Polymer Bulletin 35, 137–142 (1995)

Polymer Bulletin

Stabilization of the living end in the anionic polymerization of 2-(trimethylsiloxy)ethyl methacrylate

Role of surrounding monomer molecules

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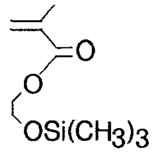
Received: 24 November 1994/Revised version: 19 January 1995/Accepted: 31 January 1995

Summary

In an anionic polymerization of 2-(trimethylsiloxy)ethyl methacrylate (**ProHEMA**), the loading rate of the monomer was found to influence the polymerization. When the monomer loading was run quickly via a dropping funnel, the **ProHEMA** polymerization occurred quantitatively to form poly(**ProHEMA**) with a narrow molecular weight distribution (MWD). Based on the results, we propose a mechanism in which monomer molecules surrounding the propagating species take part, *viz,* the surrounding monomer molecules prevent a possible termination reaction. In the presence of LiCl for **ProHEMA** polymerization, a polymer with a rather narrower MWD was obtained.

Introduction

Microphase separated polymers have been studied extensively owing to unique characteristics such as high mechanical strength (1) and surface functionality (2). Syntheses of model polymers with well defined structures are one of the most important subjects to understand structure-functionality relationships. An anionic living polymerization technique is primarily utilized for syntheses of such multiphase separated polymers (3). Actually, numerous types of block copolymers were synthesized through anionic polymerization techniques (4). The anionic polymerization technique was, however, limited to hydrocarbon monomers before Nakahama and his coworkers' methodology (5), which is a living anionic polymerization technique using protective monomers, monomers with active hydrogen(s) being protected by a certain moiety such as trialkylsilyl groups. Using this technique, several types of functional polymers were synthesized with predictable molecular weights (MW) and narrow molecular weight distributions (MWD).



ProHEMA

Because α,β-unsaturated ester monomers such as methyl acrylate and methyl methacrylate (MMA) are known to have extremely high reactivity in an anionic polymerization system (6), it is very difficult to control the polymerization reaction. Actually, Van Beylen, et al. reported (7) that the anionic polymerization of 2-(trimethylsiloxy)ethyl methacrylate (**ProHEMA**) yielded polymers with relatively broad MWD owing to certain side reactions. Nakahama's group also reported that the living end in the polymerization of **ProHEMA** was not stable enough compared to other α, β-unsaturated ester monomers, though the resulting polymers had a narrow MWD(8). In

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the anionic polymerization of **ProHEMA**, we recently found that the polymerization was strongly influenced by the surrounding monomers. This paper reports a mechanistic study of the anionic polymerization of **ProHEMA** in order to determine the nature of the growing species.

Experimental

All experiments were carried out under argon atmosphere in order to eliminate oxygen and moisture.

Materials

Commercial tetrahydrofuran (THF) and diphenylethylene (DPE) were purified by conventional methods(9). Butyllithium (BuLi) was used as a hexane solution, the concentration of which was determined by Gilman's double titration method (10). **ProHEMA** was prepared according to the literature (8) and purified by fractional distillations in vacuo.

Polymerization Procedures

A typical anionic polymerization was performed in a 100 mL round bottomed flask with a 3-way stopcock. The reactor was first carefully washed with a hexane solution of **BuLi**, and then THF (10.0 mL), BuLi (0.20 mmol) and **DPE** (0.40 mmol) were added via a syringe at -74 °C. After a few minutes agitation for complete formation of 1,1-diphenylhexyllithium (DPL) as an initiator, **ProHEMA** (10.0 mmol) was added by dropping funnel. Temperature of the reaction mixture increased up to -50 °C within 30 s due to the heat of polymerization in addition to the monomer temperature. The reaction was allowed to continue for further 10 min, before a small amount of methanol was added to quench it. The resulting mixture was analyzed by gas chromatography (GC) and gel permeation chromatography (GPC) to determine the conversion of **ProHEMA** and to obtain information on the MW and MWD of the polymer formed.

Characterization

A Hewlett-Packard 5890 Series II GC was used (column: glass capillary column DB-1 0.25 mmϕ • 30 m). GPC measurements were performed on a Toyo Soda HLC-8020 with an IR detector and TSK-Gel G4000HXL + G3000HXL + G2500HXL Columns. ^{13}C NMR spectra were measured on a JEOL FX90Q spectrometer using $CDCl_3$ as a solvent at room temperature. Chemical shifts relative to $CDCl_3$ (^{13}C: $\delta = 77.0$) were employed.

