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Poly(ethylene oxide) Macromonomers. 8. Preparation and Polymerization of ω-Hydroxypoly(ethylene oxide) Macromonomers

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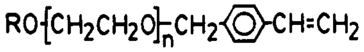
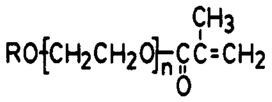
ABSTRACT: The potassium alkoxide (3) of *tert*-butyldimethylsilyl ether of ethylene glycol successfully initiated a living polymerization of ethylene oxide to a controlled degree of polymerization with a narrow distribution. End-capping with *p*-vinylbenzyl chloride and methacryloyl chloride, followed by desilylation with tetra-*n*-butylammonium fluoride afforded the corresponding ω-hydroxypoly(ethylene oxide) macromonomers (**1a** and **2a**). The radical copolymerization of the macromonomers with styrene and their homopolymerization in benzene have revealed reactivities similar to those of the corresponding ω-methoxy derivatives. Micellar polymerization in water, however, occurred more rapidly to give an apparently simpler, starlike polymer with a number of hydrophilic, poly(ethylene oxide) arms with ω-hydroxy end groups.

Introduction

Poly(ethylene oxide) (PEO) macromonomers, 1 and 2, are amphiphilic, being soluble in a variety of solvents including benzene and water, a unique property that cannot be expected for conventional monomers. Indeed the polymerizations of 1 or 2 with ω-alkoxy groups (C_1 to C_{18} for R) were found in water to occur unusually rapidly to give amphiphilic comb- or starlike polymers of very high molecular weights.[1] Organization of their α-terminal double bonds into the micelle was considered as a key factor for their enhanced polymerization. The significant effects of the ω-alkoxy groups and the PEO chain lengths on the polymerizability were observed, indicating the importance of their relative molecular density or arrangement in the micelle. Since both the ω-alkoxy group, higher than methoxy, and the α-polymerizing group are hydrophobic, they tend to organize into the micelle core, so that the hydrophilic, internal PEO chains are forced to assume loop conformations to make the surrounding shell. On the other hand, either a ω-methoxy or ω-hydroxy group will take full advantage of the hydrophilic PEO chains, allowing them to extend freely into the aqueous media, while the hydrophobic α-polymerizing groups will aggregate compactly to make the core, resulting in a simpler micelle of starlike structure.[2] The PEO macromonomers with ω-methoxy groups were in fact found to polymerize more rapidly than those with longer ω-alkoxy groups including *n*-butyl and *tert*-butyl, just as expected from their relative molecular density in the micelle as estimated by the light scattering measurement of their nonpolymerizable models.



(1) R-PEO-VB-n



$RO{-}[CH_2CH_2O]_n{-}C(=O)C(CH_3){=}CH_2$

(2) R-PEO-MA-n

a: R=H, b: R=tBuMe$_2$Si

To extend the possibility of the micellar organized polymerization of the PEO macromonomers, this paper will discuss the preparation and polymerization of the ω-hydroxy derivatives, **1a** and **2a**, as the simplest and the most hydrophilic PEO macromonomers. The alcoholic group as the ω-end may be further utilized to introduce the other functions such as drugs.

Three approaches have so far been reported for preparation of the PEO derivatives with a hydroxy group at one end and another group at the other. Tanizaki[3] reported the synthesis of the ω-hydroxypoly(ethylene oxide) meth-

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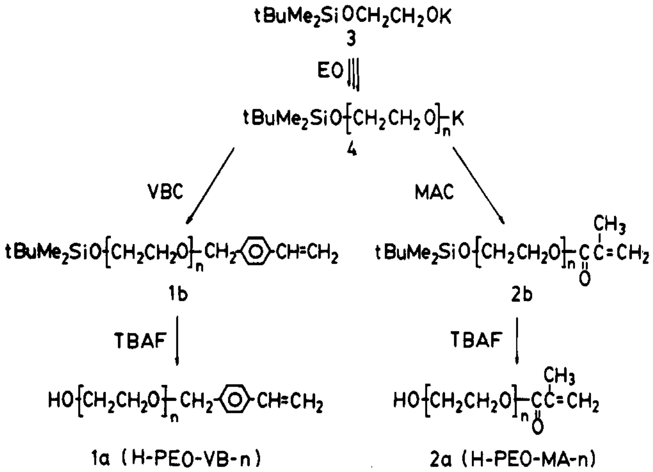
Scheme I



