Table II
Characterization of Poly(styryl)amine

analytical method	$\bar{M}_n$	analytical method	$\bar{M}_n$
VPO[a]	2360	elem anal.[b]	2420
VPO[b]	2260	elem anal.[d]	2590
VPO[c]	4430	end-group titration[b]	2090

[a] Polystyrene sample from methanol quenching of poly(styryl)lithium prior to amination; $\bar{M}_w/\bar{M}_n$(GPC) = 1.15. [b] Poly(styryl)amine. [c] Terephthaloyl derivative of poly(styryl)amine; $\bar{M}_w/\bar{M}_n$(GPC) = 1.15. [d] Benzoyl derivative of poly(styryl)amine; $\bar{M}_w/\bar{M}_n$(GPC) = 1.15.

terephthaloyl derivative with twice the molecular weight ($\bar{M}_n$, VPO) is also consistent with high amine end-group functionality (eq 7). Finally, in support of the ability to

$$\underset{\bar{M}_n^{\mathrm{VPO}} = 2260}{\mathrm{PsNH_2}} + \mathrm{ClCOC_6H_4COCl} \xrightarrow[\text{toluene}]{\text{pyridine}} \underset{\bar{M}_n^{\mathrm{VPO}} = 4430}{\mathrm{PsNHCOC_6H_4CONHPs}} \quad (7)$$

prepare poly(styryl)amine of high end-group functionality, it should be noted that a polymeric amine sample, exhibiting one TLC spot, could be isolated in 85% yield by column chromatography of the products from an amination reaction which proceeded in 92% yield by amine end-group titration. Thus, although the amine functionalization reaction described herein using the reagent generated from methoxyamine and methyllithium is not quantitative, pure amine end-group functionalized polymer can be isolated in high yield.[25] Therefore, this procedure should be extremely useful for the preparation of difunctional[26] and polyfunctional polymeric amines.

Registry No. Poly(styryl)lithium, 36345-04-7.

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Polymerization of Monomers Containing Functional Groups Protected by Trialkylsilyl Groups. 5. Synthesis of Poly(2-hydroxyethyl methacrylate) with a Narrow Molecular Weight Distribution by means of Anionic Living Polymerization

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ABSTRACT: Anionic polymerization of 2-[(trimethylsilyl)oxy]ethyl methacrylate (1) was investigated with various initiators. They included 1,4-dilithio-, 1,4-disodio-, and 1,4-dipotassio-1,1,4,4-tetraphenylbutane, (1,1-diphenylhexyl)lithium, phenylmagnesium chloride, benzylmagnesium chloride, and lithium aluminum hydride. Polymers of predictable molecular weights with relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ = 1.17–1.33) were obtained when either 1,4-dilithio-1,1,4,4-tetraphenylbutane or (1,1-diphenylhexyl)lithium was used in tetrahydrofuran (THF) at −78 °C. After complete removal of the trimethylsilyl protective group by hydrolysis, linear polymers of 2-hydroxyethyl methacrylate (HEMA) were produced. Addition of 1 to poly(α-methylstyryl)lithium capped with 1,1-diphenylethylene resulted after hydrolysis in the formation of triblock copolymers of the type poly(HEMA-*b*-α-methylstyrene-*b*-HEMA). The molecular weights of these polymers ranged between 38 000 and 71 000. $\bar{M}_w/\bar{M}_n$ lay in the range 1.14–1.37. The incorporation of HEMA in these copolymers was in the range 16–86 mol %. Microphase separation of the copolymers could be observed.

Introduction

Anionic living polymerizations of vinyl monomers have attracted both potential and practical interest because these systems permit the synthesis of polymers of predictable molecular weight and of narrow molecular weight distribution and the preparation of block copolymers of uniform composition and molecular weight.[1] However, a disadvantage of this method is that monomers with

