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ORIGINAL CONTRIBUTION

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Synthesis, polymerization, and dispersion copolymerization of poly(ethylene oxide) macromonomers carrying methacryloyloxyalkyl end groups

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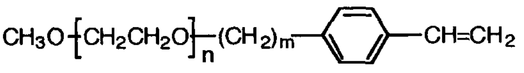
Abstract Poly(ethylene oxide) macromonomers carrying methoxy group on the one (α-) end and methacryloyloxyhexyl or methacryloyloxydecyl group on the other (ω-) end were prepared, homopolymerized in water, and dispersion-copolymerized with styrene or methyl methacrylate in a methanol–water mixture. They were found to polymerize more rapidly and to produce stable polystyrene dispersions more effectively, as compared to the corresponding macromonomers carrying either α-methoxy and or α-dodecyloxy and ω-methacryloyloxy end groups. Thus, the amphiphilic constitution of the macromonomers such that favors the polymerizing methacrylate end groups to locally concentrate into the micelle core or to the particle surface while the poly(ethylene oxide) chains extending to the medium appears to be most important in enhancing their polymerizability and effectiveness as reactive steric stabilizers. On the other hand, stable poly(methyl methacrylate) particles with a number of craters or pleats on the surface were produced with a PEO macromonomer with α-methoxy and ω-methacryloyloxy end groups.

Key words Poly(ethylene oxide) – macromonomer – micelle – polymerization – dispersion (co)polymerization

Introduction

We have reported an unusually rapid radical polymerization of poly(ethylene oxide) macromonomers in water of a general structure [1–5]:



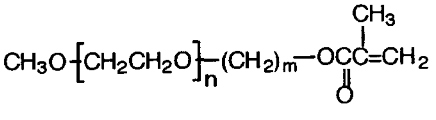
(**1**) C1-PEO-VB-n (m=1)

(**2**) C1-PEO-Cm-S-n (m>1)

where C1 stands for methoxy group as an ω-end, PEO for poly(ethylene oxide), VB for p-vinylbenzyl ($m = 1$), C_m-S for p-styrylbutyl ($m = 4$) or -heptyl ($m = 7$) as an α-end, and n specifies number-average degree of polymerization of PEO. Because of their amphiphilic constitution, with PEO chains being soluble while p-styrylalkyl groups insoluble in water, they organize into micelles with those polymerizing end groups locally concentrated in the cores, to apparently enhance their polymerization. In fact, **2**, with a more hydrophobic styryl group, was found to polymerize more rapidly [3]. Their micelle formation has been confirmed by means of static light scattering [1] and fluorescence probe methods [6]. As an important application, **2** was also found to be very effective in preparing monodisperse polymeric microspheres of submicron to micron size by emulsion or dispersion copolymerization with a large excess of styrene or butyl methacrylate [7–9].

Interestingly, a corresponding PEO macromonomer with ω-methacrylate (MA) end group **4** with $m = 11$ and

$n = 8$, and its polymers have been independently studied in terms of the micelle formation in water [10, 11]:



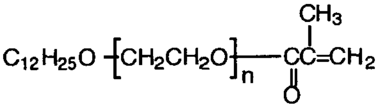
$CH_3O\text{-}[CH_2CH_2O]_n\text{-}(CH_2)_m\text{-}OC(=O)C(CH_3){=}CH_2$

(**3**) C1-PEO-MA-n (m=1)

(**4**) C1-PEO-Cm-MA-n (m>1)

Emulsion copolymerization of styrene with the macromonomers such as **2** and **4** as an effective reactive emulsifier has also been recently reported [12]. To our knowledge, however, there has been no report on the homopolymerization and dispersion copolymerization behaviors of **4** [see Appendix].