acrylate (**2a**) by cationic oligomerization of ethylene oxide (EO) in the presence of 2-hydroxyethyl methacrylate. In spite of the simplicity of this process, the degree of polymerization, DP_n, attained was low, less than 20, and its distribution is relatively broad. Rempp and co-workers[4] used potassium *p*-isopropenylbenzylate to initiate the anionic polymerization of EO to obtain a derivative of **1a**. This method, however, cannot apply to the preparation of the α-methacryloyl derivative, **2a**. Wagener and co-workers[5] employed an acetal-masked initiator, potassium alkoxide of monoacetalized 1,5-pentanediol, to polymerize EO, and then pivalolactone mediated by succinic anhydride, to prepare a block telechelomer carrying ω-hydroxy and α-carboxy end groups. Although this method appears to be also applicable to the present objective, the initiator is rather complicated in preparation, and it may suffer from a problem in acid-catalyzed demasking after introduction of a polymerizable *p*-vinylbenzyl group at the α-end. Therefore, we have developed here a silyl protection method as a simpler and probably more generally applicable procedure. We attempted polymerization of EO with potassium trimethylsilanolate in tetrahydrofuran (THF), but the molecular weight was controlled with difficulty and with a broad distribution, probably because of a slow initiation of the silanolate as compared to propagation of the alkoxide and a possible redistribution of the chain ends involving trimethylsilyl ethers. Then, a potassium alkoxide of ethylene glycol *tert*-butyldimethylsilyl ether (**3**), having the same alkoxide structure as the propagation species, was found to be very effective for the present purpose. Scheme I summarizes the preparation. The polymerization of EO was living to give a well-controlled polymer with a sharp distribution in DP and good end functionality. *p*-Vinylbenzyl chloride (VBC) and methacryloyl chloride (MAC) were used for the α-end-capping, and an ω-silyl group was successfully deprotected by use of tetra-*n*-butylammonium fluoride (TBAF) according to Corey and Venkateswarlu.[6]

Experimental Section

Materials. Ethylene glycol *tert*-butyldimethylsilyl ether was prepared from ethylene glycol, sodium hydride, and *tert*-butyldimethylsilyl chloride, kindly supplied from Shinetsu Chemical Co., Ltd., according to the procedure described by McDougal and co-workers.[7] It was distilled under vacuum over calcium hydride and dissolved in THF. The solution was reacted under vacuum by titrating with a THF solution of potassium naphthalene, until the green did not disappear after addition of 1 or 2 drops of excess of the latter, to afford a THF solution of the alkoxide **3** with no free alcohol. EO, from Seitetsu Chemical Co., Ltd., was distilled twice over potassium hydroxide under argon and twice under vacuum over calcium hydride and finally stirred over a potassium mirror for 1 h at 0 °C and distilled into a tube with a breakable seal. TBAF was used as supplied commercially as a 1 M THF solution, Janssen Chimica. VBC, MAC, THF, and other reagents were used as previously described.[1,8]

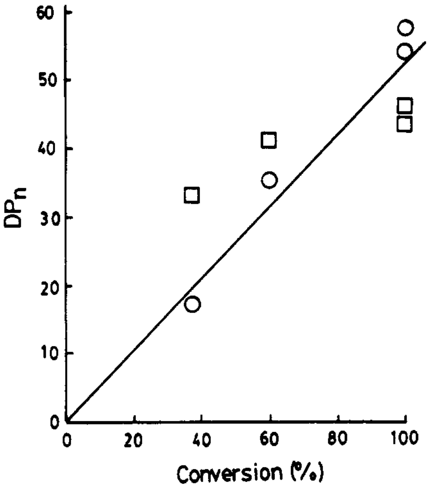
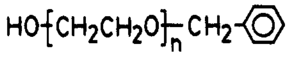
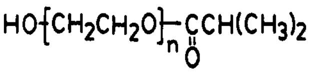


Figure 1. DP_n vs conversion plots for polymerization of EO with $tBuMe_2SiOCH_2CH_2OK$ (**3**) in THF at 40 °C. The straight line is thereotical for living polymerization. DP_n determined by ^1H NMR (○) and GPC (□).

