Macromolecules **1995**, *28*, 1159−1166 **1159**

Dispersion Copolymerization of *n*-Butyl Methacrylate with Poly(ethylene oxide) Macromonomers in Methanol−Water. Comparison of Experiment with Theory

Seigou Kawaguchi[1] **and Mitchell A. Winnik***

Department of Chemistry and Erindale College, University of Toronto,
Toronto, Ontario, Canada M5S 1A1

Koichi Ito

Department of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 441, Japan

Received March 10, 1994; Revised Manuscript Received November 8, 1994[⊗]

ABSTRACT: The dispersion copolymerization of *n*-butyl methacrylate (BMA) in methanol−water media has been investigated. The reactions were carried out in the presence of a series of poly(ethylene oxide) (PEO) macromonomers (**1**) ($C_1{-}EO_n{-}(CH_2)_m{-}S$), with a *p*-alkylstyrene (S) end group, with $m = 1$, 4, and 7 and $n = 53$ and 110. Nearly monodisperse PBMA latex particles from 90 to 500 nm in diameter are obtained. Factors which affect the particle size are the structure and molecular weight of the macromonomers, initial BMA, initiator, and macromonomer concentrations, temperature, and the composition of the solvent. The particle radius (R) follows the relationship $R \propto [\mathrm{BMA}]_0^{0.82\pm0.06}[\mathrm{macromonomer}]_0^{-0.54\pm0.03}n^{-0.30\pm0.02}[\mathrm{initiator}]_0^{-0.10\pm0.01}$. The power law exponents are close to those predicted from a coagulative nucleation model, particularly the multibin kinetics model for coalescence among unstabilized particles developed by Paine [*Macromolecules* **1990**, *23*, 3109]. R is also found to decrease with an increase in temperature and also with an increase in m (in **1**). R, however, also increases with an increasing volume fraction of water in the reaction medium. The mechanism for the dispersion copolymerization is discussed in detail.

Introduction

Over the past several years, we have been interested in the process of film formation from latex dispersions.[2,3] In these experiments, we have used poly(*n*-butyl methacrylate) (PBMA) microspheres as a model polymer. Film formation is thought to be very sensitive to the nature of substances at the surface of the latex.[4,5] Many industrial applications involve latex with a surface rich in carboxylic acid groups.[6] Another useful strategy for surface modification of polymeric microspheres is to prepare them in such a way that water-soluble polymers are attached to the surface. For this reason, several groups have reported the synthesis and some properties of latex particles containing poly(ethylene oxide) (PEO) chains attached to the particle surface. For example, Westby[7] and Satgurunathan and Ottewill[8,9] reported the preparation of such particles in a multistage emulsion polymerization process in which PEO−methacrylate was introduced in the final stage.

Because of our interest in film formation, we wished to prepare PBMA particles containing PEO chains at the surface. We followed a strategy originally developed by Ito and his co-workers using PEO macromonomers containing various substituted styrene groups at one end.[10] Monodisperse, or nearly monodisperse, polystyrene (PS) particles in size could be prepared by dispersion copolymerization in alcoholic media.[11] In order to optimize the synthesis to meet the needs of our film formation studies, we undertook a rather detailed examination of the dispersion polymerization of *n*-butyl methacrylate (BMA) in methanol−water media. These experiments provide an interesting test of a theoretical model of dispersion polymerization recently presented by Paine.[12]

Brief Review of Dispersion Polymerization

Dispersion polymerization is defined as a heterogeneous polymerization by which latex particles are formed in the presence of a suitable steric stabilizer from an initially homogeneous reaction mixture. Under favorable circumstances, this polymerization can yield in a batch process monodisperse, or nearly monodisperse, latex particles with a relatively large diameter (up to 15 μm).[13] The solvent selected as the reaction medium must be a good solvent for both the monomer and the steric stabilizer but a poor solvent or a nonsolvent for the polymer being formed. This restriction on the choice of solvent means that these reactions can be carried out only with solvents with extremely low or high solubility parameters. Historically, nonaqueous dispersion (NAD) polymerization was first carried out in aliphatic hydrocarbon media. The NAD technique was invented by Osmond and co-workers at ICI.[14] More recently, the technique has been extended to polar media, especially alcohols and their mixtures with water as the continuous phase.[15−17] There is a considerable interest in the latter systems, because of the wider range of monomers that can be used.

Three types of polymers have been employed as steric stabilizers to prevent the flocculation of growing particles.[13] Originally, amphiphilic graft polymers were generated in situ by reaction of radicals in the system with homopolymer precursors. A classic example is the use of butyl rubber (poly(isobutylene-*co*-isoprene)) to generate a steric stabilizer during polymerization of methyl methacrylate (MMA) in aliphatic hydrocarbons.[14,18] We have used poly(2-ethylhexyl methacrylate) to generate a steric stabilizer for poly(vinyl acetate) in

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

0024-9297/95/2228-1159$09.00/0

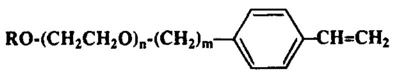
this way.[19] Hydrophilic polymers such as (hydroxypropyl)cellulose,[20-22] poly(acrylic acid),[15,23] and poly(*N*-vinylpyrrolidone)[16,17] have been employed for the preparation of PS latex particles in alcoholic media.

A second strategy involves the use of AB and ABA block polymers as steric stabilizers. Block copolymers used in this way include poly(styrene-*b*-methyl methacrylate),[24] poly(styrene-*b*-dimethylsiloxane) (PS-*b*-PDMS),[25] and poly(styrene-*b*-ethylene oxide).[26] When a selective solvent for the block copolymer is used as the continuous phase, these polymers adsorb onto the surface of particles formed to improve their colloidal properties. Unless grafting of block copolymers occurs, the adsorption can be weak. That may be the reason that in such systems broad or bimodal size distributions are often observed.[26]

The third strategy involves the use of macromonomers. Macromonomers can be prereacted to form graft copolymers which are subsequently introduced into the dispersion polymerization reaction, or they can be allowed to react in situ to form graft copolymers. The use of a macromonomer to make a preformed graft copolymer was pioneered by ICI. Their approach involved the use of a poly(12-hydroxystearic acid) (HSA) macromonomer with a methacrylate end group.[14] This was polymerized with MMA to produce a comb-graft copolymer which has limited solubility in pure aliphatic hydrocarbons but has adequate solubility in hydrocarbon−monomer mixtures. It is particularly effective in stabilizing PMMA NAD particles.