Since methacrylates are generally more reactive in radical polymerization [13], but apparently much less hydrophobic, as compared to styrene derivatives, we are interested in the macromonomers, **4**, to have an idea of their micellar polymerization in water together with their effectiveness in a dispersion system, particularly in view of their amphiphilic consitution. This paper intends to report the results with **4** ($m = 6$ or 10, $n = 17$ or 48) in comparison with corresponding macromonomers, **3** with no alkylene spacer, and **5** with a hydrophobic alkyl group in ω-position:



$C_{12}H_{25}O\text{-}[CH_2CH_2O]_n\text{-}C(=O)C(CH_3){=}CH_2$

(**5**) C12-PEO-MA-n

Experimental

Materials

Macromonomers, **4** ($m = 6$ and 10), were prepared by reaction of the corresponding tBuMe$_2$Si-protected ω-bromoalkanols **6**, with sodium alkoxide of poly(ethylene glycol) monomethyl ether (MPEGNa), followed by deprotection, sodium alkoxidation, and coupling with methacryloyl chloride (MAC) as follows:

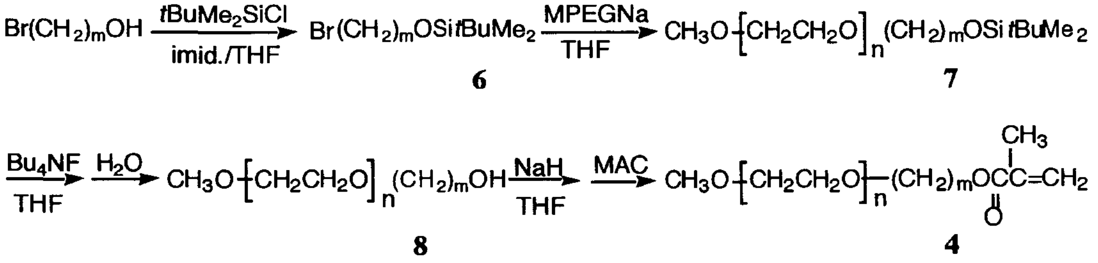
For example, 6-bromohexanol (Aldrich), 2 g (11 mmol), with imidazole (Sigma), 27 mmol, in dry tetrahydrofuran (THF), 100 mL, was reacted with *tert*-butyldimethylsilyl chloride (Aldrich), 13 mmol, according to a procedure by Corey [14], with stirring at 30 °C overnight, to obtain **6** in 95% yield. MPEG (Aldrich, $M_n = 2000$ and 750) was reacted with excess sodium hydride and **6** in dry THF at 40 °C for 2 days to isolate **7** in 70% yield after a similar procedure as described previously [3]. Deprotection of **7** with tetrabutylammonium fluoride to **8** (80% yield) and reaction with MAC to obtain the macromonomer **4** ($m = 6$) (yield 95%) were done according to a procedure similar to the one described [2].

Macromonomers **3** and **5** were prepared form MPEG and poly(ethylene glycol) monolauryl ether (Takemoto Oil&Fat Co., Ltd.), respectively, by the same methods as described [1, 15]. ^{1}H NMR spectra of **4** ($m = 6$ and 10) and characterization data of all the macromonomers used in this work are given in Fig. 1 and Table 1, respectively.

Styrene and methyl methacrylate (MMA) were washed with aq sodium thiosulfate, aq sodium hydroxide, and distilled over calcium hydride under reduced pressure. Milli-Q water and distilled methanol were used as dispersion media. Deuterated water (D_2O) from Aldrich, 4,4′-azobis(4-cyanovaleric acid) (AVA) from Aldrich, 2,2′-azobisisobutyronitrile (AIBN) from Kishida Chem., and dimethyl 2,2′-azobisisobutyrate (MAIB) from Wako Pure Chem. were used as supplied.

Polymerization

Radical polymerization of the macromonomers in water (D_2O) at 60 °C with AVA or MAIB as an initiator was monitored by ^{1}H NMR following the disappearance of the double bond peak in reference to the oxyethylene peak (Fig. 1), according to a similar procedure as described [1]. Monomer and initiator concentrations used were 45 and 4.5 mmol/l, respectively. Dispersion (co)polymerization of styrene or MMA in the presence of the macromonomers was conducted with magnetic stirring at 60 °C in a mixture of methanol and water with AIBN. Styrene or MMA, 0.5 g, a desired amount of macromonomer, and AIBN, 10 mg,



