Poly(ethylene oxide) Macromonomers XI. Solvent Effects on Homopolymerization Rates

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ABSTRACT: Radical homopolymerization of poly(ethylene oxide) (PEO) macromonomers carrying *n*-dodecyl or *n*-octadecyl group as the ω-end and *p*-vinylbenzyl or methacryloyl group as the α-end was carried out in benzene, cyclohexane, and water. The micellar polymerization in water with an exceptionally high rate was confirmed as previously found, while the polymerization in cyclohexane was considerably faster than in benzene. The significant effects of the ω-alkyl groups and the PEO chain lengths on the polymerization rate were observed in cyclohexane, suggesting formation of some loosely organized, inverse micelles of these amphiphilic macromonomers, but not in benzene.

KEY WORDS Poly(ethylene oxide) / Macromonomer / Homopolymerization / Micelle / Inverse Micelle /

In a series of studies on poly(ethylene oxide) (PEO) macromonomers,[1-7] we have been interested in how their amphiphilic properties affect the polymerization behavior in relation to that of the conventional monomers. In particular, radical homopolymerization of these macromonomers was found to occur unusually rapidly in water to afford regular comb polymers of very high molecular weights.[4-7] Organization of their hydrophobic α-terminal double bonds into the micelle core was considered to be a key facter for their enhanced polymerization. The significant effects of the end groups and the PEO chain lengths were observed, indicating the importance of their relative molecular density as estimated by m/V_m, where m and V_m are the average number of aggregation and the volume of each micelle, respectively, measured by light scattering for the nonpolymerizable macromonomer models.

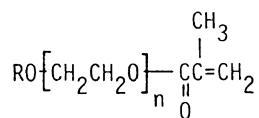In view of the amphiphilic properties of the PEO macromonomers, which usually consist of hydrophilic PEO chains and the hydrophobic terminal groups, it remains another challenging problem to examine their polymerization in a nonpolar hydrocarbon medium in comparison with that in water. Recent interest in inverse emulsion or microemulsion polymerization systems involving water-soluble monomers[8] has also prompted us to this investigation. Unlike the conventional monomers of low molecular weights, the PEO macromonomers are very unique in that they are soluble in a very wide range of solvents including water through various hydrocarbons, depending on the terminal groups and the PEO chain lengths.

This paper describes and discusses the results of polymerization of the PEO macromonomers, **1** and **2**, in water, benzene, and cyclohexane, all the systems being apparently homogeneous throughout. Cyclohexane was chosen as a nonpolar extreme of the solvents against the most polar water, since the other simple hydrocarbons such as heptane produced some precipitates during polymerization. It was first expected that the macro-

monomers, 1 and 2, will polymerize also rapidly in cyclohexane as a result of inverse micelle formation, just like those in water as a result of (normal) micelle formation.

$$RO\left[CH_2CH_2O\right]_n CH_2 \langle\bigcirc\rangle CH=CH_2$$
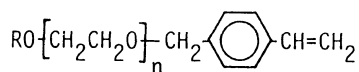
1 (R-PEO-VB-n): R $= n$C$_{12}$H$_{25}$; $n = 13$

$$RO\left[CH_2CH_2O\right]_n \overset{CH_3}{\underset{\underset{O}{\parallel}}{C}}C=CH_2$$

2 (R-PEO-MA-n): R $= n$C$_{12}$H$_{25}$, nC$_{18}$H$_{37}$; $n = 11$—23

Table I. Charactrization of macromonomers

| | PEO chain length, n | | M_w/M_n |
Code[a]	NMR[b]	GPC[c]	GPC[c]
C$_{12}$-PEO-VB-13	13	13	1.06
C$_{12}$-PEO-MA-14	14	15	1.17
C$_{12}$-PEO-MA-19	19	20	1.05
C$_{18}$-PEO-MA-11	11	11	1.08
C$_{18}$-PEO-MA-23	23	21	1.04

[a] See 1 and 2 in the text for the code representation. C$_{12}$ and C$_{18}$ stand for dodecyl and octadecyl as the ω-alkyl group, and the last numbers indicate n as determined by ^{1}H NMR.

[b] Determined by ^{1}H NMR in CDCl$_3$ using the ratio of the peak areas of oxyethylene (peak d in Figure 1) to methyl (a) or α-olefin protons (g or h).

[c] Determined by GPC calibrated with standard PEO samples.

