SYNTHESIS OF CATIONIC MACROMONOMERS BY LIVING POLYMERIZATIONS FOR COMB-BRANCHED POLYELECTROLYTES

By

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ABSTRACT

Cationic macromonomers of poly [2-(dimethylamino) ethyl methacrylate dimethylsulfate] (polyDMAEMA-DMS) were synthesized by both living nitro-anionic polymerization with a novel capping technique and atom-transfer radical polymerization (ATRP). The macromonomers were copolymerized with acrylamide to give well-defined comb-branched polyelectrolytes having polyacrylamide (PAM) backbone and polyDMAEMA-DMS side chains by free radical processes.

First, the radical mechanism involved in ATRP was investigated using an electron spin resonance (ESR) spectrometer and a differential scanning calorimeter (DSC). Poly (ethylene glycol) dimethacrylate (PEGDMA) was used as a model system for this purpose of mechanism elucidation. The network-forming feature of the system imposed diffusion limitations to radical deactivation reactions and thus allowed us to directly observe the radical intermediates during the polymerization by the first time.

The polyDMAEMA macromonomers bearing terminal allyl moieties were synthesized by the ATRP method using allyl-containing organic halide as initiator. The polyDMAEMA macromonomers with styrenic end groups were prepared by the living nitro-anionic polymerization. A novel capping technique was developed to improve the initiator efficiency in the anionic polymerization. The polyDMAEMA macromonomers were quaternized with dimethyl sulfate yielding cationic polyDMAEMA-DMS macromonomers.

The copolymerization of acrylamide with polyDMAEMA-DMS macromonomers was conducted using 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) as free radical initiator in aqueous solution. The reactivity ratios in copolymerization were measured for the two series of cationic macromonomers with terminal styrenic or allyl groups. PolyDMAEMA-DMS macromonomer with styrenic end group was found to have a much higher reactivity than acrylamide. It was attributed to the hydrophobic characteristic of styrenic group and the micelle formation of the macromonomer in aqueous media. In contrast, the PolyDMAEMA-DMS macromonomer with terminal allyl group had lower reactivity than acrylamide. This difference in reactivities caused a chemical composition drifting during the copolymerization. A semi-batch method was used to control the copolymer composition for synthesizing comb-branched cationic polyelectrolytes.

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This sandwich-type thesis is based on the following publications in referred journals

1. F. Zeng, Y. Shen, S. Zhu, R. Pelton, "Synthesis and characterization of comb-branched polyelectrolytes - preparation of cationic macromonomer of 2-(dimethylamino)ethyl methacrylate by atom transfer radical polymerization" *Macromolecules,* **33**, 1628-1635, 2000.

2. F. Zeng, Y. Shen, S. Zhu, R. Pelton, "Atom transfer radical polymerization of 2-(dimethylamino)ethyl methacrylate in aqueous media" *Journal of Polymer Science Part A: Polymer Chemistry*, **38**, 3821-3827, 2000

3. Y. Shen, F. Zeng, S. Zhu, R. Pelton "Novel cationic macromonomers by living anionic polymerization of 2-(dimethylamino)ethyl methacrylate" *Macromolecules,* **34**, 144-150, 2001.

4. Q. Yu, F. Zeng, S. Zhu, "Atom transfer radical polymerization of poly(ethylene glycol) dimethacrylate" *Macromolecules* **34**, 1612-1618, 2001

5. F. Zeng, Y. Shen, S. Zhu, R. Pelton, "Synthesis of comb-branched polyacrylamide with cationic poly(dimethylaminoethylmethyacrylate dimethylsulfate) quat"

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6. F. Zeng, Y. Shen, S. Zhu, R. Pelton, "Synthesis of styrenic-terminated methacryalte macromonomers by nitroanion-initiated living anionic polymerization"

Macromolecular Rapid Communication, accepted in November 2001.

Chapter 1

Introduction to Water-soluble Polymers

1.1 Applications of Water-soluble Polymers

The invention and use of synthetic water-soluble polymers have grown rapidly in the past half century (Finch et al., 1996. Vorchheir et al., 1981). This can be attributed both to increasing awareness and government pressure for environmental purposes, and to increasing awareness of economic benefits derivable from the use of these versatile molecules. Water-soluble polymers are mainly classified into three types: anionic, cationic and nonionic polymers on the basis of their molecular structures and solution properties. There are many applications of water-soluble polymers, but most applications arise from their properties in solution, especially from their abilities to adsorb from solution onto particles or surfaces. The distinguished properties of water-soluble polymer especially the flocculation property have gained wide applications in industries summarized in Table 1.1, particularly as flocculants in water treatment, sludge dewatering, papermaking, and mineral processing as well as oil recovery (Hoover et al., 1970).

Raw water or wastewater contains 150 mg/L to 400 mg/L of suspended solids and organic materials (Bolto, 1995. Flock et al., 1973.). Water purification requires a

separation of these organic and inorganic materials such as humic acids, clays and bacteria. These stable colloidal particles cause turbidity and undesirable color in the water. They also interfere the filtration process by blinding the filter media. Flocculants are added to water to flocculate these small particles into larger flocs that can settle or filter easily. In sludge dewatering process, the solids concentration in sludge has increased from the original water stream concentration, however it is still very low, normally less than 5.0 (wt/vol. %) (Schwoyer et al., 1981). It is necessary to reduce the water content as the transportation and disposal costs are based on the total weight not simply on the solids concentrations. Polymer consumption will increase with the percentage of biological solids present (Rey et al., 1986). The addition of water-soluble cationic polymers produces large strong flocs so that the solids can be separated more efficiently by mechanical means such as centrifugal force or vacuum filtration. Sludge dewatering is the final solid/liquid separation step before disposal and often accounts for a large percentage of the total chemical requirement of a plant.

Pulp and paper is one of Canada's most important industries. Most of the products are exported to more than 40 countries (Mutton et al., 1990). Pulp fibers are mixed with fillers, pigments and other additives in dilute slurry. It flows over a wire mesh where the water is rapidly removed. Although the fibers form a filter layer, the pulp fines and additives can easily pass through the screen. The process of flocculation is used to retain fillers, pigments, and fiber fines. The flocculants, commonly called retention aids, save money by keeping these small particles stay on the wire and be a part of the paper sheet. On a paper machine, many different processes occur simultaneously,

Table 1.1. Some Industrial Applications of Polyelectrolytes (Wandrey et al., 1998. Hoover, 1970.).

Primary coagulants	Wet and dry strength additives in papermaking
Flocculants for solid-liquid separation processes	Emulsion stabilizers and emulsifiers(also demulsifiers)
Antistatic agents	Corrosion inhibitors
Soil conditioning	Softening agents for fabrics and paper
Flame retardants	Silver halide peptizers and sensitizers for photographic film
Hair sprays, additives to shampoos, soaps, and other cosmetics	Polysalt complexes
Sequestering agents and additives to detergents	Permselective membranes
Grease thickening	Lubricating oil additives
Electroconductive coating	Isolation of protein fractions by forming an insoluble complex and regenerating the protein
Anion exchange resins	Functional coating for adhesion, curing, etc
Biocides, nematocides, fungicides, etc	Printing inks
Dye mordants and dyeable assists in fibers and photographic film	Adhesives
Pigment retention aids and drainage aids in papermaking	

including polymer adsorption, chain conformational change, collisions between filler particles and fibers, and breakage of polymer induced bonds (Hubbe et al., 1988). The flocculation mechanism depends on the types of pulp fiber, filler and retention aid used, as well as the papermaking process itself. The most probable mechanism is that the polymer chains provide bonding to attach fillers and fines to negatively charged pulp fibers although some agglomeration of fines and fillers may cause larger particles which filter out more easily in the top and central portions of the sheet (Foster et al., 1973). The retention of fines and fillers lowers solids amount to be recycled in the white water and improve the drainage of paper sheet, and thus reduce production costs.

In mining operations, slurries of finely divided colloidal mineral and ore particles, known as slimes, are produced during processing. In the past, the mining industry simply dumped these slimes into settling lagoons, treating the slime as a waste, even though valuable minerals remained in the slurry. The mineral extracting operation was not profitable. Currently, environmental regulations and increasing awareness of the public have forced the mining industry to look for technologies to separate solids from the slimes (Richardson et al., 1987).

Synthetic flocculants such as polyacrylamide are often used to separate particles from water. The polymers must be selected wisely so that the mineral particles can be extracted from the ore. It is not advisable to choose a flocculant that gives very large cohesive flocs, as the minerals are entrapped in the flocs (Kitchener et al., 1978).

The other applications of water-soluble polymers include oil recovery, food processing. During the early exploitation reservoir, oil is produced using the natural

energy present in the reservoir. When this energy is exhausted, some fluid, usually water, can be injected into the wells in order that the remaining producing wells can continue to operate with a profit. At the economic limit, when the producing wells produce so little oil and so much water that the operations cannot profitably continue, 20-80% of the original oil may still remain in the reservoir. Much research has been done on the development of injection fluid that will assist to recover more oil (Friedman et al., 1973).

Polymers are often employed in oil recovery industry as multi-purpose additives. The principal role of polymer is to improve rheological properties, thus the fluid moves more uniformly through the formation without much fingering. Polymers can increase fluid viscosity, therefore prevent fluid flow into the porous well wall structure, and prevent sands and well cuttings from settling under gravity into the well bore bottom (Myagchenkov et al., 1991. Graham et al., 1983. MacWilliams et al., 1983.).

1.2 Flocculation Mechanisms

It is well recognized that charge neutralization and chain bridging are two major mechanisms for flocculation. In papermaking and wastewater treatment, the particles are usually negatively charged (Gregory et al., 1983). Cationic homopolymer and copolymers have been widely used as flocculants such as poly(diallyldimethyl ammonium chloride –*co*- acrylamide) (polyDADMAC-*co*-AM) and poly(dimethylaminoethyl acrylate methyl chloride –co- acrylamide) (polyDMAEMA-MCQ-*co*-AM). These polymers are effective because charge units can attach to particle surfaces while chain backbones bridge the particles together as shown in figure 1.1.

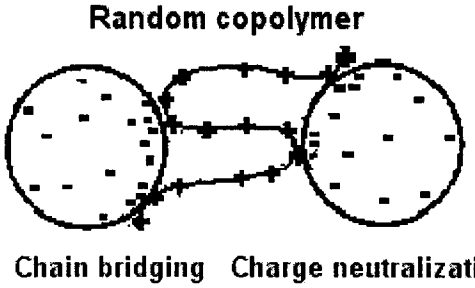

Figure 1.1. Flocculation mechanism by polymer bridging and charge neutralization of random cationic copolymer

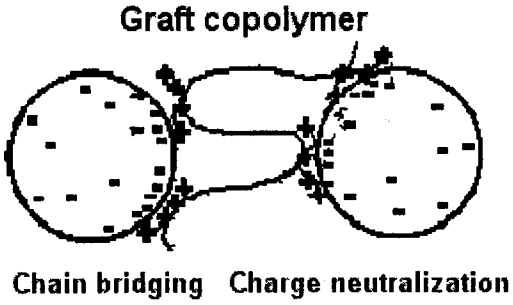

Figure 1.2. Flocculation mechanism by polymer bridging and charge neutralization of graft cationic copolymer

In today's market, more than half of polymeric flocculants are acrylamide-based copolymers. Nearly half of cationic polymeric flocculants are copolymers of acrylamide with amine- or quaternized-amine containing monomers (Rose et al., 1982). The PAM-based cationic copolymers are normally prepared by free radical polymerization. Thus, the charge units are randomly distributed along polymer backbones. Figure 1.1 shows the flocculation mechanisms for a random cationic copolymer.

In Figure 1.1, we can see these cationic charges are not most effectively used in adsorption. Besides, the monomer reactivities in copolymerization are quite different, it is difficult to control the cationic charge distribution along the polymer backbone. In order to be more effective, the cationic units would be better utilized if concentrated on side-chain branches to form cationic graft copolymer. As illustrated in Figure 1.2, these cationic graft copolymers can provide stronger attaching points to negatively charged particles by charge neutralization and chain bridging mechanisms for flocculation. The advantage to use graft copolymers is to produce strong flocs and to effectively use cationic components because polyacrylamide (PAM) is much cheaper than cationic polymers such as poly(DADMAC), and poly(DMAEA-MCQ). Therefore, the graft copolymers may increase flocculation efficiencies and reduce production costs (Ma, 1999).

1.3 Synthesis of Graft Copolymers

1.3.1 Approaches to Graft Copolymer Synthesis

In general, there are three methods to synthesize graft copolymers, namely graft-

from, graft-onto and graft-through methods (Rempp et al., 1989). Graft-from is that initiating sites or functional groups capable of generating such sites on a polymer chain initiate monomers to grow grafts from chain backbones. This method has been widely used (Ito et al., 1999. Ito, 1998. Smets et al., 1960. Bamford et al., 1958.). The sites created on backbone can be free radicals, anions, cations or Ziegler-Natta type active centers. Though this method is quite efficient in a number of cases, it can not provide accurate control over the chain structure. The number of grafts and their lengths are not controllable. Moreover, the graft copolymers often contain a large amount of homopolymers.

Attaching polymer chains by reacting chain-end moieties with functional groups on other chain backbones is called graft-onto method. In this case, grafting does not involve a monomer polymerization. The advantage of this method is that it allows a better structural characterization of the graft copolymers formed, as backbone chains and grafts are made separately and can be characterized individually. Knowing the molecular weight of each of them, and the overall composition of the graft copolymer, it is possible to evaluate the number of grafts per chain, and the average distance between two successive grafts along the backbone. However, it is difficult to control the grafts to polymer backbone and separate the ungrafted homopolymers in this method (Bywater et al., 1974). For example, Subramanian et al. used γ irradiation to graft poly(diallydimethylammonium chloride) onto polyacrylamide backbone. This method is not very selective and results in polymer microgel formation (Subramanian et al., 1999).

The graft polymerization of a monomer in the presence of a polymer carrying

pendant unsaturation, which can participate in the process, is called graft-through. However, such reactions can involve formation of crosslinks between individual chains, if a growing site happens to incorporate unsaturations belonging to two (or more) different backbones. Consequently, the process may result in gelation. Measures have to be taken to avoid gel formation if soluble species are required.

The graft-through method by macromonomer copolymerization has attracted much attention in recent years (Ito, 1998). It involves the synthesis of polymer species with terminal polymerizable unsaturation, namely macromonomer. Copolymerization of macromonomer with a suitable comonomer produces a graft copolymer. Each incorporated macromonomer forms a graft unit (Rempp et al., 1984.). Macromonomer copolymerization techniques have been widely used to synthesize well-defined graft copolymers compared with graft-from and graft-onto methods (Meijs et al., 1990). This method offers a full control over the graft length, because the molecular weight of the macromonomer can be pre-selected. In addition, the number of grafts per polymer chain can also be controlled by adjusting the molar ratio of comonomer to macromonomer.

For this method, the primary efforts have been aimed at finding effective ways to synthesize macromonomers, at understanding the influence of different unsaturation end groups of polymer chain on their copolymerization abilities. The macromonomer synthesis is the most important step.

1.3.2 Synthesis of Macromonomers

Since Szwarc first reported on living anionic polymerization in 1956 (Szwarc,

1956), the living cationic (Puskas et al., 2000. Matyjaszewski, 1996. Kennedy et al., 1982), living radical process (Rizzardo et al., 1998. Matyjaszewski et al., 1995. Sawamoto et al., 1995. Georges et al., 1994) and living covalent polymerization (Webster et al.,1983) have been subsequently reported. These living polymerization techniques have been widely used for polymeric architectural design (Coessens et al., 2001. Puskas et al., 2000. Webster, 1991) such as end-functionalized polymers, block copolymers and graft copolymers etc. These polymerization methods have also successfully been used for macromonomer synthesis.

In general, macromonomers from living polymerization are synthesized by introducing an appropriate copolymerizable end group by one of the following methods: a) end-capping method; b) initiation method; and c) chain transfer method. The end-capping and initiation methods offer most well-defined macromonomers with predefined molecular weight and narrow molecular weight distribution, but they depend on proper combination of a living polymer chain with an effective terminator or an initiator bearing a polymerizable group or its protected one. The chain transfer method utilizes end-functionalized polymers such as those obtained from chain-transfer-controlled radical polymerization and poly-condensation. By using these methods, a series of macromonomers were synthesized such as polyolefins (Okada et al., 1997. Worner et al., 1996. Haenz et al., 1996. Puskas et al., 2000), polystyrene (Hirao et al., 1996. Quirk et al., 1997. Heroguez et al., 1996.).

The end-capping method has been widely used to synthesize various macromonomers with different unsaturation end groups such as styrenic, methacryloyl

and ally end group (Rempp et al., 1988. Tsukahara et al., 1987. Rempp et al., 1958). Hirao et al. prepared styrenic-terminated polystyrene macromonomer by reacting living polystyrene chain with 4-(ω-haloalkyl) styrene derivative terminator (Hirao et al., 1996). However, the termination agent affects the macromonomer functionality and capping efficiency. It was also required to use excess amount of terminator and found that this nucleophilic substitution reactions of carbanions with alkyl halides usually proceed competitively with some side reactions such as α-metalation, β-elimination, and undesirable coupling reaction via metal-halogen interchange and/or single-electron transfer pathway. Therefore, the end-capping efficiency for macromonomer synthesis depends on monomer type, capping agent, solvent and reaction temperature.

The chain transfer method, especially catalytic chain transfer, was used to synthesize macromonomers (Moad et al., 1996.). With the radical mechanism, the product was usually not so well defined as the macromonomers from living polymerization processes.

The initiation method has been successfully used to synthesize oxirane type macromonomer such as poly(ethylene oxide) macromonomers (Masson et al., 1982. Sierra-Vargas et al., 1980) using vinyl-containing alkyloxide initiator. The advantage for this method is that every polymer chain contains unsaturated end group from the initiator. The challenges to prepare the macromonomer using the initiation method are: 1) the unsaturated end group should not allowed to react with initiator or reactive site on living polymer chain during the macromonomer preparation step; 2) the survival unsaturation group should have a compatible reactivity in successive copolymerization with

comonomer. The initiation method offers the best approach to synthesize well-defined macromonomers in terms of end functionality of the polymer product. This method is mainly applied to heterocyclic monomers such as oxirane. Recently, living nitroanionic, living oxyanionic and living radical polymerizations have also been used to synthesize methacrylate-type macromonomers (Shen et al., 2001. Nagasaki et al., 1997).

1.3.3 Synthesis of Graft Copolymer by Macromonomer Copolymerization

The kinetics of macromonomer copolymerization is often analyzed using the terminal model, Mayo-Levis equation, or its simplified model (Mayo et al., 1944). A monomer (A) reacts with macromonomer (B) to give graft copolymer with A as a backbone and B as statistically distributed branches. The chemical composition distribution of a graft copolymer in macromonomer copolymerization was determined by the reactivity of macromonomer relative to that of comonomer. In most cases, the macromonomer reactivity towards co-monomer depends on its terminal unsaturated group and chain length (Tsukahara et al., 1993). Usually the reactivity is reduced by chain length. For example, p-vinylbenzyl- or methacrylate-ended PEO macromonomers were found to copolymerize with styrene in tetrahydrofuran with increasing difficulty with the increase of the PEO chain length (Ito, 1985). The composition distribution of a graft copolymer obtained by the macromonomer method is theoretically broader than its corresponding conventional linear counterpart, due to the high molecular weight of macromonomer branches. This has been experimentally confirmed by Teramachi et al. with polystyrene macromonomers copolymerized with methyl methacrylate (Stejskal et

al., 1987). The chemical composition distribution was broadened with increasing molecular weight and decreasing frequency of the macromonomer branches, as well as with increasing conversion.

1.4 Research Objectives and Thesis Outline

The objective of this work is to conduct a systematic and fundamental investigation on the synthesis of cationic comb-structure copolymers by macromonomer copolymerization. Firstly, a series of cationic macromonomers of well-controlled structure are synthesized by living polymerization. Secondly, the macromonomers are copolymerized with water-soluble comonomers such as acrylamide to prepare a series of comb-branched copolymers with controlled chain length and density in batch processes. And thirdly, semi-batch processes are examined for the macromonomer copolymerization to control the macromonomer incorporation to polyacrylamide backbone and copolymer microstructure. The thesis consists of six chapters. The contents of each chapter are briefly described as follows:

The first chapter of the thesis gives a brief review to water-soluble polymers, their applications and synthetic methods of macromonomers and corresponding graft copolymers.

The second chapter investigates the radical mechanisms involved in atom transfer radical polymerization (ATRP) using poly(ethylene glycol) dimethacrylate (PEGDMA) as a model compound. DSC analysis is used to compare the polymerization behaviors of PEGDMA in ATRP and in conventional free radical polymerization in terms of

polymerization rate and gel formation. The radical signal and concentration are measured by electron spin resonance spectrometer (ESR). This method provides an approach to detect radical intermediates through trapping in a polymer network.

The third chapter describes the synthesis of DMAEMA macromonomers by ATRP. A series of vinyl-containing halide initiators are used to initiate DMAEMA polymerization. The optimal combination of initiator and ligand has been screened to synthesize well-defined macromonomers. The polymerization kinetics is investigated in detail. The macromonomers with different chain lengths are synthesized by ATRP method and the chain-end unsaturation is confirmed by ^{1}H NMR analysis.

The fourth chapter describes the synthesis of DMAEMA macromonomer by living anionic polymerization. Diallylamine/sBuLi and N-isopropyl vinylbenzylamine/sBuLi initiators are synthesized. A novel capping technique is developed and introduced to synthesize well-controlled macromonomers with predefined molecular weight and narrow polydispersity.

The fifth chapter describes the preparation and kinetics of comb-branched copolymers of acrylamide (AM) and polyDMAEMA-DMS macromonomers. The macromonomer copolymerization provides a series of PAM-co-PDMAEMA copolymers with well-defined structures. The reactivity ratios, r_1, of acrylamide (M_1) toward DMAEMA macromonomers (M_2) are measured. The effect of polyDMAEMA pendant chain lengths on macromonomer reactivity is determined. The copolymer compositions are controlled by semi-batch copolymerization techniques.

Finally, in Chapter 6, an overall conclusion of the thesis work and a summary of

its major contributions to knowledge as well as some recommendations for future research in this area are offered.

In addition to the main text, this thesis also includes two appendixes. Appendix A reports atom transfer radical polymerization of 2-(dimethylamino)ethyl methacrylate in aqueous media, and Appendix B reports synthesis of styrenic-terminated methacrylate macromonomers by nitroanion-initiated living anionic polymerization.

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Chapter 2

Elucidating Radical Mechanisms Involved in Atom Transfer Radical Polymerization Using Poly(ethylene glycol) Dimethacrylate as Model Compound

2.1 Introduction

Macromonomer copolymerization is one of the best approaches to prepare graft copolymers with controllable side chain length and branch density along the backbone as discussed in Section 1.3. The main challenge for this method is to synthesize macromonomers with controlled molecular weight and low polydispersity. Living polymerization is the only approach to obtain such kind of functional polymers. Living radical polymerization has many advantages for this purpose. It is not sensitive to water and polar functional groups and its reaction conditions are very mild. Especially, atom transfer radical polymerization (ATRP) has offered a new and efficient route to synthesize polymers with well-controlled molecular weight and low polydispersity (Wang et al., 1995a; Wang et al., 1995b; Kato et al., 1995; Ando et al., 1996; Percec et al., 1995; Percec et al., 1996.). ATRP is also proven successful in the living polymerization of methacrylates (Grimaud et al., 1997). Therefore, as the first choice, we use ATRP method to synthesize water-soluble cationic macromonomers of poly[2-

(dimethylamino)ethyl methacrylate] (polyDMAEMA).

Although ATRP has been intensively studied since its discovery in 1995, its radical mechanisms remain to be a hypothesis. It is arguable if a radical is involved in monomer propagation (Matyjaszewski et al., 2001; Matyjaszewski et al., 1998a; Matyjaszewski et al., 1998b; Greszta et al., 1994.). There has been no direct observation of radical intermediates in ATRP process because of extremely low radical concentration ($10^{-7} - 10^{-8}$ M, Matyjaszewski et al., 1997.), which is beyond the ESR sensitivity to detect the radical signals. Before we use ATRP for our macromonomer synthesis work, we first make effort to elucidate the radical mechanisms. We propose to use polymer network to trap radicals via diffusion limitations. Radicals are thus accumulated to reach a concentration level that can be detected by an electron spin resonance spectrometer (ESR). Because of the difficulty in ESR measurements for polar monomer/solvent systems due to energy absorption, poly(ethylene glycol)dimethacrylate oligomers are chosen as the model compound for this study. This work, if successful, will provide great fundamental understanding about the ATRP process.

In this chapter, we report the results of the ATRP of dimethacrylate oligomers, initiated by methyl α-bromophenylacetate (MBPA) with Cu(I)Br as catalyst and 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA) as ligand. The reaction behaviors of dimethacrylate in ATRP and in a conventional free radical polymerization are compared with respect to polymerization rate, gel formation, and radical concentration. The effects of initiator concentration and temperature on ATRP of dimethacrylate are also examined.

2.2 Experimental Section

2.2.1 Materials

The monomer: poly(ethylene glycol) dimethacrylate (PEGDMA, Mn 386 by ^{1}H NMR, boiling point > 200 °C/2 mmHg, glass transition temperature (Tg) -48 °C for monomer and 32 °C for the fully cured network). Methyl α-bromophenylacetate (MBPA, 97%), copper bromide (CuBr, 99.999%), and 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA, 97%), all from Aldrich, were used without further purification. Benzoyl peroxide (BPO, Aldrich, 97%) was recrystallized and used as the initiator for conventional free-radical polymerization.

2.2.2 Sample Preparation

Take the ATRP-1 system as a real synthetic example. 2 g of PEGDMA (10.36 mmol of vinyl group), 14.82 mg of CuBr (0.1036 mmol), and 23.88 mg of HMTETA (0.1036 mmol) were added into a dried glass tube. The tube was then sealed with a rubber septum and bubbled with ultrahigh-purity nitrogen for 10 min. Initiator (MBPA, 23.73 mg, 0.1036 mmol) was then added via a degassed syringe. The solution was then shaken for 2 min prior to the DSC measurement. For the conventional radical system, 25.08 mg (0.1036 mmol) of BPO was dissolved into 2 g (10.36 mmol) of PEGDMA in a 10 mL tube reactor with stirring. The detailed polymerization system used in this study is listed in Table 2.1.

Table 2.1 The polymerization recipes for ATRP and BPO polymerization systems*.

System	Initiator/catalyst system	$[Vinyl\ group]_0/[initiator]_0/[catalyst]_0/[ligand]_0$
BPO-1	BPO	100/1
ATRP-1	MBPA/CuBr/HMTETA	100/1/1/1
ATRP-2	MBPA/CuBr/HMTETA	150/1/1/1
ATRP-3	MBPA/CuBr/HMTETA	70/1/1/1
ATRP-4	MBPA/CuBr/HMTETA	50/1/1/1

* $[Vinyl\ group]_0$= 6.545 mol/L

2.2.3 Polymerization in DSC

The polymerization were conducted in a differential scanning calorimeter (DSC, 2910, TA Instrument) in an isothermal mode. Approximately 25 mg of the sample mixture was put into an open aluminum pan. The DSC cell was purged with ultra high purity nitrogen for 5 minutes prior to a temperature elevation. During the isothermal DSC scanning, a 50 mL/min of nitrogen flow was maintained to prevent the intervention from oxygen. The rate of polymerization (R_p) was monitored by following the heat flow (dH/dt) evolved in the highly exothermic reaction and was given by eq. 2.1.

$$R_p = (dH/dt)/\Delta H_o^{theor} \qquad (2.1)$$

Since the reaction heat liberated in the polymerization is directly proportional to the number of reacted vinyl groups, integrating the area under the exothermic peak yields the vinyl group conversion (C).

$$C = \Delta H_t / \Delta H_0^{theor} \qquad (2.2)$$

where ΔH_t is the reaction heat evolved up to time t, and H_0^{theor} is the theoretical heat of complete conversion. For methacrylates, it is -13.1 kcal/mol (Anseth et al., 1994).

2.2.4 GPC Measurements

The parallel polymerizations of ATRP-1 and BPO-1 were also carried out in a water bath with preset temperature to extract sol polymer fraction for molecular weight measurements by a GPC. The sample preparation followed the same procedure as for the DSC measurements. The tubes were immersed in the water bath set to 70 °C. At different time intervals, samples were taken out and immediately put into THF solvent to extract unreacted monomers and sol polymers.

A Waters 590 liquid chromatography equipped with three Varian MicroPak columns (G1000, 3000, and 7000HXL) and a 410 differential refractometer detector was used to measure the number and weight average molecular weights (M_n and M_w respectively) of the sol fractions. THF with 2% triethylamine was used as solvent. Narrow polystyrene standards (Polysciences) were used to generate the calibration curve.

2.2.5 ESR Measurements

An on-line electron spin resonance (ESR) measurement was carried out in a Bruker EPR spectrometer (EP072). The spectrometer was operated at 1.59 mW power and 100 KHz of modulation frequency. An approximately 0.5 mL sample solution was transported to a 5 mm o.d. degassed ESR tube capped with a septum. The polymerization took place when the tube was inserted into the ESR cavity, which was maintained at a desired temperature with a Bruker variable temperature unit. The ESR spectra were recorded at different time intervals during the polymerization.

Radical concentrations were calculated by the double integration of the ESR spectra. A toluene solution of 4-hydroxy-2,2,6,6-tetramethylpipieridine-1-oxyl (Tempo, Aldrich) was used as a reference for the radical concentration calibration. To estimate the Cu(II) concentration, the spectra of copper (II) trifluoroacetylacetonate in toluene under the same conditions were used as reference. The experiments were repeated and it was confirmed that the data included the next six chapters were reproducible in this thesis.

2.3 Results and Discussion

2.3.1 Polymerization Behavior

Figures 2.1-2.2 show the polymerization rate profiles for BPO-1 and ATRP-1 systems, demonstrating the significant difference in polymerization behavior between these two systems. BPO-initiated polymerization of PEGDMA exhibits characteristics of a conventional free radical polymerization of multifunctional monomers. Because the mobility of macroradicals was severely reduced after the quick formation of a three-

dimensional network at the beginning of the reaction, the bimolecular termination of the propagating radicals became difficult. The build-up of radical concentration resulted in a dramatic increase in the polymerization rate. As the reaction continued, the increased crosslinking extent also restricted the mobility of monomers, and thus the propagation reactions became diffusion-controlled as well. Therefore, the overall rate of polymerization started to decrease till the reaction eventually stopped. In contrast, the autoacceleration effect was not observed in the ATRP of PEGDMA. The highest polymerization rate appeared at the beginning of the reaction. The rate decreased gradually as vinyl groups was consumed. The increased extent of reaction also imposed resistance to monomer diffusion to slow down the propagation, leading to a further decrease in the rate of polymerization. The absence of autoacceleration effect in the ATRP of PEGDMA in the early stage could be attributed to the low radical concentration and little termination reactions between radicals. In the ATRP system, the growing radicals are in a fast dynamic equilibrium with dormant species (Wang et al., 1995a; Wang et al., 1995b; Kato et al., 1995; Ando et al., 1996).

$$R\text{-}M_n\text{-}X + Cu(I) \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} R\text{-}M_n^{\bullet} + X\text{-}Cu(II) \qquad (2.3)$$

The dormant polymeric halide, R-M_n-X, can be repeatedly activated by the transition metal species, Cu(I), to form the growing radical, R-$M_n^{\bullet}$. The oxidized transition metal species, Cu(II), can further react with the radical, R-$M_n^{\bullet}$, to regenerate R-M_n-X and Cu(I). Due to the small equilibrium constant, the concentration of growing

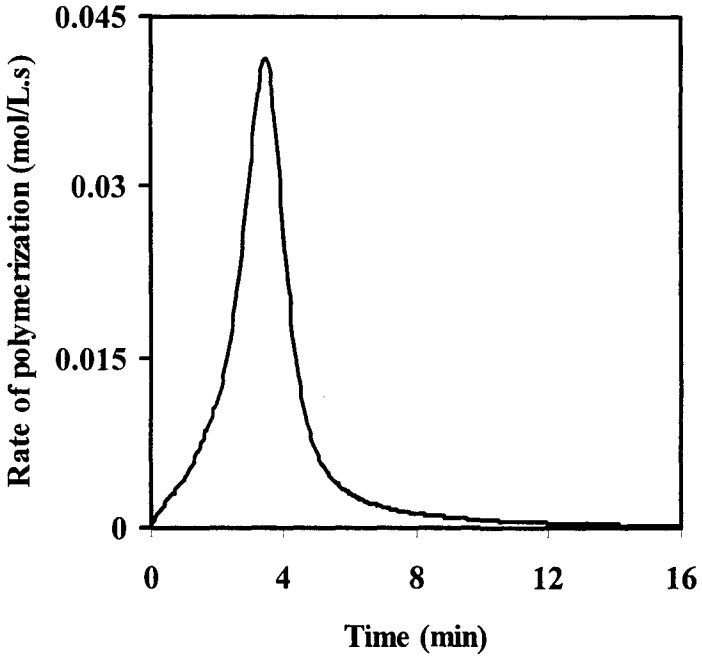

Figure 2.1. Polymerization rate profile for the BPO-initiated polymerization of PEGDMA at 70 °C: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{BPO}]_0 = 0.06545$ (mol/L)

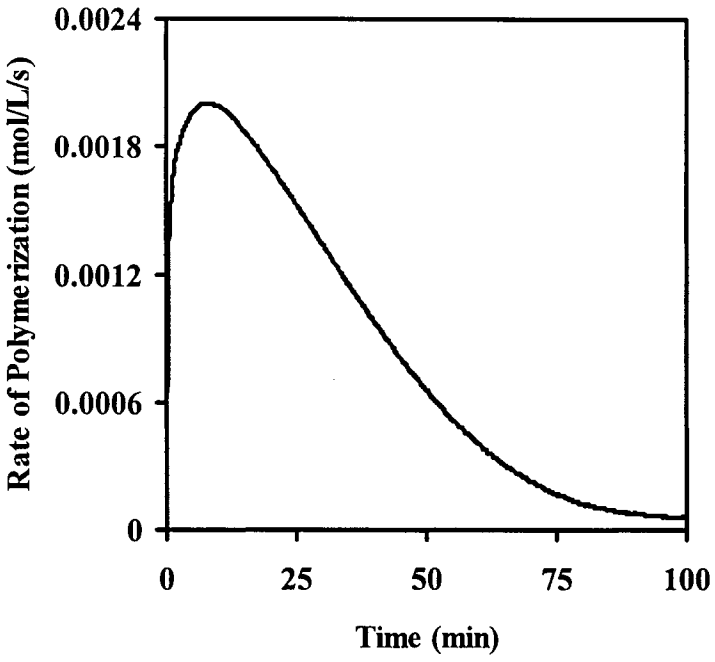

Figure 2.2. Polymerization rate profile for the ATRP-1 of PEGDMA at 70 °C: [vinyl group]$_0$ = 6.545 (mol/L), [MBPA]$_0$ = [CuBr]$_0$ = [HMTETA]$_0$ = 0.06545 (mol/L)

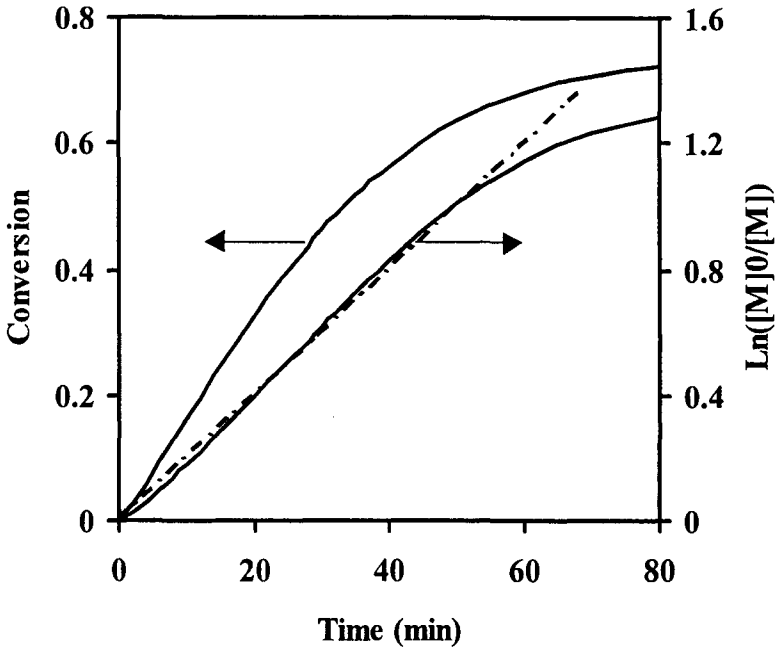

Figure 2.3. Kinetic curves for ATRP-1 of PEGDMA using the same reaction conditions as in Figure 2.2. The dash line indicates a linear portion of the $\ln([M]_0/[M])$ vs time

radicals is very low and the bimolecular termination of radicals is negligible. As long as the transitional metal species remain mobile and the reversible equilibrium is maintained, this unique mechanism would avoid the accumulation of growing radicals and eliminate the autoacceleration even in the network-forming ATRP system. Obviously, the low radical concentration also resulted in the low polymerization rate in the ATRP of PEGDMA.

