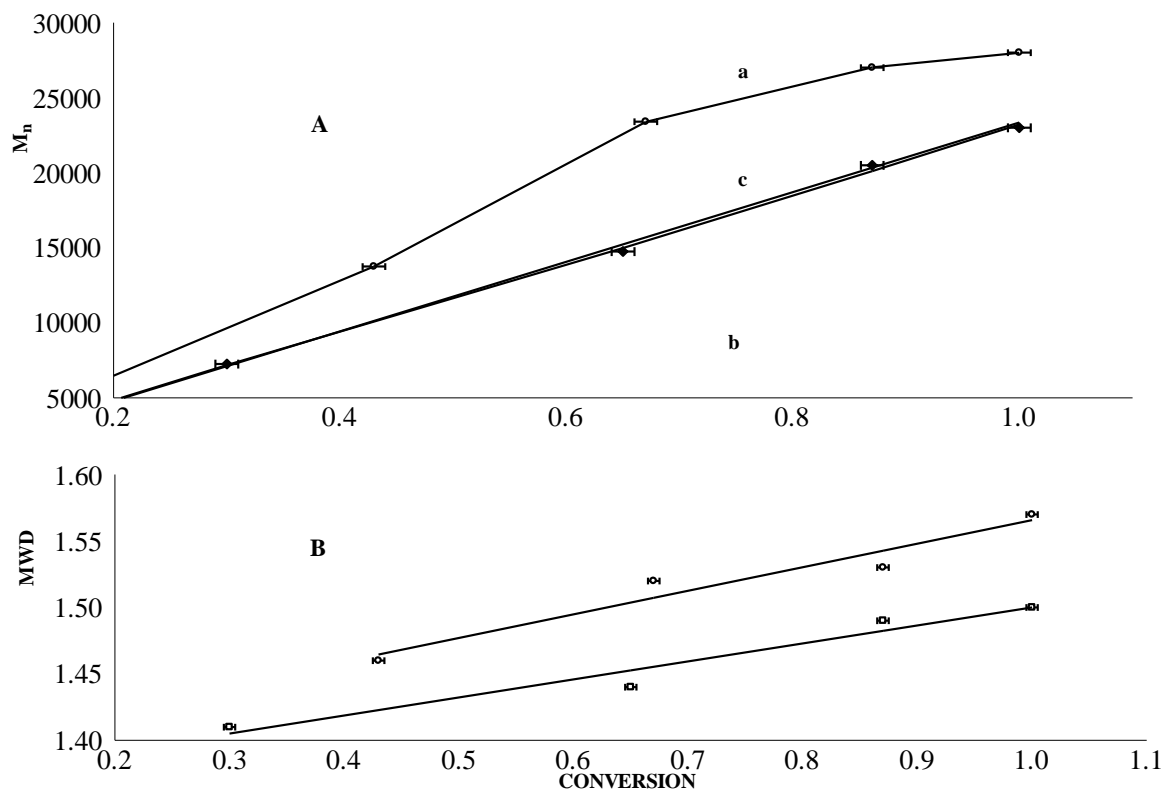


Figure 3.2.1 -1A: Effects of added ester and $[\text{CoI}] / [\text{I}]$ on the M_n (A) and MWD (B) on the polymerization of 4-(ethenyloxy)butyl acetate at -20°C : (a): $[\text{ESTER}] = \text{none}$, $[\text{CoI}] / [\text{I}] = 4.5$, $[\text{M}] = 40.0 \text{ mM}$, $[\text{HCl}] = 0.25 \text{ mM}$; (c): $[\text{ESTER}] = 10\% \text{ vol.}$, $[\text{CoI}] / [\text{I}] = 4.5$, $[\text{M}] = 40.0 \text{ mM}$, $[\text{HCl}] = 0.25 \text{ mM}$; (c): theoretical M_n .

Increasing the coinitiator / initiator ratio to 9.0 decreased the MWD but there was still an increase with conversion to 1.48 (figure 3.2.1 – 1B - b). The M_n increased linearly with conversion up to approximately 70% but again deviated from a linear increase and remained slightly above the theoretical or calculated value (figure 3.2.1 – 1A - b). The formation of the purple - brown color complex was noted approximately 18 – 20 hours following initiation.

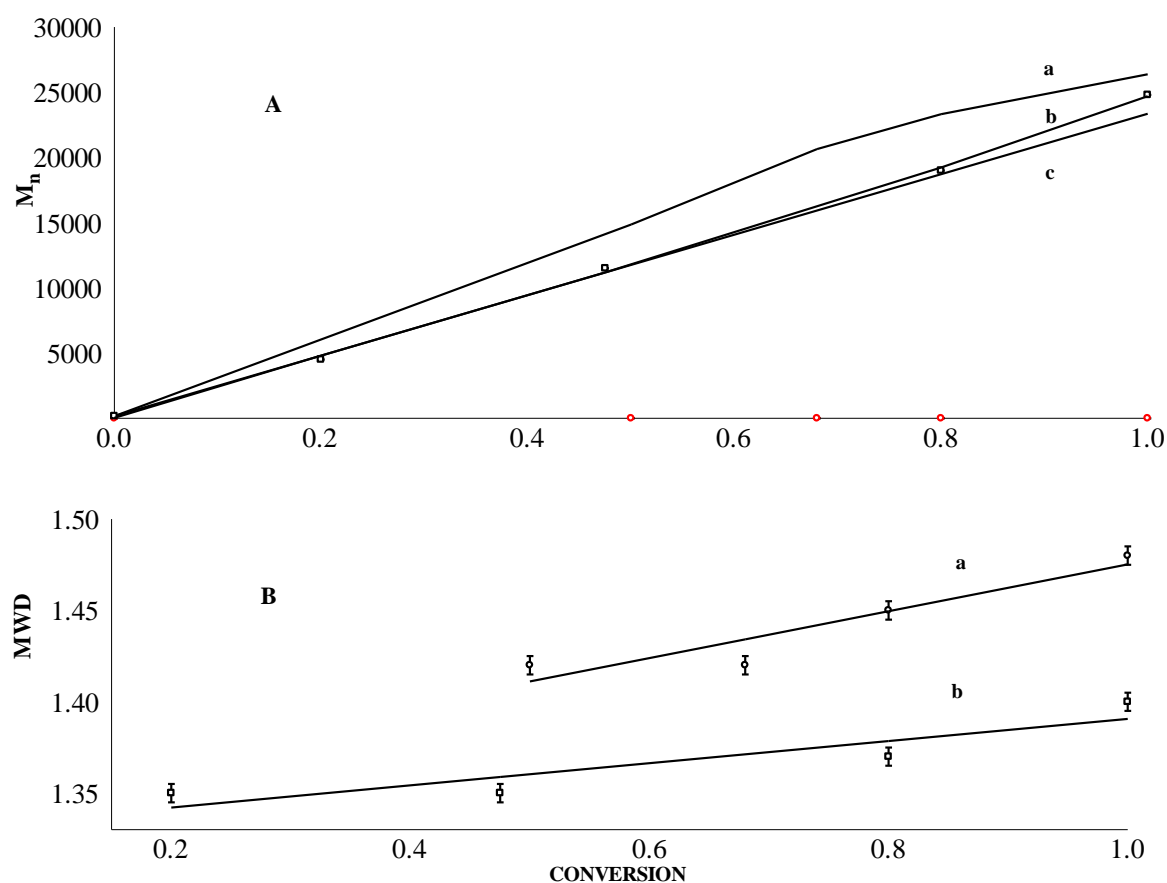


Figure 3.2.1 -1A: Effects of added ester and $[CoI] / [I]$ on the M_n (A) and MWD (B) on the polymerization of 4-(ethinyloxy)butyl acetate at $-20^\circ C$: (a): $[ESTER] = \text{none}$, $[CoI] / [I] = 4.5$, $[M] = 40.0 \text{ mM}$, $[HCl] = 0.25 \text{ mM}$: (c): $[ESTER] = 10\% \text{ vol.}$, $[CoI] / [I] = 4.5$, $[M] = 40.0 \text{ mM}$, $[HCl] = 0.25 \text{ mM}$: (c): theoretical M_n .

At a $[CoI] / [I]$ ratio of 4.5 in the presence of EA at a concentration of 10% (volume) the M_n increased linearly up to approximately 80% conversion but deviated at higher conversion falling below the theoretical or calculated value figure 3.2.1 – 1A – c). The MWD increased with conversion but was lower than in the absence of the added EA at 1.50 and 1.57, respectively (figure 3.2.1 – 1B – a & b).

Increasing the $[CoI] / [I]$ ratio to 9.0 with the addition of EA at 10% (volume) resulted in an increase in the M_n which was linear to 100% conversion and slightly lower than the theoretical or calculated value with the MWD increasing to 1.40 at complete conversion (figure 3.2.1 – 1A & 1B –c). At 100% conversion additional monomer was added to the system with coinitiator / initiator ratio of 9.0 in the presence of EA. Polymerization continued at the same rate while the M_n increased linearly up to 100% conversion and MWD continued to increase to 1.45 with conversion as shown in figure 3.2.1-2A & B. The data from this series of polymerizations is summarized in table 3.2.1 – 1.

MONOMER	ESTER	$[CoI] / [I]$	M_n	MWD	M_n vs Conversion
VOBOAC	NONE	4.50	28,000	1.57	L (to \approx 50%)
	NONE	9.00	26,200	1.48	L (to \approx 70%)
VOBOAC	EA	4.50	23,000	1.50	L (to \approx 80%)
	EA	9.00	24,800	1.40	L
VOBCOAC	NONE	4.50	29,800	1.78	NL
	NONE	9.00	28,500	1.66	NL
VOBCOAC	ECA	4.50	30,300	1.74	NL
	ECA	9.00	29,500	1.62	NL

L = linear

NL=nonlinear

Table 3.2.1-1: Polymerization characteristics of 4-(ethenyloxy)butyl acetate and 4-(ethenyloxy)butyl chloroacetate in toluene at -20° C in the presence and absence of added ester: $[M] = 40$ mM, $[HCL] = 0.25$, calculated $M_n = 25,350$

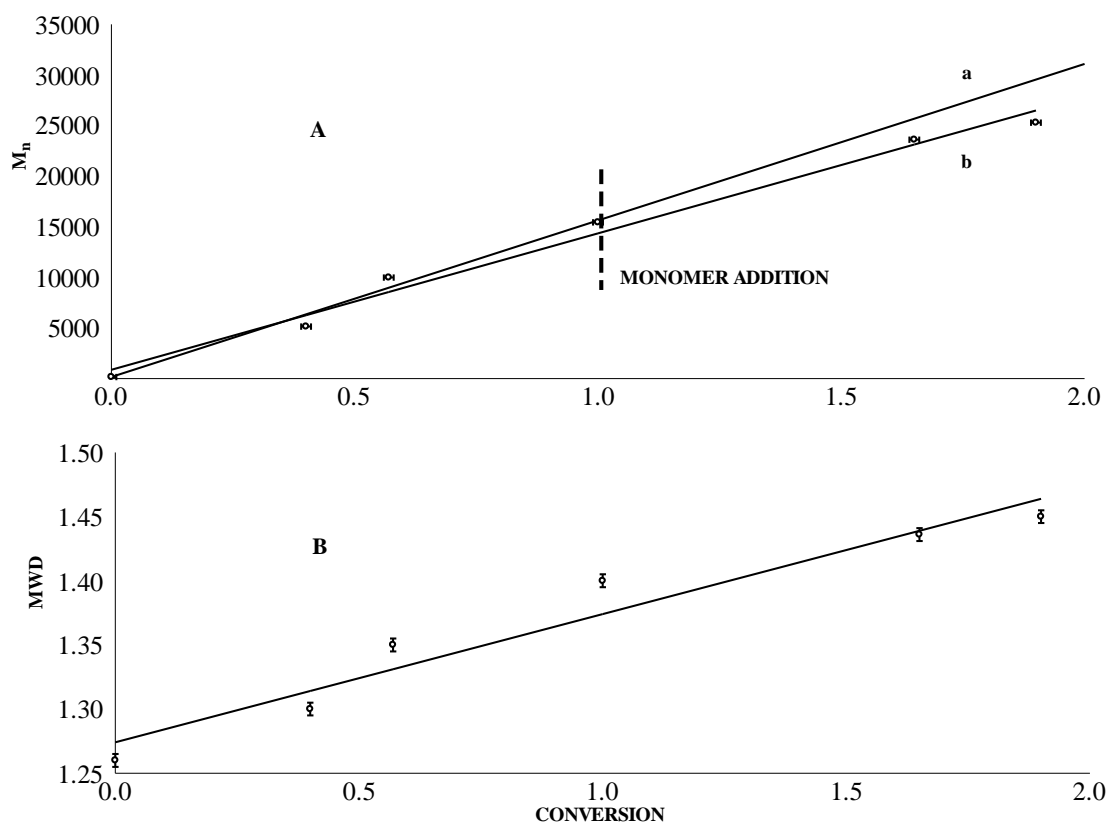


Figure 3.2.1 -2A & B: Increase in M_n with addition of additional monomer at complete conversion in polymerization of 4-(ethenyloxy)butyl acetate at -20°C in toluene: $[\text{VOBOAC}] = 25.0\text{ mM}$, $[\text{EA}] = 10\% \text{ vol.}$, $[\text{HCl}] = 0.25\text{ mM}$, $[\text{EADC}] = 2.25\text{ mM}$, (A) a = theoretical M_n , b = actual: (B) MWD versus conversion.

At 4°C and under identical conditions the polymerization of VOBOAC showed a nonlinear increase in the M_n with conversion with or without the addition of EA. At coinitiator / initiator ratios of 4.5 and 9.0, respectively, the M_n was significantly higher than the theoretical or calculated value and the MWD was relatively broad at > 1.47 increasing with conversion. The data from this series of polymerizations is summarized in table 3.2.1-2 and depicted graphically in figure 3.2.1-3A&B.

MONOMER	ESTER	[CoI] / [I]	M_n	MWD	M_n vs Conversion
VOBOAC	NONE	4.50	55,700	1.80	NL
	NONE	9.00	38,025	1.60	NI
VOBOAC	EA	4.50	47,900	1.53	NL
	EA	9.00	35,000	1.47	NL
VOBCOAC	NONE	4.50	51,000	1.88	NL

	NONE	9.00	40,000	1.80	NL
VOBCOAC	ECA	4.50	48,000	1.83	NL
	ECA	9.00	40,000	1.72	NL
L = linear		NL=nonlinear			

Table 3.2.1-2: Polymerization characteristics of 4-(ethenyloxy)butyl acetate and 4-(ethenyloxy)butyl chloroacetate in toluene at 4° C in the presence and absence of added ester: [M] = 40 mM, [HCL] = 0.25 mM, calculated Mn = 25,350

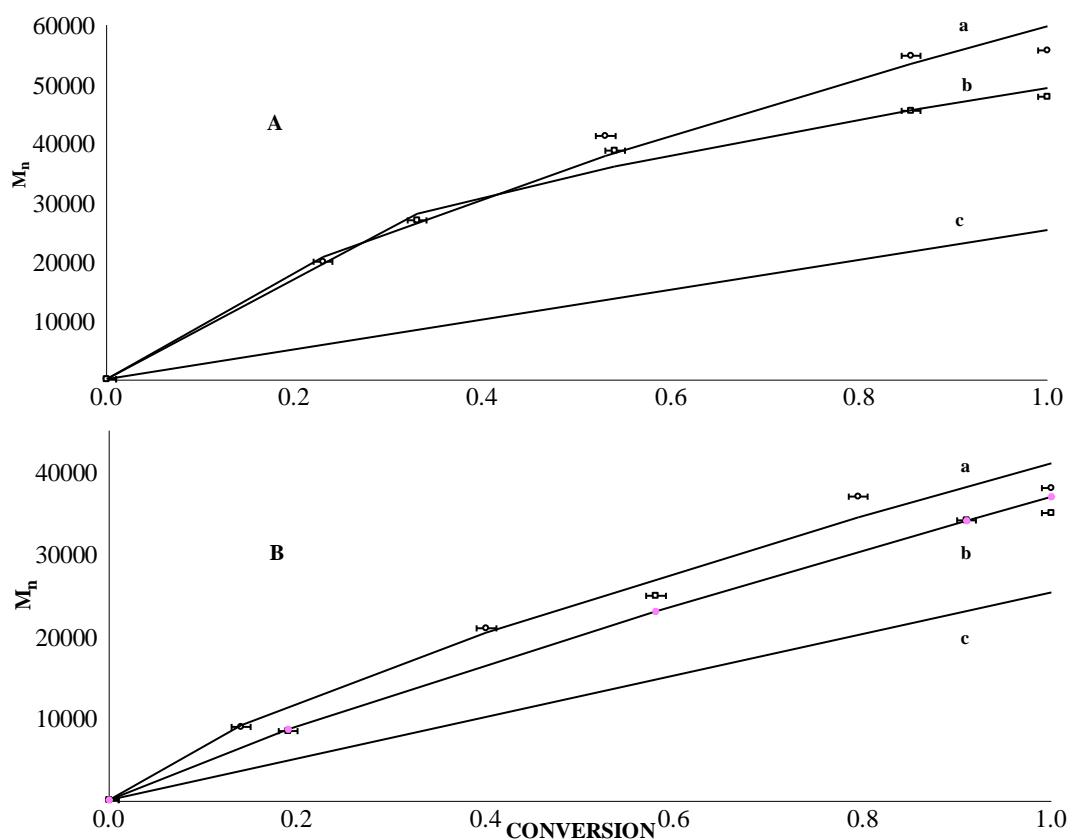


Figure 3.2.1 -3A: Effects of added ester and [CoI] / [I] on the M_n in the polymerization of 4-(ethenyloxy)butyl acetate at 4° C in toluene: A - [CoI] / [I] = 4.5, without EA (a) with EA (b); B - [CoI] / [I] = 9.0, without EA (a), with EA (b); [EA] = 10% vol., [M] = 40.0 mM, [HCl] = 0.25 mM, Theoretical M_n (c) = 25,350

3.2.2. 4-(ethenyloxy)butyl chloroacetate

In toluene at -20° C and a coinitiator / initiator ratio of 4.5, 4-(ethenyloxy)butyl chloroacetate (VOBCOAC) polymerized with the MWD increasing to ≈ 1.78 at complete conversion (figure 3.2.2 – 1B - a). The increase in the M_n was steady but was nonlinear and was above the theoretical or calculated value (figure 3.2.2- 1A - a). As noted previously a purple – brown color complex formed within 6 hours of initiation by the addition of the EADC in this system.

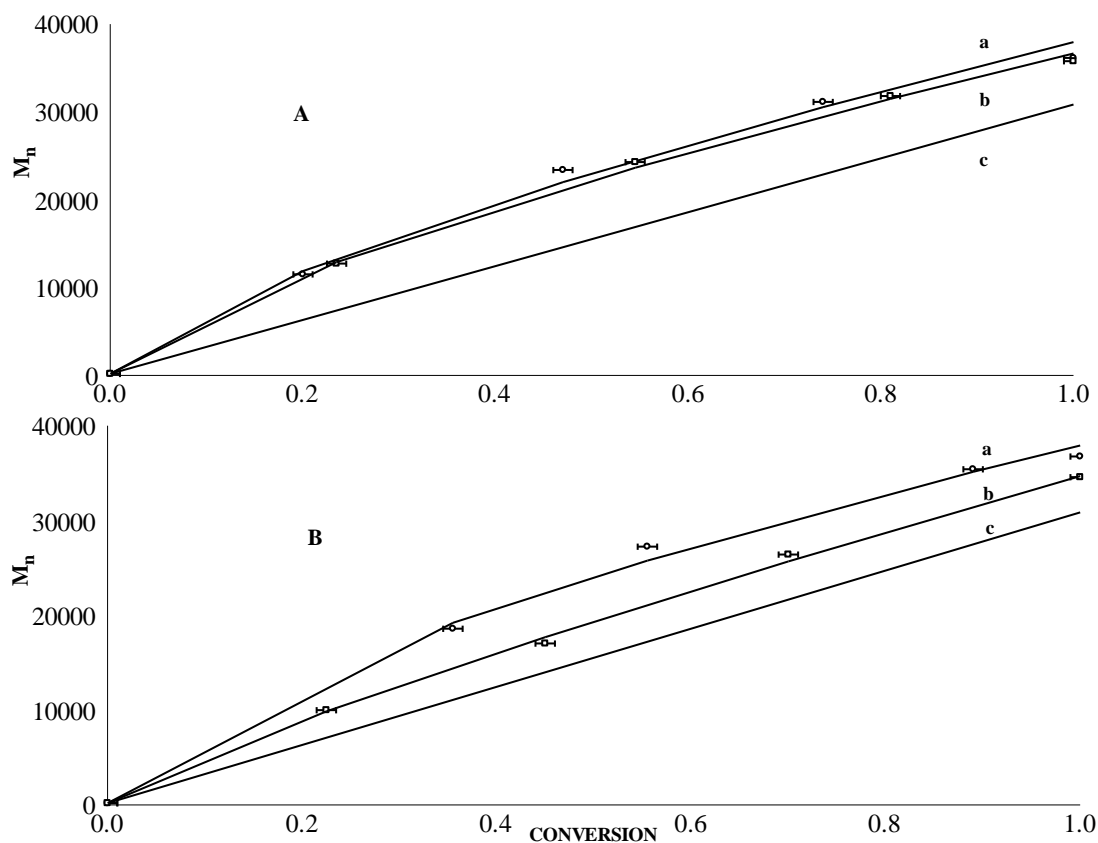


Figure 3.2.2 -1A: Effects of added ester and $[\text{CoI}] / [\text{I}]$ on the MWD in the polymerization of 4-(ethenyloxy)butyl chloroacetate at -20°C in toluene: A - $[\text{CoI}] / [\text{I}] = 4.5$, without EA (a) with EA (b); B - $[\text{CoI}] / [\text{I}] = 9.0$, without EA (a), with EA (b); $[\text{EA}] = 10\%$ vol., $[\text{M}] = 40.0\text{ mM}$, $[\text{HCl}] = 0.25\text{ mM}$,

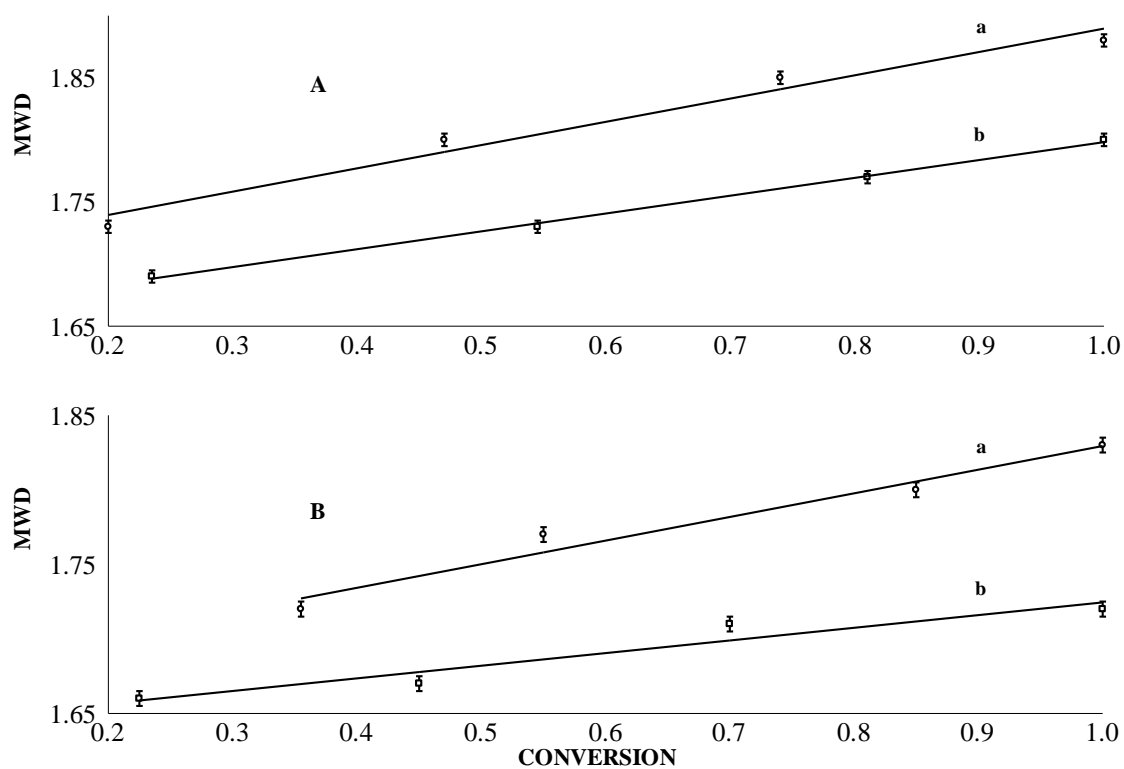


Figure 3.2.2 -1B: Effects of added ester and $[\text{CoI}] / [\text{I}]$ on the MWD in the polymerization of 4-(ethenyloxy)butyl chloroacetate at -20°C in toluene: A - $[\text{CoI}] / [\text{I}] = 4.5$, without ECA (a) with ECA (b); B - $[\text{CoI}] / [\text{I}] = 9.0$, without ECA (a), with ECA (b); $[\text{ECA}] = 10\%$, vol., $[\text{M}] = 40.0\text{ mM}$, $[\text{HCl}] = 0.25\text{ mM}$,

Increasing the coinitiator / initiator ratio to 9.0 decreased the MWD to 1.66 but there was still an increase with conversion (figure 3.2.2 – 1B -b). The M_n increased with conversion but was nonlinear and remained above the theoretical or calculated value (figure 3.2.2 – 1A -c). The formation of the purple - brown color complex was noted approximately 12 hours following initiation.

At a $[CoI] / [I]$ ratio of 4.5 and in the presence of ECA at a concentration of 10% (volume) the M_n increased steadily with conversion but remained above the theoretical or calculated value and was nonlinear. The MWD continued to increase with conversion and at 1.74 was lower than the MWD in the absence of the added ECA. Increasing the $[CoI] / [I]$ ratio to 9.0 and with the addition of ECA at 10% by volume the increase in the M_n remained nonlinear with conversion and was above the theoretical or calculated value with the MWD increasing to 1.62 at complete conversion (table 3.2.2-1A & B - c).

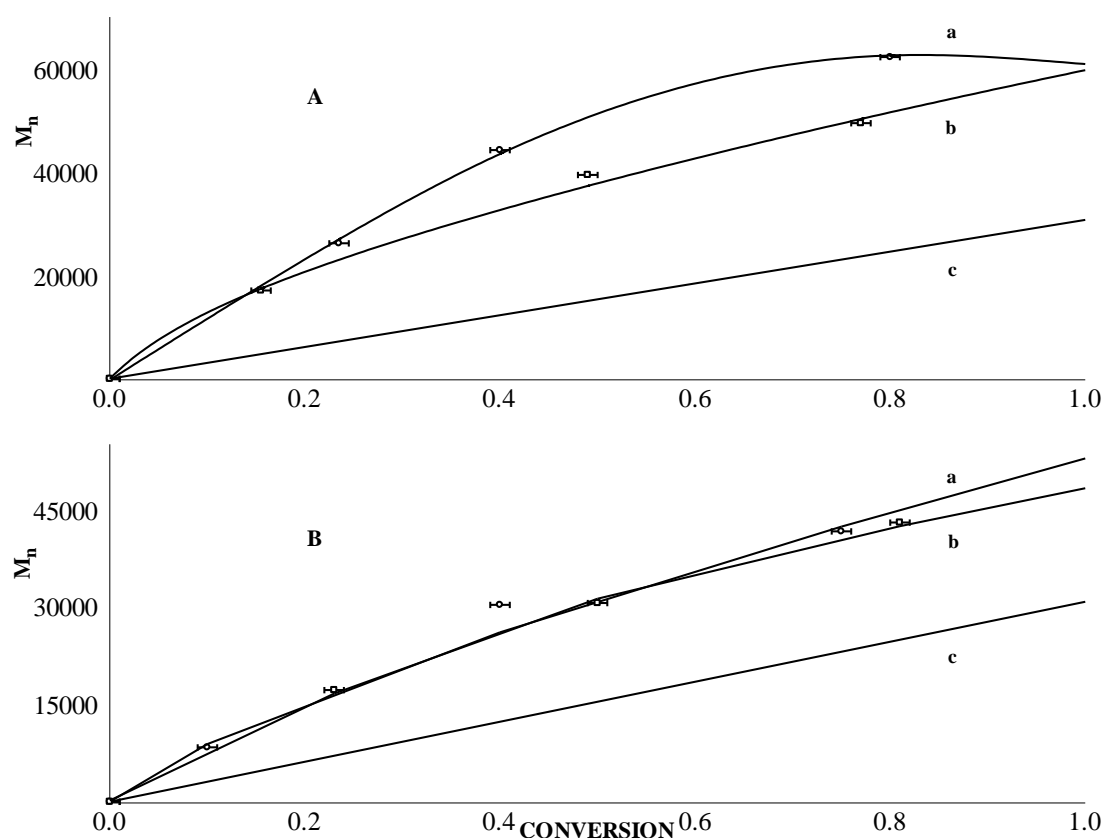


Figure 3.2.2 - 2A: Effects of added ester and $[CoI] / [I]$ on the M_n in the polymerization of 4-(ethenyloxy)butyl chloroacetate at 4° C in toluene: A - $[CoI] / [I] = 4.5$, without ECA (a) with ECA (b); B - $[CoI] / [I] = 9.0$, without ECA (a), with ECA (b): $[ECA] = 10\%$, vol., $[M] = 40.0$ mM, $[HCl] = 0.25$ mM, (c) theoretical $M_n = 30,850$

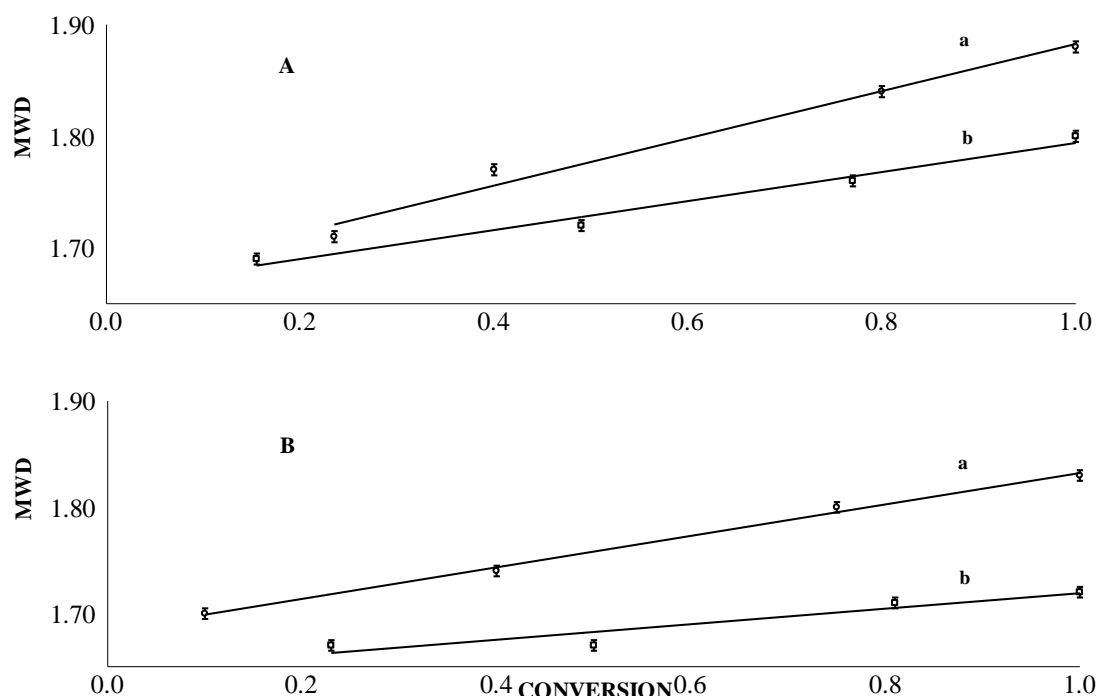


Figure 3.2.2 - 2B: Effects of added ester and $[CoI] / [I]$ on the M_n in the polymerization of 4-(ethenyloxy)butyl chloroacetate at 4° C in toluene: A - $[CoI] / [I] = 4.5$, without ECA (a) with ECA (b); B - $[CoI] / [I] = 9.0$, without ECA (a), with ECA (b): $[ECA] = 10\%$, vol., $[M] = 40.0$ mM, $[HCl] = 0.25$ mM,

At 4° C and in the absence of added ester the polymerization of VOBCOAC was conventional although conversion was complete at coinitiator / initiator ratios of 4.5 and 9.0, respectively. In both systems the increase in the M_n was steady but nonlinear and above the theoretical or calculated value based on the initiator concentration (figure 3.2.2 - 2A – a & d). The MWD increased with conversion to 1.88 and 1.80 at coinitiator / initiator ratios of 4.5 and 9.0, respectively (figure 3.2.2 – 2B – a & d). In the absence of added ester the purple - brown color complex formed within two hours of initiation by the addition of the EADC.

The addition of ECA at 10% by volume lowered the M_n at coinitiator / initiator ratios of 4.5 and 9.0 with the increase with monomer conversion remaining nonlinear and in both systems the M_n was above the theoretical or calculated value based on the initiator concentration (figure 3.2.2 – 2A – c & b). The MWD increased with conversion to 1.83 and 1.72 at coinitiator / initiator ratios of 4.5 and 9.0, respectively (figure 3.2.2 – 2B –

c&b). In the systems with added ECA the purple - brown color complex formed within 4 – 5 hours of initiation by the addition of the EADC.

CHAPTER 4

POLYMERIZATION OF AROMATIC VINYL ETHERS

4.1. POLYMERIZATION OF 4-(ETHENYLOXY)BUTYL BENZOATE

Following the same investigative strategy established for the polymerization of alkyl vinyl ethers (Chapter 3) 4-(ethenyloxy)butyl benzoate (VOBBZ) was polymerized in toluene at -20 and 4° C, respectively, in the presence and absence of butyl benzoate (BBZ) as an externally added base using the same initiator system, i., e., HCl / EADC. The data from this series of polymerization is summarized in table 4.1-1.