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Table I
Anionic Polymerization of 2-[(Trimethylsilyl)oxy]ethyl Methacrylate (1) with Various Initiators in THF at -78 °C for 5-10 min

	initiator				PHEMA benzoylated		
1, mmol	type	mmol	DPE, mmol	yield,[a] %	$\bar{M}_n$(calcd)	$\bar{M}_n$(obsd)[b]	$\bar{M}_w/\bar{M}_n$[c]
7.13	Li-nap[d]	0.245	0.703	100	14 000	13 000	1.24
11.0	Li-nap[d]	0.198	0.660	98	26 000	27 000	1.33
14.8	Li-nap[d]	0.171	0.660	100	41 000	38 000	1.23
12.1	Na-nap[e]	0.140	0.512	100	40 000	26 000	1.90
10.6	K-nap[f]	0.154	0.512	100	32 000	35 000	2.30
3.56	BuLi	0.0775	0.376	100	11 000	9 000	1.18
6.93	BuLi	0.0697	0.354	100	23 000	20 000	1.20
6.92	BuLi	0.0659	0.393	100	25 000	22 000	1.17
15.3	$LiAlH_4$	0.299		100	12 000	12 000	1.75
11.2	C_6H_5MgCl	0.200		0			
13.2	$C_6H_5CH_2MgCl$	0.220		0			

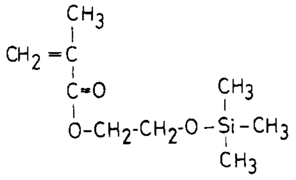
[a] Yield of PHEMA. [b] $\bar{M}_n$ (obsd) were obtained by VPO in benzene solution. [c] Ratios of $\bar{M}_w$ to $\bar{M}_n$ were calculated from their GPC peaks based on a polystyrene calibration curve. [d] Lithium naphthalide. [e] Sodium naphthalide. [f] Potassium naphthalide.

functional groups containing active protons such as hydroxyl and amino groups can not be directly employed since they react immediately with the initiators before polymerization.

One of the possible means of circumventing this difficulty is to introduce a protective group into the monomer, masking the reactive site. If anionic living polymerization of such a protected monomer could be achieved, novel types of very interesting polymeric materials could be synthesized. It is of course essential that the masking group be readily and quantitatively removable after polymerization to regenerate the original functional group.

We recently reported successful use of trialkylsilyl groups as hydroxyl and amino protecting groups in the polymerization. The new silyl-protected monomers are able to undergo anionic living polymerization. By subsequent removal of the protective groups, poly(4-vinylphenol),[2] poly[2-(4-vinylphenyl)ethanol],[3] and poly(4-vinlyaniline)[4] of known molecular weight and narrow molecular weight distribution have been obtained. Moreover, block copolymers have been produced by the sequential addition of different monomers to the living polymers.

As a part of a series of studies using silyl-protected monomers, we wish to report here on the anionic polymerization of 2-[(trimethylsilyl)oxy]ethyl methacrylate (1).



$CH_2=C(CH_3)-C(=O)-O-CH_2-CH_2-O-Si(CH_3)_3$

(1)

Anionic polymerization of 1 was attempted in the hope that the polymerization would proceed without any serious side reactions, as observed in the anionic polymerizations of some alkyl methacrylates,[5-7] and that linear poly(2-hydroxyethyl methacrylate) with a narrow molecular weight distribution and its block copolymer would be obtained.

Results and Discussion

Poly(2-hydroxyethyl methacrylate) (PHEMA) has become of interest in recent years due to the practical use of biomedically important materials as contact lenses, coating of surgical sutures, hydrogel, and hemodialysis membranes. PHEMA is generally obtained by radical polymerization. However, the synthesis of linear high molecular weight PHEMA is relatively difficult by this route because chain-transfer reactions to the hydroxyl group of HEMA often occur during the polymerization, and thereby the resulting polymers become branched and/or cross-linked.[8,9]

Some studies of the radically initiated polymerization of the hydroxyl group protected HEMAs have appeared. Most of these were the protected monomers by ester groups such as 2-acetoxyethyl, 2-(benzoyloxy)ethyl, and 2-(trityloxy)ethyl methacrylates.[8,10,11] Care may be needed to selectively remove these ester protective linkages after polymerization without interfering with the original methacrylate linkage.

There have been two references to anionic polymerization of protected HEMA. Gregonis, Russell, Andrade, and de Visser reported that 2-(benzoyloxy)ethyl methacrylate gave a polymer of 60% yield by dibutylcopper lithium initiation in toluene at -10 °C and an isotactic-rich PHEMA was produced by hydrolyzing the resulting polymer with aqueous potassium hydroxide.[8] A silyl-protected HEMA 1 of the title compound was also reported to be anionically polymerized with butyllithium in toluene at -78 °C but a disappointingly low yield (20%) of polymer was obtained, indicating that serious side reactions had occurred during the polymerization.[11] Moreover, no detailed information regarding the molecular weights and the distributions of the resulting polymers was available in these references.