Figure 2.3 gives the kinetic curves for the ATRP of PEGDMA with an initial molar ratio $[\text{vinyl group}]_0/[\text{MBPA}]_0/[\text{CuBr}]_0/[\text{HMTETA}]_0=100/1/1/1$. The reaction proceeded smoothly and the vinyl group conversion finally reached ca. 72 %. Moreover, the plot of $\ln([M]_0/[M])$ versus time was linear up to 40 % conversion, indicating that the radical concentration remained constant in this range of the conversion. This result agreed to the living character of ATRP. However, a remarkable deviation from the linearity in the later stage of the reaction was observed. This transition could be attributed to the increase in resistance to the diffusion of catalyst/ligand complex, and this will be discussed later together with the results of ESR measurements.

The gelation occurred immediately when the PEGDMA polymerization was initiated by BPO. However, there were no gels in the ATRP-1 system until the vinyl group conversion reached 5 %. Figure 2.4 shows the GPC curves of the sol fractions of the BPO-1 and ATRP-1 systems. The sol fraction in BPO-1 was completely composed of unreacted PEGDMA oligomers with M_n of 580 (GPC). However, there were two peaks in ATRP-1, indicating that the sol fraction consisted of two components, the unreacted the PEGDMA oligomers and the polymer intermediates. The variation of Mn of the sol

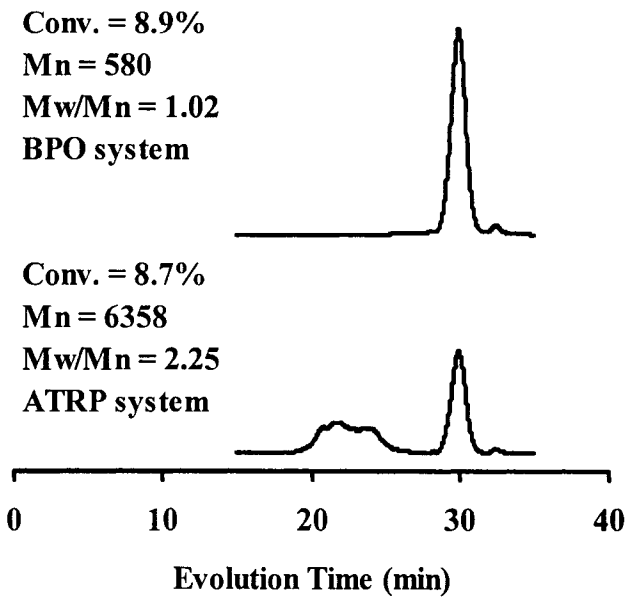

Figure 2.4. GPC curves for sol. fractions from BPO and ATRP-1 reaction systems at 70 °C.

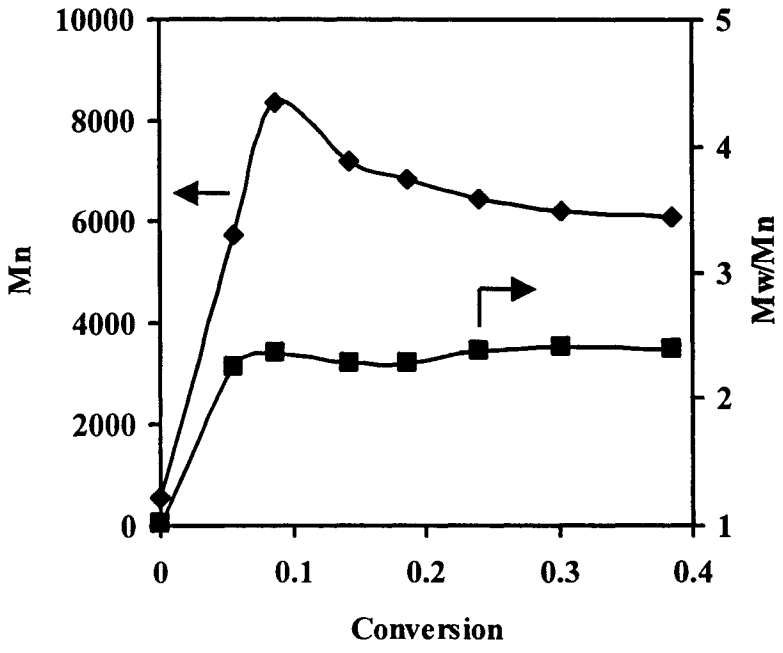

Figure 2.5. Variation of molecular weight and molecular weight distribution of sol polymer with vinyl group conversion for ATRP-1 at 70 °C.

polymer in the ATRP-1 system is given in Figure 2.5. The Mn increased initially in a linear fashion with the conversion increase, demonstrating the living nature of the ATRP process. However, after the gelation, the molecular weight slightly decreased because the sol chains of high molecular weight favored network formation. The high values of polydispersity indicated that the sol polymers were highly branched.

2.3.2 Radical Mechanism of ATRP of Dimethacrylate

The mechanism of ATRP has been extensively studied and a radical process has been suggested (Matyjaszewski, 1998a; Matyjaszewski; 1998b; Wang et al., 1995; Greszta et al. 1994.). However, some arguments still remain on the radical nature of ATRP, especially those polymerizations catalyzed by transition metals. There is a lack of direct evidence for the involvement of radical intermediates in this process.

ESR spectroscopy is an effective tool to investigate paramagnetic species. This technique has been successfully applied to the studies of free radical polymerization, mechanical or irradiation degradation, and molecular motion (Ranby et al., 1997; Kamachi, 1987.). In a typical ATRP system, based on the proposed mechanism, a halogenated initiator reacts with Cu(I) to form a primary radical and Cu(II). The primary radical then initiates chain propagation that is controlled by the reversible deactivation of the radical with Cu(II). In this process, the radicals, as well as Cu(II), are paramagnetic and ESR active. However, according to some ESR investigations on the ATRP of styrene (Matyjaszewski et al., 1998c; Kajiwara et al., 1998.), only Cu(II) species were observed due to its high concentration relative to the radicals. In a network-forming ATRP system,

the network structure may trap reactive species. Therefore, the radical concentration in the crosslinking ATRP is high and likely to be observed by ESR.

The BPO-initiated polymerization of PEGDMA was monitored by ESR for a reference. These spectra shown in Figure 2.6 have typical features of methacrylate radicals (Landin et al., 1988; Tian et al., 1992; Anseth et al., 1996.). The radical concentration versus time is shown in Figure 2.7. The rapid increase in the radical concentration at the beginning of the reaction corresponded to the autoacceleration region in the polymerization rate profile (Fig.2.1-2.2). The bimolecular radical termination via the segmental diffusion and relaxation of radical chains in the network resulted in the decrease in the radical concentration at the late stage of polymerization.

Figure 2.8 shows the ESR spectra recorded during the ATRP of PEGDMA. The ESR signals appeared were the same as those reported in the literature in the first 20 min at 70 °C (Anseth et al., 1994; Landin et al., 1988; Hathaway et al., 1981.) and they were assigned to the copper (II) species. However, it is very interesting to notice that, in addition to the copper (II) signal, a new signal started to appear after a certain period of time. These signals enlarged in Figure 2.9 were typical 9-line methacrylate radical spectra as in Figure 2.6. This observation provided an evidence that radical intermediates were involved in the ATRP process. The absence of the radical signals at the early stage of polymerization was probably due to the radical concentration below the limit of the ESR sensitivity (usually 10^{-7} mol/L).

The observation of radical signals in the ATRP of PEGDMA was the result of the build - up of radical concentration, due to the diffusion limitations experienced by the

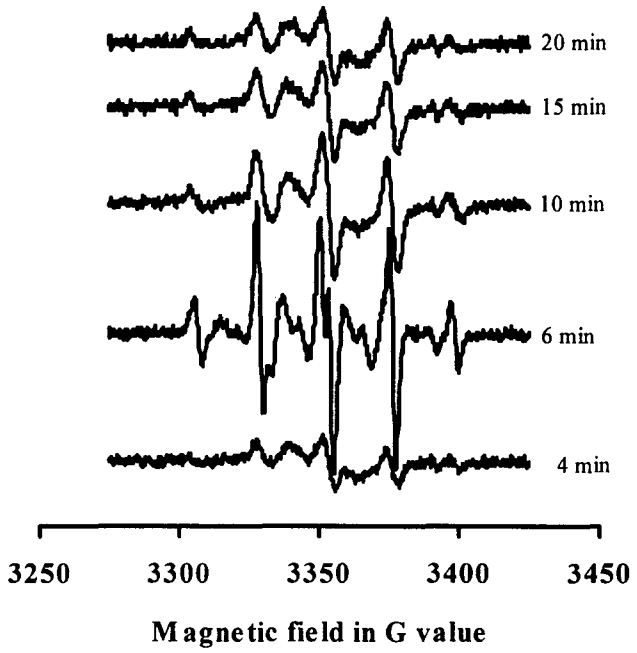

Figure 2.6. ESR spectra recorded during the BPO-initiated polymerization of PEGDMA at 70 °C: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{BPO}]_0 = 0.06545$ (mol/L).

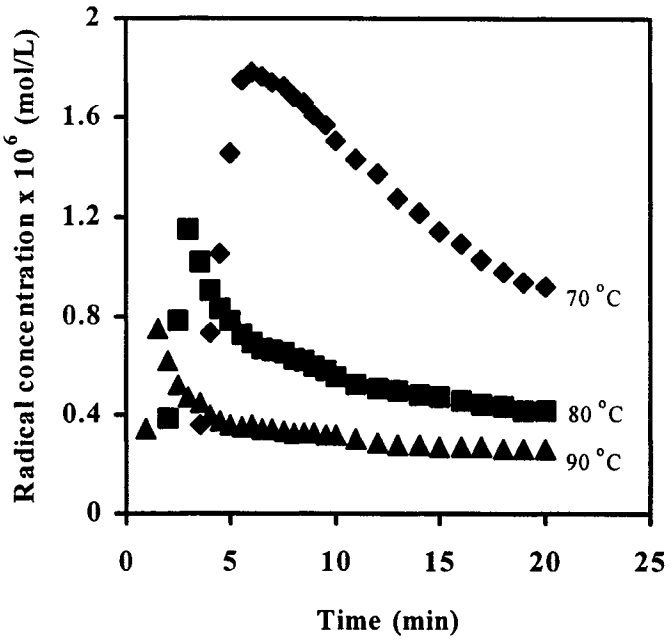

Figure 2.7. Variation of radical concentration measured by ESR during the BPO-initiated polymerization of PEGDMA at different temperatures: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{BPO}]_0 = 0.06545$ (mol/L).

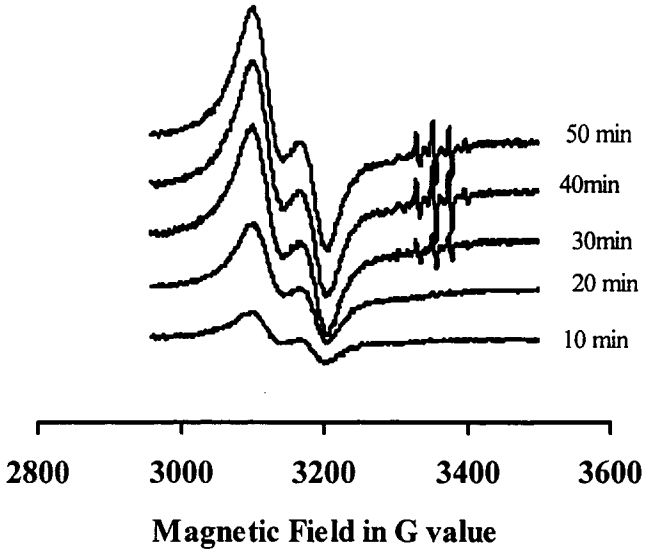

Figure 2.8 ESR spectra recorded during the ATRP process of PEGDMA at 70 °C: [vinyl group]$_0$ = 6.545 (mol/L), [MBPA]$_0$ = [CuBr]$_0$ = [HMTETA]$_0$ = 0.06545 (mol/L).

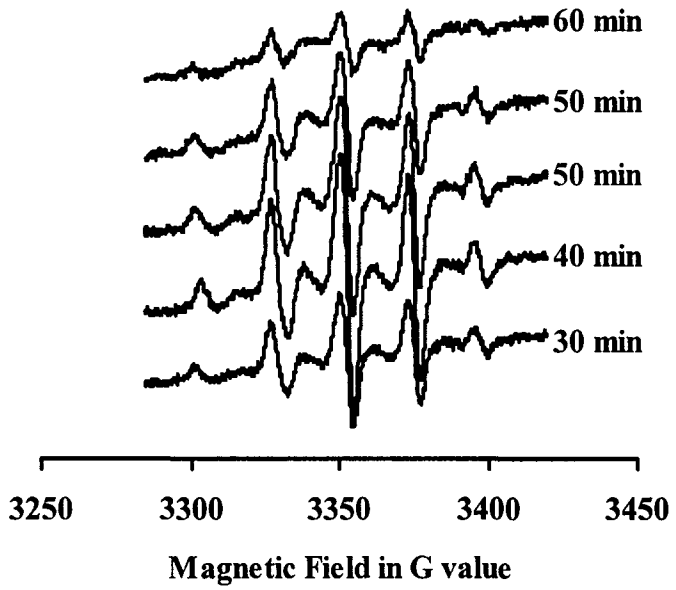

Figure 2.9 ESR signals from methacrylate radicals in the ATRP process of PEGDMA using the same reaction conditions as in Figure 2.8

catalyst/ligand complex. The times required for the radical signal to appear were 28, 18, and 12 min for the ATRP of PEGDMA at 70, 80, and 90 °C. These reaction times corresponded to approximately 42-43 % of vinyl group conversion (measured by DSC). Due to the network structure, the diffusions of the catalyst/ligand complexes (both Cu (I) and Cu (II)) were greatly restricted. Since the deactivation reaction of R-$M_n^{\bullet}$ by Cu(II) was many orders of magnitude faster than the activation of R-M_n-Br by Cu(I), the backward reaction in eq.(3) became diffusion-controlled earlier, resulting in the increase in the radical concentration.

The time dependence of the radical and Cu(II) concentrations in the ATRP-1 system is given in Figure 2.10. The Cu(II) concentration increased from the beginning of the reaction, and gradually reached a steady-state concentration. Elevating temperature resulted in faster increase and higher steady-state Cu(II) concentration. The radical concentration also increased corresponding to the increase in the Cu(II) concentration. After a maximum, it started to decrease due to significant radical termination.

The steady-state Cu(II) concentration should be governed by the redox equilibrium. However, in the network-forming ATRP system, the steady-state Cu(II) concentration is determined by the diffusion rate of Cu(II)/ligand complexes, which interrupts the equilibrium. The steady-state Cu(II) concentrations in this work were in the range of 0.86×10^{-2} to 0.92×10^{-2} mol/L, i.e., an approximately 13-14% conversion of the copper (I). This value is much higher than that found in the styrene ATRP system (4-6%).

Based on the above experimental observations, the ATRP process of PEGDMA

initiated by MBPA and catalyzed by CuBr/HMTETA complex could be divided into three stages as shown in Figure 2.11. At the beginning of the reaction, because of the fast equilibrium between the radicals and dormant species, the radical concentration remained low and constant. The polymerization proceeded in a living manner. As the reaction continued, the mobilities of Cu (I) and Cu (II) species were gradually restricted by the increased diffusion resistance, which impeded the radical deactivation and resulted in an increase in Cu (II) and radical concentrations. Due to the accumulation of radical concentration and the lack of protection of the radicals by copper complexes, the radical termination became significant, and the living nature of the polymerization started to disappear. At the final stage, the reaction behaved like a conventional free radical polymerization. The polymerization continued via the diffusion-controlled mechanism (not only the copper/ligand species, but also monomers experienced diffusion limitations). The radical termination became dominant, resulting in the decrease of the radical concentration.

2.3.3. Effect of Initiator Concentration

A series of reactions at different MBPA concentrations were carried out at 70 °C to investigate the effect of initiator concentration on the ATRP process, with a constant initiator/catalyst/ligand molar ratio of 1/1/1. Figure 2.12 shows the polymerization rate profiles. Apparently, the increase in the initiator MBPA (and also the catalyst CuBr) resulted in an increase in the radical concentration. However, while the initial rate, R_{pi}, increased, the final conversion of vinyl group decreased with the increase of the initiator

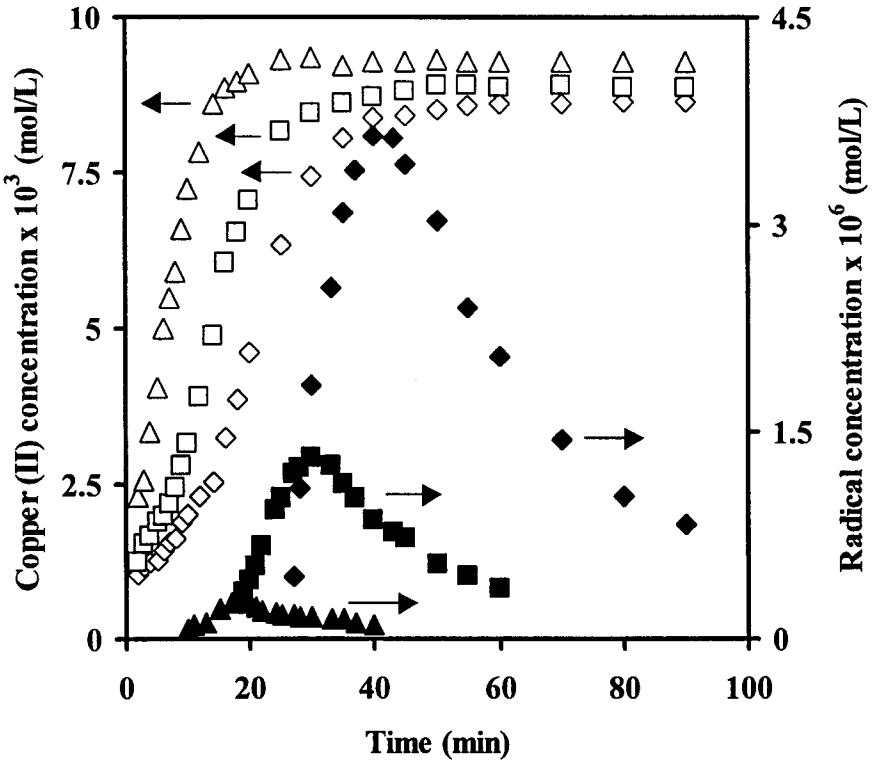

Figure 2.10. Copper (II) and radical concentrations as functions of reaction time for ATRP-1 system at different reaction temperatures: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{MBPA}]_0 = [\text{CuBr}]_0 = [\text{HMTETA}]_0 = 0.06545$ (mol/L): (◊, ♦) 70, (❑,■) 80 and (▲,Δ) 90 °C

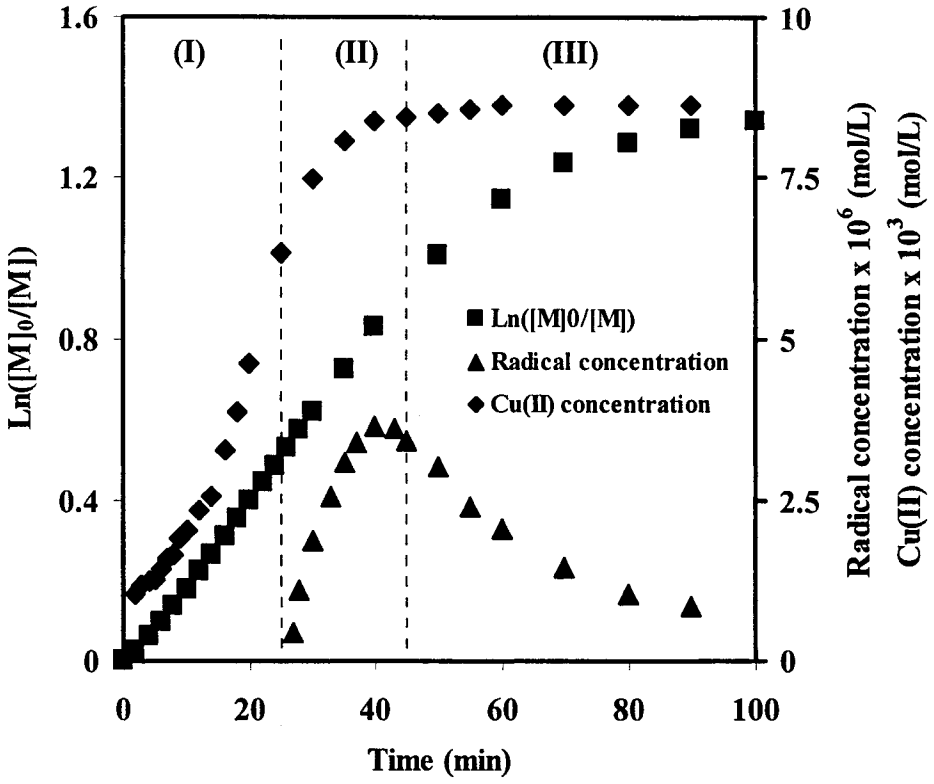

Figure 2.11. Ln($[M]_0/[M]$), radical concentration, and Cu(II) concentration vs polymerization time in the ATRP of PEGDMA at 70 °C: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[MBPA]_0 = [CuBr]_0 = [HMATETA]_0 = 0.06545$ (mol/L).

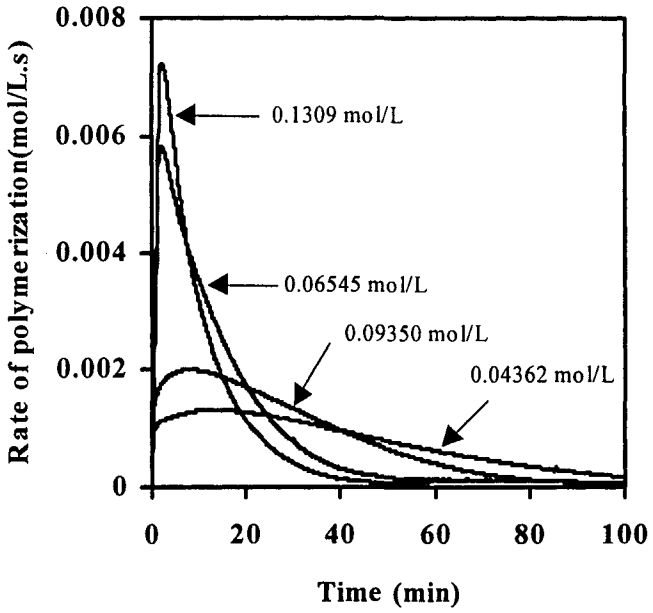

Figure 2.12. Polymerization rate profiles for ATRP of PEGDMA with different initiator concentrations at 70 °C: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{MBPA}]_0/[\text{CuBr}]_0/[\text{HMATETA}]_0 = 1/1/1$ in moles.

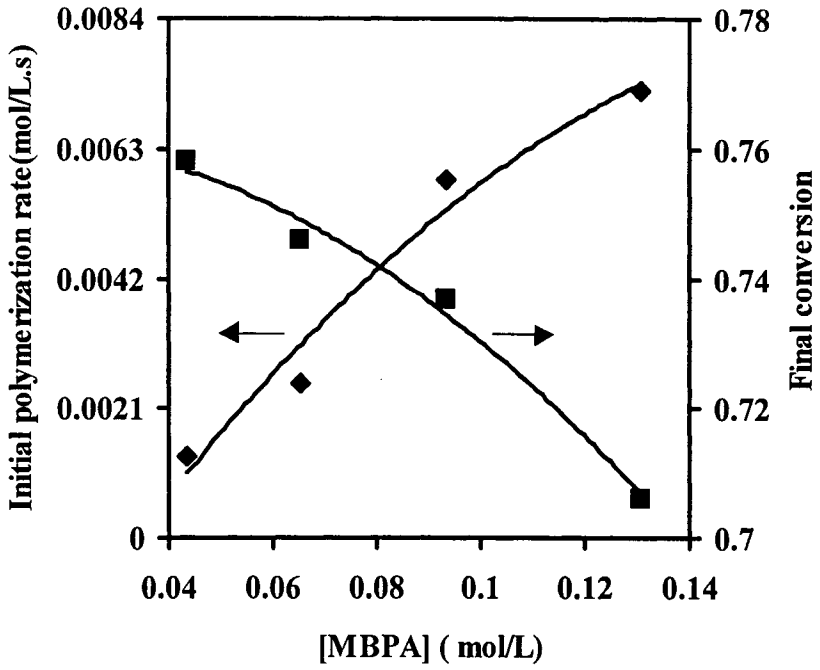

Figure 2.13. Influence of initiator concentration on the initial polymerization rate and the final vinyl group conversion in ATRP of PEGDMA at 70 °C: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{MBPA}]_0/[\text{CuBr}]_0/[\text{HMATETA}]_0 = 1/1/1$

concentration, as shown in Figure 2.13. It is believed that the early formation of three-dimensional networks and the dense network structure at the high initiator concentration were responsible for the decline of the final conversion. The densely crosslinked network trapped reactive species and stopped further polymerization.

2.3.4. Effect of Reaction Temperature

The temperature effect on the ATRP with crosslinking was also investigated at 70, 80 and 90 °C. The rate profiles are given in Figure 2.14. Similar to the effect of the initiator concentration, the initial rate increased and the final conversion of vinyl group decreased with the increase of temperature (Figure 2.15). The increase in the rate was expected because a high temperature enhanced the reactivity of polymeric halides, R-M_n-X, towards Cu(I) species, resulting a high concentration of radicals. On the other hand, increasing temperature provided little enhancement to the mobility of PEGDMA segments because of the low Tg value of the cured material. Nevertheless, the higher the temperature, the higher the reaction rate and the earlier the network formed. The early network formation restricted the reactivity of vinyl groups, leading to the reduced conversion.

The ATRP of PEGDMA at the three different temperatures gave a linear relationship of $\ln[M]_o/[M]$ versus time at the first stage of the reaction. The slope of this straight kinetic plot allows one to estimate the apparent propagation rate constant, k_p^{app}.

$$Rp = -d[M]/dt = kp[M][P^\bullet] \approx k_p^{app}[M] \qquad (2.4)$$

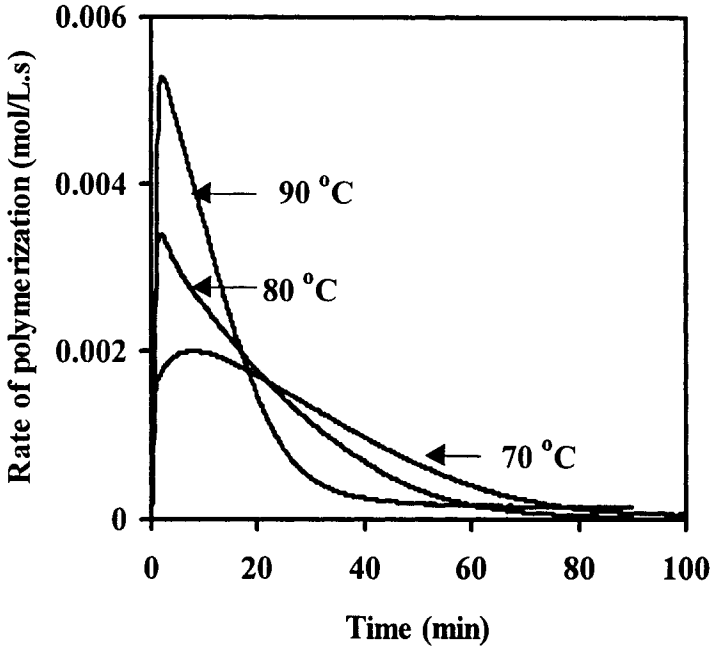

Figure 2.14. Polymerization rate profiles for the ATRP-1 system at different reaction temperatures: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{MBPA}]_0 = [\text{CuBr}]_0 = [\text{HMATETA}]_0 = 0.06545$ (mol/L)

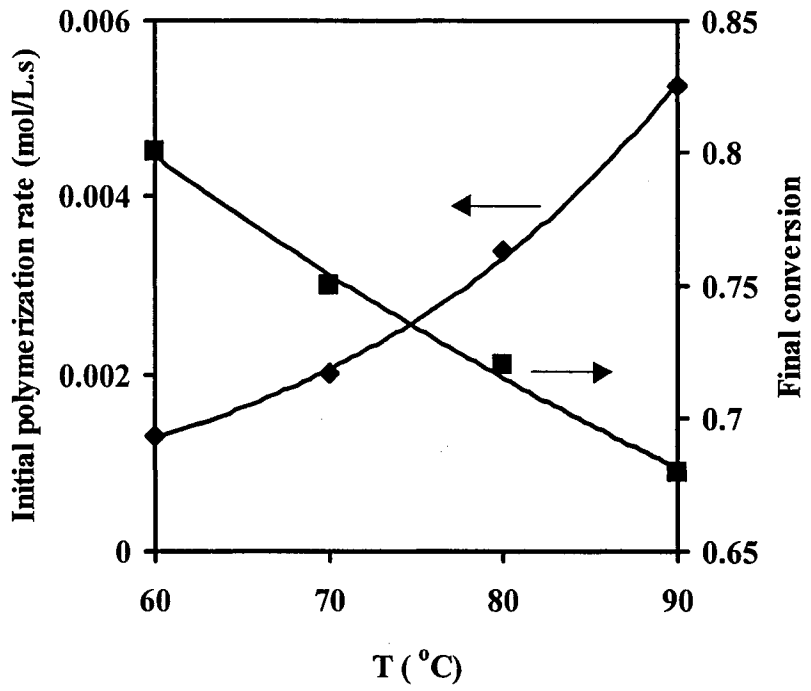

Figure 2.15. Effect of reaction temperature on the initial polymerization rate and the final vinyl group conversion in ATRP of PEGDMA: $[\text{vinyl group}]_0 = 6.545$ (mol/L), $[\text{MBPA}]_0 = [\text{CuBr}]_0 = [\text{HMATETA}]_0 = 0.06545$ (mol/L)

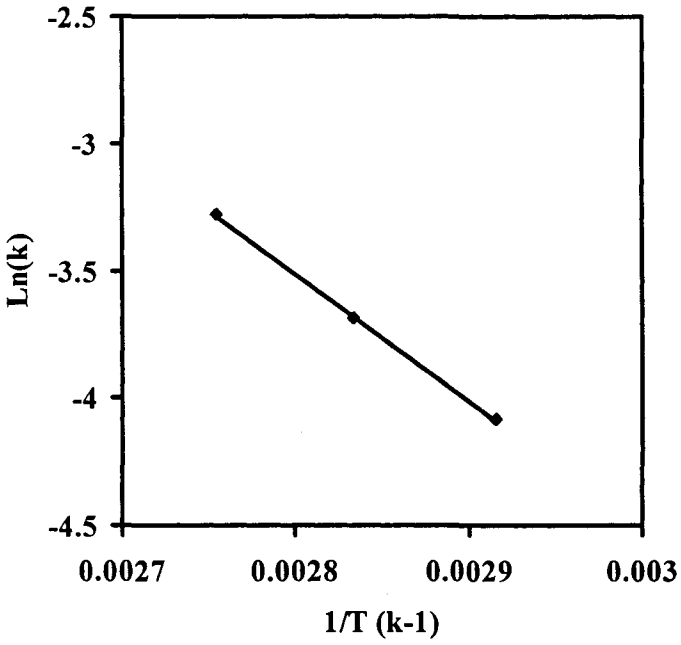

Figure 2.16. Arrhenius plot of the ATRP of PEGDMA using the same reaction conditions as in Figure 2.14.

$$\ln[M]_o/[M] = k_p^{app} t \qquad (2.5)$$

From the k_p^{app} data, an Arrhenus curve could be obtained (Figure 2.16) and the apparent activation energy, E_R, for the ATRP of PEGDMA was found to be 41.7 kJ/mol. This value is in good agreement with the reported (42 kJ/mol) for the ATRP of MMA (see Chapter 3).

2.4 Conclusions

The copper-catalyzed atom transfer radical polymerization of PEGDMA was investigated using DSC and ESR. Based on the experimental results, the following conclusions have been made:

1. The ATRP of PEGDMA proceeded with very low polymerization rates, in comparison with the BPO initiated FRP. The dynamic equilibrium between growing radicals and dormant species resulted in a lower radical concentration in the ATRP system, which avoided the accumulation of growing radicals and eliminated the autoacceleration effect.
2. Methacrylate radical signals, along with copper (II) signals, were observed by ESR measurements after a certain period of reaction time. The observation of radical signals in the ATRP of PEGDMA was attributed to the increased diffusion restriction to the Cu(II)/ligand complex, which impeded the deactivation of growing radicals. The radical signals provided an evidence for the participation of radical intermediates in the ATRP process.

3. At the beginning of the reaction, the ATRP of PEGDMA proceeded in a living manner because of the low and constant radical concentration. As the reaction continued, the mobility of catalyst/ligand complex was restricted by the increased diffusion resistance, which resulted in an increase in Cu(II) and radical concentration. Thus, radical termination became significant and the reaction was converted to a conventional FRP process. At the final stage, the polymerization continued via the diffusion-controlled mechanism.
4. The initial rate of the ATRP of PEGDMA increased and the final vinyl group conversion decreased as the initiator concentration and/or reaction temperature was increased. An apparent activation energy of 41.7 kJ/mol was obtained.

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Chapter 3

Synthesis of 2-(Dimethylamino)ethyl Methacrylate Macromonomers by Atom Transfer Radical Polymerization (ATRP)

3.1 Introduction

Well-defined macromonomers with narrow molecular weight distributions and terminal unsaturated groups are often prepared by living anionic polymerization (Varshney et al., 1992. Masson et al., 1982. Takahi et al., 1986. Asami et al., 1986), group transfer polymerization (Sogah et al., 1986.), and living cationic polymerization (Miyashita et al., 1994. Lievens et al., 1996.). The reactive terminal vinyl groups can be introduced by end capping or living polymer deactivation. For example, Ishizu and co-workers synthesized styrenic-functionalized polyacrylic acid by using chain transfer agent, followed by end-capping with 4-chloromethylstyrene (Ishizu et al., 1997a. Ishizu et al., 1997b. Ishizu et al., 1996.). There were only a few reports on the direct synthesis of polymethacrylate macromonomers because of the high selectivity of initiator type. Recently, Nagasaki et al. (Nagasaki et al., 1997.) and Lascelles et al. (Lascelles et al., 1999. Vamvakaki et al., 1999.) reported the synthesis of macromonomers of 2-(diethylamino)ethyl methacrylate (DEAEMA), and 2-(dimethylamino)ethyl methacrylate (DMAEMA) with terminal unsaturated groups by oxyanion-initiated polymerization.

However, these oxyanionic polymerizations had low initiator efficiencies and imprecise molecular weight control. In addition, living ionic polymerization requires stringent experimental conditions that often make industrial applications difficult and are limited to only a small number of monomer systems.

Living radical polymerization, particularly atom transfer radical polymerization (ATRP), has been proven to be versatile for various vinyl monomers, such as styrene (Wang et al., 1995a. Wang et al., 1995b. Xia et al., 1999.), methacrylate (Wang et al., 1995a. Kato et al., 1995. Matyjaszewski et al., 1997.), acrylonitrile (Zhang et al., 1998.), 2-(dimethylamino)ethyl methacrylate (Xia et al., 1999.), and 4-vinyl pyridine,(Zhang et al., 1998.) as well as their block copolymers. An advantage of ATRP is that it does not require strict experimental conditions as anionic and cationic polymerization do. Therefore, this living process provides a new approach for the synthesis of macromonomers with controlled molecular weight and molecular weight distribution. For example, well-defined polystyrene macromonomers were prepared by ATRP of styrene initiated by vinyl chloroacetate or allyl bromide mediated by CuBr/bipyridine (Xia et al., 1999. Matyjaszewski et al., 1998.). However, the initiators and ligands for the synthesis of macromonomers by copper-based ATRP were found to be very selective. For example, mediated by CuBr/bipyridine, vinyl chloroacetate was able to initiate styrene polymerization without damaging its vinyl group, while our work showed that vinyl chloroacetate could not initiate DMAEMA polymerization using Cu(I) Br as catalyst and BA_6-TREN or HMTETA as ligand at 60 °C. Similarly, the allyl group was found to polymerize and cause crosslinking in the ATRP polymerization of allyl acrylates

catalyzed by CuBr/bipyridine system (Nakagawa et al., 1998.). But this work showed that the allyl group in the initiator, allyl 2-bromoisobutyrate, was not consumed during the ATRP polymerization of DMAEMA catalyzed by CuBr/multidentate amine ligands and thus poly(DMAEMA) macromonomers with terminal allyl group were obtained. Most importantly, these terminal allyl groups could copolymerize with acrylamide.

