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Emulsion and dispersion polymerization of styrene in the presence of PEO macromonomers with *p*-vinylphenylalkyl end groups

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Abstract

Poly(ethylene oxide) (PEO) macromonomers with α -*p*-vinylphenylalkyl (propyl, pentyl, and hexyl) and ω -hydroxy end groups were applied to emulsion and dispersion polymerization of styrene as reactive emulsifiers and dispersants in water and in methanol-water mixture (9:1 v/v), respectively. Nearly monodisperse microspheres of submicron to micron size were obtained. Particle size in the emulsion system was one or half order of magnitude smaller than that in the dispersion system, while in both systems the size decreased approximately according to minus one half power of the macromonomer concentration in weight. The particle size was substantially independent on the PEO chain length and also on the spacer alkyl chain length of the α -polymerizing end group. The total weight of the PEO chains incorporated by copolymerization into the particle surfaces (shells), relative to that of styrene polymerized into the particle cores, appears to be a key factor for controlling the particle size. **To cite this article:** *K. Landfester et al., C. R. Chimie 6 (2003).*

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Résumé

Des macromonomères de poly(oxyde d'éthylène) PEO avec des groupes terminaux α -*p*-vinylphenylalkyles (propyle, pentyle, et hexyle) et ω -hydroxyles ont été utilisés pour la polymérisation du styrène en émulsion dans l'eau et dans la polymérisation en dispersion dans des mélanges eau-méthanol (9 :1 v/v). On a obtenu des microsphères presque monodisperses de tailles submicroniques en émulsion ou jusqu'à microniques en dispersion. Entre les deux procédés, les tailles diffèrent d'un ordre de grandeur et demi en fonction de la concentration en macromonomère. La taille des particules est pratiquement indépendante de la longueur des chaînes PEO et alkyle. Mais le rapport entre la masse de PEO incorporée à la surface des particules et la masse de styrène paraît être le facteur déterminant qui contrôle la taille des particules. **Pour citer cet article :** *K. Landfester et al., C. R. Chimie 6 (2003).*

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Keywords: PEO macromonomers; *p*-vinylphenylalkyl end-groups; styrene; emulsion copolymerization; dispersion copolymerization; particle size control

Mots clés : macromonomères de PEO ; groupes terminaux *p*-vinylphenylalkyles ; copolymérisation en émulsion, copolymérisation en dispersion ; styrène, contrôle des tailles des particules

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1. Introduction

Amphiphilic macromonomers usually consist of hydrophilic polymer chains and hydrophobic (co)polymerizable end groups as tails and heads, contrary to the conventional surfactants, and find useful application to emulsion and dispersion polymerization of hydrophobic monomers in water and alcoholic media, respectively [1]. The macromonomers copolymerize in situ with the hydrophobic monomers to afford graft copolymers that serve as effective stabilizers firmly (covalently) attached on the particle surfaces, well represented by the name ‘surfmer’ [2]. Thus the hydrophobic heads of the copolymerized macromonomers act as anchors while the hydrophilic macromonomer tails work as steric stabilizers against flocculation. So far a lot of macromonomers or surfmers have been reported for design of various kinds of polymer microspheres [1–5].

In general, emulsion and dispersion polymerizations produce polymer microspheres of submicron to micron in size. While we have proposed a kinetic model of particle size control in dispersion polymerization using macromonomers [6,7], there has been still not enough information about the mechanism of particle formation and the effects of the macromonomer structure or composition in heterogeneous polymerization system in general. Among others poly(ethylene oxide) (PEO) macromonomers have been of increasing concern in view of relatively easy design of the tail-head structure coupled with a variety of potential applications [1,8,9]. Therefore we have been interested in the project of experimental exploitation of the particle size control by using a systematically structure-designed PEO macromonomers [10]. In this paper we are intended to present some fundamental information about the effect of the tail-head composition of the styryl-ended macromonomers, **1**, which have been recently prepared by initiation method as given in Fig. 1 [11].