The idea of introducing macromonomers into a polymerization reaction to generate a steric stabilizer in situ is relatively new. It provides a simple and flexible method for stabilizing growing particles for a wide variety of monomers. These experiments have used amphiphilic macromonomers, either for emulsion polymerization[7-9,27,28] or for dispersion polymerization.[11,28] One of the most important issues in this methodology is the reactivity of the macromonomer in the solvent used for the emulsion or dispersion polymerization.

The experiments reported here use a series of PEO macromonomers containing a styrene end group. They have the structure **1** indicated below and are referred to by the notation $R{-}EO_n{-}C_m{-}S$. Here S refers to the styrene end group; *m*, to the number of CH_2 groups; and *n*, to the degree of polymerization of the PEO. Previous



(1) $R\text{-}EO_n\text{-}C_m\text{-}S$

R= H, CH_3, n-C_4H_9, $C(CH_3)_3$, n-C_8H_{17}, n-$C_{18}H_{37}$

studies of the radical homopolymerization of these macromonomers in aqueous media have shown that the polymerization proceeds rapidly as a result of organization of these macromonomers in water.[29-31] In copolymerization reactions of **1**, the apparent reactivity ratio of the macromonomers was found to increase in water and alcohol media compared to that in less polar organic solvents. The polymerization rate in water also increased as the alkyl chain length between the PEO and the styrene was lengthened, presumably as a result of the increased organization of styrene groups.[10] This type of self-association may or may not contribute to the polymerization reactions we intend to examine.

In the present study, the dispersion copolymerization behavior of *n*-butyl methacrylate (BMA) with the PEO macromonomers **1** in methanol−water media is investigated. The macromonomers used for the present study are $C_1{-}EO_n{-}C_m{-}S$, where C_1 indicates a terminal methoxy group, $m = 1$, 4, or 7, and $n = 53$ or 110. We are interested primarily on how various factors affect the size and size distribution of the latex particles produced. As variables, we examine the structure and molecular weight of macromonomers, the initial BMA, initiator, and macromonomer concentrations, temperature, and solvent composition.

The mechanism of dispersion polymerization is still poorly understood compared to that of emulsion polymerization.[32] Recently, a major contribution to this field has been made by Paine[12] in terms of both new experiments and a useful theoretical model of the dispersion polymerization mechanism. His semiquantitative model is based on the coagulative nucleation principle. He has employed a computer simulation to describe particle aggregation among unstabilized particles. While the model is attractive in terms of its underlying principles and provides a deeper quantitative understanding of the particle formation process, experimental results still cannot be explained quantitatively in terms of this model. In the present paper, we revise this model to accommodate the formation of steric stabilizer from macromonomers in the reaction. The experimental results obtained here are discussed in detail and compared with the theory.

Theory

According to the aggregative and coagulative nucleation theories[33] which all derive originally from the homogeneous nucleation theory of Fitch and Tsai,[34] the most important point in the reaction is the instant at which colloidally stabilized particles form. After this point, coagulation between similar-sized particles no longer occurs, and the number of particles present in the reaction is constant. The dispersion copolymerization of BMA with amphiphilic macromonomers **1** is considered to proceed as follows: (1) Before polymerization, the monomer, macromonomer, and initiator dissolve completely into the solvent. (2) Linear oligomers, polymers, and graft copolymers are all produced by polymerization in the continuous phase, accompanied by the decomposition of the initiator. The solubility of these polymers is a function of their molecular weight and the composition of the graft copolymer. Polymers with a molecular weight larger than a certain critical value precipitate and begin to coagulate to form unstable particles. (3) These particles coagulate on contact, and the coagulation between them continues until sterically stabilized particles form. (4) This point is referred to as the critical point, and it occurs when all of the polymers contain sufficient PEO chains at the surface to provide colloidal stability.

After this point, particles grow both by diffusive capture of oligomers and coagulation of small particles (nuclei, precursors) produced in the continuous phase and by polymerization within the particle of monomer that partitions between the two phases. The total particle number remains constant so that the particle size is only a function of amount of polymer produced. The locus of polymerization is an important consideration, both for the molecular weight and composition of graft copolymers being formed and for that of homopolymer in the particles. We will not be concerned with the molecular weight of polymers formed in this study. Our focus will be on particle size and its distribution.

The particle size is determined at the critical point by the amount of polymer produced thus far. In the discussion that follows, we use the term θ to describe the fractional conversion of monomer to polymer ($0 \le \theta \le 1$) and θ_D to describe the corresponding conversion of macromonomer. The weight (W_B in g/L) of BMA polymerized at any point in the reaction is defined as

$$W_B = W_{B0}\theta = \frac{4}{3}\pi R^3 \varrho N \qquad (1)$$

Here W_{B0} is the weight of BMA in the reactants; R is the radius (cm) of particle volume occupied by the PBMA. N is the total number of particles per liter, and ϱ is their density (1.06 g/cm^3 for PBMA).

The surface area per particle is determined by the surface area (S) occupied by a PEO chain times the number (n) of these chains grafted onto the surface

$$nS = 4\pi R^2 \qquad (2)$$

$$n = \frac{W_{D0}\theta_D N_A}{N M_D} \qquad (3)$$

W_{D0} is the weight (in g/L) of macromonomer in the reactants. N_A is Avogadro's number, and M_D is the molecular weight of the macromonomer. From eqs 1–3, one can obtain a universal relationship between the particle radius of PBMA and the extent of polymerization for sterically stabilized particles:

$$RS = \frac{3M_D W_{B0}\theta}{\varrho N_A W_{D0}\theta_D} \qquad (4)$$

At the critical point, sterically stabilized particles are formed, and coalescence between similar-sized particles is terminated. At this point one has $R = R_{crit}$, $S = S_{crit}$, $\theta = \theta_{crit}$, and $\theta_D = \theta_{Dcrit}$. Since the particle number N remains constant after this point, both R and S, at any subsequent conversion, can be described by the expressions

$$R = R_{crit}\left(\frac{\theta}{\theta_{crit}}\right)^{1/3} \qquad (5a)$$

$$S = S_{crit}\left(\frac{\theta_{crit}}{\theta}\right)^{1/3}\left(\frac{\theta}{r_1\theta_D}\right) \qquad (5b)$$

where r_1 is the reactivity ratio in copolymerization of BMA (M_1) with macromonomer (M_2). At low conversion, r_1 in this system is defined as

$$r_1 = \theta_{crit}/\theta_{D\,crit} \qquad (6)$$

The θ_D can be written in terms of r_1.