In this chapter, we report the synthesis of DMAEMA macromonomers with terminal allyl group using CuBr-based ATRP system. The effects of ligands, initiators bearing allyl or vinyl functional groups as well as experimental conditions were investigated in detail. The kinetics of the selected systems was also examined. After quaternization, the macromonomers were used to copolymerize with acrylamide to give comb-branched copolymers.

3.2 Experimental Section

3.2.1 Materials

The catalyst: Cu(I)Br; the initiators: allyl 2-bromoisobutyrate (ABIB), allyl bromide (AB), vinyl chloroacetate (VCA), vinyl benzylchloride (VBC), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA, used as a radical initiator for the conventional copolymerization of acrylamide with macromonomers); and ligands: N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 18-crown-6, tris(2-aminoethyl)amine (TREN, used as a precursor for synthesizing two new ligands described later) were obtained from Aldrich and used without further purification. Vinyl monomers: 2-

(dimethylamino)ethyl methacrylate (DMAEMA), methyl acrylate (MA) and n-butyl acrylate (BA) (MA and BA used as precursors for the two new ligands), all supplied by Aldrich, were distilled from CaH_2 prior to use. Solvents: tetrahydrofuran (THF), methanol (MeOH), ethyl acetate (EtOAc), butyl acetate (BuOAc), dimethylformamide (DMF), γ-butyrolactone, isopropanol, dimethylsulfoxide (DMSO), formamide and ethylene glycol were used after distillation. Acrylamide (AM) from Aldrich was recrytallized. Chemicals: allylamine, trichloroacetate, 2-methyl-3-buten-2-ol, 2-bromopropionyl bromide and triethylamine as precursors for preparing two new initiators were used as received from Aldrich.

3.2.2 Synthesis of Allyl Trichloroacetamide (ATCA) and (2-Methyl butenyl) 2 Bromo Propionate (MBBP)

To a solution of allyl amine (5 mL, 66.64 mmol) and triethylamine (9.30 mL, 66.80 mmol) in 50 mL dried THF cooled in ice-water bath, trichloroacetate chloride (7.48 mL, 66.64 mmol) was added dropwisely (allylamine reacted with trichloroacetate chloride to yield ATCA and HCl with the HCl absorbed by triethylamine). The mixture was magnetically stirred for 1 h at 0 °C and then 2 h at room temperature. Triethylamine hydroxy chloride salt was filtrated and washed with 10 mL THF for three times. After THF was evaporated, the crude product was distilled under vacuum. The product was recrystallized in hexane to give a colorless powder. Yield: 79.0% (10.7 g) w.r.t allylamine or trichloroacetate chloride: ^{1}H NMR ($CDCl_3$, 200 MHz): 4.05 ppm (2H, m, NH-C<u>H</u>$_2$-CH=CH$_2$), 5.29 ppm (2H, m, NH-CH$_2$-CH=C<u>H</u>$_2$), 5.93 ppm (1H, m, NH-CH$_2$-

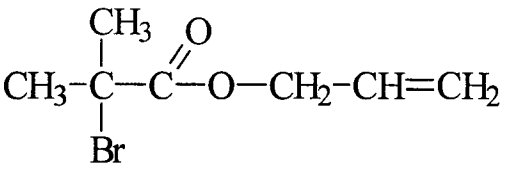
C<u>H</u>=CH_2), 6.82 ppm (1H, br, N<u>H</u>-).

Following the same procedure, (2-methyl butenyl) 2-bromo propionate (MBBP) was prepared using 2-methyl-3-buten-2-ol, 2-bromopropionyl bromide and triethylamine with the yield of 73.4%. ^{1}H NMR ($CDCl_3$, 200 MHz): 1.54 (6H, br, CH_2=CH-C(C<u>H</u>$_3$)$_2$-O), 1.75 (3H, d, C<u>H</u>$_3$-CHBr-COO-), 4.26 (1H, q, CH_3-C<u>H</u>Br-COO-), 5.13 (2H, q, C<u>H</u>$_2$=CH-C(CH_3)$_2$-O), 6.04 (1H, q, CH_2=C<u>H</u>-C(CH_3)$_2$-O).

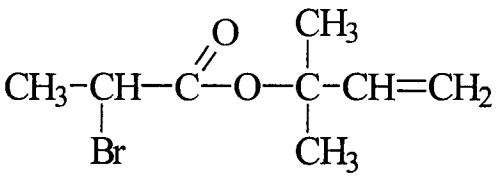
The molecular structures of all the initiators used in this paper are shown in Scheme 3.1.

3.2.3 Synthesis of Tris (2-di(butylacrylate)amino ethyl)amine (BA_6-TREN) and Tris (2-di(methylacrylate)amino ethyl)amine (MA_6-TREN)

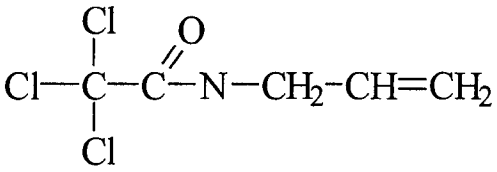
The two products were synthesized by a slightly modified method of Klee et al. (Klee et al., 1999.). To 26.3 g (0.205 mol) of butyl acrylate, tris (2-aminoethyl) amine (5.0 g, 34.2 mmol) was added dropwisely at 0-5 °C. The mixture was magnetically stirred for 2 h at 0-5 °C and then was reacted for further 24 h at room temperature. After evacuating the residual butyl acrylate, the purified crude product, yellowish liquid, was obtained:Yield: 98.7% (30.8 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 0.88 (18H, m, 6 -C<u>H</u>$_3$), 1.28 (12H, m, 6 -C<u>H</u>$_2$-CH_3), 1.55 (12H, m, 6 -C<u>H</u>$_2$-CH_2-CH_3), 2.39 [24H, m, 3 N-C<u>H</u>$_2$-C<u>H</u>$_2$-N-(C<u>H</u>$_2$-CH_2-COO)$_2$], 2.70 (12H, t, 6 N-CH_2-C<u>H</u>$_2$-COO), 4.04 (12H, 6 COO-C<u>H</u>$_2$-).



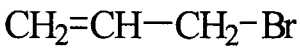
allyl 2-bromoisobutyrate
(ABIB)



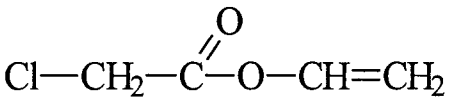
methyl butenyl 2-bromo
propionate(MBBP)



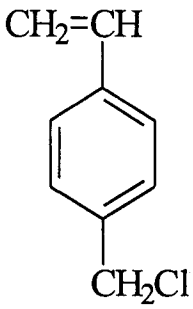
allyl trichloroacetamide(ATCA)



allylbromide(AB)

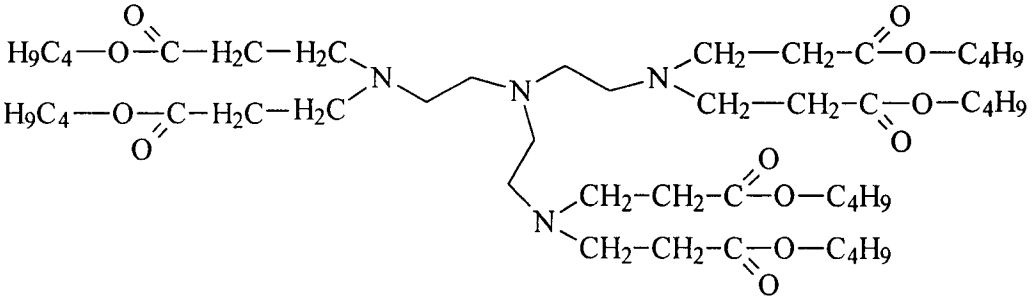


vinyl chloroacetate(VCA)

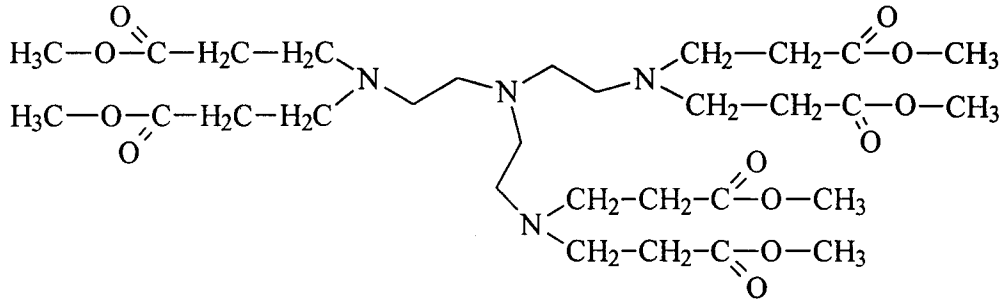


vinyl benzylchloride(VBC)

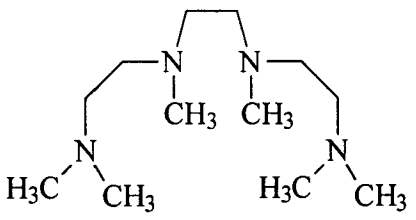
Scheme 3.1 Molecular structures of initiators



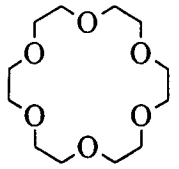
tris [2-di(butyl acrylate)amino ethyl]amine (BA_6-TREN)



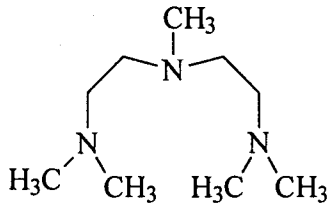
tris [2-di(methyl acrylate)amino ethyl]amine(MA_6-TREN)



1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA)



18-crown-6



N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA)

Scheme 3.2 Molecular structures of ligands

Tris (2-di(methyl acrylate)amino ethyl)amine (MA_6-TREN) was prepared by the same procedure using methyl acrylate and tris (2-aminoethyl) amine. Yield: 97.9%(22.2 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 2.44 [24H, m, 3 N-C$\underline{H}_2$-C$\underline{H}_2$-N-(C$\underline{H}_2$-CH_2-COO)], 2.72 (12H, t, 6 N-CH_2-C$\underline{H}_2$-COO), 3.63 (18H, br s, 6 -C$\underline{H}_3$).

Scheme 3.2 shows the molecular structures of the ligands used in this work

3.2.4 ATRP of DMAEMA

The ATRP polymerization of DMAEMA was carried out in bulk and in solution. In a typical experiment, 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(I)Br, 58.14 mg (0.0636 mmol) of BA_6-TREN and 1.1 ml of THF were charged to a 10 ml tube reactor. The tube was degassed with argon for ten minutes before sealed with rubber septum. Initiator was also degassed before added to the tube by a microsyringe. The tube was then immersed into an oil bath set to a required temperature. The polymerization was terminated by immersing the tube into an ice water bath. The mixture was diluted by THF and the polymer was then precipitated in hexane or petroleum ether and dried in vacuum. Conversion was determined either gravimetrically or by ^{1}H NMR (only for bulk polymerization). The resulting macromonomers were purified by passing through a silica gel column.

3.2.5 Macromonomer Quaternization and Copolymerization with Acrylamide

To a solution of 2 g purified macromonomer (0.286 mmol from 99-18-5, M_n = 6,500) in 30 mL acetone, methyl iodide (1.79 g, 12.7 mmol) was added. The mixture

was magnetically stirred for 1 h at room temperature. Then the quaternized macromonomer was separated by filtration and washed with 10 mL acetone for three times and dried under vacuum to give a colorless powder. Yield: 96.8% (3.67 g): ^{1}H NMR ($CDCl_3$, 200 MHz): 0.90 [3H, br, (-CH_2-C(C$\underline{H}_3$)-COO-], 1.92 [2H, (-C$\underline{H}_2$-C(CH_3)-COO-], 3.17 [9H, (-N(C$\underline{H}_3$)$_3^+I^-$], 3.75 [2H, (-O-CH_2-C$\underline{H}_2$-N(CH_3)$_3^+I^-$], 4.39 [2H, (-O-C$\underline{H}_2$-CH_2-N(CH_3)$_3^+I^-$], 5.19 ppm (2H, allyl proton), 5.80 ppm (1H, allyl proton).

Copolymerization of the quaternized macromonomer with acrylamide was conducted using AIBA as a radical initiator. 0.2 g (0.016 mmol from above sample, M_n = 12,400) of the macromonomer, 0.2g (2.8 mmol) of acrylamide, 1 mg of AIBA and 2 mL of water were charged to a 10 ml tube reactor. The tube was degassed with argon for ten minutes and sealed with rubber septum. The tube was then immersed into a water bath at 60 °C. After reaction for 4 h, the polymer was precipitated in methanol and dried in vacuum to yield 0.38 g of comb polymer with conversion 95% with respect to the total monomers charged.

3.2.6 Measurements

^{1}H NMR spectra were obtained on a Bruker AC-P200 Fourier transform spectrometer (200 MHz for ^{1}H) in $CDCl_3$ or D_2O solvent. The chemical shifts were reported in ppm with signals of trace of $CHCl_3$ or H_2O as internal standard. GPC measurements were carried out using a Waters 590 liquid chromatography equipped with three Varian MicroPak columns (G1,000, 3,000 and 7,000HXL) with a 410 differential

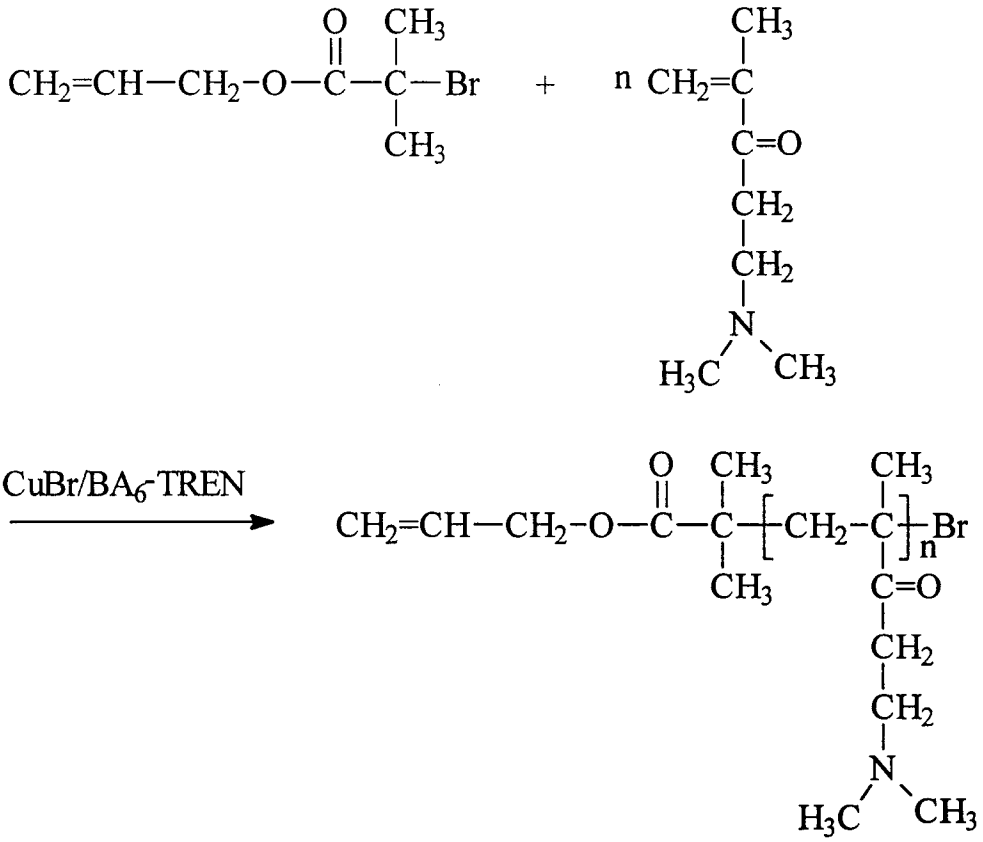
refractometer detector. THF with 2% triethylamine was used as solvent. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows based on Millenium 2.0 software package.

3.3 Results and Discussion

3.3.1 Effects of Initiator and Ligand on the Synthesis of Macromonomers by ATRP Process

A key criterion for macromonomer synthesis (see Scheme 3.3) is that the vinyl group associated with the initiator should not be consumed during macromonomer synthesis because this terminal group is needed as reactive species for subsequent macromonomer copolymerization. Various combinations of initiator and ligand types were screened for the synthesis of macromonomers by ATRP of DMAEMA mediated by copper bromide. The results are summarized in Table 3.1.

It can be seen that the initiators can be classified into three groups. The first group initiators are those who showed no activity in the ATRP of DMAEMA. For example, VCA could not initiate the DMAEMA polymerization mediated by CuBr with BA_6-TREN or HMTEMA as ligand. This is very different from Matyjaszewski's results that VCA initiated a living polymerization of styrene polymerization and produced macromonomers(Coca et al., 1997). The activity of the initiators also depended on the type of ligand used. For example, AB could initiate DMAEMA polymerization when BA_6-TREN was used as ligand, while it could not when HMTEMA used as ligand.



Scheme 3.3 Typical ATRP polymerization process

Table 3.1 Effects of initiator type and ligand type on bulk polymerization of DMAEMA at 60 °C

Run	Initiator	Ligand	Time (h)	Conv. (%)	$M_{n,cal}$	$M_{n,SEC}$	$M_{n,NMR}$	$M_{w,SEC}/M_{n,SEC}$	$f = M_{n,cal}/M_{n,NMR}$
99-18-4	VCA		20.0	0					
99-18-2	AB		5.0	53.0	4,200	30,600		2.6	0.14[b]
99-18-3	VBC		2.0	gel					
99-17-1	ABIB	BA_6-TREN	0.5	98.5	7,700	8,000	8,600	1.34	0.90
99-18-1	MBBP	BA_6-TREN	0.5	92.4	7,200	8,900	8,500	1.70	0.85
99-18-5	ATCA		5.0	89.4	7000	6500	7000	1.18	0.99
99-11-5	VCA		20.0	0					
99-11-6	AB		20.0	0					
99-11-4	VBC		5.0	0.963	7500	11400		2.01	0.66[b]
99-11-1	ABMP	HMTETA	0.5	96.7	7601	7733	8804	1.27	0.86
99-11-2	MBBP		2.0	90.3	7100	8600	8050	1.67	0.88
99-11-3	ATCA		5.0	0.762	5990	5600	6000	1.18	0.99
99-17-4a	VBC		5.0	gel					
99-17-4	ABMP	PMDETA	0.5	99.5	7800	21100		1.30	0.37
99-17-2	ABIB	MA_6-TREN	0.5	97.5	7,700	6,600	8,300	1.39	0.92
99-17-5	ABIB	18-crown-6	20	87.1	6,800	9,200		1.50	0.74[b]
99-17-6	ABIB	No ligand	20	93.3	7,300	5,500		2.31	

DMAEMA/initiator/CuBr/ligand = 50:1:1:1 in mole
f - initiator efficiency
b = $M_{n,cal}/M_{n.SEC}$

The second group of initiators could initiate the DMAEMA polymerization but caused crosslinking or broad molecular weight distribution. The typical example was VBC. For example, with VBC as initiator, DMAEMA polymerization mediated by CuBr-BA_6-TREN or CuBr-PMDETA became crosslinked even at very low conversions. This means that the VBC's styrenic group was also (co)polymerized during the ATRP process of DMAEMA. By contrast, mediated by CuBr-HMTEMA, the polymerization did not crosslink, but the molecular weight distribution of the resulting poly(DMAEMA) was up to 2.

The third group initiators initiated the ATRP of DMAEMA yielded the desired narrow molecular weight distribution macromonomers. These initiators included ABIB and ATCA. For example, with ATCA and ABIB as initiators and mediated by CuBr-BA_6-TREN, the polydispersity of polyDMAEMA were 1.18 and 1.34, respectively, with high initiator efficiencies (higher than 90%).

These results showed that for a initiator activity depended on the type of carbon-halogen bond. The secondary (MBBP) and tertiary carbon bromide (ABIB) as well as the multiple chlorine-based initiators (ATCA) were highly active, giving high initiator efficiencies, while the compounds having a strong carbon-halogen bond such as AB, VA and VBC, are poor initiators for the methacrylate. This agreed with the Matyjaszewski's results (Kato et al., 1995. Wang et al., 1997. Matyjaszewski et al., 1998.). It was also observed that the survival of the vinyl moiety in the initiator during the macromonomer preparation depended on the relative reactivity of the vinyl moiety with respect to the monomer. The low reactivity of the allyl group with respect to methacrylate was the

determining factor for the survival of the vinyl moiety in ABIB, MBBP, and ATCA. However, the catalyst also played some role in the survival of the vinyl moiety. For example, when CuBr-HMTETA was used as catalyst, VBC did not have cross-linking although the polydispersity of polyDMAEMA was high. For comparison, when CuBr-BA6-TREN or CuBr-PMDETA was used, VBC experienced gelation even at very low conversions.

The ligand type also strongly affected the activity of the initiators and the polymer properties, as shown in Table 3.1. AB could initiate the DMAEMA polymerization catalyzed by CuBr-BA_6-TREN, while it showed no activity when HMTEMA replaced BA_6-TREN. The initiator efficiency depended on the ligand type. With CuBr as catalyst and ABIB as initiator, the initiator efficiency increased by the order: PMDETA < 18-crown-6 < HMTETA < MA_6-TREN ≅ BA_6-TREN. The polydispersity of polyDMAEMA was also related to the ligand type. The polydispersity of polyDMAEMA were between 1.2 and 1.3 when BA_6-TREN, MA_6-TREN, HMTEMA and PMDEMA were used. By contrast, the polydispersity of polyDMAEMA was higher than 1.6 when 16-crown-6 ether was used.

The macromonomer structure was confirmed by ^{1}H NMR spectra (see Figure 3.1). The allyl proton signals of polyDMAEMA using ATCA as an initiator appeared at 5.15 (2H, C<u>H</u>$_2$=CH-) and 5.72 (1H, CH$_2$=C<u>H</u>-). The polymers prepared by ABIB systems also showed similar allyl proton signals. The ATCA maybe act as a difunctional initiator, resulting in chain growth in two directions with ally group in the center of the polymer chain (Destarac et al., 1998.). The higher initiator efficiencies of

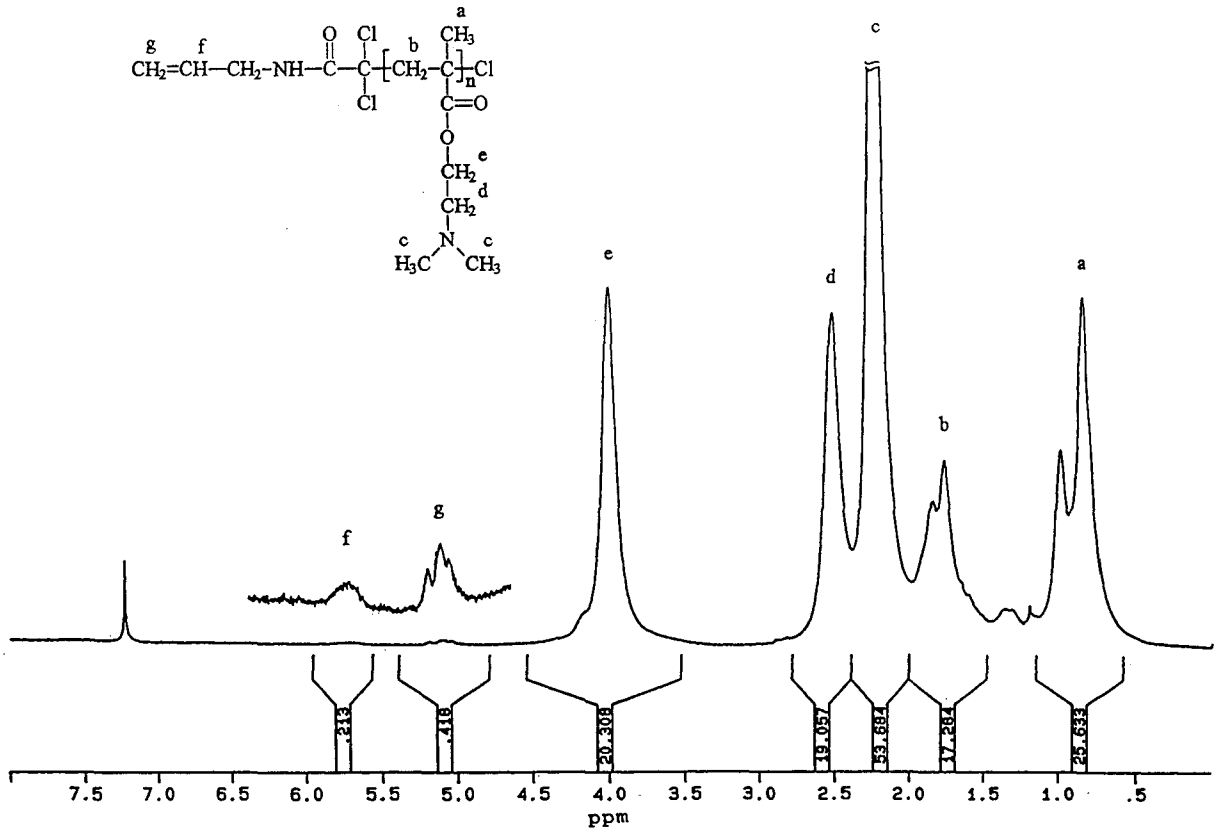


Figure 3.1. ^{1}H NMR spectrum of polyDMAEMA macromonomer: $[DMAEMA]_0/[ATCA]_0/[CuBr]_0/[BA_6\text{-}TREN]_0 = 50:1:1:1$ in mole with molecular weight M_n = 7,000 from GPC (sample 99-18-5).

ATCA/CuBr/BA_6-TREN, ABIB/CuBr/BA_6-TREN and ABIB/CuBr/HMTETA systems and the narrow molecular weight distributions of their resulting polymers indicated that the terminal allyl groups were not (co)polymerized during the ATRP process of DMAEMA. The number-average molecular weights by ^{1}H NMR were in agreement with the theoretical values. These results are different from a recent report that the allyl group of allyl acrylate was polymerized during the polymerization of allyl acrylate monomers and resulted in crosslinking when CuBr/bipyridine system was used (Klee et al., 1999).

3.3.2 Kinetics of the DMAEMA Polymerization Mediated by CuBr-PMDETA and CuBr-BA_6-TREN with ABIB as Initiator.

Table 3.1 showed that the ligand type had a very strong effect on the initiator efficiency and the polymer chain properties. To further understand the effects of other experimental factors such as temperature and solvent, two selected systems, ABIB/CuBr/PMDETA and ABIB/CuBr/BA_6-TREN, were studied in detail for the kinetics of the ATRP of DMAEMA.

Firstly ABIB/CuBr/PMDETA system, which had low initiator efficiencies, was investigated to see if varying other experimental factors such as temperature and solvent type could enhance the initiator efficiency. When PMDETA was used as ligand, the polymerization solution was heterogeneous both in bulk and in solution. The effect of temperature on the polymerization rate was investigated at temperatures 40, 50 and 60

°C. Figure 3.2 shows the conversion with time curves. At each temperature, the polymerization proceeded smoothly up to 85% conversion. The polymerization rate was increased with temperature. Figure 3.3 gives the first order kinetic plot. The linearity between $\ln([M]_0/[M])$~time in all cases indicated that the concentration of the growing species remained constant. The apparent activation energy was calculated and found to be around 42 kJ/mol.

The GPC analysis shows that the number-average molecular weight increased linearly with increasing the monomer conversion at different temperatures (Figure 3.4, 3.5 and 3.6). The polydispersities remained narrow and decreased with the increase of monomer conversion at about 1.2-1.45. The polymerization at 40 °C (Figure 3.6) yielded narrower distributions than 60 °C (Figure 3.4) and 50 °C (Figure 3.5). However, the $M_{n,SEC}$ deviated significantly from $M_{n,cal}$ at all the temperatures. The initiator efficiencies were lower than 0.50. Raising temperature did not increase the initiator efficiency.

The solvent effect on the polymerization was also investigated. When n-butyl acetate and isopropanol were used as solvent for the polymerization of DMAEMA at 60 °C, the kinetic curves deviated from the first order plot after the monomer conversion reached about 40% (Figures 3.7-3.8 and 3.9-3.10). These results indicated a significant amount of termination of the growing species. The molecular weights were also much higher than the predicted.

From the results of the ABIB/CuBr/PMDMEA system, we can conclude that the ligand plays an important role in ATRP of DMAEMA. Changing temperature or solvent

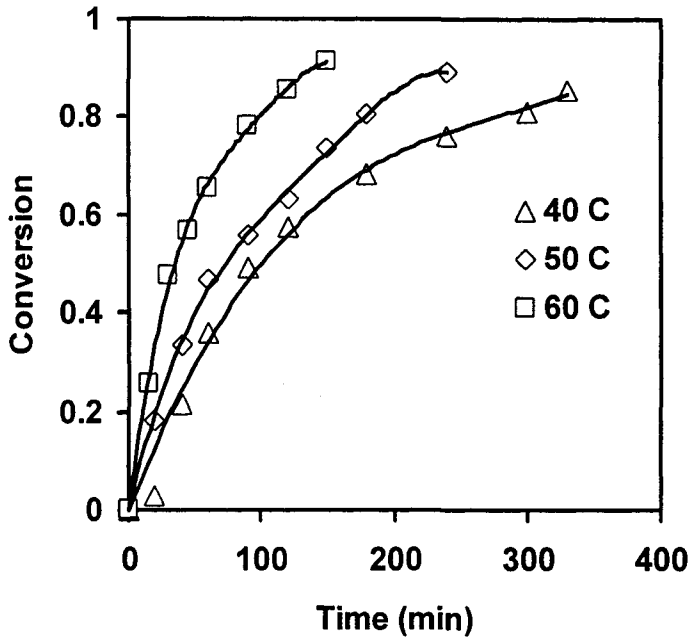


Figure 3.2. Monomer conversion of THF solution polymerization of DMAEMA vs time at 40, 50 and 60 °C with $[DMAEMA]_0 = 2.96$ (mol/L) and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ (mol/L)

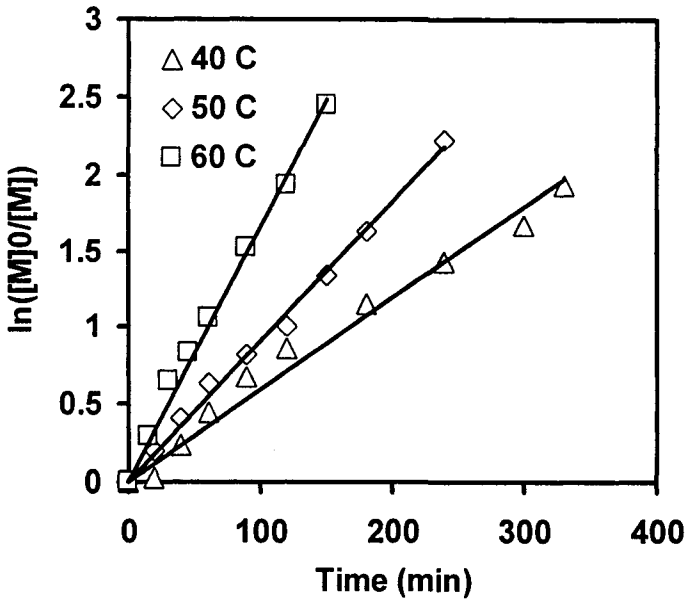


Figure 3.3. Ln$[M]_0/[M]$) of THF solution polymerization of DMAEMA vs time at 40, 50 and 60 °C with $[DMAEMA]_0 = 2.96$ (mol/L) and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ (mol/L)

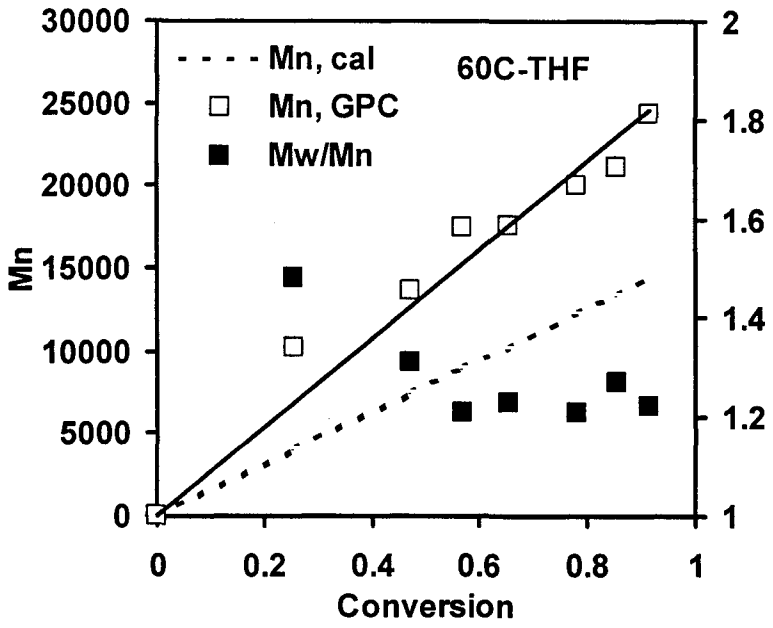


Figure 3.4 Molecular weight development of THF solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0$ = 2.96 M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0$ = 0.0296 M. The molecular weights were measured by GPC.

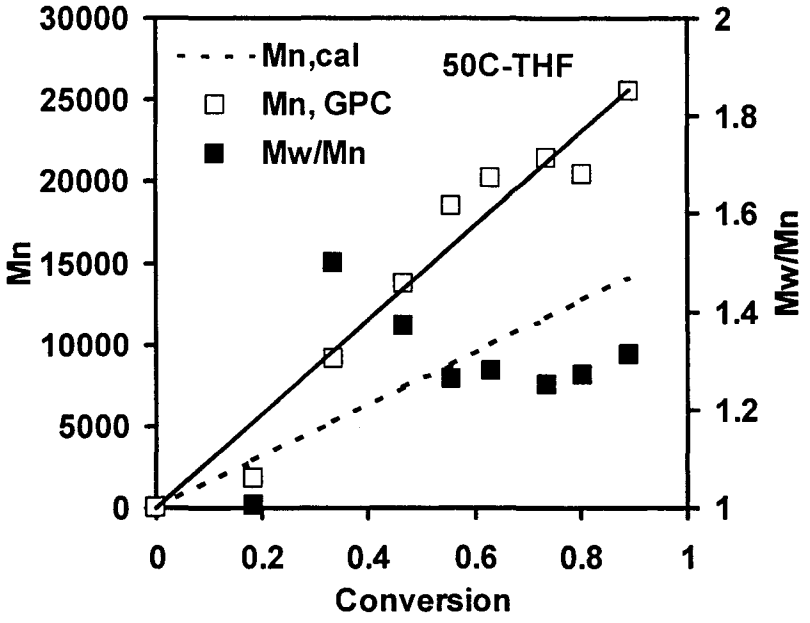


Figure 3.5. Molecular weight development of THF solution polymerization of DMAEMA at 50 °C with $[DMAEMA]_0$ = 2.96 M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0$ = 0.0296 M, The molecular weights were measured by GPC.

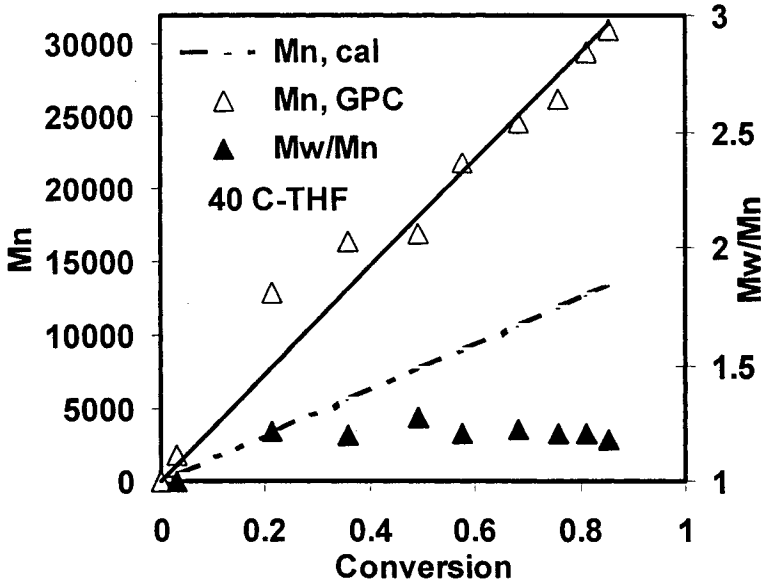


Figure 3.6. Molecular weight development of THF solution polymerization of DMAEMA at 40 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M. The molecular weights were measured by GPC.