SERIES	ESTER	[CoI] / [I]	Mn	MWD	Mn vs Conversion
A	NONE	4.50	30,300	1.66	NL
	NONE	9.00	24,700	1.58	L (to \approx 50%)
A	BBZ	4.50	25,300	1.59	L (to \approx 80%)
	BBZ	9.00	24,000	1.48	L
B	NONE	4.50	32,000	1.69	NL
	NONE	9.00	26,300	1.63	NL
B	BBZ	4.50	27,950	1.62	NL
	BBZ	9.00	25,430	1.53	NL

L = linear

NL=nonlinear

Table 4.1-1: Polymerization characteristics of 4-(ethenyloxy)butyl benzoate in the toluene at (A) -20° C and (B) 4°C in the presence and absence of BBZ as an added base: [M] = 25.0 mM, [BBZ] = 10 vol. %, [HCl] = 0.25 mM, calculated Mn = 22,000

At -20° C and in the absence of added BBZ the M_n increased steadily with conversion and was higher than the theoretical or calculated value with a coinitiator / initiator ratio of 4.5 and was nonlinear (figure 4.1-1A – a). The MWD was relatively broad at 1.66 and increased with conversion (figure 4.1-1B – a). When the coinitiator / initiator ratio was increased to 9.0 the increase in the M_n was linear up to approximately 50% but deviated at higher conversion. The MWD decreased to 1.58 but clearly showed an increase with conversion (figure 4.1-1B – a)). In both systems the polymerizations developed a deep purple – brown color within 1 – 3 hours of initiation by the addition of the EADC.

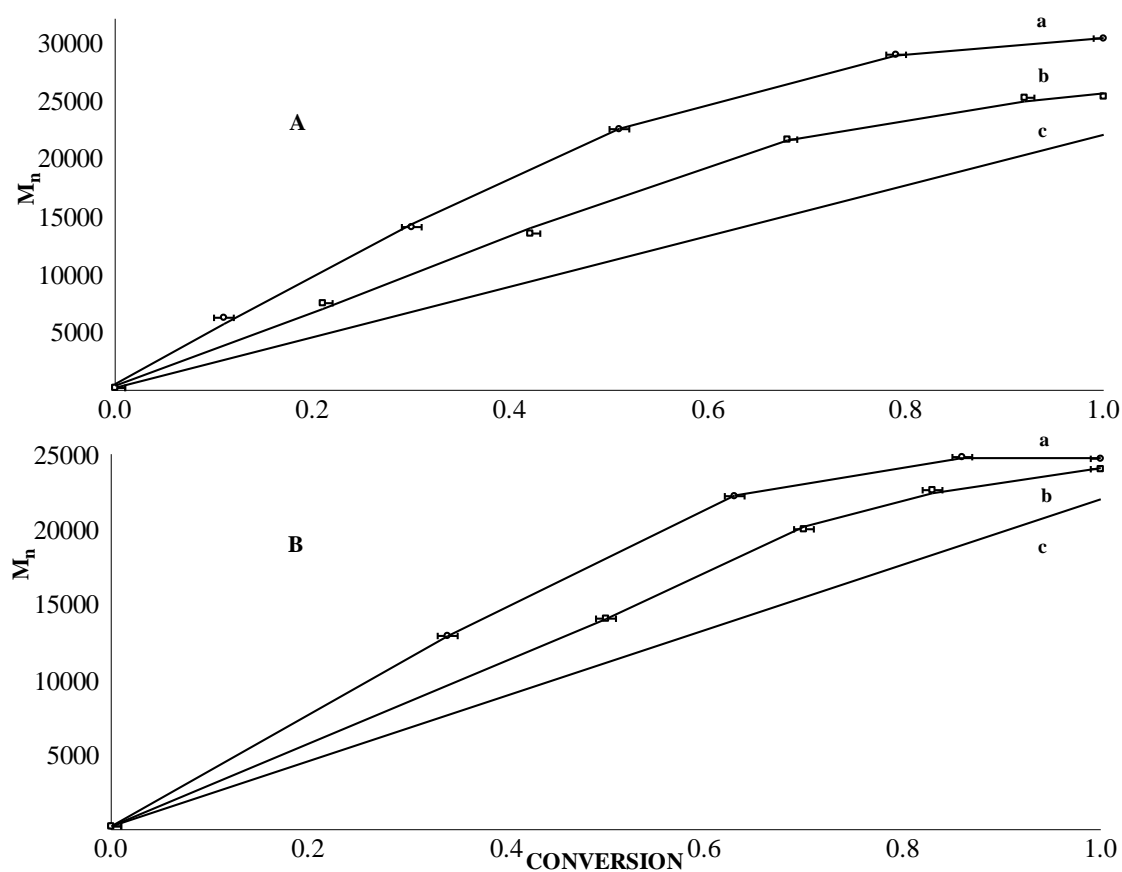


Figure 4.1- 1A: Effects of added ester (BBZ) and $[CoI] / [I]$ on the M_n of poly 4-(ethenyloxy)butyl benzoate polymerized at -20° C in toluene: A $[CoI] / [I] = 4.5$, $[BBZ] = \text{none}$ (a), 10% vol. (b): B $[CoI] / [I] = 9.0$, $[BBZ] = \text{none}$ (a), 10% vol. (b)

With the addition of BBZ and at a coinitiator / initiator ratio of 4.5 the increase in the M_n was linear up to nearly 80% conversion and deviated slightly at 100% conversion.

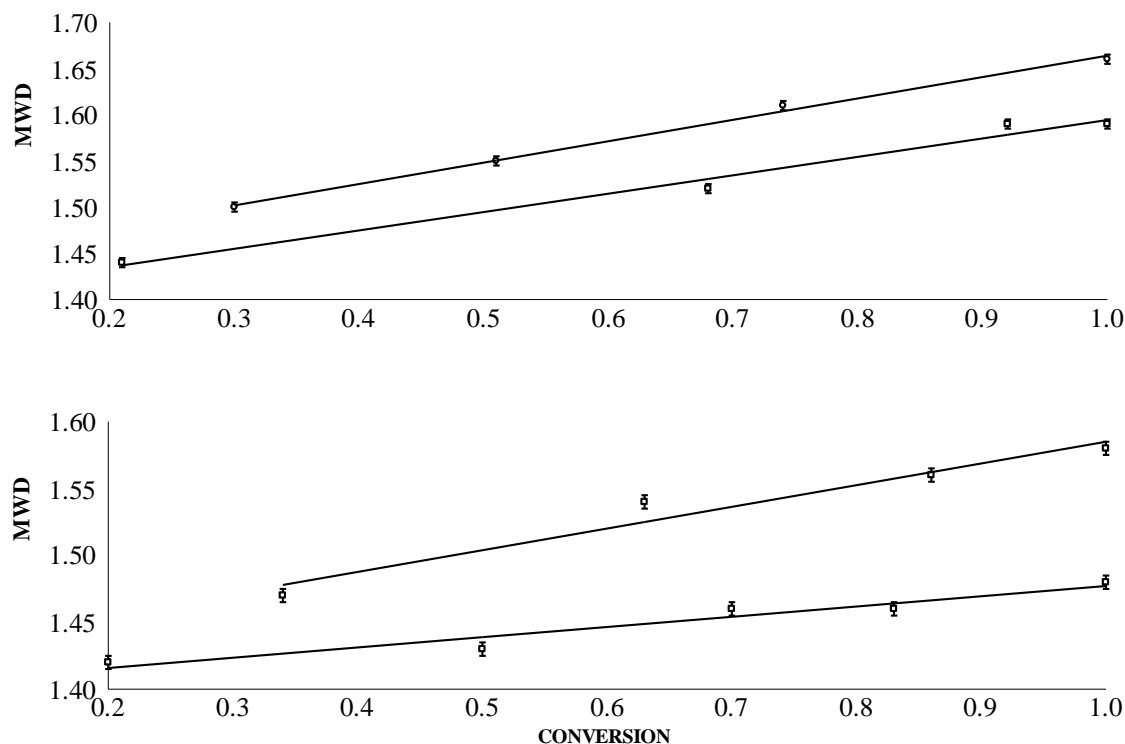


Figure 4.1- 1B: Effects of added ester (BBZ) and [CoI] / [I] on the MWD of poly 4-(ethenyloxy)butyl benzoate polymerized at -20° C in toluene: A [CoI] / [I] = 4.5, [BBZ] = none (a), 10% vol. (b): B [CoI] / [I] = 9.0, [BBZ] = none (a), 10% vol. (b)

The M_n at complete conversion was higher than the theoretical or calculated value but was lower than the M_n observed in the absence of BBZ. Again, the MWD increased with conversion but at 1.59 was lower than the 1.66 observed in the same system in the absence of BBZ. Increasing the coinitiator / initiator ratio to 9.0 resulted in a linear increase in the M_n up to 100% conversion and an MWD of 1.48 still showing an increase with conversion (figure 4.1 – 2). At both coinitiator / initiator ratios the polymerizations developed the now characteristic purple – brown color complex within 3 – 6 hours of initiation by the addition of the EADC.

At 4° C and in the absence of BBZ the increase in the M_n was nonlinear with respect to conversion at coinitiator / initiator ratios of 4.5 and 9.0, respectively. In both cases the M_n was higher than the theoretical or calculated value and the MWD increased with

conversion to 1.69 and 1.63, respectively. The formation of the purple – brown color complex was observed immediately after the addition of the EADC at a coinitorator / initiator ratio of 4.5 and at approximately 30 minutes at a ratio of 9.0 (figure 4.1-3).

With the addition of BBZ to the systems at coinitorator / initiator ratios of 4.5 and 9.0 the increase in the M_n with conversion remained nonlinear and above the theoretical or calculated value but lower than that of the equivalent system in the absence of BBZ. The addition of the BBZ decreased the MWD at both coinitorator / initiator ratios to 1.62 and 1.53, respectively, and the MWD increased with conversion in both cases (figure 4.1-4). The characteristic purple – brown color complex formed within 30 minutes at a coinitorator / initiator ratio of 4.5 and within 90 minutes at a ratio of 9.0.

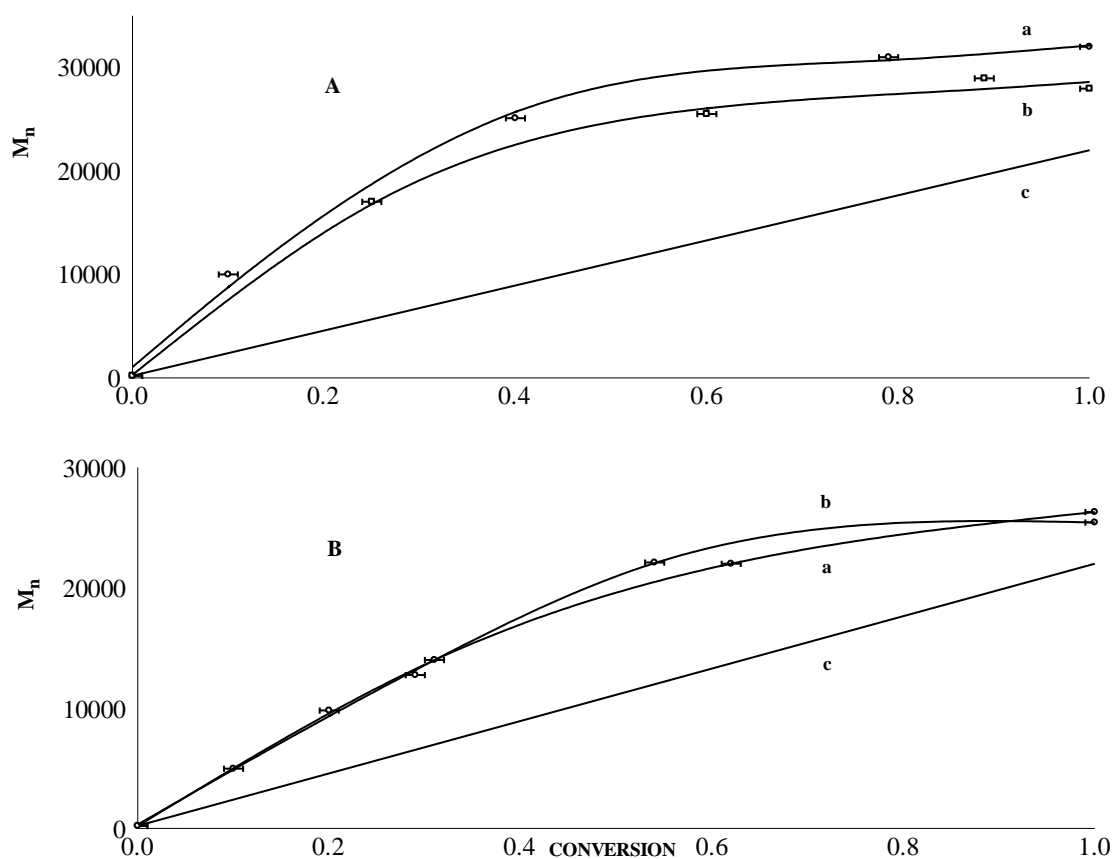


Figure 4.1 -2A: Effects of added ester (bbz) and [CoI] / [I] on the M_n and MWD on the polymerization of 4-(ethenyloxy)butyl benzoate at 4 ° C in toluene : A: [BBZ] = none (a), 10% vol. (b), [CoI] / [I] = 4.5: B: [BBZ] = none (a), 10% vol. (b), [CoI] / [I] = 9.0: [M] = 40.0 mM, [HCl] = 0.25 mM, calculated M_n = 22,000 (c)

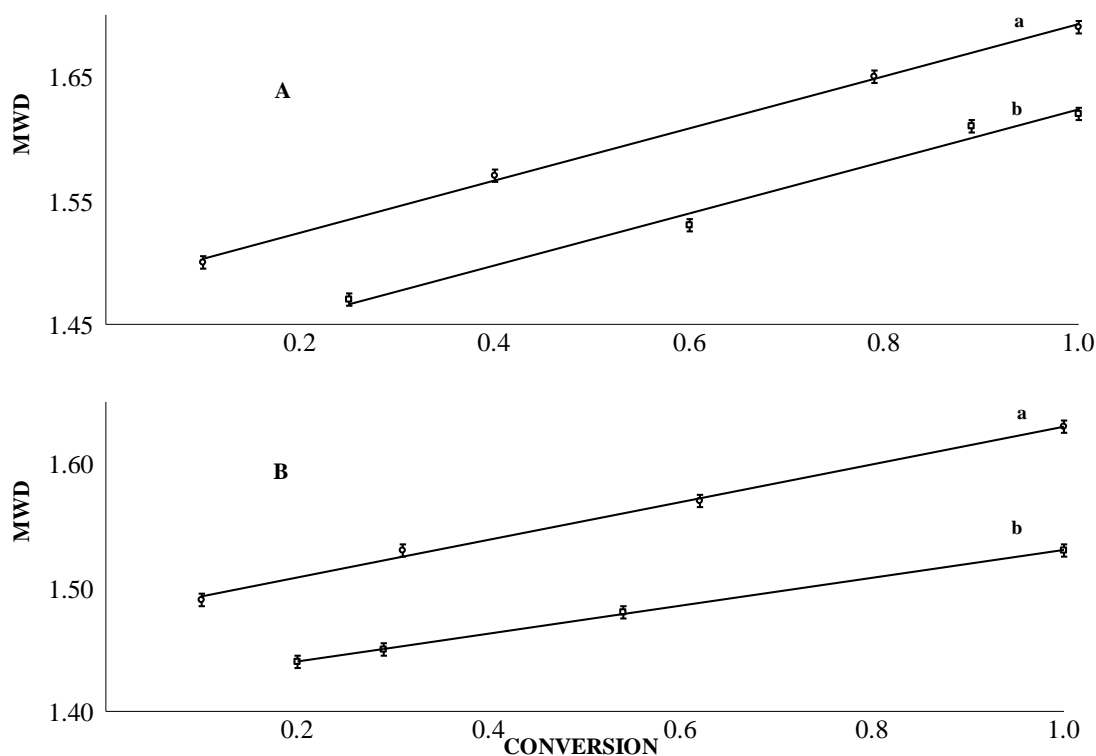


Figure 4.1 -2A: Effects of added ester (bbz) and [CoI] / [I] on the M_n and MWD on the polymerization of 4-(ethenyloxy)butyl benzoate at 4 °C in toluene : A: [BBZ] = none (a), 10% vol. (b), [CoI] / [I] = 4.5; B: [BBZ] = none (a), 10% vol. (b), [CoI] / [I] = 9.0; [M] = 40.0 mM, [HCl] = 0.25 mM, calculated $M_n = 22,000$ (c)

4.2. POLYMERIZATION OF 4-(ETHENYLOXY)BUTYL CHLOROBENZOATES

4-(ethenyloxy)butyl 3 – chlorobenzoate (VOB3CBZ) and 4-(ethenyloxy)butyl 4 – chlorobenzoate (VOB4CBZ) were polymerized following the same investigative format employed for VOBZ. In systems containing externally added esters the ester corresponding to the enchain ester moiety was used, i.e., butyl 3- chlorobenzoate (B3CBZ) with VOB3CBZ and butyl 4- chlorobenzoate (B4CBZ) with VOB4CBZ, respectively. The data from this series of polymerizations is summarized in table 4.2-1.

MONOMER	ESTER	[CoI] / [I]	Mn	MWD	Mn vs Conversion
VOB3CBZ (-20° C)	NONE	4.50	32,100	1.69	NL
	NONE	9.00	30,050	1.65	NL
	B3CBZ	4.50	29,150	1.58	NL
	B3CBZ	9.00	27,850	1.55	L (to \approx 40%)
VOB3CBZ (4° C)	NONE	4.50	33,000	1.72	NL
	NONE	9.00	31,975	1.67	NL
	B3CBZ	4.50	31,650	1.63	NL
	B3CBZ	9.00	3,100	1.60	NL
VOB4CBZ (-20° C)	NONE	4.50	31,750	1.62	NL
	NONE	9.00	29,500	1.55	NL
	B4CBZ	4.50	28,650	1.56	NL
	B4CBZ	9.00	27,000	1.47	L (to \approx 40%)
VOB4CBZ (4° C)	NONE	4.50	33,200	1.60	NL
	NONE	9.00	31,875	1.58	NL
	B4CBZ	4.50	30,450	1.60	NL
	B4CBZ	9.00	29,050	1.50	NL

L = Linear

NL= Nonlinear

Table 4.2-1: Polymerization characteristics of VOB3CBZ and VOB4CBZ in toluene at -20° C and 4°C in the presence and absence of B3CBZ and B4CBZ, respectively, as an added esters: [M] = 25.0 mM, [ESTER] = 10 vol. %, [HCl] = 0.25 mM, calculated Mn = 25,350

In the absence of an externally added ester both VOB3CBZ and VOB4CBZ exhibited a nonlinear increase in the M_n with conversion. At coinitiator / initiator ratios of 4.5 and 9.0 the MWD's were 1.69 and 1.65 for VOB3CBZ and 1.62 and 1.55 for VOB4CBZ, respectively (figure 4.2-1 – a & c and figure 4.2-3 – a & c). In both cases the MWD increased with conversion in the systems and the characteristic purple - brown color complex formed within 30 minutes of initiation by the addition of EADC.

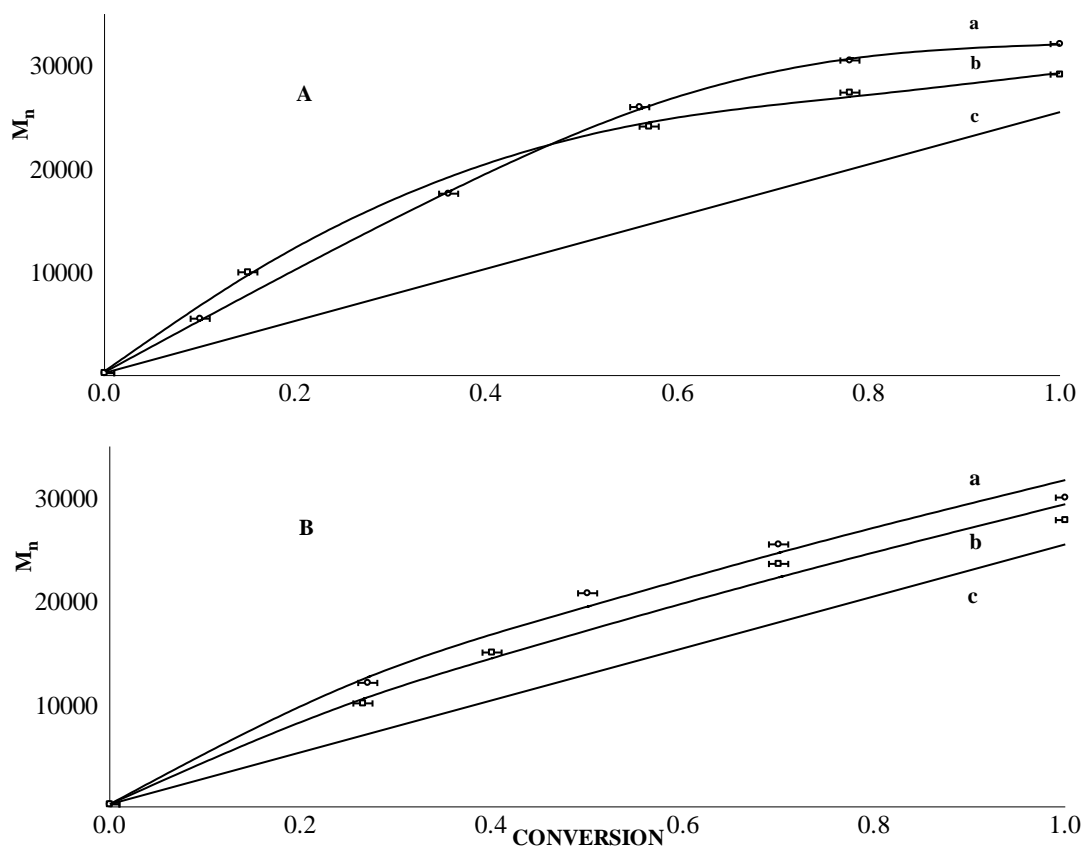


Figure 4.2-1A: Effect of added ester (B3CBZ) and $[CoI] / [I]$ on the M_n of poly - 4-(ethenyloxy)butyl 3-chlorobenzoate polymerized at $-20^\circ C$ in toluene: A: $[CoI] / [I] = 4.5$, [ESTER] = none (a), 10% vol. (b); B: $[CoI] / [I] = 9.0$, [ESTER] = none (a), 10% vol. (b); $[M] = 50.0$ mM, $[HCl] = 0.25$ mM, calculated $M_n = 25,500$ (c)

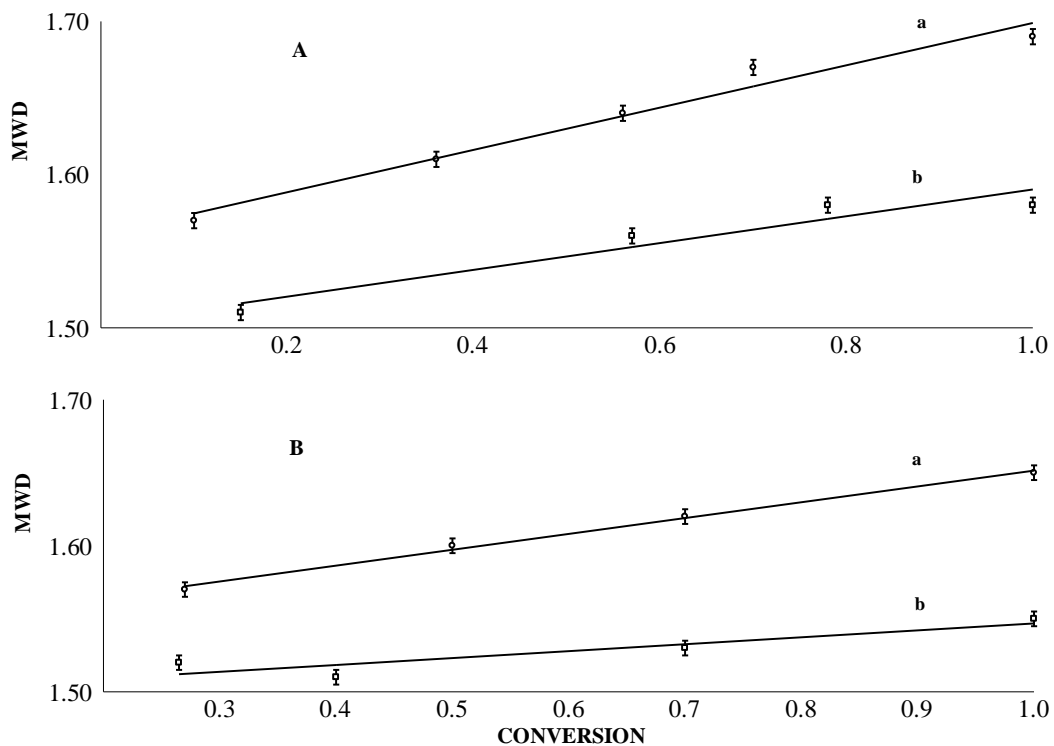


Figure 4.2-1B: Effect of added ester (B3CBZ) and $[CoI] / [I]$ on the MWD of poly - 4-(ethenyloxy)butyl 3-chlorobenzoate polymerized at $-20^\circ C$ in toluene: A: $[CoI] / [I] = 4.5$, [ESTER] = none (a), 10% vol. (b); B: $[CoI] / [I] = 9.0$, [ESTER] = none (a), 10% vol. (b); $[M] = 50.0$ mM, $[HCl] = 0.25$ mM.

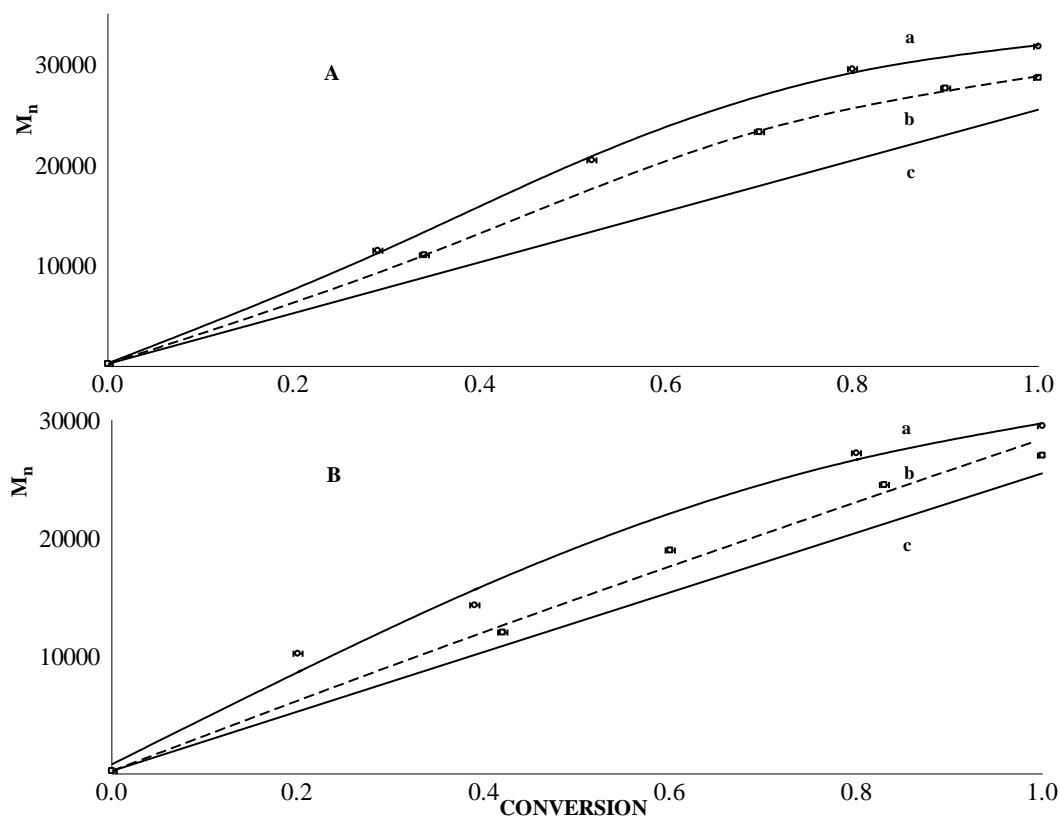


Figure 4.2-3A: Effect of added ester (B4CBZ) and $[\text{CoI}] / [\text{I}]$ on the M_n of poly - 4-(ethenyloxy)butyl 4-chlorobenzoate polymerized at -20°C in toluene: A: $[\text{CoI}] / [\text{I}] = 4.5$, $[\text{ESTER}] = \text{none}$ (a), 10% vol. (b); B: $[\text{CoI}] / [\text{I}] = 9.0$, $[\text{ESTER}] = \text{none}$ (a), 10% vol. (b); $[\text{M}] = 50.0\text{ mM}$, $[\text{HCl}] = 0.25\text{ mM}$, calculated $M_n = 25,500$ (c)

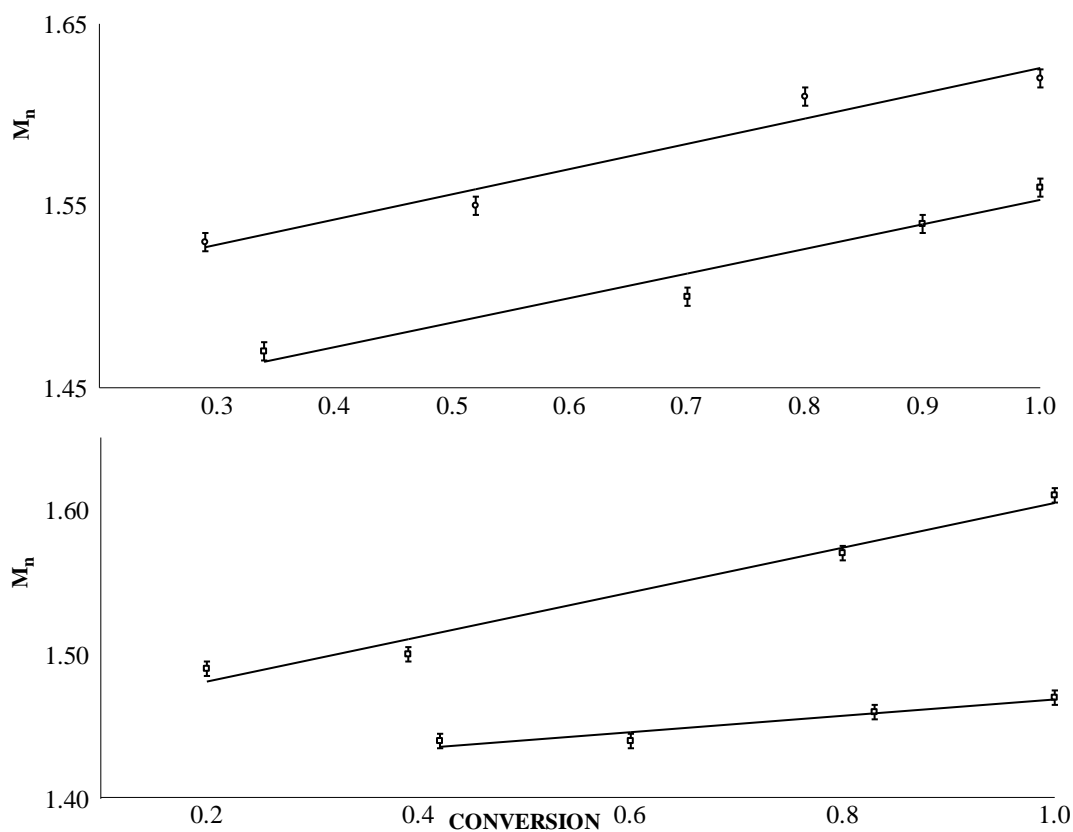


Figure 4.2-3B: Effect of added ester (B4CBZ) and $[\text{CoI}] / [\text{I}]$ on the M_n of poly - 4-(ethenyloxy)butyl 4-chlorobenzoate polymerized at -20°C in toluene: A: $[\text{CoI}] / [\text{I}] = 4.5$, $[\text{ESTER}] = \text{none}$ (a), 10% vol. (b); B: $[\text{CoI}] / [\text{I}] = 9.0$, $[\text{ESTER}] = \text{none}$ (a), 10% vol. (b); $[\text{M}] = 50.0\text{ mM}$, $[\text{HCl}] = 0.25\text{ mM}$.

The corresponding ester was added to each of the individual systems and at -20°C and at a coinitiator / initiator ratio of 4.5 the increase in the M_n was nonlinear with respect to conversion while at a ratio of 9.0 the increase in M_n was linear up to approximately 40% conversion in both systems but deviated at higher conversion with a final M_n higher than the theoretical or calculated value (figure 4.2-1 – b & d and figure 4.2 – 3 – b & d). The MWD of both systems was lower than observed in the equivalent systems without the added ester and increased with conversion as shown in figure 4.2-1B and figure 4.2 – 3B above.

At 4°C and in the absence of an externally added ester both VOB3CBZ and VOB4CBZ polymerized with a nonlinear increase in the M_n with conversion. At coinitiator / initiator ratios of 4.5 and 9.0 the MWD's were 1.72 and 1.67 for VOB3CBZ and 1.60 and 1.58 for VOB4CBZ, respectively (figure 4.2-2 – a & c and figure 4.2-4 – a & c). The MWD increased with conversion in both systems and the characteristic purple - brown color complex formed within 30 minutes of initiation by the addition of EADC.

The corresponding ester was added to each of the individual systems and at 4°C and at coinitiator / initiator ratios of 4.5 and 9.0 the increase in the M_n remained nonlinear with respect to conversion. In both systems the M_n was higher than the theoretical or calculated value (figure 4.2-2 – b & d and figure 4.2 – 4 – b & d). The MWD of both systems was lower than observed in the equivalent systems without the added ester and increased with conversion as shown in figure 4.2-1B and figure 4.2 – 3B above. The characteristic purple - brown complex formed within 40 minutes of initiation by the addition of the EADC.

