Polymer Bulletin 16, 337-344 (1986)

Polymer Bulletin

Poly(ethylene oxide) macromonomers
4. Effects of the α- and ω-terminal groups on the copolymerization reactivity

Koichi Ito, Satoshi Yokoyama, Fumitaka Arakawa, Yoshiyuki Yukawa, Tetsuo Iwashita, and Yasuhisa Yamasaki

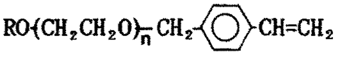
School of Materials Science, Toyohashi University of Technology, Tempaku-cho,
Toyohashi, 440 Japan

Summary

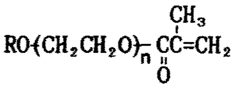
Poly(ethylene oxide) macromonomers (M_2) carrying p-vinylbenzyl or methacryloyl group at the α-end and methyl or dodecyl group at the ω-end were prepared, and radical-copolymerized with benzyl methacrylate or styrene (M_1). Relative reactivities of the macromonomers ($1/r_1$) were found to be significantly smaller than those of the corresponding model monomers of low molecular weights in all cases where the macromonomer (M_2) and the homopolymer of the comonomer (poly-M_1) are incompatible, supporting our previous suggestion of a repulsion between M_2 and poly-M_1 radical as a factor for retarding their mutual reaction.

Introduction

Poly(ethylene oxide) (PEO) has been a well-known hydrophilic polymer with a variety of practical applications, and its macromonomer has also been a subject of many recent publications (1-12) to prepare well-defined amphiphilic graft copolymers. Importantly, both the α- and ω-end groups can be rather easily designed either by living anionic polymerization of ethylene oxide by use of a known initiator and a known terminator (1,2) or by appropriate transformation reactions of their terminal groups (13). Indeed a wide range of hydrophilic-hydrophobic balance can be provided by changing R and n of the macromonomers as follow.



R-PEO-VB



$$\mathrm{RO(CH_2CH_2O)_n\underset{\overset{\|}{O}}{C}\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

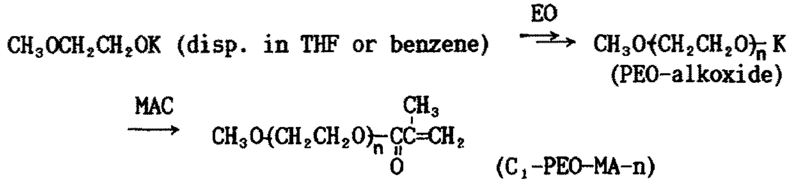
R-PEO-MA

Previously we reported the cases of R = tert-butyl for studying the effect of n on the copolymerization reactivity (10,11), and R = polystyryl for applying to a phase transfer catalyst (12).

This paper describes preparation of the macromonomers with R = methyl (C_1-PEO-VB and -MA) and R = dodecyl (C_{12}-PEO-MA) and their reactivities in copolymerization with styrene (St) or benzyl methacrylate (BzMA). BzMA was chosen as a model of methacrylic monomers for the ease of composition determination by ^1H NMR. The reactivities will be discussed in terms of the polymer-polymer compatibility as proposed before (11) as a factor affecting the corresponding polymer-polymer reactions (cross-propagation reactions).

Results and Discussion

C_1-PEO-MA was prepared by living polymerization of ethylene oxide (EO) with potassium 2-methoxyethoxide (1) followed by a reaction with excess methacryloyl chloride (MAC).



$$\mathrm{CH_3OCH_2CH_2OK}\ \text{(disp. in THF or benzene)} \xrightarrow{\mathrm{EO}} \mathrm{CH_3O(CH_2CH_2O)_{n}K}$$

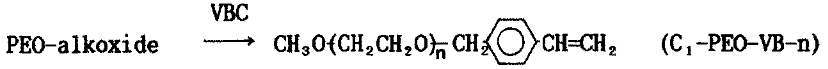
(PEO-alkoxide)

$$\xrightarrow{\mathrm{MAC}} \mathrm{CH_3O(CH_2CH_2O)_{n}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{=CH_2}$$

