

Poly(methyl acrylate) and Copolymer of Acrylic Acid and Butyl Acrylate Prepared by γ -Irradiation in the Presence of 1,1-Diphenylethene: Synthesis and Application in Emulsion Polymerization

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ABSTRACT: Poly(methyl acrylate) and amphiphilic copolymer of butyl acrylate and acrylic acid were prepared in the presence of 1,1-diphenylethene (DPE) by γ -irradiation-induced polymerization. The influences of polymerization time, amounts of DPE in system on conversion, molecular weight (MW), and its distribution (M_w/M_n) were studied. The results indicate that the polymerization in the presence of DPE and initiated by γ -irradiation shows the character of controlled radical reaction. The pre-

pared copolymer was used as the polymeric emulsifier in the emulsion polymerizations of butyl acrylate (BA) and styrene (St), respectively, to assess the possibility of making monodisperse latices of relatively high solids content (~35–45%) in an one-step batch process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3492–3499, 2007

Key words: amphiphilic copolymer; 1,1-diphenylethene; monodisperse latices

INTRODUCTION

It is well-known that the amphiphilic polymers, which consist of both hydrophobic groups and hydrophilic groups, can form aggregates, like micelles and can stabilize the polymer particles in emulsion polymerization,^{1–5} so that the amphiphilic polymers with well-defined structure, suitable molecular weight, and composition have become more attractive.

With the developed synthesis techniques, such as ionic and controlled free radical methods, “tailor-made” copolymers with very elaborate structures are becoming available. This is especially true in the light of recent advances in controlled radical polymerization chemistry, as exemplified by stable free radical polymerization (SFRP), best represented by polymerization mediated with TEMPO,^{6,7} atom transfer radical polymerization (ATRP)^{8–14} and, to a lesser extent, reversible addition fragmentation transfer (RAFT) polymerization.^{15–17} This new development of polymer chemistry enables the polymer chemists to prepare various new, well-defined amphiphilic polymers, many of them exhibit certain surfactant behaviors. However, all those techniques applied to control the radical polymerization possess

some disadvantages such as in many cases the utilization of high temperature in the case of nitroxide-mediated polymerization; the difficulties in removing the metal catalyst from the system in ATRP at the end of polymerization; and the pollution of the final polymer with halogen and sulfur in the case of ATRP and RAFT techniques.

Recently 1,1-diphenylethene (DPE) was found to be able to control the structure in the conventional free radical polymerization.¹⁸ The authors reported that DPE was used to carry out the controlled polymerization of styrene and other vinyl monomers in bulk by traditional chemical method. Furthermore, DPE is commercially available, odorless, colorless, and without known toxicity.

Compared with traditional chemical method, ⁶⁰Co γ -irradiation is a kind of environmental energy source and can initiate most monomers. The most important advantages of radiation method are that the rate of free radical formation is independent of temperature and no chemical initiator is needed so that the reaction is easy to control. More recently, it has been used to carry out controlled free radical polymerization.^{19–22} Up to now, however, no report has been found about polymers with well-controlled molecular weight (MW) and narrow distribution (M_w/M_n) prepared in a γ -radiation initiated system with DPE as the control-agent. In this article, we present our results of studies on the γ -radiation initiated

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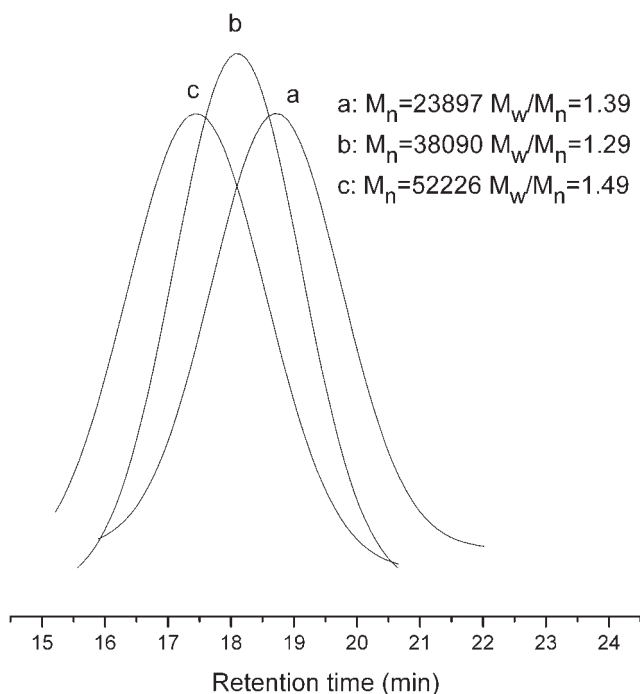


