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A potassium alcoholate-initiated polymerization of 2-(trialkylsiloxyethyl) methacrylate

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Anionic polymerization of 2-(t-butyldimethylsiloxyethyl) methacrylate (ProHEMA) was performed with potassium ethanolate as an initiator in tetrahydrofuran. It was found that the potassium ethanolate-initiated polymerization of ProHEMA proceeds smoothly at ambient temperature to 90% monomer conversion. The polymerization was initiated by the addition of ethanolate at the double bond in ProHEMA. It is considered that complexation of potassium cation with the ProHEMA molecule increased the nucleophilicity of the oxonium anion to increase the initiation ability. Based on the ^{13}C n.m.r. analysis, poly(ProHEMA) obtained with potassium ethanolate was syndiotactic rich in microstructure. This is also explained by the bulky counter cation complexed with monomer molecules, which controls monomer insertion around the growing centre. This polymerization method can be applied to a synthesis of an end-functionalized poly(2-hydroxyethyl methacrylate) (poly(HEMA)). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: anionic polymerization; poly(2-hydroxyethylmethacrylate); alkalate initiated polymerization; semi-telechelic poly(HEMA))

INTRODUCTION

Anionic polymerization of α,β-unsaturated carbonyl monomers has been studied extensively[1–3]. Among the α,β-unsaturated carbonyl compounds, methyl methacrylate (MMA) is one of the most well-investigated compounds in anionic polymerization. Because the anionic polymerizability of MMA is extremely high, several side-reactions are revealed in the alkali metal-induced anionic polymerization, especially in polar solvents. However, well-controlled poly(MMA) (PMMA) could be obtained under several reaction conditions such as very low temperature. Schulz and co-workers reported that the polymerization of MMA proceeded at −75°C in THF without any detectable side reactions if cumylcesium or α-methylstyrylcesium is used as an initiator[4–6]. Recently, Teyssié and co-workers reported that the anionic polymerization of MMA can be easily controlled when the reaction was carried out with butyllithium coupled with 1,1-diphenylethylene and/or α-methylstyrene in tetrahydrofuran (THF) in the presence of LiCl[7]. LiCl plays an important role in the stabilization of the carbanion at the growing chain end. Therefore, the synthetic method for uniform size PMMA has been improved by the anionic polymerization of MMA.

Poly(2-hydroxyethyl methacrylate) (poly(HEMA))[8], which is one of the α,β-unsaturated carbonyl monomers, has been investigated as a candidate for biomedical materials such as blood compatible surfaces and contact lenses[9,10]. For the most suitable design for the applications mentioned above, it is necessary to control precisely the molecular structure of the materials. In early studies of poly(HEMA), the polymers were synthesized by radical polymerization. Since the 1980s, anionic polymerization of HEMA derivatives has been investigated to prepare well-designed polymeric materials. 2-(Trimethylsiloxyethyl) methacrylate (ProHEMA), which is a monomer in which a hydroxyl group in HEMA is protected by a trimethylsilyl group, is one of the suitable monomers for the synthesis of well-designed poly(HEMA) by anionic polymerization because the trimethylsiloxy group in poly(ProHEMA) is easily hydrolysed by a weak acid. The anionic polymerization of ProHEMA, however, has too fast a propagation rate to control easily. For example, Van Beylen and co-workers reported that the anionic polymerization of ProHEMA in THF yielded polymers with a relatively broad molecular weight distribution (MWD) due to some side-reactions[11]. However, Nakahama and co-workers reported that the anionic polymerization of ProHEMA proceeds without any side-reaction with a narrow MWD when the polymerization was performed carefully with 1,1-diphenylhexyllithium as an initiator in THF at −78°C, though the lifetime of the living end is not long[12,13].

Recently, we investigated the reaction mechanism of the anionic polymerization of ProHEMA in THF and found that the loading rate of the monomer into the reaction mixture influenced the polymerization[14]. When the monomer loading was run quickly via a dropping funnel, the ProHEMA polymerization took place quantitatively to form poly(ProHEMA) with a narrow MWD. Based on the results, we have proposed a mechanism in which monomer molecules surrounding

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the propagating species took part, namely, the surrounding monomer molecules prevent a possible termination reaction.