(C_1-PEO-MA-n)

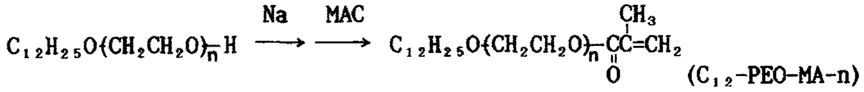
It was found that the latter end-capping reaction was more satisfactorily conducted in benzene. In tetrahydrofuran (THF) as the solvent, a very slow (dropping-wise) addition of a PEO-alkoxide solution into a MAC solution was essential, since otherwise the resulting macromonomers readily polymerized, possibly initiated by an attack of the polymer alkoxide, activated by solvation of the counter cation (K^+) by the PEO chains (14), which would be more probable in THF than in benzene.

On the other hand, the end-capping by p-vinylbenzyl chloride (VBC) was a clean reaction with no polymerization of the p-vinylbenzyl groups which are no more reactive to the attack of the alkoxide.



(C_1-PEO-VB-n)

Dodecyloxy poly(ethylene glycol) methacrylate, C_{12}-PEO-MA, was prepared from commercial poly(ethylene glycol) monododecyl ether by reactions with sodium under reflux in benzene or xylene, and then with MAC at a room temperature.



$$\mathrm{C_{12}H_{25}O(CH_2CH_2O)_{n}H} \xrightarrow{\mathrm{Na}} \xrightarrow{\mathrm{MAC}} \mathrm{C_{12}H_{25}O(CH_2CH_2O)_{n}}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{=CH_2}$$

(C_{12}-PEO-MA-n)

The macromonomers were characterized by VPO, ^{1}H NMR and GPC as before (10,11) with the results given in Table 1. The number-average degrees of polymerization, n, are in fair accord with each other, irrespective of the method of determination, supporting their satisfactory purities. Calculation of the molar composition in copolymerization, $[M_1]/[M_2]$ and $d[M_1]/d[M_2]$, was based on the n determined by VPO, as indicated in the last number of the macromonomer code, although the use of the other n resulted in almost insignificant change in the r_1 values as estimated below.

Table 1. Characterization of PEO Macromonomers

	VPO	NMR[1]	GPC[2]	
Code	n	n	n	Mw/Mn
C_1-PEO-VB-25	25.0	28.5	28.5	1.2
C_1-PEO-VB-54	53.5	64.8	-	-
C_1-PEO-MA-48	47.7	52.3	52.3	1.1
C_1-PEO-MA-84	84.1	-	100	1.1
C_{12}-PEO-MA-4	4.2	4.1	4.2	1.2
C_{12}-PEO-MA-9	9.3	9.3	12.0	1.1
C_{12}-PEO-MA-20	19.7	18.9	23.3	1.1
C_{12}-PEO-MA-25	25.4	25.4	28.9	1.1

[1] See Figure 1 for the method of estimation.

[2] Calibrated by standard PEO samples.

The radical copolymerizations of the macromonomer (M_2) with St or BzMA (M_1) were conducted in benzene at 60℃ under the condition of $[M_1]/[M_2] \gg 1$ so that the approximate composition equation, $d[M_1]/d[M_2] = r_1[M_1]/[M_2]$, should hold, where $r_1 = k_{11}/k_{12}$. The products isolated were confirmed by GPC to be free of the unreacted monomers, and analyzed for the composition by ^1H NMR using the relative peak areas of phenyl (and phenylene) to oxyethylene protons. At least three experiments with different compositions were performed in each case to give a consistent r_1 value as also confirmed in the previous papers (10,11).