Preparation of Macromonomers and Their Nonpolymerizable Models. Polymerization of EO with $tBuMe_2SiOCH_2CH_2OK$ (**3**) was conducted in THF at 40 °C under vacuum using a breakable-seal technique[8] and end-capped by reaction with excess VBC and MAC to afford the ω-silylated macromonomers (**1b** and **2b**, respectively). The polymers were freed from potassium chloride, collected, and purified as described before.[8] Desilylation was performed with TBAF in THF according to Corey.[6] TBAF solution, in 3-fold molar excess, was added to the THF solution of **1b** or **2b**, and the mixture was stirred at 0 °C for 0.5 h. The polymers were precipitated into hexane, washed repeatedly with hexane, and dried under vacuum. They were then dissolved in water, stirred about 0.5 h at room temperature with about 3-fold excess equivalents of mixed ion exchange resins, Amberlite-120 and IRA-410, to remove the free salts, filtered, and freeze-dried. The nonpolymerizable macromonomer models (**5** and **6**) were similarly prepared by reacting the living polymers (**4**) with benzyl chloride and isobutyroyl chloride, respectively, followed by desilylation with TBAF. ω-Methoxypoly(ethylene oxide) macromonomers, C_1-PEO-VB-*n*, with R = CH_3 in **1** and the degrees of polymerization, *n* = 25, 45, and 60, were prepared as previously described.[1]



(5) H-PEO-Bz-n



$HO[CH_2CH_2O]_nC(=O)CH(CH_3)_2$

(6) H-PEO-IB-n

Methods of Characterization. Gel permeation chromatography (GPC), ^1H NMR (270 MHz), vapor pressure osmometry (VPO), and laser light scattering were measured with the same apparatus and in the same procedure as previously described.[1,8]

Copolymerization of the Macromonomers with Styrene. **1a** or **2a** was copolymerized with a large molar excess of styrene (M_1) to evaluate their relative reactivity toward a polystyryl radical. The total monomer weight was ca. 2 g in 10 mL of benzene, with 1 mol % of 2,2′-azobis(isobutyronitrile) (AIBN) as

Table I
Polymerization of EO with tBuMe$_2$SiOCH$_2$CH$_2$OK (3)[a]

			polymers				
			^{1}H NMR[b]		GPC[c]		
run	polymzn time, h	convn, %	M_n	DP$_n$	M_n	DP$_n$	M_w/M_n
1	2	37	760	17	1600	34	1.12
2	4	60	1550	35	1930	41	1.10
3	24	100	2380	54	2130	46	1.08
4	24	100	2550	58	2030	44	1.06

[a] Polymerization condition: EO = 194 mmol, 3 = 3.8 mmol, THF = ca. 100 mL, 40 °C. [b] Determined from the peak intensity ratio of oxyethylene (δ 3.6) to tBuMe$_2$Si (δ 0.8 and 0.0) protons.[c] Calibrated with linear PEO standard samples.

Table II
Characterization of Macromonomers

	VPO		^{1}H NMR[a]		GPC[b]
macromonomer	M_n	DP$_n$	M_n	DP$_n$	M_w/M_n
H-PEO-VB-46	2100	46	2200	48	1.07
H-PEO-VB-65	2950	65	2750	60	1.05
H-PEO-MA-53	2400	53	2490	55	1.07
H-PEO-MA-67	3000	67	2800	62	1.07

[a] Determined from the peak intensity ratio of oxyethylene to tBuMe$_2$Si protons of the corresponding prepolymers. [b] Calibrated with linear PEO standard samples.

