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One-step synthesis of α-*p*-vinylphenylalkyl-ω-hydroxy poly(ethylene oxide) macromonomers by anionic polymerization initiated from *p*-vinylphenylalkanols

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Abstract

ω-(*p*-Vinylphenyl)alkanols, including methanol, ethanol, propanol, pentanol, and hexanol, have been partially alkoxidated with potassium naphthalene to initiate anionic polymerization of ethylene oxide (EO) in order to directly prepare the corresponding α-*p*-vinylphenylalkyl-ω-hydroxy poly(ethylene oxide) (PEO) macromonomers. *p*-Vinylphenylmethanol, i.e. *p*-vinylbenzyl alcohol (VBA) afforded the expected well-defined macromonomer via living polymerization mechanism and the kinetics have been examined as a function of extent of potassium-alkoxidation. Other alcohols such as *p*-vinylphenylpropanol (VPP), -pentanol (VPPT), and -hexanol (VPH) were also successful to afford the corresponding PEO macromonomers, while *p*-vinylphenylethanol (VPE) alkoxide polymerized EO to give *p*-divinylbenzene and poly(ethylene glycol) without *p*-vinylphenylethoxy end group, which were supposed to form by a very facile intramolecular chain transfer of the activated oligomeric alkoxide chain end to abstract a benzylic proton of the initiating fragment.

Keywords: Ethylene oxide; Anionic polymerization; Macromonomers

1. Introduction

Reactive or polymerizable amphiphiles have been of increasing concern because of their organizing properties to construct well-defined polymeric architecture [1]. Among others, so-called macromonomers have been useful in design of branched polymers by homo- and co-polymerization [2]. We have been particularly interested in poly(ethylene oxide) macromonomers carrying a hydrophilic poly(ethylene oxide) (PEO) chain and a hydrophobic polymerizable end group. They were found to organize into micelles in water and polymerize very rapidly to afford comb or brush polymers [3–10], copolymerize with a small amount of styrene solubilized in the micelles to give unimolecular nanoparticles [11], and copolymerize with excessive amounts of styrene in emulsion or dispersion system to monodisperse polymeric microspheres of submicron to micron size [12–14].

So far conventional syntheses of macromonomers have involved introduction of polymerizable functions onto living polymer chain ends, called termination method [2]. Styryl-ended PEO macromonomers have also been successfully prepared by this method by polymerizing ethylene oxide (EO) followed by termination with corresponding *p*-vinylphenylalkyl halides (Scheme 1(a)). Terminating agents, however, are needed to be used in considerable excess on molar basis, even more than 4 times excess in case of the bromides of $m = 4$ or 7 in order to overcome the consumption due to a side reaction such as elimination [4]. So here comes an idea of 'initiation' method (Scheme 1(b)) in which *p*-vinylphenylalkanols are used as the initiator for polymerization of EO.

If favorable, the initiation method utilizes all the initiator functions effectively incorporated as the chain ends to afford the expected macromonomers in one-step. Moreover, the PEO macromonomers obtained after work-up should have hydroxy groups as the other chain ends, which were introduced in the termination method in some money- and time-consuming procedure, for example by starting with silyl-protected alkoxide as an initiator to polymerize EO followed by termination and subsequent deprotection [5]. A

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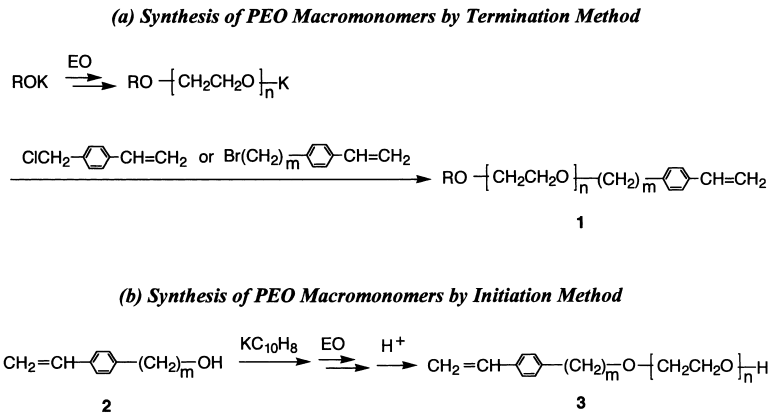


Scheme 1.

problem involved here in the initiation method is just the requirement of no reaction between the propagating chain end and the initiator fragment. Since the oxy anions are usually believed to react very hardly with styryl functions, the situation appears very favorable [15–18]. In fact, Rempp and co-workers used potassium *p*-isopropenylbenzylate successfully to polymerize EO [19] and very recently Soula and Guyot used potassium vinylbenzylate to polymerize butylene oxide and EO successively to obtain the block macromonomers [20].