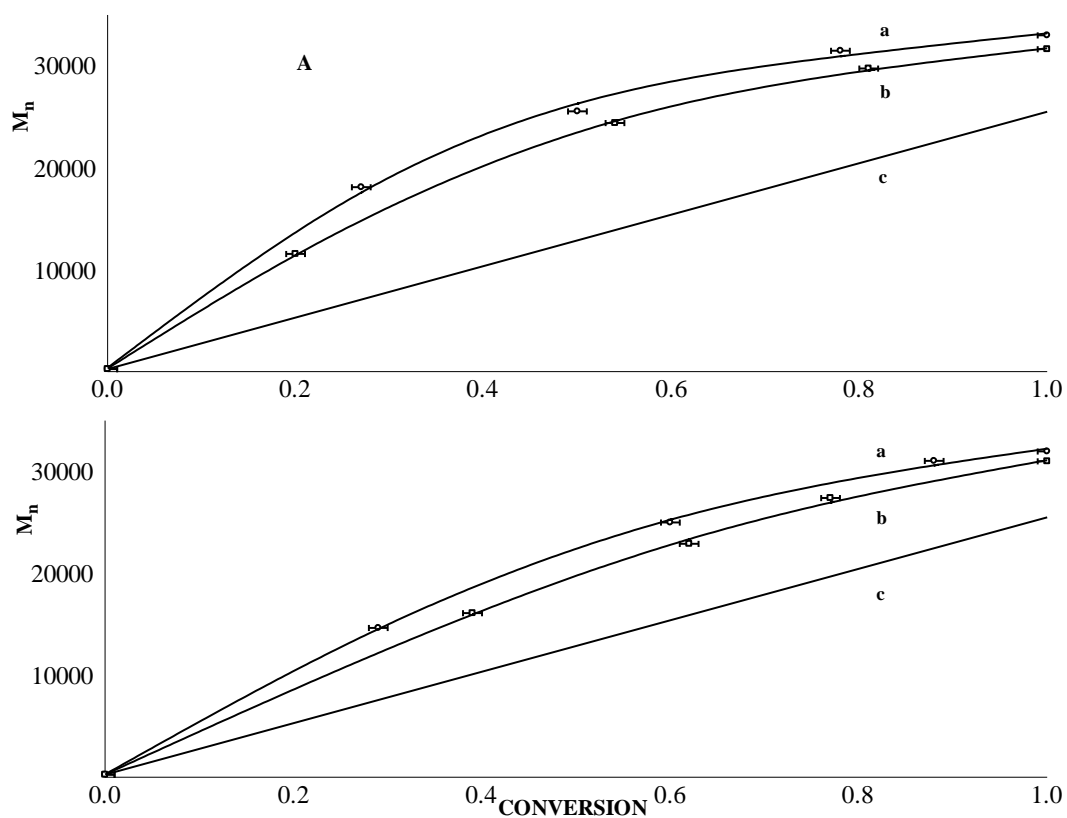


Figure 4.2-2A: Effect of added ester (B3CBZ) and $[CoI] / [I]$ on the M_n of poly - 4-(ethenyloxy)butyl 3-chlorobenzoate polymerized at 4°C in toluene: A: $[CoI] / [I] = 4.5$, [ESTER] = none (a), 10% vol. (b); B: $[CoI] / [I] = 9.0$, [ESTER] = none (a), 10% vol. (b): $[M] = 50.0$ mM, $[HCl] = 0.25$ mM, calculated $M_n = 25,500$ (c)

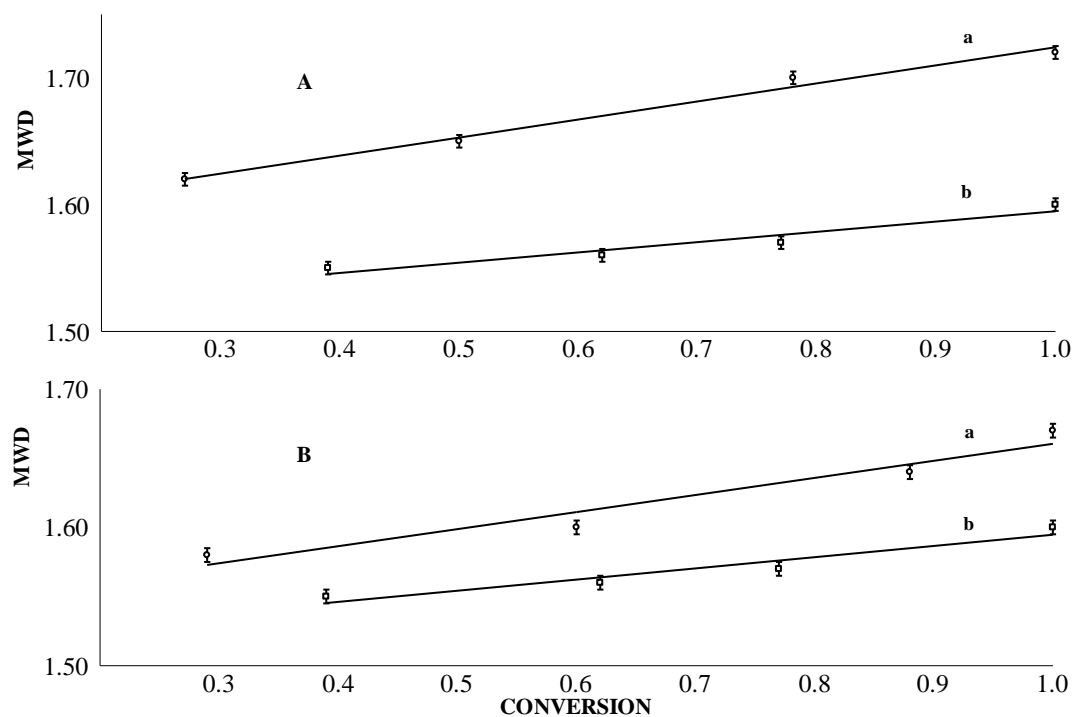


Figure 4.2-2B: Effect of added ester (B3CBZ) and $[CoI] / [I]$ on the MWD of poly - 4-(ethenyloxy)butyl 3-chlorobenzoate polymerized at 4°C in toluene: A: $[CoI] / [I] = 4.5$, [ESTER] = none (a), 10% vol. (b); B: $[CoI] / [I] = 9.0$, [ESTER] = none (a), 10% vol. (b): $[M] = 50.0$ mM, $[HCl] = 0.25$ mM.

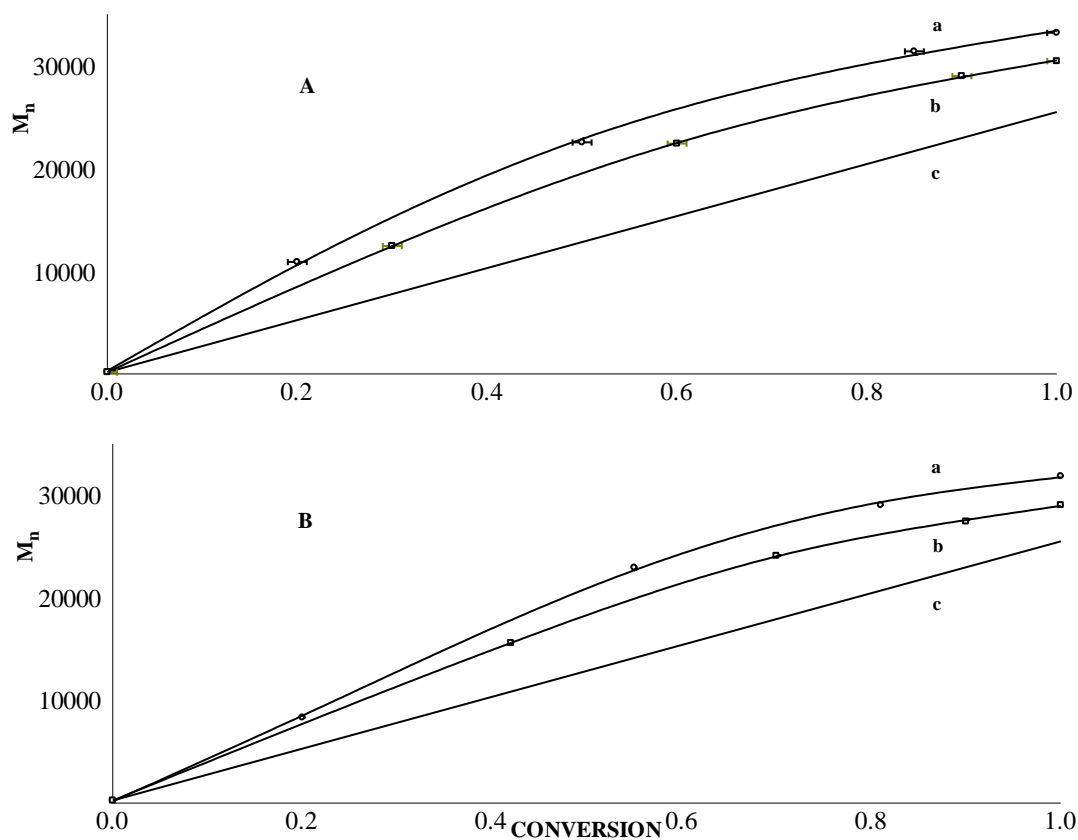


Figure 4.2-4A: Effect of added ester (B4CBZ) and $[CoI] / [I]$ on the M_n of poly-4-(ethenyloxy)butyl 4-chlorobenzoate polymerized at 4° C in toluene: A: $[CoI] / [I] = 4.5$, $[ESTER] = \text{none}$ (a), 10% vol. (b): B: $[CoI] / [I] = 9.0$, $[ESTER] = \text{none}$ (a), 10% vol. (b): $[M] = 50.0 \text{ mM}$, $[HCl] = 0.25 \text{ mM}$.

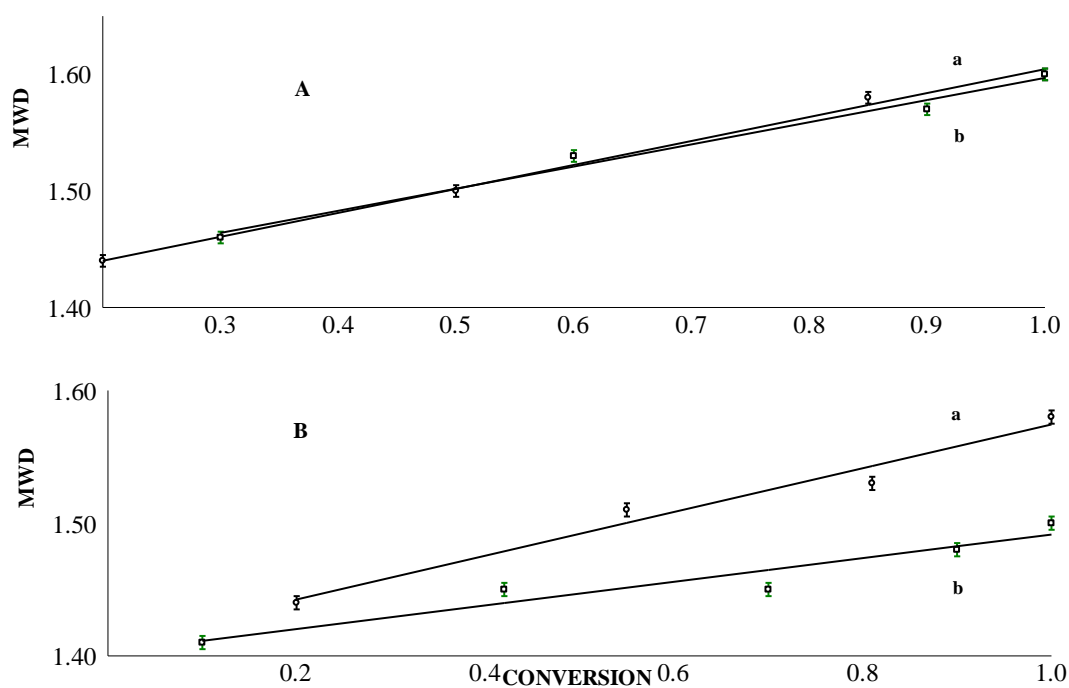


Figure 4.2-4B: Effect of added ester (B4CBZ) and $[CoI] / [I]$ on the MWD of poly-4-(ethenyloxy)butyl 4-chlorobenzoate polymerized at 4° C in toluene: A: $[CoI] / [I] = 4.5$, $[ESTER] = \text{none}$ (a), 10% vol. (b): B: $[CoI] / [I] = 9.0$, $[ESTER] = \text{none}$ (a), 10% vol. (b): $[M] = 50.0 \text{ mM}$, $[HCl] = 0.25 \text{ mM}$.

CHAPTER 5

RESULTS, DISCUSSION AND CONCLUSIONS

5.1 RESULTS & DISCUSSION

As stated earlier the aim of this investigation was to determine to what degree the enchainment of an ester group affects the living character of a polymerization as compared with the equivalent system in which there is no enchainment of ester moiety and the equivalent ester is added separately. A series of analogous systems were polymerized under identical conditions and evaluated in accordance with accepted criteria (section 1.2.4) to determine the degree of “livingness” of each system. The monomers selected for this study were derivatives 4-(ethenyloxy)butane (VOB) with ester moieties attached to the terminal carbon of the butyl side chain. The ester moieties were selected on the basis their basicity as predicted from the pK_a of the conjugate carboxylic acid of the ester (table 5.1-1).

MONOMER	CONJUGATE CARBOXYLIC ACID	pK_a
4-(ETHENYLOXY)BUTANE	NONE	NA
4-(ETHENYLOXY)BUTYL ACETATE	ACETIC ACID	4.756
4-(ETHENYLOXY)BUTYL BENZOATE	BENZOIC ACID	4.204
4-(ETHENYLOXY)BUTYL 4-CHLOROBENZOATE	4 – CHLOROBENZOIC ACID	3.986
3-(ETHENYLOXY)BUTYL 3-CHLOROBENZOATE	3 – CHLOROBENZOIC ACID	2.877
4-(ETHENYLOXY)BUTYL CHLOROACETATE	CHLOROACETIC ACID	1.260
4-(ETHENYLOXY)BUTYL DICHLOROACETATE	DICHLOROACETIC ACID	0.520

Table 5.1 – 1: pK_a values of conjugate acid of enchainment ester groups

The results from the polymerizations of the subject monomer – ester groupings polymerized at -20° and 4° C and a coinitiator / initiator ratio of 9.0 are summarized in tables 5.1 -2 and 5.1 –3, respectively.

SERIES	CALC.		CONV.	MWD	LINEARITY	pKa
	Mn	Mn				
VOB	14500	16055	0.85	2.00	NL	4.756
VOB + EA	18500	16055	1.00	1.36	L	
VOBOAC	26200	25350	1.00	1.48	L	
VOBOAC + EA	25800	25350	1.00	1.40	L	
VOB	14500	16055	0.85	2.00	NL	4.204
VOB + BBZ	17400	16055	1.00	1.45	L	
VOBBZ	24700	22000	1.00	1.58	L (to 0.80)	
VOBBZ + BBZ	24000	22000	1.00	1.48	L	
VOB	14500	16055	0.85	2.00	NL	3.986
VOB + B4CBZ	15700	16055	1.00	1.45	L (to 0.60)	
VOB4CBZ	29500	25500	1.00	1.55	NL	
VOB4CBZ + B4CBZ	27000	25500	1.00	1.47	L (to 0.40)	
VOB	14500	16055	0.85	2.00	NL	3.830
VOB + B3CBZ	15000	16055	1.00	1.66	L (to 0.50)	
VOB3CBZ	30050	25500	1.00	1.65	NL	
VOB3CBZ + B3CBZ	27850	25500	1.00	1.55	L (to 0.40)	
VOB	14500	16055	0.85	2.00	NL	2.867
VOB + ECA	15250	16055	1.00	1.72	NL	
VOBCOAC	34575	30850	1.00	1.66	NL	
VOBCOAC + ECA	35785	30850	1.00	1.62	NL	

Table 5.1-2: Summary of results of polymerization of individual monomer esters combinations showing effects of enchainment and ester basicity on degree of living character of subject vinyl ethers at -20° C in toluene: [I] = HCl, [CoI] = EADC, [ESTER]= 10 vol. %, [CoI] / [I] = 9.0, ester basicity based on pKa of conjugate acid (see table 5.1-1)

SERIES	CALC.		CONV.	MWD	LINEARITY	pKa
	Mn	Mn				
VOB	20000	16055	0.60	2.25	NL	4.756
VOB + EA	23690	16055	1.00	1.49	L (to 0.55)	
VOBOAC	38025	25350	1.00	1.60	NL	
VOBOAC + EA	35000	25350	1.00	1.47	NL	
VOB	20000	16055	0.60	2.25	NL	4.204
VOB + BBZ	19200	16055	1.00	1.45	L (to 0.40)	
VOBBZ	26300	22000	1.00	1.58	NL	
VOBBZ + BBZ	25430	22000	1.00	1.48	NL	
VOB	20000	16055	0.60	2.25	NL	3.986
VOB + B4CBZ	16650	16055	1.00	1.68	NL	
VOB4CBZ	31875	25500	1.00	1.58	NL	
VOB4CBZ + B4CBZ	29050	25500	1.00	1.50	NL	
VOB	20000	16055	0.60	2.25	NL	3.830
VOB + B3CBZ	16700	16055	1.00	1.79	NL	
VOB3CBZ	31975	25500	1.00	1.67	NL	
VOB3CBZ + B3CBZ	31000	25500	1.00	1.60	NL	
VOB	20000	16055	0.60	2.25	NL	2.867
VOB + ECA	27500	16055	1.00	1.72	NL	
VOBCOAC	48000	30850	1.00	1.80	NL	
VOBCOAC + ECA	49050	30850	1.00	1.72	NL	

Table 5.1-3: Summary of results of polymerization of individual monomer esters combinations showing effects of enchainment and ester basicity on degree of living character of subject vinyl ethers at 4° C in toluene: [I] = HCl, [CoI] = EADC, [ESTER]= 10 vol. %, [CoI] / [I] = 9.0, ester basicity based on pKa of conjugate acid (see table 5.1-1)

A review of the data in tables 5.1-2 and 5.1-3 clearly shows that the polymerization of VOB in toluene at -20 and 4° C with a coinitiator / initiator ratio of 9.0 and in the absence of an externally added ester is clearly conventional in nature with a broad MWD, incomplete monomer conversion and a nonlinear increase in the M_n with conversion. The MWD broadens and the conversion decrease with increasing polymerization temperature

at the M_n increases significantly as expected (Matyjaszewski and Sigwalt, 1987, Kennedy and Ivan, 1991, Matyjaszewski, et. al., 2007).

The addition of an ester (electron donor or Lewis base) modifies the system and at -20°C a quasi – living system (Kennedy and Ivan, 1991, Matyjaszewski, et. al., 2007) is obtained with a linear increase in the M_n with conversion, complete conversion of monomer and continued polymerization with the addition of additional monomer at complete conversion. The system is classified as quasi – living rather than ideal living due to the fact that the MWD is greater than 1.1 and bimodal (addressed later in discussion) and the M_n is higher than the theoretical or calculated value based on the $[M] / [I]$ ratio and the assumption that one active chain is formed per initiator unit.

At 4°C the system is not quasi – living but does exhibit a significant degree of living character. The MWD is broader (1.49 versus 1.36) and the M_n increases linearly up to approximately 0.55 (55%) but deviates at higher conversion with a significantly higher M_n at complete conversion, i. e., 23,690 versus 18,500 at -20°C . Although clearly not a quasi – living system the system is not conventional and exhibits a significant degree of living character.

In VOBOAC the “molecular equivalent” of the externally added ester (EA) has been incorporated in the butyl side chain of the VOB. In theory, the polymerization of the VOBOAC should exhibit the same polymerization characteristics as that of the VOB with added EA since in both cases there is an alkyl vinyl ether monomer and an ester with all other conditions and reactants being identical. Further, since the monomer contains a single ester moiety per monomer unit the ester concentration of the two systems is also

maintained at the same level by adjusting the polymerization solvent volumes thus maintaining the monomer (and ester moiety) concentration at 10% by volume.

As the data in table 5.1-2 shows the polymerization of VOBOAC in the absence of an externally added ester is not a quasi – living system. There is an increase in the MWD from 1.36 to 1.48 and the increase in the M_n is nonlinear with respect to conversion above ≈ 0.70 (70%). The M_n in this case is in good agreement with the theoretical or calculated value whereas in the VOB system with externally added ester the M_n lower than the theoretical or calculated value.

With the external addition of EA at a concentration of 10% by volume the polymerization returns to a quasi – living state with the MWD very close to that of the original system (1.40 versus 1.36), a linear increase in the M_n with conversion, complete monomer conversion and a final M_n in good agreement with the theoretical or calculated M_n based on the $[M] / [I]$ ratio.

This series of polymerizations was repeated at a coinitiator / initiator ratio of 4.5 and at 4° C at coinitiator / initiator ratios of 4.5 and 9.0, respectively. A summary of the data for the polymerizations of the VOB, EA / VOBOAC / VOBOAC, EA is given in tables 5.1-2 through 5.1-5. The data from these additional polymerizations is consistent with the data from the first series. At lower coinitiator / initiator ratios and with increased polymerization temperature the degree of living character in the system decreases.

SERIES	CALC.		CONV.	MWD	LINEARITY	pKa
	Mn	Mn				
VOB	15200	16055	0.75	2.12	NL (IC)	4.756
VOB + EA	15200	16055	1.00	1.50	L (to 0.60)	
VOBOAC	28000	25350	1.00	1.57	NL	
VOBOAC + EA	23000	25350	1.00	1.50	NL	
VOB	15200	16055	0.75	2.12	NL (IC)	4.204
VOB + BBZ	15800	16055	1.00	1.50	L (to 0.50)	
VOBBZ	30300	22000	1.00	1.66	NL	
VOBBZ + BBZ	25300	22000	1.00	1.59	NL	
VOB	15200	16055	0.75	2.12	NL (IC)	3.986
VOB + B4CBZ	15300	16055	1.00	1.52	NL	
VOB4CBZ	31750	25500	1.00	1.62	NL	
VOB4CBZ + B4CBZ	28650	25500	1.00	1.56	NL	
VOB	15200	16055	0.75	2.12	NL	3.830
VOB + B3CBZ	15650	16055	1.00	1.55	NL	
VOB3CBZ	32100	25500	1.00	1.69	NL	
VOB3CBZ + B3CBZ	29150	25500	1.00	1.58	NL	
VOB	15200	16055	0.75	2.12	NL	2.867
VOB + ECA	18000	16055	1.00	1.80	NL	
VOBCOAC	36150	30850	1.00	1.78	NL	
VOBCOAC + ECA	36750	30850	1.00	1.74	NL	

Table 5.1-4: Summary of results of polymerization of individual monomer esters combinations showing effects of enchainment and ester basicity on degree of living character of subject vinyl ethers at-20° C in toluene: [I] = HCl, [CoI] = EADC, [ESTER]= 10 vol. %, [CoI] / [I] = 4.5, ester basicity based on pKa of conjugate acid (see table 5.1-1)

SERIES	CALC.		CONV.	MWD	LINEARITY	pKa
	Mn	Mn				
VOB	25700	16055	0.60	2.34	NL	4.756
VOB + EA	40000	16055	1.00	1.55	NL	
VOBOAC	55700	25350	1.00	1.80	NL	
VOBOAC + EA	47900	25350	1.00	1.53	NL	
VOB	25700	16055	0.60	2.34	NL	4.204
VOB + BBZ	23350	16055	1.00	1.60	NL	
VOBBZ	32000	22000	1.00	1.69	NL	
VOBBZ + BBZ	27950	22000	1.00	1.62	NL	
VOB	25700	16055	0.60	2.34	NL	3.986
VOB + B4CBZ	17350	16055	1.00	1.75	NL	
VOB4CBZ	33200	25500	1.00	1.60	NL	
VOB4CBZ + B4CBZ	30450	25500	1.00	1.60	NL	
VOB	25700	16055	0.60	2.34	NL	3.830
VOB + B3CBZ	17225	16055	1.00	1.77	NL	
VOB3CBZ	33000	25500	1.00	1.72	NL	
VOB3CBZ + B3CBZ	31650	25500	1.00	1.63	NL	
VOB	25700	16055	0.60	2.34	NL	2.867
VOB + ECA	35000	16055	1.00	1.72	NL	
VOBCOAC	61050	30850	1.00	1.88	NL	
VOBCOAC + ECA	58550	30850	1.00	1.83	NL	

Table 5.1-5: Summary of results of polymerization of individual monomer esters combinations showing effects of enchainment and ester basicity on degree of living character of subject vinyl ethers at 4° C in toluene: [I] = HCl, [CoI] = EADC, [ESTER]= 10 vol. %, [CoI] / [I] = 4.5, ester basicity based on pKa of conjugate acid (see table 5.1-1)

Subsequent polymerizations of analogous series of the monomers listed in table 5.1-1 were carried out following the same investigative strategy as was followed for the VOB, EA / VOBOAC / VOBOAC, EA system. Again, the data from these series are summarized

tables 5.1 -2 through 5.1-5 for the polymerizations of the subject monomers at coinitorator / initiator ratios of 4.5 and 9.0 at -20 and 4° C, respectively.

The data from the polymerization of the subject monomers is consistent with that of the VOB, EA / VOBOAC / VOBOAC, EA system. In each case the living character of the system containing only the enchaind ester moiety is less than that of the VOB system with the corresponding ester added separately.

In the polymerization of VOB with externally added esters the degree of living character varies directly with the basicity of the added ester. The comparative strength or basicity of the individual esters is judged on the basis of the pK_a of the conjugate carboxylic acid of the ester (table 5.1-1). It has been determined by a number of investigators (Aoshima, et. al., 1986, Matyjaszewski and Stigwald, 1987, Kennedy and Ivan, 1991, Matyjaszewski, et. al., 2007) that the strength or basicity of an added ester is a critical factor in the development of living carbocationic systems.

In the polymerizations of the subject monomers the dependence of the degree of living character varies directly with the basicity of the ester whether enchaind or added externally. Systems containing more basic esters (higher conjugate acid pK_a 's), in general, had lower MWD's, higher conversion, more linearity in the increase in the M_n with conversion and in the case of EA and BBZ, quasi – living systems were obtained.

The relationship of the conjugate pK_a to the MWD for the subject monomers / ester combinations coinitorator / initiator ratio of 9.0 and 4.5 at -20 and 4° C are show in figures 5.1-1 and 5.1-2, respectively.

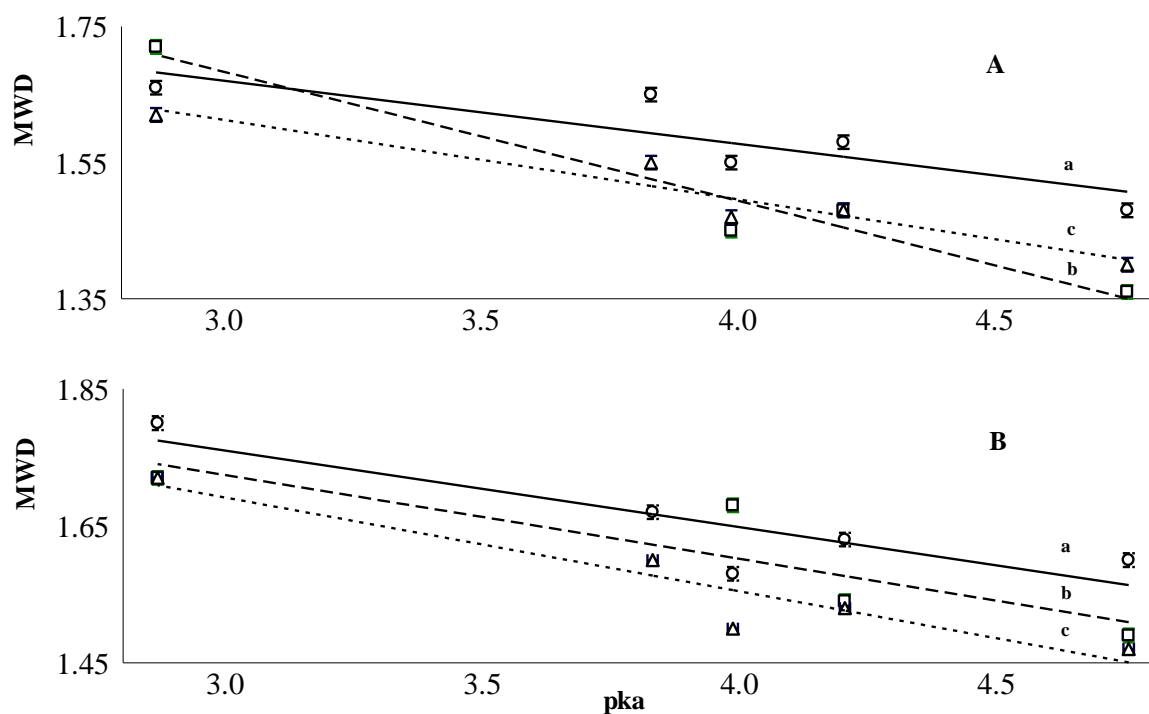


Figure 5.1 -1: Variation in the MWD with pKa of added and / or enchain ester moiety in polymerization of 4-(ethenyloxy)butane derivatives in toluene with [CoI] / [I] = 9.0 at (A) -20 °C and (B) 4 °C: a = enchain ester alone, b = externally added ester, c = enchain ester with externally added ester

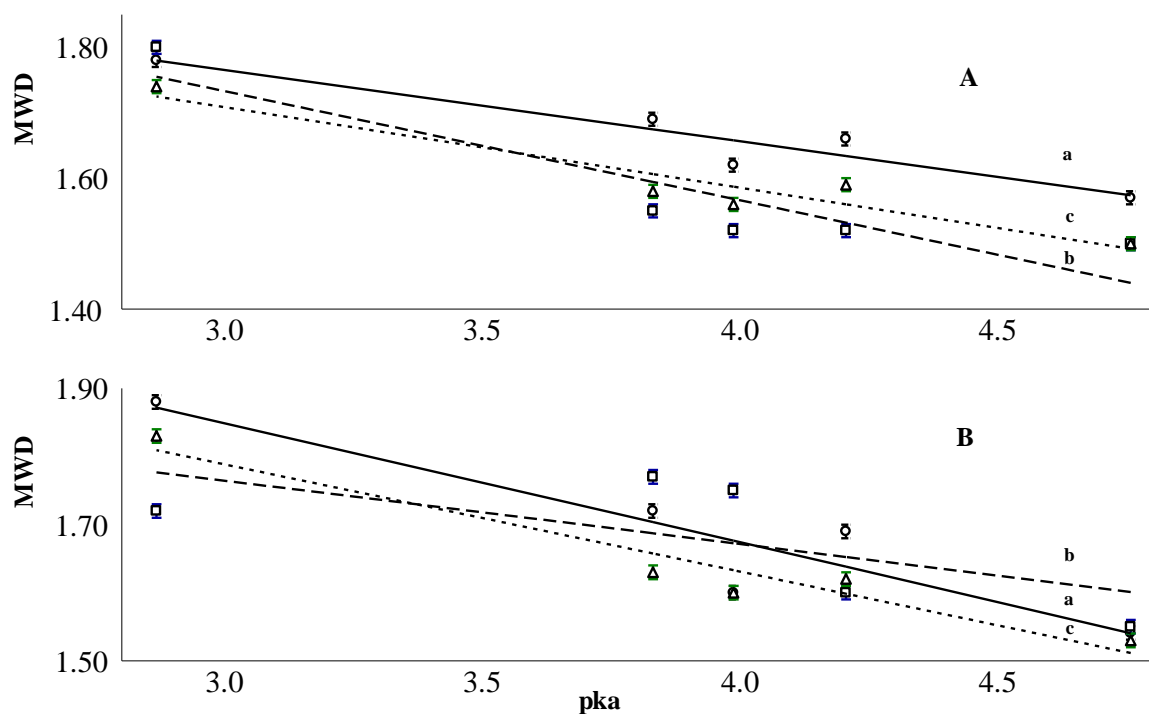


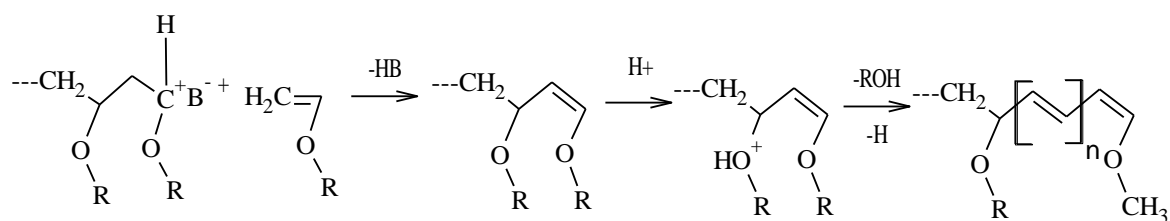
Figure 5.1 -2: Variation in the MWD with pKa of added and / or enchain ester moiety in polymerization of 4-(ethenyloxy)butane derivatives in toluene with [CoI] / [I] = 4.5 at (A) -20 °C and (B) 4 °C: a = enchain ester alone, b = externally added ester, c = enchain ester with externally added ester

Clearly, the MWD varies inversely and linearly with pK_a of the ester and / or ester moiety. Also, the enchain ester moiety (“a” in each case) is less effective in controlling the MWD than the is the corresponding externally added ester or the combination of the externally added and enchain moiety (“b” and “c”), respectively

5.1.2 COLOR COMPLEX FORMATION

As noted (Chapter 4) a deep purple – brown color complex formed in all of the polymerization mixtures irrespective of the temperature, coinitorator / initiator ratio and / or the presence or absence of an added ester. Due to the fact that the formation of the color complex was progressive it was not possible to determine the specific rates of coloration. It was possible, however to determine that in general the rate of coloration varied directly with the polymerization temperature and inversely with the basicity of the enchain ester moiety or externally added ester.

The formation of the color complex has been noted in the literature and has been attributed to the extensive occurrence of chain transfer and termination resulting in the formation of conjugated olefin termini (Aoshima, S. and Higashimura, T., 1984). The formation of the color complex has been studied and a mechanism was proposed by Jagur – Grodzinski, et. al.(2005), as shown in scheme 5.1.



Scheme 5.1: Proposed mechanism for the formation of conjugated olefin termini with possible generation of cationogen / protogen

When the conjugated polyenes (scheme 5.1) are protonated (acidified) the UV – visible absorption exhibits a large bathochromic shift to the visible range (Hafner, K. and Pelster, 1961). This bathochromic shift is reportedly responsible for the observed yellow – green to dark violet coloration of the subject polymerization systems. Further, upon re – neutralization of the color decreases in intensity and the absorption maximum decreases, i. e., the process is reversible.

In the polymerization of 2-chloroethyl vinyl ether (CEVE), Aoshima and Higashimura studied the structure of the highly colored oligomers and noted that in general the coloration occurred in the lower molecular weight oligomers and had a refined structure with an absorption maximum of 200 – 400 nm (yellow). As the molecular weight increased the color intensity increased with an absorption maximum of 500 – 700 nm (purple). The UV –VIS spectra of a non – quenched sample of a polymerization mixture of VOB was isolated in an oven dried, nitrogen purged quartz cuvette measured (figure 5.2). The spectra clearly shows that the color complex exhibits a significant degree of stability that there is an observable absorbance peak at approximately 750 nm.