2. Experimental

The PEO macromonomers, **1**, listed in Table 1, were prepared by polymerization of ethylene oxide with corresponding *p*-vinylphenylalkanols partially alkoxided with potassium naphthalene in tetrahydrofuran,

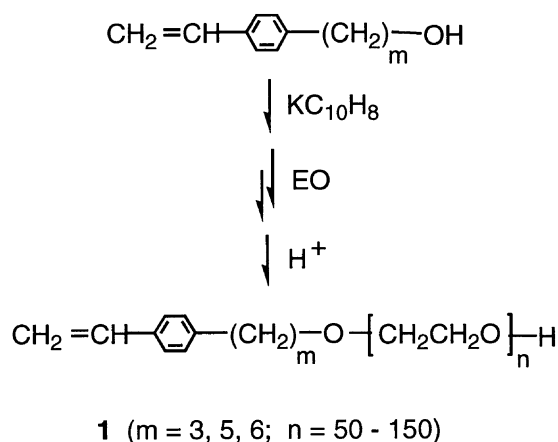


Fig. 1. Synthesis of PEO macromonomers by initiation method.

Table 1
PEO macromonomers used

Entry code ^a	M_n ^b	M_w/M_n ^c
m3n50	2340	1.07
m3n80	3660	1.16
m3n150	6740	1.12
m5n64	2990	1.10
m6n50	2430	1.24

^a The numbers following *m* and *n* stand for the alkylene and PEO chain lengths, respectively in structure **1**.

^b Number-average molecular weight determined by ¹H NMR.

^c Determined by SEC calibrated with standard poly(ethylene glycol)s.

as described in detail [11]. 2,2'-Azobis(isobutyronitrile) (AIBN) and 4,4'-azobis(4-cyanovaleric acid) (AVA) from Aldrich were recrystallized from methanol. Styrene was distilled over calcium hydride under a reduced pressure.

Emulsion polymerization of styrene in the presence of the PEO macromonomers was conducted at 65 °C in water with AVA as an initiator. Typically, 1 g of styrene, 10 mg of AVA, 10 ml of water, and a desired amount of the macromonomer were charged into a round-bottomed glass tube with a magnetic stirrer tip. The tube was degassed three times by freeze-thaw in vacuum, sealed off, and placed in a heated bath and stirred magnetically for one day. The average size and distribution were analyzed for one hundred particles in the SEM (scanning electron microscopy) photograph taken after dilution with methanol. Conversion of styrene was determined by gravimetry [12]. The particles were purified by centrifugal separation with methanol to remove the unreacted monomers, together with,

any, homopolymers of the PEO macromonomers. Removal of the unreacted macromonomers was confirmed by SEC (size-exclusion chromatography). Their composition was estimated by ^1H NMR measured in CDCl_3 from the peak intensity ratio of the phenyl to oxyethylene protons. Dispersion polymerization was similarly conducted but at 60°C in methanol-water mixture (9:1 v/v) with AIBN as an initiator.

Measurements of ^1H NMR (Mercury Varian 300), SEC (JASCO), and SEM (Hitachi S-2300) were carried out as described before [11–13].

3. Results and discussion

3.1. Theoretical consideration

We assume a core-shell structure for the polymer microspheres obtained by polymerization of excessive amount of a substrate monomer in the presence of small amount of a macromonomer [6,7]. Then the core should essentially consist of the substrate monomer polymerized and its volume in average is given by:

$$(4/3) \pi R^3 = W_{\text{So}} \theta_{\text{S}} / \rho N \quad (1)$$

where R is the particle (core) radius, W_{So} is the weight of the substrate monomer in feed, θ_{S} is its conversion of polymerization, ρ is the density of its polymer, and N is the total number of the particles. On the other hand, the surface should be covered by the macromonomer (dispersant) chains copolymerized, so that the area is given by:

$$4 \pi R^2 = W_{\text{Do}} \theta_{\text{D}} N_{\text{A}} S / M_{\text{D}} N \quad (2)$$

where W_{Do} is the weight of the macromonomer in feed, θ_{D} is its conversion copolymerized or grafted on the surface, M_{D} is the molecular weight of the macromonomer, S is the cross-sectional area occupied by each grafted macromonomer chain, and N_{A} is the Avogadro number. Then, we combine Eqs. (1) and (2) to have, for an average particle radius:

$$R = (3 M_{\text{D}} W_{\text{So}} \theta_{\text{S}}) / (\rho W_{\text{Do}} \theta_{\text{D}} N_{\text{A}} S) \\ = (3 m_{\text{S}} M_{\text{S}}) / (\rho N_{\text{A}} m_{\text{D}} S) \quad (3)$$

where $(W_{\text{So}} \theta_{\text{S}}) / (W_{\text{Do}} \theta_{\text{D}}) = (m_{\text{S}} M_{\text{S}}) / (m_{\text{D}} M_{\text{D}})$, with m_{S} and m_{D} standing for the moles of the substrate monomer and the macromonomer incorporated into the particle core and surface, respectively, and M_{S} for

the molecular weight of the substrate monomer. It is to be noted that the above relations should hold for any heterogeneous (including emulsion and dispersion) system so long as the clear-cut phase separation occurs for the core (substrate polymers) and the shell (macromonomer chains). Present copolymerization system of styrene with the PEO macromonomers appears to provide one of most suitable models because polystyrene and the PEO chains are completely incompatible with each other, while polystyrene and PEO chains are hardly and easily soluble in water or in methanol, respectively.

As expected, Eq. (3) predicts that the particle size decreases with increasing coverage of the macromonomers on the particle surfaces, i.e., with an increase in the ratio of the macromonomer to the substrate monomer polymerized, $(W_{\text{Do}} \theta_{\text{D}}) / (W_{\text{So}} \theta_{\text{S}})$ or $m_{\text{D}} / m_{\text{S}}$, and in the specific surface coverage of the macromonomer chain, S , on the surface. A problem is that S is not constant but varies with conversion according to the conformation change of the macromonomer chains tethered to the particle surface. Based on the kinetic simulation together with the homogeneous nucleation mechanism by Paine [14], we proposed an equation for the particle size in dispersion copolymerization [6,7]:

$$R = \theta_{\text{S}}^{1/3} (3 W_{\text{So}} / \rho N_{\text{A}})^{2/3} (M_{\text{D}} r_1 / W_{\text{Do}} S_{\text{crit}})^{1/2} \\ (0.386 k_2 / 4 \pi k_p)^{1/6} (k_t / 2 k_d f [I]_0)^{1/12} \quad (4)$$

where S_{crit} is S at critical point where the sterically stabilized particle formation is established, r_1 is the substrate monomer reactivity ratio in copolymerization with the macromonomer before the critical point, k_2 is diffusion-controlled rate constant for coalescence of similar-sized microparticles, k_p and k_t are the propagation and termination rate constants of polymerization of the substrate monomer, and k_d, f , and $[I]_0$ are the decomposition rate constant, initiator efficiency, and the initiator concentration, respectively. After the critical point, the sterically stabilized particles are assumed to coalesce no more, with the number of such particles remaining constant. The model successfully accounted for the results of dispersion copolymerization of *n*-butyl methacrylate or styrene with PEO macromonomers [6,7]. In general, the macromonomer chains graft-copolymerized on the particle surface are supposed to have most expanded or random conformation at the critical point (maximum S for S_{crit}), and gradually change to more extended,

upright, cylinder-like one (decrease in S) with increasing conversion (increasing frequency or density on the surface). Such a mushroom to brush transition was discussed with ^1H NMR observation of the PEO chains in dispersion copolymerization with n -butyl methacrylate [15]. In principle, Eqs. (3) and/or (4) will serve as a working hypothesis for the particle size control in emulsion and dispersion copolymerization system with a macromonomer, as will be discussed below in case of styrene copolymerization with the PEO macromonomers, **1**.

3.2. Emulsion polymerization

Styrene plus 1 to 10 wt% PEO macromonomers, **1**, with an initiator, AVA, could be readily emulsified in water under magnetic stirring. Heating to 65 °C quickly afforded polystyrene latex nearly quantitatively in weight after one day. Typical SEM photographs, recipe, and result of characterization are given in Figs. 2a and b, and Table 2. Particle size (radius, R) as a function of the macromonomer concentration, W_{Do} , is shown in double logarithmic plots in Fig. 3.