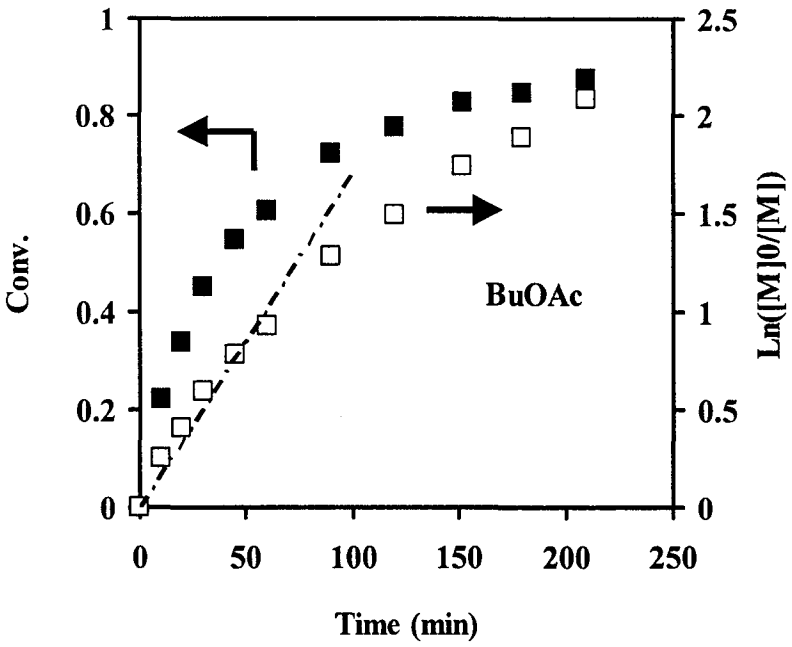


Figure 3.7 Monomer conversion and $\ln([M]_0/[M])$ vs time of n-butyl acetate solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M.

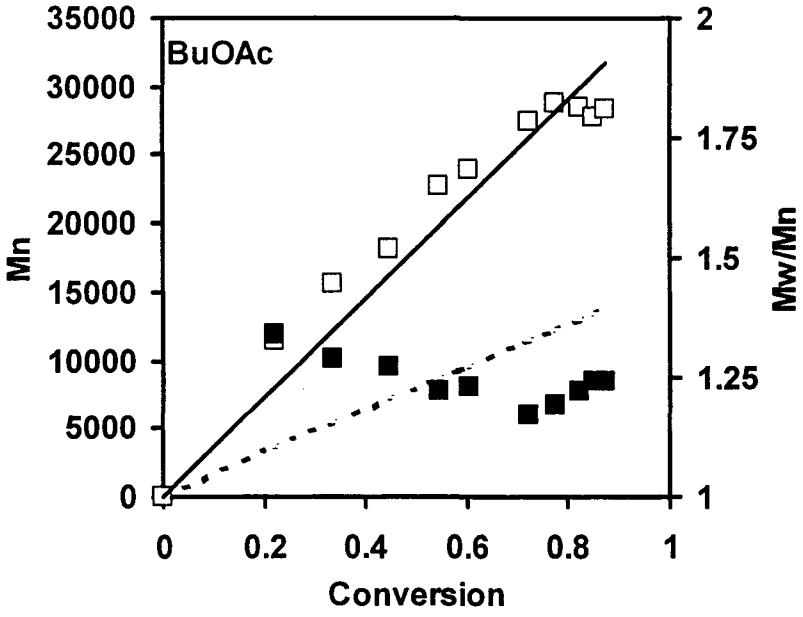


Figure 3.8 Number-average molecular weight and polydispersity versus conversion of n-butyl acetate solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M. $M_{n,GPC}$ (□), $M_{n,cal}$ (---), Mw/M_n (■).

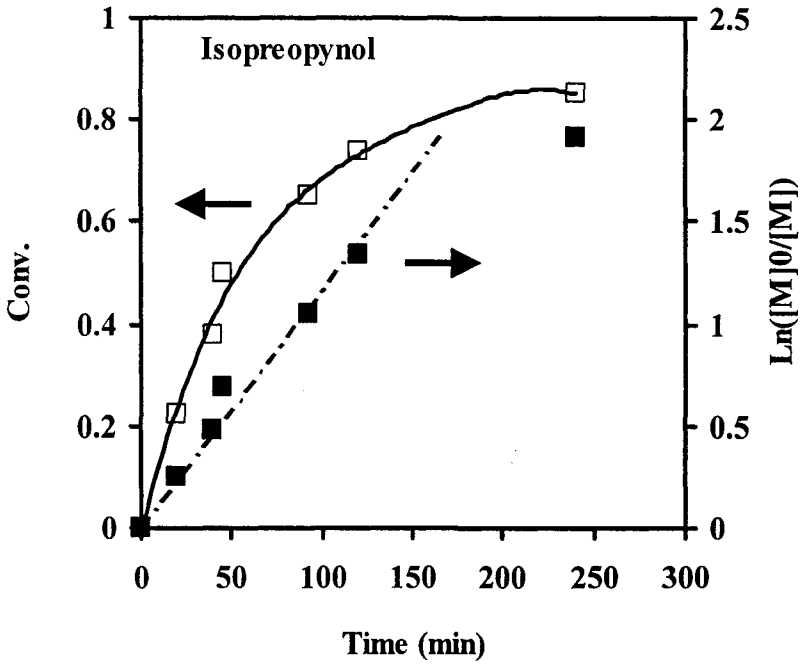


Figure 3.9 Monomer conversion and $\ln([M]_0/[M])$ versus time of isopropanol solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M.

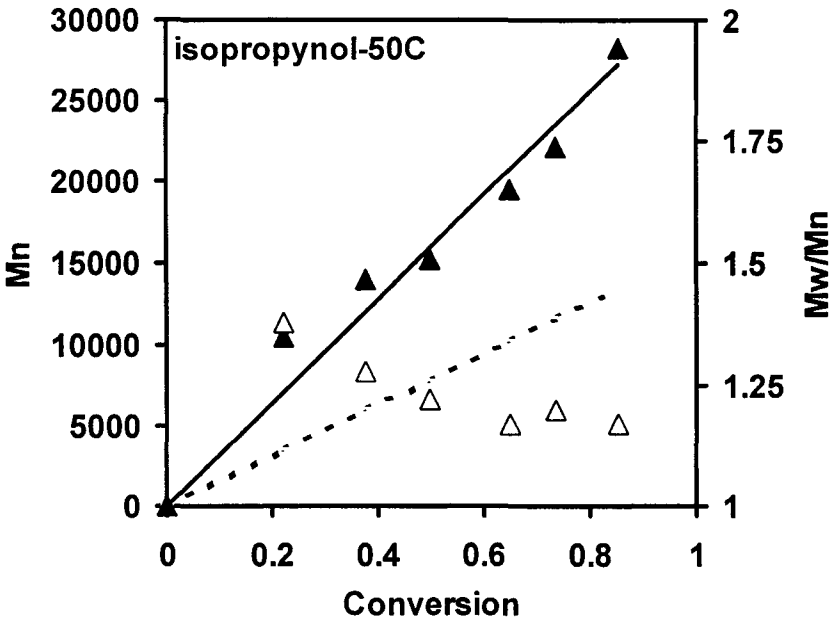


Figure 3.10. Number-average molecular weight and polydispersity versus conversion of isopropanol solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [PMDETA]_0 = 0.0296$ M. $M_{n,\,GPC}$ (▲), $M_{n,\,cal}$ (---), M_w/M_n (Δ)

type could not improve the initiator efficiency.

Table 3.1 shows that the ABIB/CuBr/ BA_6-TREN had very high initiator efficiency with good control over molecular weight and molecular weight distribution. Therefore, the ATRP polymerization of DMAEMA mediated by this system was also investigated in detail to further understand the role of ligand and other factors.

In contrast to the behavior of the ABIB/CuBr/PMDETA system, the polymerization solution was completely homogeneous in bulk as well as in solution when BA_6-TREN was used as the ligand. The polymerization proceeded smoothly up to 90% conversion without crosslinking. The linear $\ln([M]_0/[M])$~t plot also suggested a first order kinetics with a constant radical concentration. The number-average molecular weight increased linearly with the increase of monomer conversion with M_w/M_n around 1.2-1.4 (Figure 3.11-3.12). The molecular weights of polyDMAEMA were very close to the theoretical values.

Table 3.2 shows the solvent effect on the ATRP of DMAEMA catalyzed by ABIB/CuBr/BA_6-TREN. The ATRP polymerization could proceed not only in THF solvents, but also in very polar solvents such as ethylene glycol, formamide and DMSO. In high polar solvents, the polymerization was much faster than in the low polar solvent. For example, in formamide, the monomer conversion could go up to 95% in a half-hour with the molecular weight of the polymer close to the calculated value. The initiator efficiencies in polar solvents were higher than 0.9. The molecular weight distributions of polyDMAEMA prepared in polar solvents were slightly broader than those prepared in low polar solvents.

Table 3.2. Effects of solvents on solution polymerization of DMAEMA at 60 °C

Run	Solvent	Time (h)	Conv. (%)	$M_{n,cal}$	$M_{n,SEC}$	M_w/M_n
99-19-1	Ethylene glyc	0.5	81.3	6300	6300	1.60
99-19-2	Formamide	0.5	94.9	7460	7880	1.54
99-19-9	MeOH	4.5	98.3	7700	8020	1.37
99-19-3	DMSO	2.0	83.7	6600	6900	1.39
99-19-6	DMF	4.5	84.1	6600	6800	1.45
99-19-4	Isopropynol	4.5	84.8	6600	6700	1.36
99-19-5[a]	γ-Butylacton	4.5	89.94	7070	4200	1.31
99-19-7	BuOAc	4.5	87.2	6900	6800	1.37
99-19-8	EtOAc	4.5	91.2	7200	7800	1.24
99-19-10	THF	4.5	90.1	7100	7400	1.23

DMAEMA/initiator/CuBr/ligand = 50:1:1:1 in mole

f - initiator efficiency

b = $M_{n,cal}/M_{n.SEC}$

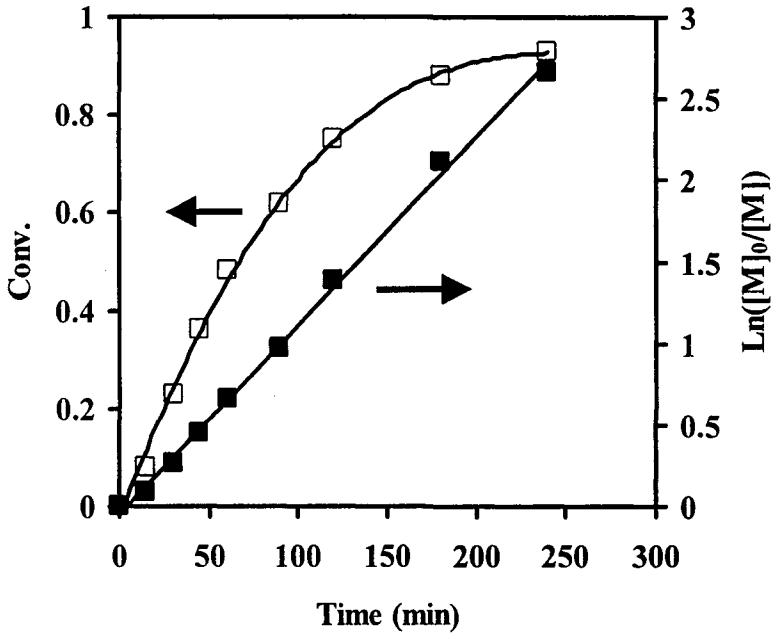


Figure 3.11. Monomer conversion and $\ln([M]_0/[M])$ versus time of THF solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0 = 2.96$ M and $[ABIB]_0 = [CuBr]_0 = [BA_6\text{-TREN}]_0 = 0.0296$ M.

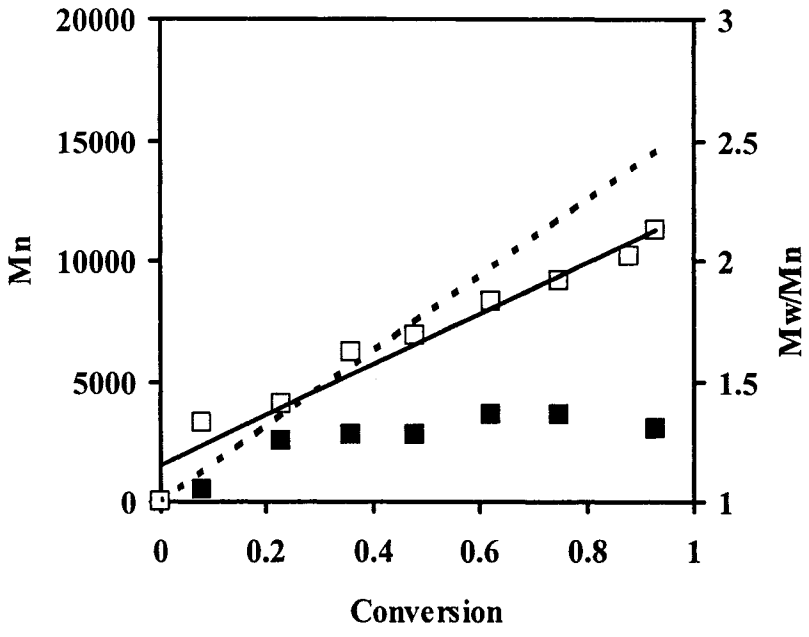


Figure 3.12. Number-average molecular weight and polydispersity versus conversion of THF solution polymerization of DMAEMA at 60 °C with $[DMAEMA]_0$ = 2.96 M and $[ABIB]_0 = [CuBr]_0 = [BA_6\text{-}TREN]_0$ = 0.0296 M. $M_{n,GPC}$ (□), $M_{n,cal}$ (---), Mw/M_n (■).

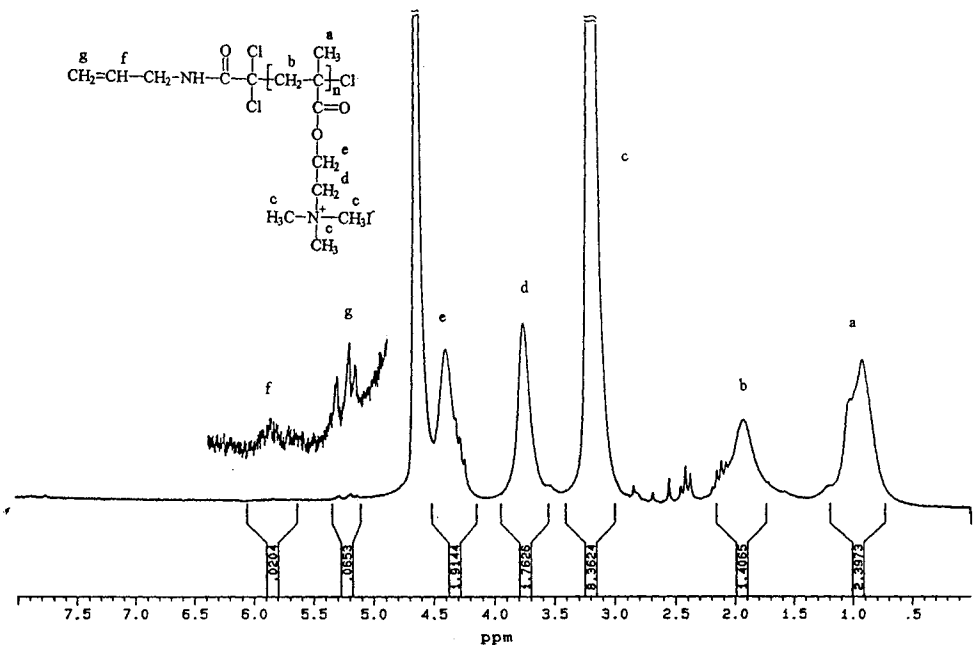
3.3.3 Preparation of Quaternary Macromonomers and Their Copolymerization with Acrylamide

To examine if the resulting macromonomers were copolymerizable, the polyDMAEMA macromonomers were quaternized and copolymerized with acrylamide using 2,2'-azobis (2-methylpropionamidine) dihydrochloride as initiator in water. After precipitated from the aqueous solution using methanol, the copolymer was separated from unreacted macromonomers because the latter was soluble in the methanol/water mixture. Figure 3.13 shows the ^{1}H NMR spectra for the quaternized macromonomer and its copolymer with acrylamide. It can be seen that beside the signals of acrylamide units (1.51, C$\underline{H}_2$; 2.05, C$\underline{H}$), the cationic macromonomer signals appeared at 3.15[-O-CH_2-CH_2-N(C$\underline{H}_3$)$_3^+$I$^-$] and 3.72 [-O-CH_2-C$\underline{H}_2$-N(CH_3)$_3^+$I$^-$]. The NMR spectra thus conformed that the cationic poly(DMAEMA) macromonomer was incorporated into the copolymer chains.

3.4 Conclusion

Base on the detailed studies on the synthesis of polyDMAEMA macromonomers by the ATRP process, the following conclusions were reached:

1. The nature of initiator and ligand type for the CuBr-based ATRP system determined whether the unsaturated group of the initiator was consumed during the ATRP process. Allyl groups in the ester or amide type of initiators survived in the ATRP of DMAEMA, while styrenyl moiety of VBC took part in the polymerization giving



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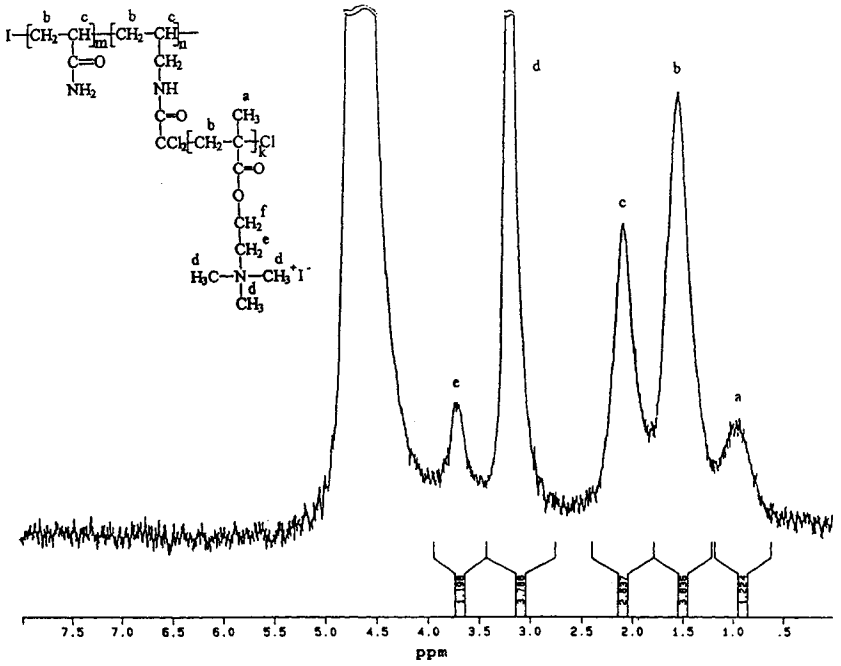

B

Figure 3.13. ^{1}H NMR spectrum of quaternized DMAEMA macromonomer and graft copolymer: (A) quaternized DMAEMA macromonomer and (B) graft copolymer of crosslinking or quaternized DMAEMA macromonomer with acrylamide. The copolymer molecular weight is M_w = 112,000 measured by GPC.

broad MWD. Vinyl chloroacetate could not initiate the polymerization of DMAEMA.

2. The type of ligand affected the initiator efficiency. With ABIB as initiator, the initiator efficiency increased by the order: PMDETA < 18-crown-6 < HMTETA ≅ MA_6-TREN ≅ BA_6-TREN. Varying temperature could not enhance the initiator efficiency of the ABIB/CuBr/PMDETA system.
3. Well-defined polyDMAEMA macromonomers with terminal allyl groups were synthesized by Cu(I)Br/BA_6-TREN with ATCA and ABIB as initiator. ^{1}H NMR showed that each polymer chain contained allyl end group. The molecular weight distributions were at Mw/Mn = 1.2-1.3.
4. The corresponding cationic macromonomers were prepared by reacting polyDMAEMA macromonomers with methyl iodide. These cationic macromonomers were copolymerizable with acrylamide.

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Chapter 4

Macromonomer Synthesis by Living Anionic Polymerization

4.1 Introduction

Chapter 3 reported the synthesis of DMAEMA macromonomers by living radical polymerization (ATRP). The ally-containing alkylhalide initiator was successfully used to initiate DMAEMA polymerization and resulted in well-defined macromonomers. However, it produced crosslinked polymers when using vinylbenzyl chloride as the initiator because styrenic group was also consumed during the polymerization. It was unsuccessful to synthesize macromonomers using styrenic-containing end group initiator by ATRP method.

Living anionic polymerization is the first and most established living polymerization process widely used for synthesizing macromonomers (Hsieh et al., 1996.). The macromonomer synthesis strategies by living anionic polymerization can be classified as end-functionalizing method using vinyl-containing agents and initiation method using functional initiator. The end-functionalizing method involves either coupling living polymer chain with termination reagent (Quirk et al., 1999. Quirk et al. 1993. Wesdemiotis et al., 2000.) or reacting functional polymer with unsaturated

compound, such as ω-hydroxyl polymer with acryloxyl chloride (Hirao et al., 1996.). The main challenge for this method is that usually not all of the end groups can be capped (low capping efficiency). For the living chain coupling, the active center of polymer chain must be stable to avoid side reactions. Therefore, this method is only applicable for a limited number of polymer systems and can not be used to synthesize DMAEMA macromonomer due to the quaternization of capping agent with $N(CH_3)_2$.

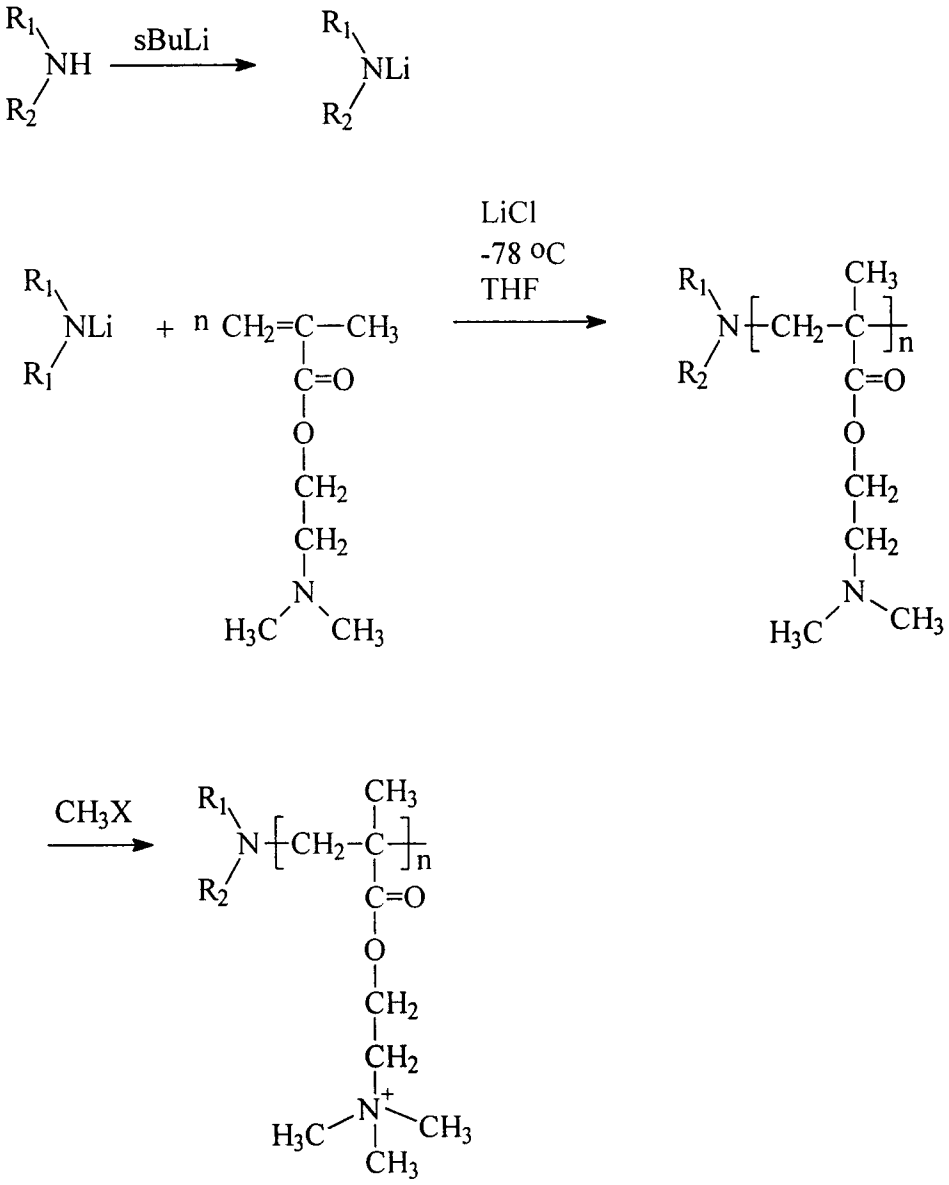
The initiation method using vinyl-containing initiators is the preferred approach for the preparation of macromonomers since each polymer chain so-prepared contains one terminal vinyl group. The challenge for this method is to select a proper initiator so that the vinyl group in it will not be reacted during the polymerization of vinyl monomers. Furthermore, the vinyl group in the initiator should not react with the initiator's active center, e.g. alkyl-metal bond. Therefore, even though the living anionic polymerization of vinyl monomers has been well developed using alkyllithium systems (Hsieh et al., 1996. Jerome et al., 1999.), the application of the initiation method in the macromonomer synthesis is still very limited because it is difficult for an initiator such as alkyllithium to bear an unsaturated group. Recently, Nagasaki (Nagasaki et al., 1997.) and Lascelles (Lascelles et al., 1999.) synthesized macromonomers of poly(diethylaminoethyl methacrylate) (polyDEAEMA) and poly(dimethylaminoethyl methacrylate) (polyDMAEMA) using less active oxyanionic initiators. However, the molecular weights of the polymers prepared were higher than predicted and the polymer polydispersities were about 1.3.

Sterically hindered lithium alkylamides initiated a living polymerization of methacrylic esters (Long et al., 1994. Antoun et al., 1997a. Antoun et al., 1997b.). Recently, we found that the nitrogen anion (nitroanion) was stable with allyl, vinyloxyl and styrenic group and therefore polyDMAEMA with allylamino, vinyl or styrenic end group can be synthesized. We here report the synthesis and characterization of cationic macromonomers of DMAEMA with diallylmethylammonium, allylmethylphenylammonium and vinylbenzylamine terminal group by nitroanion initiated living polymerization of DMAEMA and subsequent quaternization (Scheme 4.1). The macromonomers prepared are readily quaternized by quaternization agents yielding water-soluble cationic macromonomer.

4.2. Experimental

4.2.1. Reagents and Solvents

2-(Dimethylamino)ethyl methacrylate (DMAEMA, 98%), N,N-dimethyl acrylamide (DMA, 99%), *tert*-butyl methacrylate(tBMA) and methacrylnitrile (MAN) from Aldrich were stirred over CaH_2 for 24 h, then were distilled from CaH_2 under a reduced pressure and stored over CaH_2 under nitrogen in a refrigerator. 4-Vinylbenzylaldehyde (85%), N-isopropylamine (99.5%), $NaBH_3CN$ (95%), 4-vinylbenzylchloride (90%), potasium phthalimide (98%), sodium hydroxide, hydrazine hydrate, potassium, dimethyl sulfate (99%) 2,2'-azobis(2-methyl-propionamidine) dihydrochloride (AIBA), acrylamide (99%), N,N-dimethylformamide, chloroform,



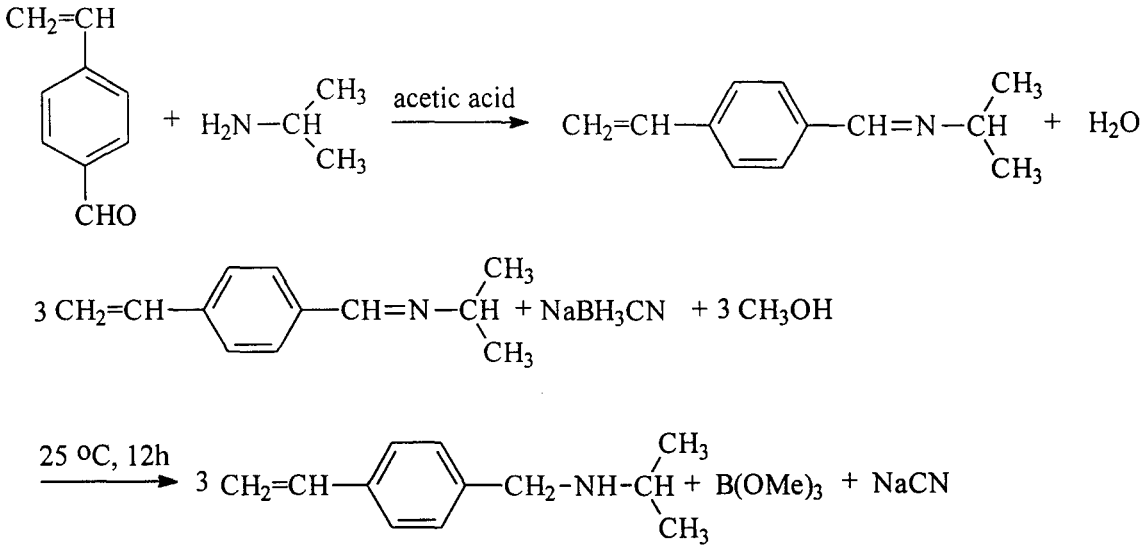
Allylamine: R_1 = H, R_2 = allyl
Diallylamine: R_1 = R_2 = allyl
Allylaniline: R_1 = allyl, R_2 = phenyl
N-isopropyl-4-vinylbenzylamine: R_1 = isopropyl, R_2 = vinylbenzyl
Vinylbenzylamine: R_1 = H, R_2 = phenyl

Scheme 4.1. Synthesis of DMAEMA macromonomers by nitroanion-initiated polymerization in THF solution at –78 °C.

methanol, ethanol, ethyl ether were all obtained from Aldrich and were used without further purification. LiCl (99.9%) from Aldrich was dried at 130 °C and then dried again at 100 °C under vacuum just before use. THF was refluxed over potassium under nitrogen atmosphere. Diallylamine, allylamine and allylaniline were distilled over CaH_2. N-isopropyl-4-vinylbezylamine and vinylbenzylamine were synthesized in our lab (see next Section). *Secondary-* butyllithium (sBuLi, 1.3 M in cyclohexane) was purchased from Aldrich and its concentration was titrated by a standard method.

4.2.2 Synthesis of N-Isopropyl-4-Vinylbenzylamine (PVBA)

N-isopropyl-4-vinylbenzylamine was synthesized based on the method of Se et al. (1983, shown in scheme 4.2). To a solution of 4-vinylbenzylaldehyde (8.0 g, 60.61 mmol) and two drops of acetic acid in 80 mL chloroform cooled in ice-water bath, isopropylamine (3.93 g, 66.66 mmol) was added dropwisely (4-vinylbenzylaldehyde reacted with isopropylamine to yield N-isopropyl-4-vinylbenzylimine (PVBI)). The mixture was magnetically stirred for 1 h at 0 °C and then 4 h at room temperature. The solution was dried by sodium sulfate. Sodium sulfate salt was filtrated and washed with 10 mL chloroform for three times. After chloroform was evaporated, the crude product was distilled under vacuum. Yield: 70% (7.33 g) with respect to 4-vinylbenzylaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): 1.24 ppm (6H, m, =N-CH-($C\underline{H}_3$)$_2$), 3.51 ppm (1H, t, =N-$C\underline{H}$-(CH_3)$_2$), 5.28 ppm (1H, d, CH=$C\underline{H}_2$), 5.78 ppm (1H, d, CH=$C\underline{H}_2$), 6.74 ppm (1H, q, $C\underline{H}$=CH_2), 7.41 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$), 7.66 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$), 8.26



Scheme 4.2 Synthesis of N-isopropyl-4-vinylbenzylamine

ppm (1H, s,2H, m, CH_2=CH-C_6H_4-C<u>H</u>=N).

To a solution of PVBI (6.0 g, 34.68 mmol) in 30 mL of dried methanol, $NaBH_3CN$ (2.3 g) was added. The mixture was allowed to react for 6 h at room temperature. .After methanol was removed, the crude was distilled under vacuum. .Yield: 85% (5.20 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.06 ppm (6H, m, NH-CH-(C<u>H</u>$_3$)$_2$), 1.40 ppm (1H, m, N<u>H</u>-CH-$(CH_3)_2$), 2.81 ppm (1H, m, NH-C<u>H</u>-$(CH_3)_2$), 3.74 ppm (2H, s, CH_2=CH-C_6H_4-C<u>H</u>$_2$-NH), 5.18 ppm (1H, d, CH=C<u>H</u>$_2$), 5.70 ppm (1H, d, CH=C<u>H</u>$_2$), 6.67 ppm (1H, q, C<u>H</u>=CH_2), 7.32 ppm (2H, m, CH_2=CH-C_6<u>H</u>$_4$), 7.66 ppm (2H, m, CH_2=CH-C_6<u>H</u>$_4$).

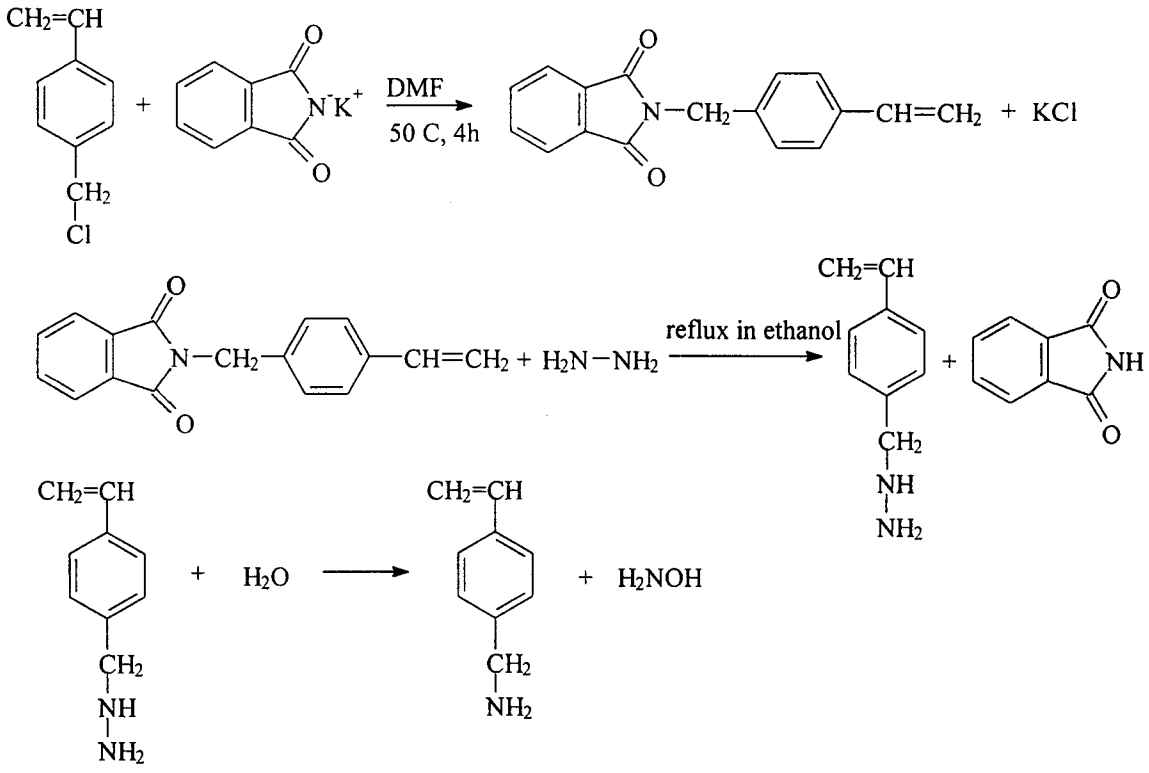
4.2.3 Synthesis of 4-Vinylbenzylamine (VBA)

4-Vinylbenzylamine was synthesized by a slightly modified method of Kobayash et al (1983). A mixture of 4-vinylbenzyl chloride (10.0 g, 65.36 mmol) and potassium phthalimide (13.30g, 71.90 mmol) was dissolved in 40 mL of N,N-dimethylformamide (DMF) and was heated to 50 °C for 4 hr. DMF was removed under vacuum and the residue was dissolved in 50 mL of chloroform. The solution was washed with 0.2 M sodium hydroxide aqueous solution followed by three times of 10 mL water. The chloroform solution was dried with sodium sulfate and then chloroform was evaporated. The product was recrystallized from methanol. Yield: 14.3 g (84%). N-4-vinylbenzylphthalimide (14.0 g, 53.23 mmol) in 40 mL of ethanol was refluxed in water bath. Hydrazine hydrate (5.0 g, 79.85 mmol) in 10 mL ethanol was added dropwisely.