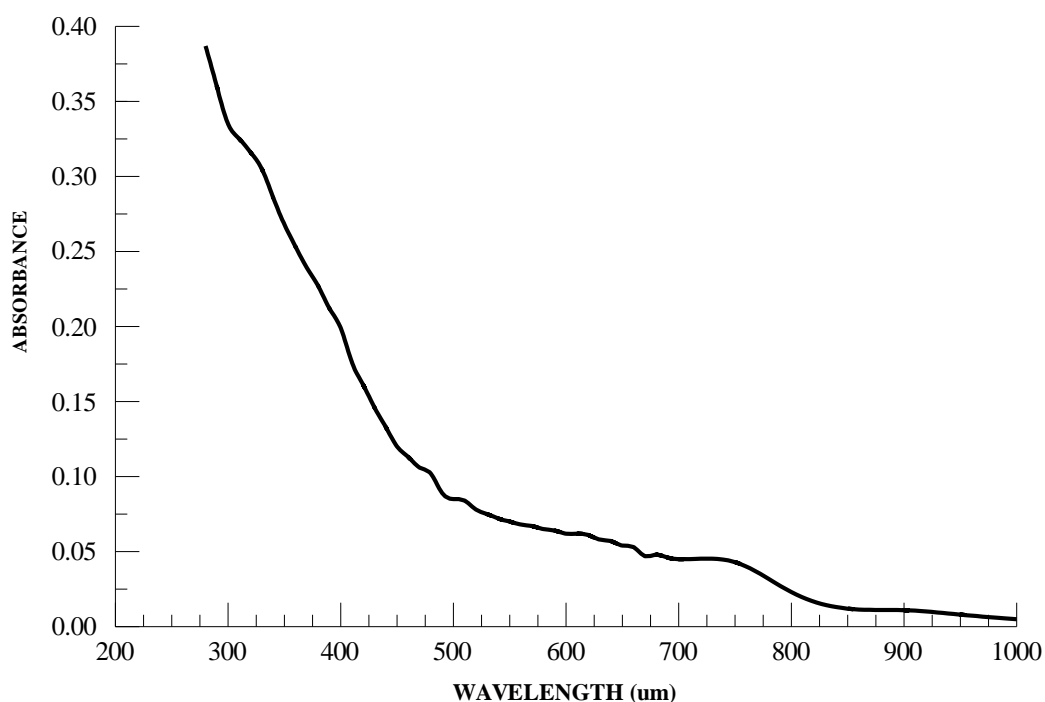


Figure 5.2 -1: UV - VIS spectrum of color complex formed in the polymerization of VOBZ at -20 °C in toluene: [VOBBZ] = 40.0 mM, [EADC] = 2.25 mM, [HCl] = 0.25 mM, [CoI] / [I] = 9.0

The NMR spectra of the isolated polyenes showed the characteristic trans – 1 – alkoxy – 1,3 – butadiene slit peaks in the $\delta = 5 - 7$ region together with the ethane proton at $\delta = 4.9 - 5.1$ attributed to the acetal end cap generated by the methanol added to quench the polymerization reaction.

All of the subject polymerization systems discolored with conversion and the intensity of the observed color varied directly with the basicity of the ester whether added or enchainned. The rate of the increase in the color intensity increased with temperature and in all cases the initial color was light yellow or amber changing to a deep brownish – purple with time / conversion. These observations are consistent with the findings of Aoshima and Higashimura and are indicative of the formation of the trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups indicating that chain transfer and /or termination did occur.

The H NMR spectra from the polymerization of VOB in the absence (A) and presence (B) of an externally added ester BA and VOBZ in the absence of an externally added ester are shown in figures 5.1.2 -1 and 5.1.2-2, respectively. The polymerization of VOB in the absence of an externally added ester was clearly conventional in nature (section 5.1) and the H NMR confirms the presence of trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups confirming that chain transfer and /or termination did occur. With the addition of BA as an externally added ester the polymerization of VOB was controlled in nature. In this instance the H NMR again confirms the presence of the trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups but at a greatly reduced concentration (figure 5.1.2 – 1B). In this case chain transfer and / or termination was present but either occurred at a level that was sufficiently low thereby allowing the

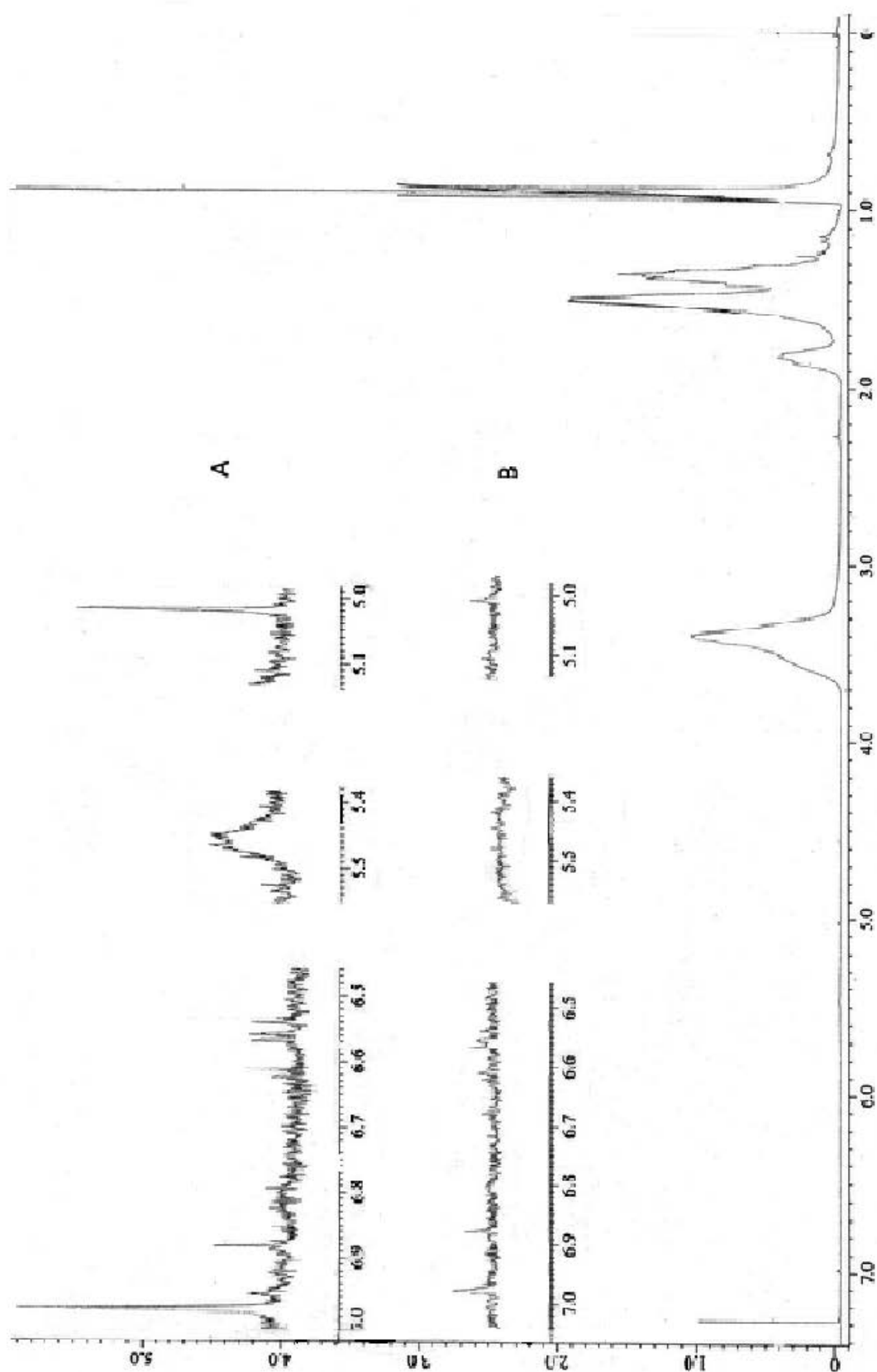


Figure 5.1.2-1: Proton NMR spectrum of poly-4-(ethyloxy)butane polymerized at 4°C in toluene (A) without the addition of an ester and (B) with butyl acetate: $[I] = HCl$, $[Co] = EADC$.

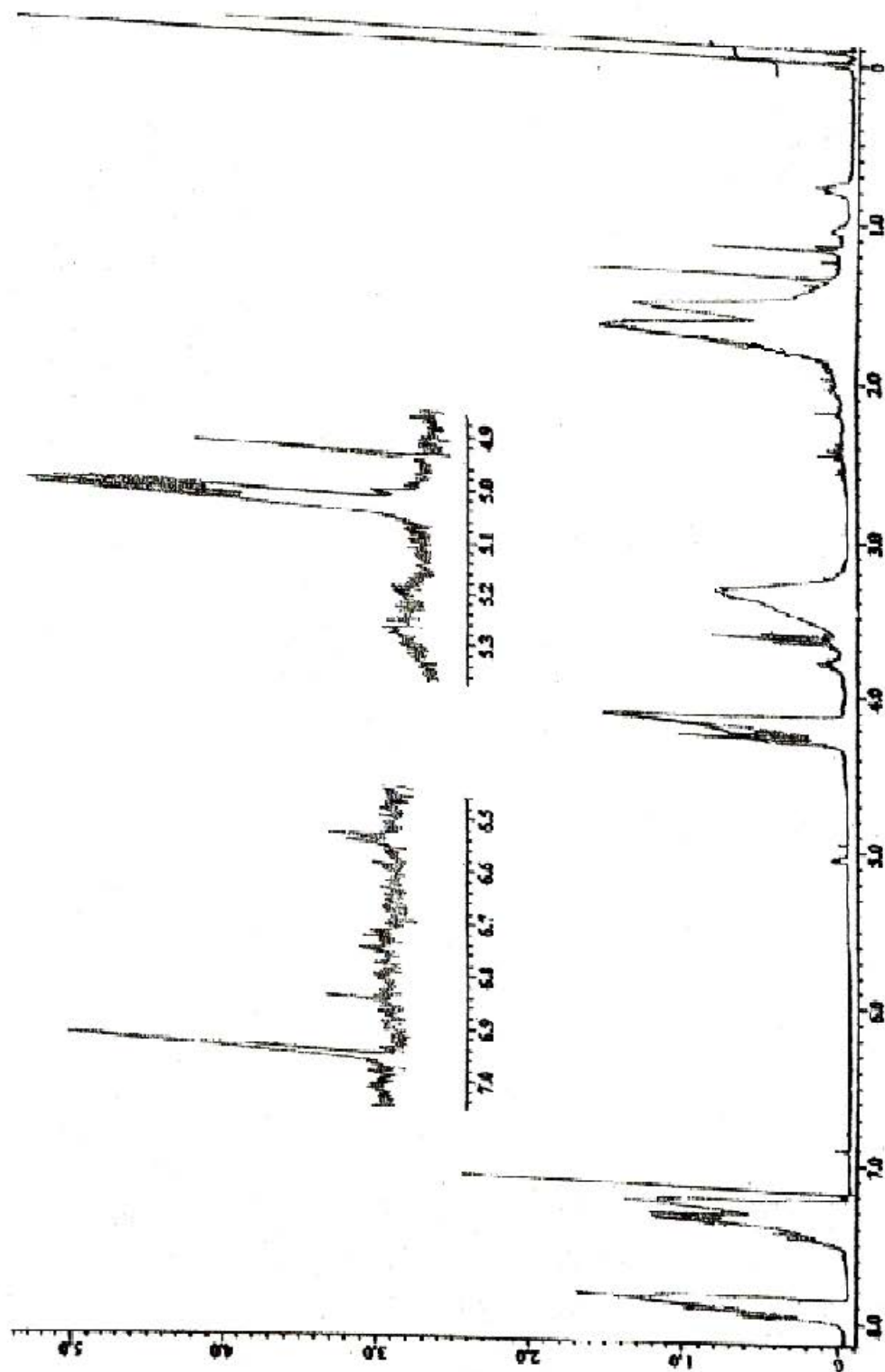


Figure 5.1.2-2: Proton NMR spectrum of poly-4-(ethyloxy)butyl benzoate polymerized at 47°C in toluene in the absence of an externally added ester: $[I] = HCl$, $[Co] = EADIC$.

polymerization to proceed as a controlled polymerization or the chain transfer and / or termination reactions were reversible and faster than propagation.

VOBBZ, a vinyl ether with an ester (benzoate) moiety enchainned at the terminal carbon of the side chain was polymerized under the same conditions and the system was conventional in nature but exhibited a considerable degree of living character and the previously described color change was observed. The ¹H NMR again confirmed the presence of the trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups indicating that chain transfer and / or termination reactions had occurred (figure 5.1.2 -2). The conjugated polyene concentration in this case was greater than that of the VOB in the presence of an added ester and slightly lower than that of the VOB in the absence of an externally added ester.

In each of the above systems the color complex was destroyed by the addition of an ammoniacal methanol solution (quenching agent) reverting back to a yellow to amber solution. The addition of the ammoniacal methanol deprotonates the conjugated polyene and reacidification regenerated the dark brownish – purple. This is again consistent with the Aoshima and Higashimura finds and is yet further evidence in support of the formation of the trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups indicating that chain transfer and / or termination reactions occurred.

From the experimental observations it is clear that the addition of an externally added ester may induce or create a living or controlled polymerization system. Further, it is clear that the enchainment of an ester moiety in the side chain of the vinyl ether is less effective in achieving a living or controlled system. In the polymerization of VOB the externally added ester induced a converted a conventional polymerization system into a controlled

system while an enchainment ester moiety, while increasing the living or controlled character of the system was not able to do so.

In all of the experimental polymerization systems as well as in those studied by Aoshima and Higashimura the initial system color was a light yellow which progressively darkened and changed to a brownish – purple or violet with conversion. When neutralized with a base the system color returns to a yellow rather than the initial clear or colorless system suggesting that yellow color may not be entirely attributable to the formation of trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups.

The formation of colored complexes and color changes with reaction progress have been cited in the literature as for example in the living polymerization of styrene in THF using a sodium naphthalenide initiator (Swarc, M., Levy, M. and Milkovich 1956). In this example the sodium naphthalenide anion is green in color and reacts with the styrene monomer to form the red styryl anion.

In a separate and limited series of experiments it was determined that the yellow color complex may be, at least in some systems, attributable to an interaction of a number of the polymerization system components and not entirely the result of the formation of the trans – 1 – alkoxy – 1,3 – butadiene (conjugated polyene) end groups from transfer and / or termination reactions. This conclusion is supported by the data in table 5.1.2-1 which shows that color complexes are in fact generated by combinations and interactions of a number of components of the polymerization system. The data also shows that (1) the ester may be, in some undefined manner, involved in the formation of the color complex and / or (2) that the EADC may form a color complex with the solvent.

SOLVENT	EADC	IBVE-OAC	EA	0 hrs	6 hrs	24 hrs	48 hrs
Toluene	50 μ l			bright yellow	yellow green	yellow green	green
Toluene	50 μ l	50 μ l		light yellow	light yellow	yellow	yellow
Toluene	50 μ l	50 μ l	50 μ l	clear	clear	clear	light yellow
Toluene	50 μ l		50 μ l	clear	clear	clear	clear
DCM	50 μ l			yellow orange	dark orange	dark amber	brown
DCM	50 μ l	50 μ l		yellow	yellow orange	orange brown	brown
DCM	50 μ l	50 μ l	50 μ l	yellow	yellow	light brown	brown
DCM	50 μ l		50 μ l	clear	clear	clear	clear

Table 5.1.2-1: Formation of color complexes at 4° C in mixtures of various polymerization components: EADC = 25.0 wt. % in toluene, IBVE-OAC = 0.0002M in toluene.

*** prechilled components added to oven dried vials using dry syringe technique, vials stored at 4° C and visually evaluated.

Complicating the situation is the fact that in the in the polymerization of CEVE using the same initiator system as was used for VOB no color complex formation was observed for the CEVE system at full conversion while a deeply purple – brown colored complex formed after 4 – 5 hours in the VOB system (see discussion on molecular weight distributions).

The formation of the color complex in the subject polymerizations does support the conclusion that transfer and /or termination reactions are present in the subject systems. This conclusion is supported by the broader than ideal MWD's, higher than theoretical or

calculated M_n 's and nonlinear increase in the M_n with conversion. The transfer / termination is more pronounced at 4° C than at -20° C and more pronounced in the absence of externally added ester and in systems with enchain esters alone.

5.1.3 MOLECULAR WEIGHT DISTRIBUTIONS

Of all of the systems investigated only five were actually living or controlled systems. The VOB / EA, VOBOAC, VOBOAC / EA, VOB / BBZ and VOBBZ / BBZ at -20° C and a coinitiator / initiator ratio of 9.0, all achieved complete monomer conversion, had M_n 's slightly above the theoretical or calculated value based on the $[M] / [I]$ ratio and exhibited a linear increase in the M_n with conversion. Also, at complete conversion the addition of fresh monomer to each of these systems resulted in the continuation of polymerization at approximately the same rate with full conversion of the added monomer and a linear increase in the M_n with conversion.

Obviously, these systems are living or controlled and exhibit all of the requisite diagnostic criteria with the exception of diagnostic criterion 5:

“Narrow molecular weight distribution polymers are produced”

As stated in section 1.2.4, this is not a critical diagnostic criterion (Quirk, R. and Lee, 1992, Kennedy, J. and Ivan, B., 1991, Matyjaszewski, K., 1996) and systems producing polymers with an MWD > 1.1 (Poisson distribution) are not necessarily nonliving just as systems producing polymers with a narrow MWD are not necessarily living (as discussed in section 1.2.4). Traditionally, living systems with MWD values of 1.15 to 1.25 are

reported as “narrow” and values above ≈ 1.35 are commonly referred to as “relatively broad” although there is a great deal of variation from author to author.

It is also worth noting that most investigators commonly calculate molecular weights and subsequently MWD's on the basis of SEC measurements using (nearly) monodisperse polymers, often polystyrene, as standards. Generally, a refractive index (RI) detector is used but ultraviolet (UV) detectors are also acceptable in most instances. It has also been noted (Matyjaszewski and Stigwalt, 1987, Snyder, et. al., 1997, Matyjaszewski, et. al., 1996, Jagur and Grodzinski, 2005) that many investigators determine molecular weights and MWD's using precipitated or otherwise purified samples where very low and / or very high molecular weight fractions may be removed. In the current study the M_n and MWD data was obtained using the RI and UV detectors for the analysis of polymer samples that were not precipitated or purified. In the current study the five systems classified as living or controlled produced polymers with MWD's of ≈ 1.35 to 1.48 with the values determined by time slice integration of SEC curves based on a 15 point polystyrene calibration curve utilizing the IR.

As noted in section 3.1 the SEC curve for the VOB / EA system at 4° C and coininitiator / initiator ratios of 4.5 and 9.0 were conventional in nature with MWD's of 1.55 and 1.49, respectively. At a coininitiator / initiator ratio of 4.5 the increase in the M_n was nonlinear and while at 9.0 it was linear up to approximately 55% conversion and both systems achieved complete conversion. The SEC chromatograms for both systems were bimodal at lower conversion with the bimodality decreasing and finally disappearing as the conversion reached 70 – 85% for the coininitiator / initiator ratios of 9.0 and 4.5, respectively.

It was first thought that the bimodality might be attributable to contamination and or the introduction of adventitious water due to errors in reactant purification or procedural errors. Consequently, the polymerizations were repeated using freshly prepared and standardized initiator and coinitiator solutions and freshly distilled VOB, EA and toluene. Additionally, a second monomer, 2 – chloroethyl vinyl ether (CEVE), previously shown to a living system under the same conditions was also polymerized (as an internal standard to identify errors in the purification and / or polymerization procedures).

The polymers for the VOB systems at both coinitiator / initiator ratios of 4.5 and 9.0 were again bimodal with an MWD's of 1.57 and 1.49, respectively. The M_n 's were significantly higher than the theoretical or calculated value (tables 5.1 – 3 & 5.1-5). Also the CEVE was not bimodal and was a living system with an MWD of 1.28 and a linear increase in the M_n with conversion and a final value of 16,800 (theoretical or calculated value = 16,000). Based on the experimental data it clear that the observed bimodality in these systems was not caused by any contamination or procedural errors and was therefore attributable to either (1) the presence of more than one active species or (2) slow exchange between ions and ion pairs of different activities (Schultz, G. V., 1973, Figini, R. V., 1967).

The exchange between ions and ion pairs of different activities has been analyzed in ionic systems and the broadening of polydispersities was used for the dynamics of the the exchange (Schultz, G. V., 1973, Figini, R. V., 1967). When the exchange becomes slower, as in the case of aggregates of ion pairs, polydispersities increase and distribution may become bimodal (Aoshima, S., Hasegawa, O. and Higashimura, T. 1985).

In the VOB polymerization systems at -20°C with coinitiator / initiator ratios of 4.5 and 9.0 no bimodal distributions were observed and the MWD's varied from 1.50 – 1.80 and

1.36 – 1.72, respectively, and in the five living or controlled systems the MWD's varied from 1.36 – 1.48 (tables 5.1-5 & 5.1-3). The higher than expected MWD's in these systems may be attributed to termination, as supported by the formation of a colored complex and the presence of conjugated polyene end groups (section 5.1.2) and the higher than theoretical or calculated M_n 's (table 5.1-2) and / or slow exchange (Matyjaszewski, K. 1996, Aoshima, S., Hasegawa, O. and Higashimura, T. 1985). The remaining systems polymerized at -20° C were conventional in nature. Only the systems with the esters having the highest pKa (EA and BBZ) either enchainned, externally added and / or in combination exhibited living or controlled characteristics and in the remaining systems the degree of livingness decreased with the decrease in the pKa of the ester added to the system and / or enchainned in the monomer side chain.

At higher temperatures the propagation rate generally decreases in cationic polymerizations. However, an increase in temperature also increases the side reactions such as termination which increases the M_n and transfer which decreases the M_n . In either case both of these side reactions broaden the MWD. The EA in the system has the highest pKa of the subject esters and is intermediate in its ability to control the side reactions thus permitting the continued growth of multiple active species generated by the side reactions and the slow exchange. In the remaining systems polymerized at 4° C the added and / or enchainned ester is not sufficiently basic (lower pKa) to exert any significant control of the side reactions and the polymerizations proceed in a conventional manner.

It should also be pointed out that bimodal or even “polymodal” distributions may actually be present but not detectable due to separation and / or detection limitations. If multiple fractions are present and their M_n 's are not sufficiently different a chromatograph may

appear to be a single peak with a broad MWD instead of two individual peaks with narrower MWD's (figure 5.1.3-1).

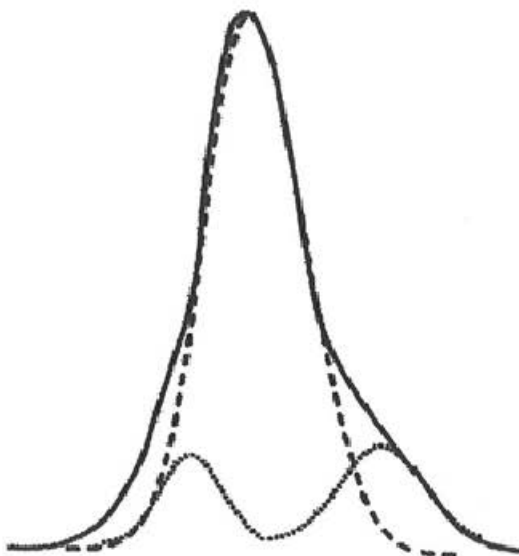


Table 5.1.3-1: Multiple peak overlap / interference

5.1.4 NMR ANALYSIS

The C^{13} and H NMR spectra for the majority of the subject polymerizations were complicated due to the presence of the externally added esters which were prohibitively high boiling – low vapor pressure compounds. Additionally, the solubility of the subject ester was generally identical to that of the corresponding monomer rendering isolation and purification difficult. A method for the isolation and purification of the polymer residues is currently being developed and will be the subject of a future study.

The ^1H and ^{13}C NMR spectra for poly(ethenyloxy)butane (VOB) polymerized in the absence and presence of an externally added ester, BA, are shown in figures 5.4.1A and 5.4.1B, respectively. A simple comparison of the two sets of spectra clearly shows that the polymer obtained in the presence and absence of the externally added ester are structurally and compositionally identical indicating that there was no reactive involvement of the ester in the polymerization i.e., no isolatable or detectable ester derivatives are present .

More specifically, in the systems containing an enchaind ester group, e. g., VOBBZ, the ^{13}C NMR shows the presence of the 166 ppm peak indicates that the carbonyl group has not been chemically modified. Further, integration of the peak shows that the carbonyl carbon is present at nearly the theoretical or calculated concentration

Under the acidic cationic reaction conditions reaction with the enchaind carbonyl or ester group is highly unlikely. The carbonyl carbon could (conceivably) be attacked by a nucleophilic counterion or gegenion (Kennedy, J. and Marechal, E., 1991) followed by attack on the carboxyl oxygen by the active carbocation resulting in an acetal (figure 5.1.4-1) which is highly unlikely.

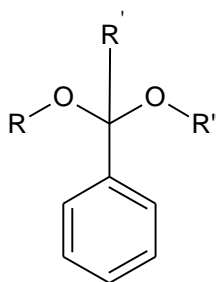


Figure 5.1.4-1: Proposed structure of acetal formed by attack on carbonyl group by active species

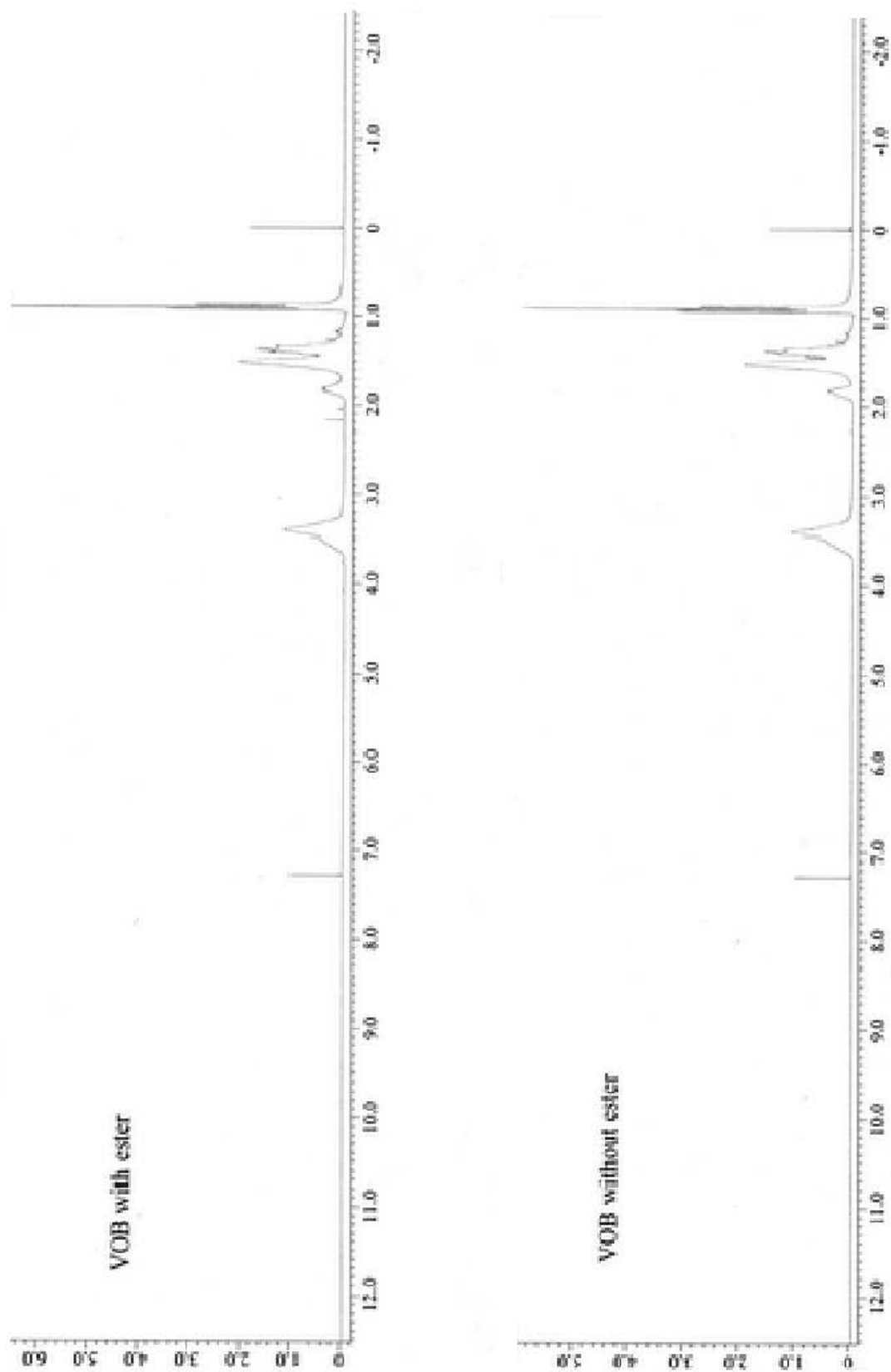


Figure 5.4.1A: ^1H NMR of poly(ethenylbutane) polymerized at -20°C in toluene in the presence and absence of an externally added ester (EA): $[\text{Ester}] = 10\%$ vol., $[\text{Cat}]/[\text{I}] = [\text{EADC}]/[\text{HCl}] = 9.0$.

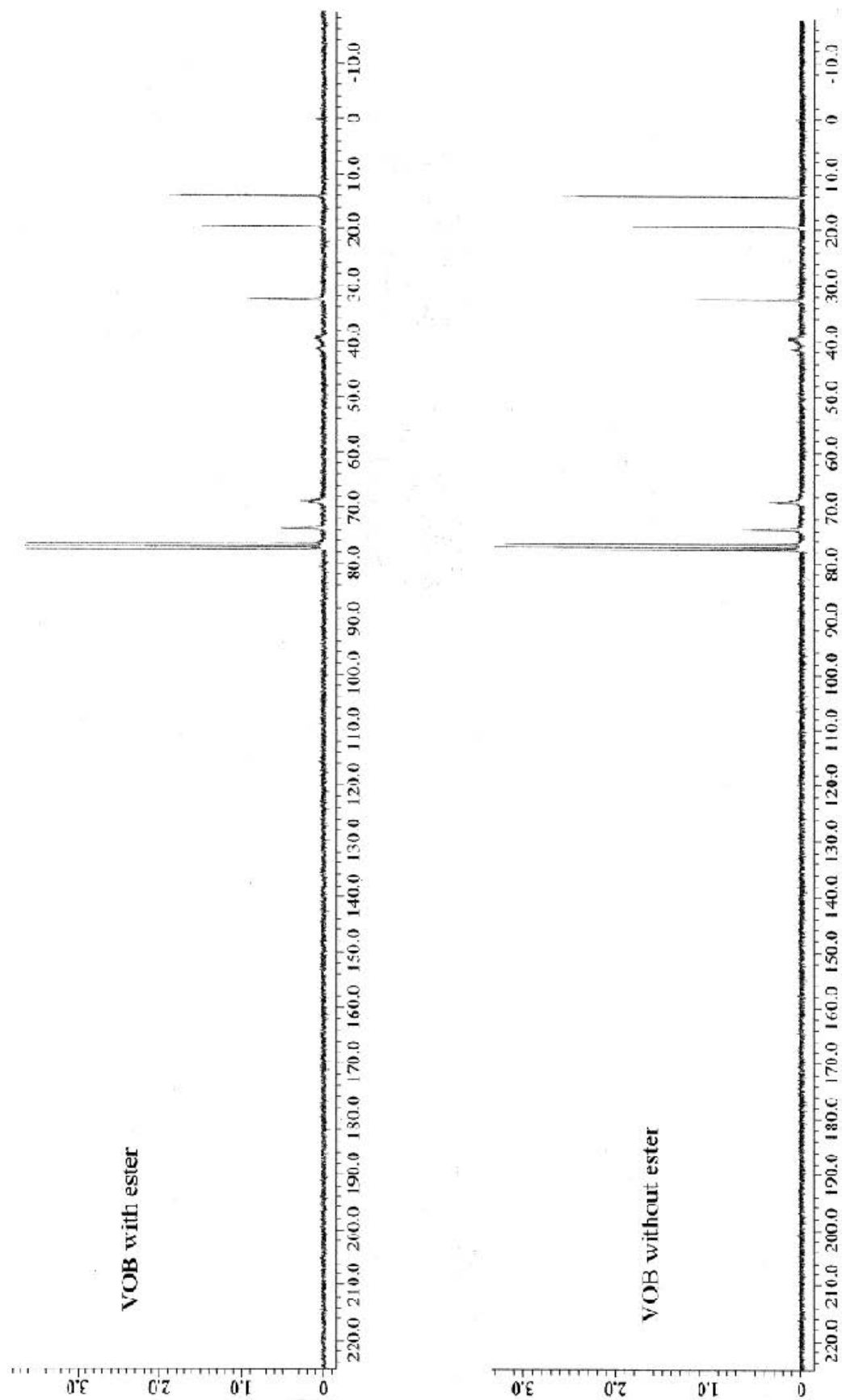


Figure 5.4 ^{13}C NMR of poly(aryleneoxy)butane polymerized at -20°C in toluene in the presence and absence of an externally added ester (EA): [Ester] = 10% vol., [Co]/[I] = [EADC]/[HCl] = 90.

All of the subject polymerizations were quenched / terminated by the addition of an ammoniacal methanol solution. The methoxy anion reacts with the active or propagating species forming a acetal end group (Figure 5.1.4-2). The presence of the acetal end group was confirmed for all systems by H NMR which showed the presence of the acetal H at 4.9 - 5.05 ppm (Figures 5.1.2 -1 and 5.1.2-2) in every case.

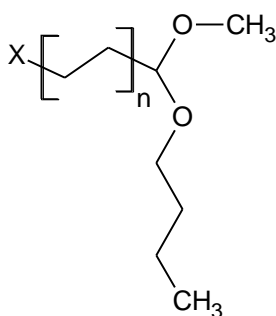


Figure 5.1.4-2 Structure of Terminal Acetal

Further analysis of the ^{13}C and H NMR spectra shows that the subject polymers were all linear with no branching or (as stated above) secondary structures attributable to side reactions (figures 5.1.4 – 3, 4, 5 and 6). The NMR spectra show no 2° or 3° structures in the five living / controlled systems or in the conventional systems including those that did not achieve complete monomer conversion.