Nearly mono-sized microparticles were obtained in the range of micron to submicron in diameter depending on the increasing macromonomer level from 1 to 10 wt%. Fig. 3 clearly shows that the size is almost one or half-order of magnitude smaller than that in dispersion copolymerization in methanol-water mixture (9:1 v/v), when compared at the same macromonomer concentration in weight. Also it appears that the size decreases according to inverse root of the macromonomer concentration ($W_{\text{Do}}^{-1/2}$), just like Eq. (4) in dispersion copolymerization, except for the data at the lowest one (1 wt%). The last fact suggests a homogeneous nucleation mechanism, as assumed previously for such a rather hydrophilic PEO macromonomer [10].

To be noted in Fig. 3, the particle size appears to be controlled almost consistently by the weight, not by the number (mole), of the macromonomer. Thus, the PEO chain length, n , appears to have little effects on the particle size. This result can be expected because, in Eq. (3), the increase in n or the molecular weight, M_{D} , of the macromonomer will decrease its incorporation in molar basis, m_{D} , and correspondingly increase the

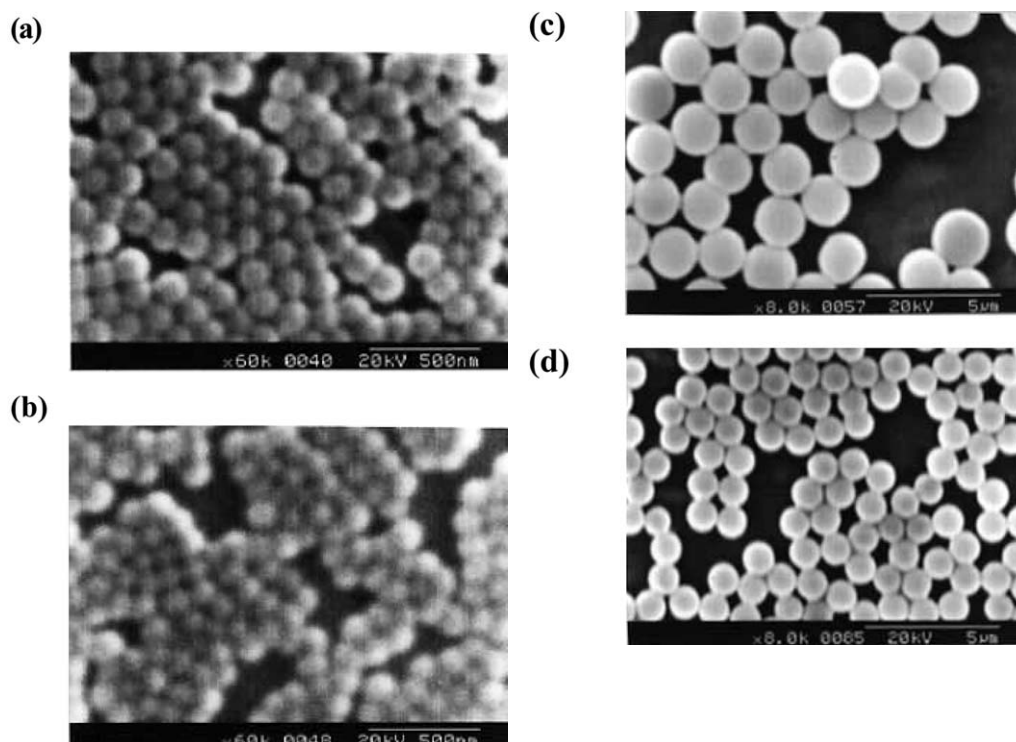


Fig. 2. Typical SEM photographs of the polystyrene microspheres obtained by emulsion (a, b) and dispersion (c, d) copolymerization with m3n50. $W_{\text{So}}/W_{\text{Do}}$: (a) 14.3, (b) 10.0, (c) 19.8, (d) 10.0.