Anionic Polymerization of 1. A representative series of polymerization of 1 was carried out with various anionic initiators in THF at -78 °C. The initiators included 1,4-dilithio-, 1,4-disodio-, and 1,4-dipotassio-1,1,4,4-tetraphenylbutane, (1,1-diphenylhexyl)lithium, phenylmagnesium chloride, benzylmagnesium chloride, and lithium aluminum hydride. The yields, the molecular weights, and the ratios $\bar{M}_w/\bar{M}_n$ for this series of polymers are listed in Table I. The data show that 1 easily undergoes anionic polymerization with each of the initiators with the exception of Grignard reagents. Almost quantitative conversions were achieved in all cases. Thus, the polymerizability of 1 toward anionic initiators resembled that of methyl methacrylate as the classic methacrylate monomer. These results clearly suggest that the trimethylsilyl protective group is unaffected by a variety of anionic initiators except for Grignard reagents.

When 1,4-dilithio-1,1,4,4-tetraphenylbutane was used as an initiator, the characteristic dark red of the initiator solution immediately disappeared upon addition of 1, indicating that ready initiation had taken place. The anionic polymerization of 1 was fast and complete within 5 min. The polymerization mixture was then quenched with a few drops of 1.5 N HCl, and the polymer was precipitated by

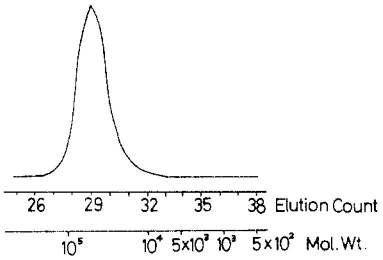


Figure 1. GPC curve for poly(2-(benzoyloxy)ethyl methacrylate): $\bar{M}_n$(obsd) = 38 000; $\bar{M}_w/\bar{M}_n$ = 1.23.

addition to excess water. The complete removal of the trimethylsilyl groups was confirmed by the ^{1}H NMR spectrum of the resulting polymer. Therefore, the resulting polymer should have been in the form of PHEMA, the ^{1}H NMR of which displayed the expected signals. Thus, the trimethylsilyl protective group can be readily and selectively cleaved without interfering with the methacrylate ester linkage by the above treatment. PHEMA thus obtained is a white solid, soluble in methanol, ethanol, *N,N*-dimethylformamide, and pyridine but insoluble in benzene, THF, chloroform, and water. To determine the molecular weight and molecular weight distribution of the polymers by VPO and GPC measurements in benzene and THF, the polymers were esterified with benzoic anhydride in pyridine to afford poly(2-(benzoyloxy)ethyl methacrylate), which was soluble in these solvents. The ^{1}H NMR study indicated a complete esterification.

The agreement between $\bar{M}_n$'s of these benzoylated polymers measured by VPO and calculated based on monomer to initiator ratios is quite good, and the molecular weight distributions are narrow (Figure 1). It should be mentioned that no low molecular weight material was detected in the polymers. The values of $\bar{M}_w/\bar{M}_n$ were calculated to be in the range 1.23–1.33 by Tung's method using the calibration curve of standard polystyrene.[12] These results suggest that the anionic initiation and subsequent propagation reactions of 1 with this initiator proceed with few, if any, side reactions during the course of the polymerization.

On the other hand, less satisfactory results were obtained in the polymerization of 1 when Na^+ or K^+ was used as the countercation. The molecular weight distributions obtained with 1,4-disodio- and 1,4-dipotassio-1,1,4,4-tetraphenylbutane were much broader than with the corresponding lithium compound, although quantitative conversions could be achieved.

Fairly narrow distribution was observed in the polymer produced with (1,1-diphenylhexyl)lithium prepared from 1,1-diphenylethylene (DPE) and butyllithium. The polymer yield was 100%. This is in sharp contrast to the previous result where only a low yield (20%) of the polymer was obtained with butyllithium alone.[11] Thus, by the use of the bulky and less reactive 1,1-diphenylhexyl carbanion we have eliminated the side reaction that is considered as the attack of the ester group by butyllithium.

Lithium aluminum hydride gave a quantitative yield of polymer with a relatively broad molecular weight distribution.

Grignard reagents, both phenylmagnesium chloride and benzylmagnesium chloride, did not initiate polymerization of 1, and no polymer was obtained from −78 to +20 °C, even after 24 h. This was entirely unexpected when compared to the anionic polymerizability of methyl methacrylate with Grignard reagents previously reported. The most plausible explanation at the present time might be the attack by the Grignard reagents at silicon atoms in a nucleophilic way.