In this paper we present the results of using various ω-(*p*-vinylphenyl)alkanols, **2**, which are partially alkoxidated with potassium naphthalene to polymerize EO to obtain well-defined PEO macromonomers, **3**, carrying styryl end groups with varying hydrophobic alkylene spacers ($m = 1$, 3, 5, 6) and controlled hydrophilic PEO chain lengths. Detailed kinetics of EO polymerization with *p*-vinylbenzyl alcohol will be also discussed as a function of degree of alkoxidation. To our knowledge, such information under extremely dry and high vacuum condition has not been available but will provide fundamental understanding of anionic polymerization of EO. Also some unexpected but interesting result with 2-(*p*-vinylphenyl)ethanol as an initiator (**2**, $m = 2$) will be included.

2. Experimental

2.1. Materials

p-Vinylbenzyl alcohol (VBA) (**2**, $m = 1$) was prepared from *p*-vinylbenzyl chloride (VBC) by reaction with sodium acetate followed by alkaline hydrolysis, according to the procedure described [20,21]. ^{1}H NMR in $CDCl_3$ (Fig. 2(A)): δ 1.8 (br, H; $-CH_2OH$); δ 4.65 (br., 2H; $-CH_2OH$); δ 5.25 (dd, 1H; $=CH_2$); δ 5.75 (dd, 1H; $=CH_2$); δ 6.75 (dd, 1H; $-CH=$), and δ 7.37 (q, 4H; C_6H_4).

2-(*p*-Vinylphenyl)ethanol (VPE) (**2**, $m = 2$) was prepared from *p*-chlorostyrene, via Grignard reagent followed by reaction with EO [22]. ^{1}H NMR: δ 2.33 (t, 1H; $-CH_2OH$); δ 2.84 (t, 2H; $-ArCH_2CH_2OH$); δ 3.80 (m, 2H; $-CH_2CH_2OH$); δ 5.24 (dd, 1H; $=CH_2$); δ 5.75 (dd, 1H; $=CH_2$); δ 6.72 (dd, 1H; $-CH=$), and δ 7.35 (q, 4H; C_6H_4).

3-(*p*-Vinylphenyl)propanol (VPP) (**2**, $m = 3$) was prepared from VBC, via Grignard reagent followed by reaction with EO as follows. A solution of VBC (0.2 mol, 30.5 g) in dry ether (80 mL) was dropped over 1 h under vigorous stirring into finely crushed magnesium turnings (0.22 mol, 5.3 g) in ether (120 mL) with a small amount of iodine. Temperature was kept at 0–10 °C. The reaction was continued for 1 h further without cooling. Then, cooled EO (0.4 mol, 20 mL) was added into the flask chilled at −78 °C, stirred for 1 h after the temperature was allowed to rise to ambient, followed by hydrolysis 2N aq. HCl. The organic layer was washed with water, dried over $MgSO_4$, and filtered. Ether was evaporated and the residue was distilled under a reduced pressure. Bp 90–95 °C/6–8 Torr. Yd. 70%. ^{1}H NMR: δ 1.38 (br, 1H; $-CH_2OH$); δ 1.9 (m, 2H; $-ArCH_2CH_2CH_2OH$); δ 2.7 (t, 2H; $-ArCH_2CH_2-$); δ 3.68 (t, 2H; $-CH_2OH$); δ 5.20 (dd, 1H; $=CH_2$); δ 5.71 (dd, 1H; $=CH_2$); δ 6.70 (dd, 1H; $-CH=$), and δ 7.26 (q, 4H; C_6H_4).

5-(*p*-Vinylphenyl)pentanol (VPPT) (**2**, $m = 5$) was prepared from *p*-(3-bromopropyl)styrene [23] via Grignard reagent followed by reaction with EO as above, except that the reaction with EO was conducted at 40 °C for 24 h in a closed system under vacuum with breakable seal technique, in a similar procedure for EO polymerization (see below). Ether extract was evaporated and freeze-dried from benzene. Yd. 40%. ^{1}H NMR: δ 1.27 (br, 1H; $-CH_2OH$); δ 1.4 (m, 2H; $-CH_2CH_2CH_2CH_2OH$); δ 1.6 (m, 4H; $-CH_2CH_2CH_2CH_2CH_2OH$); δ 2.62 (t, 2H; $-ArCH_2CH_2-$); δ 3.54 (t, 2H; $-CH_2-CH_2OH$); δ 5.19 (dd, 1H; $=CH_2$); δ 5.70 (dd, 1H; $=CH_2$); δ 6.70 (dd, 1H; $-CH=$), and δ 7.22 (q, 4H; C_6H_4).

6-(*p*-Vinylphenyl)hexanol (VPH) (**2**, $m = 6$) was prepared from *p*-(5-bromopentyl)styrene [24] via Grignard reagent followed by reaction with formaldehyde [25], worked up as above, and purified by column chromatography over silica gel with cyclohexane/ethyl acetate (80/20

v/v) as an eluent. Yd. 38%. ^{1}H NMR: δ 1.19 (br, 1H; $-CH_2OH$); δ 1.4 (m, 4H; $-CH_2CH_2CH_2CH_2CH_2CH_2OH$); δ 1.6 (m, 4H; $-CH_2CH_2CH_2CH_2CH_2CH_2OH$); δ 2.60 (t, 2H; $-ArCH_2CH_2-$); δ 3.63 (t, 2H; $-CH_2-CH_2OH$); δ 5.18 (dd, 1H; $=CH_2$); δ 5.70 (dd, 1H; $=CH_2$); δ 6.70 (dd, 1H; $-CH=$), and δ 7.23 (q, 4H; C_6H_4).