If the surrounding monomer molecules interact with the cation, it should influence the reactivity of the initiator for the ProHEMA polymerization. In this paper, we report the anionic polymerization of ProHEMA using alkali metal alcoholate as an initiator.

EXPERIMENTAL

Materials

THF and ethanol were purified by conventional methods[15]. Potassium naphthalene was prepared according to the literature and was used as a THF solution[16]. 2-(Trimethylsiloxyethyl) methacrylate (monomer **I**) was prepared according to the literature and purified by fractional distillation *in vacuo*[13]. 2-(t-Butyldimethylsiloxyethyl) methacrylate (monomer **II**) was prepared as follows: HEMA and t-butyldimethylchlorosilane were reacted for 24 h in the presence of triethylamine (TEA) at room temperature under argon. Then the mixture was filtered and distilled under reduced pressure (1 mmHg, 52°C) before use.

Polymer synthesis

One of the representative procedures for the anionic polymerization of monomer **II** is described. To the THF (15 ml) solution of ethanol (1 mmol) in a glass vessel with a three-way stopcock under an argon atmosphere, a THF solution of potassium naphthalene (1 mmol) was added at room temperature and stirred for 10 min to form the potassium ethanolate. After **II** (20 mmol) was added, the mixture was allowed to react for 90 min at 0°C. To determine the monomer conversion, the reaction mixture was analysed directly by gas chromatography (g.c.) to determine monomer conversion; then the mixture was poured drop by drop into a large excess of methanol. The precipitate was dissolved in THF and precipitated again in methanol. The polymer thus obtained was finally subjected to freeze drying from benzene solution.

Analysis

Gel permeation chromatography (g.p.c.) measurements were carried out using a Shimadzu 6A Liquid Chromatograph equipped with a TSK gel column (G4000HLX + G3000HXL + G2500HXL) and an internal RI detector (RID-6A). THF containing 2% triethylamine was used as the eluent at a flow rate of 1 ml min^{-1}. ^{1}H and ^{13}C n.m.r. spectra were obtained using chloroform-*d* solutions (^{1}H, 1.0 wt%; ^{13}C, 10.0 wt%) with a JEOL EX400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

RESULTS AND DISCUSSION

It is well known that alkali metal alcoholates cannot initiate the anionic polymerization of methacrylate monomers due to the low nucleophilicity of the oxonium anion[17]. The oxonium anion having relatively high nucleophilicity, however, initiates the polymerization of MMA. For example, Tomoi *et al.* reported that lithium 2-methoxyethanolate initiates the anionic polymerization of MMA because the 2-methoxy group in the initiator increased the nucleophilicity of the oxonium anion due to chelation with the lithium cation[18]. Therefore, a slight change in the initiation reactivity varies the polymerizability of methacrylate monomers drastically in the anionic polymerization.

We have already revealed that ProHEMA itself has a strong interaction towards alkali metal cations even in polar solvents such as THF[14]. If ProHEMA increases the nucleophilicity of oxonium anions, alkali metal alcoholates can be anticipated to show the initiation ability of ProHEMA itself. Using potassium ethanolate as an initiator, the polymerization ability of ProHEMA derivatives were examined. When ProHEMA **I** was added to the THF solution of potassium ethanolate at ambient temperature, a cross-linked gel was formed, indicating that potassium ethanolate had initiation activity towards the vinyl group of **I**, though undesirable side-reactions such as an ester exchange reaction preceded the cross-linking during the polymerization reaction. This result supports our hypothesis, namely, **I** increases the nucleophilicity of potassium ethanaolate to initiate the polymerization of **I** itself, though a non-soluble gel was obtained. To obtain a soluble polymer with a highly designed structure, suppression of the side-reactions was examined. If the cross-linking reaction takes place due to the attack of the growing carbanion on the pendant ester group and/or siloxy group, a monomer carrying a bulky side-group can be anticipated to prevent the side-reaction. Because ProHEMA **II** has a bulky t-butyl group, the polymerizability of **II** using potassium ethanolate was examined. The mixture of **II** with potassium ethanolate in THF at 0°C was homogeneous for 90 min, and no gel formation was observed. Based on the g.c. analysis, it was confirmed that the monomer was consumed completely within 90 min. From a g.p.c. analysis of the reaction product shown in *Figure 1*, **II** was converted to a polymer having a number-average molecular weight (M_n) of 7300 with a molecular weight distribution (M_w/M_n) of 1.43. The M_n of the polymer determined from g.p.c. was higher than that calculated by the initial monomer/initiator ratio (4900), suggesting low initiator efficiency. From these results, it is concluded that potassium ethanolate initiates the polymerization of ProHEMA **II** without