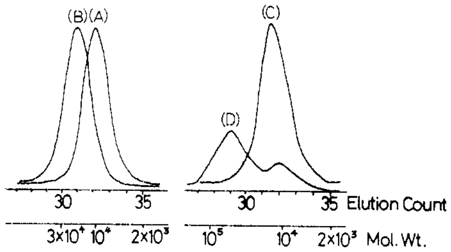


Figure 2. GPC curves for poly(2-(benzoyloxy)ethyl methacrylates) at the first polymerization (A) and at the second polymerization (B) (the second monomer was added after 5 min of the first monomer addition): peak A, $\bar{M}_n$(obsd) = 9000, $\bar{M}_w/\bar{M}_n$ = 1.18; peak B, $\bar{M}_n$(obsd) = 20 000, $\bar{M}_w/\bar{M}_n$ = 1.20. GPC curves for poly(2-(benzoyloxy)ethyl methacrylates) at the first polymerization (C) and at the second polymerization (D) (the second monomer was added after 15 min of the first monomer addition).

Postpolymerization of 1. The preparation of copolymers containing HEMA blocks was one goal of anionic polymerization studies. Therefore, it was of interest to investigate if any polymer chains might be living in the (1,1-diphenylalkyl)lithium-initiated systems.

The polymerization of 1 was carried out with (1,1-diphenylhexyl)lithium in THF at −78 °C for 5 min. The resulting solution was then divided into two portions. The first portion was terminated, while fresh 1 was added to the second portion, which was held an additional 30 min at −78 °C. After benzoylation of each sample, GPC studies were compared. As can be seen in Figure 2, the GPC curve of the second sample was found to shift to the higher molecular weight side. This clearly indicates that a living 2-[(trimethylsilyl)oxy]ethyl methacrylate polymer existed after the initial consumption of 1.

Similar experiments with 1,4-dilithio-1,1,4,4-tetraphenylbutane as an initiator were performed with a longer reaction time (15 min and 1 h) in the first polymerization of 1. From the GPC studies it is seen that a portion of the living polymer was already deactivated after 15 min, as shown in Figure 2. When fresh 1 was added after 1 h of the first polymerization, no polymerization of additional 1 could be observed. The GPC curve of the second sample was found to be virtually identical with that of the sample obtained by the first polymerization, thus indicating that all the active chain ends were deactivated after 1 h.

In conclusion, it would appear from this study that the living polymer yielded from 1 remains stable in practice within 5 min at −78 °C. The resulting polymer had therefore the predictable molecular weights with relatively narrow distribution. However, the living end of the polymer was gradually deactivated with the passage of time.

Block Copolymerization of 1 with α-Methylstyrene. The synthesis of a block copolymer by the combination of HEMA and a nonpolar monomer has stimulated a great deal of interest since the block copolymer generally leads to heterophase materials in which hydrophobic and hydrophilic domains are separated. Okano, Katayama, and Shinohara previously synthesized triblock copolymers of poly(HEMA-*b*-sytrene-*b*-HEMAs) by the reaction of amino-semitelechelic oligo-HEMA and isocyanate-telechelic oligostyrene.[9] Moreover, it was found that the microdomain structure of surface of the block copolymer acted to suppress the shape change of adhered platelets both with and without protein preadsorption.[13] However, there are some problems with respect to the molecular weights and the molecular weight distributions of the block copolymers due to the synthetic method.

Table II
Anionic Block Copolymerization of α-Methylstyrene with 2-[(Trimethylsilyl)oxy]ethyl Methacrylate by Lithium Naphthalide Initiation in THF at –78 °C[a]

	poly(HEMA-*b*-α-methylstyrene-*b*-HEMA)[b]		
sample	$\bar{M}_n$(calcd)	$\bar{M}_n$(obsd)[c]	$\bar{M}_w/\bar{M}_n$[d]
1	67 000 (53 000)	62 000 (51 000)	1.14
2	35 000 (22 000)	40 000 (29 000)	1.27
3	43 000 (25 000)	41 000 (25 000)	1.15
4	41 000 (15 000)	38 000 (14 000)	1.28
5	64 000 (9 500)	71 000 (9 300)	1.37
6[e]	39 000 (18 000)	33 000 (16 000)	1.12

[a] Polymerizations were carried out for 1 h for the first polymerization and for an additional 1 h for the second polymerization. [b] The values in parentheses indicate the $\bar{M}_n$'s of the starting poly(α-methylstyrene). [c] $\bar{M}_n$'s obsd were obtained from $\bar{M}_n$'s of the starting poly(α-methylstyrene) and the composition determined by ^{1}H NMR. [d] The ratios of $\bar{M}_w/\bar{M}_n$ were calculated from their GPC peaks based on a polystyrene standard curve. [e] Butyllithium initiation; the resulting polymer was an AB type diblock copolymer.