$$\theta_D = 1 - (1 - \theta)^{1/r_1} \qquad (7)$$

According to Paine,[12] computer simulations using the multibin kinetic model for the coalescence between the unstable moieties indicate that the particle number (N) at the critical point is given by

$$N = \frac{N_A k_p}{0.386 k_2 \theta}\left(\frac{2fk_d[\mathrm{I}]}{k_t}\right)^{1/2} \qquad (8)$$

where k_p is the propagation rate constant (M^{-1} s^{-1}), k_t is the termination rate constant (M^{-1} s^{-1}), and k_2 is the diffusion-controlled rate constant for coalescence between similar-sized particles (M^{-1} s^{-1}). [I] is the initiator concentration (mol/L), and fk_d is the product of the decomposition rate constant (s^{-1}) for the initiator and the fraction of initiator fragments initiating polymerization.

From eqs 1 and 8, θ_{crit} can be written as

$$\theta_{crit} = (R_{crit})^{3/2}\left(\frac{{}^4/_3\pi\varrho N_A k_p}{0.386 k_2 W_{B0}}\right)^{1/2}\left(\frac{2fk_d[\mathrm{I}]}{k_t}\right)^{1/4} \qquad (9)$$

Substituting eqs 1 and 9 into eq 5 yields the equations

$$R = \theta^{1/3}\left(\frac{3W_{B0}}{\varrho N_A}\right)^{2/3}\left(\frac{M_D r_1}{W_{D0}S_{crit}}\right)^{1/2}\left(\frac{0.386k_2}{4\pi k_p}\right)^{1/6}\left(\frac{k_t}{2fk_d[\mathrm{I}]}\right)^{1/12} \qquad (10)$$

$$S = \theta^{-1/3}\left(\frac{3W_{B0}}{\varrho N_A}\right)^{1/3}\left(\frac{M_D S_{crit}}{r_1 W_{D0}}\right)^{1/2}\left(\frac{4\pi k_p}{0.386k_2}\right)^{1/6}\left(\frac{2fk_d[\mathrm{I}]}{k_t}\right)^{1/12}\left(\frac{\theta}{\theta_D}\right) \qquad (11)$$

In eq 10, one sees that the radius of latex particle follows simple scaling relationships with the key parameters in the system: $\theta^{1/3}$, $[\mathrm{BMA}]_0^{2/3}$, $[\text{macromonomer}]_0^{1/2}$, and $[\text{initiator}]_0^{1/2}$, where $[\ ]_0$ means initial concentration. These equations also predict that the particle size and stabilization are determined by the magnitude of r_1. In addition, one sees in eq 11 that the surface area occupied by a PEO chain follows $\theta^{-1/3}$ in the case of azeotropic copolymerization, $\theta = \theta_D$. This means that the PEO chain conformation for chains grafted onto the latex particle will change with grafting density, as will be discussed later.

Estimation of S_{crit}. To proceed, one must estimate the S value at the critical point. We begin by making two assumptions, first that no PEO becomes buried inside the particles as a consequence of macromonomer polymerization, and second that no PEO macromonomer is adsorbed onto the surface of the particles. The first assumption may not necessarily hold in dispersion copolymerization, particularly in the case of aggregative nucleation. However, it should be noted that eq 10 does not change much even if both of these effects are considered. These processes should be incorporated into the terms r_1 and S_{crit}. In this paper, we estimate S_{crit} only for the simplest case.

The value of S is dependent upon the conformation of a single PEO chain grafted onto the surface of a latex particle. According to the de Gennes "mushroom" model[35] for a polymer grafted to a surface with which it does not interact, the polymer chain occupies a volume determined by its mean-squared radius of gyration $\langle S^2\rangle$. When the surface becomes crowded with chains, additional energy is needed to deform the polymer mushrooms into brushes. When the particle surfaces are covered completely with random coils of the PEO polymer, the particles are also sterically stabilized against coagulation.

We define S_{crit} in terms of a surface covered by undeformed polymer coils, calculating the maximum surface area occupied by a single PEO chain from its dimensions in the continuous phase. In this approximation, we treat the PEO chain as a rigid sphere with

Table 1. Molecular Characteristics of Macromonomers

	GPC			NMR	
samples	n^a	$10^{-3}M_n$	M_w/M_n	n^b	f^c (%)
$C_1-EO_{53}-C_1-S$	52	2.40	1.07	50	99
$C_1-EO_{53}-C_4-S$	53	2.50	1.06	53	100
$C_1-EO_{53}-C_7-S$	54	2.48	1.06	52	98
$C_1-EO_{110}-C_1-S$	110	4.96	1.05	115	96
$C_1-EO_{110}-C_4-S$	111	5.05	1.04	112	100
$C_1-EO_{110}-C_7-S$	114	5.20	1.04	117	97

[a] Determined by GPC calibrated with PEO standards. [b] Number of EO units per chain, determined by ^{1}H-NMR from the ratio of peak areas of oxyethylene to ω-methoxy protons. [c] The functionality of double bonds per molecule (in percent) determined by ^{1}H-NMR from the ratio of peak areas of vinyl to ω-methoxy protons.

random coil dimensions, affixed on the surface of a latex particle. In this case, S_{crit} can be written as[36]

$$S_{\text{crit}} = {}^5/_3\pi\langle S^2\rangle \tag{12}$$

Values of $\langle S^2\rangle_z$ for PEO in methanol at 25 °C are available in the literature and fit the expression[37]

$$\langle S^2\rangle_z^{1/2} = 0.16M_D^{0.585} \tag{13}$$

In our system, the two PEO macromonomers have degrees of polymerization of ca. 53 and 110. These are sufficiently short, so that the polymer dimensions will resemble the unperturbed dimensions of the chains. This may mitigate two factors that we are unable to take into account. The copolymerization reactions were run at 70 °C in methanol–water mixtures with BMA. Both temperature and solvent will affect the magnitude of $\langle S^2\rangle$ and $\langle S^2\rangle_{crit}$. In this paper, we use the values in methanol at 25 °C.