The copolymerization results are summarized in Table 2, together with those including the model monomers of low molecular weights such as 2-methoxyethyl methacrylate (MEO-MA), St, and dodecyl methacrylate (C_{12}MA). Just as in the case of the copolymerization of tert-butoxy PEO macromonomers with St (10,11), the monomer reactivity ratio, r_1, again increased with n of the present macromonomers in copolymerization either with St or with BzMA. Therefore it can be concluded that the relative reactivities of the PEO macromonomer, $1/r_1 = k_{12}/k_{11}$, toward both poly-BzMA and poly-St radicals are generally smaller than those of the corresponding model monomers.

An apparent exception is the copolymerization between BzMA and C_{12}-PEO-MA, where r_1 is almost constant with n below about 10, but appears to increase barely with n of about 20. The reactivity ratio at a much higher n should approach that ($r_1 \fallingdotseq 1.7$) obtained for C_1-PEO-MA-48 or -84, since the effect of ω-terminals should vanish there. Also C_1-PEO-VB-25 in copolymerization with BzMA appears to be an exception in that it has a relative reactivity similar to its model monomer, St.

It is most interesting to note in Table 2 that the polymer-polymer compatibility (forming a transparent film) and incompatibility (forming a cloudy film) between the macromonomer (M_2) and the M_1-homopolymer closely corresponded to the constancy and the decrease, respectively, of the relative reactivity ($1/r_1$) of the macromonomer as compared to the

Table 2. Monomer Reactivity Ratio of St or BzMA (M_1) in Copolymerization with PEO Macromonomers and Model Monomers (M_2)[1]

M_1	M_2	r_1	r_2	Compatibility[2]	Reference
BzMA	MEO-MA	0.93±0.02	0.95±0.02	Yes	This work
	C_1-PEO-MA-48	1.68±0.04	-	No	This work
	C_1-PEO-MA-84	1.68±0.13	-	No	This work
BzMA	St	0.51±0.01	0.44±0.01	Yes	Otsu et al[3]
	St	0.62±0.10	0.46±0.05	Yes	Ito et al[4]
	C_1-PEO-VB-25	0.61±0.02	-	Yes	This work
	C_1-PEO-VB-54	0.82±0.02	-	No	This work
BzMA	C_{12}MA	1.20±0.04	0.94±0.03	Yes	This work
	C_{12}-PEO-MA-4	1.24±0.12	-	Yes	This work
	C_{12}-PEO-MA-9	1.23±0.09	-	Yes	This work
	C_{12}-PEO-MA-20	1.49±0.15	-	Yes	This work
St	C_{12}MA	0.56±0.02	0.36±0.04	Yes	Otsu et al[3]
	C_{12}MA	0.63±0.04	0.53±0.09	Yes	This work
	C_{12}-PEO-MA-4	0.74±0.04	-	No	This work
	C_{12}-PEO-MA-9	0.79±0.05	-	No	This work
	C_{12}-PEO-MA-20	0.82±0.02	-	No	This work
	C_{12}-PEO-MA-25	1.04±0.04	-	No	This work
	tC_4-PEO-MA-62	1.18±0.11	-	No	Ito et al[5]

[1] Total monomers, 10 % w/v in benzene; AIBN, 1 mol %; 60℃.

[2] Compatibility of the monomer M_2 and the homopolymer of M_1.

[3] Ref. 15. [4] Ref. 16. [5] Ref. 10.

respective model monomer. Thus the general incompatibility between the PEO chain and poly-St or poly-BzMA chain implies a corresponding repulsion between these different polymers, which is in turn responsible for a reduced reactivity ($1/r_1$) for the reaction between these polymers, i. e., a PEO macromonomer (M_2) and a growing polymer radical ($-M_1\cdot$) which approximates an M_1 homopolymer radical under the present condition. On the other hand, the exceptions noted above can be explained by the compatibility (meaning no repulsion) between PEO macromonomers with n less than about 25 and poly-BzMA.