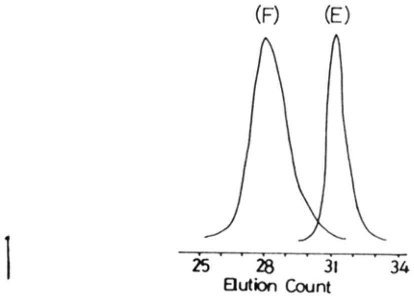


Figure 3. GPC curves for poly(α-methylstyrene) (E) and for poly(2-(benzoyloxy)ethyl methacrylate-*b*-α-methylstyrene-*b*-2-(benzoyloxy)ethyl methacrylate) (F): peak E, $\bar{M}_n$(obsd) = 9300, $\bar{M}_w/\bar{M}_n$ = 1.08; peak F, $\bar{M}_n$(obsd) = 71 000, $\bar{M}_w/\bar{M}_n$ = 1.37.

In order to obtain a well-defined block copolymer that should be linear, free of homopolymer, and with a narrow molecular weight distribution of each block, we have synthesized block copolymers of α-methylstyrene with HEMA by two-step anionic living polymerization followed by hydrolysis of the protecting group.

Bifunctional DPE-capped living poly(α-methylstyrene) was prepared by the lithium naphthalide initiated polymerization of α-methylstyrene at –78 °C in THF followed by the addition of DPE (2–3 M excess of the initiator) to convert the propagating polymer ends to 1,1-diphenylmethyl carbanions. It is possible that the utilization of such a polymeric anion as an initiator of polymerization of **1** results in a triblock copolymer of ABA type where A and B blocks are poly(2-[(trimethylsilyl)oxy]ethyl methacrylate) and poly(α-methylstyrene), repectively. The A blocks were easily hydrolyzed to generate HEMA units by treatment with a few drops of 1.5 N HCl. A quantitative yield of polymer was obtained. Block copolymers with various compositions could be prepared simply by varying the ratio of each monomer charged in the polymerization. In a similar manner, a diblock AB type copolymer was successfully synthesized by the addition of **1** to the polymeric monoanion of α-methylstyrene, initially prepared from α-methylstyrene and butyllithium followed by addition of DPE.

The results of the block polymer synthesis are summarized in Table II, and the GPC curves of the representative samples are shown in Figure 3. For GPC studies block copolymers were benzoylated in a similar manner in the case of the HEMA homopolymer. As can be seen, the GPC curves show that the peak of starting poly(α-methylstyrene) shifts completely toward the higher molecular weight side after addition of **1** and that the resulting block copolymer still possesses a single peak. The compositions in all samples were determined by ^{1}H NMR and were found to be about the same as those calculated from the amounts of both monomers fed at the polymerization. The molecular weights of the polymers could be estimated by their compositions and the $\bar{M}_n$'s of the starting poly(α-methylstyrenes). They were reasonably well in agreement with those expected from monomer to initiator ratios in each sample. These results indicate that the block copolymerization is efficiently performed by this anionic method.

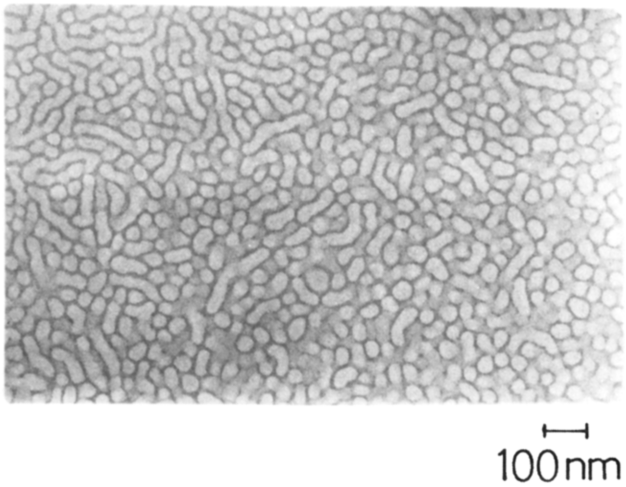


Figure 4. Electron micrograph of the film of sample 3.