Table 2
Emulsion copolymerization of styrene with PEO macromonomers^a

Macromonomer code	W_{S_0}/W_{D_0} (g g ⁻¹)	D_n^b (nm)	D_w/D_n^b	m_s/m_D^c (mol mol ⁻¹)	S^d (nm ²)	$\langle R_g \rangle^e$ (nm)	θ_s/θ_D^f
m3n50	91.0	1370	1.008	2200	1.7	0.73	1.1
m3n50	14.3	220	1.025	570	2.7	0.93	1.8
m3n50	10.0	181	1.015	440	2.6	0.90	1.9
m3n80	97.3	1450	1.052	8100	5.8	1.4	2.3
m3n80	25.3	292	1.011	1410	5.0	1.3	1.5
m3n150	104.0	1405	1.045	10500	7.8	1.6	1.5
m3n150	14.1	169	1.014	1390	7.6	1.7	1.5

^a Feed: styrene (W_{S_0}) = 1 g, AVA = 10 mg, water = 10 ml. Temperature: 65 °C. Polymerization time: 24 h. Styrene conversion: nearly quantitative ($\theta_s = 1$).

^b D_n and D_w : number- and weight-average particle diameter from SEM.

^c Styrene/macromonomer mole ratio in particle from ¹H NMR.

^d Cross-sectional area per macromonomer chain on particle surface from $R = D_n/2$ and m_s/m_D with Eq. (3), with $M_s = 104$ and assuming $\rho = 1 \text{ g cm}^{-3}$.

^e Average radius of gyration of each macromonomer chain occupying the cross-sectional area on particle surface: $\langle R_g \rangle = (S/\pi)^{1/2}$.

^f Ratio of conversion of styrene to macromonomer: $\theta_s/\theta_D = (m_s M_s/m_D M_D) (W_{D_0}/W_{S_0})$.

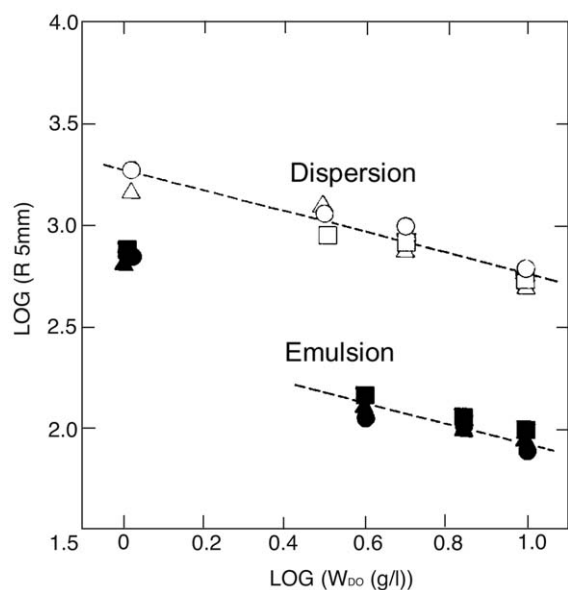


Fig. 3. Double logarithmic plots of particle radius vs macromonomer concentration in dispersion (○, △, □) and emulsion (●, ▲, ■) copolymerization of styrene with PEO macromonomers with various chain lengths: (○, ●) m3n50, (□, ■) m3n80, (△, ▲) m3n150. Broken lines are reference with a slope of $-1/2$.

specific surface coverage, S , occupied by that chain on the surface, as can be seen in Table 2.

The values of S or its corresponding radius, $\langle R_g \rangle$, reflect the size of each macromonomer chain tethered on the particle surface. These values are significantly smaller as compared to those of the free PEO chains with the corresponding molecular weights. Thus for a

random coil conformation in water at 25 °C [16], a PEO chain with a weight-average molecular weight, M_w , will have the square-root radius of gyration:

$$\langle R_g^2 \rangle^{1/2} = 0.020 M_w^{0.58} \quad (5)$$

which gave $\langle R_g \rangle_{\text{random}} = 1.7, 2.3,$ and 3.3 nm for $n = 50, 80,$ and $150,$ respectively, by assuming $M_w = M_n$. The corresponding surface area, $S_{\text{random}} = (5/3) \pi \langle R_g^2 \rangle$ [5a], are calculated as 15, 28, and 57 nm², respectively. This comparison, though not so critical because of temperature difference, supports the previous conclusion that the macromonomer chain must have the extended, cylinder-like conformation upright on the particle surface [6,9,15]. This picture was proved independently by the TEM and DLS (dynamic light scattering) observation of the particles obtained by emulsion copolymerization of styrene with a PEO macromonomer carrying *p*-styrylheptyl end group ($m = 7$ and $n = 45$ with ω -end group = OCH₃ instead of OH in **1**) [9,17].