Experimental Section

Materials. The PEO macromonomers (**1**) were prepared by the method reported in previous papers from the Ito group.[10] In short, $C_1-EO_n-C_1-S$ was prepared under nitrogen by reacting the C_1-EO_n-OH (Aldrich) with a slight excess of sodium hydride followed by *p*-vinylbenzyl chloride in dry THF at room temperature. *p*-(4-Bromobutyl)styrene and *p*-(7-bromoheptyl)styrene were prepared by the reactions of (*p*-vinylbenzyl)magnesium chloride, either with 1,3-dibromopropane or 1,6-dibromohexane in dry ether at 0 °C. $C_1-EO_n-C_4-S$ and $C_1-EO_n-C_7-S$ were prepared in dry THF by reacting C_1-EO_n-OH with a fivefold excess of either *p*-(4-bromobutyl)styrene or *p*-(7-bromoheptyl)styrene in the presence of a fivefold excess of sodium hydride at room temperature. The reaction solutions were twice poured into dry acetone from THF to precipitate salts, which were then removed by filtration. The filtrate was recovered by precipitation into hexane and purified by three reprecipitation cycles from THF. Finally, the macromonomers were freeze-dried from benzene. The molecular characteristics of the macromonomers are presented in Table 1. The degrees of polymerization of the PEO chains (*n*) determined by gel permeation chromatography (GPC) are ca. 53 and 110, in agreement with results obtained from end group analysis by ^{1}H-NMR. The functionality (*f*) of double bonds determined by ^{1}H-NMR is also satisfactory.

BMA (Aldrich) was distilled just before use. Spectroscopic grade methanol (Caledon Laboratories Ltd.) was used without further purification. Water was purified by a Millipore Milli Q purification system. α,α'-Azobis(isobutyronitrile) (AIBN) (Polysciences Ltd.) was purified by recrystallization three times from ethanol.

Dispersion Copolymerization. Dispersion copolymerizations were carried out with a 50 mL three-neck reactor fitted with a condenser and a mechanical stirrer (200 rpm) under nitrogen.[26] The half-moon-type impeller was used. The solvent composition varied from 5 to 25 vol % water in methanol. BMA concentration was varied from 0.32 to 1.0 mol/L. Initiator concentrations ranged from 3.4 to 108 mmol/L. Macromonomer concentrations ranged from 0.85 to 14.2 mmol/L. The polymerization temperature range was from 60 to 85 °C. Under these experimental conditions, the solution before polymerization was completely clear. After purging with nitrogen for 20 min, the polymerization was commenced by immersing the reactor in an oil bath at the appropriate temperature.

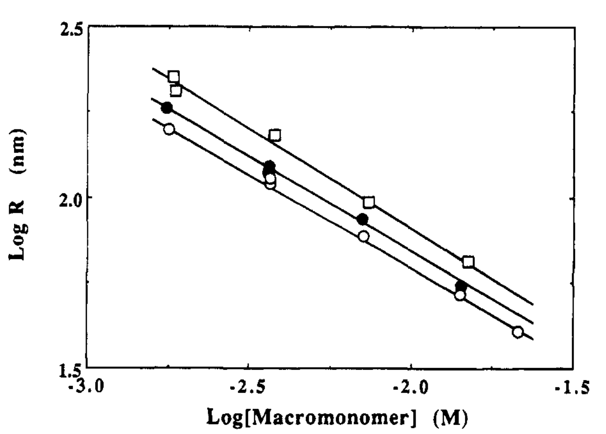


Figure 1. Double-logarithmic plots of latex particle radius (*R*) vs [macromonomer]. [BMA] = 0.744 M, [I] = 13.4 mM, and *T* = 70 °C. The solvent is methanol containing 20 vol % water. (□) $C_1-EO_{53}-C_1-S$, (●) $C_1-EO_{53}-C_4-S$, and (○) $C_1-EO_{53}-C_7-S$.

Measurements. GPC measurements were run with an HPLC (Jasco, TRIROTOR-III) equipped with an RI detector (Shodex SE-11) and GPC columns (Shodex A-802 and A-803). THF was used as the eluent at a flow rate of 1 mL/min at 40 °C. Molecular weights were calibrated by using a series of standard PEO samples from Tosoh Co., Ltd. ^{1}H-NMR spectra (JEOL JNM-GX 270 FT spectrometer) were run on samples in $CDCl_3$ with tetramethylsilane as an internal standard. Particle size and size distribution were measured with a dynamic light scattering photometer (Brookhaven Instruments BI-90 particle sizer) with a fixed scattering angle of 90° at 20 °C. The solvent used was methanol (viscosity is 0.597 cP). The data analysis was carried out using an algorithm of the inverse Laplace transformation method.[26] The intensity median diameter in the BI-90 was used as an average diameter of the particles. As a measure of the size distribution, the GSD (geometric standard deviation) was used. In all experiments, the GSD values are from 1.1 to 1.2. This means that the size distribution is monodisperse or nearly monodisperse.[38]

Results and Discussion

To compare the theory with the dispersion copolymerization behavior, the influence of various factors on the latex particle size was examined. All experimental results discussed here are from experiments carried out to 100% conversion. We used an interesting approach to monitoring the extent of monomer and macromonomer conversion by ^{1}H-NMR which will be described in detail in a future publication.[39] Reactions were run using deuterated solvent as the reaction medium. In this way we could follow the residual methacrylate and *p*-alkylstyrene group concentrations by direct ^{1}H-NMR measurements on the reaction mixture. We confirmed that both conversions are 100% after 6 h of polymerization.