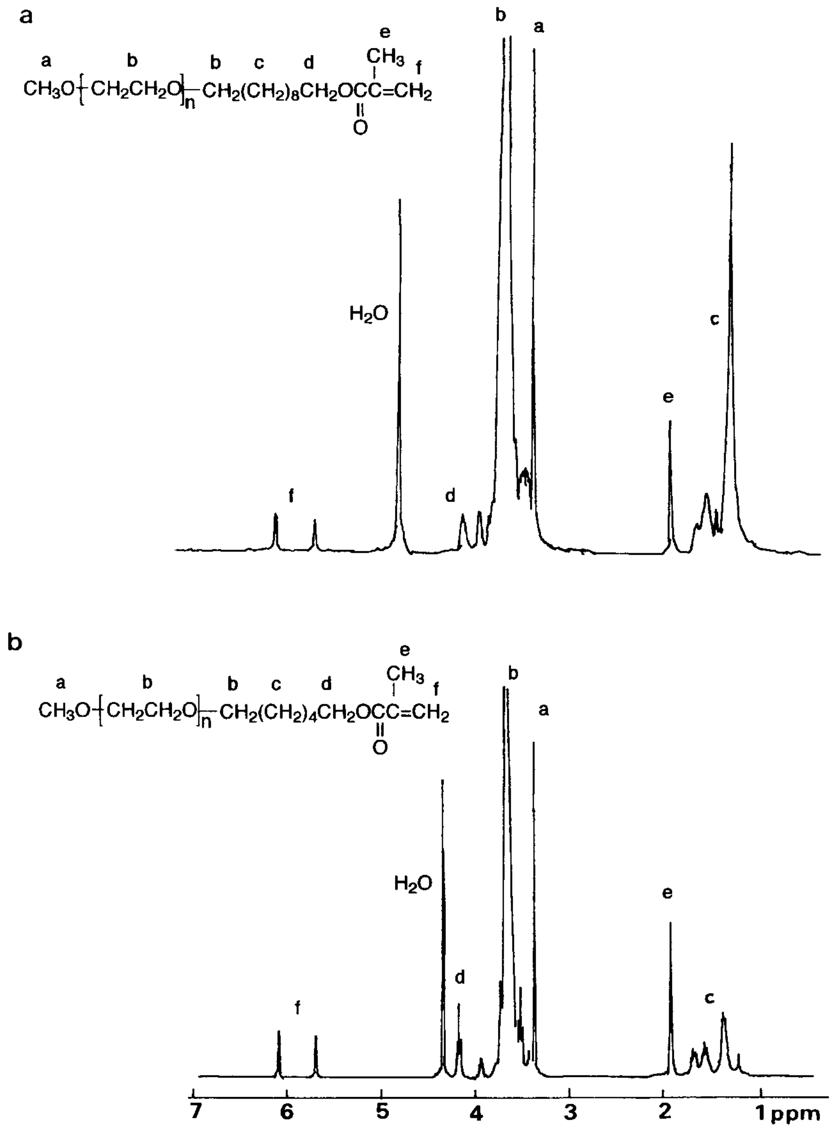


Fig. 1 ^{1}H NMR spectra of the macromonomers in D_2O: (a) C1-PEO-C10-MA-48, (b) C1-PEO-C6-MA-48

Table 1 Characterization of the macromonomers used

Code[a]	M_n	M_w/M_n[b]	f[c]	HLB[d]
C1-PEO-MA-17	848	1.07	0.95	17.6
C1-PEO-MA-48	2212	1.04	1.00	19.1
C1-PEO-C6-MA-48	2312	1.04	0.99	18.3
C1-PEO-C10-MA-17	1004	1.04	0.90	14.9
C1-PEO-C10-MA-48	2368	1.04	1.00	17.8
C12-PEO-MA-19	1004	1.12	0.93	15.6

[a] The last figure indicates the number-average degree of PEO as determined by ^{1}H NMR from the peak area ratio of oxyethylene to ω-methoxy protons.
[b] Determined by GPC calibrated with PEO standard samples.
[c] Functionality of the methacrylate double bond as determined by ^{1}H NMR from the peak area ratio to the ω-methoxy protons.
[d] Hydrophile–lypophile balance as calculated by $HLB = E/5$ [16], where E is the weight percentage of the PEO segment involved.

were weighed into a glass tube with a mixture of methanol and water, 5 ml, degassed three times by freeze-thawing, sealed off, and stirred in a bath of 60 °C for 48 h, to almost complete conversion of the substrate monomer. The polymer particles were characterized for the size by SEM after dilution with methanol. Their composition was determined by ^{1}H NMR, as described previously [17], with the sample obtained after purification by reprecipitation from THF into methanol to remove unreacted monomers as confirmed by GPC.