an initiator. The molar ratio, $[M_1]/[M_2]$, was changed over ca. 140 through ca. 2000. Polymerization was done at 60 °C, usually for several hours, to less than 20% conversion. Purification of copolymers and the composition analysis by ^{1}H NMR were performed by the same procedure as previously described.[8]

Homopolymerization of Macromonomers. The rate of homopolymerization of **1a** or **2a** was monitored by ^{1}H NMR at 60 °C either in water (D$_2$O) with 4,4′-azobis(4-cyanovaleric acid) (AVA) or in benzene (C$_6$D$_6$) with AIBN, by following the disappearance of the double bond peak in reference to the oxyethylene peak (see Figures 3 and 4), similar to that described in a previous paper.[1]

Results and Discussion

Polymerization of EO with tBuMe$_2$SiOCH$_2$CH$_2$OK (3) and Preparation of ω-Hydroxypoly(ethylene oxide) Macromonomers. It is well-known that polymerization of EO with alkali alkoxides in aprotic solvents proceeds without termination or transfer, though the kinetics may be complicated because of aggregation of the active species.[9] Potassium alkoxides, among others, appear to have been the most convenient to initiate the polymerization under a mild condition to a polymer with a narrow DP distribution.[1,4,5,8] A recent kinetic study by Reuter and co-workers[10] using cumyl or diphenylmethyl potassium clearly demonstrates the living polymerization of EO with potassium as the counterion.

The initiator **3** in THF was also found to initiate the living polymerization of EO, with a reasonable activity to get a quantitative yield at 40 °C in less than 1 day. Figure 1 and Table I show the linear increase in DP$_n$, as estimated from ^{1}H NMR, with conversion, in accord with the expression for a living polymerization, DP$_n$ = conversion × $[M]_0/[I]_0$, where $[M]_0$ and $[I]_0$ are the initial molar concentrations of the monomer and the initiator, respectively.[11] Distribution in DP was also narrow, with M_w/M_n less than 1.1. The DP$_n$ estimated from GPC was considerably different from that from ^{1}H NMR, probably because the calibration of GPC by use of PEO standard samples cannot properly apply to the present PEO polymers of relatively low DP and with bulky *tert*-butyldimethylsilyl end groups. The living nature of polymerization was also clear by the result in Figure 2, which shows the linear increase in DP$_n$, with the same narrow distribution, even after complete polymerization of the second EO monomers added to the first polymerized batch.

Table III
Monomer Reactivity Ratio (r_1) in Copolymerization of Styrene (M$_1$) with Macromonomers and Their Models (M$_2$)

M$_2$	r_1	M$_2$	r_1
styrene	(1.0)	methyl methacrylate[a]	0.30–0.62
p-methylstyrene[a]	0.89		
H-PEO-VB-46	1.45 ± 0.06	2-hydroxyethyl methacrylate[a]	0.33–0.59
H-PEO-VB-65	1.68 ± 0.06		
C$_1$-PEO-VB-25	1.31 ± 0.09	H-PEO-MA-53	0.83 ± 0.12
C$_1$-PEO-VB-45	1.48 ± 0.03	H-PEO-MA-67	1.12 ± 0.08
C$_1$-PEO-VB-60	1.71 ± 0.11		

[a] The data are from ref 14. Other data are the results of this work in copolymerization at 60 °C in benzene with AIBN.

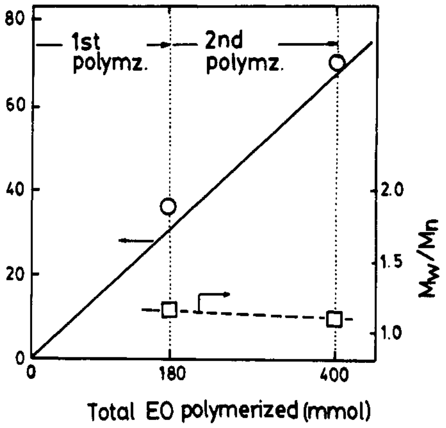


Figure 2. Dependence of DP$_n$ (by ^{1}H NMR) and M_w/M_n (by GPC) on the amount of EO polymerized in two times. The straight line is theoretical for living polymerization. tBuMe$_2$SiOCH$_2$CH$_2$OK (3) = 6 mmol, THF = ca. 100 mL, EO = 180 mmol (initial charge), and 220 mmol (2nd charge), polymerization time = 24 h each.