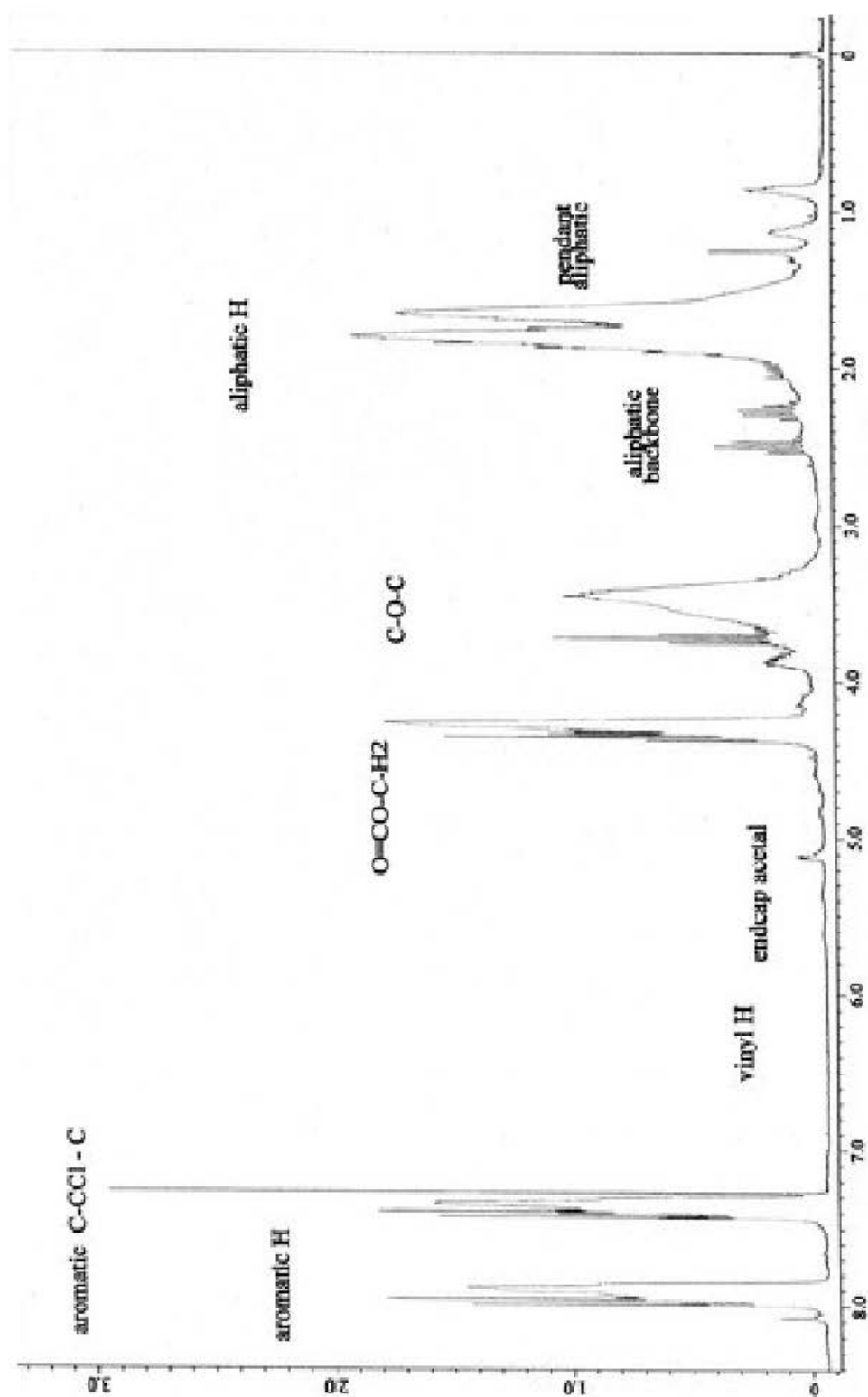


Figure 5.1.4-3: Proton NMR of 4-(ethenyl-oxy)butyl 4-chlorobenzoate polymerized at -20° C in the presence of butyl-4-chlorobenzoate [ester] = 10% vol., [Co(I)/II] = [EADC]/[HCl] = 9.0

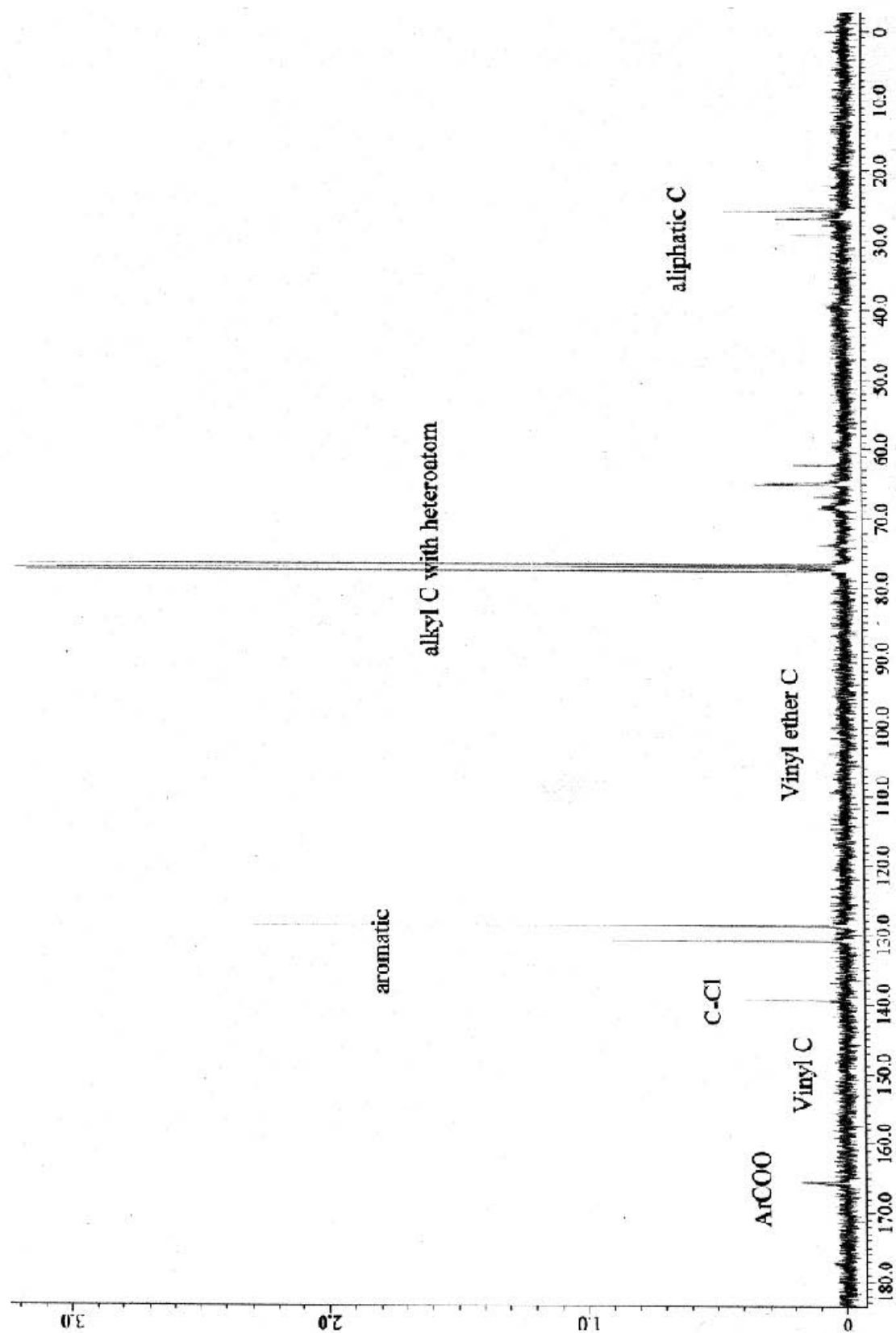


Figure 5.1.4-4: ^{13}C NMR of 4-(ethenyl)butyl 4-chlorobenzoate polymerized at -20°C in the presence of butyl-4-chlorobenzoate [ester] = 10% vol., $[\text{Cat}]/[\text{I}] = [\text{EADC}]/[\text{HCl}] = 9.0$

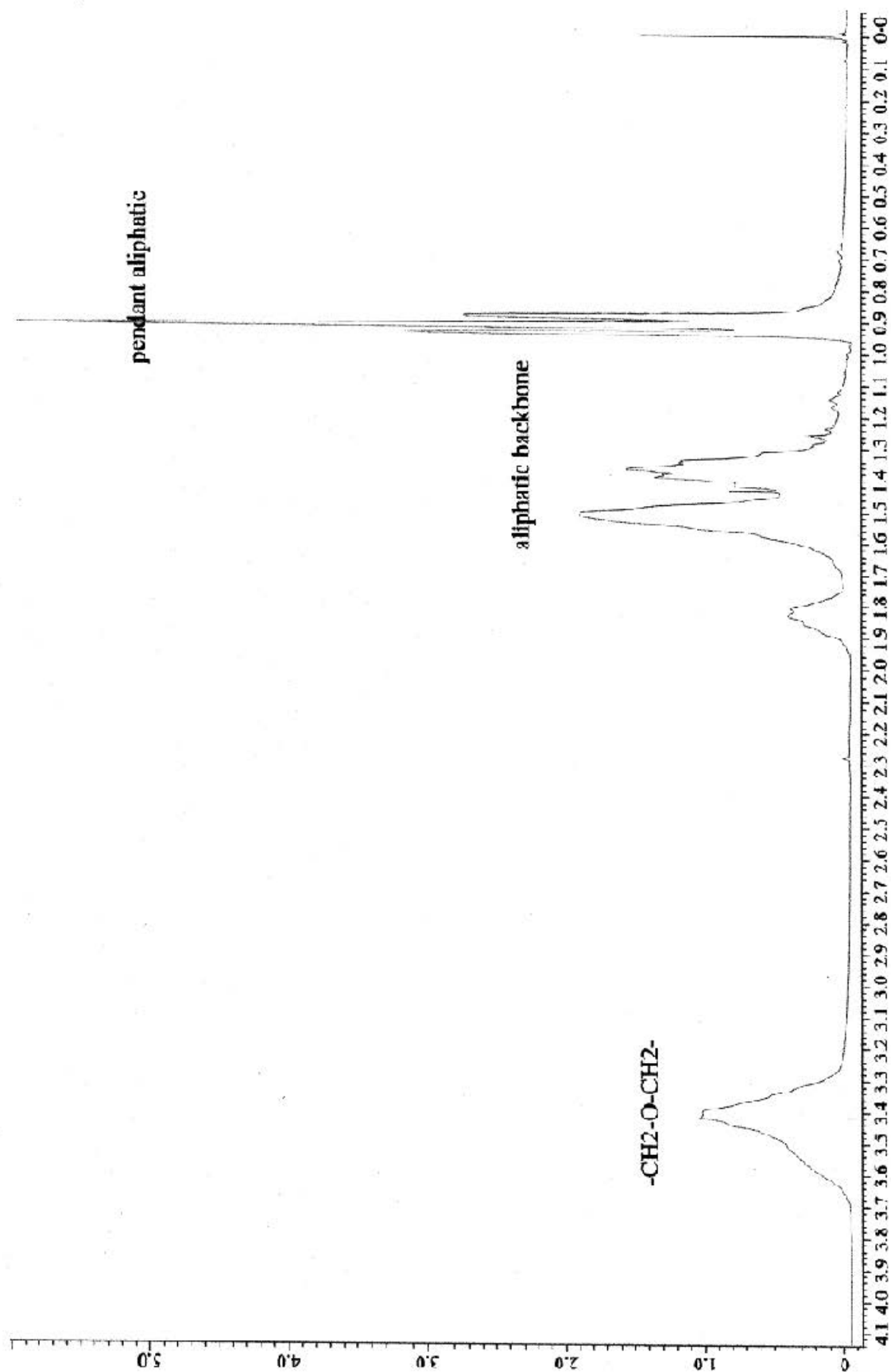


Figure 5.1.4-5: ^1H NMR of 4-(ethenyl)oxybutane polymerized at -20°C in toluene in the presence of butyl acetate: [ester] = 10% vol., [Co]/[I] = [ADC]/[HCL] = 9.0.

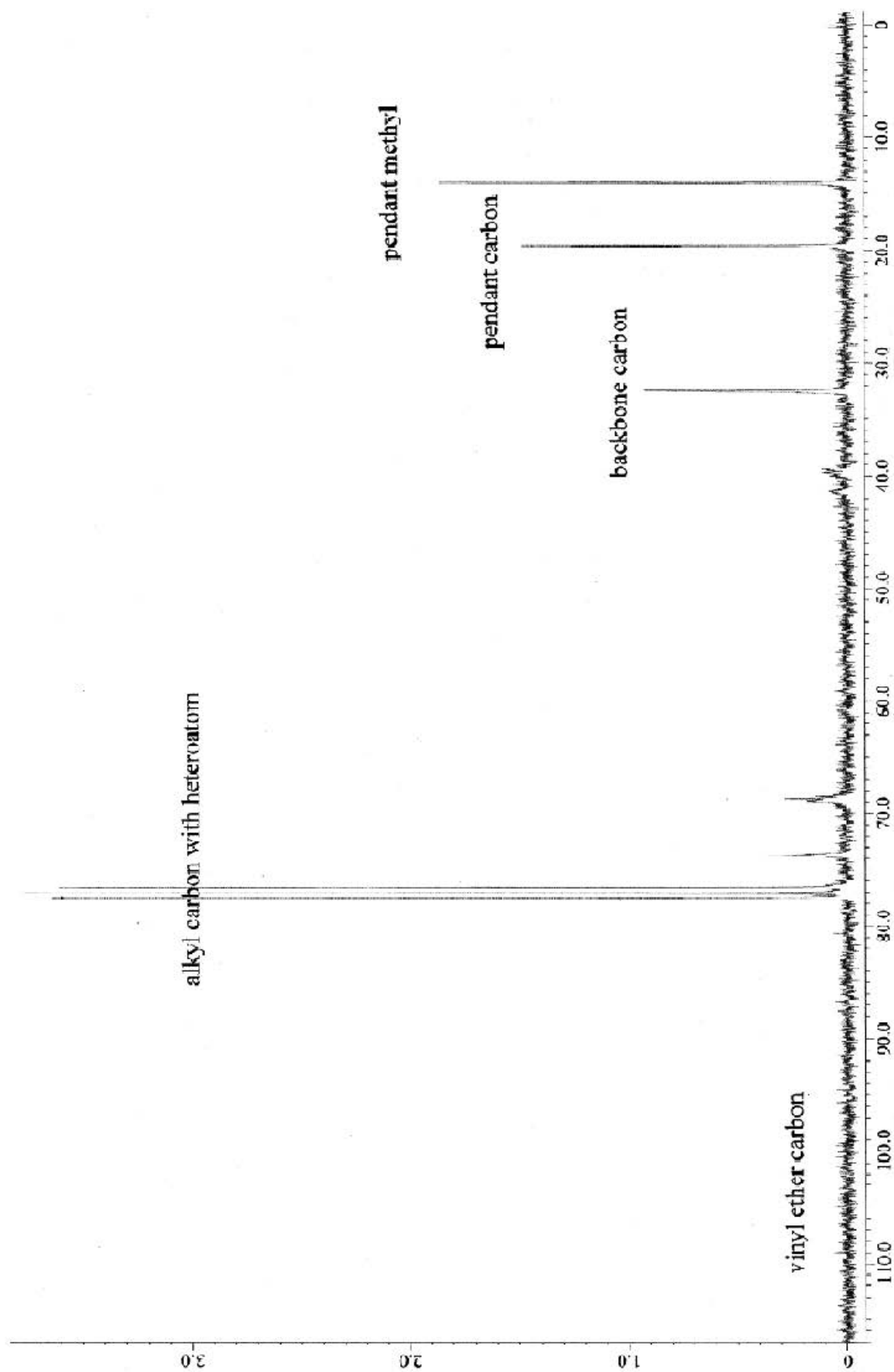


Figure 5.1.4-6: ^{13}C NMR of 4-(ethenyloxy)butyl 4-chlorobenzoate polymerized at -20°C in the presence of butyl-4-chlorobenzoate [ester] = 10% vol., [Coll]/[I] = [EADC]/[HCl] = 9.0

5.2 CONCLUSIONS

The ability of an ester to induce or create a living system is directly related to the basicity of the ester. The relative basicity of an ester is a function of the pK_a of the conjugate carboxylic acid forming the ester with the higher pK_a corresponding to a more basic ester. The characterization of a polymerization system is determined by the analysis of the polymerization process in accordance with an established and generally accepted set of diagnostic criteria that define a living system. Based on these criteria three distinct types of systems, living, controlled and conventional may be defined (section 1.3.4).

The external addition of an ester to a vinyl ether polymerization system has been shown to induce a living system with the judicious selection of an appropriate initiator, coinitiator and solvent.

The polymerization systems of the current study were designed to serve as a basis for determining if an ester moiety attached to the C1 carbon of the side chain of 4-(ethenyloxy)butane (VOB) would induce a living system in the same manner and to the same extent as the [same] added externally / separately. Following the established conventions (Kennedy, J. and Ivan, B., 1991) the subject systems are described as follows:

HCl / EADC / Monomer or Monomer - Ester/ \pm Ester / Toluene / -20°C & 4°C

The conclusions drawn from the experimental observations relative to the study objectives are summarized as follows:

1. How does the basicity or strength of an added ester (Lewis base) affect the degree of livingness of a polymerization?

In the absence of an enchainment or externally added ester the polymerization of VOB is conventional in nature yielding polymers with broad MWD's, uncontrolled M_n 's and in most cases incomplete monomer conversion. At -20°C and at a $[\text{CoI}] / [\text{I}]$ ratio of 9.0 the addition of EA or BBZ (at 10% by volume) induces a living or controlled polymerization system yielding polymers with narrower MWD's, controlled M_n 's and complete monomer conversion. Also, at full conversion the addition of more monomer results in continued polymerization at approximately the same rate and continuing until the additional monomer is consumed.

The EA and BBZ are the most basic esters and the addition of the less basic ester, i.e., B4CBZ, B3CBZ, ECA and EDCA, respectively, resulted in systems that were conventional with varying "degrees of living character". The living character of the various systems increased with the increase in the basicity of the added ester (table 5.1-1).

At -20°C all of the systems were conventional or exhibited minimal living or controlled character when the $[\text{CoI}] / [\text{I}]$ ratio was reduced to 4.5 and at 4°C all systems were conventional irrespective of the added ester or $[\text{CoI}] / [\text{I}]$ ratio.

2. Does an enchainment ester moiety function in the same manner and to the extent as the same ester added separately / externally?

The polymerization of vinyl ether monomers with enchainment ester moieties generally followed the same pattern as was observed for the externally added esters, i. e., the degree

of living character induced by the presence of the ester moiety varies directly with the basicity of the ester. Also, at -20°C and a $[\text{CoI}] / [\text{I}]$ ratio of 9.0 only the monomers with the most basic ester moieties yielded living or controlled systems, i. e., VOBOAC and VOBBZ, respectively. All other systems were conventional in nature at -20°C and 4°C irrespective of the $[\text{CoI}] / [\text{I}]$ ratio.

The data also shows that although the VOBOAC and VOBBZ living or controlled, they were in fact less ideal than the corresponding system in which the ester was added separately. Also, it was noted that in a system containing a monomer with an enchain ed ester moiety that the external addition of the corresponding ester increases the living character of the system. Clearly, the data from this investigation demonstrates that an enchain ed ester moiety does not function in the same fashion or to the same extent as the structurally equivalent ester added separately at an equivalent concentration.

3. How can monomer conversion be accurately measured when the monomer, polymer and system additives have excessively high boiling points and the individual components have similar solubility characteristics?

A new method has been developed and validated based on the direct analysis of the polymer, monomer and ester following the removal of the reaction solvent (toluene) and reaction quenchant (ammoniacal methanol). A detailed discussion of a newly devoped and validated method is given in Chapter 7.

CHAPTER 6

EXPERIMENTAL

6.1 MATERIALS

Commercial grades of 4-(ethenyloxy)butan-1-ol, 2-(ethenyloxy)ethanol, 4-(ethenyloxy)butane and ethenyloxy ethyl ether were donated by BASF Corporation. The monomers were washed with aqueous sodium hydroxide and water and dried over calcium sulfate for twelve hours. The monomers were then distilled twice over calcium hydride at reduced pressure and stored under nitrogen at 4° C in amber vials. Boiling ranges and physical properties for each monomer are shown in table 6 .1.

4-(ethenyloxy)butyl benzoate and 2 – (ethenyloxy) chloroethane (Aldrich Chemical Company) were washed with aqueous and water and dried over calcium sulfate for twelve hours. The monomers were then distilled twice over calcium hydride at reduced pressure and stored under nitrogen at 4° C in amber vials. Boiling range and physical properties of the monomers are shown in table 6.1.

Toluene, anhydrous, 99.8%, anhydrous n - hexane, 95 %, anhydrous dichloromethane, 99.8 %, anhydrous carbon tetrachloride, 99.8 % (Aldrich Chemical Company) were dried for twelve hours over calcium sulfate, distilled twice over calcium sulfate at atmospheric pressure and stored over 4A molecular sieves, under dry nitrogen at 4° C in amber glass bottles.

Methyl benzoate, ethyl benzoate, propyl benzoate, n – butyl benzoate, 2 – methylpropyl benzoate, methyl benzoate, ethyl benzoate, methyl acetate, methyl chloroacetate and

methyl dichloroacetate, methyl trichloroacetate (Aldrich Chemic Company) were dried with calcium sulfate, distilled over calcium sulfate at reduced pressure and stored over 4A molecular sieves, under dry nitrogen at 4° C in amber glass bottles.

Benzoyl chloride, 3 – chlorobenzoyl chloride, 4 – chlorobenzoyl chloride, 3 – methylbenzoyl chloride, 4 – methylbenzoyl chloride, chloroacetyl chloride, dichloroacetyl chloride, trichloroacetyl chloride, triethylamine – 99%, glacial acetic acid, tetrahydrofuran, benzene and methanol (Aldrich Chemical Company) were used as received.

Ethylaluminum Dichloride (EADC) – 25% in toluene and hydrogen chloride (HCl), 1.0 molar in ethyl ether (Et₂O) were used as received but were assayed prior to use. The HCL etherate was assayed by titration with standardized, alcoholic potassium hydroxide using a Brinkman Titrimo 360 autotitrator. The EADC was assayed by manual titration of the aluminum using a microburet

6.2 ANALYTICAL AND CHARACTERIZATION EQUIPMENT

NMR SPECTROSCOPY

¹H and ¹³C spectroscopic analysis was performed on a Jeol EX 270 MHz or Jeol ECS 400 MHz spectrophotometer with Delta™ NMR software using CDCl₃, CD₂Cl₂ or DMSO – d₆ as solvents.

INFRARED SPECTROSCOPY

Infrared spectroscopic analysis was performed on a Buck Scientific Model 500 Scanning IR spectrophotometer with GRAMS AI™ software.

POLYMER CHARACTERIZATION

Polymer molecular weights and molecular weight distributions (M_w / M_n) were determined by size exclusion chromatography (SEC) in THF on a Buck Scientific BLC – 20 Integrated Isocratic HPLC system with PeakSimple™ 2000 integration software with an internal variable frequency UV detector and a Knauer K – 2401 RI detector with three ES Industries Chromegapore™ polystyrene columns (MSE-100, MSE-300 and MSE-500; 4.6 mm dia. X 300 mm). Calculations of the molecular weights and molecular weight distributions (M_n , M_w and M_w / M_n) were based on calibration curves obtained from fifteen narrow molecular weight polystyrene standards (Aldrich Chemical Company and Pressure Chemical Company).

GAS CHROMATOGRAPHY

Chromatographic separations were performed on a Buck Scientific Model 910 gas chromatograph with FID and TCD detectors, PeakSimple™ 2000 integration software and a Restek™ Rtx – VMS column.

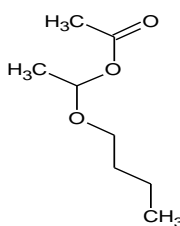
6.3 SYNTHESIS

6.3.1 INITIATORS

1-butoxyethyl acetate (1)

Using a dry syringe technique acetic acid (12.010g, 0.20 mol.), 1-(ethenyloxy)butane (25.032g, 0.25 mol.) and dry benzene (100 mls) were added to an oven dried flask. The reaction mixture was heated to 60° C in a water bath with continuous mixing for six hours and then cooled to room temperature and transferred to a separatory funnel. The reaction mixture was washed twice with aqueous sodium hydroxide, twice with water and dried

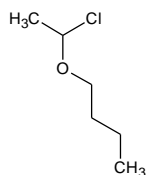
over calcium sulfate. The excess benzene was removed by rotoevaporation at reduced pressure and the crude product was then distilled twice over calcium hydride at reduced pressure to give 27.2g (85% yield) of 1-butoxyethyl acetate. Boiling point °C @ mm Hg. ^1H NMR, δ 5.7 (q, 1 H, OCHO), δ 3.3 – 3.6 (m, 2 H, OCH₂C), δ 1.8 (s, 3H, OCOCH₃), δ 1.4 (m, 2H, CH₃COO), δ 1.3 (d, 5H, CH₂ CH₃), δ 10.9 (m, 3H, CH₂CH₃); ^{13}C NMR, δ 170.7 (C=O), δ 95.7 (OCHO), δ 65.5 (OCH₂), δ 31.5 (CH), δ 21.1, 19.4, 14.1 (all CH₃).



(1)

1 - butoxyethyl chloride (2)

(2) was synthesized in benzene from 1-(ethenyloxy)butane and anhydrous hydrogen chloride in ethyl ether using the same procedure as described for (1). The excess ether and benzen were removed by rotoevaporation at reduced pressure and the crude product was then distilled twice over calcium hydride at reduced pressure to give 21.9g (80% yield) of 1-butoxyethyl chloride. Boiling point °C at mm Hg. ^1H NMR, δ 5.5(m, 1 H, CH₃ClO), δ 3.6 (m, 2 H, OCH₂C), δ 1.7 (d, 3 H, CH₃CHClO), δ 1.5 (m, 4 H, OCOCH₃), δ 0.5 (m, 3H, CH₃CH₂); ^{13}C NMR, δ 85.0 (CCl), δ 68.6 (OCH₂C), δ 32.4 (CCH₂C), δ 24.6 (CH₃CCl), δ 19.5 (C CH₂CH₃), δ 14.1 (CH₃CH₂).



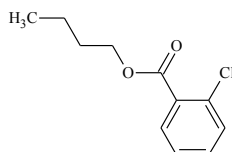
(2)

6.3.2. ESTERS

Butyl 2-chlorobenzoate (3)

(6) was synthesized in benzene from 2-methylbenzoyl chloride (30.9180g, 0.2mol.) 2-(ethenyloxy)butan-1-ol (24.486g, 0.21mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess benzene and 2-(ethenyloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 40.768 g (87.0% yield) of the crude product. ^1H NMR, δ 7.9 (m, H, Bz, C6), δ 7.21(m, 3 H, Bz, C3, C4 & 5), δ 6.45 (q, 1H, =CHO), δ 4.35 (t, 2 H, O=COCH₂), δ 4.15 (d, 1 H, HCH=CHO), δ 3.97 (m, 1 H, HCH=CHO), δ 3.7 (m, 2 H, CH₂OCH=), δ 2.6 (s, 3 H, CH₃), δ 2.3 (m, 2 H, HCH OC=), 1.2 (m, 2 H, HCH CH₂CH=); ^{13}C NMR, δ 169.0 (C=O), δ 151.1 (=CHO), δ 140.8 (CCH₃), δ 132.7 (Bz, C3 & C4), δ 131.1 (Bz, C6), δ 130.4 (Bz, C1), δ 126.3 (Bz, C5), δ 84.0 (CH₂=), δ 67.3 (=CHOC), δ 62.9 (CH₂O), δ 26.1 (HCHCH₂OC=), δ 25.6 (HCH CH₂O), δ 21.5 (CH₃).



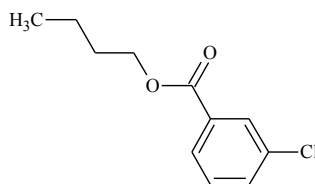
(3)

Butyl 3- chlorobenzoate (4)

(6) was synthesized in benzene from 2-(ethenyloxy)butan-1-ol (24.486g, 0.21 mol.), 3-methylbenzoyl chloride (30.9180g, 0.2mol.), triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess benzene and 2-(ethenyloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 41.705 g (89.0% yield) of the crude product. ^1H NMR, δ 7.9 (m,

1H, Bz, C6), δ 7.25 (m, 2 H, Bz, C4 & 5), δ 7.15 (d, 1H, Bz, C3), δ 6.5 (q, 1H, CH₂=CHO), δ 4.35 (t, 2 H, O=COCH₂), δ 4.15 (d, 1 H, HCH=CHO), δ 3.97 (m, 1 H, HCH=CHO), δ 3.7 (m, 2 H, CH₂OCH=), δ 2.4 (s, 3 H, CH₃), δ 2.3 (m, 2 H, HCH OC=), 1.2 (m, 2 H, HCH CH₂CH=); ¹³C NMR, δ 168.0 (C=O), δ 151.1 (=CHO), δ 137.6 (CCH₃), δ 132.0 (Bz, C4), δ 130.8 (Bz, C1), δ 129.3 (Bz, C2), δ 127.7 (Bz, C5 & C6), δ 84.0 (CH₂=), δ 67.3 (=CHOC), δ 62.9 (CH₂O), δ 26.1 (HCHCH₂OC=), δ 25.6 (HCH CH₂O), δ 21.5 (CH₃).



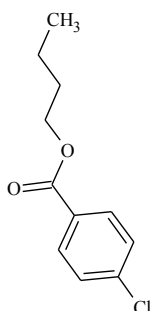
(4)

Butyl 4-chlorobenzoate (5)

(8) was synthesized in benzene from 2-(ethenyloxy)butan-1-ol (24.486g, 0.21 mol.), 4-methylbenzoyl chloride (30.9180g, 0.2mol.), triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess benzene and 2-(vinylloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 41.705 g (89.0% yield) of the crude product. ¹H NMR, δ 7.8 (m, 2H, Bz, C2 & 6), δ 7.25 (m, 2 H, Bz, C4 & 5), δ 6.5 (q, 1H, CH₂=CHO), δ 4.35 (t, 2 H, O=COCH₂), δ 4.15 (d, 1 H, HCH=CHO), δ 3.97 (m, 1 H, HCH=CHO), δ 3.7 (m, 2 H, CH₂OCH=), δ 2.4 (s, 3 H, CH₃), δ 2.3 (m, 2 H, HCH OC=), 1.2 (m, 2 H, HCH CH₂CH=); ¹³C NMR, δ 168.8 (C=O), δ 151.1 (=CHO), δ 143.9 (CCH₃), δ 129.2 (Bz, C1), δ 129.5

(Bz, C2 & C6), δ 128.6 (Bz, C3 & C5), δ 84.0 ($\text{CH}_2=$), δ 67.3 ($=\text{CHOC}$), δ 62.9 (CH_2O), δ 26.1 ($\text{HCHCH}_2\text{OC}=\text{}$), δ 25.6 ($\text{HCH CH}_2\text{O}$), δ 21.2 (CH_3).



(5)

TABLE 6.3.2 -1: PHYSICAL PROPERTIES OF ESTERS

ESTER	MW	d @ 25 C	RI (20 C)	BP(760mm)
Ethyl Acetate	88.11	0.902	1.372	77
Ethyl Chloroacetate	122.55	1.145	1.421	143
Ethyl Dichloroacetate	172.18	1.280	1.438	158
Ethyl Trichloroacetate	191.44	1.378	1.453	168
Butyl Acetate	116.16	0.880	1.394	125
Butyl Benzoate	178.23	1.010	1.498	249
Butyl-2-Chlorobenzoate	212.72	1.110	1.500	279
Butyl-3-Chlorobenzoate	212.72	1.140	1.500	284
Butyl-4--Chlorobenzoate	212.72	1.140	1.502	274

6.3.3. MONOMERS

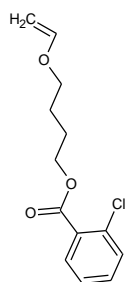
4-(ethenyloxy)butyl 2-chlorobenzoate (3)

Using a dry syringe 2-chlorobenzoyl chloride (35.002g, 0.2mol.) and dry benzene (75 mls) was added to an oven dried, three necked flask containing a magnetic stirrer bar and fitted with a reflux condenser carrying a calcium chloride drying tube and a vented addition funnel.

Using a dry syringe 2-(ethenyloxy)butan-1-ol (24.486g, 0.21mol.) and triethylamine (21.250g, 0.21 mol.) were added to the vented addition funnel and mixed by swirling. The flask was mounted in a water bath on a magnetic stirrer / heating plate. With continuous stirring the 2-(ethenyloxy)butan-1-ol / triethylamine mixture was added at a rate sufficient to heat the reaction mixture to reflux. The addition funnel was rinsed with dry benzene (20 mls) and the reaction mixture was heated to maintain a gentle reflux for 1 hour.

The flask was cooled to ambient and 100 mls deionized water was added and mixing was continued until the precipitated solid (triethylamine chloride) was dissolved. The reaction mixture was transferred to a 500 ml separatory funnel and the organic (upper) layer washed three times with aqueous sodium hydroxide, twice with deionized water and dried over calcium sulfate for twenty four hours.

The excess benzene and 2-(ethenyloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 47.296 g (92.8% yield) of the crude product. ^1H NMR, δ 7.9 (m, 2H, Bz, C2 & 6), δ 7.3 (m, 2 H, Bz, C3 & 5), δ 6.4 (q, 1H, $\text{CH}_2=\text{CHO}$), δ 4.3 (t, 2 H, $\text{O}=\text{COCH}_2$), δ 4.15 (d, 1 H, $\text{HCH}=\text{CHO}$), δ 3.97 (m, 1 H, $\text{HCH}=\text{CHO}$), δ 3.71 (m, 2 H, $\text{CH}_2\text{OCH}=\text{}$), δ 1.8 (m, 4 H, $\text{CCH}_2\text{CH}_2\text{C}$); ^{13}C NMR, δ 165.7 ($\text{C}=\text{O}$), δ 151.9 ($=\text{CHO}$), δ 139.4 ($=\text{CCl}$), δ 131.0 (Bz, C2 & 6), δ 128.9 (Bz, C1), δ 128.6 (Bz, C3 & 5), δ 86.6 ($\text{CH}_2=\text{}$), δ 67.3 ($=\text{CHOC}$), δ 65.0 (CH_2O), δ 25.9 ($\text{CH}_2\text{HCHCH}_2$), δ 25.65 ($\text{HCH CH}_2\text{O}$).

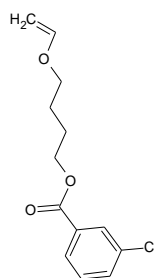


(3)

4-(ethenyloxy)butyl 3-chlorobenzoate (4)

(4) was synthesized in benzene from 3-chlorobenzoyl chloride (35.002g, 0.2mol.), 2-(ethenyloxy)butan-1-ol (24.486g, 0.21mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess benzene and 2-(ethenyloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 45.848 g (90.0% yield) of the crude product. ^1H NMR, δ 7.9 (m, 2H, Bz, C2 & 6), δ 7.3 (m, 2 H, Bz, C3 & 5), δ 6.4 (q, 1H, $\text{CH}_2=\text{CHO}$), δ 4.3 (t, 2 H, $\text{O}=\text{COCH}_2$), δ 4.15 (d, 1 H, $\text{HCH}=\text{CHO}$), δ 3.97 (m, 1 H, $\text{HCH}=\text{CHO}$), δ 3.71 (m, 2 H, $\text{CH}_2\text{OCH}=\text{}$), δ 1.8 (m, 4 H, $\text{CCH}_2\text{CH}_2\text{C}$); ^{13}C NMR, δ 165.7 ($\text{C}=\text{O}$), δ 151.9 ($=\text{CHO}$), δ 139.4 ($=\text{CCl}$), δ 131.0 (Bz, C2 & 6), δ 128.9 (Bz, C1), δ 128.6 (Bz, C3 & 5), δ 86.6 ($\text{CH}_2=\text{}$), δ 67.3 ($=\text{CHOC}$), δ 65.0 (CH_2O), δ 25.9 ($\text{CH}_2\text{HCHCH}_2$), δ 25.65 ($\text{HCH CH}_2\text{O}$).