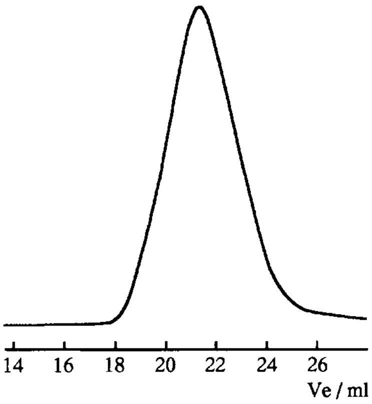


Figure 1 G.p.c. profile of poly(ProHEMA) (poly(**II**)) prepared by anionic polymerization initiated with potassium ethanolate (the same sample as run 2 in *Table 1*)

any gel formation. In order to obtain suitable polymerization conditions, the polymerizations of **II** under various conditions were examined and the results are summarized in *Table 1*. When the polymerization was carried out at −30°C, the M_n of the polymer obtained was considerably higher than that at 0°C (run 3 in *Table 1*). This is explained by the decreased initiation efficiency due to the relatively lower temperature. Actually, the polymerization did not proceed at all at −75°C (run 4 in *Table 1*). In this way, with increasing polymerization temperature (−75 to 0°C), the initiation efficiency increased from 0 to 67%. At a polymerization temperature above 0°C, however, the M_n was higher than that at 0°C, though the initial monomer/initiator ratios were the same (run 1 in *Table 1*). The obtained polymer had a shoulder on the high-*MW* side in the g.p.c. profile, indicating a branching reaction between the growing chain and the preformed polymers, though the initiation efficiency might be higher than that prepared at lower temperature. To obtain further information on this polymerization reaction at high temperature, the time courses of the polymerization were investigated. From the time course of the monomer consumption in the polymerization of **II** initiated with potassium ethanolate at 23°C shown in *Figure 2*, it is found that more than 90% of the monomer was consumed within 5 min, indicating a rapid polymerization rate even though the alcoholate was used as the initiator. *Figure 3* shows the change in the molecular weight of the polymer formed as a function of the monomer conversion. With increasing monomer conversion, the molecular weight of the polymer increased directly though the slope of the line is slightly larger than that calculated by the monomer/initiator ratio. When the monomer was almost consumed, however, the molecular weight of the polymer increased significantly, indicating that an intermolecular side-reaction took place during the later stage of the polymerization. On the basis of these results, it is concluded that the potassium ethanolate-initiated polymerization of ProHEMA **II** proceeds smoothly at ambient temperature to 90% monomer conversion.