EXPERIMENTAL

The PEO macromonomers, 1 and 2, were prepared from monolauryl or monostearyl ether of poly(ethylene glycol), Takamoto Oil & Fat Co., Ltd, by reaction with excess sodium hydride, followed by reaction with excess p-vinylbenzyl chloride and methacryloyl chloride, respectively. They were isolated by precipitation into cooled hexane, purified and characterized in a smilar procedure as previously described.[1,4,6] Figure 1 shows typical ^{1}H NMR spectra, and Table I summarizes characterization of the macromonomers used in this study.

Deuterated solvents were used as supplied commercially, chloroform-d and cyclohexane-d_{12} from Aldrich, benzene-d_6 and water-d_2 from CEA. 2.2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol, and 4,4′-azobis (4-cyanovaleric acid) from Aldrich was used as supplied.

Polymerization of Macromonomers

Radical polymerization of the macromonomers was carried out at 60°C in an NMR tube. The conversions were monitored by means of ^{1}H NMR following the disappearance of the double bond peaks (g or h in Figure 1) in reference to the oxyethylene peak (d), as previously described.[4−6] Essentially the same results were obtained for some runs by monitoring the conversions by means of GPC assuming same RI responce of the poly(macromonomer)s and the unreacted macromonomers. Molecular weights of the poly(macromonomer)s were roughly estimated to be higher than 10^4 at least, by calibration with linear PEO standard samples, which severely underestimate the molecular weights of these comb polymers.[7]

Measurements

^{1}H NMR (270 MHz), gel permeation chromatography (GPC), and light scattering were measured as previously described.[1−7]

RESULTS AND DISCUSSION

Polymerization in Benzene

Figure 2 shows the time–conversion plots for the polymerization in benzene with AIBN. Similarly as previously observed,[4] the polymerizations proceeded relatively slowly at the employed condition of very low, absolute concentrations of both the monomer and the
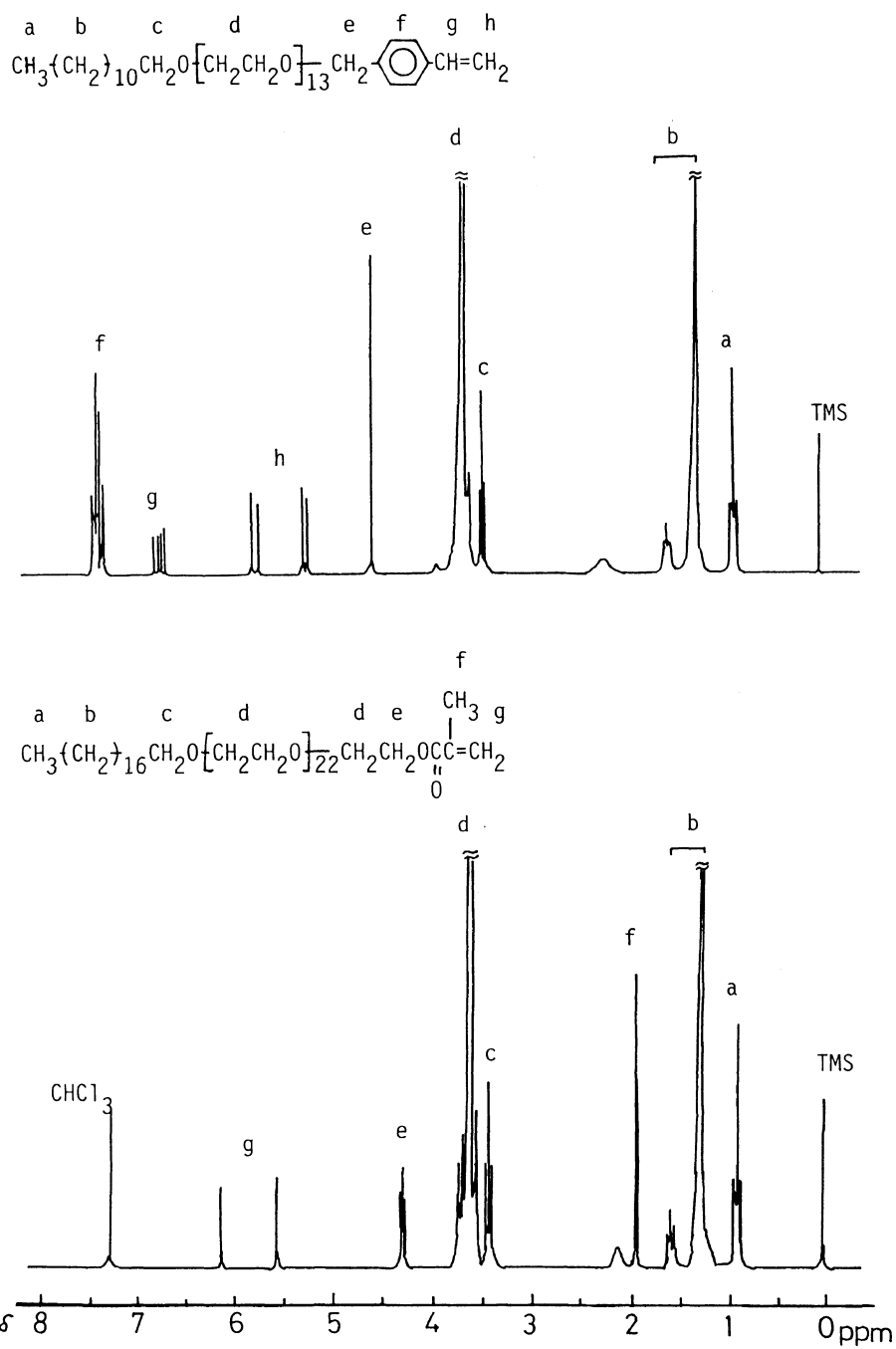
Figure 1. ^{1}H NMR spectra (270 MHz) of the macromonomers, C_{12}-PEO-VB-13 (upper) and C_{18}-PEO-MA-23 (lower), in CDDl$_{3}$. Broad peaks at *ca.* 2.2 ppm due to water.
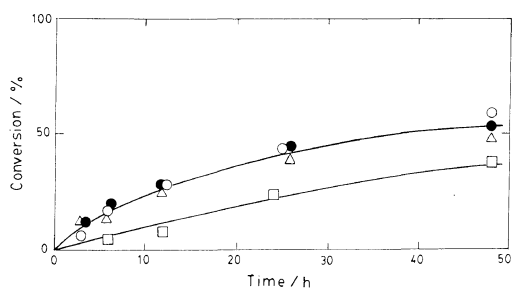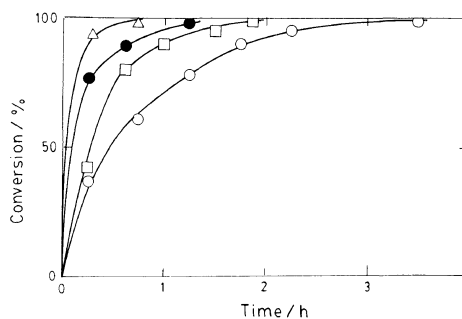
Figure 2. Conversion *vs.* time plots for polymerization of C_{12}-PEO-MA-14 (○), C_{18}-PEO-MA-23 (●), C_{18}-PEO-MA-11 (△), and C_{12}-PEO-VB-13 (□) in benzene-d_6 with [M] = 45 mmol$\,l^{-1}$ and [AIBN] = 2.25 mmol$\,l^{-1}$.