Measurements

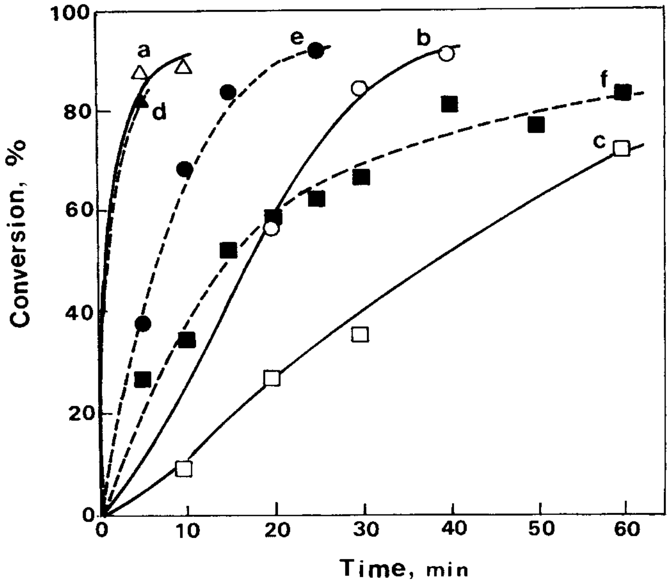
^{1}H NMR on a JEOL JNM-GX-270 FT spectrometer and GPC on a JASCO TRIROTAR III with an RI detector, Shodex RI SE-11, were measured as described before [1]. GPC was calibrated with standard samples of poly(ethylene oxide) and polystyrene for the molecular weights of the macromonomers and the (co)polymers obtained in a dispersion system, respectively. Polymer particles were observed by SEM on a Hitachi S-2300 microscope with Pt-coated polymer dispersions. Number- and weight-average diameters of the particles were calculated by $D_n = \sum n_i D_i / \sum n_i$ and $D_w = \sum n_i D_i^4 / \sum n_i D_i^3$, respectively, where n_i is the number of the particles with diameter D_i.

Results and discussion

Homopolymerization of macromonomers

The macromonomers **3** and **4** polymerized apparently clearly while **5** with a little cloudy appearance, in water at 60 °C with a radical intiator. Conversions were monitored by ^{1}H NMR. The time-conversion plots of **4**, C1-PEO-C6-MA-48 and C1-PEO-C10-MA-48, with AVA and MAIB are given in Fig. 2 in comparison with those of **3**, C1-PEO-MA-48. Most interestingly, the rate of polymerization apparently increases with increasing hydrophobicity around the polymerizing methacrylate end group in the order: C1-PEO-C10-MA-48 > C1-PEO-C6-MA-48 > C1-PEO-MA-48. This result clearly supports the micellar polymerization mechanism for **4**, just as reported for the PEO macromonomers with styryl end groups **1**, and **2** [1, 3, 5]. Thus polymerization of **4** is apparently favored by micellar organization, with their hydrophobically enhanced methacrylate groups enriched into the cores, just like that found for C1-PEO-C11-MA-8 [10].

Fig. 2 Time-conversion plots for homopolymerization of the macromonomers in D_2O at 60 °C. $[M] = 45$ mmol/l, $[I] = 4.5$ mmol/l: (a) C1-PEO-C10-MA-48 with AVA, (b) C1-PEO-C6-MA-48 with AVA, (c) C1-PEO-MA-48 with AVA, (d) C1-PEO-C10-MA-48 with MAIB, (e) C1-PEO-C6-MA-48 with MAIB, (f) C1-PEO-MA-48 with MAIB



As for the macromonomer **3**, C1-PEO-MA-48, with no explicitly hydrophobic group, the initial conversion rate in water is higher than that of its lower analog C1-PEO-MA-3, which is less than 10%/h in the same condition as in Fig. 2 [1], or even higher than that of methyl methacrylate, which is calculated from the rate data with AIBN in bulk at 60 °C to be about 10% in 10 min [18]. Since the decomposition rates of AIBN, AVA, and MAIB are, roughly speaking, not so much different [1, 19], the result suggests a hindered diffusion-controlled termination of macromonomers as compared to the corresponding monomers of lower molecular weights, as is often observed [1, 5, 20, 21]. Alternatively, the result may be accounted for by assuming some loose, if not very extensive, micelle formation due to aggregation through relatively hydrophobic methacrylate groups, as proposed previously [1]. Higher polymerization rates generally observed with MAIB as compared with AVA (Fig. 2) appear to be due to slightly but significantly higher decomposition rate [19] of the former which may be more extensively solubilized in the micelle cores [22]. A reason for the apparently similar conversion rates for C1-PEO-C10-MA-48 with MAIB and AVA (curves a and d), however, is not clear because of the too rapid polymerization.