The end capping of the living polymer alkoxide (**4**) by VBC or MAC was successful to afford the α-polymerizable end groups as was confirmed by ^{1}H NMR for the satisfactory relative peak intensities of the corresponding α- and ω-standing end groups, i.e., *p*-vinylbenzyl or methacryloyl and *tert*-butyldimethylsilyl groups, in reference to those of the oxyethylene protons. Figure 3a shows an example for the polymer **1b** with n (by VPO) = 46.[12]

Desilylation from the ω-end to afford ω-hydroxyl was also successful by treatment with TBAF at 0 °C without any reaction on the α-end polymerizable groups. Figures 3b and 4 show their ^{1}H NMR spectra. Complete absence of the peaks due to *tert*-butyldimethylsilyl protons and instead the appearance of those due to ω-hydroxyl protons are clear in the spectra. Figure 3c shows that the peak due to ω-hydroxyl disappeared in measurement in D$_2$O. Table II summarizes the characterization of the macromonomers used for copolymerization and homopolymerization studies that follow. The agreement between the DP$_n$ determined by ^{1}H NMR and that by VPO also supports the satisfactory end-group functionality.

Copolymerization of Macromonomers with Styrene. Reactivity of the ω-hydroxypoly(ethylene oxide) macromonomers (**1a** and **2a**) was first evaluated in copolymerization with a very large molar excess of styrene as M$_1$ so that the conventional composition equation can be reduced to the approximate expression as follows.[8,13]

$$d[M_1]/d[M_2] = r_1[M_1]/[M_2] \qquad (1)$$

Here r_1 is the monomer reactivity ratio of M$_1$, $r_1 = k_{11}/k_{12}$, where k_{11} and k_{12} are the rate constants of the correspond-

Table IV
Micelle Formation of Macromonomer Models in Water at 25 °C[a]

macromonomer model	cmc × 10^{-5}, mol/L	M_m	m	$\langle s^2\rangle^{1/2}$, m	V_m, m^3	m/V_m, m^{-3}
H-PEO-Bz-53	$1._1$	$8._7 \times 10^4$	$4._5 \times 10$	$5._1 \times 10^{-8}$	$1._2 \times 10^{-21}$	$3._8 \times 10^{22}$
C_1-PEO-Bz-45[b]	$3._0$	$1._1 \times 10^6$	$5._2 \times 10^2$	$1._7 \times 10^{-7}$	$4._5 \times 10^{-20}$	$1._2 \times 10^{22}$
H-PEO-IB-51	$6._4$	$1._8 \times 10^4$	$7._7$	$2._5 \times 10^{-8}$	$1._4 \times 10^{-22}$	$5._5 \times 10^{22}$
C_1-PEO-IB-25[b]	$7._1$	$2._3 \times 10^4$	$1._9 \times 10$	$2._5 \times 10^{-8}$	$1._4 \times 10^{-22}$	$1._4 \times 10^{23}$

[a] Subscript figures in the first decimal place indicate an uncertainty of ±0.1 to ±0.3 in determining cmc, M_m, and $\langle s^2\rangle^{1/2}$. [b] Data of ref 1.