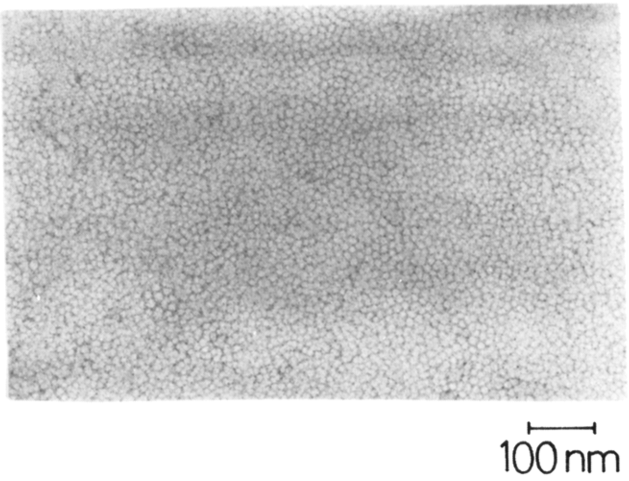


Figure 5. Electron micrograph of the film of sample 4.

Solubilities of the block copolymers are summarized in Table III. The poly(α-methylstyrene) and PHEMA data are added for convenience. As expected, a block copolymer with high HEMA content is soluble in methanol, whereas those with low HEMA content are soluble in THF and 1,4-dioxane and swollen in chloroform, dichloroethane, benzene, and toluene.

Transparent films of block copolymers could be cast from dilute solutions in either THF–acetone (5/1 (v/v)) or THF–ethanol (1/1 (v/v)) mixed solvents.

Films thus prepared were stained in an aqueous solution of uranyl acetate. The morphological observations were made with an electron microscope. As shown in Figures 4 and 5, it is clear that microphase separation occurs. The films of sample 3 with a HEMA content of 37 mol % exhibited cylinder-like (300 × 1000–2000 Å) poly(α-methylstyrene) domains embedded in a continuous PHEMA matrix, which was stained selectively by uranyl acetate. When sample 4 with a higher molecular weight

Table III
Solubilities of Block Copolymers of Poly(HEMA-*b*-α-methylstyrene-*b*-HEMAs) and Poly(α-methylstyrene) and PHEMA[a]

		block copolymers[b]				
solvent	poly(α-methylstyrene)	sample 1 (16)	sample 3 (37)	sample 4 (61)	sample 5 (86)	PHEMA
benzene	○	△	△	×	×	×
toluene	○	△	×	×	×	×
carbon tetrachloride	○	×	×	×	×	×
chloroform	○	△	×	×	×	×
dichloromethane	○	△	×	×	×	×
diethyl ether	○	×	×	×	×	×
1,4-dioxane	○	○	○	○	×	×
tetrahydrofuran	○	○	○	○	×	×
ethyl acetate	○	×	×	×	×	×
acetone	×	×	×	×	×	×
methyl ethyl ketone	○	×	×	×	×	×
N,N-dimethylformamide	○	○	○	○	○	○
pyridine	○	○	○	○	○	○
methanol	×	×	×	×	○	○
ethanol	×	×	×	×	△	○
water	×	×	×	×	×	×

[a] The symbols (○), (△), and (×) indicate soluble, swelling, and insoluble, respectively. [b] The values in parentheses indicate the mole percent of HEMA fraction in the block copolymers.

HEMA block and a lower molecular weight α-methylstyrene block was cast from a THF–ethanol solution, smaller spherical domains (100–200 Å) could be observed. Incompatibility of the segments in the block copolymer is thus apparent from these results.

The present method permits the synthesis of well-defined block copolymers with various chain lengths of each segment [polyHEMA and poly(α-methylstyrene)] in which microphase separation of the hydrophilic and hydrophobic domains occurs in different sizes and geometries.