Macromonomer Concentration and Structure. Double-logarithmic plots of the radius of the latex particles as a function of macromonomer concentration [macromonomer] are shown in Figure 1. With increasing [macromonomer], the latex size decreases. The

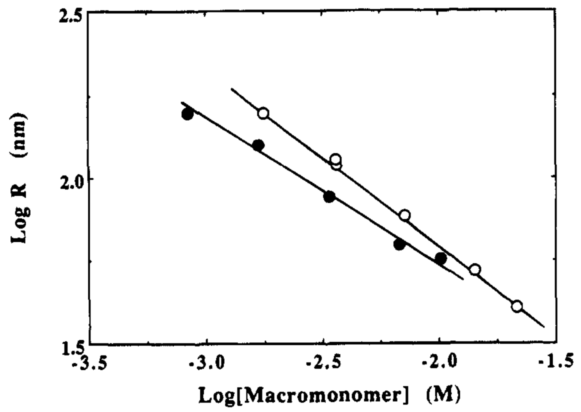


Figure 2. Double-logarithmic plots of latex particle radius (R) vs [macromonomer]. The conditions are the same as in Figure 1. (○) $C_1-EO_{53}-C_7-S$ and (●) $C_1-EO_{110}-C_7-S$.

following scaling behavior is obtained, irrespective of the choice of macromonomer used:

$$R = K[\text{macromonomer}]_0^{-0.56\pm0.02} \qquad (14)$$

The value of the exponent is only slightly larger than that (0.50) in eq 10. A range of dependence of particle size on stabilizer concentration has been reported for NAD polymerization in hydrocarbon and alcohol media.[14,17,25] The values of the exponent vary from −0.30 to −0.80.

Another important feature of the reaction shown in Figure 1 is the dependence of the final particle size on the structure of the macromonomer. Decreasing the length of the alkyl chain separating the styrene group from the PEO leads to an increase in the particle size. This result can be interpreted in terms of differences in r_1 values. The r_1 value is determined to be 1.0 ± 0.2 for the $C_1-EO_{53}-C_7-S$ macromomer.[39] It is reasonable to assume that the apparent reactivity of the macromonomer ($1/r_1$) in a polar medium increases with the length of the alkyl chain.[10] Macromonomers with long alkyl chains are more liable to adsorb onto those portions of the hydrophobic latex particle surface which are not sterically stabilized. This would increase both the local concentration of macromonomer and the particle stability. As a result, the number of sterically stabilized particles would increase at the critical point. Therefore, the value of m in the macromonomers of structure **1** should be considered to be an important parameter for designing reactions to produce a particular particle size.

Molecular Weight of Macromonomer. Figure 2 presents double-logarithmic plots of particle radius vs [macromonomer] for $C_1-EO_{53}-C_7-S$ and $C_1-EO_{110}-C_7-S$. One can see in this figure that the longer the PEO chain, the smaller the particle size at the same macromonomer concentration. This result corresponds to the increase in surface area occupied by a single PEO chain. From eqs 10, 12, and 13, the PEO chain-length dependence of the particle radius at a given macromonomer concentration (mol/L) can be written as

$$R \propto (n_{\mathrm{EO}})^{-0.585} \qquad (15)$$

We have only two PEO chain lengths. Also the slope changes with PEO chain length, so that we cannot estimate exactly the PEO chain-length dependence over the entire range of our experiments. At low and high [macromonomer], we obtain $R \sim n^{-0.31}$ and $R \sim n^{-0.28}$, respectively.

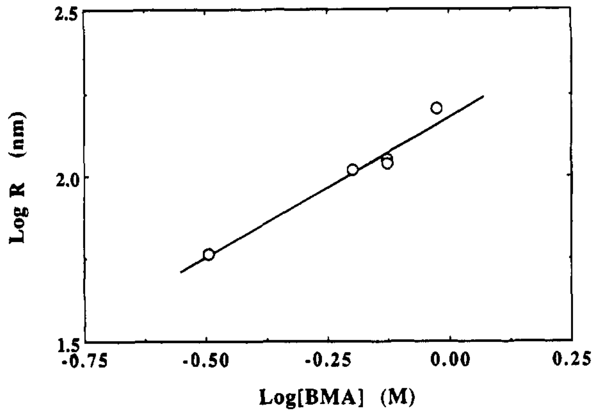


Figure 3. Double-logarithmic plot of latex particle radius (R) vs [BMA]. $[C_1-EO_{53}-C_7-S] = 3.66$ mM, [I] = 13.4 mM, and $T = 70$ °C. The solvent is methanol containing 20 vol % water.

The experimental values of the exponent are significantly smaller than that in eq 15, but this is not so surprising. Possible reasons for this difference are related to the solvency of the medium for the macromonomer and to the molecular weight of the PEO chain. The PEO macromonomers do not dissolve in pure BMA. Since BMA is a nonsolvent for PEO, its presence in significant quantities at the beginning of the reaction should tend to decrease the PEO chain dimensions. The particle number is determined at an early stage in the reaction, when the BMA concentration is high. For the macromonomer in a poor solvent, the value of the exponent should be smaller than that in eq 13. In addition, eq 13 does not necessarily hold for low molecular weight polymers. In dilute solutions of homologous polymers, it is known that stiffness effects become important in the low molecular weight region, and the scaling exponent between $\langle S^2 \rangle$ and molecular weight deviates from the asymptotic behavior.[40,41]

Paine also reported a smaller value of this exponent in a very different system (i.e., 0.27−0.36).[17] A molecular weight dependence was reported by Dawkins and Taylor[25] for a series of PS-*b*-PDMS block copolymers used as a steric stabilizer in NAD polymerizations of styrene. A double-logarithmic plot of particle diameter against the molecular weight of the PDMS gave a power law dependence of about −1.8. This exponent, however, seems to be too large to be explained only in terms of the chain conformation of PDMS in hexane. It should be noted here for $C_1-EO_{110}-C_7-S$ that $R \propto [\text{macromonomer}]^{-0.51}$, in better agreement with the theoretical value than for the macromonomer with $n = 53$.