Figure 3 shows another interesting fact that **4** polymerized significantly more rapidly than **5** with a hydrophobic alkyl (C12) group in ω-position, i.e., in a formally farthest position from the polymerizing methacrylate group. Since **4** (C1-PEO-C10-MA-17) and **5** (C12-PEO-MA-19) here have very similar HLB values (Table 1), they are expected to have an apparently similar micelle-forming ability. Therefore, the result clearly indicates importance of the location of the hydrophilic and hydrophobic segments relative to the polymerizing group. It is reasonable to expect a higher polymerizability for **4** than **5** as observed, because the former will locally concentrate the methacrylate groups into the micelle core together with the hydrophobic alkyl (C10) spacer groups, a situation very suitable for polymerization. In contrast, **5** has to relatively disperse the methacrylate groups among or around the micelle shells composed of the hydrated hydrophilic PEO chains. Also, a factor to be considered is that polymethacrylate backbone chains are apparently rather hydrophobic, insoluble in water, so that polymerization of **5** will force some of the PEO chains to take loop conformations, giving rise to a flower-like polymerized

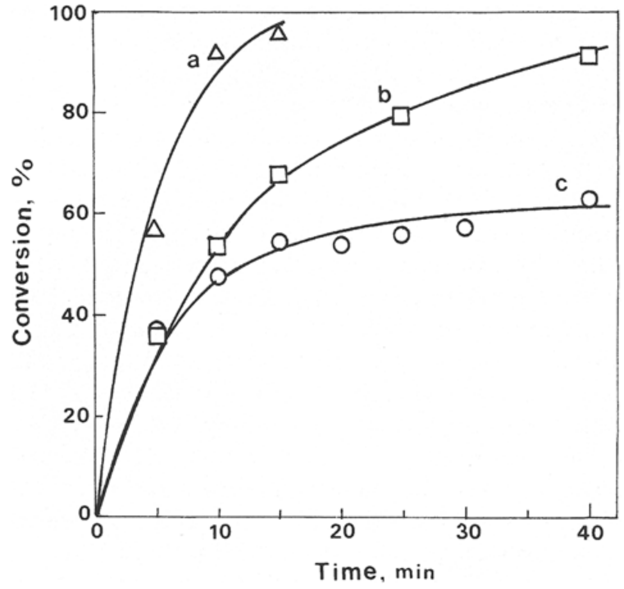


Fig. 3 Time-conversion plots for homopolymerization of the macromonomers in D_2O at 60 °C. $[M]$ = 45 mmol/l, $[I]$ = 4.5 mmol/l. (a) C1-PEO-C10-MA-17, (b) C12-PEO-MA-19, (c) C1-PEO-MA-17

micelle, which is entropically unfavored. Another possibility is intermicellar association through penetration of long ω-alkyl chains among different micelles. In fact, PEO macromonomers with longer alkyl chains such as C18-PEO-MA-23 or -29 were found to gel during polymerization in water at 60 °C with AVA, $[M]$ = 45–4.5 mmol/l, and $[I]$ = 4.5–0.45 mmol/l, suggesting extensive intermicellar aggregation.

In spite of this consideration, however, Fig. 3 also shows a significantly higher polymerizability of **5**, C12-PEO-MA-17, when compared to **3**, C1-PEO-MA-17, particularly at extended polymerization time. Apparently, a higher micelle-forming ability of **5** will favor its eventually higher conversion while a much more hydrophilic **3** appears to polymerize to a limited conversion. Further discussion needs information of surface-active properties such as CMC and micellar sizes of these macromonomers and their polymers, which remain to be elucidated.