VBA, VPE, VPP, and VPPT were finally distilled over CaH_2 under high-vacuum line and sealed into calibrated tubes with a breakable seal. VPH was evacuated under high vacuum, dissolved in tetrahydrofuran (THF), and sealed into calibrated tubes with a breakable seal.

THF, distilled from a blue solution with sodium benzophenone, was dried and purified under vacuum by distillation over $LiAlH_4$ and then over sodium anthracene, and finally from a red solution with disodium salt of α-methylstyrene tetramer (Na_2MS_4) into calibrated flasks with a breakable seal. A solution of Na_2MS_4 in THF was prepared by reaction of α-methylstyrene with sodium mirror at room temperature, filtered, and stocked as dilute solutions in ampoules with a breakable seal. EO was distilled trap-to-trap twice over KOH pellets, three times over CaH_2 powder, and finally over Na mirror into calibrated tubes with a breakable seal.

Potassium naphthalene ($KC_{10}H_8$) was prepared under high vacuum by reacting naphthalene with excess potassium mirror in THF. Naphthalene was purified by sublimation and dissolved in THF. Potassium mirror was prepared on the wall of a flask after careful trap-to-trap distillations over a small oxygen-free flame. The dark green solution obtained was filtered and divided into calibrated tubes with a breakable seal. The concentration was usually 0.2–0.5N, as determined by titration of an aliquot in water with a potassium hydrogen phthalate solution.

2.2. Polymerization of EO

Polymerization was conducted under high vacuum (5×10^{-5} Torr or 3.7×10^{-3} Pa) with all the reagents sealed into appropriate, calibrated ampoules which were also prepared under the vacuum with breakable seal technique.

Kinetics of EO polymerization with VBA was followed in a procedure as follows. Ampoules including a washing solution (Na_2MS_4 in THF), VBA as an initiator, THF as a solvent, potassium naphthalene solution ($KC_{10}H_8$/THF), and EO were, respectively, attached into an apparatus with the reaction flask and several tubes for sampling as shown in Fig. 1. The apparatus was attached upside-down to a vacuum line, evacuated, baked over an oxygen-free flame, and sealed off from the line. The breakable seal of the ampoule of the washing solution (a) was broken with a magnetic bar to rinse all the inner walls. The walls were then completely washed and cleaned by fresh THF, which comes on distillation by cooling on the outer walls with cotton tips wetted with chilled isopropanol by dry ice, until the red color of the Na_2MS_4disappeared from the wall. The washing

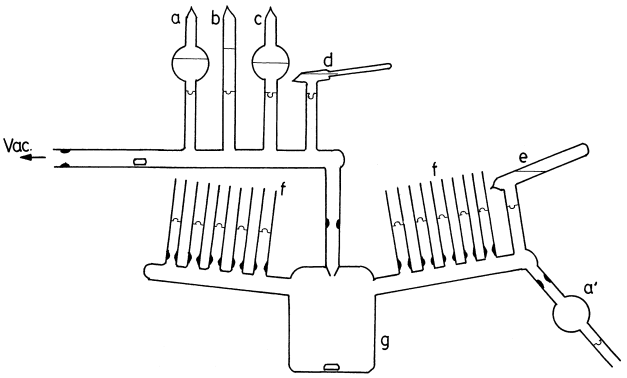


Fig. 1. Apparatus for kinetics measurement of EO polymerization. (a) Washing solution (Na_2MS_4/THF); (a′) ampoule for recovering a washing solution; (b) potassium naphthalene solution ($KC_{10}H_8$/THF); (c) THF; (d) initiator alcohol (VBA); (e) EO; (f) sampling tubes; (g) reaction flask.

solution was recovered into the flask (a′) and sealed off. Initiator (VBA) and solvent (THF) were introduced into the reaction flask. Then the $KC_{10}H_8$/THF solution was introduced drop by drop into the flask under vigorous magnetic stirring, so that the dark green color immediately disappeared upon mixing, indicating the reaction with VBA to the alkoxide. The lower half of the apparatus was sealed off above the reaction flask. The breakable seal of the chilled ampoule of EO was finally broken to introduce the monomer into the reaction flask. The flask was then placed in a bath of 40 °C to start the polymerization. From time to time, the aliquots were transferred by inverting the apparatus into sampling tubes (f) and sealed off to check for conversion or degree of polymerization. Thus the content was terminated with small amounts of methanol and poured into a large amount of hexane to precipitate out the polymers, which were collected by filtration or by decantation, washed with hexane, and finally freeze-dried from benzene, and characterized by ^{1}H NMR and size exclusion chromatography (SEC).