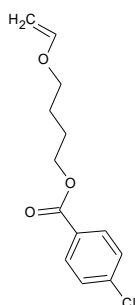


(4)

4-(ethenyloxy)butyl 4-chlorobenzoate (5)

(5) was synthesized in benzene from 4-chlorobenzoyl chloride (35.002g, 0.2mol.), 2-(ethenyloxy)butan-1-ol (24.486g, 0.21mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess benzene and 2-(ethenyloxy)butane-1-ol was removed by rotoevaporation at reduced pressure to give 45.848 g (90.0% yield) of the crude product. ^1H NMR, δ 7.9 (m, 2H, Bz, C2 & 6), δ 7.3 (m, 2 H, Bz, C3 & 5), δ 6.4 (q, 1H, $\text{CH}_2=\text{CHO}$), δ 4.3 (t, 2 H, $\text{O}=\text{COCH}_2$), δ 4.15 (d, 1 H, $\text{HCH}=\text{CHO}$), δ 3.97 (m, 1 H, $\text{HCH}=\text{CHO}$), δ 3.71 (m, 2 H, $\text{CH}_2\text{OCH}=\text{}$), δ 1.8 (m, 4 H, $\text{CCH}_2\text{CH}_2\text{C}$); ^{13}C NMR, δ 165.7 ($\text{C}=\text{O}$), δ 151.9 ($=\text{CHO}$), δ 139.4 ($=\text{CCl}$), δ 131.0 (Bz, C2 & 6), δ 128.9 (Bz, C1), δ 128.6 (Bz, C3 & 5), δ 86.6 ($\text{CH}_2=\text{}$), δ 67.3 ($=\text{CHOC}$), δ 65.0 (CH_2O), δ 25.9 ($\text{CH}_2\text{HCHCH}_2$), δ 25.65 ($\text{HCH CH}_2\text{O}$).

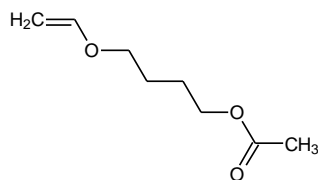


(5)

4-(ethenyloxy)butyl acetate (9)

(9) was synthesized in dichloromethane from 2-(ethenyloxy)butan-1-ol (23.23g, 0.20 mol.), acetyl chloride (16.485g, 0.21 mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3)

The excess dichloromethane was removed by rotoevaporation at reduced pressure to give 30.246g (95.0% yield) of the crude product. ^1H NMR, δ 6.6 (m, 1 H, $\text{OCH}=\text{C}$), δ 4.1 (q, 2 H, $\text{HCH}=\text{CHO}$), δ 4.05 (t, 2 H, $\text{O}=\text{COCH}_2\text{C}$), δ 3.95 (d1, 1 H, $\text{HCH}=\text{CHO}$), δ 3.68 (m, 2 H, $=\text{CHOCH}_2$), δ 2.2 (m, 2 H, $\text{O}=\text{cOCH}_2\text{HCH}$), δ 2.0 (d, 3 H, $\text{CH}_3\text{C}=\text{OO}$), δ 1.25 (m, 2 H, $\text{CH}_2\text{HCHCH}_2$); ^{13}C NMR, δ 172.8 ($\text{C}=\text{O}$), δ 150.6 ($\text{OCH}=\text{CH}_2$), δ 84.0 ($\text{CH}_2=\text{C}$), δ 67.4 ($\text{CH}_2\text{OCH}=\text{}$), δ 64.5 (OCH_2), δ 25.9 ($\text{O}=\text{COC}$), δ 25.4 (OCH_2C), δ 20.8 (CH_3)

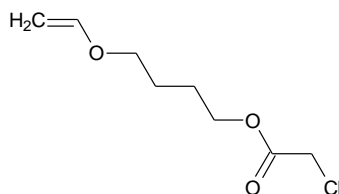


(9)

4-(ethenyloxy)butyl chloroacetate (10)

(10) was synthesized in dichloromethane from 2-(ethenyloxy)butan-1-ol (23.23g, 0.20 mol.), chloroacetyl chloride (23.717g, 0.21 mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3)

The excess dichloroethane was removed by rotoevaporation at reduced pressure to give 37.564g (97.0% yield) of the crude product. ^1H NMR, δ 6.6 (m, 1 H, $\text{OCH}=\text{C}$), δ 4.2 (q, 1 H, $\text{HCH}=\text{CHO}$), δ 3.9 (d, 2 H, OCH_2C), δ 4.2 (q, 1 H, $\text{HCH}=\text{CHO}$), δ 0.5 (m, 1H, $\text{OCH}=\text{C}$), δ 3.8 (d, 2 H, ClCH_2), δ 3.7 (m, 2 H, $=\text{CHOCH}_2$), δ 2.2 (m, 2 H, OCH_2CH_2), δ 1.3 (m, 2 H, OCH_2CH_2); ^{13}C NMR, δ 168.0 ($\text{C}=\text{O}$), δ 150.6 ($\text{OCH}=\text{CH}_2$), δ 84.0 ($\text{CH}_2=\text{C}$), δ 67.4 ($\text{CH}_2\text{OCH}=\text{C}$), δ 66.2 (OCH_2), δ 64.4 ($\text{O}=\text{COC}$), δ 41.2 (OCH_2C), δ 26.0, δ 25.2 (all CH_2)

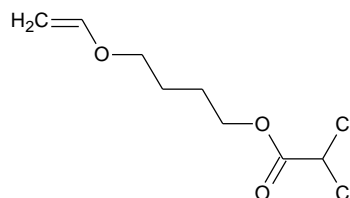


(10)

4-(ethenyloxy)butyl dichloroacetate (11)

(11) was synthesized in dichloromethane from 2-(ethenyloxy)butan-1-ol (23.23g, 0.20 mol.), dichloroacetyl chloride (30.952g, 0.21 mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3)

The excess dichloromethane was removed by rotoevaporation at reduced pressure to give 45.614g (97.0% yield) of the crude product. ^1H NMR, δ 6.6 (m, 1 H, $\text{OCH}=\text{C}$), δ 6.0 (d, 1 H, ClCHCl), δ 4.2 (t, 2 H, OCH_2C), δ 4.2 (q, 1 H, $\text{HCH}=\text{CHO}$), δ 0.5 (m, 3H, CH_3CH_2); ^{13}C NMR, δ 165.3 ($\text{C}=\text{O}$), δ 150.6 ($\text{OCH}=\text{CH}_2$), δ 84.0 ($\text{CH}_2=\text{C}$), δ 67.4 ($\text{CH}_2\text{OCH}=\text{C}$), δ 66.2 (OCH_2), δ 64.2 (CHCl_2), δ 26.0 (OCH_2C), δ 25.0 ($=\text{CHOCH}_2\text{C}$)

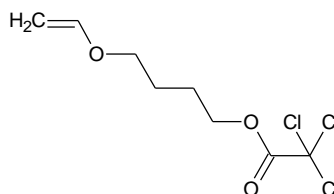


(11)

4-(ethenyloxy)butyl trichloroacetate (12)

(12) was synthesized in dichloromethane from 2-(ethenyloxy)butan-1-ol (23.23g, 0.20 mol.), trichloroacetyl chloride (38.184g, 0.21 mol.) and triethylamine (21.250g, 0.21 mol.) using the same procedure as described for (3).

The excess dichloromethane was removed by rotoevaporation at reduced pressure to give 49.352g (94.0% yield) of the crude product. ^1H NMR, δ 6.5 (q, 1 H, $\text{OCH}=\text{C}$), δ 4.8 (t, 2 H, $\text{CH}_2\text{OC}=\text{O}$), δ 4.2 (d, 1 H, $\text{HCH}=\text{CHO}$), δ 4.0 (d, 1 H, $\text{HCH}=\text{CHO}$), δ 3.9 (t, 2 H, OCH_2), δ 3.9 (m, 2 H, CH_2CH_2); ^{13}C NMR, δ 162.7 ($\text{C}=\text{O}$), δ 150.6 ($\text{OCH}=\text{CH}_2$), δ 89.9 (CCl_3), δ 84.0 ($\text{CH}_2=\text{C}$), δ 67.4, 67.2 ($\text{O}-\text{CH}_2$), δ 26.1, 24.8 (CH_2CH_2).



(12)

TABLE 6.3.3 -1: PHYSICAL PROPERTIES OF MONOMERS

MONOMER	SYMBOL	BP, ° C	Density
4-(ETHENYLOXY)BUTANE	VOB	94	0.774
4-(ETHENYLOXY)BUTYL ACETATE	VOBOAC	199	0.870
4-(ETHENYLOXY)BUTYL BENZOATE	VOBBZ	304	1.060
4-(ETHENYLOXY)BUTYL 4-CHLOROBENZOATE	VOB4CBZ	350	1.064
4-(ETHENYLOXY)BUTYL 3-CHLOROBENZOATE	VOB3CBZ	357	1.064
4-(ETHENYLOXY)BUTYL CHLOROACETATE	VOBCOAC	259	1.050
4-(ETHENYLOXY)BUTYL DICHLOROACETATE	VOBDCOAC	283	1.062

6.4 POLYMERIZATION PROCEDURE

6.4.1 SINGLE MONOMER ADDITION

Polymerizations were carried out at – 20° and 4° C under nitrogen in oven dried three necked flasks containing a magnetic stirrer bar and closed with rubber septa. Reactants were added using oven dried, nitrogen purged syringes. Quantities were determined by back weighing of the syringes and flasks. For reaction times of eight (8) hours or less the flasks were mounted in constant temperature ice (H₂O) baths (4° C) or ice (H₂O) / sodium chloride baths (-20° C) on magnetic stirrer plates and were equilibrated at the specified temperature for twenty minutes before initiating reactions. For reaction times exceeding eight (8) hours the reaction flasks were transferred to a laboratory freezer (Fisher Isotemp® model 97-926-1) after the initial eight (8) hours

Initiators were added either as solutions in the polymerization solvent or directly using oven dried, nitrogen purged microliter syringes. Polymerizations were initiated by the addition of a solution of ethylaluminum dichloride in either hexane or toluene at the polymerization temperature.

At predetermined time intervals the polymerization reactions were quenched by the addition of ammoniacal methanol solution (5% vol.) at the reaction temperature using oven dried, nitrogen purged syringes. Alternately, aliquots of the reaction mixture were removed by syringe and quenched by injection into a sealed vial containing ammoniacal methanol at the polymerization temperature.

The quenched reaction mixtures were sequentially washed with dilute aqueous hydrochloric acid (2% vol.) and water to remove the initiator residues and the excess solvent and other volatile components were removed by rotevaporation at reduced pressure.

6.4.2. INCREMENTAL MONOMER ADDITION

Incremental monomer addition polymerizations were conducted following the same procedure used for the single monomer additions (section 6.4.1) and monomers were adjusted to the reaction temperature prior to addition.

Monomer additions were made at predetermined intervals and varied based on the observed reaction rates of the individual systems. Samples were quenched at predetermined intervals and analyzed as described in the procedure for single monomer addition.

6.4.3 MONOMER CONVERSION DETERMINATION

Where the ester and /or monomer was sufficiently volatile to remove by rotoevaporation or oven drying for extended periods at reduced pressure the conversion was determined gravimetrically . In many cases however, the monomer and ester boiling points were sufficiently high as to prevent removal without thermal degradation of the polymer or in some cases thermally induced polymerization of the residual monomer. To determine the monomer conversion in systems with monomers and / or esters having prohibitively high boiling points a novel HPLC method was developed (Chapter 7).

From an examination of the SEC chromatograms from the molecular weight determinations it was noted that the monomer and ester components of each of the systems studied co – eluded, i., e., had identical V_E values. Further, the UV spectra of the monomers and esters were compared and it was noted that for each reaction pairing the spectra were essentially identical. As an example, Figure 6.1 shows the UV spectra of 4-(ethenyloxy)butyl benzoate and butyl benzoate in THF. In this example both the ester and the monomer spectra show characteristic absorbance peaks at 270 nm in THF and have identical V_E values. It was further noted that the UV spectra of the polymer also exhibited a UV spectral peak at 270 nm. (figure 6.4.3 -2).

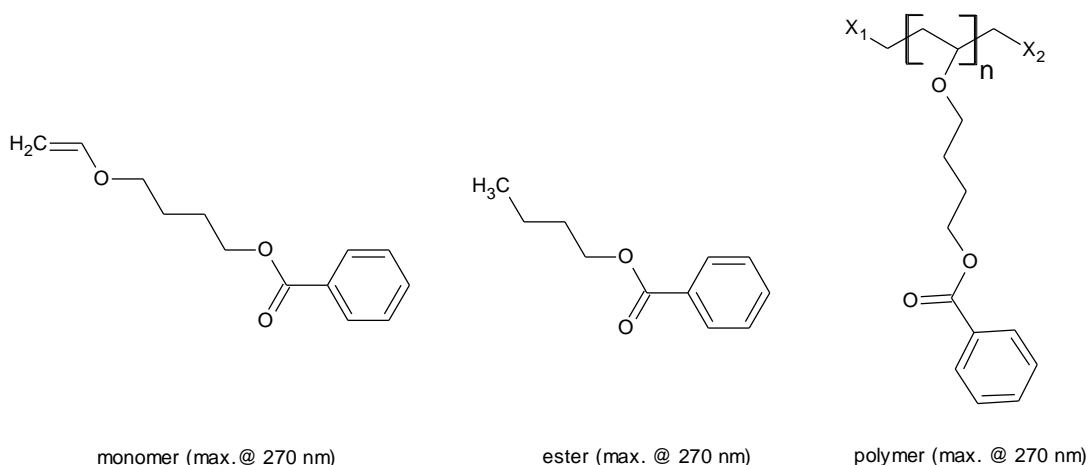


Figure 6.2

As noted previously (section 6.2) the HPLC used in this study was equipped with variable frequency UV and refractive index detectors. In each of the subject polymerization systems the monomer and added ester components were by design analogous in structure and have similar refractive indices as shown in table 6.4.3 - 1. This being the case it was possible to use the UV and / or RI detector response to quantify the monomer, ester and polymer concentration in a given sample and therefore to determine the monomer conversion, and subsequently the M_n , M_w and M_w / M_n from a single chromatographic scan.

TABLE 6.4.3 - 1: REFRACTIVE INDEX OF MONOMER - ESTER PAIRS

MONOMER / ESTER PAIR	REFRACTIVE INDEX
Butyl Benzoate	1.498
4-(ethenyloxy)butyl Benzoate	1.509
Butyl 3- Chlorobenzoate	1.500
4-(ethenyloxy)butyl 3-Chlorobenzoate	1.507
Butyl 4-Chlorobenzoate	1.502
4-(ethenyloxy)butyl 4-Chlorobenzoate	1.507

Since the SEC molecular weight determination separates the polymer from the monomer and ester components, the area and / or height of the combined monomer / ester peak is proportional to the combined quantity of monomer and ester in the sample. Therefore, if the quantity of either the monomer or the ester is know the quantity of the other component can be determined.

Obviously, the monomer concentration will decrease as polymerization proceeds while the ester (added Lewis base) will remain constant. This being the case it is possible to use the

ester component as an internal standard (Snyder, et. al., 1997, Meyer, 1998) and thereby quantitatively determine the monomer concentration in a given sample.

The ester concentration in each reaction mixture can be determined by simply weighing all components in the reaction mixture (solvent, ester, initiator, coinitiator and monomer). In polymerizations where aliquots are sequentially removed from the reaction mixture the aliquot weight is determined by back weighing of a pre - weighed quenching vial containing a known quantity of quenching agent. Following aqueous acid washing to remove initiator residues and removal of the polymerization solvent and quenchant by nitrogen assisted evaporation at atmospheric pressure (section 7.2) the quantity of ester in the sample is arithmetically calculated.

For polymerizations where the entire reaction mixture was quenched at a predetermined time (AMI or “all monomer in method” – Kennedy, J.P. and Ivan, B., 1991) the calculations were obvious and for sequential monomer addition studies the aliquots removed and monomer added are determined by back weighing of the dry syringes used for the extractions and additions and the quantity of ester in the sample calculated arithmetically.

A detailed discussion and description of the newly developed methods for the determination of the monomer conversion and molecular weight distributions in polymerization reactions involving relatively non – volatile monomers and polymerization additives / modifiers and solvents is discussed in Chapter 7.

CHAPTER 7

METHOD DEVELOPMENT

7.1 BACKGROUND AND DISCUSSION

Early in the experimental investigations of the current project it was noted that the traditionally accepted procedures for the determination of the monomer conversion did not appear to be directly and / or reliably applicable. Generally the traditional methods rely on either the volatility of the monomer versus the polymer formed or on the solubility of the monomer versus that of the polymer in various solvents or solvent mixtures.

Conversion determinations based on the monomer volatility are common with studies involving styrenes, vinyl ethers and dienes and other volatile monomers (Faust, R., et. al., 1987; Aoshima, S. and Higashimura, T., 1984; Faust, R. and Kennedy, J., P., 1986). In these studies the subject monomers, reaction solvents and system additives often have relatively low boiling points and / or vapor pressures which facilitates the quantification of the polymer by the evaporation of the other system components. As an example consider the following polymerization system (Aoshima, S. and Higashimura, T., 1986):

IBVE - Acetate / EADC / IBVE / Ethyl Acetate / n-Hexane / 0 ° C

In this example the reaction mixture is quenched at a predetermined reaction time by the addition of an ammoniacal methanol solution and then sequentially washed with dilute acid and water to remove initiator residues and then evaporated to dryness under reduced pressure giving the weight of polymer in the sample. Since the original weight of monomer in the reaction mixture is known the monomer conversion is readily determined as:

$$[1 - (M_i - P_{wt}) / (M_i)] 100 = \% \text{ Conversion} \quad (\text{eq. 7-1})$$

where M_i is the initial monomer weight and P_{wt} is the polymer weight. Generally a series of identical reactions are run and quenched at predetermined times and the monomer conversion at the selected time intervals are determined as described above.

An alternative or modified method for the determination of the monomer conversion with time involves the sequential removal and quench of aliquots of a single reaction mixture at predetermined time intervals and is referred to as the AMI or “all monomer in” method (Kennedy, J. P. and Ivan, B., 1991). In this case monomer conversion is determined by the gravimetric quantification of the polymer by evaporation of the volatile system components or in some cases the unreacted monomer may be determined by GC or HPLC (Heroguez, V., Deffleux, A. and Fontanille, M., 1987).

In other cases investigators have relied on the determination of polymer concentration based on the precipitation of the polymer in a secondary solvent (Lee, J., Kim, J. and Kim, M., 1990). In such cases the reaction mixture or an aliquote thereof is transferred and extracted with a suitable neutralizing solution to solubilize the initiator residues. The solvent layer is then poured into an excess of a solvent in which the polymer is insoluble and the polymer is quantified by filtration or by evaporation if the monomer is sufficiently volatile.

Either of these two methods are suitable for the determination of the monomer conversion and subsequent isolation of the subject polymers if and only if all of the components of the polymerization system are volatile or have differential solubilities as compared with the polymer. If the subject monomers or system additives have high boiling points and low vapor pressures removal by evaporation, even at reduced pressure is difficult and / or

incomplete. In some cases it is possible to remove monomers with limited volatility at high vacuum and temperature but this often results in thermal polymerization of residual monomer or degradation of the polymer.

In the current study the limitations of the of the accepted or traditional analytical methods for the determination of monomer conversion were problematic. In a number of the subject systems the monomers and system additives (added esters) were sufficiently volatile to permit the determination of the monomer conversion by evaporative removal of the nonpolymeric components. Examples of such systems were those in which the monomer was 4-(ethenyloxy)butane and the acetate and the mono-, di- and trichloroacetate derivatives thereof. In these systems the added esters were the corresponding ethyl acetate, ethyl chloroacetate, ethyl dichloroacetate and ethyl trichloroacetate which were sufficiently volatile to be removed by evaporation at reduced pressure or at atmospheric pressure under a continuous nitrogen flow (section 7.1.1). In either case the polymer concentration remained constant and there was no evidence of thermal polymerization of residual monomer since the processing temperatures were relatively low, i.e., $< 125^{\circ}\text{C}$ at reduced pressure and $< 100^{\circ}\text{C}$ under a continuous nitrogen flow. In the remaining systems the monomers were 4-(ethenyloxy)butyl benzoate and the 2, 3 and 4 monochloro derivatives with the added esters being butyl benzoate and the 2-, 3- and 4 monochloro derivatives thereof. In these systems both the monomers and the added esters bases were essentially non – volatile and not readily removable by either thermal evaporation at reduced pressure or by atmospheric evaporation under a continuous nitrogen stream. In most cases the required heat either degraded the polymer or induced thermal polymerization of the residual monomer. Clearly, the need for a more robust and applicable method for the determination of the monomer conversion in

polymerization systems containing high boiling and non – volatile components was indicated.

As noted earlier (section 6.4.3) the molecular weight and molecular weight distribution determinations of the subject polymers were determined by SEC chromatography against polystyrene standard using a standard calibration curve (Collins, E., Bares, J. and Billmeyer, F., 1973). SEC chromatography is basically different from all other chromatic methods in that a simple molecular size classification process rather than any interaction phenomena forms the basis of separation (Meyer, V. 1998).

Basically, a porous material is used as the column packing and molecules that are too large to diffuse into the pores are excluded and pass through the column relatively quickly since they can only flow through the spaces between the column packing particles while smaller molecules in the mobile phase penetrate the pores and are only able to escape by diffusion and as a result move more slowly through the column. In short, SEC is essentially a fractionation process in which molecules are separated on the basis of molecular size or more precisely, molar mass.

If the subject polymerization systems are examined solely on the basis of the molar mass of the individual components it is noted that there are actually only two fractions, i. e., the polymeric fraction (high molar mass) and the combined monomer, ester and reaction solvent fraction (low molar mass). Also, due to the similarity of the subject monomer / ester pairs used in the individual polymerizations and the inherent limitations of the SEC columns the monomer and ester are co – eluted with the reaction solvent generating a

single peak which is proportional to the combined concentration of the monomer, ester and solvent (Berek, D., 2010).

As stated earlier (section 7.1) the monomer conversion is typically determined gravimetrically from the isolated polymer and / or the residual monomer. In either case it is necessary or advantageous to remove the reaction solvent and any other substances that may interfere with the quantification of the analytes in the sample. By far the most common process for the isolation of the polymer and / or monomer is evaporation at reduced pressure most commonly achieved using a rotary evaporator. The rotary evaporator facilitates the removal of the volatile components based on the boiling points of the individual components. At reduced pressure the boiling points of the components are reduced facilitating the removal of the volatile components at lower temperatures and reducing the possibility of thermal degradation or reaction.

As noted earlier the subject benzoate monomers have boiling points above 300 °C and the corresponding ester are generally above 250 °C all with very low vapor pressures. This being the case it was found that the residual monomer and ester in a given reaction could not be removed without thermal degradation of the polymer and / or thermally induced polymerization of the residual monomer. In some cases it was noted that at very low pressures (ca. 15 Torr) and extended times (> 8 hrs) it was possible to remove the major portion of the esters at temperatures between 115 - 145°C but the removal was often incomplete and there was evidence of partial loss of residual monomer and darkening of the polymer.

It was determined that the most viable option would be to remove only the reaction solvent and quenchant and then to quantify the remaining polymer, monomer and ester by SEC. Since the monomer and ester co – elude and the ester concentration remains constant it was possible to determine the monomer and ester concentrations from standard calibration curves of the pure substances using the ester as an internal standard with the polymer weight being determined by mass balance.

7.2 SOLVENT EVAPORATION UNDER CONTINUOUS NITROGEN FLOW

By far the most common method employed for the removal of solvents and subsequent isolation or concentration of an analyte is evaporation or more precisely, distillation at reduced pressure. Generally, this is accomplished using a rotary evaporator and references citing its use are common throughout the literature.

Rotary evaporation is most efficient when applied to the removal of lower boiling solvents such as hexane, petroleum ethers, diethyl ether and other commonly used reaction and / or extraction solvents. However, it is also possible to remove higher boiling solvents if sufficient vacuum is applied and if other components of the subject sample are not adversely affected by the applied heat. A further consideration with multi – component mixtures is possibility of azeotropic interactions (co – evaporation) and whether or not there is a sufficient difference in the boiling points of the components at the required temperature and pressure.

When removing higher boiling solvents it is advantageous to reduce the boiling point of the solvents being removed by reducing the pressure (figure 7.2 – 1). However, reducing the system pressure lowers the boiling points of all the components of the subject sample and may result in the removal of portions of the higher boiling analytes in the sample. The possibility of the partial loss of analyte is further affected by that fact that as the applied heat increases so does the vapor pressure of the other components of the sample and the tendency of a substance to enter the vapor phase by evaporation increases with the increase in the vapor pressure (Price, D.M., 1999; Price, D.M. and Hawkins, M., 1999a). Thus it is seen that at reduced pressure and increased temperature the possibility of the partial loss of the analyte from a sample containing high boiling components increases. This situation is further exasperated by the fact that the removal of the high boiling components even at higher temperatures and lower pressures usually requires longer processing times which increases the potential loss.

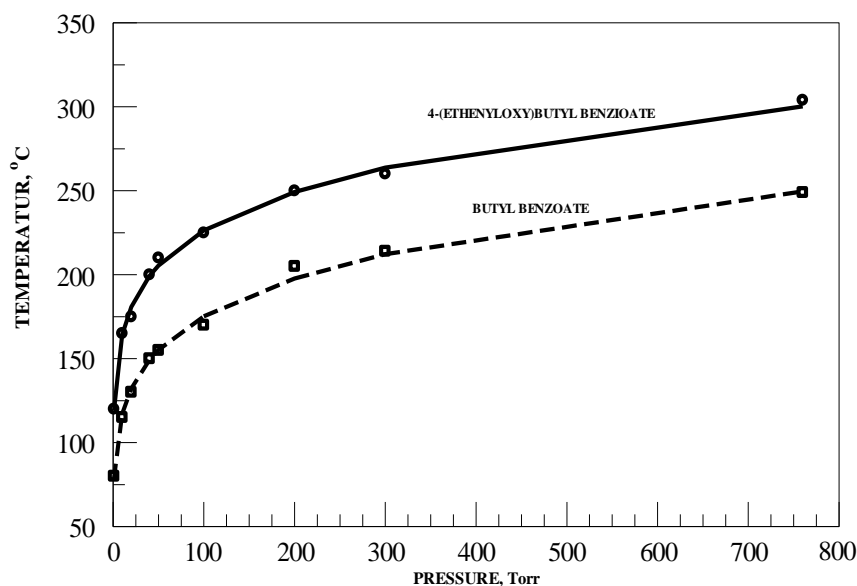


Figure 7.2 - 1: VARIATION IN BP OF 4-(ETHENYOXY)BUTYL BENZOATE AND BUTYL BENZOATE WITH PRESSURE

Another disadvantage of the rotary evaporator is that the apparatus processes only one sample at a time and this factor combined with the longer processing times can cause severe delays in sample processing and data acquisition.

Again, the most plausible solution to the presence of the high boiling was to selectively remove only the polymerization solvent and quenchant, i., e., toluene and methanol and then to quantify the remaining monomer and ester components with the polymer weight being determined by a simple mass balance. A prerequisite to the successful development of an acceptable analytical method was obviously the co – development of a sample preparation method capable of achieving the following performance criteria:

1. Selectively and totally removing the toluene and methanol from the samples.
2. Operation at relatively low temperatures ($< 50^{\circ}\text{C}$) to eliminate the possibility of thermally induced polymerization of residual monomer or thermal degradation of the polymer.
3. Eliminating the partial removal of high boiling components from the samples.

It was experimentally determined that the desired result could not be achieved using the traditional rotary evaporatory but might be possible using a nitrogen evaporator at atmospheric pressure (Organomation Associates Inc., N – EVAP).

Basically a nitrogen evaporator is a device consisting of a multi position sample holder submersed in a heating bath. The sample is contained in a glass vial of appropriate size and dry nitrogen or atmospheric air is directed into the sample holder through a cannula. The gas flow is manually regulated to control the evaporation rate while preventing sample loss from spattering.

In general the evaporation of a liquid may be divided into two components: (1) the amount of the liquid that is converted into vapor being dependent on the temperature dependant

vapor pressure (VP) and (2) then actual weight or mass of the vapor collected or accumulated in the space above the liquid which is dependent on the vapor density (VD) of the substance and is independent of the temperature.

In a typical gas flow assisted evaporative system the solvent being removed is vaporized by the applied heat and the vapor collects in the sample container in the area above the liquid surface until equilibrium is reached at which point the vapor concentration remains constant (the sample container being a semi – closed or “restricted” system). The continuous flow of gas into the sample container physically flushes the vapor from the sample container thereby forcing the equilibrium to the left thus generation additional vapor. In general terms, the temperature dependent vapor pressure of the substance determines the rate and volume of vapor generated and the vapor density determines the force required to remove the vapor from the sample container.

It was originally assumed that the relative rates of evaporation of the sample components would be directly related to the boiling point of the individual components. However, the data from the validation of the preparative process and associated procedure clearly demonstrated that this was not the case. Since the evaporation rates did not appear to be directly related to the solvent boiling point or vapor pressure, respectively, it was determined that it would be necessary to demonstrate that the method was capable of achieving the required performance criteria and further to determine the relationship between the boiling point (BP), vapor pressure (VP), vapor density (VD) and the observed evaporation rates in an open, gas flow assisted evaporation system.

7.2.1 EXPERIMENTAL

The apparatus used for this series of experiments was a standard twenty four (24) position N – EVAP nitrogen evaporator, model # 112, with a heated water bath. Operational specifications and diagram of the unit are attached. Standard borosilicate glass vials with rubber lined plastic closures were used as sample containers and all test solvents (Sigma – Aldrich Group) were ACS reagent grade and were used as received without further purification. Physical properties of the subject solvents are given in table 1.

Both commercial grade (99.99%) and UHP (99.999%) grade nitrogen (Air Liquide) were used and atmospheric air was generated using a diaphragm vacuum pump. Gases flows were regulated using standard multistage cylinder regulators (Fisher Scientific) and dried by passing through

Solvents were dispensed using a Finnpiette variable volume pipetter (Fisher Scientific) and verified by weighing. Bath temperatures were measured with NIST traceable digital thermometers with type K thermocouple probes. Relative humidity was measured using an NIST traceable hygrometer (Fisher Scientific) and atmospheric pressure was measured using an NIST traceable barometer (Fisher Scientific).

In the first series of experiments six (6) pre – weighed, oven dried sample vials were charged with predetermined volumes of the subject solvents and weighed. The charge volume was verified by calculations based on the density of the solvent at 25° C. The sample vials were then sealed to prevent evaporation prior to mounting in the N -EVAP unit.

Gas delivery needles one (1) through six (6) were adjusted to the desired depth and the gas flow valves fully opened. The remaining eighteen (18) needles were turned off and the

manifold gas flow was adjusted to the desired flow rate. The water bath was adjusted to the desired temperature and allowed to equilibrate for thirty (30) minutes prior to the start of the test run.

Following the thirty (30) minute equilibration the sample vials were opened and, as rapidly as possible, mounted in the corresponding positions in the sample carousel. Gas flow to the gas delivery needles was started and the sample carousel immediately lowered into the water bath.

At predetermined time intervals the sample carousel was removed from the water bath and the sample vials removed, closed and weighed. The sample vials were then opened and, as rapidly as possible, remounted in the corresponding positions in the sample carousel. Gas flow to the gas delivery needles was restarted and the sample carousel immediately lowered back into the water bath. The sequence was repeated at three (3) different temperatures using nitrogen and atmospheric air, respectively.

In the second series of experiments six (6) pre – weighed, oven dried sample vials were charged with equal volumes of a single solvent and weighed. The charge volume was again verified by calculations based on the density of the solvent at 25° C. The sample vials were then sealed to prevent evaporation prior to mounting in the N -EVAP unit.

Following the same procedure as used for the first series the sample tubes were mounted in the N-EVAP unit at a predetermined temperature. Sample tubes were sequentially removed at predetermined intervals and weighed to determine solvent loss. The sequence was repeated at three (3) different temperatures using nitrogen and atmospheric air, respectively.

In the third series of experiments, following the same procedure, the sample vials were charged with solvent mixtures of known composition. The solvent mixtures in experimental series three contained toluene and methanol together with the subject monomers and esters and polystyrene ($M_w = 25,000$, $M_w/M_n = 1.01$) as a substitute for the polyvinyl ether fraction in the actual samples.

7.2.2 RESULTS AND DISCUSSION

The data from the first series of experiments shows that the rate of evaporation of solvent is linear with respect to time at a given temperature, atmospheric pressure, relative humidity and gas flow rate (figures 7.2.2- 2, 3, 4, 5, 6 & 7). This conclusion was verified by subsequent sets of evaporation rate determinations on selected solvents (toluene, acetone and hexane) run individually. Further, the evaporation rate (ER) of a solvent increases with temperature and is linear at constant temperature (figure 7.2.2-8).

Increasing the gas flow rate, in general increases the apparent evaporation rate (figure 7.2.2- 6). There appears to be a minimum and maximum limit to the effects of the gas flow rate. At zero gas flow the solvent will “slowly” evaporate at a rate dependent on the (VP) and (VD) varying directly with the (VP) and inversely with the (VD). The apparent evaporation rate increases with increased gas flow up to a critical gas flow rate at which the physical “flushing” of the vapor from the sample container equals the rate at which the solvent vapor fills the fixed volume of the sample container. As this maximum effective gas flow rate is reached and / or exceeded the increase in the apparent evaporation rate (ΔER) decreases.

As shown in figure 7.2.2- 1, there appears to be no significant differentiation between the use of nitrogen (or other inert gases) and atmospheric air (approximately 70% nitrogen, 29% oxygen, 1% other gases). Dry atmospheric air appears to be suitable for use in evaporative solvent removal procedures (figure 7.2.2-1). The effects of relative humidity (moisture content of the air) will be studied in subsequent studies.

The data from the first series of experiments clearly shows that the relative evaporation rate (R_r) of a solvent at a given temperature is not determined solely by the solvent boiling point (BP). Referring to the data in table 7.2.2 - 1 for example, we see that the evaporation rate for methanol (BP = 65° C) is approximately one half that of hexane (BP = 69° C) and slightly slower than benzene (BP = 80° C).

