

EFFECTS OF ω -ACRYLOYL POLY(ETHYLENE OXIDE) MACROMONOMER ON EMULSIFIER-FREE EMULSION COPOLYMERIZATION OF METHYL METHACRYLATE AND *n*-BUTYL ACRYLATE*

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Abstract Well-defined nonionic hydrophilic ω -acryloyl poly(ethylene oxide) macromonomer (PEO-A) has been prepared by living anionic polymerization of ethylene oxide with diphenyl methyl potassium as the initiator and acryloyl chloride as the reaction terminating agent. The polymer was characterized by FTIR and SEC. The emulsifier-free emulsion polymerization of methyl methacrylate (MMA) and *n*-butyl acrylate (BA) containing various concentrations of PEO-A was studied. In all cases stable emulsion copolymerizations of MMA and BA were obtained. The stabilizing effect was found to be dependent on the molecular weight and the feed amount of the macromonomer.

Keywords Macromonomer; ω -Acryloyl poly(ethylene oxide); Emulsifier-free emulsion copolymerization; Methyl methacrylate-*n*-butyl acrylate copolymer

INTRODUCTION

Polymeric latex, particularly in aqueous medium, is nowadays a topic of prime importance for both basic science and applied research^[1]. Latex stability is the key problem of emulsion polymerization technique. In order to achieve latex stability one of the ways is copolymerization with hydrophilic monomers such as sulfoderivatives of vinyl monomers^[2,3], 2-hydroxyethyl methacrylate^[4], glycidyl methacrylate^[5] and methyloamide of acrylic acid^[6]. These functional monomers have the potential advantage of being copolymerization in situ on the surface of latex particles. This surface modification can cause an increase in stability under different conditions. In this article, a nonionic hydrophilic macromonomer(PEO-A) was prepared. The effect of this macromonomer on the emulsifier-free emulsion copolymerization of MMA and BA was studied.

EXPERIMENTAL

Anionic polymerization and characterization

Anionic polymerization of EO was carried out in a repeatedly flamed glass reactor under vacuum. The temperature of the reactor was then slowly raised from -78°C up to 35°C (ca. 1h). Polymerization was commenced at 35°C for 24h then terminated by using acryloyl chloride.

FTIR spectra (KBr disk) were obtained on a Nicolet-5DX FTIR spectrometer (USA). Size exclusion chromatography (SEC) was carried out in THF at 30°C using a Waters 510 HPLC (USA) to measure the number-average molecular weights of the macromonomers.

Emulsion copolymerization and characterization

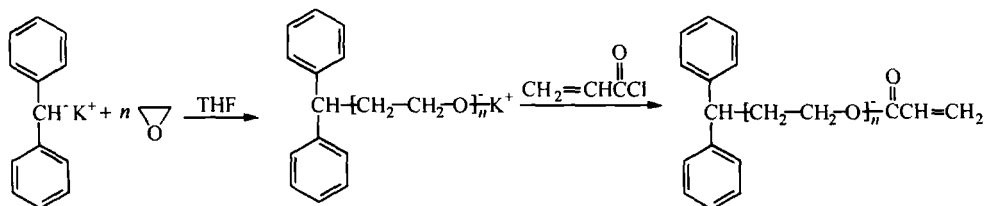
All of the semicontinuous emulsifier-free emulsion copolymerizations were carried out at 70°C in a liter glass reactor. The rate of conversion was measured gravimetrically and the particle size d_p was determined by transmission electron microscope HITACHI-600 (Japan) and image processing system.

RESULTS AND DISCUSSION

Synthesis of PEO-A

Hydrophilic macromonomers with various molecular weight were synthesized in THF by using diphenyl methyl potassium as an initiator. Table 1 shows that the theoretical molecular weights and calculated values determined by SEC are in good agreement within the investigated range in agreement with a possible living mechanism. Fig.1 shows the characteristic adsorption peaks of C—O—C band at 1062 and 948.7 cm^{-1} . The peaks at 1640 cm^{-1} and 1735 cm^{-1} indicate that there are

C=C bands and $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ groups respectively in the products. These indicate that it is successful to terminate the anionic polymerization with acryloyl chloride and to produce PEO-A.



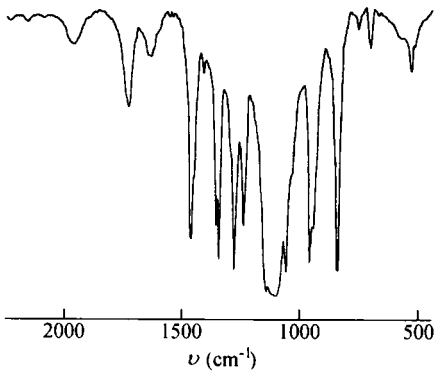


Fig. 1 FTIR spectrum of PEO-A macromonomer (sample 2)

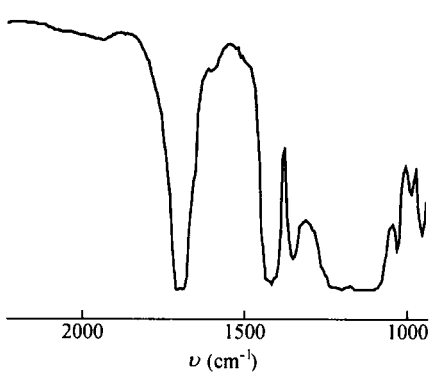


Fig. 2 FTIR spectrum of the copolymer of MMA and BA in the presence of PEO-A (sample 2)

Table 1 Characterization of PEO-A macromonomers synthesized in THF Using Φ_2 CHK as initiator

PEO-A	$M_n \times 10^{-3}$ Theoretical	$M_n \times 10^{-3}$ Calculated	SEC	Yield (wt%)
1#	2	2.3		93.4
2#	3	3.5		94.5
3#	5	5.7		94
4#	9	10.2		95

Effect of PEO-A macromonomer on emulsifier-free emulsion copolymerization of MMA and BA

Semicontinuous emulsifier-free emulsion copolymerizations of MMA and BA were carried out in the presence of PEO-A macromonomers. Theoretical solid content was 40%. Monomer feed rate was 0.9g/min. Reaction temperature was 70°C at stirring speed of 400 rpm.