Experimental Section

Materials. HEMA was purified from the commercial product by distillation at 67 °C (3.5 mmHg). THF was refluxed over sodium wire for 5 h and distilled from sodium naphthalide solution. Hexamethyldisilazane was kindly supplied from Shinetsu Chemical Co., Ltd. DPE was prepared by a literature procedure[14] and purified by fractional distillation. It was finally distilled together with THF from benzylmagnesium chloride in THF solution under vacuum and stored in ampules equipped with breakseals. Butyllithium was obtained from Japan Synthetic Rubber Co., Ltd. 1,1-Diphenylhexyllithium was freshly prepared just prior to polymerization from butyllithium and DPE in THF at 30 °C for 5 min. 1,4-Dilithio-, 1,4-disodio-, and 1,4-dipotassio-1,1,4,4-tetraphenylbutane were also freshly prepared just prior to polymerization from the corresponding metal naphthalides and DPE in THF at 30 °C for 5 min. The concentration of metal naphthalide was previously colorimetrically titrated with standard 1-octanol in THF in a sealed reactor through breakseals under vacuum. Phenylmagnesium chloride and benzylmagnesium chloride were prepared in THF according to standard procedure and stored in ampules equipped with breakseals. Lithium aluminum hydride was sealed in ampules equipped with breakseals as a THF solution after filtration to remove insoluble portions.

2-[(Trimethylsilyl)oxy]ethyl Methacrylate. Hexamethyldisilazane (30 g, 0.18 mol) was added dropwise over a 1-h period to 2-hydroxyethyl methacrylate (24 g, 0.18 mol). The temperature was maintained at 10 °C during the addition. A few drops of trimethylsilyl chloride were then added to the mixture at once. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. The crude product was obtained by direct distillation from the mixture. It was purified by fractional distillation at 61–62 °C (3 mmHg) to give 27 g (0.16 mol, 72%) of colorless, liquid 2-[(trimethylsilyl)oxy]ethyl methacrylate (lit.[15] 71–72 °C (2 mmHg)): 60 MHz ^{1}H NMR ($CDCl_3$) δ 6.15 (1 H, m, $HC{=}CCO$), 5.60 (1 H, m, $\mathit{HC}{=}CCH_3$), 4.40 (2 H, t, $OCOCH_2$), 3.60 (2 H, t, $CH_2\mathit{CH_2}OSi$), 2.19 (3 H, s, CH_3), 0.16 (9 H, s, $Si(CH_3)_3$).

The silylated monomer thus obtained was dried over calcium hydride with stirring for 24 h and distilled under vacuum for storage in ampules with breakseals.

Polymerization Procedures. All the operations were carried out at −78 °C under high-vacuum conditions (~10^{-6} mmHg) in an all-glass apparatus equipped with breakseals as previously reported by Morton and his co-workers.[16] All the polymerizations were carried out at −78 °C with shaking except for the polymerizations with Grignard reagents that were performed at 20 to −78 °C. The polymerizations were completed within 5 min and were terminated with a few drops of 1.5 N HCl. The polymers were collected after adding a large excess of water to precipitate. They were redissolved in methanol, precipitated into diethyl ether two additional times, and dried at 40 °C by vacuum pump.

Benzoylation of PHEMA. To 0.5 g of HEMA in 6 mL of dry pyridine under a nitrogen atmosphere was added 4.5 g of benzoic anhydride over a 30 min period at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was poured into water, and the polymer precipitated was obtained by filtration. The polymer was redissolved in THF, precipitated into methanol two additional times, and freeze-dried. The ^{1}H NMR spectrum of the resulting polymer indicates complete benzoylation of PHEMA.

Measurements. IR spectra were run with a Jasco IR-G spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL JNM-PMX 60 instrument. Gel permeation chromatograms (GPC) were obtained with a Toyo Soda HCL-802 instrument with UV or refractive index detection, THF being the elution solvent. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution. Polymer films were cast from THF–acetone or THF–ethanol solution. The as-cast films were exposed to a 1% aqueous solution of uranyl acetate, which stained the hydrophilic PHEMA domains selectively. The films were observed by transmission electron microscopy with a Hitachi TS-7 instrument.

Registry No. $LiAlH_4$, 16853-85-3; C_6H_5MgCl, 100-59-4; $C_6H_5CH_2MgCl$, 6921-34-2; BuLi, 109-72-8; Li-nap, 7308-67-0; Na-nap, 3481-12-7; K-nap, 4216-48-2; hexamethyldisilazane, 999-97-3; 2-hydroxyethyl methacrylate, 868-77-9; 2-[(trimethylsilyl)oxy]ethyl methacrylate, 17407-09-9; 1,4-dilithio-1,1,4,4-tetraphenylbutane, 7307-17-7; 1,4-disodio-1,1,4,4-tetraphenylbutane, 3970-44-3; 1,4-dipotassio-1,1,4,4-tetraphenylbutane, 52681-96-6; (1,1-diphenylhexyl)lithium, 3462-81-5.