Dispersion (co)polymerization of styrene and MMA with macromonomers

Macromonomer technique has been of increasing importance in preparation of soap-free, relatively monodisperse polymeric microspheres of submicron to micron size in emulsion and dispersion systems [23, 24]. Here the macromonomers, very soluble in the media, are copolymerized with an excessive amount of substrate monomers to afford graft copolymers with the soluble macromonomer chains as the branches which act effectively as steric stabilizers for the insoluble (co)polymer particles produced in situ. Now **3** and **4** were also found to be effective in dispersion (co)polymerization with styrene or MMA in a methanol–water mixture (9/1 or 7/3 v/v, respectively).

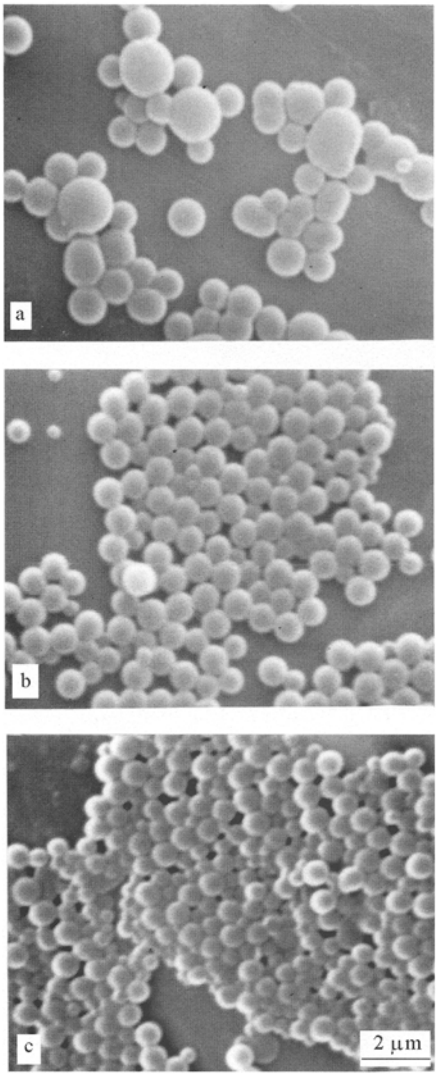


Fig. 4 SEM photographs of the particles obtained from dispersion (co)polymerization of styrene with macromonomers: (a) Styrene/C1-PEO-MA-48, (b) styrene/C1-PEO-C6-MA-48, (c) styrene/C1-PEO-C10-MA-48

Typical SEM photographs are given in Figs. 4 and 5, and the particles data are summarized in Table 2. In (co)polymerization of styrene, more monodispersed and smaller-sized particles were obtained with the PEO methacrylate macromonomer with a longer alkylene spacer group, thus indicating their effectiveness as reactive dispersant decreasing in the order: C1-PEO-C10-MA-48 > C1-PEO-C6-MA-48 > C1-PEO-MA-48. The last one

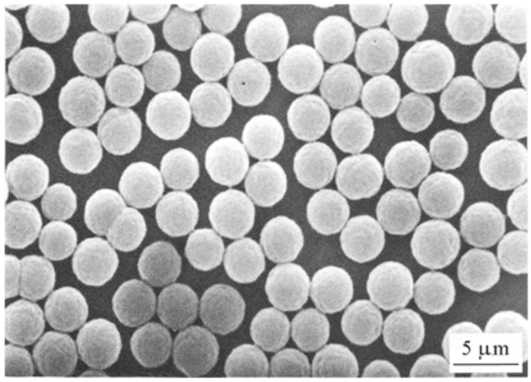


Fig. 5 SEM photograph of the particles obtained from dispersion (co)polymerization of MMA with C1-PEO-MA-48

induced some precipitation. This result is in accord with the fact in Table 2 that the more hydrophobically enhanced methacrylate end groups are more effectively graft copolymerized into the particles surface, as expected from a higher affinity of these methacrylate groups with styrene monomer or with the polystyrene particles, although the incorporation of the macromonomers was in general much less than the composition in the feed. It is also interesting to note that the incorporation of the present macromonomers, C1-PEO-C6-MA-48 and C1-PEO-C10-MA-48, into the polystyrene particles was significantly higher than what was found in dispersion (co)polymerization with **2** (C1-PEO-C4-S-45) [9]. This resulted in the correspondingly smaller particles here, as expected theoretically [8, 9] from a higher copolymerizability of the present methacrylate-ended macromonomers, **4**, with styrene, as compared with the styryl-ended ones **2**, by assuming their similar cross-sectional areas or steric repulsion effects of the PEO chains of similar lengths.