The conversion ratio of styrene to the macromonomer, θ_s/θ_D in Table 2, estimated from the particle composition, reveals that θ_D is much higher than that in dispersion system (Table 3). Indeed, roughly azeotropic incorporation ($\theta_s/\theta_D = 1$) was observed in case of micellar and emulsion copolymerization with a more hydrophobic PEO macromonomer ($m = 7$ and $n = 17$ with ω -end group = OCH₃) [10,12]. Such a behavior may even suggest a type of ‘mini-emulsion’ mechanism [18,19] for the present emulsion copolymerization, since almost all the macromono-

Table 3
Dispersion copolymerization of styrene with PEO macromonomers ^a

Macromonomer code	W_{S0}/W_{D0} (g g ⁻¹)	D_n^b (nm)	D_w/D_n^b	m_S/m_D (mol mol ⁻¹) ^c	S^d (nm ²)	$\langle R_g \rangle^e$	θ_S/θ_D^f
m3n50	19.8	1940	1.004	1520	0.8	0.51	3.4
m3n50	10.0	1190	1.002	1170	1.0	0.57	5.2
m3n80	31.2	1760	1.004	5000	3.0	0.97	4.5
m3n80	19.8	1620	1.002	4700	3.1	0.98	6.7
m3n150	33.0	2500	1.007	9700	4.0	1.1	4.5
m3n150	20.3	1550	1.003	7800	5.2	1.3	5.9

^a Feed: styrene (W_{S0}) = 1 g, AIBN = 20 mg, methanol–water (9:1 v/v) = 10 ml. Temperature: 60 °C. Polymerization time: 24 h. Styrene conversion: nearly quantitative ($\theta_S = 1$).

^b D_n and D_w : number- and weight-average particle diameter from SEM.

^c Styrene/macromonomer mole ratio in particle from ¹H NMR.

^d Cross-sectional area per macromonomer chain on particle surface from $R = D_n/2$ and m_S/m_D with Eq. (3), with $M_S = 104$ and assuming $\rho = 1 \text{ g cm}^{-3}$.

^e Average radius of gyration of each macromonomer chain occupying the cross-sectional area on particle surface: $\langle R_g \rangle = (S/\pi)^{1/2}$.

^f Ratio of conversion of styrene to macromonomer: $\theta_S/\theta_D = (m_S M_S/m_D M_D) (W_{D0}/W_{S0})$.

mers charged not only effectively emulsified the initial styrene droplets but also appear to continue to stabilize the final polystyrene particles as such by covering with the graft copolymers produced in situ. Further study including the droplet size measurements is needed to confirm a clear mechanism. Anyway the macromonomers may appear to work as effective steric stabilizers throughout to protect the droplets and the so produced particles against flocculation.

As shown in Fig. 4, the effect of the spacer alkyl length, m , in the polymerizing end group of the macromonomer on the particle size appears also insignificant in the emulsion system, though the data are somewhat scattered to say conclusively.

3.3. Dispersion polymerization

Clear solution containing styrene and 1 to 10 wt% PEO macromonomers, **1**, with AIBN in methanol/water mixture (9:1 v/v) quickly changed turbid upon heating to 60 °C with magnetic stirring. Polystyrene latex was obtained nearly quantitatively in weight after one day. Typical results are given in Table 3, with the SEM photographs in Fig. 1c and d, and the dependence of the particle size on macromonomer concentration in Figs. 3 and 4.

Nearly monodisperse, micron-sized microspheres were obtained while the dependence of the particle size on the macromonomer concentration, Fig. 3 and 4, is in accord with the theory in Eq. (4), i.e., $R \propto W_{D0}^{-1/2}$ over the whole concentration range investigated,

$W_{D0} = 1\text{--}10 \text{ g L}^{-1}$ (1–10 wt% to styrene). The much larger size in the dispersion system, as compared to the emulsion system, can be related to the much less incorporation (smaller m_D or θ_D) coupled with smaller surface coverage (S or $\langle R_g \rangle$) of the macromonomers copolymerized in the particles, as can be seen by comparison of Tables 2 and 3.