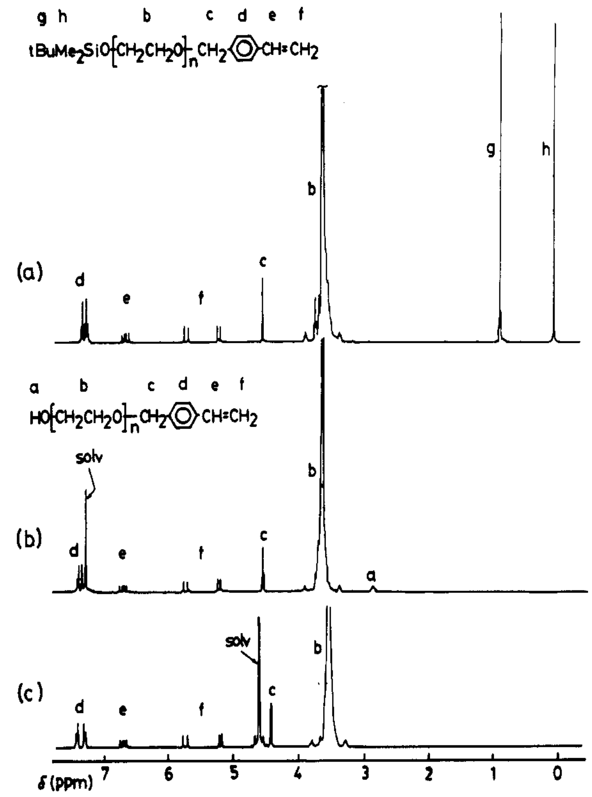


Figure 3. ^1H NMR spectra of macromonomers: (a) **1b** ($n = 46$) in $CDCl_3$, (b) **1a** ($n = 46$) in $CDCl_3$, (c) **1a** ($n = 46$) in D_2O.

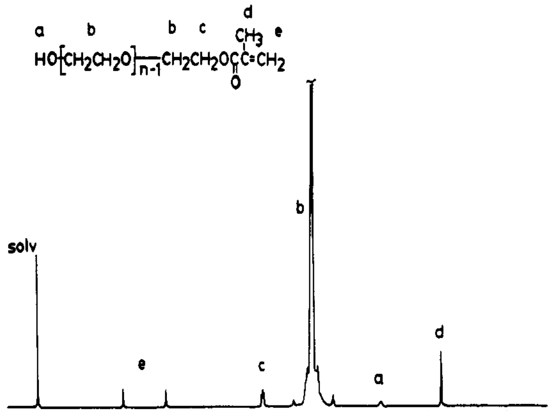


Figure 4. ^1H NMR spectrum of a macromonomer, **2a** ($n = 53$) in $CDCl_3$.

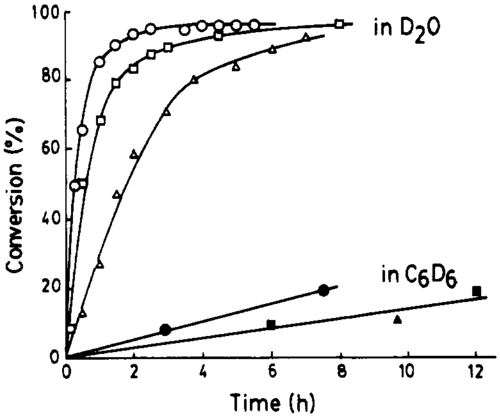


Figure 5. Conversion vs time plots for polymerization of H-PEO-MA-67 (○), H-PEO-VB-65 (□), and C_1-PEO-VB-60 (△) in water at 60 °C with [M] = 45 mmol/L and [AVA] = 0.45 mmol/L. The solid symbols refer to the corresponding polymerization in benzene with [M] = 45 mmol/L and [AIBN] = 2.25 mmol/L.

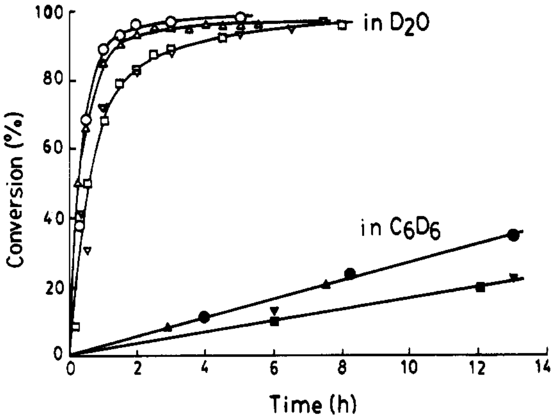


Figure 6. Conversion vs time plots for polymerization of H-PEO-MA-53 (○), H-PEO-MA-67 (△), H-PEO-VB-46 (▽), and H-PEO-VB-65 (□) in water at 60 °C with [M] = 45 mmol/L and [AVA] = 0.45 mmol/L. The solid symbols refer to the corresponding polymerization in benzene with [M] = 45 mmol/L and [AIBN] = 2.25 mmol/L.

ing propagation reactions.