Figure 3. Conversion *vs.* time plots for polymerization of C_{18}-PEO-MA-11 (△), C_{18}-PEO-MA-23 (●), C_{12}-PEO-MA-14 (□), and C_{12}-PEO-MA-19 (○) in water-d_2 with [M] = 45 mmol$\,l^{-1}$ and [AVA] = 0.45 mmol$\,l^{-1}$.

initiator on the molar bases, and they appeared to level off below *ca.* 60% conversions, very probably as a result of the "dead-end" phenomenon.[9] Interestingly, the ω-alkyl group (*R*) and the PEO chain length (n) affected very little on the rates, at least within the experimental range investigated, while the macromonomer with α-methacrylate polymerized considerably faster than that with α-vinylbenzyl ether just like the conventional monomers such as methyl methacrylate *vs.* styrene.

The results can be reasonably understood by considering that the macromonomers will be little aggregated and almost molecularly dissolved in benzene, as confirmed by the light scattering measurement of a nonpolymerizable macromonomer model, C_{18}-PEO-Bz-35, carrying benzyl ether group instead of *p*-vinylbenzyl ether as the α-end in **1**.[4] Therefore, their apparent polymerizabilities will be essentially determined by the chemical nature, *i.e.*, the intrinsic reactivities of the α-terminal double bonds, as has been also reported in highly diffusion-controlled polymerization of polystyrene macromonomers.[10,11]

Polymerization in Water

As previously reported for the *p*-vinylbenzyl ether-ended macromonomers, **1**,[4] the methacrylate-ended macromonomers, **2**, were also found to polymerize unusually rapidly in

water, even with a very low concentration of AVA, as given in Figure 3. Since the decomposition rate of AVA in water and that of AIBN in benzene were found to be only a little different from each other,[4] the result can be most reasonably understood by a micellar polymerization mechanism with an enhanced propagation rate constant (k_p) and/or a depressed termination rate constant (k_t).