Initial BMA Monomer Concentration. Initial monomer concentration has a major influence on the final particle radius. According to the data in Figure 3, particle radius increases significantly with increasing initial BMA concentration. The scaling relationship obtained is

$$R = K[\text{BMA}]_0^{0.82\pm0.06} \qquad (16)$$

The value of the exponent in eq 16 is significantly larger than that in eq 10. This is also likely to be due to a solvency effect. BMA is good solvent for the PBMA polymer being formed in the reaction but, as we pointed out, a poor solvent for the PEO chain. We can rationalize this kind of solvent effect in terms of the value of S_{crit} in eq 10. With increasing [BMA], S_{crit} decreases.

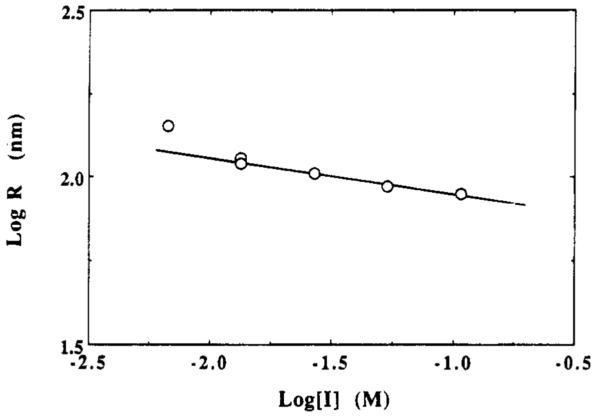


Figure 4. Double-logarithmic plot of latex particle radius (R) vs [I]. [C_1–EO_{53}–C_7–S] = 3.66 mM, [BMA] = 0.744 M, and T = 70 °C. The solvent is methanol containing 20 vol % water.

As a consequence, the latex particle size increases with a larger exponent than the one predicted from eq 10. Another factor is that the polymerized macromonomer may not adsorb onto the particle surface, particularly if it has low molecular weight in the BMA chain, when the BMA content is higher.

Initiator Concentration. There have been relatively few publications about the effect of initiator concentration on particle size.[16,42,43] Croucher and Winnik[42,43] reported that the greater the initiator concentration, the larger the final particle size in the NAD polymerization of MMA. Also, Vanderhoff, El-Aasser,[16] and Paine[17] observed a power law dependence of +0.40 in the dispersion polymerization of styrene in alcohol. Figure 4 presents our results. In marked contrast to previous results, we find that the final particle radius slightly decreases with increasing initiator concentration. We obtain the following scaling relationship:

$$R = K[\mathrm{I}]_0^{-0.10\pm0.01} \tag{17}$$

This exponent value is consistent with that predicted in eq 10. This may imply a fundamental difference in nucleation mechanism between the two systems. This needs further study. Here, one can conclude that the model describes the present system better than the previous systems including chain transfer reaction.

θ-Dependence of Latex Particle Radius. According to eq 10, the particle radius is proportional to the fractional conversion of monomer as $\theta^{1/3}$. Here we determined θ values separately by ^{1}H-NMR. These dispersion copolymerization reactions were carried out in deuterated solvent.[39] We find that R is indeed proportional to $\theta^{1/3}$, which indicates that, above the critical point, the particle number remains constant throughout the reaction.

Solvent Composition. Solvent quality is well known to play a key role in the final particle size. One explanation for the influence of initial monomer concentration on particle size is through its effect on the solvency of the medium. In Figure 5 we examine the effect of the volume percent water in the reaction medium on the radius of the particles produced. Particle size increases with increasing amounts of water. This is a striking result for us.[44] Water is a good solvent for PEO and should increase S_{crit}. As a consequence, latex particle size should decrease with increasing water content in the system if the solvency of the medium for the steric stabilizer were the dominant factor. In the limiting case of pure water as the reaction medium, the polymerization reaction becomes one of emulsion polymerization, which affords smaller size particles.

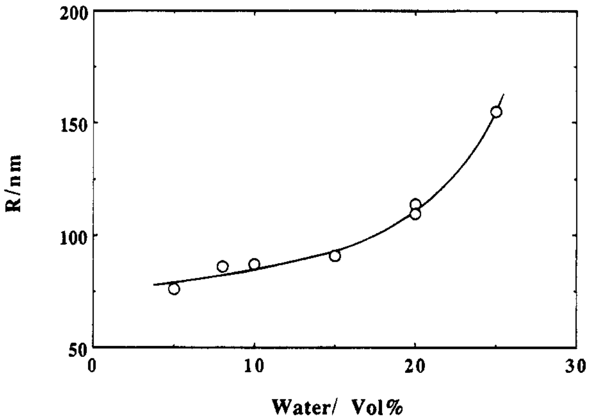


Figure 5. Plot of latex particle radius (R) vs water concentration (vol %). [C_1–EO_{53}–C_7–S] = 3.66 mM, [BMA] = 0.744 M, [I] = 13.4 mM, and T = 70 °C.

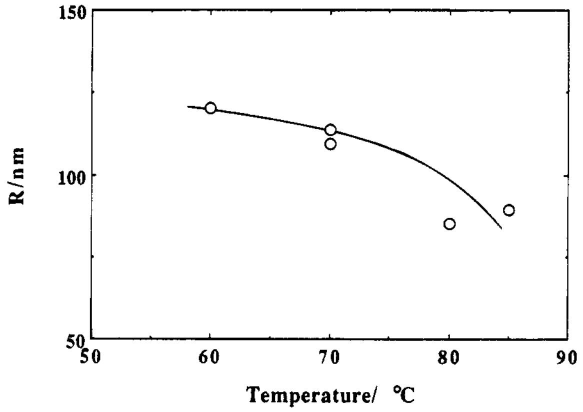


Figure 6. Plot of latex particle radius (R) vs temperature. [C_1–EO_{53}–C_7–S] = 3.66 mM, [BMA] = 0.744 M, and [I] = 13.4 mM. The solvent is methanol containing 20 vol % water.

Ober and Lok[15] reported that the final latex radius in their system is inversely proportional to the solubility parameter of the medium. In contrast, Paine reported that the final particle diameter shows a maximum when the Hansen polarity and the hydrogen-bonding term in the solubility parameter are close to those of the steric stabilizer.[20] Our results are not necessarily at odds with Paine's ideas. The behavior of PEO in water and in water–methanol mixtures is rather complex, and this complexity is only exacerbated by the presence of decreasing amounts of BMA in the medium as the reaction proceeds. We conclude that we cannot interpret these results with the present model.