A structural analysis of the obtained polymers was carried out by n.m.r. spectroscopies. *Figure 4* shows the ^{1}H and ^{13}C n.m.r. spectra of the polymer obtained at 0°C (run 2 in *Table 1*). The assignments of the signals in *Figure 4* were carried out referring to the previous reports and are shown in the figure[13,14]. From these assignments, it is confirmed that the products thus obtained were formed via the addition polymerization of **II**. In the ^{13}C n.m.r. spectrum shown in *Figure 4B*, three signals appeared at 14.7, 63.2 and 69.2 ppm, which are assignable to $\underline{CH_3}$–CH_2–CH_2–, to CH_3–$\underline{CH_2}$–O–CH_2, and to CH_3–CH_2O–$\underline{CH_2}$–, at the end of the polymer chain, respectively, according to the calculation data using an empirical equation as shown in *Table 2*[19]. This result shows that the initiation took place by the addition reaction of potassium ethanolate at the double bond of **II**. This fact indicates that a new semi-telechelic poly(HEMA) synthesis can be anticipated using potassium alcoholate possessing a functional group such as a vinyl benzyl group.

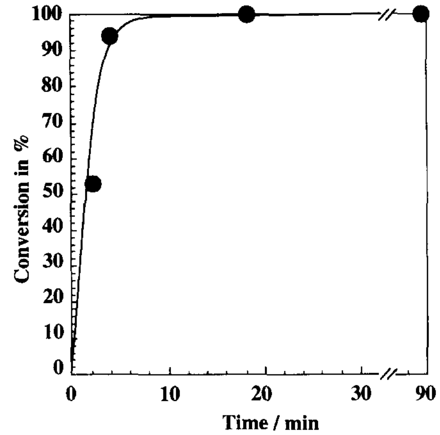


Figure 2 Time course of ProHEMA **II** conversion in the potassium-initiated polymerization at 23°C

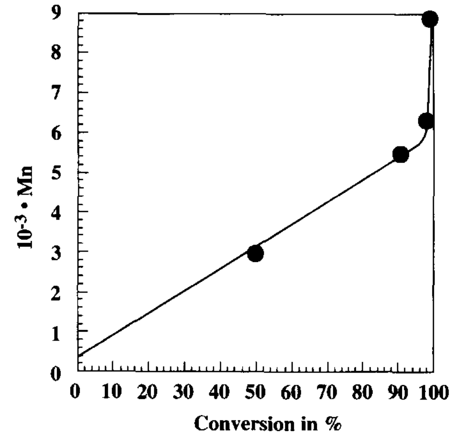


Figure 3 Change in the M_n of poly (**II**) as a function of time (the same condition as *Figure 2*)

Table 1 Results of polymerization of ProHEMA II[a]

	Polymerization		$10^{-3} \times M_n$				
Run	Temperature (°C)	Time (min)	Calculated	Observed[b]	M_w/M_n	Conversion (%)	Initiator efficiency (%)[d]
1	23	90	4.9	8.8	1.59	100	—
2	0	90	4.9	7.3	1.43	99.2	67
3	−30	90	4.9	12.0	1.78	100	41
4	−75	90	4.9	NP[c]	—	0	0

[a] Solv.: THF, initiator : potassium ethoxide, $[\text{Monomer}]_0/[\text{initiator}]_0 = 20$

[b] Determined from g.p.c. results

[c] NP, no polymerization

[d] Initiator efficiencies were calculated by the degree of polymerization determined from g.p.c. patterns and the monomer conversions determined from g.c. patterns, assuming no side-reaction