In conclusion, the present data of the effects of of the α- and ω-end groups on the macromonomer's reactivity also support our previous suggestion that a repulsive interaction between different polymer chains is responsible for the reduced reactivity in copolymerization. A kinetic expression taking account of the effects of any polymer-polymer interactions in solution appears to be an important subject to be studied to understand the polymer-polymer reactions in general. C_{12}-PEO-MA is by itself an amphiphilic macromonomer which functions also as an effective dispersant in emulsion system, as will be published in a forthcoming paper.

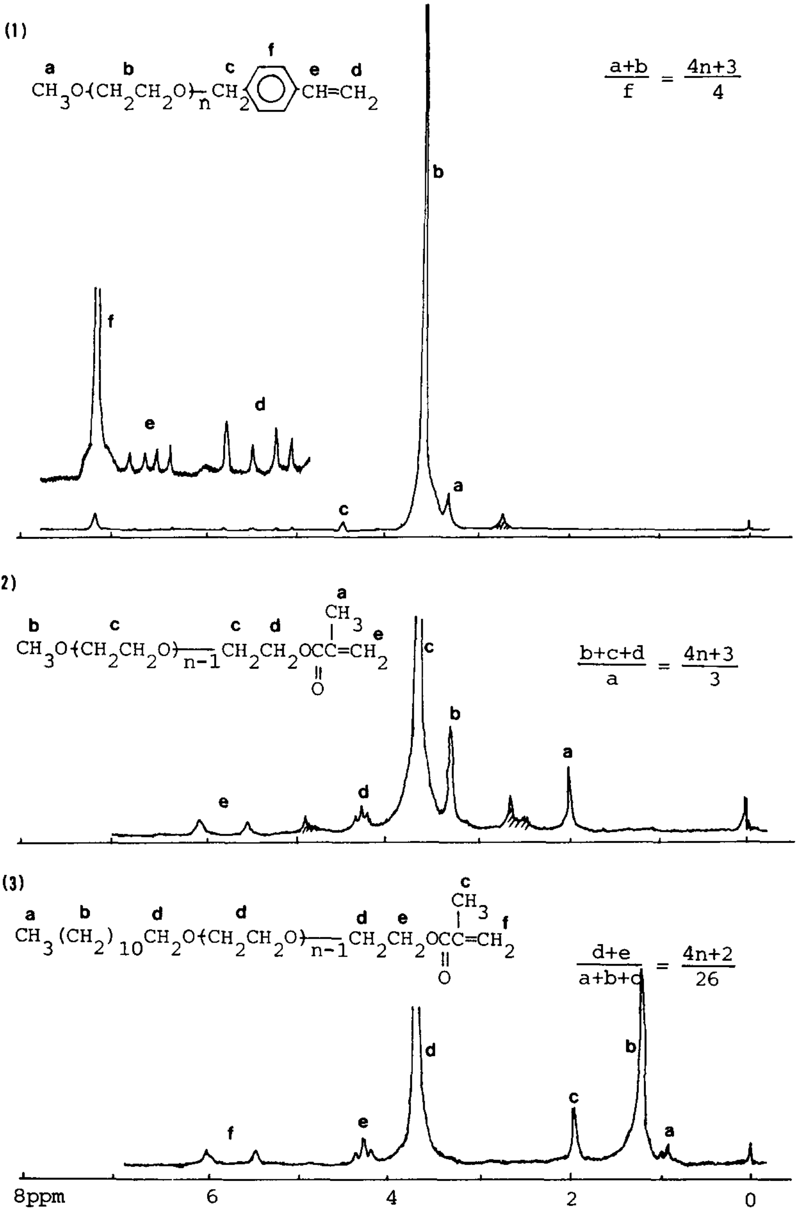


Figure 1. ^{1}H NMR spectra (60 MHz) of PEO macromonomers; (1) C_1-PEO-VB-25, (2) C_1-PEO-MA-48, (3) C_{12}-PEO-MA-9.