The preparative syntheses of the macromonomers were similarly carried out starting from partially (about 40%) alkoxidated VBA, VPP, VPPT, and VPH with the apparatus as in Fig. 1 but without sampling tubes. The polymerization was conducted at 40 °C for more than 2 days to achieve almost quantitative conversion, and the polymers were purified by re-precipitation from THF into hexane and finally freeze-dried from benzene.

The polymerization of EO with partially alkoxidated VPE was similarly conducted to almost quantitative conversion. The polymers isolated as the hexane-insoluble part, however, were found to be just poly(ethylene glycol) without any *p*-vinylphenylethyl groups as judged by ^{1}H NMR. So the hexane soluble part was evaporated and the residue was analyzed by ^{1}H NMR to be identified as *p*-divinylbenzene: δ 5.2 (dd, 2H; $=CH_2$), δ 5.7(dd, 2H; $=CH_2$), δ 6.7 (q, 2H; $=CH-$), and δ 7.37 (s, 4H; C_6H_4). The amount was almost comparative to that expected from the original VPE used. Independent experiment starting with

2-phenylethanol instead of VPE produced poly(ethylene glycol) and styrene just as expected. The attempted reaction just between 2-phenylethanol and $KC_{10}H_8$ in THF without EO polymerization, however, resulted in recovery of the alcohol after work-up. Also the reaction between 2-phenylethanol and K-alkoxide of poly(ethylene glycol) monomethyl ether, $KO(CH_2CH_2O)_nCH_3$ ($n = 15$), resulted in recovery of the alcohol and poly(ethylene glycol) monomethyl ether, as the hexane-soluble and -insoluble parts, respectively. These experiments show that the polymerization of EO with potassium VPE must have produced *p*-divinylbenzene and poly(ethylene glycol) by some intramolecular transfer involving hydrogen abstraction of the propagating alkoxide anion from the initiator fragment as will be discussed with Scheme 3.

2.3. Characterization

^{1}H NMR spectra were measured on Mercury Varian 300 with deutero-chloroform ($CDCl_3$) solutions, with tetramethylsilane as an internal standard. Pulse width and delay were 7.25 μs and 1.5 s, respectively, to allow complete relaxation of the protons. Number of accumulation was 16 times. SEC was recorded on JASCO PU980 as a pump, with JASCO RI980 as an RI detector, and Shodex GPC KF-802 and -803 as columns. The eluent was THF with the flow rate of 1 mL/min at 40 °C. The standard poly(ethylene glycol)s were used for calibration of the molecular weights.

3. Results and discussion

3.1. General scheme

Since the propagating species in anionic polymerization of EO is an oxy anion via ring-opening of EO, the polymerization can be initiated by alkoxide and the propagation will continue without termination even in the presence of free alcohols because any proton exchange will reproduce the same oxy anion:

$$RO^-K^+ + RO{-}H \rightleftarrows RO{-}H + RO^-K^+ \quad (1)$$

$$RO^-K^+ + EO \rightarrow RO{-}CH_2CH_2O^-K^+ \quad (2)$$

Here RO can be any alcohol residue or poly(ethylene oxide) chain. Therefore, so long as the equilibrium in Eq. (1) is much faster than the propagation in Eq. (2), the system looks like 'living' polymerization with all the initial alcohol residues as the initiator fragments, just as observed in 'immortal' polymerization of epoxides by aluminum porphyrin complexes [26]. Thus in practical view of synthesis of PEO macromonomers, we thought the styryl-alkanols as convenient initiators as given in Scheme 2, since the styryl double bonds are known to be inactive to oxy anions [15–20]. We used potassium naphthalene solution ($KC_{10}H_8$/THF) to convert the alcohols fractionally to alkoxides because the solution is easy to handle in a vacuum system. A problem is to avoid any reaction with the styryl groups which could occur easily via charge transfer as is well known since the discovery of the living polymerization of styrene [27]. This was accomplished by slowly adding (drop by drop) the $KC_{10}H_8$ solution to the excess alcohols in THF under vigorous stirring as described in Section 2. Detailed study was conducted first on kinetics of EO polymerization with VBA.

3.2. Kinetics of EO polymerization with VBA

EO was polymerized in THF at 40 °C with VBA ($m = 1$) partially alkoxidated by potassium naphthalene ($KC_{10}H_8$). Polymerization was followed by ^{1}H NMR with the samples isolated from time to time. Typical spectra are shown in Fig. 2 for the polymerization at 32% alkoxidation ($x = 0.32$). Polymerization or incorporation of EO units can be seen in the appearance and increase of the oxyethylene peak around δ 3.7, while the upfield shift of the benzyl methylene protons from δ 4.65 for VBA (A) to δ 4.55 after polymerization (B and C) indicates that initiation incorporated all the *p*-vinylbenzyloxy groups as the initiator fragments in the polymer chains. It also appears that the vinylphenyl groups remain intact during polymerization of EO. So the increase in the peak of oxyethylene protons around δ 3.7 relative to that of benzylmethylene or vinyl protons was taken as the measure of conversion or degree of polymerization by assuming no reaction of the vinylbenzyl groups.