The mixture was allowed to reflux 1.5 hr under vigorous stirring. After cooled to room temperature, the precipitate was collected and dried. The solid was treated with potassium hydroxide aqueous solution (20.0 g of KOH in 120 ml of water) for 2 hr. The aqueous mixture was extracted with ethyl ether (one time140 mL followed by four times 70 mL) and dried on potassium carbonate. The solvent was removed and the residue was distilled under vacuum. Yield: 5.4 g (76%). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.61 ppm (2H, m, -N$\underline{H}_2$), 3.85 ppm (2H, m, -C$\underline{H}_2$-NH_2), 5.22 ppm (1H, d, C$\underline{H}_2$=CH-), 5.72 ppm (1H, d, C$\underline{H}_2$=CH-), 6.71 ppm (1H, q, CH_2=C$\underline{H}$-), 7.28 ppm (4H, m, -$C_6\underline{H}_4$-CH_2-NH_2). The synthesis process was shown in Scheme 4.3.

4.2.4. Preparation of Initiator and Polymerization

In a glass reactor previously treated with chlorotrimethylsilane and flame dried, weighted LiCl was added and heated to 100 °C under vacuum and purged with nitrogen 5 cycles. Then 30 mL THF and required amount of N-substituted allylamine/vinylamine were charged to the reactor. The reactor was cooled down to -78 °C. A stoichiometric amount of s-butyllithium was added dropwisely with stirring. After 1h of stirring, the monomer was introduced. In the runs with a capping agent, 2-fold (molar) dimethylacrylamide or *tert*-butyl methacrylate with respect to N-substituted allylamine/vinylamine was introduced and stirred at –78 °C for 0.5h before adding monomer. The polymerization was terminated by adding 0.2 mL methanol. The aliquot was then poured into 200-mL petroleum ether. Finally the polymer was separated and



Scheme 4.3 Synthesis of vinylbenzylamine

dried in vacuum at 30 °C for 24h.

4.2.5. Polymer Quaternization

1 g polymer was dissolved in 10 mL acetone or DMSO or dimethylforamide (DMF) at room temperature. 0.5 mL CH_3I was then added dropwisely and stirred for 2 h. 0.1 mL dimethyl sulfate was then added and the solution was stirred for another hour. When using acetone as solvent, the quaternized polymer precipitated very quickly after adding CH_3I. The precipitate was isolated and dried in the vacuum oven. When DMSO or DMF was used as solvent, the quaternized polymer was soluble in DMSO and therefore the reaction in DMSO or DMF was homogenous. The quaternized polymer was precipitated in acetone and also dried in vacuum.

4.2.6. Characterization

4.2.6.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton ^1H NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 MHz. ^1H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using residual $CHCl_3$ signal at 7.23 ppm as an internal reference. When D_2O was used as solvent, residual H_2O signal at 4.63 ppm was used as internal reference.

4.2.6.2 Molecular Weight Measurements

Number and weight average molecular weights (M_n and M_w, respectively) were

determined by gel permeation chromatography (GPC) using THF-2%(v/v) trimethylamine as eluent at 25 °C with RI detector. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve (Varian MicroPak column G1000, 3000, 7000 HXL). Data were recorded and processed using the Windows based Millenium 2.0 software package.

4.3. Results and Discussion

4.3.1 DMAEMA Polymerization by N-Substituted Allylamine-sBuLi Initiator System

The initiators, lithium N-substituted allylamides, were prepared *in situ* by the reaction of N-substituted allylamine with s-butyllithium (Scheme 4.1). The reaction was thus investigated using diallylamine as model compound to see if the reaction had side reactions such as the addition reaction to the double bond and α-proton abstraction. Firstly, diallylamine was allowed to react with equimolar sBuLi in THF at anionic polymerization terminated by equimolar water. An oil-like liquid (*a*) was isolated. ^{1}H-NMR spectra indicated that the product obtained was a dimer of tBMA with terminal diallylamino group (Figure 4.1). The signals of the allyl group appeared at 5.7 ppm (m, CH=), 5.1 ppm (m, CH_2=) and 3.1 ppm (m, -CH_2-), slightly shifted to high field compared to those of diallylamine. Most importantly, the intensity ratio of the signals of the methylene proton (CH_2=), methine (=CH) and methylene (-CH_2-) was close to 2:1:2, and there was no sign of N-H proton. This clearly indicates that sBuLi abstracted proton

from N-H without reaction with the allyl groups, yielding lithium diallylamide. Therefore, lithium N-substituted allylamides were prepared by the reaction of corresponding N-substituted allylamine with sBuLi.

After the catalyst was prepared, DMAEMA monomer was injected for polymerization. The effects of catalyst preparation and polymerization conditions were summarized in Table 4.1. If both the initiator preparation and polymerization of DMAEMA were carried out at 0 °C, the polymerization gave only 33% polymer (Table 4.1, entry 1). When the initiator was prepared at 0 or 25 °C while the polymerization was carried out at -78 °C, the conversion was almost complete, but the molecular weight of the resulting polymer was much higher than predicted (Table 4.1, entries 2 and 3). The initiation efficiency (the ratio of calculated Mn over measured Mn) with respect to diallylamine was only about 15%. When both of the initiator preparation and successive polymerization were carried out at –78 °C, the initiator efficiency increased to about 25% as shown in Table 4.1. The corresponding GPC trace (Figure 4.2, a) shows a unimodal and extremely narrow molecular weight distribution. This result indicates that the initiation reaction was very fast and once a polymer chain started to propagate, the propagating anions had no side reactions such as the reaction with carbonyl group. Experimental conditions were optimized in order to increase the initiator efficiency. The amount of added LiCl had some effect on the polymerization. In the absence of LiCl, the polymerization produced polymer with very broad molecular weight distribution (Mw/Mn = 2.36, table 4.1, entry 4). But in the presence of LiCl, the polymer appeared to

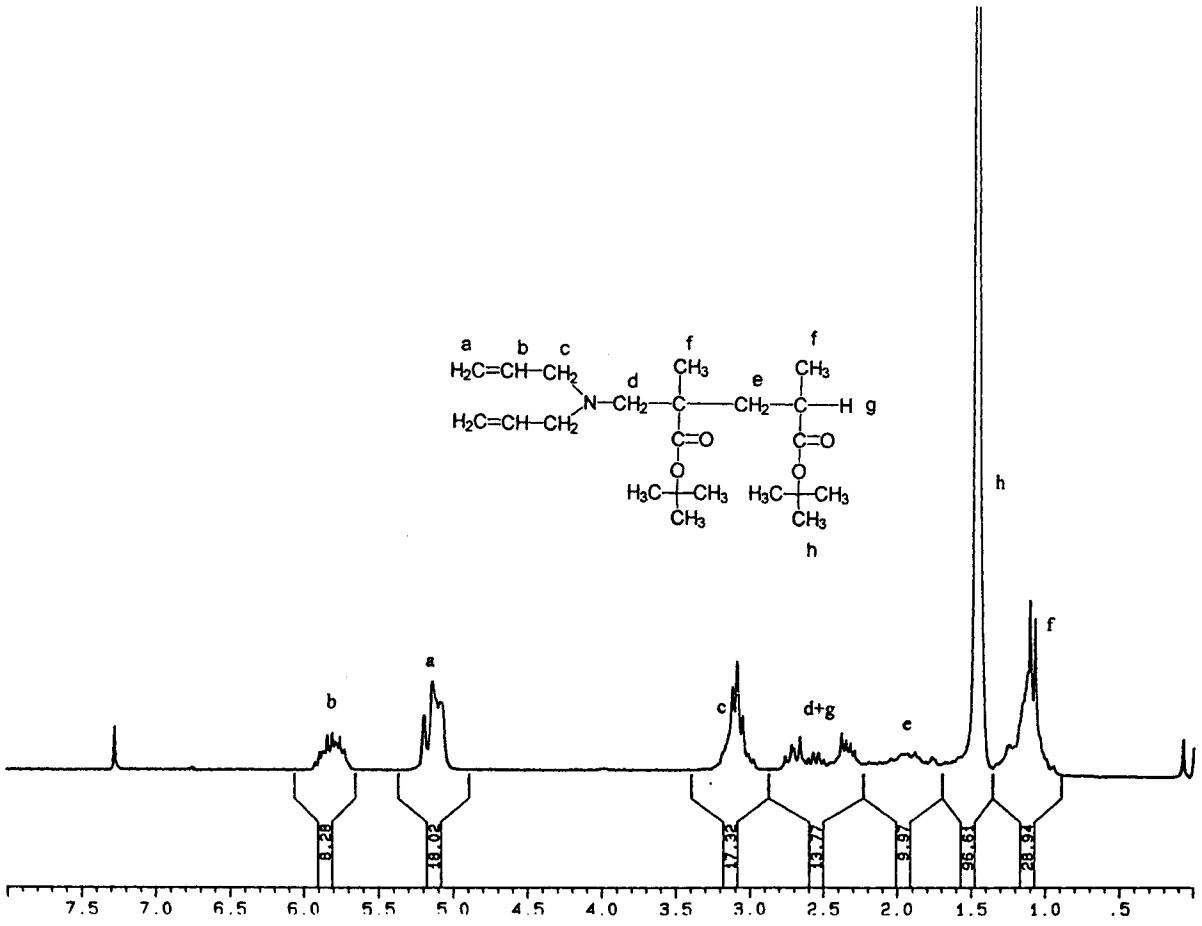


Figure 4.1. ^{1}H NMR spectra of the compound isolated from the reaction of diallylamine with sBuLi and tert-butyl methacrylate. [diallylamine]/[sBuLi] = 1/1, [tBMA]/[diallylamine] = 2/1 in THF; -78 °C

Table 4.1. Synthesis of PDMAEMA macromonomers by living polymerization of DMAEMA initiated by alkylamine/s-butyllithium in the presence of lithium chloride [a]

Run	Initiator	Reaction Temp(°C)	Polym. Temp(°C)	LiCl/ BuLi	DA/ BuLi	Conv. (%)	Mn (calcd)	Mn (GPC)	Efficiency	Mw/Mn
1	DA	0	0	10	1	33	1884	3500	-	1.11
2	DA	25	-78	10	1	99	4700	32700	0.16	1.09
3	DA	0	-78	10	1	99	4700	29700	0.14	1.10
4	DA	-78	-78	0	1	99	4700	17700	0.27	2.36
5	DA	-78	-78	1	1	99	4700	19000	0.24	1.07
6	DA	-78	-78	3	1	98	4700	18800	0.25	1.08
7	DA	-78	-78	10	1	99	4700	19000	0.24	1.15
8	DA	-78	-78	10	10	97	9600	24500	0.39	1.06
9	DA	-78	-78	10	10	97	12700	36600	0.35	1.02
10	AAN	-78	-78	10	10	98	4700	5888	0.79	1.06
11	AAM	-78	-78	10	10	0	-	-	-	-
12	VBA	-78	-78	3	1	0	-	-	-	-

a: -78 °C; [lithium amide]=0.017 mol/L in THF; AAN = allylaniline; AAM = allylamine; VBA = vinylbenzylamine

be nearly monodispersed (Table 4.1, entries 5-7). This is agreeable with report that the presence of LiCl suppressed side reactions of carbon anions attacking the carbonyl groups in the polymer and monomer (Jerome et al., 1999.). However, the presence of LiCl had no influence on the initiation efficiency. With or without LiCl, the initiation efficiencies of diallylamine were about 0.25.

The effect of added amount of diallylamine was also investigated. The presence of excessive diallylamine slightly increased the initiator efficiency, as shown in Table 4.1 entries 8 and 9. The molecular weight distribution of prepared polyDMAEMA remained very narrow, regardless of the amount of added diallylamine. This indicates that the formed propagating carbonanions did not abstract the proton in N-H of diallylamine (Scheme 4.4). This allows us to let sBuLi to react with an excess amount of diallylamine to minimize possible side reactions of sBuLi during the initiator preparation.

Allylaniline (AAn), allylamine (AAm) and vinylbenzylamine (VBA) were also tested for the polymerization of DMAEMA to further investigate the effect of substituents on the initiator efficiency (Table 4.1, entries 10, 11 and 12). With lithium monoallylamide (Scheme 4.5 b) and lithium vinylbenzylamide as initiator, no polymer was obtained, while lithium allylphenylamide (Scheme 4.5 c), derived from the reaction of allylaniline with sBuLi, had much higher initiator efficiency, 0.79, than that of lithium diallylamide (Scheme 4.5 a). Apparently, the substituents on the nitroanion influences the initiator efficiency. For N-substituted allylamines, the efficiency increased by the order $0 < 25\% < 79\%$ with the substituents changed from H, allyl, to phenyl. This trend

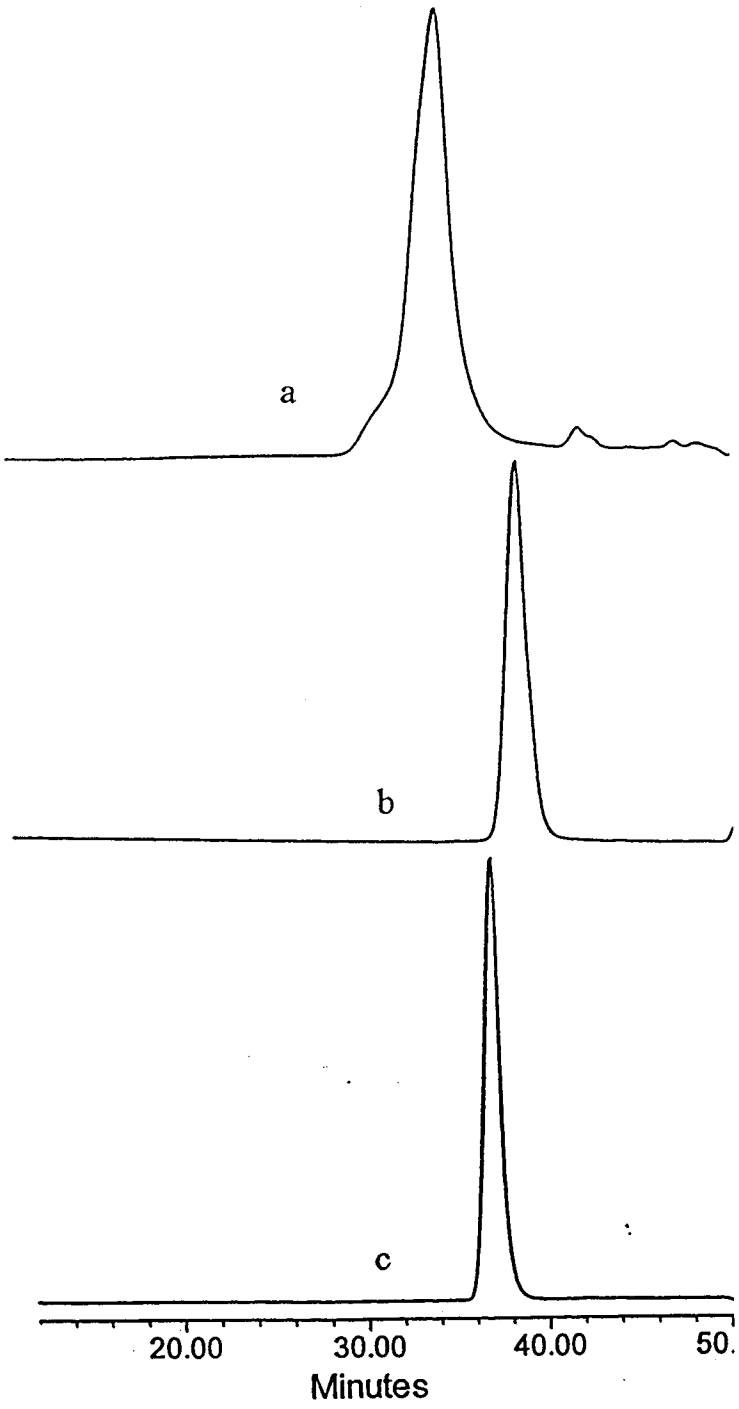


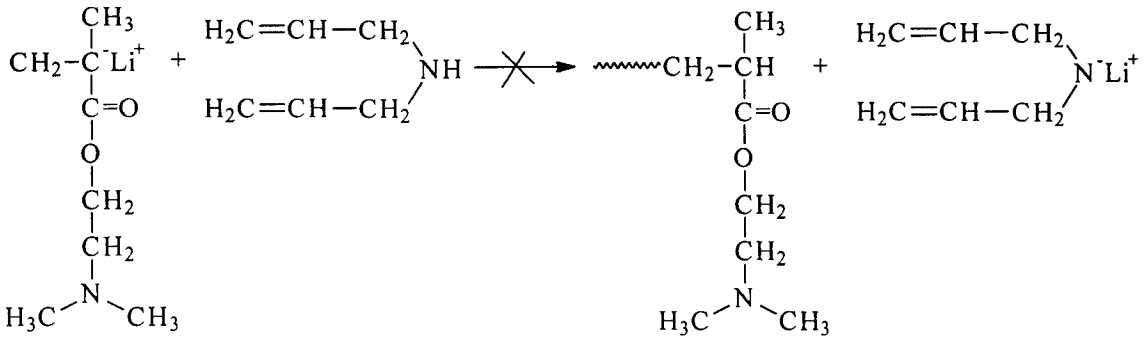
Figure 4.2 GPC traces of polyDMAEMA initiated by DMA-capped lithium diallylamide (a) without LiCl (Table 4.2. entry 1, (b) with 3-fold LiCl (Table 4.2, entry 3), and (c) with 10-fold LiCl (Table 2, entry 7).

suggests that the low initiator efficiency of lithium diallylamide was inherent due to its low steric hindrance of the two allyl groups. In fact, similar initiator efficiency was obtained when using lithium diethylaminde as initiator.

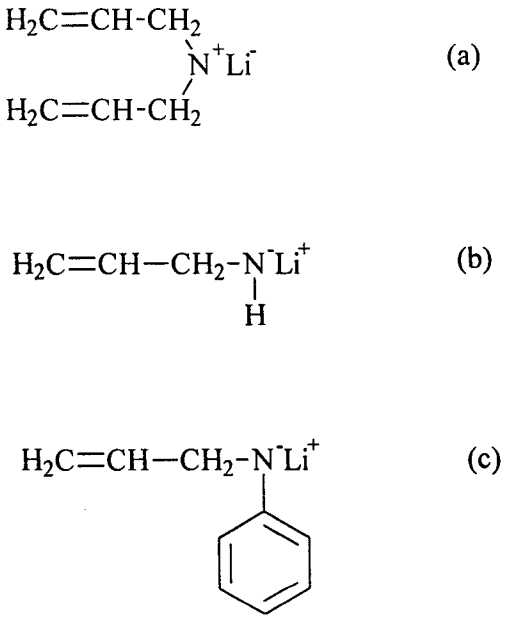
4.3.2. Diallylamine/sBuLi-Capping Agent Initiated Polymerization of DMAEMA

The low initiator efficiency of lithium amide of less bulky substituents was ascribed to the initiator's association and side reactions with carbonyl groups in the monomer and polymer (Antoun et al., 1997b). Increasing steric hindrance of the substituent decreased such association and minimizes these side reactions and thus increased initiator efficiency. Therefore, the lithium diallylamide was modified by reacting with dimethylacrylamide (DMA), *tert*-butyl methacrylate (tBMA) or methacrylnitrile (MAN) (capping reaction) respectively to convert it into an anion with bulky substituents (Scheme 4.6). Table 4.2 summarizes the results of the DMAEMA polymerization with capped lithium diallylamide.

Table 4.2 shows that DMA or tBMA-capped lithium diallylamide had very high activities. The monomer conversions were almost complete. More importantly, the molecular weights of the polymers agreed well with predicted. The initiator efficiencies were as high as 0.90, in contrast to the low initiator efficiency of uncapped lithium diallylamide (Table 4.2, entries 2-5, 9-11). The molecular weight distributions were also narrow, less than 1.1. The narrow GPC traces of the resulting polymers (Figure 4.2 b, c) demonstrated that there was only a single type of initiation species. These results suggest



Scheme 4.4. No chain transfer of polymer anion to diallylamine



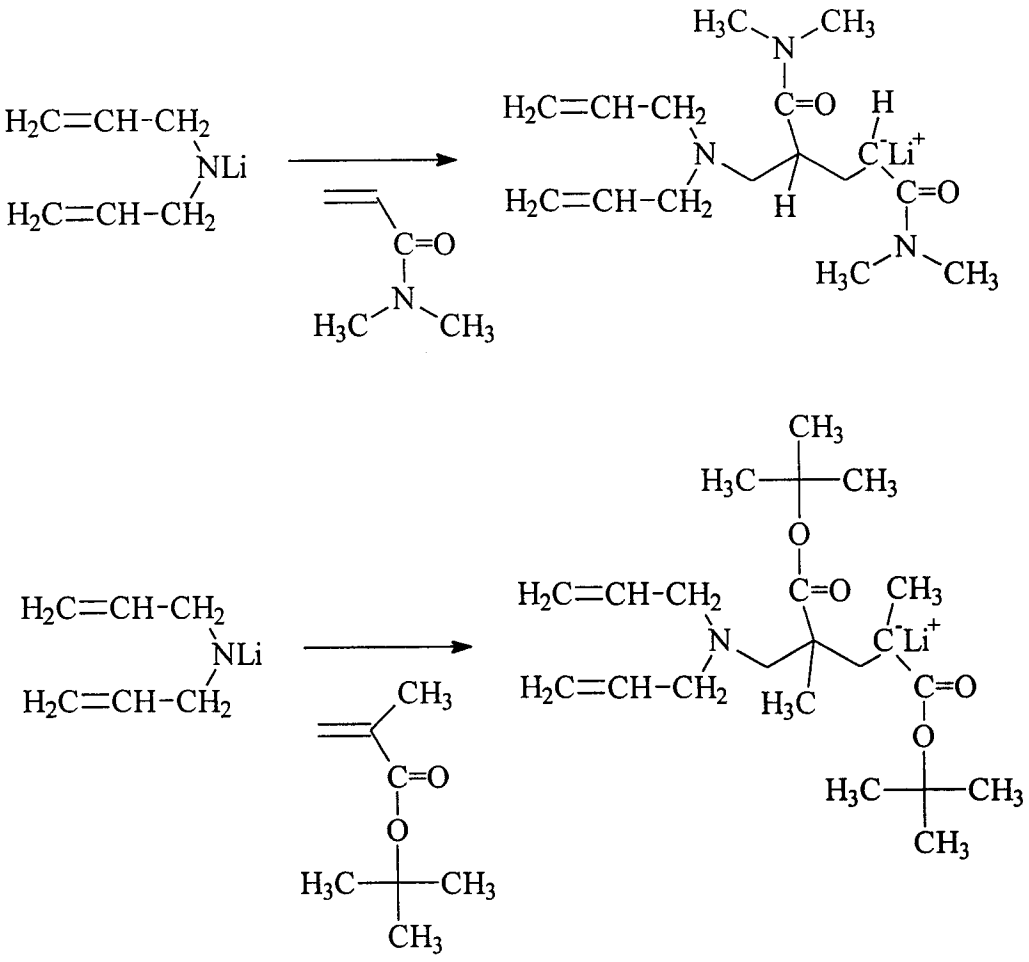
Scheme 4.5. Schematic structures of the N-substituted allylaminolithium

DMAEMA polymerization with capped lithium diallylamide.

that the capping reaction of lithium diallylamide with DMA or tBMA was complete, and the capped initiators did not associate in the solution and had no reactions with carbonyl groups. The complete capping reaction also indicates that lithium diallylamide did not strongly associate in the presence of LiCl, as observed in the lithium diethylamide (Antoun et al., 1997b). This conclusion was also confirmed by the lithium diallyamide-initiated homopolymerization of tBMA, in which high initiator efficiencies were also obtained (Shen et al., 2001). Therefore, the low efficiency in the lithium diallylamide-initiated polymerization of DMAEMA (Table 4.1) was due to the reaction of lithium diallylamide with the carbonyl group, other than diallylamide initiator association (Antoun et al., 1997b).

When methacrylnitrile (MAN), which has similar vinyl group of tBMA but without the bulky *tert*-butyl group, was used as capping agent, the polymerization was less controlled (Table 4.2 entry 13). The resulting polymer had a much higher molecular weight than predicted with a broad molecular weight distribution. Actually it was found that when MAN was added to the lithium diallylamide solution at –78 °C the solution turned into red, which suggested that some lithium diallylamide reacted the CN group.

The LiCl concentration had a dramatic effect on the DMAEMA polymerization initiated by the capped lithium diallylamide. Without LiCl, DMA-capped lithium diallylamide had a very low initiation efficiency (Table 4.2 entry 1), even lower than that of uncapped initiator (Table 4.1). The polymer produced had a broad molecular weight distribution (Figure 4.2 a). Adding 1 to 3-fold LiCl with respect to lithium diallylamide



Scheme 4.6. Capping reaction of diallylaminolithium with DMA and tBMA

Table 4.2. DMAEMA polymerization initiated by capped-lithium diallylamide at –78 °C [a]

Run	Capping agent	DMAEMA/Amide ratio	LiCl/Amide	Solvent	Conv. (%)	Mn Calcu.	Mn GPC	Initiator Efficiency	Mw/Mn
1	DMA	30	0	THF	99	4700	38500	0.12	2.89
2	DMA	30	1	THF	98	4700	5310[b]	0.89	1.06
3	DMA	27	3	THF	99	4200	4440	0.95	1.04
4	DMA	78	3	THF	98	12300	13800	0.90	1.08
5	DMA	150	3	THF	99	23300	25500	0.93	1.04
6	DMA	30	3	THF-Toluene [b]	95	4700	24600	0.19	4.86
7	DMA	30	10	THF	99	4700	9600	0.49	1.06
8	DMA	60	10	THF	100	7720	15200	0.51	1.08
9	tBMA	30	3	THF	99	4700	4900	0.96	1.03
10	tBMA	50	3	THF	99	7800	8300	0.94	1.05
11	tBMA	64	3	THF	99	10000	11500	0.87	1.07
12	tBMA	60	10	THF	97	9420	17000	0.55	1.04
13	MAN	30	3	THF	100	4700	19500	0.21	1.31
14	DMA	50	3	THF	100	7850	12300	0.63	1.19

[a] [Diallylaminolithium]=0.017 mol/L, [b] Toluene/THF =9/1 (v/v).

substantially increased the initiator efficiency to 0.90 and yielded polymers with extremely narrow molecular weight distributions (Table 4.2 entries 2-5) (Figure 4.2 b). This is agreeable with the results in other polymerization system (Zune et al., 1999). However, we found that too much excess LiCl had a detrimental effect on the initiation efficiency for both DMA and tBMA-capped lithium diallylamide (Table 4.2, entries 7, 8, 12). For example, the efficiencies of the capped lithium diallylamide decreased to about 0.5 with a 10-fold LiCl. This effect of excess LiCl may be due to the fact that too many LiCl molecules surround an initiator anion and thus some initiators may become dormant in clusters and inactive in the initiation of DMAEMA. We also tested toluene/THF (9:1 v/v) as a solvent and found low initiator efficiency and very poor control of molecular weight (Table 4.2 entry 6).

4.3.3 Synthesis of DMAEMA Macromonomer Without Capping Reaction Initiated by N-Isopropyl-4-Vinylbenzylamide

The N-isopropyl-4-vinylbenzylamide initiator with isopropyl and phenyl substituents was also synthesized by reacting PVBA with equal molar sBuLi in THF at -78° C. After the addition of sBuLi, the solution turned to yellow-brown color, which indicated the reaction of sBuLi with N-isopropynol-4-vinylbenzylamine. It was confirmed that sBuLi abstracted the proton from amine (NH) and did not react with the styrenic moiety.

The prepared initiator, lithium N-isopropyl-4-vinylbenzylamide (LiPVBA), was

used to initiate the polymerization of DMAEMA at –78 °C in the presence of LiCl. The results are summarized in Table 4.3.

In contrast, LiPVBA, which has a bulky isopropyl and phenyl group on the nitro-anion, initiated a living polymerization of DMAEMA in the presence of three times of LiCl (molar). The molecular weight of polyDMAEMA could be precisely controlled by DMAEMA/initiator ratio, as shown in Figure 4.3. The polydispersity of resulting polymer was very narrow (Mw/Mn ≈ 1.06). Lithium chloride was required for producing low polydispersity polymer samples. Without LiCl, the polydispersity of PDMAEMA was about 1.2. However, the initiator efficiency was not affected by LiCl. These results indicate that the nitro-anion with bulky substituents could effectively initiate living polymerization of DMAEMA in the presence of LiCl and required no capping reactions.

4.3.4. Characterization and Quaternization of the Macromonomers

The macromonomers prepared were characterized by ^{1}H-NMR. Figure 4.4 shows the NMR spectrum of polyDMAEMA. Signals of polyDMAEMA backbone are at 2.25 ppm ($N(C\underline{H}_3)_2$), 2.55 ($NC\underline{H}_2$), 4.05 ppm ($COOC\underline{H}_2$), 1.65~2.05 ppm ($C\underline{H}_2$-C-CH_3), 0.87~1.05 ppm ($C\underline{H}_3$-C). Signals due to diallylamino group appear at 5.1 ppm (m, CH_2=) and 5.7 ppm (m, =CH) (Figure 4.4 A), which are very similar to the signals of diallylamine. The signals of allyl group in allylphenylamino appear at up-field, 5.6 ppm (m, =CH) and 5.05 ppm (m, CH2=), due to the conjugation of benzene ring with the nitrogen atom. These results indicated that the polymers had the desired diallylamino or

Table 4.3. Synthesis of macromonomers from DMAEMA initiated by LPVBA and LVBA in THF at -78 °C.

Entry	Amine	M/ Amide	LiCl/ sBuLi	capping agent	Conv. (%)	Mn,cal	$Mn_{,SEC}$	$M_{n,NMR}$	Mw/ Mn	f[a]
1	PVBA	50	0	-	100	7850	8100	8100	1.20	0.97
2	PVBA	50	3	-	100	7850	8100	8000	1.06	0.97
3	PVBA	50	3	DMA	100	7850	9050	7950	1.08	0.87
4	PVBA	15	3	-	100	2355	2700	2300	1.04	0.87
5	PVBA	20	3	-	100	3140	3300	3500	1.03	0.95
6	PVBA	30	3	-	100	4710	5600	5200	1.06	0.85
7	PVBA	75	3	-	100	11800	12400	-	1.05	0.95

a-f = $M_{n,cal}/M_{n,SEC}$

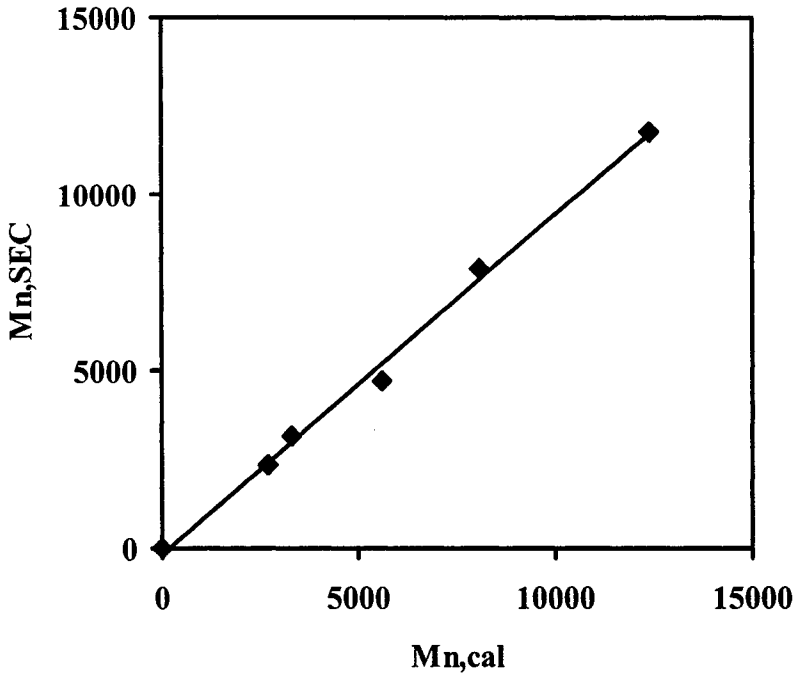


Figure 4.3 Molecular weight data of the nitro-anionic polymerization of DMAEMA with LiPVBA as initiator in THF at –78 C. Mn measured by SEC versus calculated Mn

allylphenylamino terminal groups. For the macromonomers with vinylbenzylamine terminated group, the signals due to vinylbenzylamine group appear at 5.09 ppm (1H, d, $C\underline{H}_2$=CH), 5.63 ppm (1H, d, $C\underline{H}_2$=CH), 6.64 ppm (1H, m, CH_2=C$\underline{H}$), which are very similar to those of vinylbenzylamine.

The allyl group is not an effectively polymerizable group. But allyl on quaternary nitrogen atom is readily polymerizable. For example, diallyldimethylammonium chloride (DADMAC) is an important cationic monomer for homo- and random copolymers popularly used in industry (Bolto, 1995; Brand et al., 1997). Therefore the allyl-terminated polymers were reacted with quaternization agents to prepare polymerizable cationic macromonomers. Two types of nitrogen atoms, in pendant dimethylamino and terminal diallylamino or allylphenylamino groups, need to be quaternized. The two types of nitrogen atom groups showed very different activities. The nitrogen atoms in dimethylamino groups were easily quaternized by CH_3I at room temperature or by benzyl chloride at 40 °C. For example, after 1 h reaction with CH_3I at room temperature, all the nitrogen atoms in dimethylamino groups were converted into trimethylammonium ($(CH_3)_3N^+$), as shown in Figure 4.5. The signal of $NC\underline{H}_3$ at 2.25 ppm disappeared completely while a strong peak for $N^+C\underline{H}_3$ appeared at 3.20 ppm. However, the signals of allyl groups did not change at all (Figure 4.5 A). Increasing quaternization temperature or prolonging the reaction time could partially quaternize these terminal groups, but caused some double bonds to disappear, possibly due to reaction with I_2 generated from the decomposition of CH_3I.

The more powerful methylizing agent, $(CH_3)_2SO_4$, can quantitatively quaternize both types of tertiary amino groups in the polymer. For example, after 1 h reaction in DMSO at room temperature, the terminal diallylamino group was completely quaternized, as seen in NMR spectra (Figure 4.5 B). The allyl proton signals at 5.1 ppm (CH_2=) in non-quaternized diallylamine shifted to 5.45 ppm after quaternization, which was the same as the signals of that in diallyldimethylammonium chloride. The complete quaternization of allylphenylamino group with dimethyl sulfate required longer time (Figure 4.5 C). This lower reactivity of allylphenylamino group may be due to the combination of high steric hindrance effect of the benzene ring and the conjugation of the nitrogen atom with benzene ring, which substantially decreases the electron density on the nitrogen atom. In contrast, there is no need to quaternize N-isopropyl-4-vinylbezylamino group for macromonomer copolymerization.