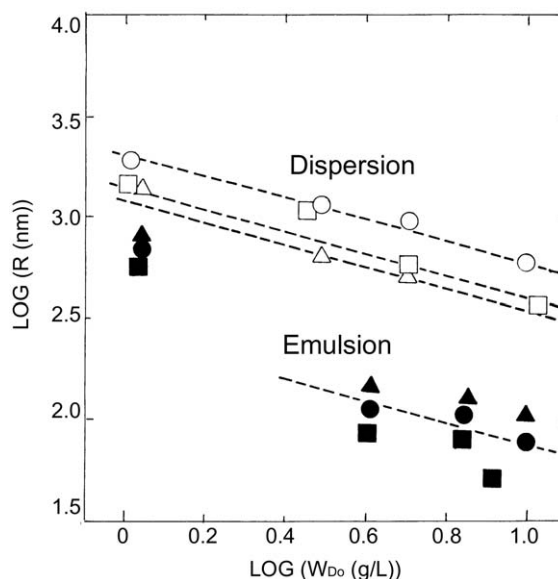


Fig. 4. Double logarithmic plots of particle radius vs macromonomer concentration in dispersion (○, △, □) and emulsion (●, ▲, ■) copolymerization of styrene with PEO macromonomers with various spacer alkyl lengths: (○, ●) m3n50, (□, ■) m5n63, (△, ▲) m6n50. Broken lines are reference with a slope of $-1/2$.

We can suppose in the dispersion system [6,7] that excessive molar amounts of styrene and the macromonomers dissolved molecularly in methanol-water (9:1 v/v) mixture will polymerize and/or copolymerize to give insoluble polystyrenes and styrene-rich copolymers, which will coalesce together to originate the sterically stabilized microparticles, which will in turn grow in size by polymerization and copolymerization of the monomers. Here styrene appears to be more easily occluded in the particles because the incorporation of the macromonomers will be hindered sterically by the already grafted PEO chains covering the surface. As a consequence, the final particles characterized by small m_D or θ_D (large m_S/m_D or θ_S/θ_D) will result with larger size as compared to the emulsion system. Here it is to be noted that the values of S or $\langle R_g \rangle$ in the dispersion system are appreciably smaller but substantially in the same level as compared to those in the emulsion system. In fact, free PEO polymers exhibited random conformations with the same molecular size, $\langle R_g \rangle_{\text{random}}$, in methanol and in water [16]. The presence of $-\text{OH}$ end group in the present macromonomers may lead to somewhat larger $\langle R_g \rangle$ or S in the aqueous emulsion system.

Concerning the very little effect of the PEO chain length, n , of the macromonomer on the particle size, R , as observed in Fig. 3, can be explained by considering Eqs. (4) and (5), which are combined with $S_{\text{crit}} = S_{\text{random}}$ to give the relation: $R \propto M_D^{-0.08}$.

The spacer alkyl length, m , of the macromonomer also appears to have little effects on R (Fig. 4), but some trend of smaller size with increasing m may reflect increasing copolymerizability of the macromonomer to styrene (smaller r_1) in nucleation stage.

4. Conclusion

PEO macromonomers, **1**, with various chain lengths, $m = 3, 5, 6$ and $n = 50\text{--}150$, were found to be effective in emulsion and dispersion copolymerization with styrene to afford nearly monodisperse microspheres of submicron to micron size. The smaller particle size in the emulsion system can be a result of higher copolymerizability and larger surface coverage

of the macromonomers in water as compared to the dispersion system in methanol–water (9:1 v/v). More detailed mechanism, particularly of nucleation in the emulsion system, whether homogeneous or droplets, still remains to be studied. In the emulsion system in Figs. 3 and 4, the upward deviation (or higher slope) observed in $\log R$ vs $\log W_{D0}$ plots at the lowest W_{D0} may suggest possible change in nucleation mechanism, say, from homogeneous to droplets.

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