Fig. 3 shows the conversion vs time plots for various degree of alkoxidation (x). Clearly, the rate becomes increasingly higher with x. Table 1 summarizes the data

Table 1
Characterization of PEO macromonomers obtained at complete conversion of EO polymerization with VBA

VBA (mmol)	x[a]	EO (mmol)	Time (h)	$M_{n,calc}$[b]	$M_{n,NMR}$[c]	$M_{n,SEC}$[d]	$M_w/M_{n,SEC}$[d]
13.5	0.09	250	600	950	970	1060	1.09
11.3	0.18	308	300	1320	1410	950	1.20
11.9	0.32	299	150	1440	1320	1220	1.09
10.5	0.43	353	48	1610	1700	1400	1.16
11.6	0.63	214	24	940	1090	990	1.17
12.6	0.73	226	6	920	1010	1020	1.10
9.7	0.94	223	3	1120	1100	1270	1.17
10.4	0.45	587	168	2630	2660	2500	1.03
5.1	0.42	552	168	4900	4820	4100	1.05
3.6	0.59	467	168	5890	5950	5700	1.08

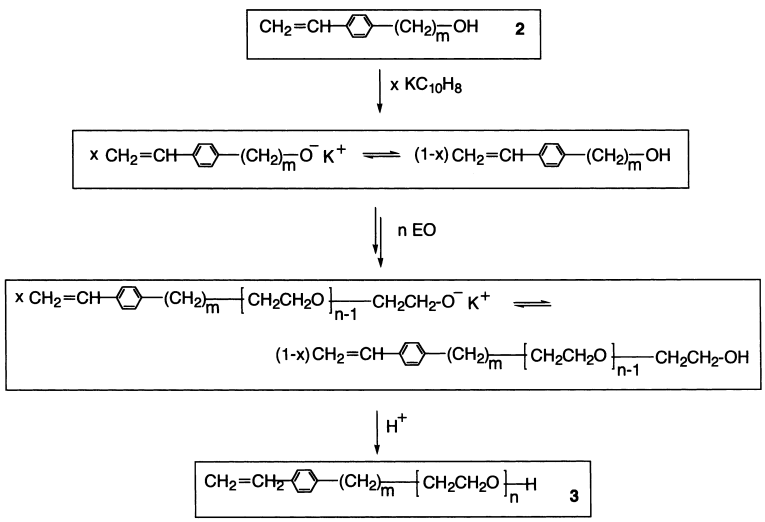
THF = ca. 80 mL, 40 °C, conversion = nearly quantitative.

[a] Degree of alkoxidation, $x = [KC_{10}H_8]/[VBA]_0$.

[b] $M_{n,calc} = M_A + 44[M]_0/[A]_0$, where M_A = molecular weight of initiator alcohol, here 134 for VBA.

[c] $M_{n,NMR} = M_A + 44(I_{EO}/4)/(I_{VBA}/2)$, where I_{EO} = peak intensity of the oxyethylene protons at δ 3.7 and I_{VBA} = peak intensity of the VBA benzylic methylene protons at δ 4.55.

[d] Determined by SEC calibrated with standard poly(ethylene glycol)s.



Scheme 2.

of characterization of the polymers obtained under various conditions after almost complete conversion. The number-average molecular weights as determined from ^{1}H NMR ($M_{n,NMR}$) and those from SEC calibrated with standard poly(ethylene glycol)s ($M_{n,SEC}$), and those calculated from the molar ratio of EO to VBA charged ($M_{n,calc}$) are in fair accord with each other, strongly supporting the living polymerization mechanism just as shown in Scheme 2. The chromatograms in SEC are unimodal in each case with nearly monodisperse distribution in the molecular weight ($M_w/M_n \leq 1.2$). Thus all the alcohol molecules charged in the feed can be initiator fragments to afford the PEO macromonomers with the number-average degree of polymerization ($DP_n = n$, in Scheme 2) given as follows.

$$DP_n = n = [M]_0\theta/[A]_0 \quad (3)$$

where $[M]_0$ and $[A]_0$ are the initial molar concentrations of EO and alcohol, respectively, and θ is the conversion of EO polymerized and $\theta = 1$ in Table 1.

The data in Fig. 3 were re-plotted in Fig. 4 to follow the first-order kinetics:

$$\ln[M]_0/[M] = -\ln(1-\theta) = k_{p,app}[P^*]t \quad (4)$$

where [M] is the monomer concentration after time t, with $\theta = ([M]_0 - [M])/[M]_0$, $[P^*]$ is the concentration of active