Figure 1 GPC curves of poly(methyl acrylate) obtained from bulk polymerization induced by γ -irradiation in the presence of 0.05 mol % DPE; (a) 2 h, (b) 3 h, (c) 4 (h) dose rate: 97 Gy/min.

DPE controlled free radical polymerizations of several systems: methyl acrylate (MA) in bulk and solution, butyl acrylate (BA) and acrylic acid (AA) in solution. In this article, we also show a primary testing result about the application of the fabricated amphiphilic copolymers (copolymer of BA and AA) in emulsion polymerization as the emulsifier.

EXPERIMENTAL

Materials

MA, BA, St were washed with 10% of sodium carbonate solution and dehydrated with calcium chloride and distilled under a reduced pressure. Tetrahydrofuran

(THF) employed in experiments is analytical reagent grade. Distilled water was used throughout the experiments. A 2.22×10^{15} Bq ^{60}Co γ -ray source was applied to initiate the polymerization in the experiments.

Synthesis of DPE

DPE was synthesized using the method reported elsewhere.²³ The product is obtained with a yield of 70%. ^1H NMR (300MHz, CDCl_3): $\delta = 5.41(\text{s}, 2\text{H}, =\text{CH}_2)$, 7.26–7.56(m, 10H, aromatic H).

Polymerization

Bulk polymerization of MA

Solution of DPE in the monomer were prepared gravimetrically. Bulk polymerizations were carried out in some 5 mL glass sample vials and deoxygenated by nitrogen gas and initiated by ^{60}Co γ -irradiation at a dose rate of 97 Gy/min. Each sample was taken out at a chosen time. The conversion of each sample was determined gravimetrically.

Polymerization of MA and copolymerization of AA and BA in solution

The solution polymerizations were carried out in a 250 mL glass-made reactor equipped nitrogen inlet and outlet, a valve on the bottom. Similarly, the polymerizations were induced by ^{60}Co γ -irradiation at a dose rate of 97 Gy/min. The samples for testing were taken out from the systems through the valve on the reactor bottom.

Emulsion polymerization of butyl acrylate and styrene

Batch emulsion polymerizations were carried out in a 100-mL glass sample vials. Distilled water, the copolymer stabilizer (prepared BA-AA copolymer), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (to partly neutralize the carbonic acid group in BA-AA copolymer) and monomer were introduced, and the emulsion was bubbled with nitrogen gas for

TABLE I
Data of M_n , M_w/M_n , and Conversion for Bulk Polymerization of MA Initiated by γ -Irradiation

No.	DPE (mol %)	Monomer	Water	Time (min)	$M_{n,\text{GPC}}$	Conv. (%) ^a	M_w/M_n
1	0	MA	– ^b	8	392,550	6.1	1.44
2	0.1	MA	–	180	17,057	6.8	1.46
3	0.1	MA	+ ^c	180	17,383	9	1.38
4	0.4	MA	+	125	5,270	1.4	1.16
5	0.3	MA	+	125	7,803	1.8	1.21
6	0.2	MA	+	125	10,503	2.2	1.29
7	0.1	MA	+	125	16,421	4.2	1.43

Condition: dose rate = 97 Gy/min; polymerization was carried at room temperature.

^a Conversions were determined gravimetrically.

^b –, No trace water in system.

^c +, Trace water in the system.