Polymerization Temperature. A plot of particle size against temperature is shown in Figure 6. One sees that particle size increases with decreasing temperature. This is also in contrast to the results of Ober and Hair.[45] They showed that larger particles are obtained at higher temperature. The effect of temperature on particle size is predicted from the temperature dependence of the various rate constants in eq 10.

$$\frac{\mathrm{d}\ln \mathrm{R}}{\mathrm{d}(1/kT)} = -\frac{2E_2 - 2E_{\mathrm{p}} + E_{\mathrm{t}} - E_{\mathrm{d}}}{12} \tag{18}$$

where E_2, E_{p}, E_{t}, and E_{d} are the activation energies for particle coalescence, polymerization, the termination step for BMA, and initiator decomposition, respectively. Here k is the Boltzmann constant. We have ignored the

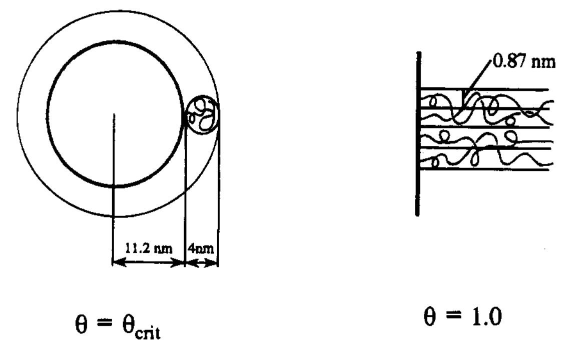


Figure 7. Schematic representation for the PEO sterically stabilized latex particles at the critical point and at $\theta = 1.0$. The picture is drawn by using calculated values in the text. The solid lines represent PEO chain.

temperature dependence of $\langle S^2 \rangle$. For BMA, $E_p = 20.4$ kJ mol^{-1}, $E_t = 12.7$ kJ mol^{-1}, and $E_d = 123.4$ kJ mol^{-1} for AIBN.[46] The activation energies for coalescence, polymerization, and termination are rather low in comparison to E_d. Thus, increasing temperature primarily increases the initiation rate, which in our system decreases the particle size.

Calculation of Absolute Particle Size. We now compare directly the experimental particle sizes with those calculated from eq 10. We obtained $R = 110$ nm under the following conditions: $[C_1-EO_{53}-C_7-S] = 3.66 \times 10^{-3}$ M, [BMA] = 0.77 M, $[I] = 13.4 \times 10^{-3}$ M, and $T = 70$ °C. For the calculation, we used $k_p = 640$ M^{-1} s^{-1}, $k_t = 27.5 \times 10^6$ M^{-1} s^{-1}, $f = 1.0$, $k_2 = 10^9$ M^{-1} s^{-1}, and $k_d = 4.0 \times 10^{-5}$ s^{-1} as the rate constants[46] and $N_A = 6.02 \times 10^{23}$ mol^{-1}, $\theta = 1.0$, and $r_1 = 1.0$.[39] Substituting these parameters into eqs 9 and 10, we obtain the values $S_{crit} = 12.6$ nm^2, $R_{crit} = 11.2$ nm, $\theta_{crit} = 0.01\%$, and $R = 237$ nm. It is remarkable that the equation can predict particle size even within a factor of 2. Therefore, one can conclude that the theory is capable of predicting particle size in the dispersion polymerization reactions, irrespective of the extent of grafting.[12]

Using eq 11, the surface area (S) occupied by a PEO chain at $\theta = 1.0$ can be calculated to be 0.59 nm^2.[47] This value is significantly smaller than S_{crit}. Also, the number of grafted PEO chains per particle (n) is calculated to be 125 at the critical point and 2.58×10^5 at $\theta = 1.0$. These values allow us to draw the schematic picture presented in Figure 7 for PEO-stabilized latex particles at the critical point and at $\theta = 1.0$. From the values of n and S, one can see that the conformation of the PEO grafted onto the particle changes from a random coil to an extended conformation with increasing grafting density. We assumed in our model that particle size was determined by the presence of close-packed PEO mushrooms on the particles at the critical point. Here we see that further growth in particle size is accompanied by a crossover to a polymer brush for the PEO at the particle surface.

Conclusion

We have examined the dispersion copolymerization behavior of n-butyl methacrylate in aqueous methanol media with a series of PEO macrmonomers as steric stabilizers. Monodisperse or nearly monodisperse PBMA particles, ranging in size from 90 to 500 nm in diameter, were obtained. Various factors affect the size and size distribution of the particles. A model for this dispersion copolymerization was developed based upon ideas originally presented by Paine.[12] The radius of the latex R follows a power law dependence upon the individual initial reactant concentrations in the system, viz., $R = K[\mathrm{BMA}]_0^{0.82\pm0.06}[\mathrm{macromonomer}]_0^{-0.54\pm0.03}n^{-0.30\pm0.02}[\mathrm{initiator}]_0^{-0.10\pm0.01}$. Here n refers to the chain length EO_n of the PEO chain in the macromonomer. These exponents are close in value to those predicted from the model and for our system.

Acknowledgment. The authors would like to thank ICI, ICI Canada, The Glidden Co., and NSERC Canada for their support of this research. The authors also thank Dr. A. Paine, Xerox Research Centre of Canada, for his many valuable comments and suggestions on the manuscript and for use of a disk centrifuge to measure PBMA particle size and size distribution. S.K. would like to express his grateful acknowledgment to the Ministry of Education, Science and Culture of Japan for supporting his stay in Toronto.