The two characteristic adsorption peaks at 948.7 and 1062 cm^{-1} (Fig. 2) indicate that PEO-A has taken part in the copolymerization of MMA and BA.

Instantaneous conversion vs. time plots are shown in Fig. 3. As shown in Table 2 and Fig. 3, when the M_n of PEO-A was over 10000 coagulation occurred

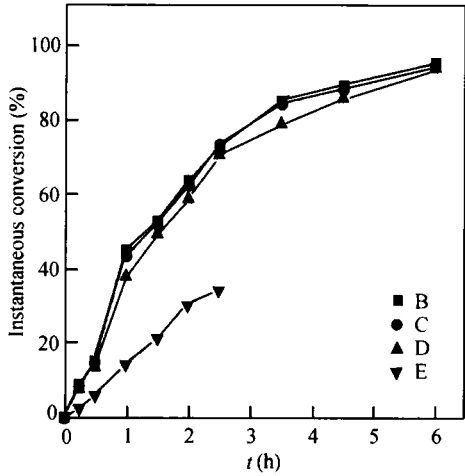


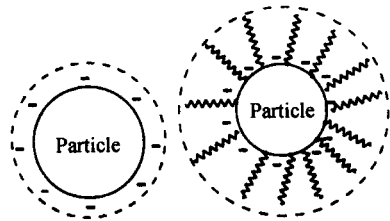
Fig. 3 Instantaneous conversion for the reactions with PEO-A various molecule weight of PEO-A
B: 1#, C: 2#, D: 3#, E: 4#

at very low conversion. This can be explained as the length of hydrophilic chains located on the surface of particle is too long to link the particles with one another. Thus coagulation occurred. This result indicates that the M_n of PEO-A has a critical value. An effective hydrophilic macromonomer must have a suitable M_n value under the critical one.

Table 2 Data of reaction time, total amount of scrap, d_p , N_p and yield of the finished latex

PEO-A (1 wt%)	Reaction time (h)	Scrap (g)	d_p (nm)	$N_p \times 10^{-13}$ (mL, H ₂ O) ⁻¹	Yield (%)
1#	6	no	384	0.96	95
2#	6	no	410	0.91	94
3#	6	no	452	0.88	93
4#	—	—	—		40 (coagulation occurs)
PEO-A 0	6	12.3	323	2.04	90
(2#) 0.5	6	no	470	0.65	94
wt% 1	6	no	430	0.90	94
3	6	no	734	0.23	92

Results shown in Table 2 demonstrate that the particle diameter decreases (or the particle number N_p increase) with the concentration of PEO-A. But when the amount of PEO-A was high up to 3% N_p decrease on the contrary. These results indicate that PEO-A play an important role in the latex stability during the polymerization process. The stabilizing mechanism can be depicted by scheme 1.



A. MMA/BA B. MMA/BA/PEOA
Scheme 1 The schematic diagrams of the stabilizing mechanism during the polymerization process

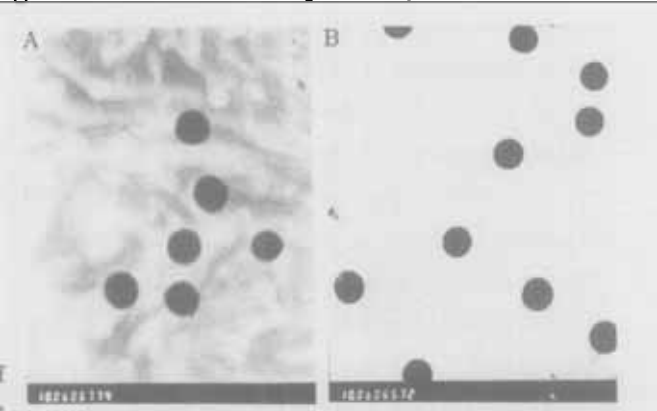


Fig. 4 TEM micrographs ($\times 15000$) of latex particles prepared (A) with PEO-A; (B) without

Since SO_4^- and hydrophilic groups on the surface of the latex particles can produce a hydrate layer surrounding the particle and the hydrate layer for the system

of PMMA\BA\PEO-A with long hydrophilic chains located on the particle surface is thicker than that for the system of PMMA\BA without hydrophilic monomer, it is clear that more effective steric barriers can be generated in the former particles. However, PEO-A can be initiated in the aqueous phase to produce water soluble homopolymers in addition to the residue of unreacted macromonomer in the finished latex which may be unfavorable to the latex stability. Thus PEO-A macromonomer can be a good comonomer to achieve stable MMA/BA latex if the concentration is appropriate.

Fig. 4 shows the micrographs of finished latex. The common characteristics of both (A) and (B) are that the latex particle size distribution is very narrow. This result could be attributed to the homogeneous nucleation mechanism of emulsifier-free emulsion polymerization. However, the differences between the two different polymerization system are also obvious. The interface between particle and aqueous phase of the system without PEO-A (in Fig. 4B) is very clear and that with PEO-A (in Fig. 4A) is obscure. This can be attributed to the differences of the thickness of the two kinds of hydrate layers. The hydrate layer of the later system consisting of soft macromolecule chains is thicker than that of the former system.

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