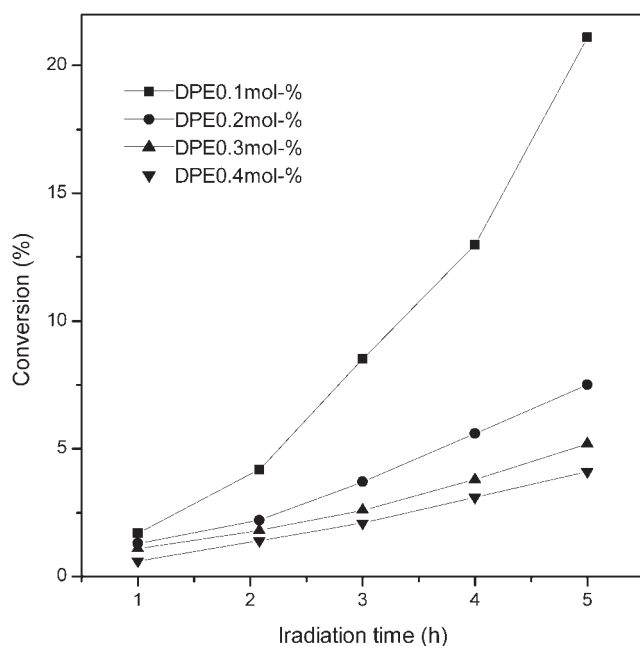


Figure 2 Variation of conversion versus time in the bulk polymerization of MA in the presence of DPE; dose rate: 97 Gy/min.

20 min and was initiated by ^{60}Co γ -irradiation at a dose rate of 67 Gy/min. The conversion of each sample in reaction was determined gravimetrically.

Characterization

MW and M_w/M_n were determined by means of gel permeation chromatography (GPC) equipped with

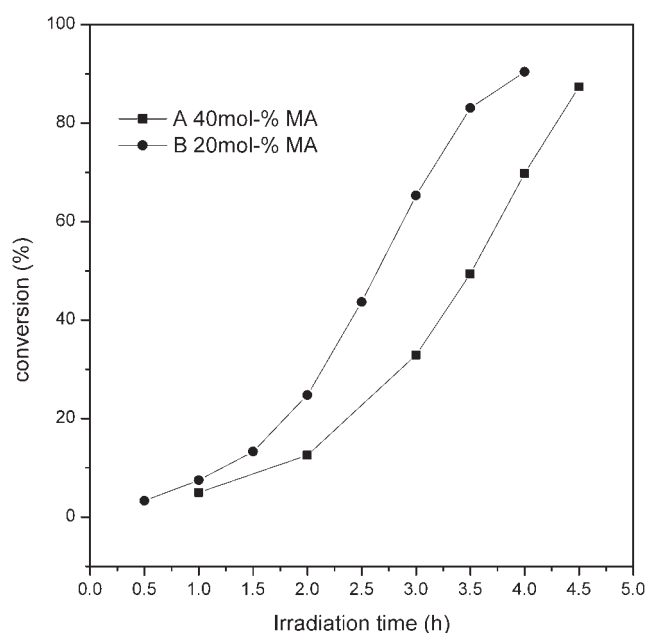


Figure 3 Variation of conversion versus time in solution polymerization of MA; DPE/(DPE + MA) mol %: (a) 0.05; (b) 0.1; dose rate: 97 Gy/min.

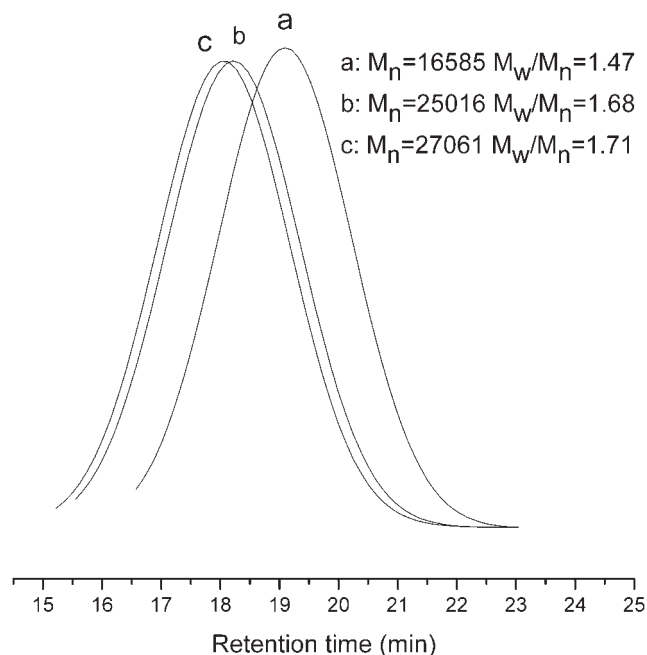


Figure 4 GPC curves of poly(methyl acrylate) obtained from solution polymerization initiated by γ -irradiation with 40 mol % MA in THF; DPE/(DPE + MA) mol % = 0.05; (a) 2 h, (b) 3 h, (c) 3.5 h.