References and Notes

(1) Permanent address: Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441, Japan.
(2) Zhao, C.-L.; Wang, Y.; Hruska, Z.; Winnik, M. A. *Macromolecules* **1990**, *23*, 4082.
(3) Wang, Y.; Zhao, C.-L.; Winnik, M. A. *J. Chem. Phys.* **1991**, *95*, 2143.
(4) Kim, H.-B.; Wang, Y.; Winnik, M. A. *Polymer* **1994**, *35*, 1779.
(5) Kim, H.-B.; Winnik, M. A. *Macromolecules* **1994**, *27*, 1007.
(6) Paton, T. C. *Paint Flow and Pigment Technology*; Wiley: New York, 1979.
(7) Westby, M. J. *Colloid Polym. Sci.* **1988**, *266*, 26.
(8) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1988**, *266*, 547.
(9) Ottewill, R. H.; Satgurunathan, R. *Colloid Polym. Sci.* **1987**, *265*, 845.
(10) Chao, D.; Itsuno, S.; Ito, K. *Polym. J.* **1991**, *23*, 1045.
(11) Nugroho, M. B.; Kawaguchi, S.; Ito, K. *Polym. Prepr. Jpn.* **1993**, *42*, 437.
(12) Paine, A. J. *Macromolecules* **1990**, *23*, 3109.
(13) Croucher, M. D.; Winnik, M. A. *An Introduction to Polymer Colloids: Preparation of Polymer Particles by Dispersion Polymerization*; Candau, F., Ottewill, R., Eds.; Kluwer Academic Press: Dordrecht, The Netherlands, 1990.
(14) Barret, K. E. J. *Dispersion Polymerization in Organic Media*; Wiley-Interscience: New York, 1975.
(15) Ober, C. K.; Lok, K. P. *Macromolecules* **1987**, *20*, 268.
(16) Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1986**, *24*, 2995.
(17) Paine, A. J.; Luymes, W.; McNulty, J. *Macromolecules* **1990**, *23*, 3104.
(18) Williamson, B.; Lukas, R.; Winnik, M. A.; Croucher, M. D. *J. Colloid Interface Sci.* **1987**, *119*, 559.
(19) Egan, L. S.; Winnik, M. A.; Croucher, M. D. *Polym. Eng. Sci.* **1986**, *26*, 15.
(20) Paine, A. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2485.
(21) Chen, Y.; Yang, H.-W. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2765.
(22) Lok, K. P.; Ober, C. K. *Can. J. Chem.* **1985**, *63*, 209.
(23) Corner, T. *Colloid Surf.* **1981**, *3*, 119.
(24) Dawkins, J. V.; Shakir, S. A.; Croucher, T. G. *Eur. Polym. J.* **1987**, *23*, 173.
(25) Dawkins, J. V.; Taylor, G. *Polymer* **1979**, *20*, 599.
(26) Winzor, C. L.; Mrazek, Z.; Winnik, M. A.; Croucher, M. D.; Riess, G. *Eur. Polym. J.* **1994**, *30*, 121.
(27) Chao, D.; Itsuno, S.; Ito, K. *Polym. Prepr. Jpn.* **1991**, *40*, 2588.
(28) Kobayashi, S.; Uyama, H. *Kobunshi Ronbunshu* **1993**, *50*, 209.
(29) Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* **1991**, *24*, 2348.
(30) Ito, K.; Hashimura, K.; Itsuno, S.; Yamada, E. *Macromolecules* **1991**, *24*, 3977.
(31) Kawaguchi, S.; Yekta, A.; Duhamel, J.; Winnik, M. A. *J. Phys. Chem.* **1994**, *98*, 7891.
(32) Piirma, I., Ed. *Emulsion Polymerization*; Academic Press: New York, 1982.
(33) Feeney, P. J.; Napper, D. H.; Gilbert, R. G. *Macromolecules* **1987**, *20*, 2922.
(34) Fitch, R. M.; Tsai, C. H. In *Polymer Colloids*; Fitch, R. M., Ed.; Plenum Press: New York, 1971.

(35) (a) de Gennes, P.-G. *Adv. Colloid Interface Sci.* **1987**, *278*, 189. (b) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.

(36) The mean-squared radius of gyration $\langle S^2 \rangle$ for a rigid sphere of radius $= R'$ and density $= \varrho$ is given by the expression

$$\langle S^2 \rangle = \frac{\int_0^{R'} 4\pi \varrho r^4 \, dr}{\int_0^{R'} 4\pi \varrho r^2 \, dr} = \frac{3}{5}(R')^2$$

(37) Zhou, P.; Brown, W. *Macromolecules* **1990**, *23*, 1131.

(38) Scanning electron micrograph (SEM) analyses were carried out for one set of particles, with a median diameter of 250 nm (GSD = 1.2) as determined by dynamic light scattering using a BI-90 instrument. Because of the low T_g of the PBMA latex, some deformation and coagulation of the latex occurred during sample preparation for SEM measurements. Latex particles with diameters between 223 and 260 nm were observed in the SEM. The number-average diameter, D_n, and D_w/D_n were calculated to be 244 nm and 1.06, respectively. Here D_w is the weight-average diameter. In addition, disk centrifugation measurement for the same latex dispersion was carried out. We obtained 1.23 as a value of the GSD. Therefore, we think that the BI-90 provides reliable information about the polydispersity, at least for relatively small particles, i.e., with $D_n < 500$ nm. In addition, we think that GSD values between 1.1 and 1.2 from the BI-90 indicate nearly monodisperse particle dispersions.

(39) Kawaguchi, S.; Winnik, M. A.; Ito, K. Manuscript in preparation.

(40) Kawaguchi, S.; Suzuki, J.; Imai, G.; Kitano, T.; Ito, K. Manuscript in preparation. We investigated the conformational properties of PEO of molecular weight ranging from 76 to 2×10^6 by means of light scattering and intrinsic viscosity measurements. We observed deviations from asymptotic behavior in the low molecular weight range. These data could be analyzed in terms of the helical wormlike chain model.[39]

(41) (a) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971. (b) Fujita, H. *Polymer Solutions*; Elsevier: New York, 1992.

(42) Winnik, M. A.; Lukas, R.; Chen, W. F.; Furlong, P.; Croucher, M. D. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 483.

(43) Croucher, M. D.; Winnik, M. A. *Future Directions in Polymer Colloids*; El-Aasser, M. S., Fitch, R. M., Eds.; *NATO ASI Ser. E: Appl. Sci.* **1988**, *138*, 209.

(44) We also observed the decrease of particle size with increasing water concentration in the dispersion copolymerization of styrene.

(45) Ober, C. K.; Hair, M. L. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1395.

(46) Brandrup, J.; Immergut, E. H., Eds. In *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.

(47) We consider that this experimental value is too small. One explanation may be that some fraction of the copolymerized PEO is buried in the PBMA particle interior.

MA9412086