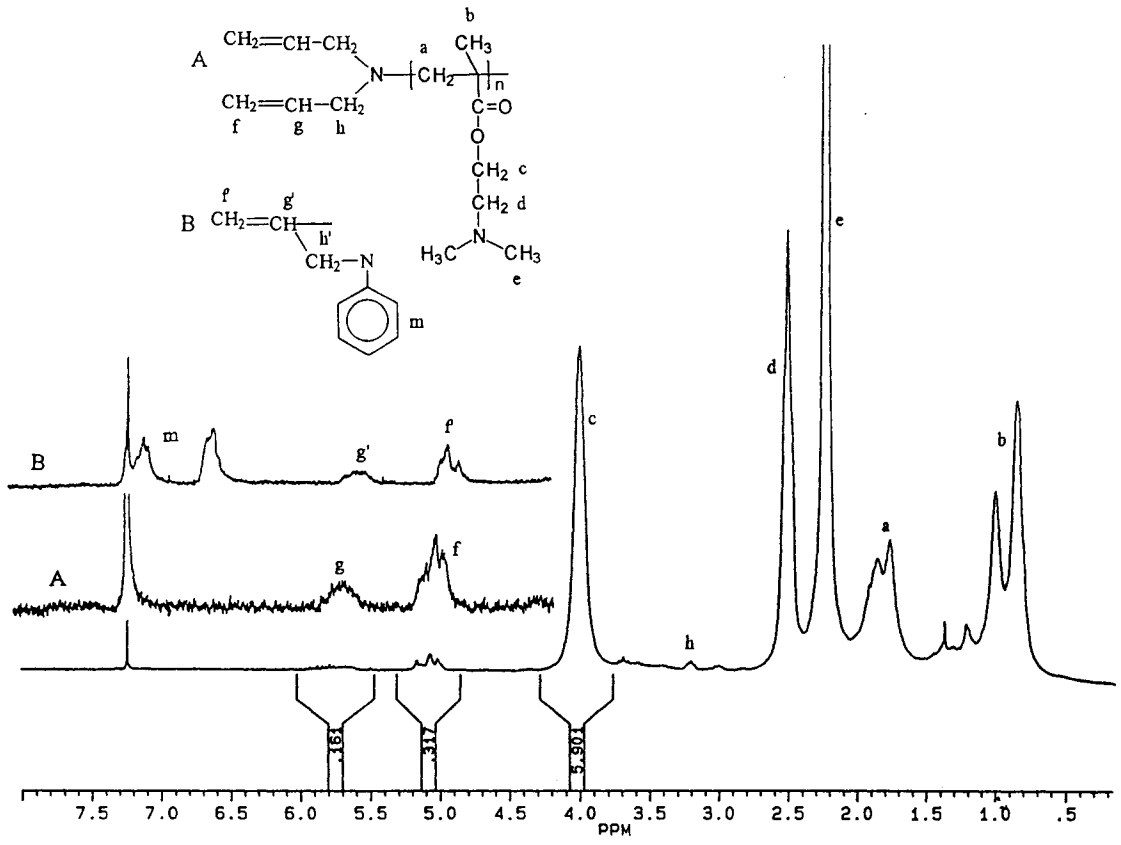


Figure 4.4. ^{1}H NMR spectra of polyDMAEMA macromonomers prepared by (a) diallylamine-sBuLi and (b) allylphenylamine-sBuLi

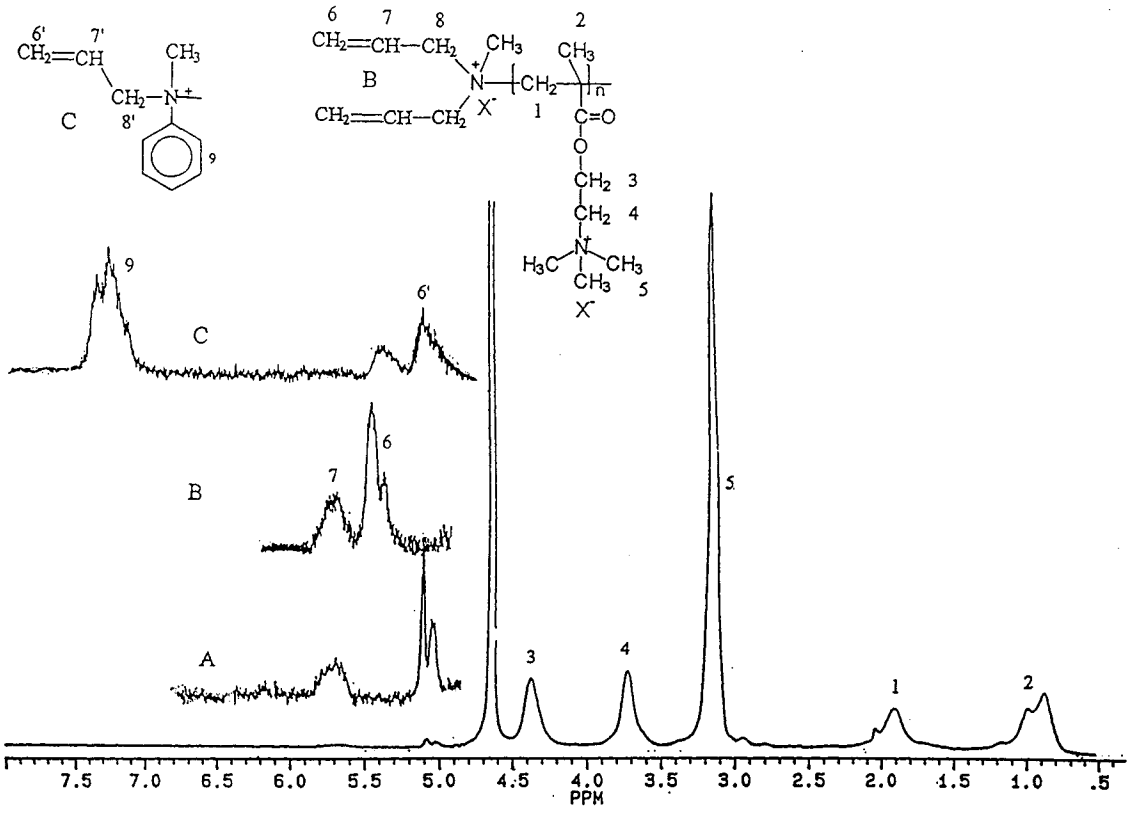


Figure 4.5. [1]HNMR spectra of quaternized polyDMAEMA macromonomers: (a) diallylamino-terminated polyDMAEMA reacted with CH_3I at room temperature for 1 h, (b) diallylamino-terminated polyDMAEMA reacted with $(CH_3)_2SO_4$ in DMSO for 1 h, and (c) allylphenylamino-terminated polyDMAEMA reacted with $(CH_3)_2SO_4$ in DMSO for 6 h.

4.4 Conclusion

(1) Cationic PolyDMAEMA macromonomers with polymerizable terminal vinyl and styrenic groups were successfully synthesized by a living anionic polymerization initiated by N-substituted lithium allylamide systems and subsequent quaternization.

(2) The substituent on the nitroanion strongly affected on the initiator efficiency, which increased by 0 < 25% < 79% with the substituent changed from H, allyl to phenyl.

(3) A capping method for nitroanion was developed to increase the initiator efficiency. The initiator efficiency of lithium diallylamide was thus increased from 0.25 to 0.9 by capping it with dimethylacrylamide or t-butyl methacrylate.

(4) For LiPVBA initiator with bulky substituent, no capping is required.

(5) One to three-fold LiCl with respect to initiator was necessary for a well controlled polymerization of DMAEMA. However, too much excess of LiCl reduced the initiator efficiency.

(6) The quaternization of terminal diallylamino and allylphenylamino groups required a strong methylizing agent such as $(CH_3)_2SO_4$, while the dimethylamino group in the polymer chain was quaternized by CH_3I.

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Chapter 5

Synthesis of Comb-Branched Polyelectrolytes by Macromonomer Copolymerization in Batch and Semi-batch Processes

5.1 Introduction

Since the works by an ICI group (Walbridge et al, 1975.) and Milkovich (Milkovich et al., 1974.), a number of recent papers have been published on macromonomer copolymerization (Rempp et al., 1984. Gnanou et al., 1989.). The chemistry of macromonomer synthesis and copolymerization has also received considerable attention and a variety of such polymers and materials have been produced which now have found applications in adhesive, coating, painting, surfactant and bio-materials fields (Takemoto et al., 1987. Ceresa, 1973). However, most of the studies have involved hydrophobic-hydrophobic and hydrophobic-hydrophilic copolymerization such as styrene and methyl methacrylate macromonomers. Recently, Xiao et al. synthesized water-soluble nonionic graft copolymer of PEG macromonomer with acrylamide (Xiao et al., 1996a.). The graft copolymers demonstrated better properties as retention and drainage agents compared to the random copolymer and PEO homopolymer in papermaking (Xiao et al., 1996b.). In our group, we have shown that graft copolymers with active cationic units concentrated on pendant chains gave better flocculation perfor-

mance than the corresponding random copolymers (Li et al., 1999. Ma et al., 1999). However, the graft copolymers were prepared by gamma irradiation of the aqueous mixtures of polyacrylamide and poly(diallyldimethyl ammonium chloride). This procedure was not very selective and was difficult to control and resulted in a mixture of structures.

The extension of macromonomer copolymerization may offer an approach for synthesizing cationic graft copolymers. However, few studies have been reported on the copolymerization of cationic macromonomers with hydrophilic monomers such as acrylamide and vinylformamide. For most of the work, the graft copolymers were synthesized by batch processes. The grafts are thus not uniformly distributed along chain backbones. For example, when the reactivity of macromonomer was low compared to comonomer, i.e. $r_1 > 1$ (here M_1 is comonomer and M_2 macromonomer), the macromonomer was less incorporated into polymer backbone at the early stage (Kawakami, 1985). This would result in a composition drift. With increase in conversion, the comonomer concentration decreases and macromonomer incorporation to polymer backbone increases.

Semi-batch technology has been widely used to control copolymer composition and microstructure for conventional monomer copolymerization (Snuparek et al., 1977.) Hernandez-Barajas used a semi-batch technique to control copolymer composition of acrylamide and 2-(dimethylamino)ethyl methacrylate or 2-(dimethylamino)ethyl acrylate (Hernandez-Barajas et al., 1997.). The chemical composition and structural homogeneity of the yielding copolymers were improved by this method. In order to overcome the

composition drifting during macromonomer copolymerization, the extension of semi-batch control methods to macromonomer copolymerization may improve the control over composition drifting and/or copolymer microstructure (Zeng et al., 2001.).

In this chapter, we report the copolymerization kinetics of polyDMAEMA macromonomer with acrylamide by free radical copolymerization in aqueous media. The reactivity ratios of acrylamide with respect to macromonomers were measured. The effects of macromonomer end group and chain length on the reactivity and those of polymerization method on polymer composition and microstructure were examined.

5.2. Experimental Section

5.2.1. Materials

Acrylamide (98%), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (used as a radical initiator for the conventional copolymerization of acrylamide with macromonomers) were obtained from Aldrich and recrystallized before use. Methanol (MeOH) from Aldrich was used without purification.

5.2.2. Synthesis of Macromonomer with Different Molecular Weight

Three polyDMAEMA macromonomers with allyl end group were synthesized by ATRP process (see Chapter 3). One macromonomer with styrenic end group was synthesized by living nitro-anionic method (see Chapter 4).

The resulting macromonomers were quaternized by dimethyl sulfate at acetone solution. To a solution of 12 g purified macromonomer (76.43 mmol) in 120 mL

acetone, dimethyl sulfate (10.60 g, 84.07 mmol) was added. The mixture was magnetically stirred for 1 h at room temperature. Then the quaternized macromonomer was separated by filtration and washed with 10mL acetone for three times and dried under vacuum to give a colorless powder. Yield: 95.1% (20.50 g).

5.2.3 Copolymerization of polyDMAEMA-DMS Macromonomer with Acrylamide

5.2.3.1 Batch Process

The kinetic study on the batch copolymerization of polyDMAEMA-DMS macromonomer with acrylamide was carried out in an aqueous solution using AIBA as a radical initiator. The mixture of polyDMAEMA-DMS macromonomer (0.040 g), acrylamide (0.16 g, 2.25 mmol), AIBA (1 mg) and water (2mL) was charged to a glass ampoule reactor and degassed by three freeze-to-thaw cycles. The ampoules were then immersed into a preset water bath with circulating water at the polymerization temperature. The ampoules were taken out one by one at different time intervals and frozen quenched. The reactant mixture was dissolved in water and the polymer was precipitated in methanol and washed three times with 5 mL of methanol. All samples were dried under vacuum at room temperature for 36 h. The monomer conversions were determined gravimetrically and the copolymer composition was measured by ^{1}H NMR in D_2O solvent. The total conversion was calculated from the ratio of the weight of dried copolymer sample over that of total comonomers initially charged to ampoule. The acrylamide conversion was calculated from the weight of acrylamide component in dried copolymer sample divided by that of acrylamide monomer initially charged to ampoule.

The conversion of polyDMAEMA macromonomer was calculated following the same procedure.

5.2.3.2 Semi-batch Process

Take the copolymerization of styrenic terminated macromonomer as an example. 0.8 g of acrylamide and 40 mg of polyDMAEMA-DMS macromonomer (i.e., 20 wt% of the total macromonomer) and 3 mg of AIBA (30 wt% of the total AIBA) in 16.8 mL (5 wt% of the total solution) of deionnized water were initially charged to a reactor equipped with magnetic stirrer, then purged with high purity nitrogen for 30 min. 160 mg of polyDMAEMA-DMS macromonomer and 7 mg of AIBA in 3.2 mL of deionized water was fed to the reactor at a constant feeding rate controlled by a tubing pump during a 2-hour period. 0.5 mL of sample was taken each time at preset time intervals by a degassed syringe and was precipitated in methanol. The conversion was calculated from the ratio of the weight of dried polymer collected over that of total comonomers initially charged to the sample (5 wt% of the solution).

5.2.4. Measurements

^{1}H NMR spectra were obtained on a Bruker AC-P200 Fourier transform spectrometer (200 MHz for ^{1}H) in $CDCl_3$ or D_2O solvent. The chemical shifts were reported in ppm with signals of trace of $CHCl_3$ or H_2O as internal standard. GPC measurements were carried out using a Waters 590 liquid chromatography equipped with three Varian MicroPak columns (G1,000, 3,000 and 7,000HXL) with a 410 differential

refractometer detector. THF with 2% triethylamine was used as solvent. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows based Millenium 2.0 software package.

5.3 Results and Discussion

5.3.1 Synthesis and Characterization of Macromonomers

The polyDMAEMA macromonomers with allyl end group were synthesized by an ATRP process (see Chapter 3) with ABIB as initiator, and Cu(I)Br/BA_6-TREN as catalyst. The resulting macromonomers were purified by passing through a silica gel column. The polyDMAEMA macromonomer with styrenic unsaturated end group was synthesized by living nitro-anionic method (Table 5.1, entry 4). The quaternary salts of polyDMAEMA macromonomer were prepared by reacting polyDMAEMA macromonomer with DMS in 10% (by weight) acetone solution (Bogoeva-Gaceva et al., 1983.). All the macromonomers synthesized were summarized in Table 5.1.

The molecular structures of the resulting macromonomers with allyl or styrenic end group are shown in Scheme 5.1. The macromonomer molecular weights measured by GPC using polystyrene as standard and by end group analysis by ^{1}H NMR were agreeable, which indicate the allyl or styrenic end group was not consumed during the synthesis of macromonomer by ATRP or living nitro-anionic processes.

The macromonomers were characterized by ^{1}H NMR. Figure 5.1a shows the ^{1}H NMR spectra of polyDMAEMA macromonomer. The signals of polyDMAEMA

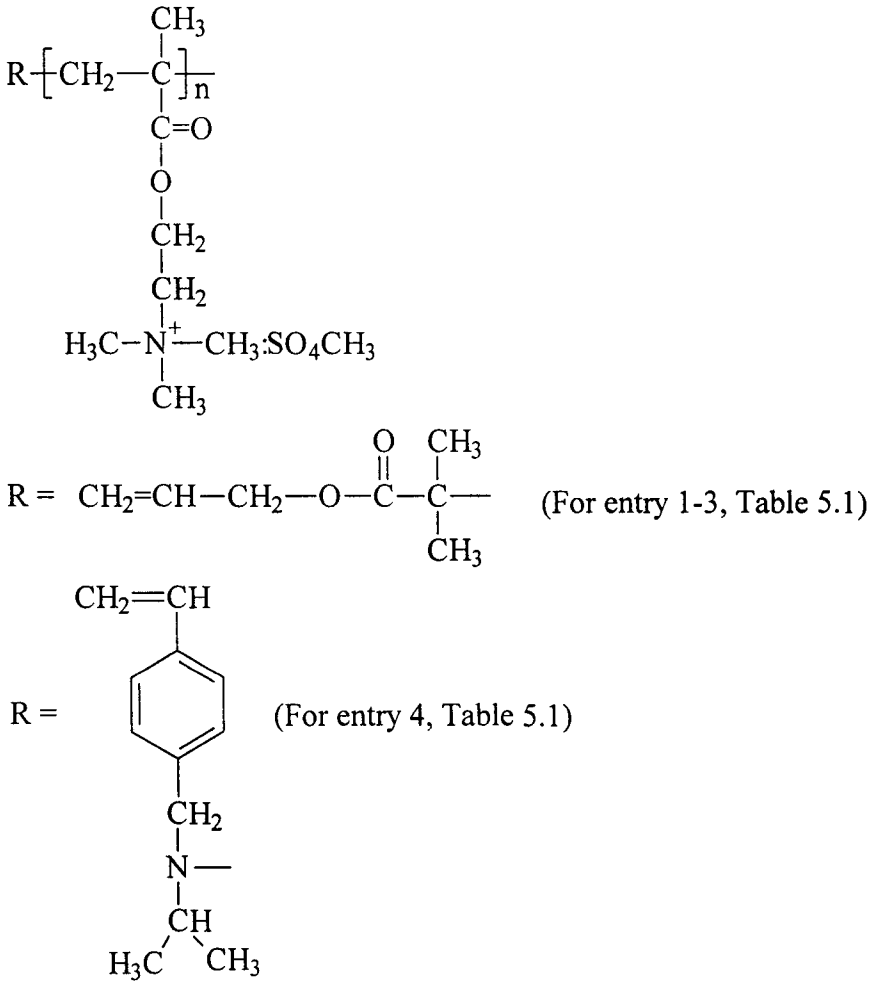
backbone are at 2.20 ppm (6H, $N(C\underline{H}_3)_2$), 2.47 ppm (2H, $NC\underline{H}_2$), 3.97 ppm (2H, $COOC\underline{H}_2$), 1.73-1.82 ppm (2H, $C\underline{H}_2$-C-CH_3), 0.82 and 0.97 ppm (3H, $C\underline{H}_3$-C). The signals due to allyl group appear at 5.16 ppm (2H, $C\underline{H}_2$=CH-) and 5.72 ppm (1H, CH_2=C$\underline{H}$-) which are very similar to the unsaturated ally group from ABIB.

The subsequent quaternization by dimethylsulfate converted polyDMAEMA to cationic macromonomers, polyDMAEMA-DMS. Figure 5.1b shows the ^{1}H NMR spectrum of the cationic polyDMAEMA-DMS macromonomer. After quaternization, the NCH_3 signal at 2.47 ppm disappeared completely while a strong peak for N^+CH_3 appeared at 3.06 ppm, which indicated the nitrogen atom in dimethylamino group quaternized by dimethyl sulfate. The signals at 5.16 ppm (2H, $C\underline{H}_2$=CH-) and 5.72 ppm (1H, CH_2=C$\underline{H}$-) did not change, which indicated the vinyl group was not consumed during quaternization (Figure 5.1b). The slightly shift of ^{1}H NMR signals to the lower field is due to the use of D_2O as solvent.

Table 5.1 Preparation of macromonomer with predicted chain length

Entry	Initiator	DMAEMA /Initiator	Time (h)	Conv (%)	Mn,cal	$M_{n,GPC}$	$M_{n,NMR}$	Mw/ Mn	f[c]	$M_{n,MCQ}$ By cal.
1	ABIB[a]	100:1	3.0	85.3	13400	14600	-	1.19	0.92	24300
2	ABIB[a]	50:1	3.0	87.5	6900	7700	7450	1.15	0.90	12500
3	ABIB[a]	30:1	3.0	90.1	4300	4500	4400	1.16	0.96	7700
4	VBA[b]	100:1	1.0	99	15540	15180	-	1.09	1.0	27360

a - using living radical polymerization method: b - using living nitro-anionic polymerization method; c - initiator efficiency



Scheme 5.1. Molecular structures of cationic PDMAEMA macromonomer with allyl and vinyl end group

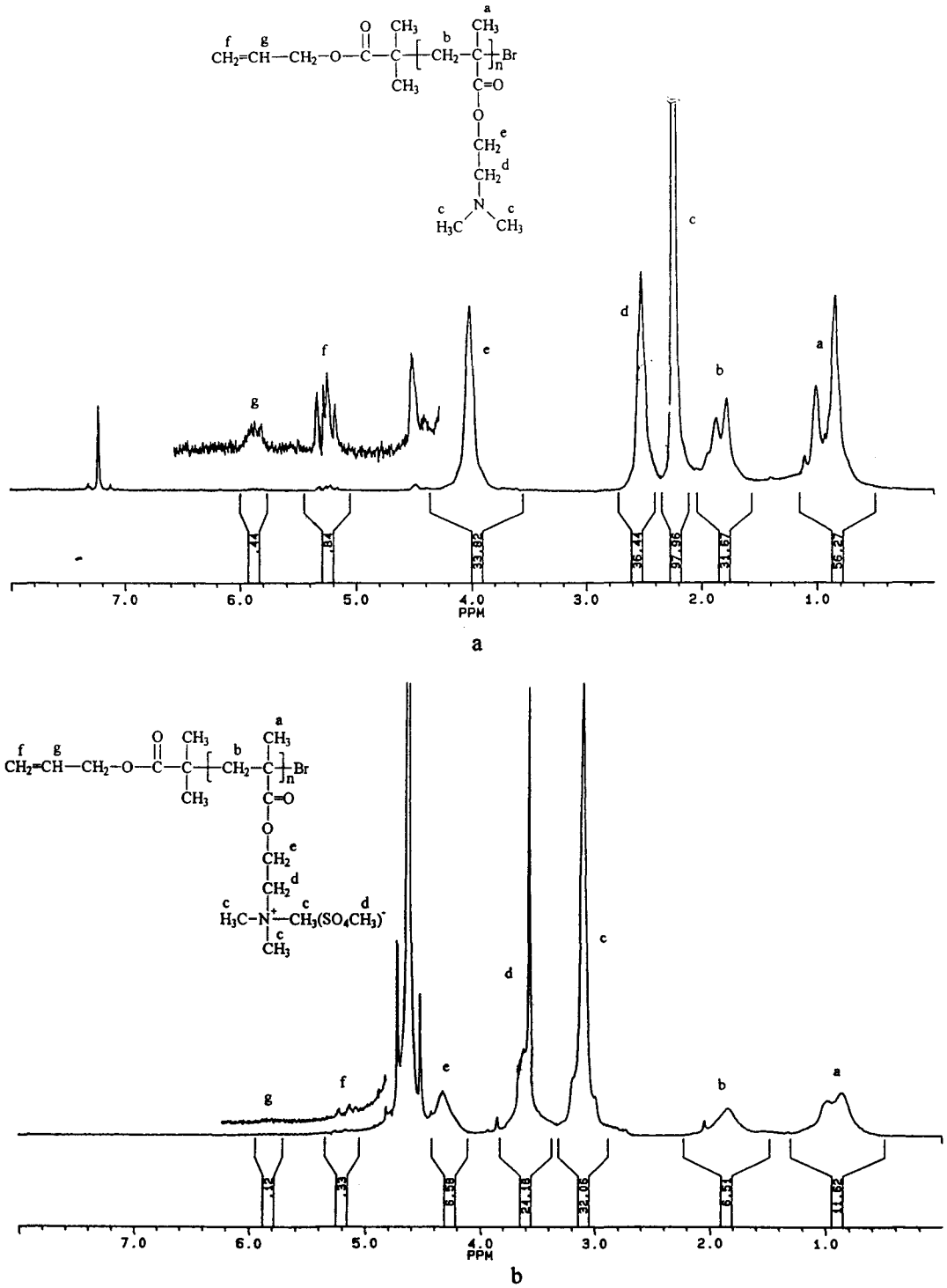


Figure 5.1 ^{1}H NMR spectra of polyDMAEMA macromonomer and cationic macromonomer: (a) From Table 5.1, entry 3; (b) the cationic macromonomer from Table 5.1, entry 3.

5.3.2 Copolymerization Kinetics of Acrylamide with polyDMAEMA-DMS Macromonomer

The copolymerization of acrylamide with PDMAEMA-DMS macromonomer was conducted in deionized water with AIBA as radical initiator at 50 °C. Figures 5.2-5.3 show the conversion versus time plots for acrylamide and macromonomers with allyl and styrenic end group for f_{10} = 0.8 by weight respectively. The macromonomer with styrenic end group had higher incorporation rate than acrylamide during copolymerization (Figure 5.2). However, when the macromonomer with allyl end group was copolymerized with acrylamide, the incorporation rate was much slower under the same copolymerization condition as shown in Figure 5.3. The conversion reached 90% in 1 hour for macromonomer with styrenic end group compared to 24% for that with allyl end group in 1 h. These results indicate that their reactivities are essentially determined by the chemical nature of their terminal copolymerizing groups as observed by Tsukahara et al. and Gnanou et al. (Tsukahara et al., 1987. Gnanou et al., 1989.). The difference in the macromonomer reactivities may be attributed to two major reasons: 1) the chemical nature of end group (styrenic or ally end group) - the styrenic end group is more reactive than ally end group; 2) the micelle formation due to hydrophobic styrenic end group in water solution, which has been observed by Ito et al. in micellar polymerization of poly (ethylene oxide) macromonomers in water (Ito et al., 1991.). These results suggested that the macromonomer reactivity was determined by the unsaturated end functional group.

The effect of cationic macromonomer content on the polymerization rate was also investigated by comparing acrylamide homopolymerization to its copolymerization with

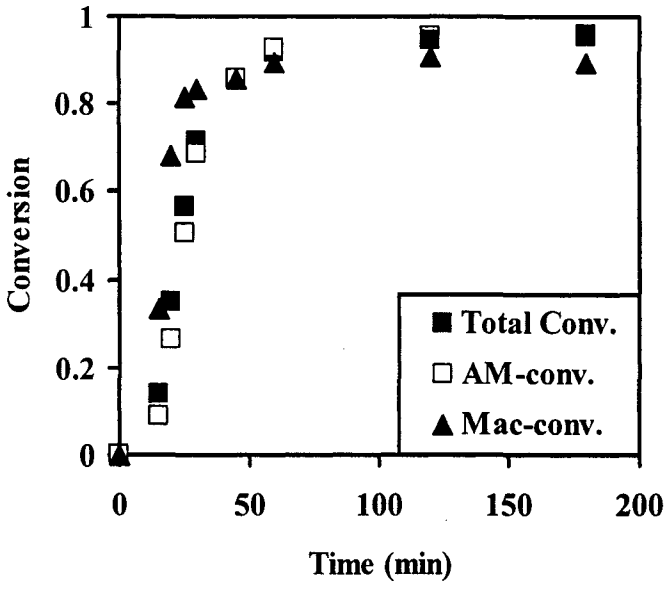


Figure 5.2 Monomer conversion vs time in 10% (weight) aqueous solution for macromonomer with styrenic end group at 50 °C: $[AM]_0$ = 1.13 mol/L, [PDMAEMA-DMS]$_0$ = 0.071 mmol/L, $[AIBA]_0$ = 1.85 mmol/L

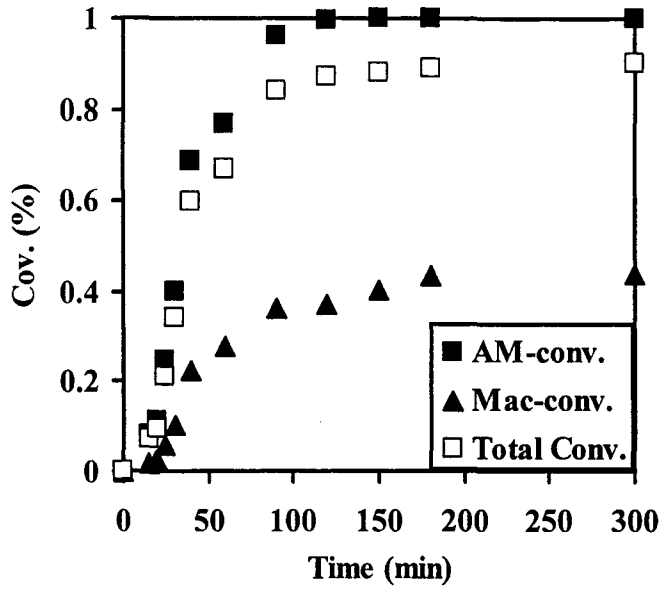


Figure 5.3 Monomer conversion vs time in 10% (weight) aqueous solution for macromonomer with allyl end group at 50 °C: $[AM]_0$ = 1.13 mol/L, $[PDMAEMA\text{-}DMS]_0$ = 0.142 mmol/L, $[AIBA]_0$ = 1.85 mmol/L

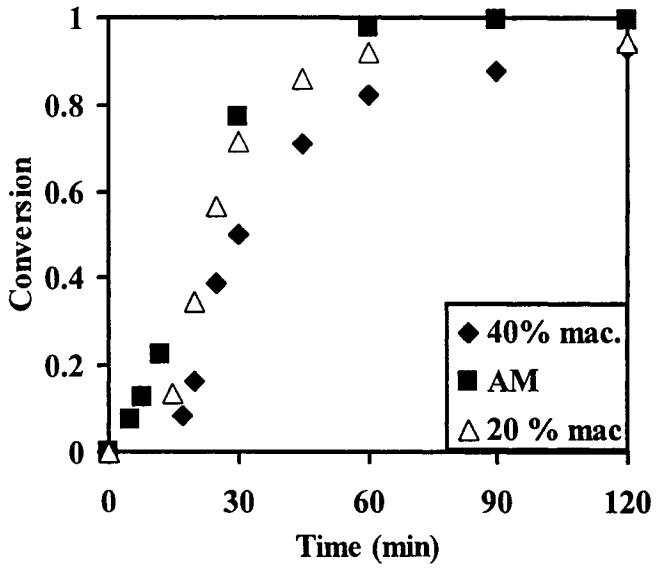
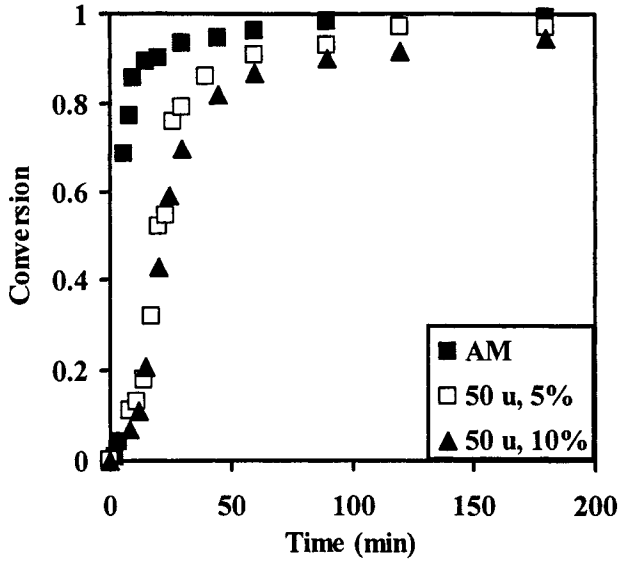
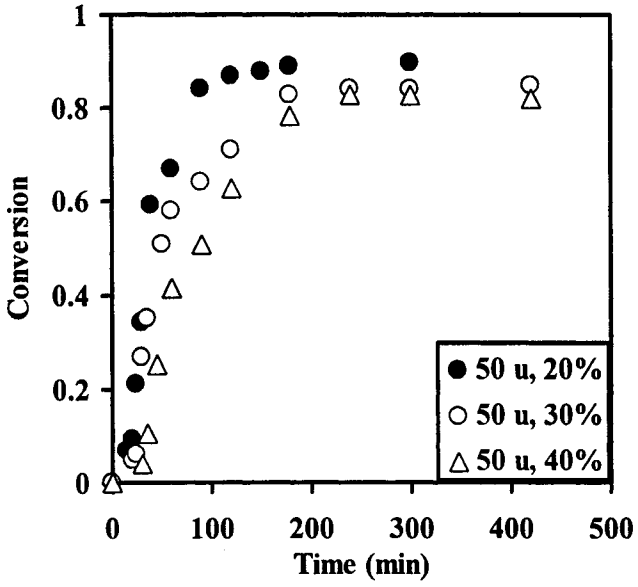


Figure 5.4 Total conversion vs time for different PDMAEMA-DMS with styrenic end group contents in 10% (weight) aqueous solution at 50 °C:

(■) f_{10} = 1.0, (Δ) f_{10} = 0.8, (♦) f_{10} = 0.6



(a)



(b)

Figure 5.5 Total conversion vs. time for different contents of PDMAEMA-DMS with ally end group in 10% (weight) aqueous solution at 50 °C: (■) $f_{10} = 1.0$, (❑) $f_{10} = 0.95$, (▲) $f_{10} = 0.9$, (●) $f_{10} = 0.80$, (○) $f_{10} = 0.70$, (Δ) $f_{10} = 0.60$.

macromonomer at different compositions. Figures 5.4 and 5.5 (a, b) show the total conversions of acrylamide copolymerization with PDMAEMA-DMS macromonomers in aqueous solution at 50 °C. As the macromonomer content increased, the total polymerization rate decreased. This reduction in rate was caused by lower molar monomer concentration at higher macromonomer content in the reactor (due to high molecular weight of the macromonomer) and the lower reactivity for ally-containing macromonomer.

The accumulation composition curve shows that the cationic macromonomer composition decreased with the total conversion increase for the macromonomer with styrenic end group macromonomer (Figure 5.6), while the cationic macromonomer composition increased with the total conversion increase for the macromonomer with allyl end group (Figure 5.7). For the copolymerization of macromonomer with allyl end group, the macromonomer incorporation was slow compared with acrylamide. With conversion increase, the macromonomer incorporation increased. In contrast to the macromonomer with allyl end group, the macromonomer with styrenic end group incorporation was much better (Figure 5.6).

5.3.3 Reactivity of PDMAEMA-DMS Macromonomer Towards Acrylamide.

The copolymerization of macromonomer with comonomer is governed by the general rules of copolymerization. The relative incorporation ability of the two polymerizable species is determined by the reactivity ratio r. Let us denote the comonomer, acrylamide, as M_1 and the macromonomer, polyDMAEMA-DMS macromonomer, as M_2. The well-known Mayo-Lewis equation for instantaneous composition applies to the copolymer formed (Mayo et al., 1944.):

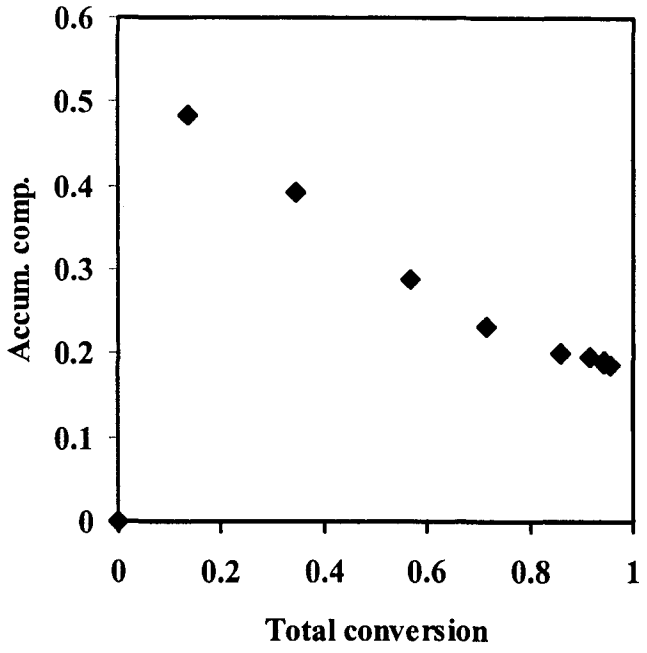


Figure 5.6 The accumulation composition vs total monomer conversion for PDMAEMA-DMS with styrenic end group copolymerization in 10% (weight) aqueous solution at 50 °C: $[AM]_0$ = 1.13 mol/L, $[PDMAEMA\text{-}DMS]_0$ = 0.071 mmol/L, $[AIBA]_0$ = 1.85 mmol/L

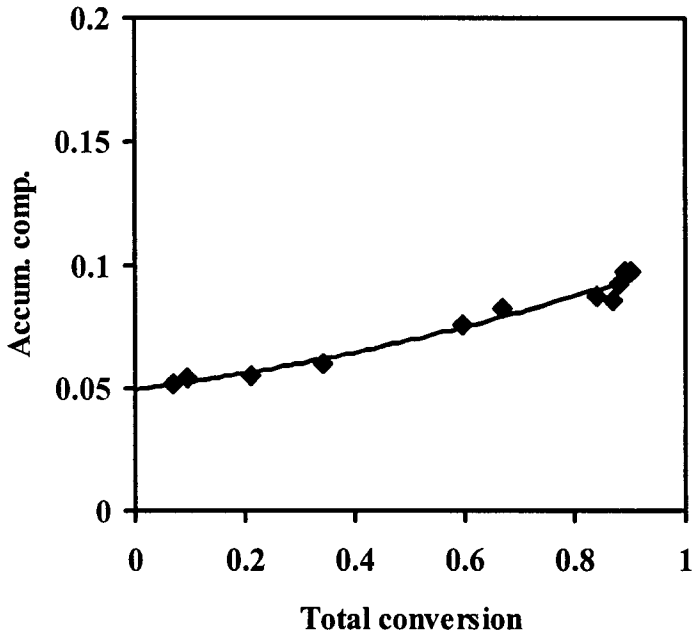


Figure 5.7 The accumulation composition vs total monomer conversion 10% (weight) aqueous solution at 50 °C: $[AM]_0$ = 1.13 mol/L, $[PDMAEMA\text{-}DMS]_0$ = 0.142 mmol/L, $[AIBA]_0$ = 1.85 mmol/L

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]} \tag{5.1}$$

where M_1 is acrylamide and M_2 is the polyDMAEMA-DMS macromonomer. The reactivity ratio of acrylamide is defined as $r_1 = k_{p11}/k_{p12}$. The rate constants are illustrated with the following reactions:

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{p11}} \sim\sim M_1^{\bullet} \tag{5.2}$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{p12}} \sim\sim M_2^{\bullet} \tag{5.3}$$

Because of the high molecular weight of polyDMAEMA-DMS macromonomer (with chain length of 30-100 units of DMAEMA), the molar concentration of the macromonomer is very low, i.e. $[M_2]/[M_1] << 1$. Eq. (5.3) can be reduced to the simple form:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \tag{5.4}$$

This equation can be used to estimate r_1. The reciprocal of r_1 ($1/r_1 = k_{12}/k_{11}$) is a measure of the macromonomer reactivity towards acrylamide radical. The parameter r_2 can not be estimated due to the extremely low macromonomer concentration.