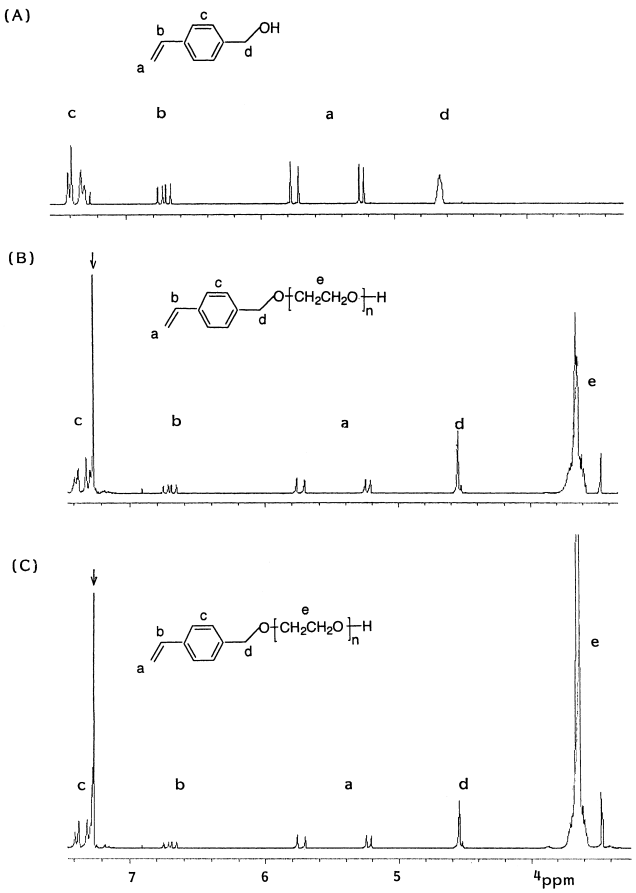


Fig. 2. Typical ^{1}H NMR spectra of VBA and products of EO polymerization at $x = 0.32$: (A) original VBA; (B) after 10 h ($n = 4.5$); and (C) after 25 h ($n = 13.9$). Peak with an arrow due to impurity ($CHCl_3$).

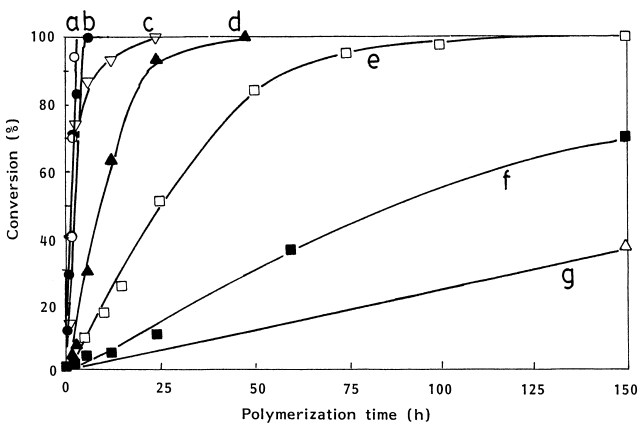


Fig. 3. Time-conversion plots of EO polymerization at various degree of alkoxidation: (a, ○) $x = 0.94$; (b, ●) $x = 0.73$; (c, ▽) $x = 0.63$; (d, ▲) $x = 0.43$; (e, □) $x = 0.32$; (f, ■) $x = 0.18$; (g, △) $x = 0.09$. See upper seven rows in Table 1 for the feed composition of VBA and EO.

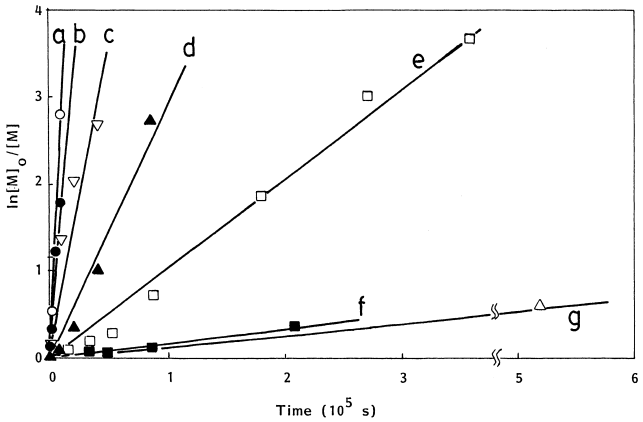


Fig. 4. First-order plots of the data in Fig. 3: (a, ○) $x = 0.94$; (b, ●) $x = 0.73$; (c, ▽) $x = 0.63$; (d, ▲) $x = 0.43$; (e, □) $x = 0.32$; (f, ■) $x = 0.18$; (g, △) $x = 0.09$.

chain ends, and $k_{p,app}$ is the corresponding apparent propagation constant. Since the polymerization is accelerated with x, we took the total potassium alkoxide concentration as [P*], i.e. $[P^*] = x[A]_0$, to calculate even roughly the value of $k_{p,app}$, which will provide an idea of activity of each potassium alkoxide species in ring-opening polymerization of EO. Since the living nature of the present polymerization is evident by the data in Table 1, the scattering in the first-order plots in Fig. 4 may be due to sampling procedure in such a closed vacuum system (Fig. 1) which may change the concentrations of the species involved to some extent. Nevertheless, the results in Fig. 5 clearly shows as a fact that the $k_{p,app}$ values are not constant but increases with x, indicating that the free alcohols interfere the propagation reaction of the alkoxides as the active chain ends. We suppose that the exchange equilibrium and/or the complex formation among the free alcohols and the potassium alkoxides may apparently reduce the reactivity of the alkoxide moiety in ring-opening of EO. Further discussion, however, should be made after more detailed examination of the kinetics and some spectroscopic investigation of the possible complexes.