Results and Discussion

Since Szwarc had discovered a living anionic polymerization of styrene (11), reactors with breakable seals have been used in order to maintain high purity of the polymerization system. We have reported recently, however, that an anionic polymerization of styrene derivatives proceeded without any side reaction even in a flask equipped with 3-way stopcock when the polymerization was run carefully (12). An anionic polymerization of MMA initiated with DPL in THF at -74 °C also proceeded quantitatively to form a polymer with a predictable MW and a narrow MWD using the same reactor stated above. In the anionic polymerization of **ProHEMA**, however, only 52.1 % of the monomer was consumed under the same conditions, indicating that certain side reactions occurred during the polymerization. This is a striking contrast to MMA polymerizations. Actually, it is reported that termination reactions proceeded much more slowly than the propagation in the anionic polymerization of MMA initiated with organolithium compounds at low temperature (13).

The extent of the anionic polymerization of **ProHEMA** was found to be influenced by the loading time of the monomers into the system. Table 1 summarizes the results of the polymerizations with different monomer loading times, keeping other conditions the same. It was found that the **ProHEMA** polymerization took place quantitatively when the monomer loading was run quickly via a dropping funnel.

Table 1. Results of anionic polymerizations of **ProHEMA** in THF at -74 °C$^{a)}$.

Run	**ProHEMA** Loading		Conversion$^{b)}$
	Method	Time in s	in %
1	Dropping funnel	< 1	100.0
2	Syringe	5 - 10	52.1
3	Dropping funnel	60	8.2

a) [**ProHEMA**]$_0$ / [**DPL**]$_0$ = 1.0 / 0.02 mol • dm^{-3}; Reaction time after loading: 10 min.
b) Determined from GC results

It should be noted that the loading of the monomer into the polymerization flask required 5 to 10 s via syringe, while that from the dropping funnel took less than 1 s. In contrast, when the monomer was added via syringe dropwise for 1 min, only 8% of the monomer was consumed. This may be explained by a mechanism in which monomer molecules surrounding the propagating species took part, *viz,* the surrounding monomer molecules prevented a possible termination reaction. Using a dropping funnel, the monomer could be loaded fast enough to supply surrounding monomers to suppress commencement of a certain side reaction.

Fig. 1 shows the GPC trace of the polymer obtained by the fast loading technique, in which the resulting polymer shows monomodal distribution and relatively broader MWD (1.30). When **ProHEMA** was added into the mixture after the monomer was consumed completely, however, no further polymerization took place, which supports the above mechanism.

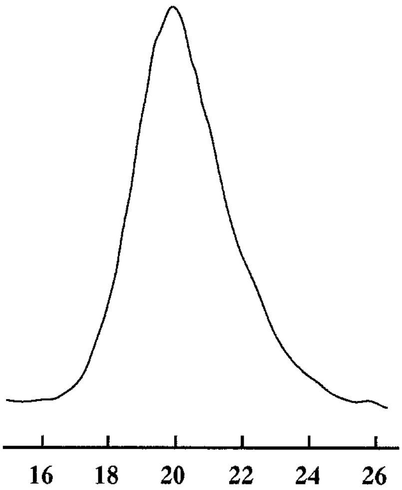
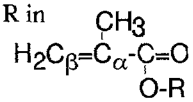


Fig. 1. GPC of poly(ProHEMA) formed by the anionic polymerization (The same conditions as Run 1 in Table 1; Mn = 7.5 • 10^3; Mw / Mn = 1.30)

Teyssié et al. (14,15) reported that LiCl stabilized the growing carbanion in the anionic (meth)acrylate ester polymerizations with organolithium compounds as an initiator to form polymers with predictable MW and narrow MWD. Müller, et al. (16) revealed that this effect was due to the lowered propagation rate owing to stabilization of the growing species by a μ-type complex formation between LiCl and the growing species. In the case of **ProHEMA** polymerization, it is considered that surrounding monomer molecules influenced the growing species as stated above. To obtain information on the role of the surrounding monomers, spectroscopic measurements were carried out.