Assume negligible drifting in copolymer composition at low monomer conversions (<25%), and instantaneous composition approximately equal to the

composition in accumulated copolymers. Under these conditions, Eq (5.4) can be simplified to (Kennedy et al., 1982.):

$$r_1 = \frac{\ln(1-X_1)}{\ln(1-X_2)} \tag{5.5}$$

where X_1 and X_2 are the conversions of acrylamide and polyDMAEMA-DMS macromonomer, respectively. Figures 5.8-5.10 show the plots of $\ln(1-X_1)$ versus $\ln(1-X_2)$ for macromonomer with ally unsaturated end group. The r_1 for polyDMAEMA-DMS of chain length 100 is 5.38. The $\ln(1-X_1)$ verse $\ln(1-X_2)$ plot is presented in Figure 5.11 for the macromonomer with styrenic unsaturated end group. The r_1 for polyDMAEMA-DMS of chain length 100 is 0.127. The reactivity ratios were summarized in Table 5.2. For the macromonomers with allyl end group, the reactivity ratios ($1/r_1$) are 0.186-0.192. However, the reactivity was much higher for the macromonomer with styrenic end group ($1/r_1$ = 7.87) in water solution. This high reactivity may be attributed to two reasons. Firstly, styrenic group is more reactive than allyl group. The reactivity ratios for the copolymerization of acrylamide (M_1) and styrene (M_2) are r_1 = 0.2 ($1/r_1$ = 5) and r_2= 1.05 (Chung, 1970.). Secondly, the unusual high reactivity of the styrenic-terminated macromonomer may also be due to the formation of micelles. The hydrophobic styrenic group aggregates in water solution. The high styrenic concentration inside the micelles facilitates a rapid polymerization of the macromonomer.

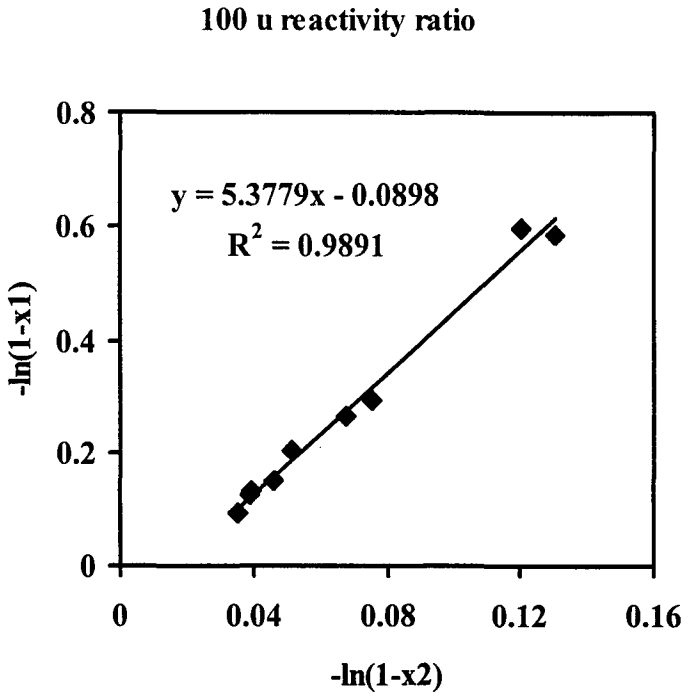


Figure 5.8 Reactivity ratio estimation for acrylamide with 100-unit polyDMAEMA-DMS macromonomer with allyl end group in aqueous solution polymerization at 50 °C

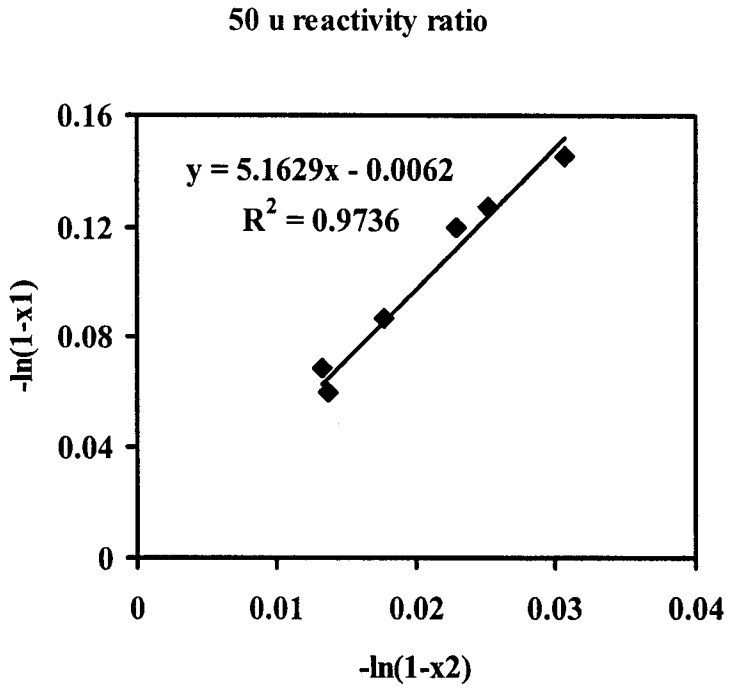


Figure 5.9 Reactivity ratio estimation for acrylamide with 50-unit polyDMAEMA-DMS macromonomer with allyl end group in aqueous solution polymerization at 50 °C

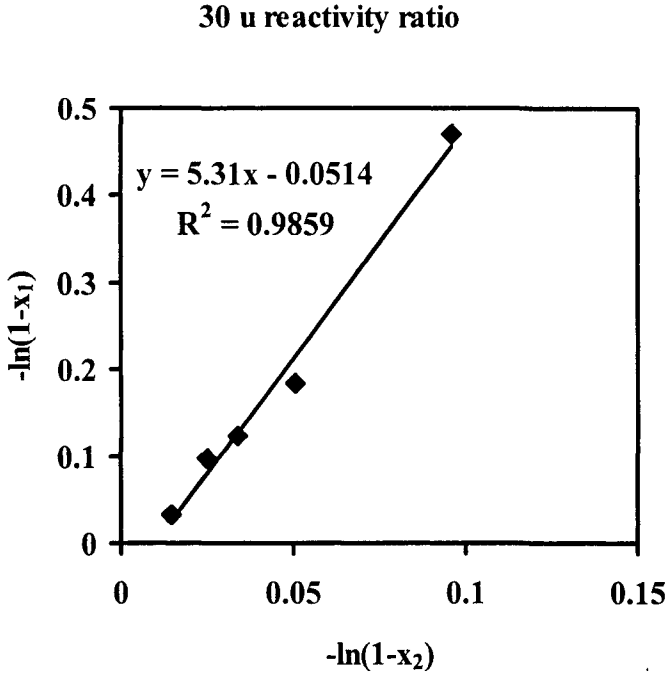


Figure 5.10. Reactivity ratio estimation for acrylamide with 30-unit polyDMAEMA-DMS macromonomer with allyl end group in aqueous solution polymerization at 50 °C

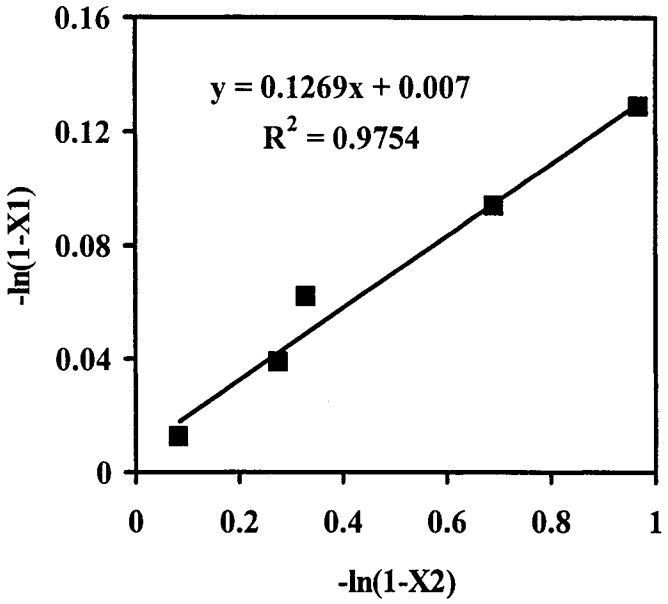
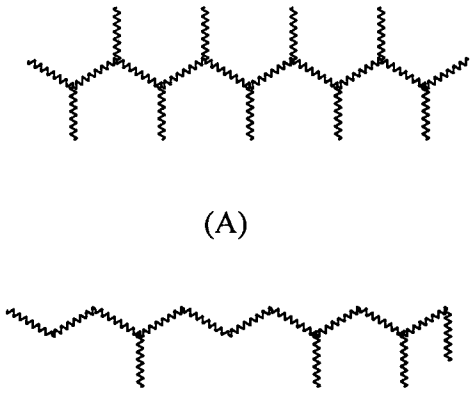


Figure 5.11. Reactivity ratio estimation for acrylamide with 100-unit polyDMAEMA-DMS macromonomer with styrenic end group in aqueous solution polymerization at 50 °C

Table 5.2 Values of r_1 estimated from low conversion data

Macromer	End group	Chain length	Reactivity ratio r_1	IR* $1/r_1$
PDMAEMA-A-100	Allyl	100	5.38	0.186
PDMAEMA-A-50	Allyl	50	5.16	0.194
PDMAEMA-A-30	Allyl	30	5.31	0.188
PDMAEMA-V-100	Vinylbenzyl	100	0.127	7.874

* Inverse reactivity ratio



(A)

(B)

Figure 5.12. Graft copolymers: (A) homogeneous graft copolymer; (B) heterogeneously graft copolymer

The graft copolymers produced in the batch processes are heterogeneous in terms of the distribution of grafts along polymer backbones as shown in Figure 5.12(b) due to the incompatible reactivities between macromonomer and its comonomer. The semi-batch method may offer a better approach for synthesizing the homogeneous graft copolymers (Ito et al., 1991.).

5.3.4. Semi-batch Copolymerization of Acrylamide with polyDMAEMA-DMS Macromonomer

For a comonomer system having a large difference in reactivities, there exists a severe drifting in the copolymer composition during copolymerization. The more reactive monomer molecules are preferably incorporated into polymer chains. The chains produced at the early stage are mainly composed of this type of monomeric units, while those produced later contain more slow monomers. The copolymer composition changes significantly with conversion, as shown in Figure 5.6-5.7. In the batch copolymerization of acrylamide with polyDMAEMA-DMS macromonomer with styrenic or allyl group, the copolymer products are very heterogeneous in terms of copolymer composition.

Semi-batch technologies have been widely used for controlling copolymer composition (Hernandez-Barajas et al., 1997. Hamielec et al., 1983). A semi-batch process was also applied in this work to optimize the macromonomer incorporation during copolymerization. Two feeding strategies were developed. In the first method, all the slow monomer was fed to the reactor first. The fast monomer mixed with the initiator was fed to the reactor by a pump in a linear decreasing manner. In the second method, all

the slow monomer and a part of the fast monomer were initially added to the reactor to provide a desired comonomer ratio (N_{10}/N_{20}). The other part of the fast monomer was subsequently fed to the reactor at a constant flow rate. The polyDMAEMA-DMS macromonomer with styrenic end group was selected for semi-batch process investigation.

For the first method, 0.8 g of acrylamide in 5% aqueous solution was charged to the reactor. The polyDMAEMA-DMS macromonomer (0.2 g) and initiator (10 mg) were fed to the reactor at a flow rate linearly decreasing from 0.075 mL/min to 0 within 2 h. Figure 5.13 shows the total conversion and accumulative composition. The results indicate that the polyDMAEMA-DMS macromonomer content in the copolymer increased with the total conversion. For the second method, 0.8 g of acrylamide and 40 mg of polyDMAEMA-DMS macromonomer (it accounts for 20% of the total polyDMAEMA-DMS used in this experiment), 3 mg of AIBA (30% of the total AIBA) in 5% aqueous solution were initially charged to the reactor. The rest macromonomer and initiator in 5% aqueous solution was fed to the reactor at a constant flow rate in 2 h. Figure 5.14 shows the polyDMAEMA-DMS content in the copolymer remained constant during the whole process of polymerization.

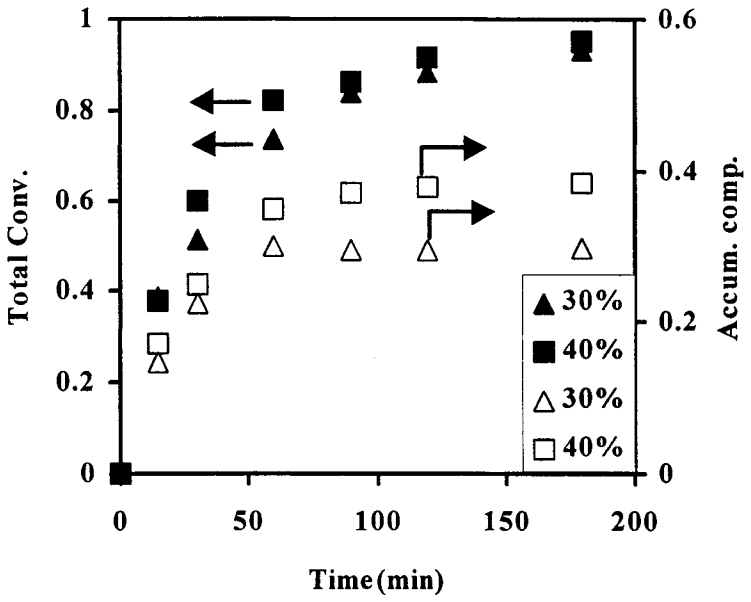


Figure 5.13. Total conversion and accumulative composition versus time for the semi-batch copolymerization of acrylamide with polyDMAEMA-DMS macromonomer in aqueous solution at 50 °C. Feeding policy: 0.8 g of acrylamide in 5% aqueous was initially charged to reactor; the macromonomer with initiator (0.2 g of polyDMAEMA-DMS and 10 mg of AIBA) in 5% solution was fed in a linearly decreasing mode from 0.075 mL/min to 0 mL/min in 2 h.

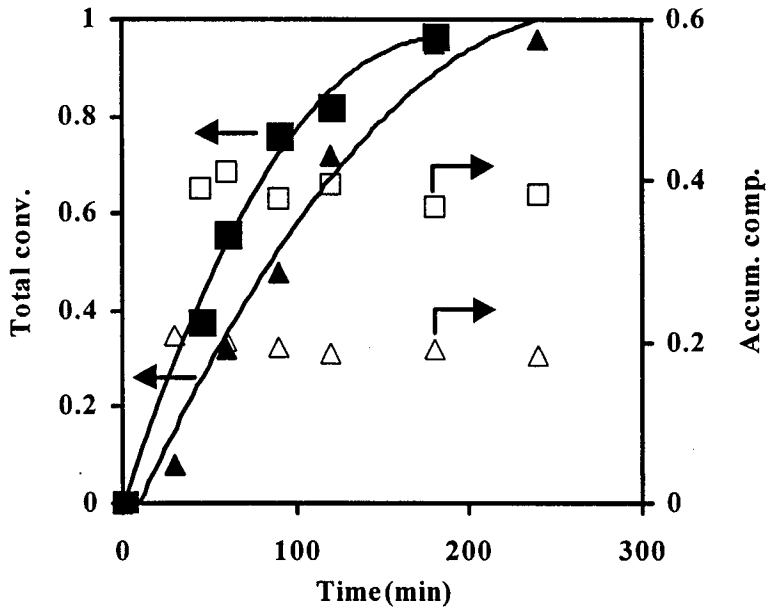


Figure 5.14. Total conversion and accumulative composition versus time for the semi-batch copolymerization of acrylamide with polyDMAEMA-DMS macromonomer in aqueous solution at 50 °C. Feeding policy: 0.8 g of acrylamide, 0.04 g of polyDMAEMA and 3 mg of AIBA in 5% aqueous was initially charged to reactor; the macromonomer with initiator (0.16 g polyDMAEMA-DMS, 7 mg of AIBA) was fed at a constant rate for 2 h.

5.4 Conclusion

Well-defined polyDMAEMA macromonomers with allyl end group and those with styrenic end group were synthesized by ATRP process and living nitro-anionic polymerization method, respectively. The corresponding cationic polyDMAEMA-DMS macromonomers were prepared by reacting polyDMAEMA with dimethylsulfate. The copolymerization results of acrylamide with polyDMAEMA-DMS showed that the incorporation of macromonomer with styrenic end group to polyacrylamide backbone was faster than that of macromonomer with allyl end group. The cationic macromonomer with styrenic end group had much higher reactivity than acrylamide (r_1 = 0.127). However, the macromonomer with ally end group had lower reactivity than acrylamide (r_1 = 5.16-5.36 for DMAEMA chain length 30-100). The batch copolymerization processes experienced severe drifting in copolymer composition and yielded heterogeneous graft copolymers. Two semi-batch policies were used to control the chemical composition. With all acrylamide and a part of polyDMAEMA-DMS macromonomer initially charged to the reactor, a constant feeding rate of the rest macromonomer yielded the copolymer products having homogeneous composition.

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Chapter 6

Summary of the Thesis

6.1 Conclusion

Well-defined comb-branched cationic polyelectrolytes have been synthesized via macromonomer copolymerization processes. The semi-batch technique was applied to control copolymer chemical composition and chain microstructure. The challenge for this work is to synthesize cationic macromonomers with controlled molecular weight and narrow polydispersity and to control the cationic macromonomer incorporation to polyacrylamide backbone.

1) We first proposed to use polymer network of PEGDMA combined with ESR technique to investigate the radical mechanisms involved in ATRP. The radicals were trapped in polymer network with the increase in monomer conversion due to diffusion controlled radical deactivation. This led to a dramatic increase in the radical concentration. The radical intermediates in ATRP were directly observed by the first time confirming its radical mechanisms.
2) The initiation method (initiator bearing unsaturation moiety) was used to synthesize polyDMAEMA macromonomers. The initiators with allyl or vinyl unsaturation group were screened for the synthesis of macromonomer via ATRP. The

multidentate amine ligands were also evaluated for this system. A new ligand, BA_6-TREN with high solubility in organic solvent, was synthesized and applied to macromonomer synthesis of polyDMAEMA. The cationic macromonomers with allyl end group were prepared by reacting the polyDMAEMA macromonomer with dimethyl sulfate in acetone solution at ambient temperature. The ATRP initiation method was applied to synthesize polyDMAEMA macromonomer with ally end group, which had relatively low reactivity.

3) In order to synthesize polyDMAEMA macromonomers with styrenic end group, a novel nitro-anionic capping method was developed. Vinyl or allyl amines were used as initiator and DMA or t-BMA was used as capping agents for the living nitro-anionic process. After capping, the initiator efficiencies reached 90% and the polymer polydispersities were less than 1.1.

4) Comb-branched polyelectrolytes having polyacrylamide (PAM) backbone and poly(dimethylaminoethylmathacrylate methylsulfate) (polyDMAEMA-DMS) side chains were prepared by free radical macromonomer copolymerization. Two series of cationic macromonomers with ally and styrenic end groups were used for the copolymerization with acrylamide in aqueous solution. The reactivity ratios were measured in batch process. The results showed that the inverse reactivity ($1/r_1$, M_1 is acrylamide and $1/r_1$ is a measure of macromonomer reactivity) for the styrenic-containing macromonomer of chain length 100 was 7.87. The reactivity ratios for the macromonomers with allyl end group and chain length 30-100 were 0.186-0.194.

The high reactivities of the styrenic-containing macromonomer were attributed to possible micelle formation.

6.2 Recommendations

This thesis has explored the approaches to synthesize macromonomers by living radical polymerization and living anionic polymerization as well as to synthesize comb-branched graft copolymers by batch and semi-batch processes. The preliminary testing results showed that the graft polyelectrolytes had improved performance in flocculation than their linear counterparts commercially available. Further developments should focus on the relationship between polymer chain structure and flocculation performance in application such papermaking. Future work is recommended as follows:

6.2.1 To establish the relationship between graft copolymer structure and their flocculation performance

There are four structural parameters of the graft copolymer that may affect the flocculation property, namely, the molecular weight of backbone, the molecular weight of grafts, the density of grafts, and the distribution of grafts along backbone. In order to relate the application performance to the polymer chain structural properties, comb-branched graft polyelectrolytes having well-controlled parameters need to be synthesized first. The thesis has shown that the molecular weight of grafts can be controlled by macromonomer molecular weight, the graft density can be controlled by feeding composition in copolymerization, and the graft distribution can be controlled by semi-

batch policies. High purity in both macromonomer and its comonomer is essential for obtaining high molecular weight graft copolymer. Therefore, a series of graft copolymer samples with controlled chain structure (parameters) can be synthesized and their corresponding flocculation properties can be tested. The relationship of the polymer chain structure and its flocculation property can thus be established.

6.2.2 To synthesize hydrophobic-hydrophilic graft copolymers and to explore their applications

Hydrophilic-hydrophobic graft copolymers have wide applications in industry. One of the applications is for painting and coating industries such as anti-setting agent or thickeners. For example, the graft copolymers with polyDMAEMA backbone and polyMMA branches will form physically crosslinked gels in water. The hydrophobic PMMA branches aggregate together to form the crosslinking points. These physically crosslinked points can be broken at high shear rate (when coating is applied), while at low shear rate they are to improve dripping properties of the coating or painting. This thixotropic property may lead copolymers to find many applications.

In this thesis, we have already developed the methods for synthesizing hydrophilic and hydrophobic macromonomers. Copolymerization of hydrophobic (or hydrophilic) macromonomer with hydrophilic (or hydrophobic) comonomers produces hydrophobic-hydrophilic graft copolymers. Subsequent developments may focus on synthesizing well-controlled graft copolymers.

APPENDIX A

Atom Transfer Radical Polymerization of 2-(Dimethylamino)ethyl Methacrylate in Aqueous Media

A 1 Introduction

Living radical polymerization mediated by metal complex, termed as atom transfer radical polymerization (ATRP), is a versatile method for various types of vinyl monomers.[1,2] ATRP is usually performed in bulk or in an organic solvent. Water is always the most preferable reaction media due to its environmental and cost advantages. Coca et al first reported the polymerization of 2-hydroxyethyl acrylate in aqueous media at 90 °C.[3] Recently, Ashford et al. reported the polymerization of sodium methacrylate using poly(ethylene oxide)-based macro-initiator in water solution at 90 °C.[4] Wang et al reported the monomethoxy-capped oligo(ethylene oxide) methacrylate and sodium 4-vinylbenzoate polymerization at ambient temperature.[5,6] However, the polymerization of aminoethyl methacrylate was not successful with poor control over molecular weight.[7] We are interested in the polymerization+ of 2-(dimethylamino)ethyl methacrylate (DMAEMA) because poly(DMAEMA) is an useful water-soluble and temperature-sensitive polymer. Poly(DMAEMA) has a lower critical solution temperature (LCST) around 50 °C.[8,9] DMAEMA has been polymerized via living anionic,[10] group transfer,[11] and ATRP [12-14] in various organic solvents, but ATRP of DMAEMA in aqueous media

remains to be a challenge.

In this appendix, we report an aqueous ATRP of DMAEMA using a CuBr-based catalyst system. The effects of ligand and initiator types on the polymerization behavior were examined.

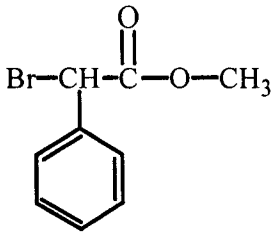
A 2 Experimental Section

A 2.1 Materials

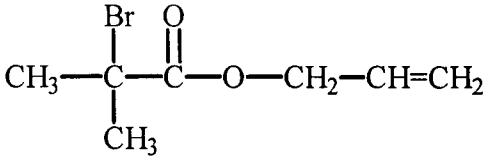
The catalyst: Cu(I)Br; the initiators: methyl α-bromophenylacetate (MBP), allyl 2-bromoisobutyrate (ABIB), ethyl 2-bromoisobutyrate (EBIB), α-bromo γ-butyrolactone (γ-BBL) and the ligands: 2,2'-bypyridine (Bpy), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) were provided by Aldrich and used without further purification. 2-Vinyloxyethyl 2-bromoisobutyrate (VBIB) was synthesized by our group.[14] 2-(Dimethylamino)ethyl methacrylate (DMAEMA) also from Aldrich was distilled from CaH_2 prior to use. Deuterium oxide (D_2O) (Cambridge Isotope Laboratories, Inc) and de-ionized water was used as the reaction solvent. The molecular structures of all the initiators and ligands used in this work are shown in Scheme A 1.

A 2.2. Polymerization

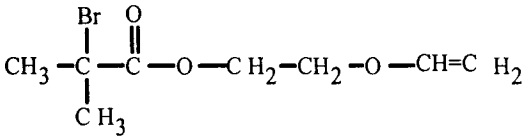
The ATRP polymerization of DMAEMA was carried out in deuterium oxide or de-ionized water solution by two methods. Method one: 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(1)Br, 19.87 mg (0.1272 mmol) of Bpy were first charged to a 10 ml glass ampoule. The ampoule reactor was sealed with



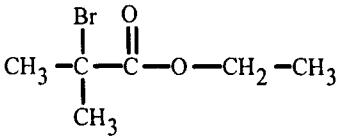
methyl bromophenyl acetate (MBP)



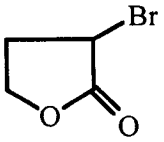
allyl 2-bromoisobutyrate (ABIB)



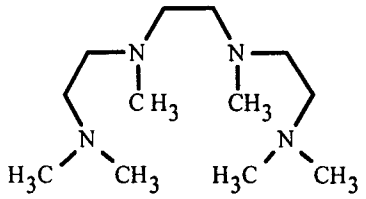
vinyl 2'-oxyethyl 2-bromoisobutyrate (VBIB)



ethyl 2-bromoisobutyrate (EBIB)

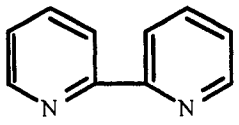


a-bromo r-butyrolactone(r-BBL)



1,1,4,7,10,10-hexamethyltriethylenetetram

(HMTETA)



2,2'-bipyridine (Bpy)

Scheme A1 Molecular structures of initiators and ligands.

rubber septum. The mixture was allowed to react for ten minutes under nitrogen protection, then 1g of D_2O was added and degassed for another ten minutes. 10.0 μl (0.0636 mmol) of degassed MBP was added to the reactor by a microsyringe. The ampoule was then immersed into a 20 °C water bath. Method two: 1 g (6.36 mmol) of DMAEMA, 9.14 mg (0.0636 mmol) of Cu(1)Br, 19.87 mg (0.1272 mmol) of Bpy and 1 g of D_2O were charged to a 10 ml glass ampoule. The ampoule reactor was sealed with rubber septum and degassed for ten minutes under nitrogen. Sampling was done by a degassed syringe in time intervals. The polymerization was terminated by adding the sampled polymer mixture to a 0.1 ml of $CuBr_2$ deuterium oxide solution. Conversion was determined by ^1H NMR. Molecular weight and molecular weight distribution of the polymer were measured by GPC using THF containing 2% triethylamine (v/v) as eluent and polystyrene standards were used to generate the calibration curve.

A 3 Results and Discussion

A3.1 Effects of Solvent, Initiator and Ligand on ATRP Polymerization of DMAEMA

CuBr combined with multidentate amines was proven to be a good catalyst system for the ATRP of DMAEMA in organic solvents such as dichlorobenzene or THF.[12-14] However, the polymerization in high polar solvents such as ethylene glycol had the lack of control.[13] The molecular weight distributions of the resulting poly(DMAEMA) were broad (Mw/Mn ≅ 1.6). Further studies indicated that the DMAEMA ATRP could also be

carried out in aqueous media and the initiator, ligand and catalyst preparation strongly affected the polymerization. Table A1 summarizes the results for the ATRP of DMAEMA in water catalyzed by CuBr-Bpy or CuBr-HMTETA with various initiators.

The initiator type was found to be the most important factor for the DMAEMA ATRP. Catalyzed by CuBr-Bpy, MBP initiated a living polymerization of DMAEMA in water producing polymers with controlled molecular weight and very low polydispersities, while others such as bromoisobutyrate and α-bromo r-butyrolactone yielded polymers with broad molecular weight distributions. We found that all the initiators dissolved quickly once they were added to the DMAEMA/H_2O mixture (1/1, w/w). Therefore, this difference was not resulted from the initiator solubility.

The ligand type also affected the aqueous ATRP of DMAEMA. When HMTETA was used, DMAEMA polymerization was very rapid but poorly controlled, producing polymers with moleulcar weight much higher than predicted and high polydispersity, as shown in Runs 7 and 8 in Table A1. When Bpy was used as ligand with MBP as initiator, the polymerization rate was relatively slow, but well-controlled as seen in Runs 1 and 2 in Table A1. The molecular weight of PDMAEMA was agreeable with the predicted and the polydispersity of the polymer was about 1.20.

The procedure of the catalyst preparation also had influence on the polymerization rate and molecular weight development. When CuBr, Bpy and DMAEMA were mixed first under nitrogen prior to water addition (Method One), the polymerization proceeded smoothly and the resulting polymers had pre-defined molecular weight and narrow molecular weight distribution. However, if water were added with CuBr, Bpy and

Table A1 Effects of initiator type and ligand type on aqueous ATRP of DMAEMA at 20°C

Run	Initiator	Ligand	Time (h)	Conv. (%)	$M_{n,cal}$	$M_{n,SEC}$	$M_{w,SEC}/M_{n,SEC}$	$f = M_{n,cal}/M_{n,SEC}$
1[a]	MBP	BPY	0.5	32.6	5130	5340	1.12	0.96
2[a]	MBP	BPY	2	84.5	13000	12800	1.21	1
3[a]	ABIB	BPY	0.5	91.1	14330	16300	1.77	0.87
4[a]	VBIB	BPY	0.5	95.2	14900	19100	2.10	0.78
5[a]	EBIB	BPY	0.5	88.2	13860	15900	1.71	0.87
6[a]	r-BBL	BPY	0.5	81.3	12800	59700	2.09	0.21
7[a]	MBP	HMTETA	0.5	53.28	8370	12680	1.46	0.66
8[a]	MBP	HMTETA	2.0	84.5	13280	18400	1.50	0.72
9[a]	ABIB	HMTETA	0.5	92.70	14570	17900	1.66	0.81
10[a]	VBIB	HMTETA	0.5	94.5	14850	18500	2.18	0.80
11[a]	EBIB	HMTETA	0.5	94.8	14900	17180	1.95	0.86
12[a]	r-BBL	HMTETA	0.5	90.3	14190	28000	1.74	0.51
13[b]	MBP	BPY	1.0	89.1	14000	21300	1.46	0.66

DMAEMA/initiator/CuBr/ligand = 100:1:1:2(for Bpy)/100:1:1:1(for HMTETA) in mole.

DMAEMA/water = 1:1(w/w)

f - initiator efficiency

a - The catalyst was prepared in method one.

b - The catalyst was prepared in method two.

DMAEMA at the same time using Method two, the polymerization solution was very rapid and the polymers had high molecular weight and broad molecular weight distribution (Mw/Mn>1.5) (Table A1, run 13).

The effects of initiator, ligand and catalyst preparation on the controllability of the polymerization may result from the different reaction rate. The lower critical solution temperature (LCST) of DMAEMA monomer is very low (ca. 36 °C).[8,9] Therefore, it is very sensitive to temperature change. If the polymerization is fast, the polymerization heat released will raise the solution temperature to a level higher than the LCST of DMAEMA and thus DMAEMA separates from the solution. We observed that the polymerization media was clear only for CuBr/Bpy/MBP system, while others were cloudy, suggesting that there was a phase separation. This heterogeneity may result in poor control in the polymerization.

A 3.2 Kinetics of ATRP of DMAEMA in Aqueous Media

All the aqueous ATRPs of DMAEMA were carried out in 50% (w/w) of water solution. Figure A1 shows DMAEMA polymerization at 20 and 30 °C with MBP/CuBr/Bpy (1:1:2 in mole). The polymerization reached 90% conversion in 1h at 30 °C. However the reaction was much slower at 20 °C. It took 6 h to reach 90% conversion. The linear plots of $\ln([M]_0/[M])$ versus time suggests a first-order kinetics with a constant concentration of growing radicals. Lowering the catalyst concentration to half (DMAEMA:MBP:CuBr:Bpy = 100:1:0.5:1 in mole) slightly decreased the

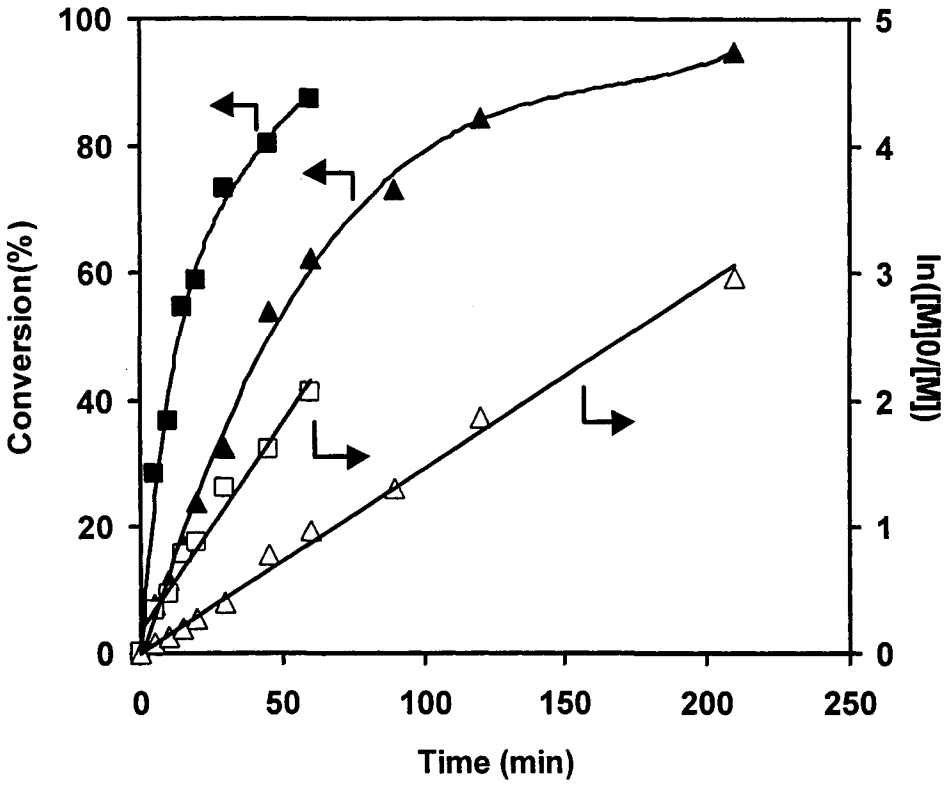


Figure A1. The aqueous ATRP of DMAEMA catalyzed by CuBr-Bpy at 20 and 30 °C. $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0$ = 100:1:1:2 in mole, DMAEMA/D_2O = 1:1 (w/w). Temperature: 20 °C (■, □), 30 °C (▲, Δ).

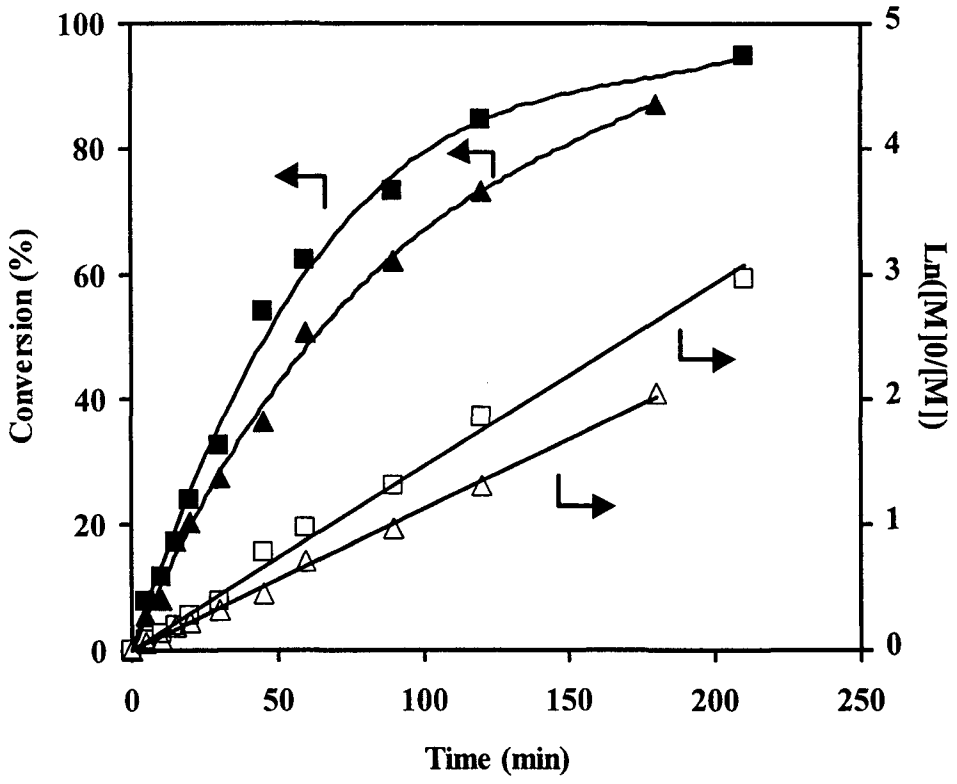


Figure A2. The aqueous ATRP of DMAEMA catalyzed by CuBr-Bpy at 20 °C at different catalyst concentration. $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0 = 100:1:1:2$ (in mole) (■, □), $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0 = 100:1:0.5:1$ (in mole) (▲, Δ)

polymerization rate (Figure A2).