TABLE 1 - SOLVENTS PROPERTIES

SOLVENT	MW	DENSITY	BP	VP	VD
1-Propanol	60.10	0.804	97.0	14.9	2.1
2-Propanol	60.10	0.785	82.0	33.0	2.1
Acetone	58.08	0.791	56.0	184.0	2.0
Acetonitrile	41.05	0.786	81.0	72.8	1.4
Benzene	78.11	0.874	80.0	74.6	2.8
Carbon Tetrachloride	153.82	1.594	76.5	91.0	5.3
Chloroform	119.38	1.492	61.0	160.0	4.1
DMF	73.09	0.944	153.0	2.7	2.5
DMSO	78.13	1.100	189.0	0.4	2.7
Ethanol	46.07	0.789	78.0	44.6	1.6
Heptane	100.20	0.684	98.0	40.0	3.5
Hexane	86.18	0.659	69.0	132.0	3.0
Methanol	32.04	0.791	65.0	97.7	1.1
THF	72.11	0.889	66.0	143.0	2.5
Toluene	92.14	0.865	110.0	22.0	3.2
Water	18.02	1.000	100.0	17.5	1.0

It is further worth noting that, as shown in table 7.2.2 - 1, the evaporation rates of the subject solvents do not correlate directly with the vapor pressure (VP) or the vapor density

(VD). Arithmetic manipulation of the data led to the observation that at a given temperature the relative evaporation rate (R_r) of a solvent varies directly with the product of the vapor density and the vapor pressure, $R_r = (VD)(VP)$.

TABLE 7.2.2 -2: SOLVENTS BY (VP)/(VD)

RELATIVE SOLVENT EVAPORATION RATE	MW	DENSITY	BP	VP	VD	(VP)(VD)
Chloroform	119.38	1.49	61.00	160.00	4.10	656.00
Carbon Tetrachloride	153.82	1.59	76.50	91.00	5.32	484.12
Hexane	86.18	0.66	69.00	132.00	3.00	396.00
Acetone	58.08	0.79	56.00	184.00	2.00	368.00
THF	72.11	0.89	66.00	143.00	2.50	357.50
Benzene	78.11	0.87	80.00	74.60	2.77	206.64
Heptane	100.20	0.68	98.00	40.00	3.50	140.00
Methanol	32.04	0.79	65.00	97.70	1.11	108.45
Acetonitrile	41.05	0.79	81.00	72.80	1.41	102.65
Ethanol	46.07	0.79	78.00	44.60	1.59	70.91
Toluene	92.14	0.87	110.00	22.00	3.20	70.40
2-Propanol	60.10	0.79	82.00	33.00	2.10	69.30
1-Propanol	60.10	0.80	97.00	14.90	2.10	31.29
Water	18.02	1.00	100.00	17.50	1.00	17.50
DMF	73.09	0.94	153.00	2.70	2.50	6.75
DMSO	78.13	1.10	189.00	0.42	2.70	1.13

As a test of the validity of the above relationship a series of commonly used laboratory solvents were classified according to their R_r values (table 7.2.2- 2). From the data we see that carbon tetrachloride with a BP of 76.5° C has a higher R_r value than hexane, acetone or THF. We also see that hexane, acetone and THF all have a lower BP than carbon tetrachloride at 69, 56 and 66° C, respectively. If the R_r relationship is valid, carbon tetrachloride should evaporate more rapidly than hexane, acetone and THF at a given temperature.

Following the procedure outlined for experimental series one the relative evaporation rates for carbon tetrachloride, hexane, acetone and THF were determined. The data from this experiment is given in table 7.2.2 -2 and clearly shows that the relative evaporation rates for the four (4) solvents are in the order carbon tetrachloride > hexane > acetone > THF which is in agreement with the relative rates predicted by the R_r relationship.

The evaporation rate obviously increases with temperature but the relationship between the R_f and $((VP)(VD))$ remains linear as shown in figures 7.2.2- 8 & 9. Also, the plot of the calculated R_r values from the $(VP)(VD)$ product for selected solvents at various temperatures supports the conclusion that it should be possible to determine the vapor pressure of a substance from a comparative study of the evaporation rate of the substance relative to a standard with a known vapor pressure.

In experimental series three the evaporation rates of a solvent mixture containing known concentrations of a volatile and non – volatile component was compared with that of the individual components, i. e., toluene and butyl benzoate, respectively. The toluene (volatile component) was totally evaporated in approximately 60 – 65 minutes at 40° C while the butyl benzoate (non – volatile component) remained relatively constant showing only a 0.3% weight loss (figure 7.2.2 – 10). The evaporation rate was linear for toluene and butyl benzoate while there was a decrease in evaporation rate of the toluene portion of the toluene / butyl benzoate mixture with the complete evaporation of the toluene fraction taking 70 – 75 minutes versus 60 – 65 minutes for an equal weight of the pure toluene. Further, it was determined that following the evaporation of the toluene portion of the mixture the butyl benzoate evaporation rate was the same as that of the pure butyl benzoate (figure 7.2.2 – 11).

FIGURE 7.2.2- 1: SOLVENT EVAPORATION RATES WITH NITROGEN & AIR AT CONSTANT TEMPERATURE & PRESSURE (T= 41.5 °C, P = 735 Torr, RH = 58%)

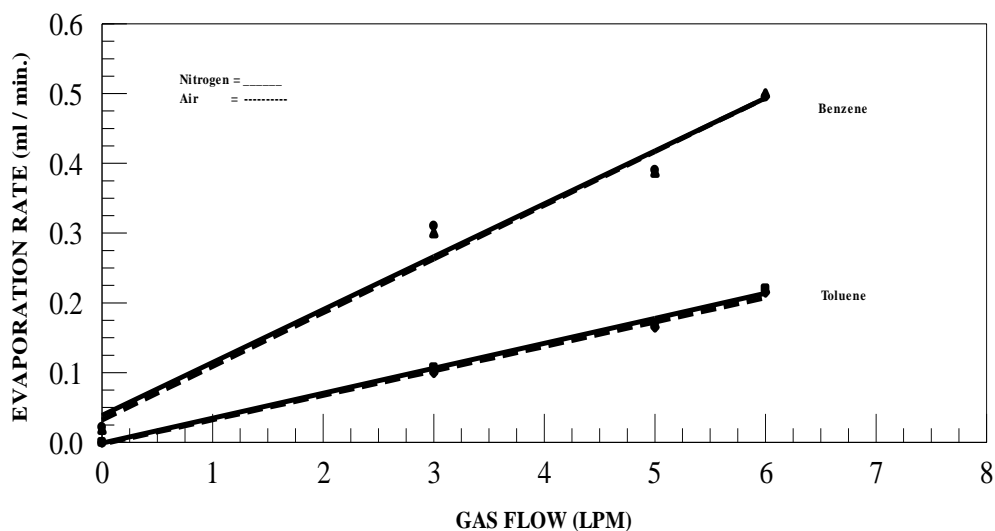


FIGURE 7.2.2 -2: EVAPORATION RATES OF VARIOUS SOLVENTS AT CONSTANT TEMPERATURE & PRESSURE (T= 22°C, P= 738 Torr, RH= 52 %, Air @ 5 LPM)

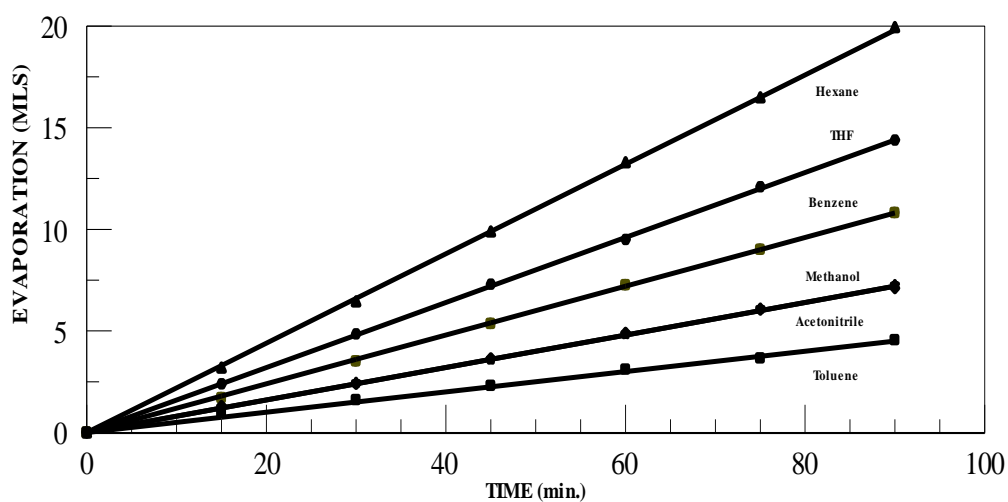


FIGURE 7.2.2- 3: EVAPORATION RATES OF VARIOUS SOLVENTS AT CONSTANT TEMPERATURE & PRESSURE (T= 41.5°C, P= 734 Torr, RH= 57 %, Air @ 5 LPM)

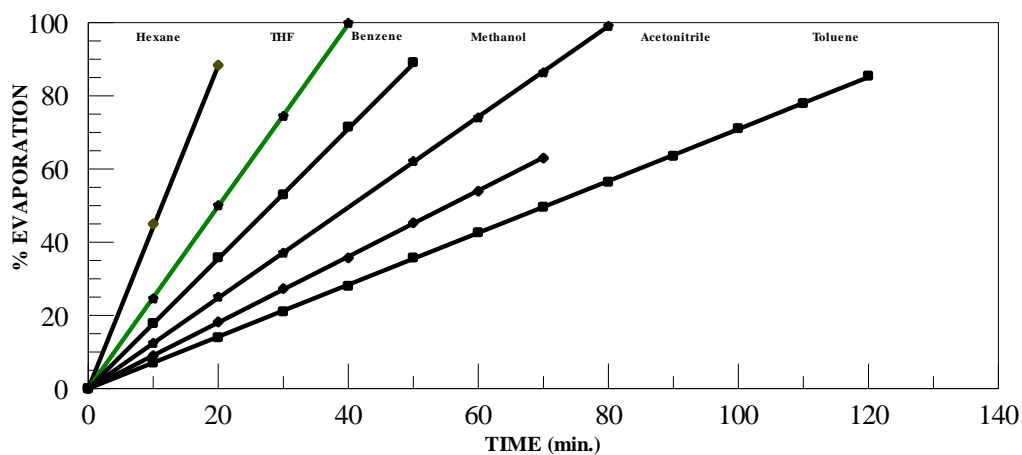


FIGURE 7.2.2- 3: EVAPORATION RATES OF VARIOUS SOLVENTS AT CONSTANT TEMPERATURE & PRESSURE (T= 41.5° C, P= 734 Torr, RH= 57 %, Air @ 5 LPM)

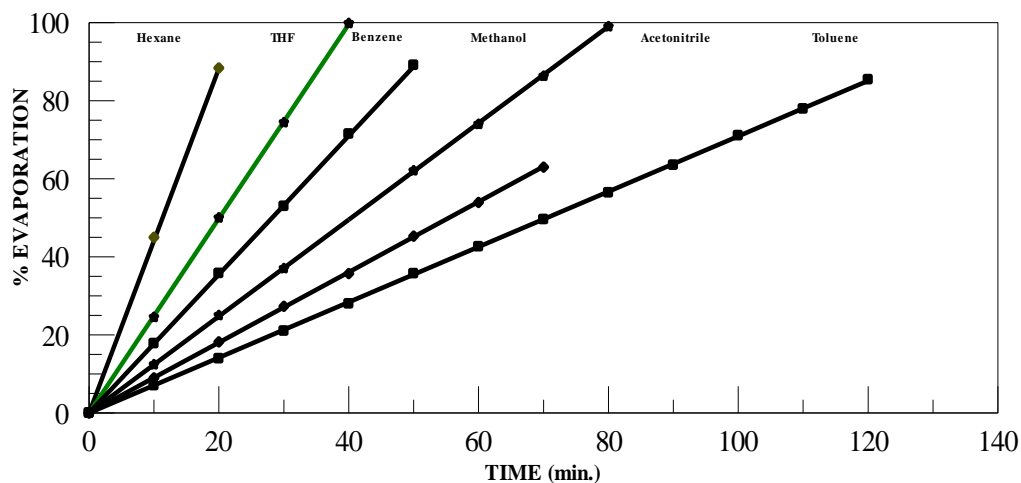


FIGURE 7.2.2- 4: EVAPORATION RATES OF VARIOUS SOLVENTS AT CONSTANT TEMPERATURE & PRESSURE (T= 5° C, P = 732 Torr, RH = 48 %, Air @ 5 LPM)

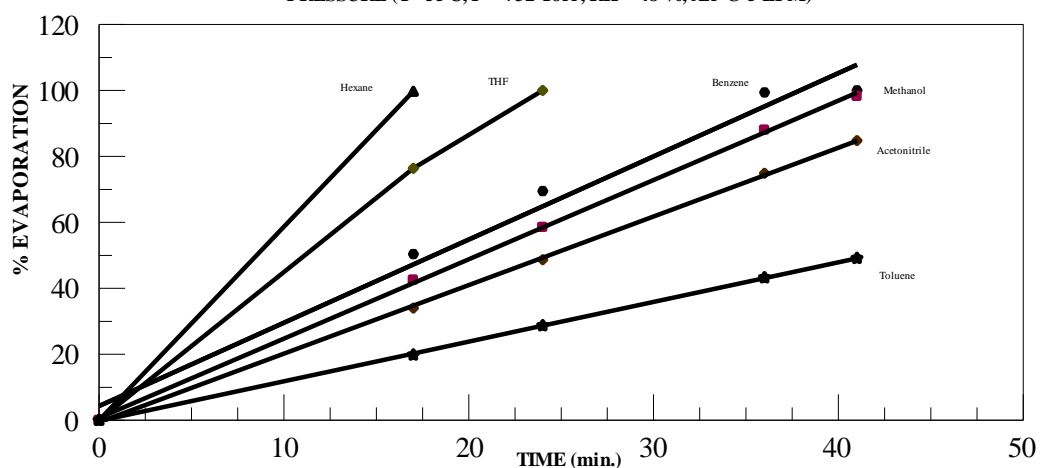


FIGURE 7.2.2- 5: EVAPORATION RATES OF VARIOUS SOLVENTS AT CONSTANT TEMPERATURE & PRESSURE (T= 41.5° C, P= 734 Torr, RH= 58 %, Air @ 3 LPM)

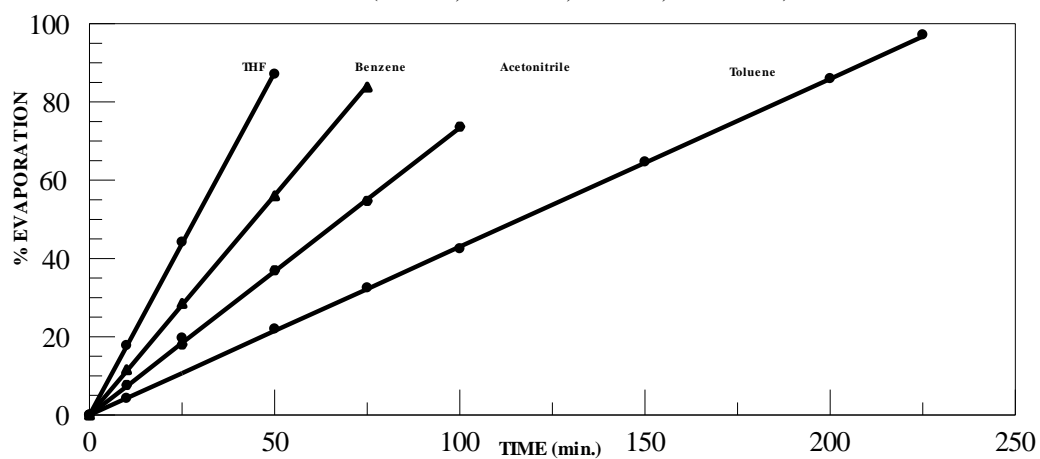


FIGURE 7.2.2-6: EVAPORATION RATES AT VARIOUS GAS FLOW RATES (Air @ 41.3°C)

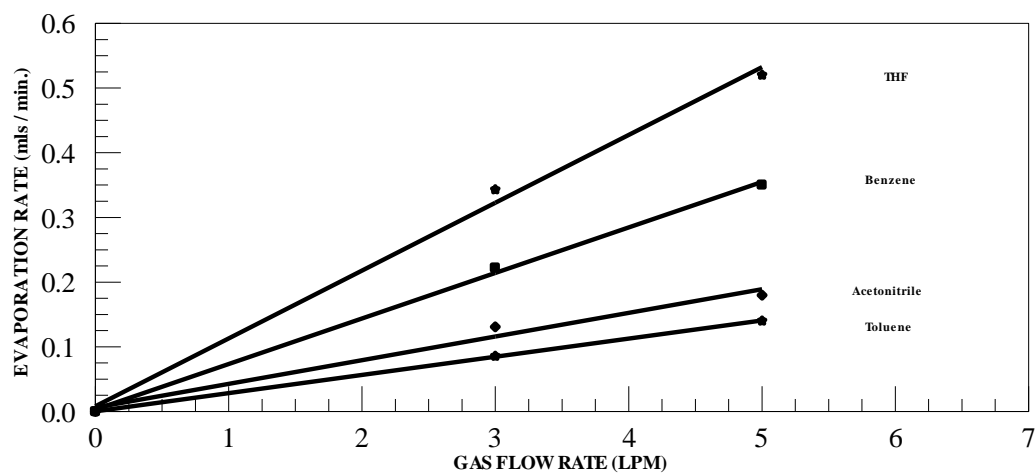


FIGURE 7.2.2-8: EVAPORATION RATE VERSUS (VP)(VD) AT VARIOUS TEMPERATURES
(P= 735 Torr, AIR @ 5 lpm)

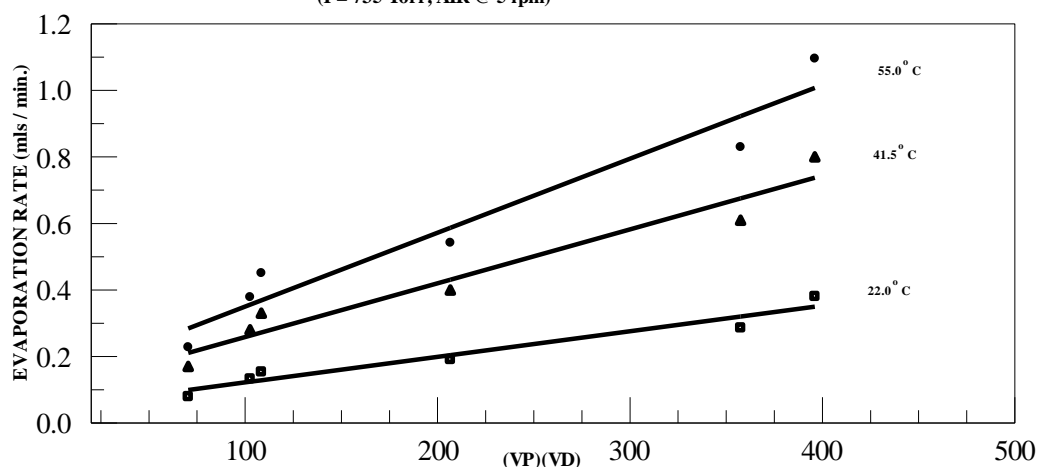


FIGURE 7.2.2-9: CALCULATE EVAPORATION RATES OF VARIOUS SOLVENTS
(P= 735 Torr, Air @ 5 LPM)

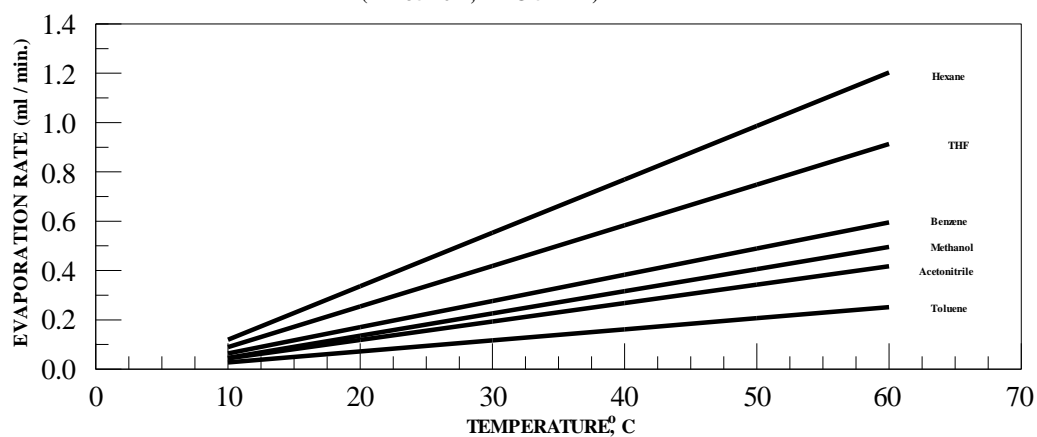


FIGURE 7.2.2- 10: EVAPORATION RATES OF BINARY BLEND OF TOLUENE & BUTYL BENZOATE
VERSUS THE INDIVIDUAL SOLVENTS - 40C, nitrogen flow @ 5 LPM

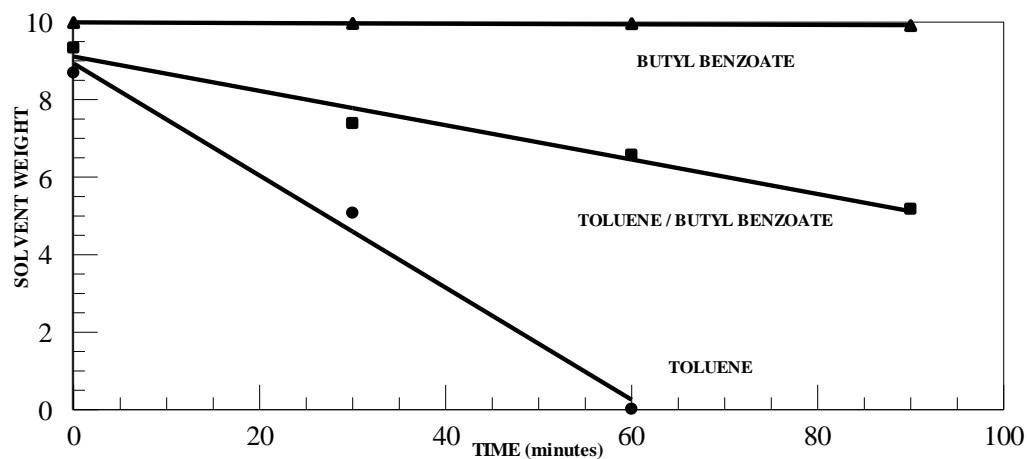


FIGURE 7.2.2-11: SELECTIVE EVAPOORATION RATES OF SOLVENTS OF VARYING VOLATILITY
AT CONSTANT TEMPERATYURE & PRESSUIRE

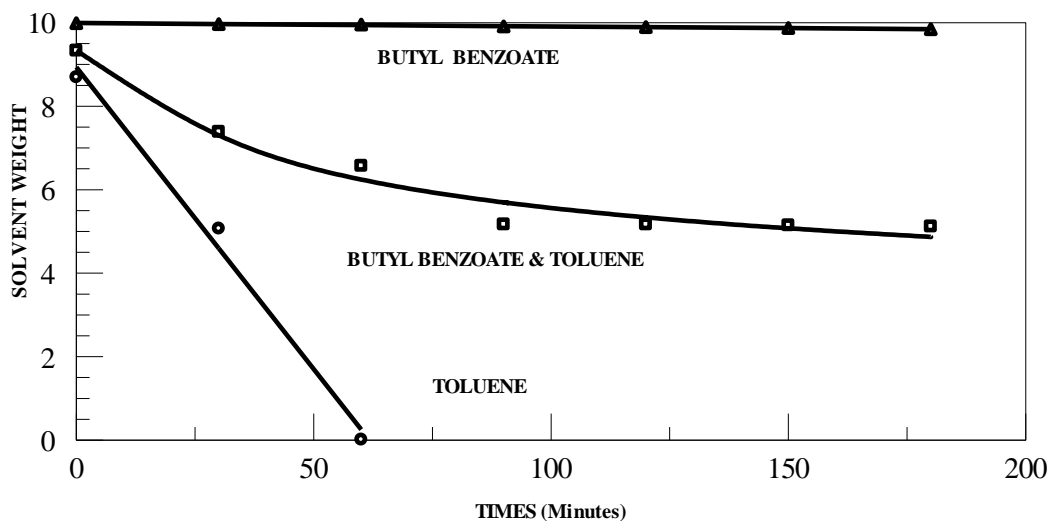
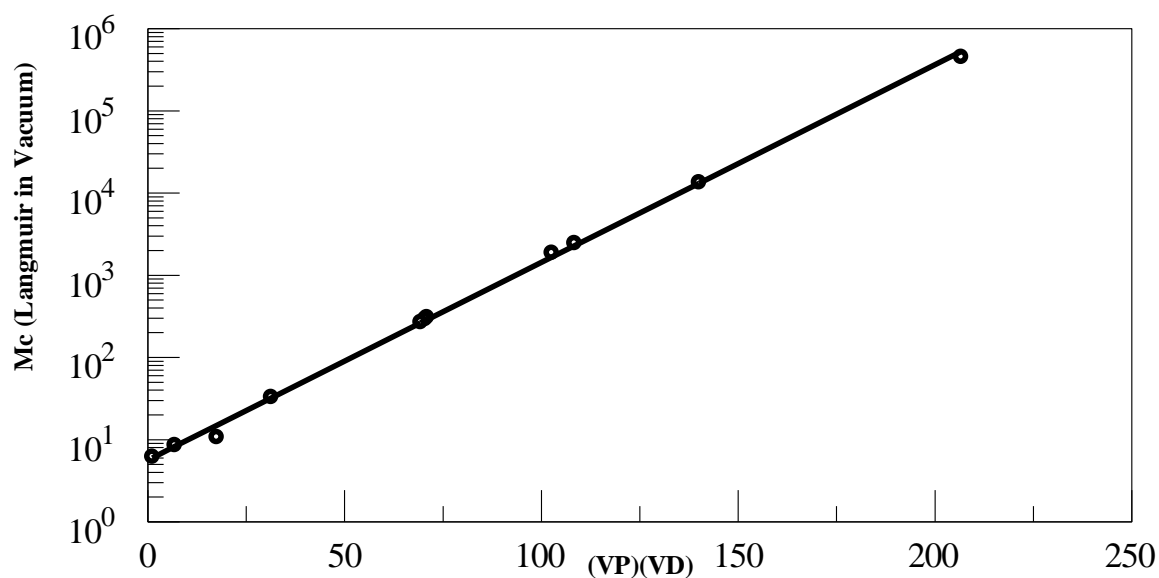


FIGURE 7.2.2-12: EVAPORATION RATES IN CONTINUOUS NITROGEN FLOW ERSUS
CALCULATED RATES IN VACUUM USING THE LANGMUIR EQUATION



7.2.3 CONCLUSIONS

The process by which a solvent evaporates in the N-EVAP nitrogen evaporator is to a large degree a physical process. The vapor pressure (VP) and vapor density (VD) determine the quantity of solvent vapor generated and the weight of the vapor, respectively. As the air above the sample becomes saturated equilibrium is reached and the evaporation rate decreases in accordance with the law of partial pressure. The gas flow into the sample holder physically “flushes” the solvent vapor from the sample holder thereby shifting the equilibrium to the right allowing evaporation of the solvent to continue.

The “solubility” of the solvent vapor in the gas is not a critical factor in determining the apparent evaporation rate although it is a contributing factor. The solubility of the solvent vapor in the gas increases the amount of vapor that is removed / displaced by the gas flow into the sample container but does not appear to be as important as the “flushing volume” in general. This conclusion is supported by the observed “near equivalency” of nitrogen and atmospheric air in the experimental investigations. The increase in the apparent evaporation rate with temperature is attributable to the increase in vapor pressure and subsequent increase in generated vapor. As long as the gas flow is sufficient to remove the vapor the apparent evaporation rate will increase with increasing temperature.

The vapor density (VD) is also a key factor in determining the optimum gas flow rate. In general terms, the gas flow rate requirement varies directly with the vapor density (VD). The heavier the vapor the greater the gas flow required to remove the collected vapor. The data from experimental series three clearly demonstrates that given a sample mixture containing volatile and non – volatile components it is possible to quantitatively separate

the volatile components from the non – volatile components by gas flow assisted evaporation at atmospheric pressure and relatively low temperatures ($\leq 50^{\circ}\text{C}$).

7.3 COMPONENT SEPARATION AND QUANTIFICATION BY SEC

As stated earlier the quantification of the various components of the subject polymerization systems is dependent on the following factors:

1. The ability to remove the reaction solvent and quenching agents from the subject polymerization mixture without the loss of residual monomer, ester additive or lower molecular reaction products.
2. The co-elution (by SEC chromatography) of the residual monomer and ester additives from the polymerization mixture following the removal of the reaction solvent and quenching agent.
3. The verification of the additive nature of the individual components of the composite (co-eluted) peak as calculated from calibration curves of the individual components (residual monomer and ester) based on peak area and / or height.

The feasibility of the removal of the reaction solvent and quenching agent without the subsequent loss of the subject analytes (residual monomer and added ester) was clearly demonstrated and was discussed in detail (section 7.2.).

The co – elution and additive response of the of the monomer and added ester fraction was confirmed by the analysis of standard solutions of a subject monomer (4-(ethenyloxy)butyl benzoate), added ester (butyl benzoate) and a reference polymer

(polystyrene, MW = 25,000) and is discussed in detail in sections 7.3.2 and 7.3.3, respectively.

7.3.1 EXPERIMENTAL

7.3.1.1 INSTRUMENTS & REAGENTS

Anhydrous, inhibitor free, HPLC grade THF (Sigma Aldrich) was used as the mobile phase and for the preparation of all standards and analytical solutions. The solvent was purified as described in the literature (Perrin, D. D, and Armarego, W. L. F., 1988).

Solvent purity was verified by GC analysis on a Buck Scientific Model 910 gas chromatograph with FID and TCD detectors, PeakSimple™ 2000 integration software and a Restek™ Rtx – VMS column.

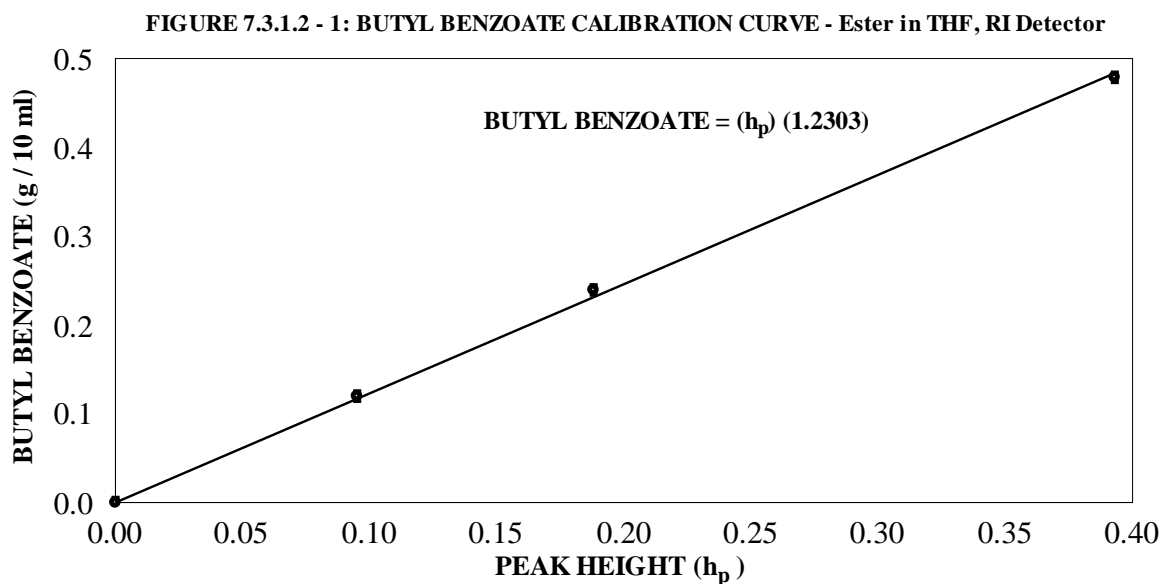
Component separation and quantification was determined by size exclusion chromatography (SEC) in THF on a Buck Scientific BLC – 20 Integrated Isocratic HPLC system with PeakSimple™ 2000 integration software and three ES Industries Chromegapore™ polystyrene columns (MSE-100, MSE-300 and MSE-500; 4.6 mm dia. X 300 mm). The instruments internal variable frequency UV detector was set at $\lambda = 280$ nm when in use but for the majority of the analytical determinations was bypassed in favor of a Knauer K – 2401 RI detector to minimize the solvent path for maximum accuracy and precision (Meyer, Veronika, 1998: Snyder, L. R., Kirkland, J. J. and Glajch, J. L., 1997).

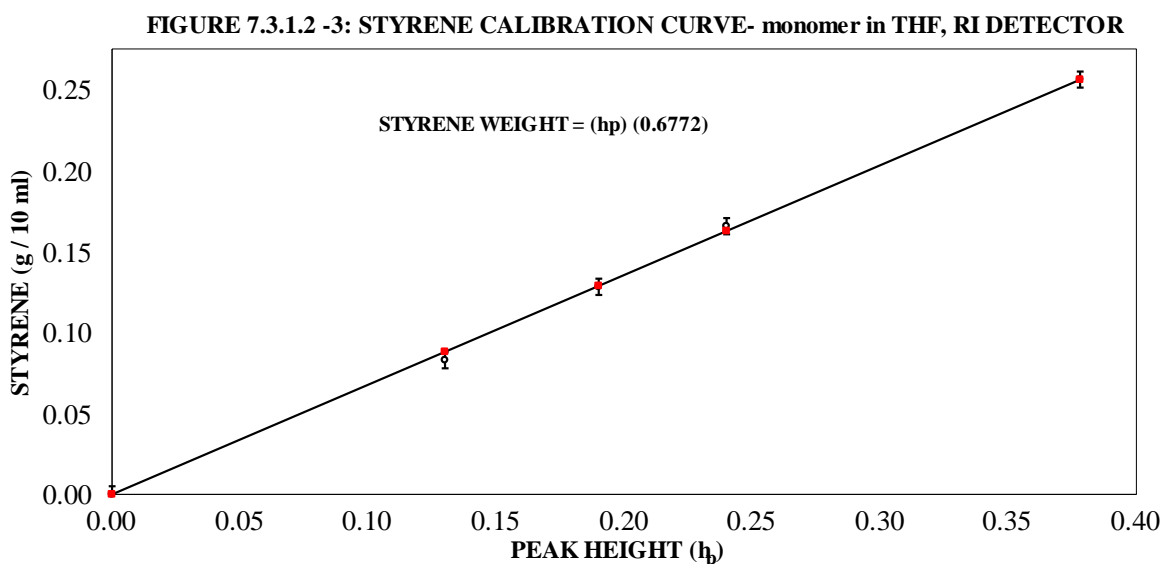
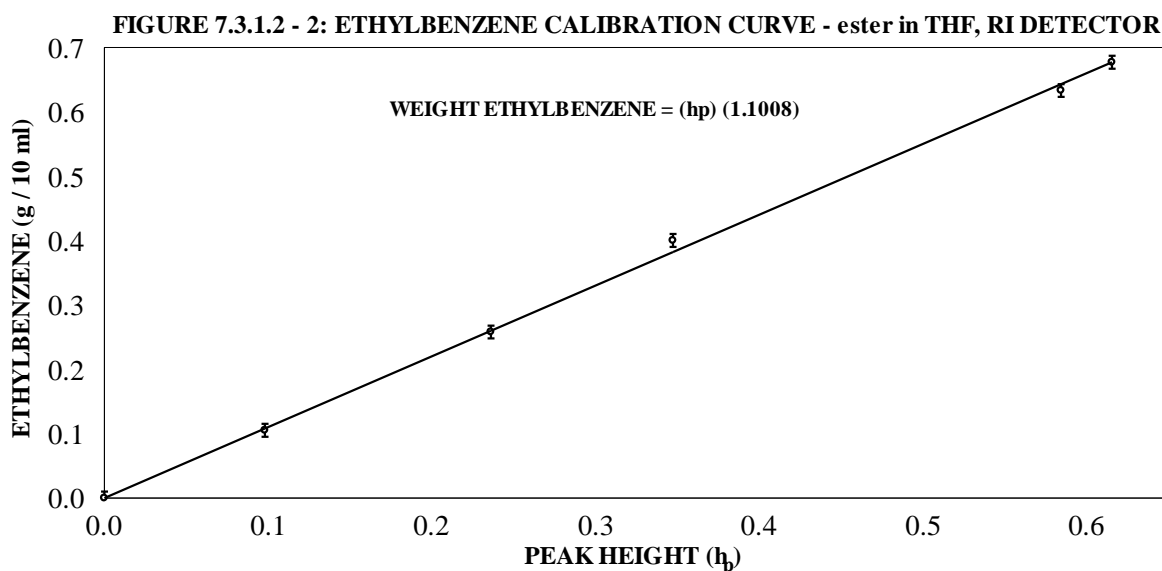
Excess solvent was removed from samples using a twenty four (24) position semi - automatic N – EVAP nitrogen evaporator, model # 112, with a thermostatically regulated water bath. Both commercial grade (99.99%) and UHP (99.999%) grade nitrogen (Air Liquide) were used and atmospheric air was generated using a diaphragm vacuum pump.