Because the growing carbanion of the anionic polymerization of methacrylate monomers can be regarded as a stabilized carbanion existing mainly in an enolate form, trimethylsiloxy lithium (**TMSOLi**) was used as a model of the propagating species. Chemical shifts in the NMR spectrum are one of the most suitable techniques to obtain information on the coordination of monomers with Li species. ^{13}C NMR measurements of **ProHEMA** and MMA with and without **TMSOLi** were carried out, the results of which are listed in Table 2. Signals of the vinyl β-carbon and carbonyl carbon of MMA in the presence of **TMSOLi** shifted by 27.9 and 25.2 Hz, respectively, to the upper

Table 2. ^{13}C NMR chemical shifts of MMA and **ProHEMA** in the presence and absence of **TMSOLi**[a), b)]

R in  $H_2C_\beta=C_\alpha(CH_3)-C(=O)-O-R$	$(CH_3)_3SiOLi$	$\delta(H_2C_\beta)$	$\delta(C{=}O)$	$\delta[(CH_3)_3SiOLi]$
		in ppm from TMS		
CH_3	Absence	125.254	167.767	
CH_3	Presence	125.533	168.019	3.108
$CH_2CH_2OSi(CH_3)_3$	Absence	125.417	167.197	
$CH_2CH_2OSi(CH_3)_3$	Presence	125.600	167.324	3.007

a) $[Monomer]_0 = [$**TMSOLi**$]_0$; Monomer = 1,0 g/dl

b) Chemical shift of methyl carbon in **TMSOLi** is 3.610 ppm.

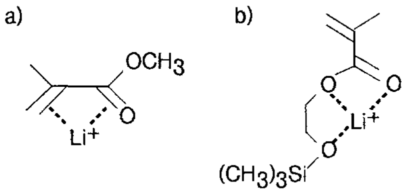


Fig. 2. Possible structure of MMA (a) and ProHEMA (b) with lithium cation

frequency field compared to that in the absence of **TMSOLi**, although the upper field shifts (18.3 and 12.7 Hz for the vinyl β-carbon and carbonyl carbon, respectively) for the corresponding carbons of **ProHEMA** were less than those for MMA, which indicates that the interaction of the vinyl and carbonyl π-conjugation of MMA with the Li cation was much greater than that of **ProHEMA**. However, the signals of the methyl carbon in **TMSOLi** (3.61 ppm) shifted by 50.2 and 60.3 Hz to the lower frequency field when MMA and **ProHEMA** were added to the solution, respectively, which means that the **ProHEMA** molecule is coordinated more tightly to the Li cation than that of MMA. The ethylene glycol unit in **ProHEMA** may play an important role in the chelation to the Li cation as shown in Fig. 2(b). Such coordination of **ProHEMA** to the Li cation may prevent possible interaction between the Li cation and functional groups of the penultimate unit(s) of the growing species, which is known to induce several side reactions such as cyclization and ester exchange reactions (13). After the consumption of the surrounding monomers, such side reactions may take place predominantly.

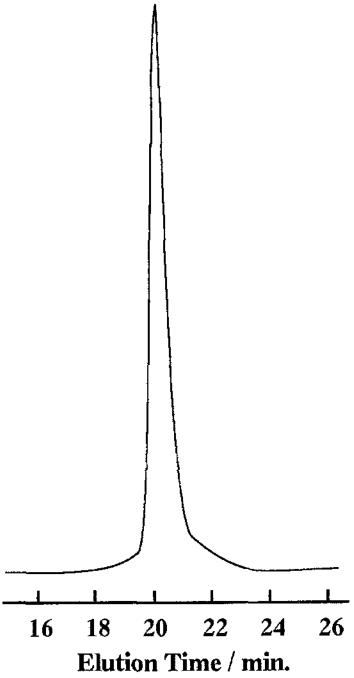


Fig. 3. GPC of poly(ProHEMA) formed by the anionic polymerization in the presence of LiCl ($[ProHEMA]_0/ [DPL]_0/ [LiCl]_0$ = 1.0 / 0.029 / 0.29 mol • dm ; Solv.: THF; Temp.: -74 °C; Time: 10 min.; Mn = 8.5 • 10^3; Mw / Mn = 1.08)

The effect of lithium chloride on the **ProHEMA** polymerization was investigated. As shown in Fig. 3, the resulting polymer had a narrow MWD (Mw / Mn = 1.08), indicating that the μ-type complexation of LiCl increased the stabilization of the growing species also in the **ProHEMA** polymerization. Actually, post polymerization took place by addition of a second monomer after the monomer was consumed completely though a certain amount of prepolymer was deactivated. Therefore, it was concluded that poly(HEMA) with a predictable MW and with a narrow MWD could be obtained without the breakable seal method.

Further studies on the synthesis of a block copolymer consisting of poly(HEMA) as one segment by this method will be published elsewhere.

Acknowledgment

We would like to express our sincere appreciation to the *Watanabe Foundation* for the financial support of part of this research.

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