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1^{\bullet} \qquad (2)$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_2^{\bullet} \qquad (3)$$

Therefore the reciprocal ($1/r_1$) can be a measure of the relative reactivity of the macromonomer (M_2) toward the polystyryl radical ($\sim M_1^{\bullet}$).

The copolymerization was conducted to low conversions in benzene with AIBN as an initiator and analyzed for the copolymer composition by ^1H NMR according to the same procedure as described before.[8] The parameters r_1 determined were found to be independent of the monomer molar ratios, supporting the approximation in eq 1 under the present condition. Table III summarized the r_1 data for H-PEO-VB (**1a**) and H-PEO-MA (**2a**), in comparison with those for the corresponding ω-methoxy macromonomers, C_1-PEO-VB, together with the literature data for the low molecular weight monomers.[14] By comparing their reciprocal values ($1/r_1$), it is reasonable to conclude as before[8] that all the macromonomers have similarly lower relative reactivities toward a polystyryl radical as compared to the corresponding low molecular weight monomers such as styrene and methyl methacrylate. The effect is more pronounced with increasing DP_n of the macromonomer.

Therefore, a thermodynamic repulsion between these incompatible polymer pairs, PEO and polystyrene,[8] appears to be a factor in retarding their mutual reaction. The difference in the ω-end groups, ω-hydroxy vs ω-methoxy, however, had little effect on their copolymerization reactivity in benzene, as expected because the ω-end itself cannot significantly affect the polymer–polymer interaction in such a good solvent.

Homopolymerization of Macromonomers. Radical homopolymerizations of the macromonomers (**1a** and **2a**) were conducted either in benzene with AIBN or in water with AVA, with the results given in Figures 5 and 6. As observed before with ω-alkoxy macromonomers,[1] ω-hydroxy derivatives also polymerized apparently homogeneously throughout.[15] Again, the polymerization in water was much more rapid in water than in benzene, and α-methacrylate was considerably more reactive than α-p-vinylbenzyl ether, as expected. Interestingly in Figure 5, ω-hydroxy macromonomers in water were found to be somewhat more reactive than the corresponding ω-methoxy derivatives, but not so in benzene as in the case of copolymerization with styrene. Laser light scattering measurements were made in water with the corresponding nonpolymerizable macromonomer models (**5** and **6**) to confirm their micelle formation. Table IV gives the critical micelle concentration (cmc), micellar weight (M_m), average number of aggregations in a micelle (m), root-mean-square radius of gyration ($\langle s^2 \rangle^{1/2}$), micellar volume ($V_m$) assuming a sphere, and relative molecular density in a micelle (m/V_m), estimated similarly as described before.[1] In accord with the previous discussion,[1] the parameter m/V_m appears to parallel the rate of polymerization. Thus the ω-hydroxy derivative organized into a more compact, denser micelle, giving rise to a higher rate of polymerization than the corresponding ω-methoxy derivative with a comparable DP_n. It may be speculated that the more hydrophilic PEO chains with ω-hydroxy ends will cause their hydrophobic, polymerizable α-ends to organize more compactly into the core, while ω-methoxy groups may interact even a little with the α-ends, allowing a somewhat looser organization.[16] The effect of the PEO chain lengths on the polymerizability was almost negligible within the range of DP_n investigated as in Figure 6.

The molecular weights of the homopolymers isolated appear to be higher than 10^5, as evaluated from GPC calibrated with linear PEO standard samples, which will severely underestimate the MW of these highly branched, starlike polymers.[1,17] So by dividing by the MW of about 2×10^3 for each macromonomer, the DP_n of the corresponding hydrophobic trunk chains in a polymerized micelle would be estimated to be on the order of 50 or more.