The GPC analysis showed that the number-average molecular weight increased linearly with the increase of monomer conversion for the polymers at 20, and 30 °C or at lower catalyst concentration (Figure A3). The polydispersities remained low, about 1.2-1.3, throughout the polymerization. These results demonstrated the living feature of the aqueous ATRP of DMAEMA catalysized by CuBr/Bpy with MBP initiator.

Figure A4 shows the DMAEMA polymerization at 20 ^{0}C in water with CuBr/HMTETA as catalyst. The polymerization was very fast at the early stage, but slowed down later. For example, the conversion reached 59% in first 30 minutes, but was only 84% in 2 hours. The kinetic plot showed a significant curvature, indicating significant radical termination in the first 25 minutes. Correspondingly, the molecular weights were much higher than their theoretical values and the molecular weight distributions were rather broad (2.2-2.4) as shown in Figure A5.

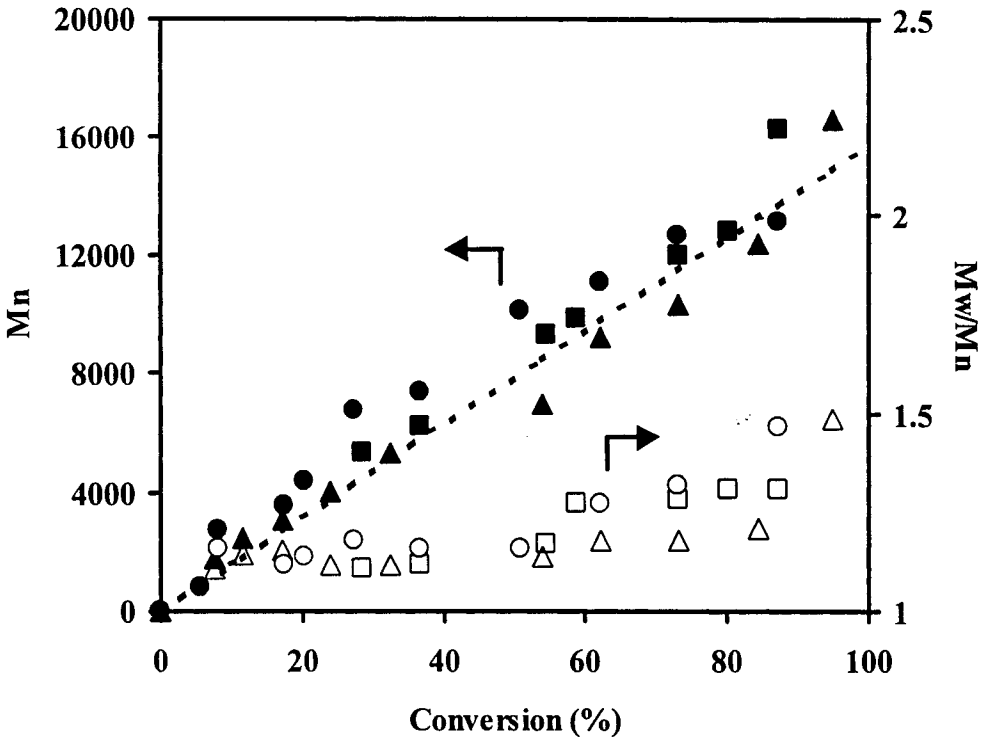


Figure A3. Molecular weight of poly(DMAEMA) as a function of conversion in aqueous ATRP of DMAEMA at: $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0 = 100:1:1:2$, DMAEMA/$D_2O$ = 1:1 (w/w) at 20 °C (■, □), 30 °C (▲, Δ), $DMAEMA]_0/[MBP]_0/[CuBr]_0/[Bpy]_0 = 100:1:0.5:1$, DMAEMA/$D_2O$ = 1:1 (w/w), 20 °C (●, O), calculating molecular weight (---).

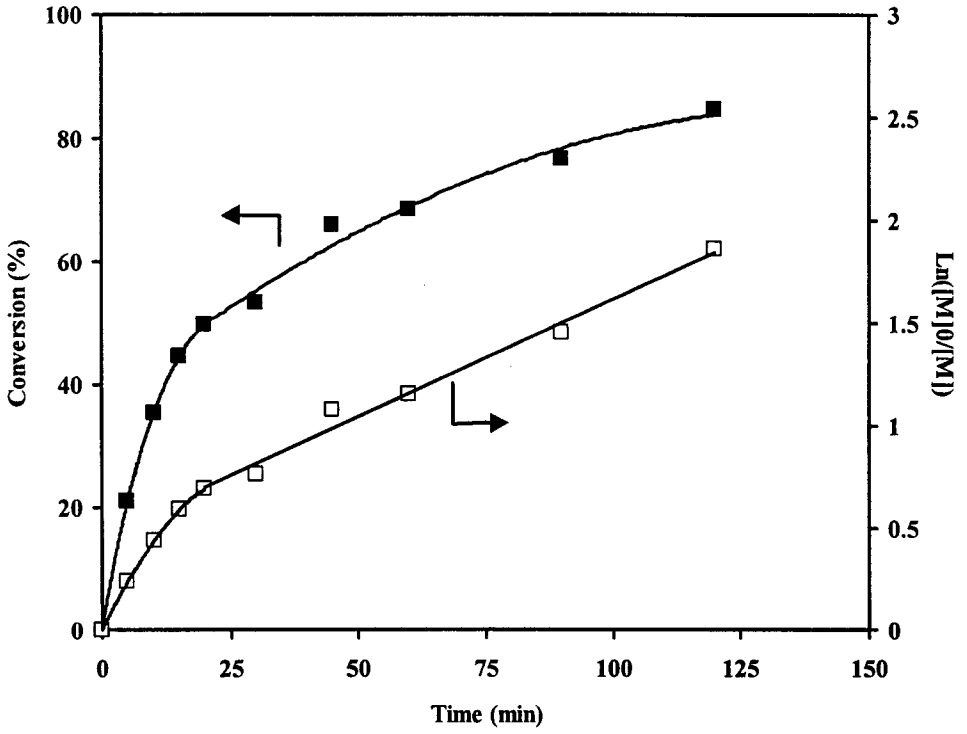


Figure A4. The aqueous ATRP of DMAEMA catalyzed by CuBr-HMTETA at 20 °C. $[DMAEMA]_0/[MBP]_0/[CuBr]_0/[HMTETA]_0 = 100:1:1:1$, $DMAEMA/D_2O = 1:1$ (w/w).

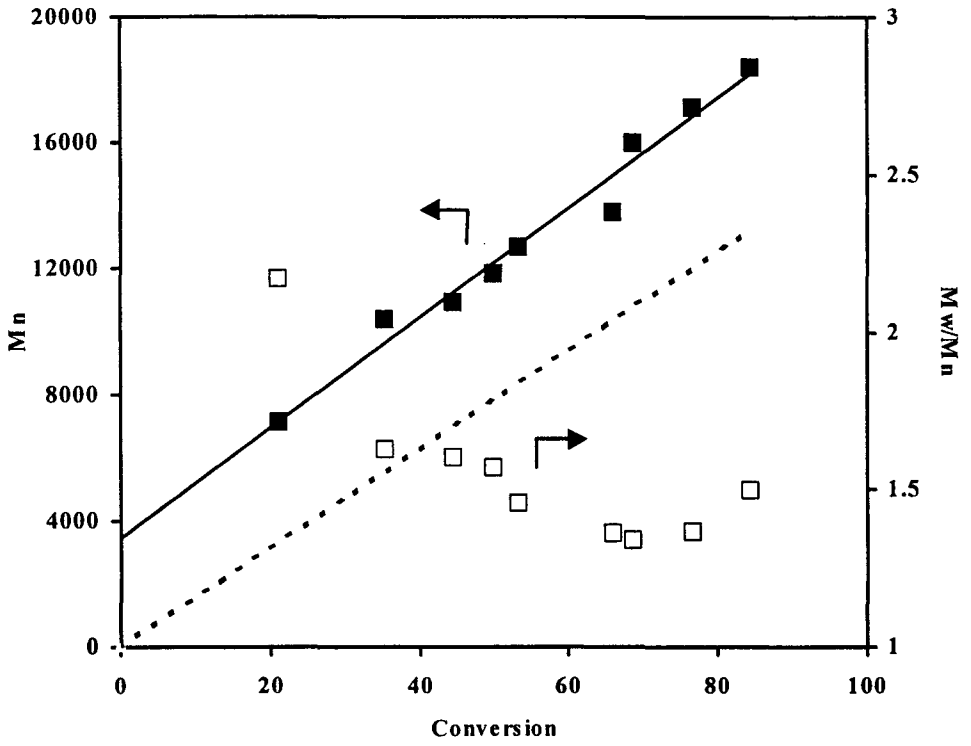


Figure A5. Molecular weight of poly(DMAEMA) as a function of conversion in aqueous ATRP of DMAEMA. See Figure 4 for conditions.

A 4. Conclusion

Various combinations of two ligands and five initiators were examined for the ATRP of DMAEMA in aqueous media catalyzed by CuBr. The types of ligand, initiator and catalyst, as well as the recipe preparation method, had strong effects on the polymerization. The living behavior was observed only with CuBr/Bpy as catalyst and MBP as initiator, indicated from the first-order kinetics and linear increase in the number-average molecular weight with monomer conversion. The molecular weight distribution of poly(DMAEMA) was narrow with its polydispersity about 1.20.

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APPENDIX B

Synthesis of Styrenic-Terminated Methacryalte Macromonomers by Nitroanion-Initiated Living Anionic Polymerization

B 1 Introduction

Macromonomer is a polymer chain that bears a reactive terminal unsaturated group. It is an important intermediate for constructing super-macromolecular structure such as comb-branched graft copolymers,[1)] and star-shaped copolymers.[2)] For example, well-defined comb-branched graft copolymers with controlled chain length and density of side chains were prepared by macromonomer copolymerization, in which the chain length and density of side chains were readily adjusted by varying the molecular weight and content of macromonomer.[1,3)] The homogeneity in the side chain distribution along backbone depends on the macromonomer reactivity relative to its comonomer. When the reactivities of macromonomer and its comonomer are comparable, the side chains are homogeneously distributed along the backbone of graft copolymer. The challenge in preparing a well-defined graft copolymer is to synthesize a macromonomer with unsaturated end group having proper reactivity.

Styrenic-terminated macromonomers can be copolymerized with various comonomers at good reactivities.[4,5)] These macromonomers were commonly synthesized

by the end capping method, where a living polymer chain is allowed to react with vinylbenzyl-containing terminating agent.[6-9] However, the drawback for this method is that usually not all chain ends can be capped.

The initiation method by living polymerization is preferred because it can guarantee that each polymer chain contains a targeted unsaturated group.[10-13] The styrenic-terminated macromonomers were usually not synthesized by the initiation method since the styrenic group could react with organometallic initiator in a living anionic polymerization and/or be consumed during the polymerization.[14] Oxyanion-initiated anionic polymerization was used to synthesize styrenic terminated polymethacrylate macromonomers for self-coordination monomers such as dimethylaminoethyl methacrylate, but oxyanion is not active enough to initiate non-self coordination monomers such as MMA.

Nitro-anion is active for the polymerization of various methacrylate monomers.[15,16] but does not react with unsaturated groups such as vinyloxyl and allyl group. The nitroanion-initiated polymerization has been therefore used to synthesize various macromonomers of methacrylates.[11,13] It was found that the control of polymer molecular weight (initiator efficiency) strongly depended on the substituents of the nitroanion. Nitroanions with less bulky substituents had low initiator efficiencies. An initiator capping step was required to enhance the initiator efficiency.[11,13] In this appendix, we report the direct synthesis of polymethacrylate macromonomers with terminal styrenic group using a nitroanion with bulky substituents.

B 2 Experimental Section

B 2.1 Materials

Methyl methacrylate (MMA, 98%), 2-(dimethylamino)ethyl metacrylate (DMAEMA, 98%), and tert-butyl methacrylate (tBMA, 99%) from Aldrich were stirred over calcium hydride for 24 h, vacuum-distilled over calcium hydride and stored under a nitrogen atmosphere at –20 °C. 4-Vinylbenzylaldehyde (85%), N-isopropylamine (99.5%), $NaBH_3CN$ (95%), potassium were obtained from Aldrich and used without further purification. Chloroform, methanol, ethyl ether were purchased from Aldrich. Secondary-butyllithium (sBuLi, 1.3 M in cyclohexane) was also purchased from Aldrich and its concentration was titrated by a standard method. Tetrahydrofuran (THF) was purified by refluxing over fresh potassium-benzophenone complex (a deep purple color indicating solvent free of oxygen and moisture) and distilled before use.

B 2.2 Synthesis of N-Isopropyl-4-Vinylbenzylamine (PVBA)

To a solution of 4-vinylbenzylaldehyde (8 g, 60.61 mmol) and two drops of acetic acid in 80 mL chloroform cooled in ice-water bath, isopropylamine (3.93 g, 66.66 mmol) was added dropwise. 4-Vinylbenzylaldehyde reacts with isopropylamine to yield N-isopropyl-4-vinylbenzylimine (PVBI). The mixture was magnetically stirred for 1 h at 0 ^{o}C and then 4 h at room temperature. The solution was dried by sodium sulfate. Sodium sulfate salt was filtrated and washed with 10 mL chloroform for three times. After chloroform was evaporated, the crude product was distilled under vacuum. Yield: 70% (7.33 g) with respect to 4-vinylbenzylaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): 1.24 ppm

(6H, m, =N-CH-($C\underline{H}_3$)$_2$), 3.51 ppm (1H, t, =N-C$\underline{H}$-(CH_3)$_2$), 5.28 ppm (1H, d, CH=C$\underline{H}_2$), 5.78 ppm (1H, d, CH=C$\underline{H}_2$), 6.74(1H, q, C$\underline{H}$=CH_2), 7.41 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$), 7.66 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$), 8.26 ppm (1H, s,2H, m, CH_2=CH-C_6H_4-C$\underline{H}$=N).

To a solution of PVBI (6 g, 34.68 mmol) in 30 mL of dried methanol, $NaBH_3CN$ (2.3 g) was added. The mixture was allowed to react for 6 h at room temperature. After methanol was removed, the crude was distilled under vacuum. Yield: 85% (5.20 g). ^{1}H NMR ($CDCl_3$, 200 MHz): 1.06 ppm (6H, m, NH-CH-($C\underline{H}_3$)$_2$), 1.40 ppm (1H, m, N$\underline{H}$-CH-(CH_3)$_2$), 2.81 ppm (1H, m, NH-C$\underline{H}$-(CH_3)$_2$), 3.74 ppm(2H, s, CH_2=CH-C_6H_4-C$\underline{H}_2$-NH), 5.18 ppm (1H, d, CH=C$\underline{H}_2$), 5.70 ppm (1H, d, CH=C$\underline{H}_2$), 6.67(1H, q, C$\underline{H}$=CH_2), 7.32 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$), 7.66 ppm (2H, m, CH_2=CH-$C_6\underline{H}_4$).

B 2.3 Preparation of Initiators and Polymerization

In a round bottom flask previously treated with chlorotrimethylsilane and flame dried, weighted LiCl was added and heated to 100 °C under vacuum and purged with nitrogen 5 times. THF (20mL) and required amount of PVBA were charged to the reactor with degassed syringe. The solution was cooled down to –78 °C in dry ice-acetone solution. A stoichiometric amount of s-butyllithium was added with stirring. After stirring half hour, the monomer was introduced. After 1 hr reaction, the polymerization was terminated by adding 0.5 mL methanol. The solution was poured into 300 mL of petroleum ether. The polymer was dried at room temperature under vacuum for 24 h.

B 2.4 Measurements

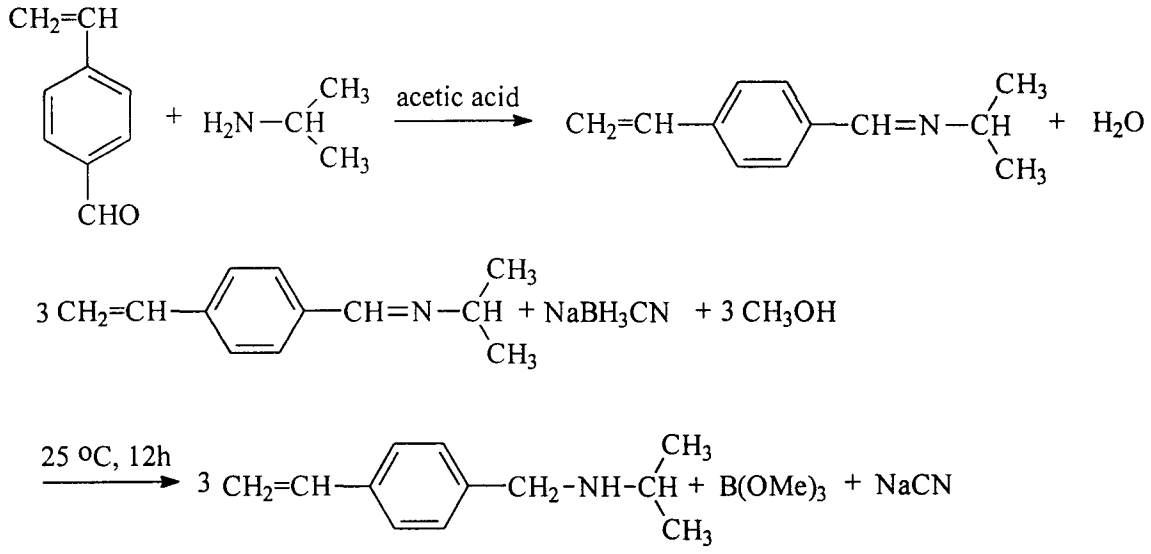
^1H NMR spectra were obtained on a Bruker AC-P200 Fourier transform spectrometer (200 MHz for ^1H) in $CDCl_3$ solvent. The chemical shifts were reported in ppm with signals of trace of $CHCl_3$ as internal standard. GPC measurements were carried out using a Waters 590 liquid chromatography equipped with three Varian MicroPak columns (G1000, 3000 and 7000HXL) with a 410 differential refractometer detector. THF with 2% triethylamine was used as solvent. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows based on Millenium 2.0 software package.

B3 Results and Discussion

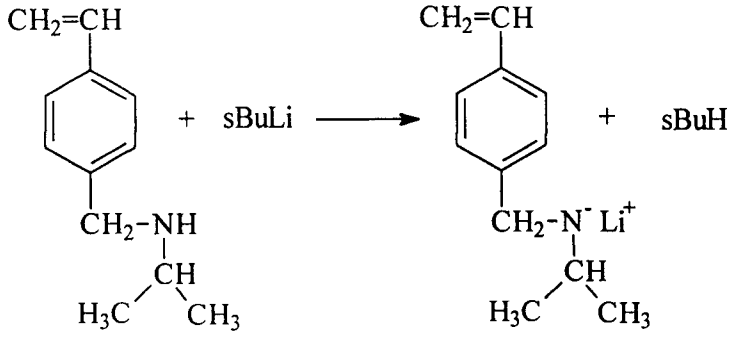
B3.1 Synthesis of N-Isopropyl-4-Vinylbenzylamide Initiators

Alkylamine reacts with butyllithium to yield lithium alkylamide, which initiates a living polymerization of methacrylates.[11,13] N-isopropyl-4-vinylbenzylamine (PVBA) was synthesized in this work for preparing macromonomers with styrenic moiety. Scheme B1 (a) shows the synthesis procedures. For synthesis of PVBA, the addition of acetic acid as catalyst is important for the system to have a high yield of PVBI.

The corresponding N-substituted amide initiator was prepared by reacting PVBA with an equal mole of sBuLi in THF at -78° C (Scheme B1(b)). After the addition of sBuLi, the solution turned to yellow-brown color from colorless which indicated the product of amide.



(a)



(b)

Scheme B1. Synthesis of N-isopropyl-4-vinylbenzylamine (a) and N-isopropyl-4-vinylbenzylamide (b)

B 3.2 Polymerization of MMA, *t*BMA and DMAEMA Initiated by LiPVBA

The polymerizations of MMA, tert-BMA, and DMAEMA initiated by the prepared initiator, lithium N-isopropyl-4-vinylbenzylamide (LiPVBA), are summarized in Table B1. The LiPVBA-initiated living polymerizations produced polymers with well-controlled molecular weight and narrow polydispersity in THF at -78 °C. The initiator efficiencies for all the monomers were generally higher than 90%. This is much higher than that of lithium diallyamide-initiated polymerizations, in which the initiator efficiencies for MMA and DMAEMA were about 25%. This suggests that the bulky isopropyl and vinylbenzyl groups on the nitroanion in LiPVBA greatly suppressed side reactions of the nitroanion with carbonyl groups, which consumed initiator molecules. The polymer polydispersities were less than 1.1 for the polymerizations with 3 fold of LiCl. Without LiCl, the polydispersities increased slightly, about 1.2. This suggests that the aggregation of LiPVBA in the solution was very weak due to the bulkiness of the substituents. The aggregation of nitroanion with less bulky substituents was much stronger and thus caused broad molecular weight distribution in the absence of LiCl.[11,13] The results demonstrate that LiPVBA is a versatile initiator for the living anionic polymerization of methacrylates.

B 3.3 Block Copolymerization of DMAEMA, MMA and tBMA

Block copolymers bearing terminal unsaturated group become block macromonomers. Amphiphilic block macromonomers are useful precursors for reactive dispersants, emulsifiers, microspheres, and coating materials.[17,18] Upon completing the

Table B1 Synthesis of macromonomers from MMA and tBMA initiated by LiPVBA complexed by three times of LiCl(mol) in THF at -78 °C

Entry	monomer	M/Amide	Conv.(%)	Mn,cal	$Mn_{,SEC}$	M_{NMR}	Mw/Mn	f[a]
1	MMA	30	100	3000	3100	2900	1.05	0.97
2	MMA	50	100	5000	5100	5050	1.06	0.98
3	MMA	75	100	7500	8000	8200	1.05	0.93
4	MMA	100	100	10000	10050	-	1.08	0.99
5	tBMA	25	100	3550	3600	-	1.07	0.98
6	DMAEMA	50	100	7850	8100	8000	1.06	0.97

a-f = $M_{n,cal}/M_{n,SEC}$

Table B2. Diblock Copolymerization of Different Methacrylate Pairs Initiated by LiPVBA Complexed with 3 equiv of LiCl (mol)

	first block					second block					
entry	monomer 1	Mn,cal	$Mn_{,SEC}$	Mw/Mn	f[a]	monomer 2	Mn,cal	$Mn_{,SEC}$	Mw/Mn	f[b]	comp.[c]
7	DMAEMA	3900	3800	1.03	0.97	MMA	6400	7400	1.06	0.86	50-50
8	DMAEMA	3140	3340	1.03	0.94	MMA	11,140	11,340	1.14	0.98	20-80
9	DMAEMA	3930	4200	1.03	0.93	tBMA	7400	8100	1.06	0.91	49-51
10	tBMA	3550	3600	1.07	0.98	MMA	5550	5400	1.09	1.0	55-45

Condition: THF solvent, -78 °C.

a- $f = M_{n,cal}/M_{n,SEC}$ for first block

b- $f = M_{n,cal}/M_{n,SEC}$

c- block copolymer composition measured by ^1H NMR

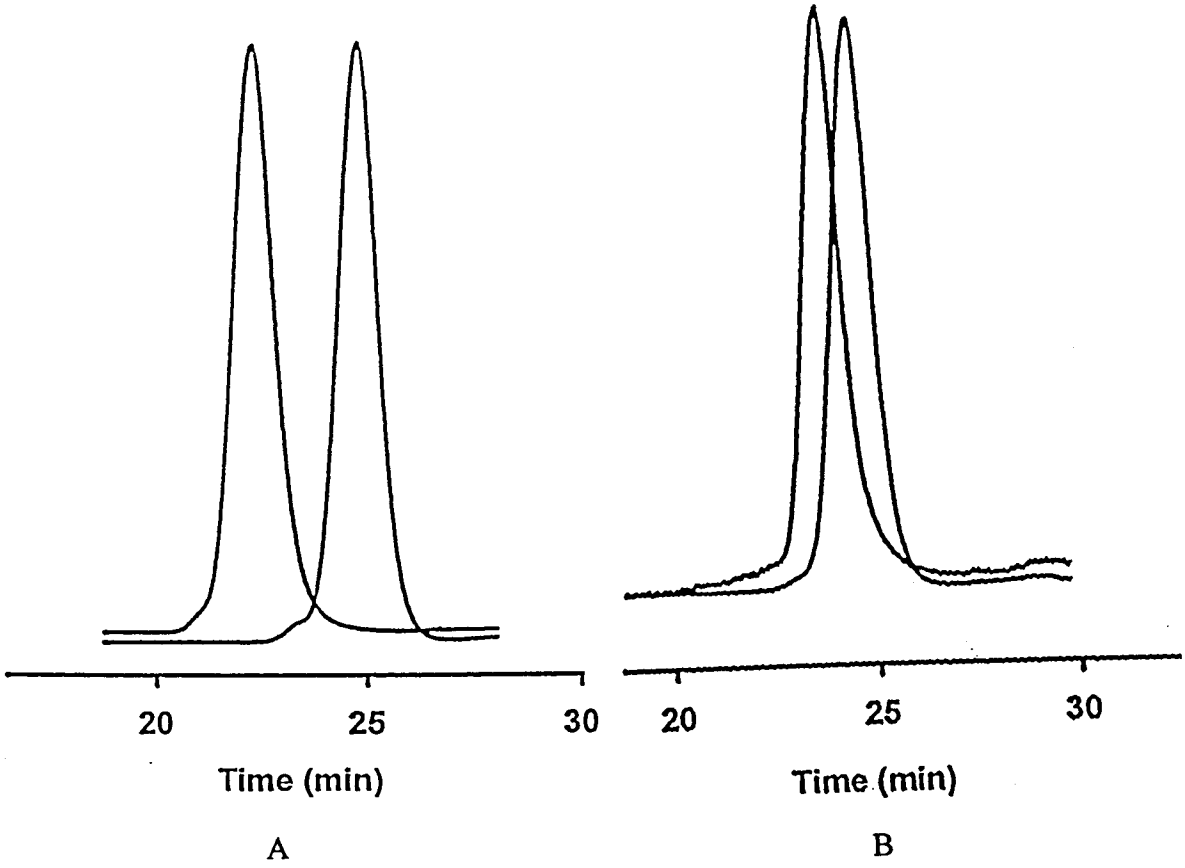
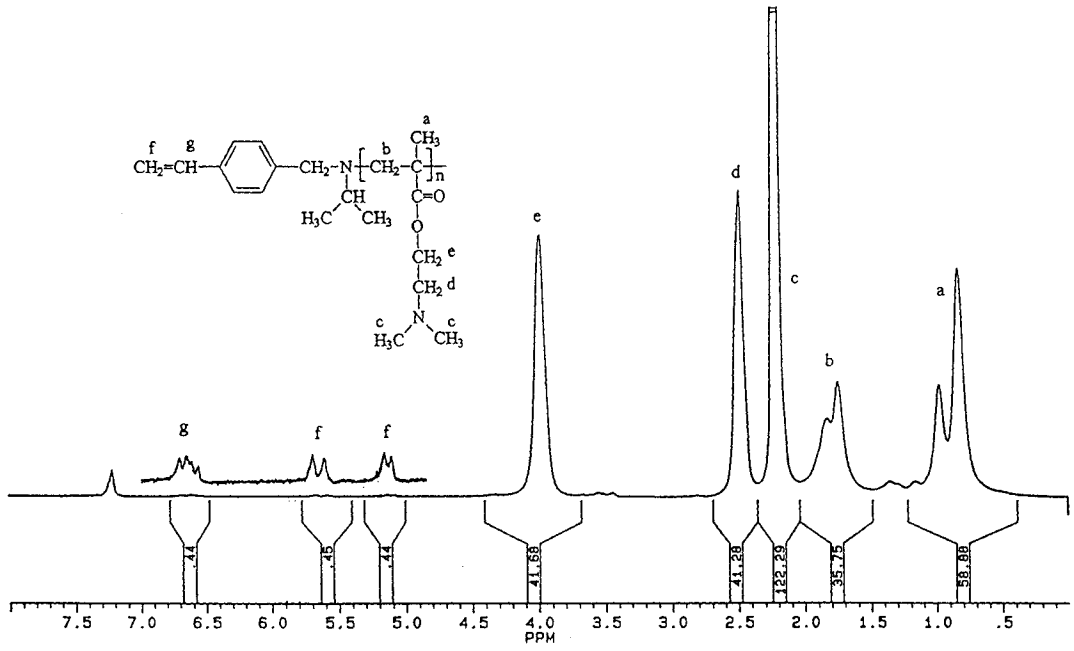


Figure B1. SEC traces for poly(DMAEMA-*block*-MMA) and poly(tBMA–*block*-MMA) synthesized by a two-step process with LiPVBA initiator: A) prepolymer, Mn =3,340; block, Mn = 11,340 (Table 2, entry 8); B) prepolymer: Mn = 3,600 ; block copolymer, Mn = 5,400 (Table B2, entry 10).

first monomer, living polymer chains initiated by LiPVBA were allowed to propagate with a second type of monomer and produced block copolymers with terminal styrenic group. Table B2 shows that the living polyDMAEMA chains quantitatively initiated MMA and tBMA. The chain length of each block was well controlled by the monomer/initiator ratio. The molecular weight distributions were very narrow for both prepolymers and block copolymers (Mw/Mn = 1.05-1.1). No homopolymer was detected in the crude diblock polymer samples as shown by size exclusion chromatography (Figure B1)

B 3.4 Characterization of Macromonomers

The macromonomers were characterized by ^{1}H NMR. Figure B2 shows the ^{1}H NMR spectra of polyMMA, polyDMAEMA, and the block macromonomer of poly(DMAEMA-*block*-MMA). For polyDMAEMA macromonomer, signals of polyDMAEMA backbone are at 2.20 ppm ($N(C\underline{H}_3)_2$), 2.47 ppm ($NC\underline{H}_2$), 3.97 ppm ($COOC\underline{H}_2$), 1.73-1.82 ppm ($C\underline{H}_2$-C-CH_3), 0.82 and 0.97 ppm ($C\underline{H}_3$-C). Signals due to vinylbenzylamine group appear at 5.09 ppm (1H, d, $C\underline{H}_2$=CH), 5.63 ppm (1H, d, $C\underline{H}_2$=CH), 6.64 ppm (1H, m, CH_2=C$\underline{H}$), which are very similar to the signals of vinylbenzylamine. The assignments for polyMMA and poly(DMAEMA-*blk*-MMA) are very similar to those for polyDMAEMA and are shown in Figure B2.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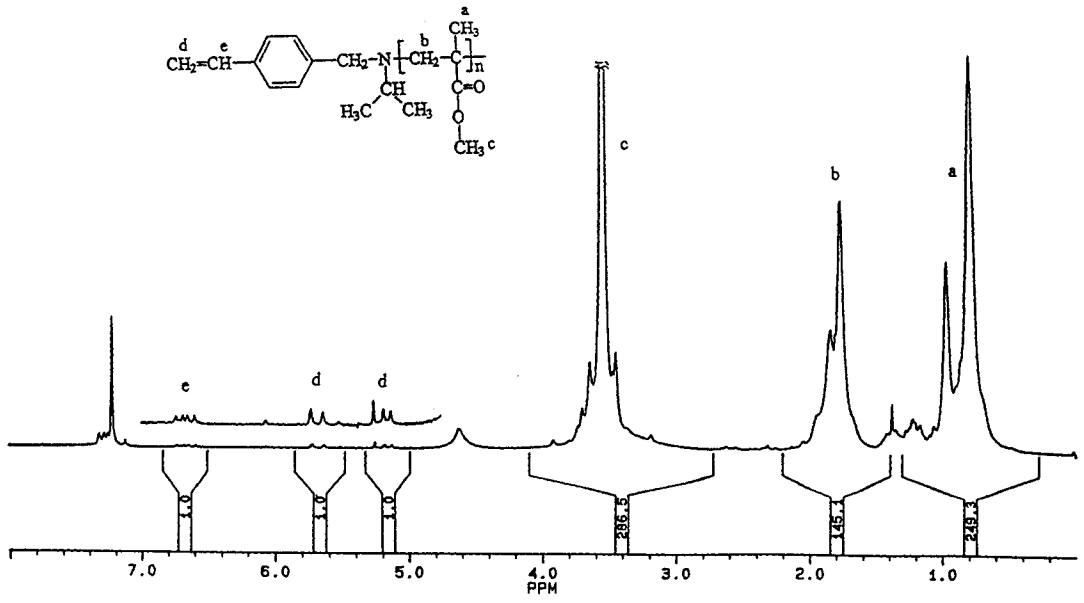
CH2-N
b
CH2
a
CH3
Jn
C=O
O
CH2 e
CH2 d
CH
H3C CH3
c
H3C
N
c
CH3
g
f
f
e
d
c
b
a
.44
.45
.44
41.68
41.28
122.29
35.75
58.88
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5
PPM

A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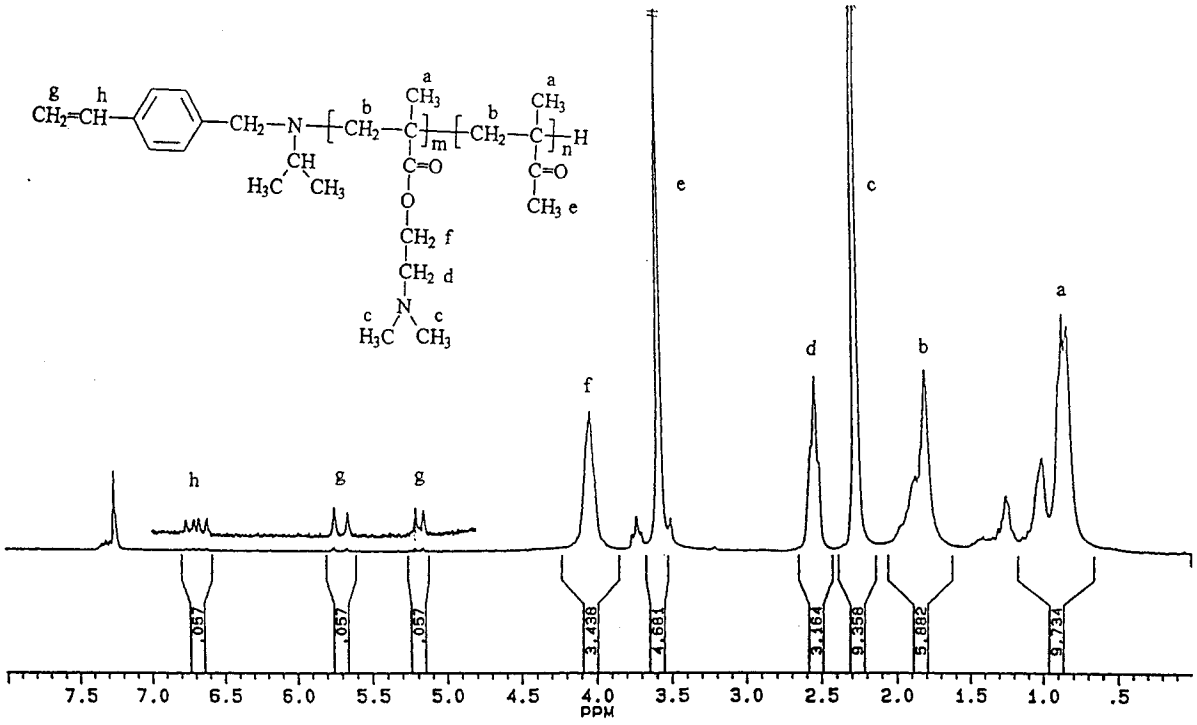
CH2-N
b
CH2
a
CH3
Jn
C=O
CH
H3C CH3
O
CH3 c
e
d
d
c
b
a
1.0
1.0
1.0
286.5
145.1
249.3
7.0 6.0 5.0 4.0 3.0 2.0 1.0
PPM

B



C

Figure B2. ^{1}H NMR spectra of polyDMAEMA, polyMMA and poly(DMAEMA-*block* MMA) macromonomers: A) from Table B1, entry 6; B) from Table B1, entry 2; and C) from Table B2, entry 7.

B 4 Conclusion

N-isopropyl-4-vinylbenzylamine (PVBA) was synthesized and reacted with secondary butyl lithium to result in lithium N-isopropyl-4-vinylbenzylamide (LiPVBA). LiPVBA was successfully used to initiate the living anionic polymerizations of MMA, DMAEMA and tBMA for synthesizing macromonomers and their block macromonomers with terminal styrenic groups. The resulting polymers had well-controlled molecular weight and narrow polydispersity (Mw/Mn < 1.1). The macromonomer and block macromonomer structures were confirmed by ^{1}H NMR analysis.

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