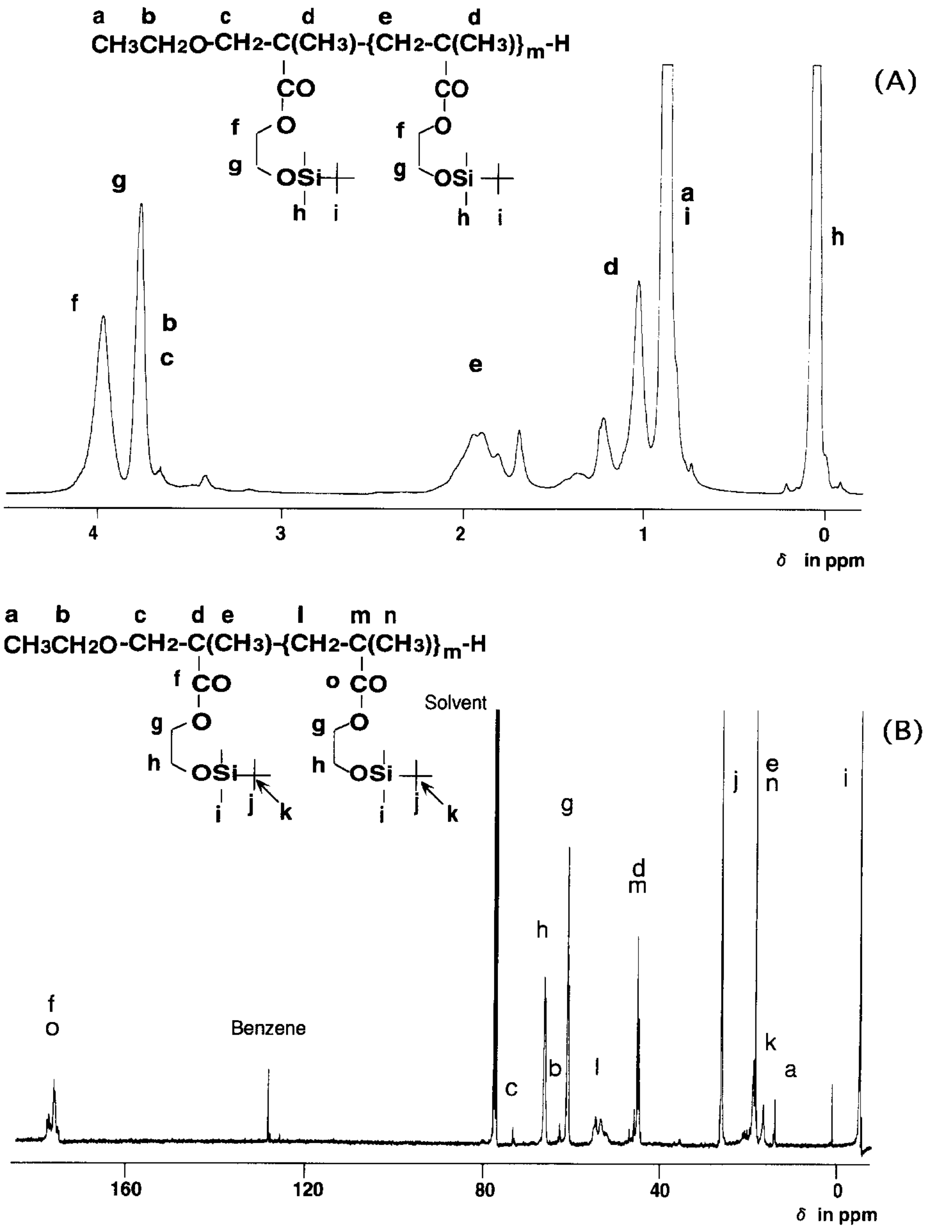
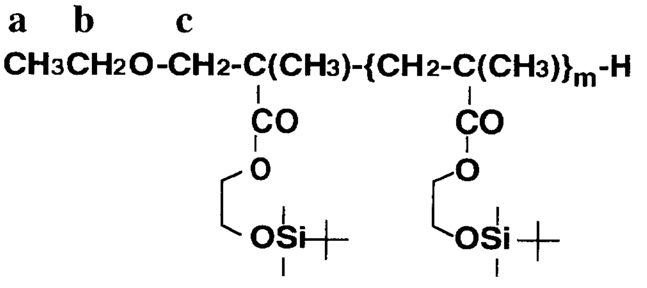


Figure 4 ^{1}H and ^{13}C n.m.r spectra of poly (**II**) (the same sample as run 2 in *Table 1*): (a) ^{1}H and (b) ^{13}C

Our hypothesis for the alcoholate-initiated polymerization of ProHEMA was that the chelation of the ProHEMA molecule with the counter cation (K^+) of ethanolate increases the reactivity of the initiator as

Table 2 ^{13}C n.m.r chemical shifts of poly(ProHEMA **II**) initiated with potassium ethoxide (ppm)