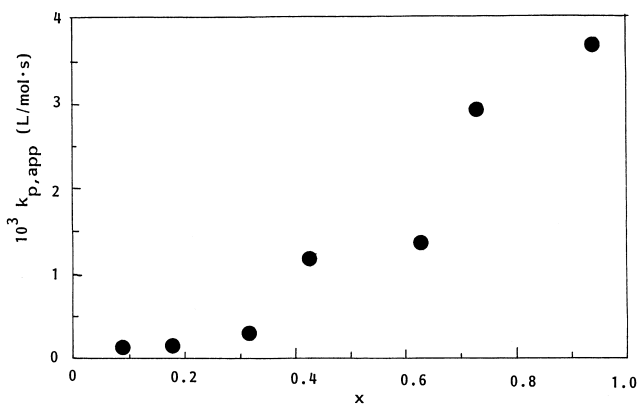


Fig. 5. Change of $k_{p,app}$ as a function of degree of alkoxidation, x.

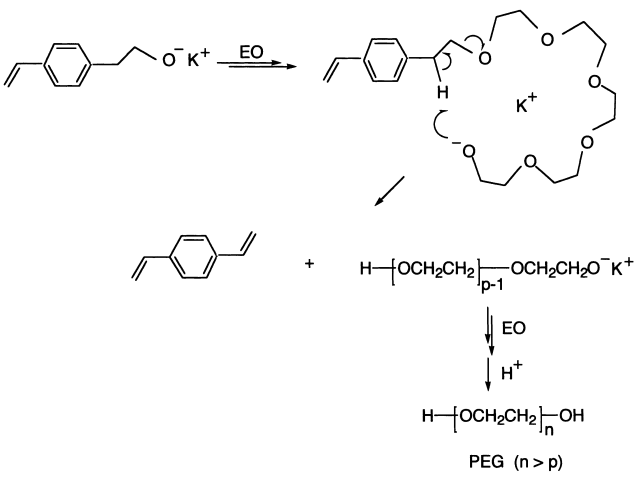
3.3. Polymerization of with VPE to poly(ethylene glycol) and p-divinylbenzene

VPE (10 mmol) was partially alkoxidated with potassium naphthalene ($x = 0.44$) to polymerize EO (250 mmol) under a condition similar to the legend to Table 1. The polymers were isolated as usual in quantitative yield by precipitation into hexane but identified just as poly(ethylene glycol) (PEG) with $M_{n,SEC}$ around 10^3 without any *p*-vinylphenylethoxy fragments. Instead, *p*-divinylbenzene was isolated from hexane-soluble part, with no indication of the initial VPE residue in the ^{1}H NMR spectrum. Similar polymerization starting with 2-phenylethanol instead of VPE produced styrene and PEG as the hexane-soluble and -insoluble fractions, respectively. On the other hand, no apparent reaction occurred and just the original alcohols were recovered after work-up either when VPE was just alkoxidated by potassium naphthalene or when 2-phenylethanol was reacted with potassium alkoxide of PEG monomethylether (see Section 2).

These results strongly suggest an intramolecular hydrogen-transfer reaction after some degree of normal polymerization to release *p*-divinylbenzene and potassium alkoxide of oligo(ethylene glycol), which will continue to propagate to PEG. Thus we propose Scheme 3 as a mechanism. Activation of the oxy anion by crown ether-like complexation of the counter ion (K^+), say, after normal addition of about 5 or 6 EO units, appears to be a driving force for intramolecular abstraction of the benzylic proton, together with formation of elongated conjugated phenylalkenes, i.e. *p*-divinylbenzene from VPE and styrene from 2-phenylethanol here.

3.4. Polymerization with VPP, VPPT, and VPH for syntheses of hydrophobically enhanced styryl-ended PEO macromonomers

PEO macromonomers carrying hydrophobically-enhanced polymerizing end groups are particularly inter-



Scheme 3.

esting in view of so enhanced organization to micelles and (co)polymerizability [4,6,13,28,29]. Therefore successful use of *p*-styrylalkanols as initiators for EO polymerization is valuable for application. The results of preparation of the PEO macromonomers by use of VPP ($m = 3$), VPPT ($m = 5$), and VPH ($m = 6$) are summarized in Table 2 together with typical ^{1}H NMR spectra in Fig. 6. The agreements in the number-average molecular weights by ^{1}H NMR ($M_{n,NMR}$), SEC ($M_{n,SEC}$), and calculation ($M_{n,calc}$) are usually satisfactory to support the living polymerization mechanism in Scheme 2. Some difference observed in the values of M_n appears to be due to probable errors involved in calibration of very small amounts of the alcohols charged and calibration of SEC with poly(ethylene glycols). Thus we conclude that all the alcohols charged are effectively incorporated as the initiating fragments of the PEO macromonomers to initiate polymerization of EO in living fashion.