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Photoinduced Electron Transfer in Acceptor Polymer Poly(vinyl methyl terephthalate) and Its Anion Radical Behavior Studied by Laser Photolysis

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ABSTRACT: Photoinduced electron transfer in a heteroexcimer system of excited *N*-ethylcarbazole (electron donor)–poly(vinyl methyl terephthalate) (electron acceptor) was studied by nanosecond ruby-laser photolysis in benzonitrile at room temperature. The behavior of the ion radicals thus formed in the polymer system was investigated in comparison with those in model compounds: dimethyl terephthalate and three dimer model compounds. The transient absorption spectrum of the acceptor polymer system was the same as those of the monomer and dimer model compounds. However, anion radical transfer experiments show that the anion radical formed in the polymer chain does not transfer to an acceptor *p*-dicyanobenzene, while the anion radical in the monomer and dimer systems easily transfers the electron to the acceptor *p*-dicyanobenzene. The results suggest that the anion radical in the polymer system is stabilized by the interaction with neighboring chromophores and its electron transfer is suppressed.

Introduction

Polymer systems show several photophysical and photochemical behaviors characteristic of a high local concentration of chromophores in contrast to dilute homogeneous systems. For example, efficient energy migration along the polymer chain[1] and considerable annihilation of excited states under high-intensity excitation have been reported.[2,3] As for the photoionization process of polymer systems, peculiar solvent effects,[4-6] e.g., emission spectra of transient excited species are not much affected by solvent polarity and have been observed for copolymers that have pendant electron donor and acceptor groups. Also, the cation radical formed in poly(*N*-vinylcarbazole) (PVCZ) was reported to be stabilized by the neighboring chromophores.[7] As for the stabilization of ion radicals, dimer cation radicals have been well investigated by ESR[8] and optical spectroscopy after γ-ray irradiation in rigid media[9-12] and by the pulse radiolysis method.[13] However, very little knowledge about dimer anion radicals has been obtained thus far,[14] since only under special conditions are the dimer anion radicals of aromatic compounds formed.[15]

It is known that excited singlet carbazole residue interacts with dimethyl terephthalate (DMTP) and forms a heteroexcimer in nonpolar solvents and that in polar solvents photoionization occurs and carbazole cation radical and DMTP anion radical are produced.[16,17] In this study, the photoinduced electron-transfer process and the behavior of ion radicals thus formed were investigated for the system of *N*-ethylcarbazole (ECZ)–poly(vinyl methyl terephthalate) (PMTP). With regard to photoinduced electron transfer, the electron-transfer rate constant, the quantum yield of ion radical formation, and the ion radical recombination rate constant for the polymer were compared with those of the monomer and dimer model compounds. The stabilization of anion radicals in the polymer was investigated by the ion radical transfer method.[18] The results show several polymer effects, e.g., higher yield of ion radical formation and stabilization of ion radicals in the polymer chains.

Results

Photoionization of Methyl Terephthalate (MTP) Derivatives. The compounds studied in this investigation are denoted in Figure 1 with their abbreviations. DMTP is a monomer model of PMTP, whereas, 1,2-MTP, 1,3-MTP, and 2,4-MTP (racemate) are the dimer models of PMTP. In this paper, MTP represents the methyl terephthalate residue $CH_3OCOPhCOO-$.

The fluorescence quenching rate constant of $^1ECZ^*$ by MTP residue was obtained from the Stern–Volmer plot and is listed in Table I. Quenching rate constants (k_q) for DMTP and dimer models are all approximately the diffusion-controlled values, ca. 10^{10} M^{-1} s^{-1}. The k_q value for the $^1ECZ^*$–PMTP system is not listed since the effective chromophore concentration of the polymer system cannot be estimated.

Laser photolysis experiments were carried out for the systems of ECZ–electron acceptors in benzonitrile solvent at room temperature. ECZ was excited by a second harmonic pulse of a *Q*-switched ruby laser (347 nm, 14-ns pulse width). The electron-transfer process from excited singlet ECZ ($^1ECZ^*$) to MTP residue produces the cation

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