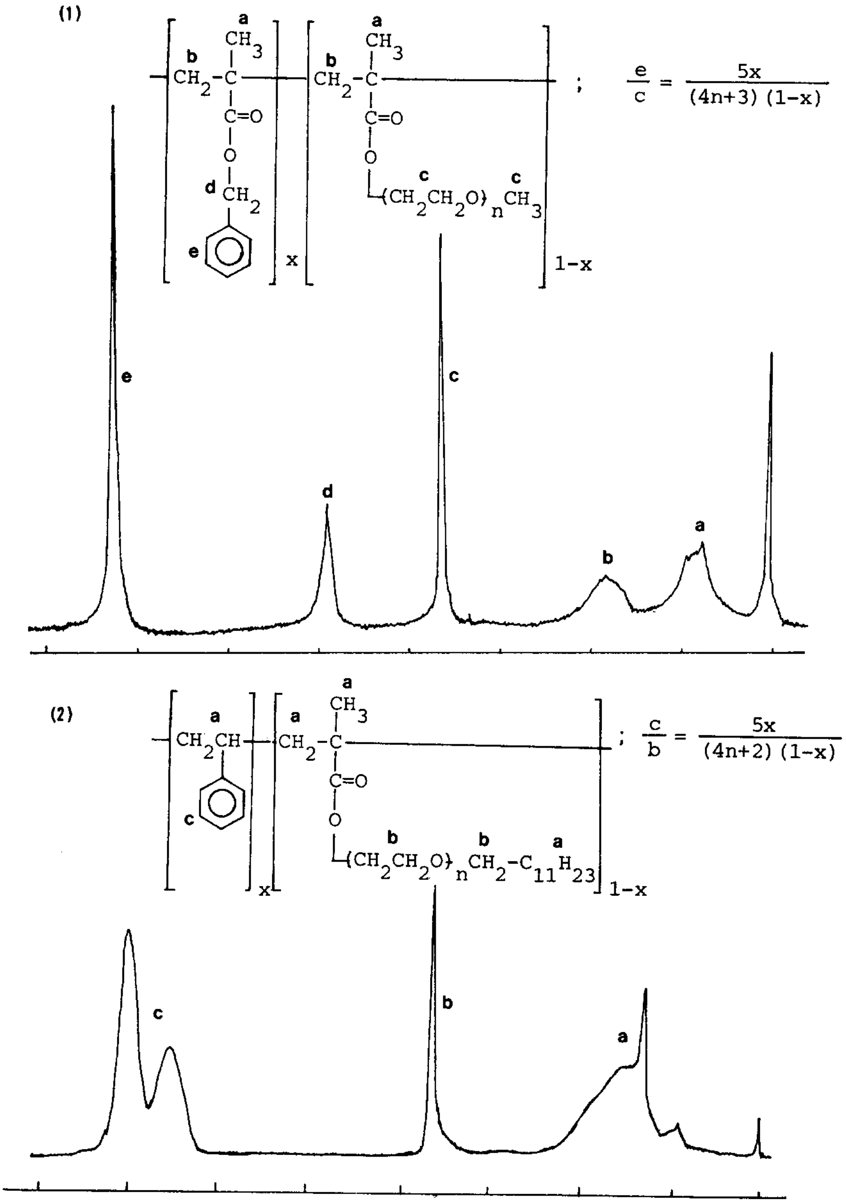


Figure 2. ^1H NMR spectra (60 MHz) of the copolymerization products from (1) BzMA and C_1-PEO-MA-48, and (2) St and C_{12}-PEO-MA-9.