4. Conclusions

Partially alkoxidated alcohols, including VBA, VPP, VPPT, and VPH ($m = 1$, 3, 5, 6) successfully initiated polymerization of EO to afford the expected α-styrylalkyl- and ω-hydroxy-ended PEO macromonomers, just as shown in Scheme 2, with the degree of polymerization controlled by initial ratio of EO/alcohol. VPE ($m = 2$), however, gave *p*-divinylbenzene and PEG very probably as a result of intramolecular chain transfer as given in Scheme 3. The initiation method proposed appears applicable to design of various kinds of hetero-telechelic PEO macromonomers and polymers in general. The study along this line as well as application of the macromonomers to emulsion and dispersion polymerization are to be published in due course.

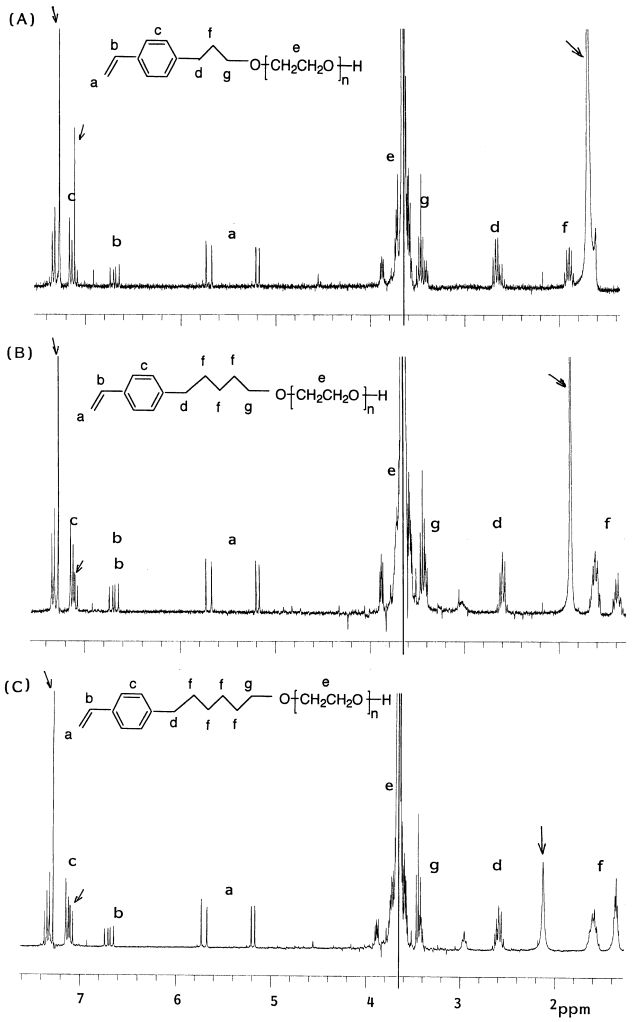


Fig. 6. Typical ^{1}H NMR spectra of PEO macromonomers prepared from (A) VPP ($m = 3$, $n = 50$); (B) VPPT ($m = 5$, $n = 63$), and (C) VPH ($m = 6$, $n = 50$). Peaks with an arrow are due to impurities ($CHCl_3$, C_6H_6, and H_2O from low to upfield).

Table 2
Characterization of PEO macromonomers obtained at complete conversion of EO polymerization with VPP ($m = 3$), VPPT ($m = 5$), and VPH ($m = 6$)

Alcohol (mmol)	x[a]	EO (mmol)	Time (h)	$M_{n,calc}$[b]	$M_{n,NMR}$[c]	$M_{n,SEC}$[d]	$M_w/M_{n,NMR}$[d]
VPP 6.3	0.50	240	48	1820	2340	1970	1.07
VPP 4.3	0.27	208	72	2110	2080	2000	1.09
VPP 3.8	0.40	343	64	4150	3660	2830	1.16
VPP 3.7	0.43	522	54	6390	6740	4390	1.12
VPPT 8.9	0.63	298	72	1660	2130	2300	1.12
VPPT 4.3	0.49	247	72	2720	2990	2930	1.10
VPH 5.7	0.61	278	72	2340	2650	2320	1.10
VPH 8.1	0.36	262	168	1640	2430	2000	1.24

THF = ca. 90 mL, 40 °C, conversion = nearly quantitative.

[a] Degree of alkoxidation, $x = [KC_{10}H_8]/[VBA]_0$.

[b] $M_{n,calc} = M_A + 44[M]_0/[A]_0$, where M_A = *molecular* weight of the initiator alcohol used.

[c] $M_{n,NMR} = M_A + 44(I_{EO}/4)/(I_A/2)$, where I_{EO} = *peak* intensity of the oxyethylene protons and I_A = peak intensity of the benzylic methylene protons of the initiator alcohol fragnents.

[d] Determined by SEC calibrated with standard poly(ethylene glycol)s.

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