Gas flows were regulated using standard multistage cylinder regulators (Fisher Scientific) and dried by passing through a gas drying trap (Drierite™).

7.3.1.2 STANDARDS

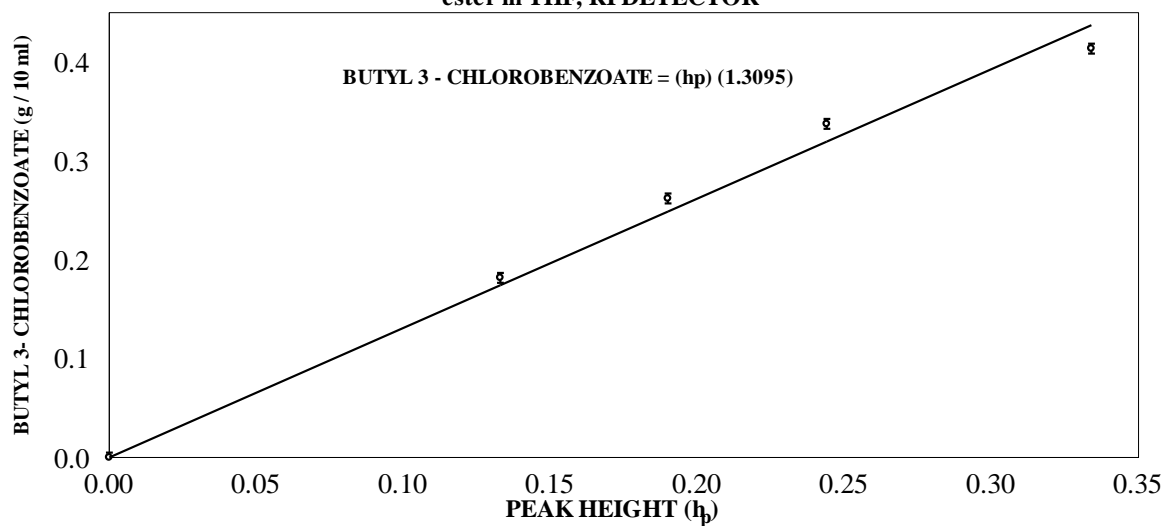
Standard / reference solutions of butyl benzoate, ethylbenzene and styrene were prepared in THF using ACS grade primary standards which were used as received without further purification. Solutions of varying concentrations were prepared and five (5) point calibration curves were prepared for each standard. The linear correlation and COD of the calibration curves was greater than 98% for all standards (Figures 7.3.1.2 -1, 2 & 3).



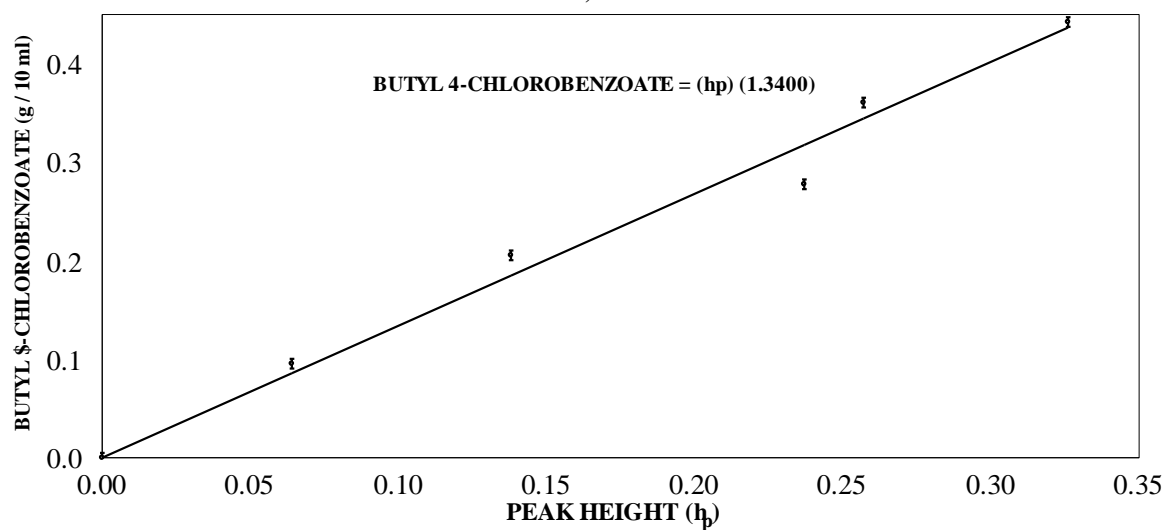


Laboratory prepared samples of butyl 3- chlorobenzoate, butyl 4 – chlorobenzoate, 4-(ethenyloxy)butyl benzoate, 4-(ethenyloxy)butyl 3 – chlorobenzoate and 4-(ethenyloxy)butyl 4 – chlorobenzoate were distilled twice over calcium hydride at reduced pressure and were used for the preparation of the standard / reference solutions. Solutions of varying concentrations were prepared and five (5) point calibration curves were prepared for each standard. The linear correlation and COD of the calibration curves were greater than 98% for all standards (Figures 7.3.1.2 – 4 through 9).

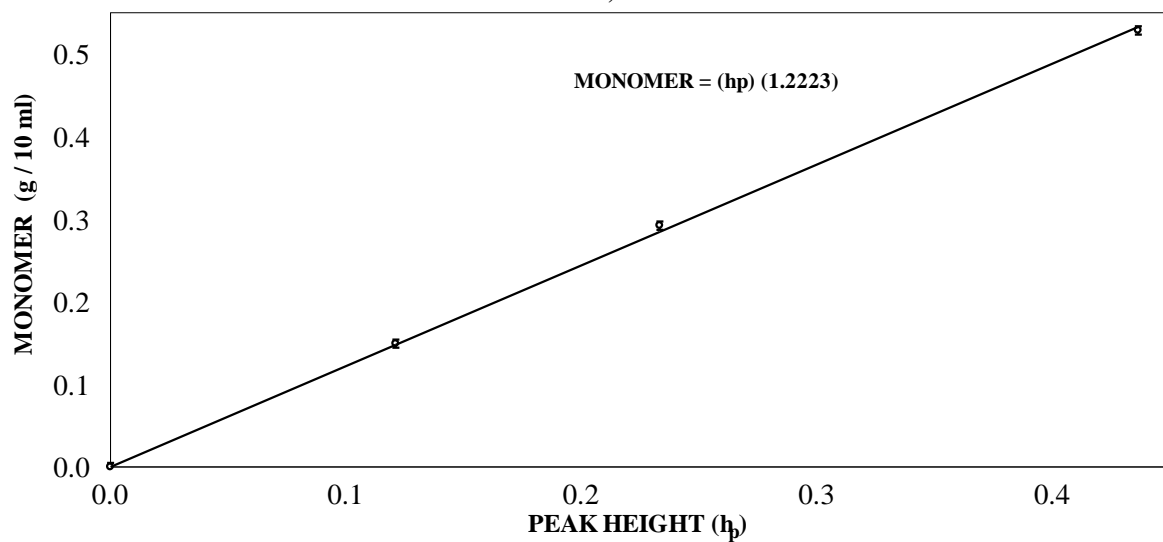
**FIGURE 7.3.1.2 -4: BUTYL 3-CHLOROBENZOATE CALIBRATION CURVE -
ester in THF, RI DETECTOR**



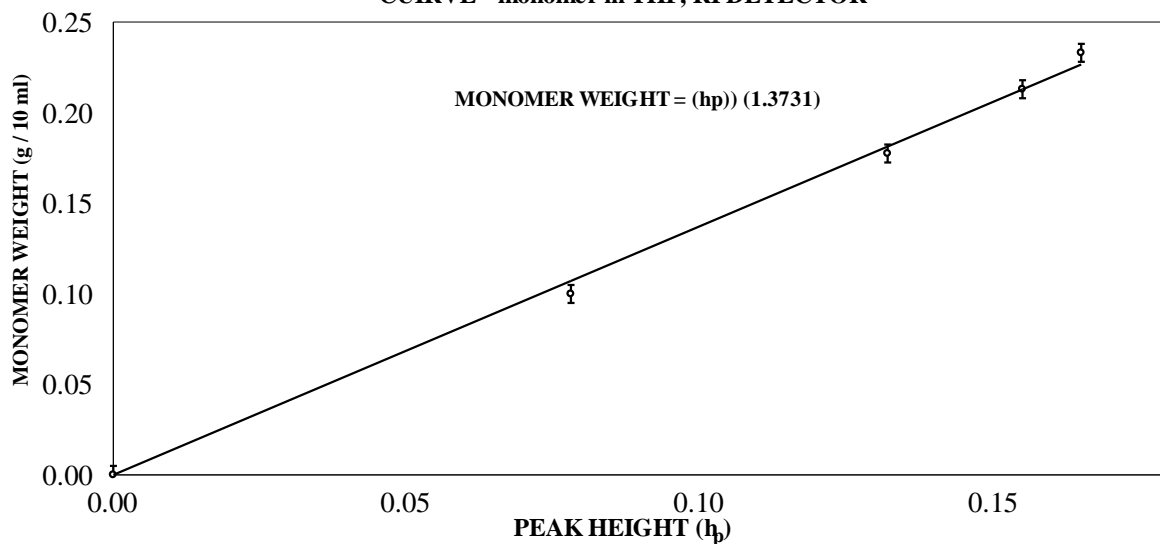
**FIGURE 7.3.1.2 - 5: BUTYL 4-CHLOROBENZOATE CALIBRATION CURVE -
ester in THF, RI DETECTOR**



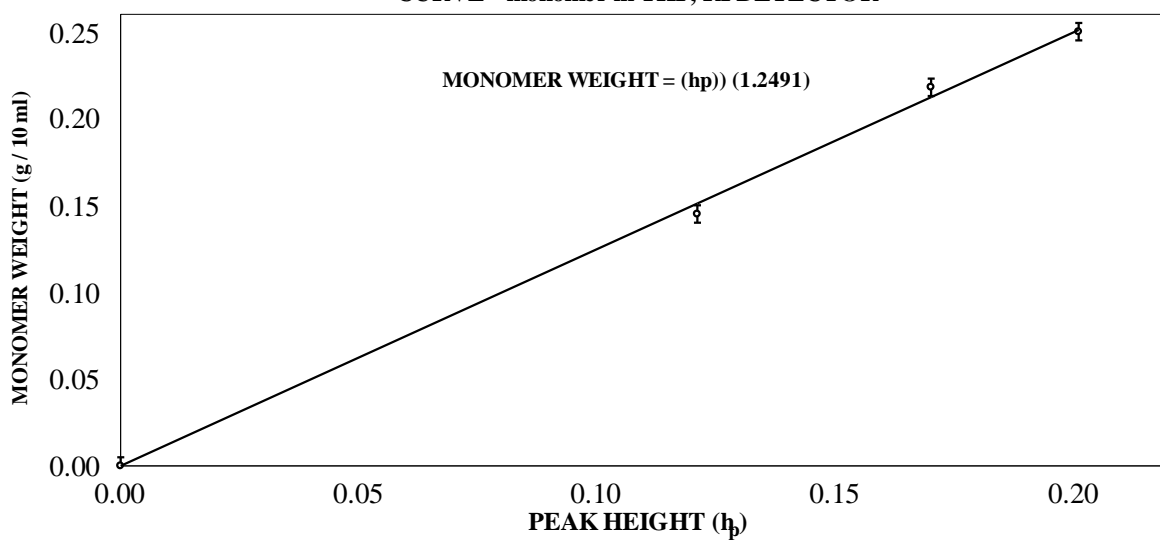
**FIGURE 7.3.1.2 - 6: 4-(ETHENYLOXY)BUTYL BENZOATE CALIBRATION CURVE -
monomer in THF, RI DETECTOR**



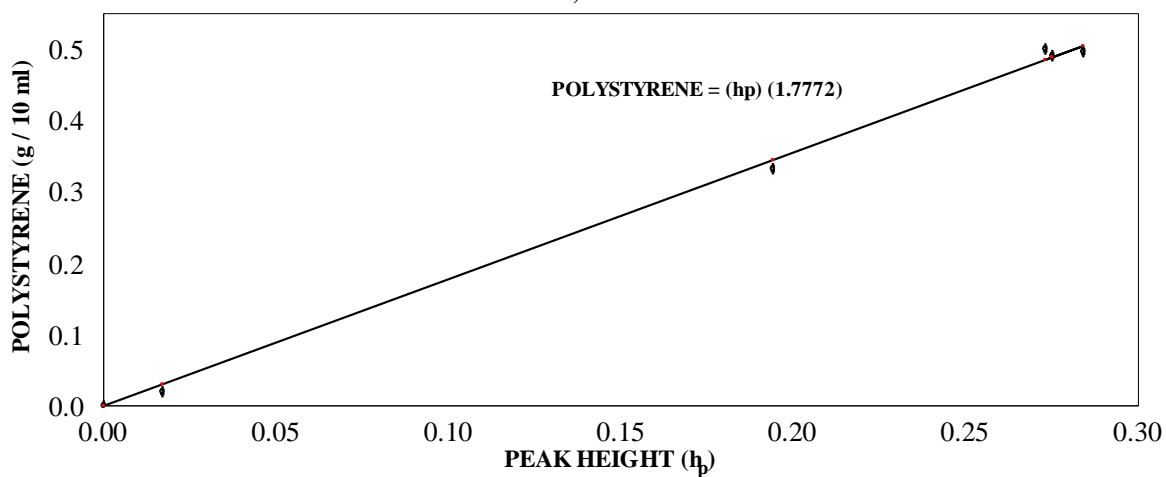
**FIGURE 7.3.1.2 - 7: 4-(ETHENYLOXY)BUTYL 3-CHLOROBENZOATE CALIBRATION
CURVE - monomer in THF, RI DETECTOR**



**FIGURE 7.3.1.2 - 8: 4-(ETHENYLOXY)BUTYL 4-CHLOROBENZOATE CALIBRATION
CURVE - monomer in THF, RI DETECTOR**



**Figure 7.3.1.2 - 9: SEC calibration curve, polystyrene in THF, mobile phase = THF,
F = 0.75 ml / min., RI detector**



Three (3) series of test solutions were also prepared for use in the evaluation and validation of the sample preparation and analytical procedures. Each series consisted of three (3) test solutions each containing a fixed concentration of an ester and varying concentrations of a monomer and polymer. Within each series the monomer to polymer ratios were varied while the combined weight of the monomer and polymer remained constant thereby simulating a polymerization system consistent with the subject investigation, i. e., monomer concentration decreases as polymer concentration increases and the ester concentration remains constant. In each series polystyrene (MW = 25,000, $M_w/M_n = 1.01$) was used as the polymeric component.

Obviously, the polymeric component in an actual polymerization system would normally exhibit an increase in molecular weight with conversion rather than remaining constant. However, for the purposes of the method development the molecular weight is not significant since the actual objective is the quantification of the individual analytes following the SEC separation. Further, the polymeric component of the subject systems would not necessarily have a narrow PDI as was the case with the polystyrene standard. The effects of the PDI on the quantification of the polymeric component was investigated and is discussed in detail in section 7.3.3.

The individual test solutions for series two (2) and three (3) were prepared volumetrically from stock solutions of the individual components in toluene at a concentration of 5.0g / 25 mls total volume and diluted to a final volume of 10 mls by the addition of 5.0 mls toluene and 1.0 mls methanol. The solutions were prepared in preweighed 20 ml glass vials with rubber lined closures. The test solutions for series one (1) were prepared in THF from stock solutions at a concentration of 5.0g / 25 mls total volume and diluted

to a final volume of 10 mls with THF. The actual compositions of the individual test solutions from the three series are shown in table 7.3.1.2 – 1.

TABEL 7.3.1.2 - 1: TEST SOLUTIONS

SERIES 1	#1 - 1	#1 - 2	#1 - 3
STYRENE	0.4000	0.2000	0.0000
POLYSTYRENE	0.0000	0.2000	0.4000
ETHYLBENZENE	0.4000	0.4000	0.4000
THF	6.0 ml	6.0 ml	6.0 ml
SERIES 2	#2 - 1	#2 - 2	#2 - 3
4-(ETHENYLOXY)BUTYL BENZOATE	0.4000	0.2000	0.0000
POLYSTYRENE	0.0000	0.2000	0.4000
BUTYL BENZOATE	0.4000	0.4000	0.4000
METHANOL	1.0 ml	1.0 ml	1.0ml
TOLUENE	5.0 ml	5.0 ml	5.0 ml
SERIES 3	#3 - 1	#3 - 2	#3 - 3
4-(ETHENYLOXY)BUTYL 4 - CHLOROBENZOATE	0.4000	0.2000	0.0000
POLYSTYRENE	0.0000	0.2000	0.4000
BUTYL 4- CHLOROBENZOATE	0.4000	0.4000	0.4000
METHANOL	1.0 ml	1.0 ml	1.0 ml
TOLUENE	5.0 ml	5.0 ml	5.0 ml

Sample series one (1) was intended to serve as a basis for the evaluation of the separatory capabilities of the SEC column assembly, establish general guidelines for analyte concentration and to test the accuracy and precision of the detection system. The standard test solutions did not contain toluene or methanol and therefore required no sample preparation prior to analysis. These test solutions were in effect representative of a standard test solution prepared from the components that were isolated from a polymerization sample by evaporative removal of the reaction solvent and quenchant.

Sample series 2 and 3 were compositionally consistent with actual polymerization system samples in that they contained a fixed concentration of a non – volatile ester and varying concentrations of a non – volatile monomer and polymer in the volatile reaction solvent containing a quenchant, i. e., toluene and methanol, respectively.

7.3.1.3 SAMPLE PREPARATION

Sample series 1 test solutions were used as prepared without further processing. As noted above (section 7.3.1.2) these standard test solutions did not contain toluene or methanol and therefore required no sample preparation prior to analysis. These samples were intended to serve as a control demonstrating that it was possible to quantify two co – eluted components one with a fixed concentration serving as an internal standard.

For sample series 2 and 3 the sample vials were placed directly into the nitrogen evaporator and evaporated at 40° C under a continuous flow of nitrogen at 5.0 LPM for 70 minutes. The sample vials were then removed from the evaporator, closed and weighed.

The sample vials were then returned to the evaporator under the same conditions and evaporated for an additional 10 minutes and reweighed. This procedure was repeated until the loss in weight between two consecutive weighings was less than 2%. The residue was then taken up in THF and quantitatively transferred to a 10 ml volumetric flask and diluted to volume.

7.3.1.4 ASSAY

The test solutions were analyzed with a fixed sample volume of 20 μ l injected at 25° C using THF as the mobile phase at a flow rate setting of 0.75 mls / minute. The actual flow rate was measured every second analysis and averaged 0.643 mls / minute over the course of the analysis of all of the test samples with a 1.88% RSD.

The RI detector with a minimized flow path was autozeroed prior to each sample run and the flow cell was flushed every second analysis. It was determined that a time constant of 0.5 provided adequate sensitivity and a relatively low signal – to – noise ratio. The columns were insulated with a polystyrene foam and the laboratory temperature was maintained at 25° C, \pm 2.0° and verified before each sample injection.

The elution times were recorded with each sample determination and the actual flow were measured every second analysis. The flow rate was measured manually by collection of the effluent in a graduate cylinder and measurement of the collection time with a standard laboratory timer (Snyder, L. R., Kirkland, J. J. and Glajch, J. L., 1997). The average actual flow rate was 0.643 ml / minute with a 1.88% RSD.

7.3.1.5 RECOVERY

Recovery studies were conducted using a “spiking” procedure. In the first series individual analytes were first quantified from peak heights using standard calibration curves. The test solutions at concentrations of 100, 200, 300 and 500 mg /10 mls were first analyzed following the proposed procedure. The test solution was then spiked with a known amount of the analyte and then re – analyzed following the same procedure with the recovery calculated as:

$$(W_t - W_o / W_s)(100) = \% \text{ Recovery}$$

where W_t is the total weight of the analyte in the final (spiked) test solution, W_o is the weight of the analyte in the original (unspiked) test solution and W_s is the weight of the analyte added to the original test solution.

In the second series of recovery studies the above procedure was repeated with the the test solution containing a fixed concentration of a second analyte (representative of the added ester in the subject polymerization systems). In this case the recovery is calculated as above after subtraction of the peak height attributable to the second analyte.

7.3.1.6 METHOD VALIDATION

The proposed method was validated following established guidelines (Gadkari, Parag, 2012: FDA, Federal Registry, USA, 2000:Shabir, G. A., 2003: Snyder, L. R., Kirkland, J.

J. and Glajch, J. L., 1997). The system suitability was also evaluated following the same guidelines.

7.3.2 RESULTS AND DISCUSSION

The co – elution and additive nature of the composite peak from the monomer and added ester components was verified based on the data from the analysis of the series 1 and series 2 test solutions (table 7.3.1.2 -1). The series I samples contained no reaction solvent or quenchant and were intended to served as a control simulating the progressive decrease in monomer with conversion as would be observed in a typical polymerization reaction. The ethylbenzene and styrene monomer are essentially equal in molecular weight and analogous in structure and would therefore have equal retention times based on the fact that SEC is, as stated earlier, a physical process in which molecules are separated solely on the basis of molecular mass. The polystyrene having a higher molecular weight would obviously be eluted at a lower elution volume (shorter time)

The data from the SEC analysis of series 1 test solutions (samples #1-1, #1-2 and #1-3) are shown in figure 7.3.2-1. The samples were analyzed separately under identical conditions (section 7.3.1.4) and the chromatograms were then co – plotted on a common axis. The SEC chromatogram clearly shows two sets of peaks, i. e., polystyrene and the co – eluted ethylbenzene and styrene. Peaks A and B (samples #1-1 and #1-2) are composite peaks of ethylbenzene and styrene while peak C is a single component peak of ethylbenzene (equal concentration in all of the series 1 samples). Correspondingly, peaks a,b &c are single component peaks of polystyrene and are shown to increase progressively as the styrene decreases.

Based on the standard calibration curves for each of the components the individual SEC chromatographs were quantified as shown in table 7.3.2 – 1. The recovery was greater than 98.0% for each of the individual components and the 5% tailing factor ($T_{0.05}$) was less than 2.5 (calculated using USP method) for all determinations. The standard deviation (STDEV) was 0.005 with a %RSD of less than 5.0 for all determinations.

A secondary standard test solution was prepared from equal concentrations (0.5000 g / 10 ml) of polystyrene standards of different molecular weights, i.e., 2500 and 25000, respectively. The sample was analyzed following the same procedure as was used for the series 1 test solutions and the chromatograms from three (3) consecutive determinations, plotted on a common axis are shown in figure 7.3.2 – 2.

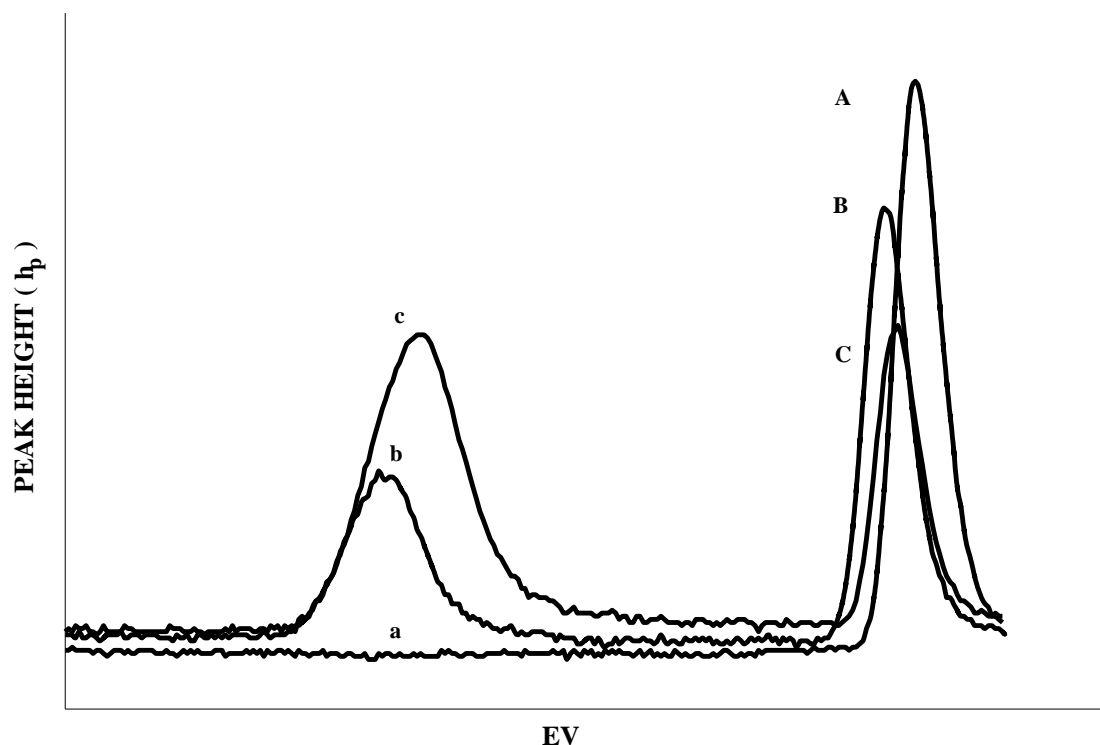


FIGURE 7.3.2-1: SEC chromatogram of three sample fractions of a theoretical polymerization mixture showing the co - elution of the low molecular Weight styrene and ethyl benzene. The ethyl benzene concentration (C) remains constant while the styrene concentration (A & B) decreases with a corresponding increase in the polystyrene concentration (a,b & c).

After correcting for base line drift it was shown that the individual h_p are equal for all three (3) sample analyses. In each individual analysis the polystyrene standards are separated based on their molecular weights and the individual h_p values were proportional to the weight of polystyrene in the sample based on the standard polystyrene calibration curve (figure 7.3.1.2 – 9). The analyte recovery was 98.0% with $T_{0.05}$ of 1.25 and a 1.5% RSD.

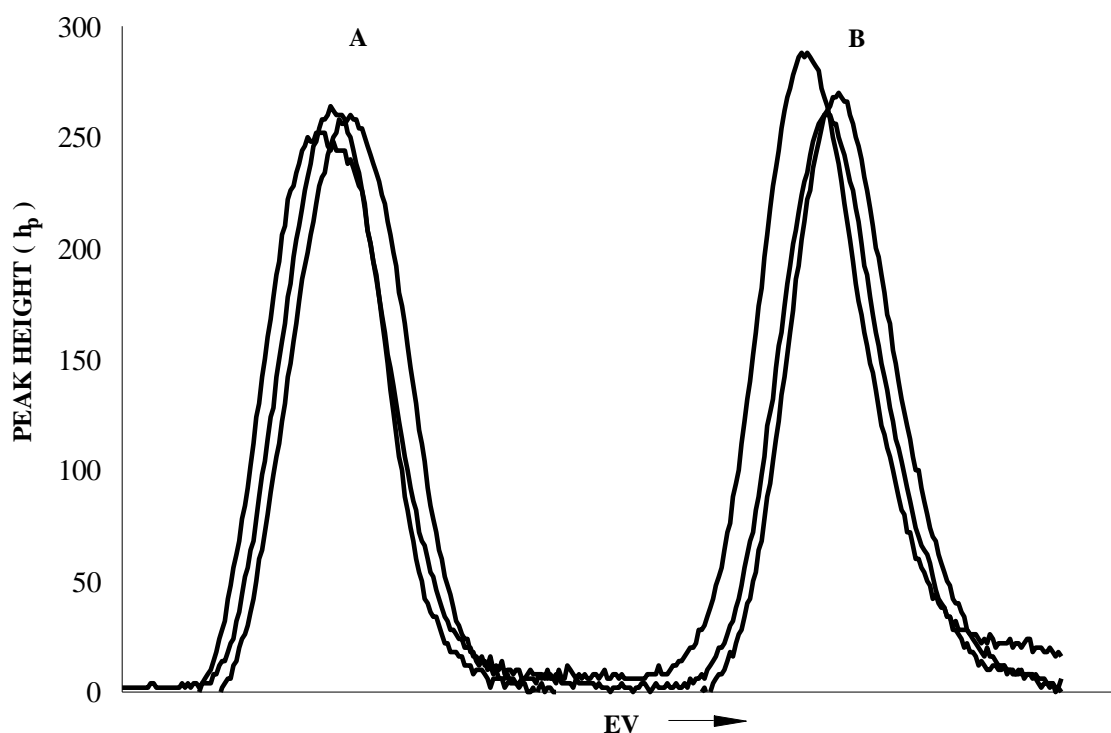


FIGURE 7.3.2 - 2: Chromogram of three separate samples of polystyrene of different molecular weights at equal concentrations, A = polystyrene , 25000 MW: B = polystyrene, 2500 MW, concentration = 0.5 g / 10 ml in THF

TABLE 7.3.2 - 1

SAMPLE	ADDED CONCENTRATION		RECOVERED		% RECOVERY	
	STYRENE	POLYSTYRENE	STYRENE	POLYSTYRENE	STYRENE	POLYSTYRENE
#1-1	0.3000	0.0000	0.2970	0.0000	99.00	
#1-2	0.1500	0.1500	0.1480	0.1530	98.67	102.00
#1-3	0.0000	0.3000	0.0030	0.2950		98.33

The series 2 and 3 test solutions are analogous in composition to the subject polymerization systems with the noted exception of the addition of polystyrene as the polymer component (section 7.3.1.3). In addition to the monomer, ester and polymer this series of test solutions contain the subject polymerization solvent (toluene) and reaction quenchant (methanol). This series of test solutions were processed as previously described (section 7.3.1.3) to remove the reaction solvent and quenchant and were then analyzed following the same procedure as was used for the analysis of the series 1 test solutions. The sample preparation procedure (nitrogen assisted evaporation at atmospheric pressure, 40°C) successfully removed the reaction solvent and quenchant with no appreciable loss of analyte (Table 7.3.2 – 2).

TABLE 7.3.2 - 2

SAMPLE	THEORETICAL ANALYTE WEIGHT	RECOVERED ANALYTE WEIGHT	% RECOVERY
#2 - 1	0.6000	0.5950	99.20
#2 - 2	0.6000	0.5975	99.60
#2 - 3	0.6000	0.6000	100.00
#3 - 1	0.6000	0.6015	100.30
#3 - 2	0.6000	0.6000	100.00
#3 - 3	0.6000	0.5980	99.70

The sample residues were treated as described (section 7.3.1.3) and analyzed following the exact procedure as was used for the analysis of the series 1 test solutions. The results of the analysis of the series 2 and 3 test solutions are shown in table 7.3.2 – 3. The recovery was greater than 97.0% for each of the individual components and the 5% tailing factor ($T_{0.05}$) was less than 2.5 (calculated using USP method) for all determinations.

TABLE 7.3.2 - 3

SAMPLE	ADDED CONCENTRATION		RECOVERED		% RECOVERY	
	VOBBZ	POLYSTYRENE	VOBBZ	POLYSTYRENE	VOBBZ	POLYSTYRENE
#2-1	0.3000	0.0000	0.2955	0.0000	98.50	
#2-2	0.1500	0.1500	0.1470	0.1490	98.00	99.33
#2-3	0.0000	0.3000	0.0000	0.2944		98.13

SAMPLE	VOB4CBZ		POLYSTYRENE		% RECOVERY	
	VOB4CBZ	POLYSTYRENE	VOB4CBZ	POLYSTYRENE	VOB4CBZ	POLYSTYRENE
#3-1	0.3000	0.0000	0.2962	0.0000	98.73	
#3-2	0.1500	0.1500	0.1456	0.1505	97.07	100.33
#3-3	0.0000	0.3000	0.0010	0.2940		98.00

7.3.3 CONCLUSIONS

The analysis of the test solutions clearly demonstrates that the newly developed procedure is suitable for use in the determination of the monomer conversion in the subject polymerization systems. The nitrogen assisted evaporation at atmospheric pressure and relatively low temperatures ($\leq 40^{\circ}\text{C}$) was shown to be effective in the selective removal of the reaction solvent and quenchant thereby facilitating the quantification of the subject monomer, polymer and ester additive.

The analysis of the series 1 test solutions demonstrated that it was possible to accurately quantify individual components of a multi - component mixture following separation of the components by SEC. The recovery was greater than 98.0% for each of the individual components and the 5% tailing factor ($T_{0.05}$) was less than 2.5 (calculated using USP

method) for all determinations. The standard deviation (STDEV) was 0.005 with a RSD of less than 5.0% for all determinations.

The analysis of the series 2 and 3 test solutions further demonstrated that it was possible to accurately quantify individual components of a multi - component mixture isolated from a mixture of a reaction solvent and quenchant solution following separation of the components by SEC. The recovery in this case was greater than 97.0% for each of the individual components with a 5% tailing factor ($T_{0.05}$) of less than 2.5 (calculated using USP method) for all determinations. The standard deviation (STDEV) was again 0.005 with a RSD of less than 5.0% for all determinations.

The data from the method validation clearly supports the conclusion that the new method is sufficiently accurate and precise and that it may therefore be utilized in the determination of the monomer conversion in the subject polymerization systems.

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