	Carbon		
	a	b	c
Calculated	14.7	63.3	69.2
Observed	14.7	63.2	73.7



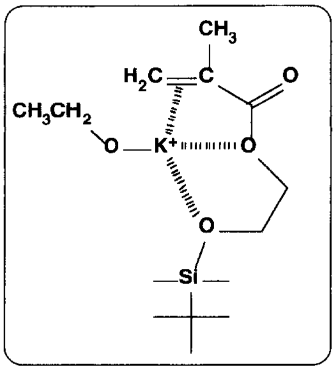
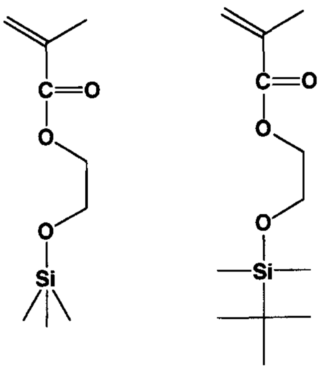


Figure 5 Proposed structure of the potassium–ProHEMA complex

Table 3 Microstructure of vinyl polymers initiated with alkali metal alcohlate[a]

Initiator	Monomer	Reaction temperature (°C)	Tacticity (%) I	H	S
CH_3CH_2OK	ProHEMA **II**	0	8	22	70[b]
			8	14	78[c]
$MeOCH_2CH_2ONa$[20]	MMA	20	22	38	40
$Et(OCH_2CH_2)_2OK$[20]	MMA	20	27	34	39
2,2′-Azobisisobutyronitrile (AIBN)	ProHEMA **II**	60	30	14	56[c]

[a] Solvent: THF
[b] Determined from ^1H n.m.r (400 mHz) spectra
[c] Determined from ^{13}C n.m.r (400 mHz) spectra



2-(trimethylsiloxy)-ethyl methacrylate
ProHEMA (I)

2-(t-butyldimethylsiloxy)-ethyl methacrylate
ProHEMA (II)

Scheme 1

mentioned above. An ether oxygen in the side-chain of ProHEMA plays an important role as shown in *Figure 5*. If the initiation reactivity was truly increased by the chelating structure and the chelation continued until the monomers were consumed completely, it might affect the microstructure of the polymer formed during the propagation process. A triad microtacticity determined by the peak areas originating from the α-methyl group in the ^1H n.m.r. spectrum and by the quaternary carbon group in the ^{13}C n.m.r. spectrum are listed in *Table 3* along with the PMMAs, prepared with alkali metal alcoholate as an initiator[21–23]. In the anionic polymerization of MMA initiated with alkali metal alcoholate, the obtained polymers showed no specific stereoregularity. On the other hand, poly(ProHEMA) (poly(**II**)) obtained with potassium ethanolate was syndiotactic rich in microstructure. It is reported that propagation of methacrylate monomers possessing a bulky ester group such as triphenylmethyl methacrylate in anionic polymerization is governed by the helix structure of the growing chain[24]. In the case of the polymerization of **II**, however, because the bulky t-butyl group is far from the vinyl group, it must not affect the microtacticity. Actually, poly(**II**) prepared by radical polymerization has no stereoregularity as is the case with PMMA. Teyssié and co-workers reported that syndiotactic PMMA was obtained when the polymerization was carried out in the presence of crown ether[25]. They explained that the bulky counter cation complexed with crown ether governed the insertion of the monomer molecule at the growing chain end. The highly syndiotactic rich microstructure of poly(ProHEMA) (poly(**II**)) is one of the proofs that a free monomer molecule interacts with potassium cation similar to that with crown ether during the polymerization process. This may be one of the reasons for obtaining the syndiotactic-rich polymer.

CONCLUSION

On the basis of the reported results, it is confirmed that potassium ethoxide can initiate the anionic polymerization of 2-(t-butyldimethylsiloxyethyl) methacrylate. These new anionic polymerizations of HEMA derivatives initiated with alcoholates can be expected to lead to new molecular designs.

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