Experimental

MEO-MA was prepared as described before (10). C_1-PEO-MA and -VB were also prepared by the procedure described (10) except that the initiator used was potassium 2-methoxyethoxide which was prepared from potassium and 2-methoxyethanol under vacuum, evacuated and finely dispersed in THF or benzene. C_{12}-PEO-MA was prepared from poly(ethylene glycol) monododecyl ether supplied from Takemoto Oil & Fat Co., Ltd., by reactions with excess sodium under reflux in benzene or xylene, followed by removal of the excess sodium and by reaction with excess MAC. Typical ^{1}H NMR spectra are given in Figure 1 with the assignments. The number-average degree of polymerization, n, was estimated from the appropriate peak areas as indicated in the figure.

Copolymerizations were carried out at 60℃ in benzene to conversions less than 20 wt %, and the products were isolated by precipitation into hexane (in copolymerizations with BzMA) or into methanol (in copolymerizations with St). In the case of C_1-PEO-MA or -VB with BzMA, the products were further reprecipitated from acetone into water to remove the unreacted macromonomer. The product was confirmed in each case by GPC to be free of the unreacted monomers, and analyzed for the composition by ^{1}H NMR. Typical spectra are given in Figure 2, together with the assignments and the equations used for the estimation of the molar composition, $d[M_1]/d[M_2] = x/(1-x)$. Copolymerizations of BzMA with MEO-MA and C_{12}MA, and those of St with C_{12}MA were similarly carried out, and the reactivity ratios were estimated by use of the Kelen-Tüdös method (17).

The compatibility test was made using poly-BzMA (Mn = 4×10^4), poly-St (Mn 1.2×10^4) and the PEO macromonomers according to the procedure as described before (11).

Acknowledgement

We thank Takemoto Oil & Fat Co., Ltd. for the supply of poly(ethylene glycol) monododecyl ether.

References

1) P. Masson, G. Beinert, E. Franta, P. Rempp, Polym. Bull., 7, 17 (1982).
2) P. Rempp, P. Lutz, P. Masson, E. Franta, Makromol. Chem., Suppl., 8, 3 (1984); 13, 47 (1985).
3) W. W. Shulz, J. Kaladas, D. W. Shulz, J. Polym. Sci., Polym. Chem. Ed., 22, 3795 (1984).
4) S. Nagaoka, Y. Mori, H. Takiuchi, Y. Yokota, H. Tanzawa, S. Nishiumi, ACS Polym. Prepr., 24 (1), 67 (1983).
5) Y. Tanizaki, Yukagaku, 31, 253 (1982).
6) T. Hamaide, M. Marriaggi, J. L. Foureys, P. LePercechec, A. Guyot, J. Polym. Sci., Polym. Chem. Ed., 22, 3091 (1984).

7) T. Suzuki, T. Tomono, J. Polym. Sci., Polym. Chem. Ed., 22, 2829 (1984).
8) S. Kobayashi, M. Kaku, T. Mizutani, T. Saegusa, Polym. Bull., 9, 169 (1983).
9) S. Kobayashi, T. Mizutani, T. Saegusa, Makromol. Chem., 185, 441 (1984).
10) K. Ito, H. Tsuchida, A. Hayashi, T. Kitano, E. Yamada, T. Matsumoto, Polym. J., 17, 827 (1985).
11) K. Ito, H. Tsuchida, T. Kitano, Polym. Bull., accepted for publication.
12) S. Itsuno, K. Yamazaki, F. Arakawa, T. Kitano, K. Ito, E. Yamada, T. Matsumoto, Kobunshi Ronbunshu, 43, 91 (1986).
13) J. M. Harris, J. Macromol. Sci., Rev., C25, 325 (1985).
14) D. Garg, S. Höring, J. Ulbricht, Makromol. Chem., Rapid Comm., 5, 615 (1984).
15) T. Otsu, T. Ito, M. Imoto, Kogyo Kagaku Zasshi, 69, 986 (1966).
16) K. Ito, Y. Yamashita, Kogyo Kagaku Zasshi, 68, 1469 (1965).
17) T. Kelen, F. Tüdős, J. Macromol. Sci., Chem., A9, 1 (1975).

Accepted August 6, 1986 S