While a stable dispersion was also obtained with C1-PEO-C10-MA-17, a macromonomer, C12-PEO-MA-19 with a similar HLB, was found to produce extensive coagulation almost from begining of the polymerization, indicating ineffectiveness of the hydrophobic group introduced on the other end of the polymerizing group. This can be expected because the α-methacrylate group has to copolymerize with styrene and thus anchor into a particle surface possibly together with the ω-C12 group. This means a central PEO chain, either bridging between particles, or looping on a particle surface, just as discussed above in the case of homopolymerization in water.

Dispersion (co)polymerization of MMA was also successful in producing very stable PMMA dispersions of micron size. In this case, however, C1-PEO-MA-48 was more effective in giving monodisperse particles than C1-PEO-C6-48. Interestingly, the particles obtained were found to have uneven surfaces with a number of craters or pleats (Fig. 5), somewhat resembling "golf" balls as reported by Okubo et al. [25]. Such particles were also obtained in (co)polymerization of MMA with a macromonomer **1**, C1-PEO-VB-45 [26]. These results suggest that some compatibility between PMMA and PEO chains and also between PMMA and the medium (methanol/water) may play a role in controlling the particle formation, in a different way from that of styrene system [8, 9]. This is to be discussed in a forthcoming paper [26].

Table 2 Dispersion (co)polymerization of styrene[a] and MMA[b] with the macromonomers

Monomer (M_1)	Macromonomer (M_2)	M_1/M_2 [10^2 mol/mol]	m_1/m_2[c] [10^2 mol/mol]	D_n [μm]	D_w/D_n
Styrene	C1-PEO-MA-48	4.2	38	0.50[d]	1.18
Styrene	C1-PEO-C6-MA-48	4.2	19	0.46	1.04
Styrene	C1-PEO-C10-MA-48	4.2	11[e]	0.32	1.05
Styrene	C1-PEO-MA-17	0.78	3.3	0.50[d]	1.10
Styrene	C1-PEO-C10-MA-17	0.78	2.9	0.28	1.12
Styrene	C12-PEO-MA-19	0.78	—f)	—f)	—f)
MMA	C1-PEO-MA-48	4.3	7.6	1.19	1.01
MMA	C1-PEO-C6-MA-48	4.3	6.0	0.2–1.7[g]	—

[a] Styrene 0.5 g in methanol/water ($\frac{9}{1}$ vol/vol) 5 ml, at 60 °C for 48 h.

[b] MMA 0.5 g in methanol/water ($\frac{7}{3}$ vol/vol) 5 ml, at 60 °C for 48 h.

[c] Monomer/macromonomer molar ratio in polymer particles isolated as determined by ^{1}H NMR.

[d] Data for dispersed particles. Partial precipitation was observed.

[e] M_n and M_w/M_n were around 2×10^5 and 5, respectively, as estimated by GPC calibrated with standard polystyrenes.

[f] Coagulated in the whole system.

[g] Bimodal with small particles of 0.2 μm and their aggregated spheres around 1.7 μm.

Conclusion

The PEO macromonomers, **4**, with hydrophobically enhanced methacrylate end groups were prepared and found to homopolymerize very rapidly in water. They were also very effective in producing stable dispersion particles from styrene in methanol/water mixture. Stable, uneven-surfaced microspheres from MMA were obtained, however, with a rather simple PEO macromonomer, **3**, with just a methacrylate end group. Proper balance and location of the hydrophilic and hydrophobic segments relative to the polymerizing group appears to be a factor of key importance in determining the macromonomer's polymerizability and effectiveness in dispersion (co)polymerization in a particular polar medium.

Acknowledgments This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. Support from Technical Research Laboratory of Kansai Paint Co., Ltd., Hiratsuka, Japan is also gratefully acknowledged.

Appendix

(Note added in proof)

To our notice after submission of this article, a very rapid micellar polymerization of C1-PEO-C11-MA-40, according to our notation, and its application to emulsion (co)polymerization with styrene have been published [Liu J, Chew CH, Gan LM (1996) J Macromol Sci-Pure Appl Chem A33:337, and Liu J, Chew CH, Wong SY, Gan LM (1996) J Macromol Sci-Pure Appl Chem A33:1181].

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