The effects of the ω-alkyl groups and the PEO chain lengths on the apparent polymerizability were also significant, reflecting their relative ability to organize micelles. Thus, by analogy with the previous discussion based on the light scattering measurements for the micelle formation,[4] a macromonomer with a higher ω-alkyl group and/or with a lower PEO chain length will make more densely organized micelles in water, resulting in a higher rate of polymerization.

Polymerization in Cyclohexane

Figure 4 typically shows the solvent effects on the time–conversion plots as observed for the polymerization of a macromonomer, **2**, C_{12}-PEO-MA-14. Very clearly, the polymerization in cyclohexane is faster than that in benzene but by far slower than that in water. The effects of the ω-alkyl groups and the PEO chain lengths were also significant in cyclohexane but just reversed from those in
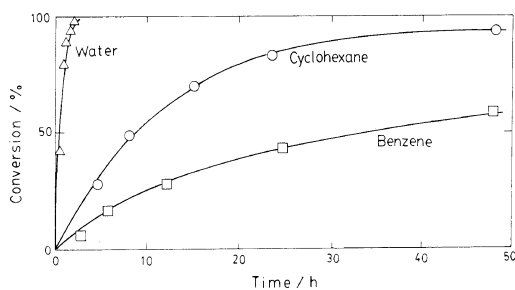
Figure 4. Conversion *vs.* time plots for polymerization of C_{12}-PEO-MA-14, $[M] = 45 \, \text{mmol} \, l^{-1}$, in water-$d_2$ with AVA ($0.45 \, \text{mmol} \, l^{-1}$) ($\triangle$), in cyclohexane-$d_{12}$ ($\bigcirc$) and in benzene-d_6 ($\square$) with AIBN ($2.25 \, \text{mmol} \, l^{-1}$).
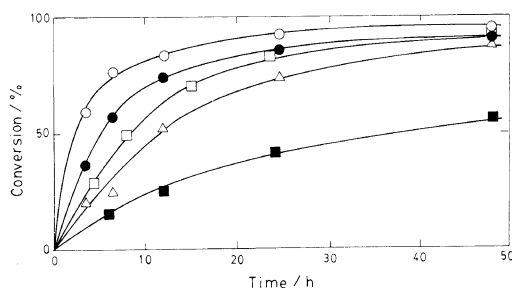
Figure 5. Conversion *vs.* time plots for polymerization of C_{12}-PEO-MA-19 ($\bigcirc$), C_{12}-PEO-MA-14 ($\square$), C_{18}-PEO-MA-23 ($\bullet$), C_{18}-PEO-MA-11 ($\triangle$), and C_{12}-PEO-VB-13 ($\blacksquare$) in cyclohexane-d_{12} with $[M] = 45 \, \text{mmol} \, l^{-1}$ and $[AIBN] = 2.25 \, \text{mmol} \, l^{-1}$.

water, as in Figure 5. Thus a macromonomer with a lower ω-alkyl group and/or with a higher PEO chain length was found to polymerize more rapidly. These results are just as expected by assuming inverse micelle formation in cyclohexane, since either longer PEO chain or lower ω-alkyl group will enhance the hydrophilicity and so favor the aggregation to form the inverse micelles.

The polymerization in cyclohexane, however, was not so markedly enhanced as compared to that in water. This appears to be related to the fact that the inverse micelle formation of the nonionic surfactants in nonpolar solvents are in general of open association type without any definite cmc or aggregation number.[12,13] In fact, we have observed no indication of micelles in cyclohexane by a

laser light scattering measurement with a non-polymerizable model, C_{12}-PEO-IB-10, which carries α-isobutyrate end group in place of α-methacrylate in **2**, at least below a concentration of $5 \times 10^{-4} \, \text{g} \, \text{ml}^{-1}$ at 25°C. This is in sharp cntrast to the distinct scattering due to the micelle formation as observed in water under the same condition.[4]

Therefore in cyclohexane we assume somewhat loosely organized, inverse micelles which will favor the polymerization to some significant extent as observed. The aggregation, even if it may be transient, will probably depress a diffusion-controlled termination (k_t) between the highly branched polymer radicals. An enhanced propagation (k_p) appears to be improbable in cyclohexane since the α-polymerizable terminal groups are also hydrophobic so that they will rather freely extend into the medium as compared to those assumed for the normal micelles in water.[4] Any evidence for the assumed inverse micelles other than the polymerization rates remains to be studied further.

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