Conclusions

The potassium salt of monosilylated ethylene glycol (**3**) effectively initiated the living polymerization of EO to afford ω-hydroxypoly(ethylene oxide) macromonomers (**1a** and **2a**), after end-capping with VBC and MAC followed by desilylation with TBAF. The macromonomers in water organized into simple, compact micelles with the α-polymerizable end groups as the core, resulting in very rapid polymerization to an apparently starlike, soluble polymer with a number of fully extended hydrophilic PEO chains terminated with ω-hydroxy groups, which can be the simplest model of a fixed PEO micelle.

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(11) The data in Table I for the polymerization time (t) of 2 and 4 h were satisfactorily fitted to the kinetic expression; $-\ln(1-\theta) = k_p[I]_0 t$, where θ is a fractional conversion and k_p the apparent rate constant of propagation. Estimated $k_p[I]_0$ and k_p were 6.4×10^{-5} s^{-1} and 1.9×10^{-3} L mol^{-1} s^{-1}, respectively.
(12) The relative intensities (areas) for the peaks b/c/d/e/f/g/h were 192/2/4/1/2/9/6 in satisfactory accord with those expected, 184/2/4/1/2/9/6.
(13) (a) Schulz, G. O.; Milkovich, R. *J. Polym. Sci., Polym. Chem. Ed.* 1984, *22*, 1633. (b) Sierra-Vargas, J.; Franta, E.; Rempp, P. *Makromol. Chem.* 1981, *182*, 2603.
(14) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 3rd ed.; Wiley-Interscience: New York, 1989.
(15) The radical chain transfer through the benzylic hydrogens with the transfer constant around 0.0021 has been reported for the polymerization of butyl acrylate in the presence of a benzyl ether model compound; Hamaide, T.; Revillon, A.; Guyot, A. *Eur. Polym. J.* **1987**, *23*, 787. Although this transfer, if it occurs, may complicate the polymerization of PEO–VB macromonomers (**1**), all the systems were apparently homogeneous both in benzene and in water at least under the conditions investigated. We suppose that the transfer constant may be even smaller for the present case involving a more resonance-stabilized styrenic polymer radical and a PEO–VB macromonomer of a much higher DP or its polymer. An organized micellar polymerization in water may also be a factor for reducing the possibility of chain transfer as well as termination reactions.
(16) In Table IV, it can be seen as generally expected, that the more hydrophilic model gives a micelle of a lower degree of aggregation, m, and of a smaller size, $\langle s^2 \rangle^{1/2}$, if compared at a similar DP. Thus the decreasing order of m (or $\langle s^2 \rangle^{1/2}$) such that C_1–PEO–Bz-45 > H–PEO–Bz-53 > C_1–PEO–IB-25 > H–PEO–IB-51 appears to be in accordance with the expected increasing order of hydrophilicity. The observed trend in cmc, however, is not necessarily in line with that expected from the hydrophilicity, and the values of the cmc's are significantly lower than those cited for the conventional nonionic surfactants such as a nonyl phenyl ether of poly(ethylene glycol), e.g., cmc $= 7.5 \times 10^{-6}$ and 1.8×10^{-4} mol/L for DP = 10 and 31, respectively: Rossen, M. J. *Surfactants and Interfacial Phenomena*; Wiley-Interscience: New York, 1978; through *Kagaku Binran (Handbook of Chemistry)*, 3rd ed.; Maruzen: Tokyo, 1984. We can say nothing for the reason at present, but we have determined the cmc as the concentration above which the scattering intensity or the Rayleigh ratio significantly increased (ref 1), and cmc may be a quantity of only phenomenological importance, which can vary depending on the method of measurement, rather than a strict thermodynamic constant, as pointed out by: Elias, H. G. *J. Macromol. Sci., Chem.* **1973**, *A7*, 601.
(17) (a) Tomi, Y.; Imai, G.; Ito, K. *Polym. Prepr., Jpn.* **1989**, *38*, 1657. (b) Tomi, Y.; Imai, G.; Kawaguchi, S.; Ito, K. *Polym. Prepr., Jpn.* **1990**, *39*, 166. (c) Kawaguchi, S.; Tomi, Y.; Ito, K., to be published.