10^3 , 10^4 , 10^5 Å columns, THF (1.0 mL/min) as the eluent, and a calibration based on styrene standard was taken. ^1H nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DMX-500 instru-

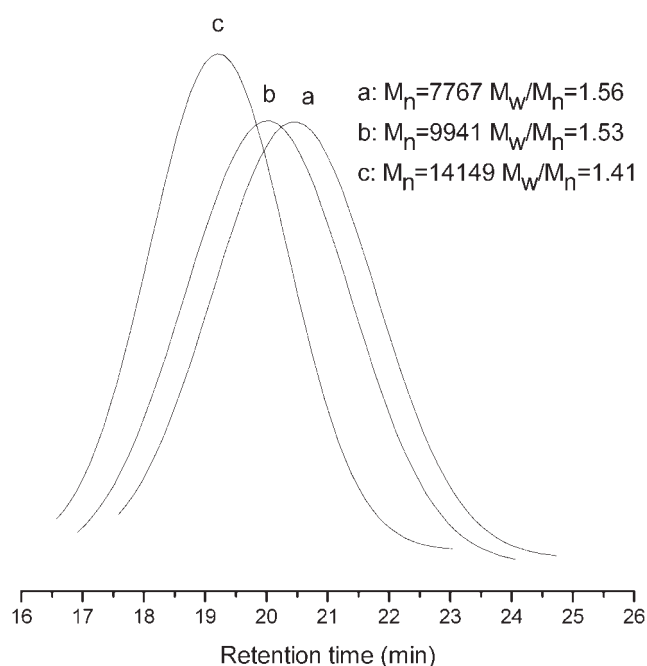


Figure 5 GPC curves of poly(methyl acrylate) obtained from solution polymerization induced by γ -irradiation with 20 mol % MA in THF; DPE/(DPE + MA) mol % = 0.1; (a) 1 h, (b) 1.5 h, (c) 2.0 h.

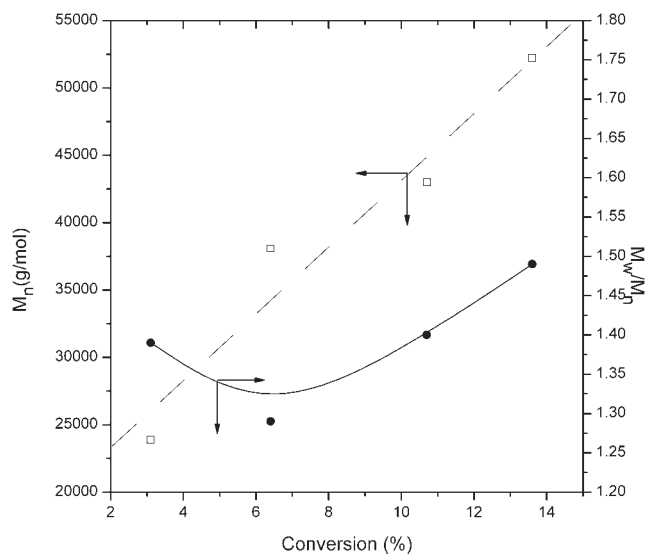


Figure 6 Evolution of molecular weight and polydispersity with conversion for the bulk polymerization of MA induced by γ -irradiation in the presence of 0.1 mol % DPE.

ment with CDCl_3 as the solvent and tetramethylsilane (TMS) as an internal standard. To determine the size and polydispersity of the particles, dynamic light scattering (DLS) measurement on highly diluted dispersion was obtained on MS-800 spectrophotometer and transmission electron microscope (TEM) was performed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

Bulk polymerization of MA by the DPE-method

MA was polymerized in the presence of different DPE concentration at the dose rate of 97 Gy/min. The GPC measurements show that the MW of poly (methyl acrylate) increases with the conversion going up (Fig. 1). However, in the absence of DPE, the MW reaches high value within a short time (Sample 1 in Table I). It means that DPE, as an additive, is incorporated into the polymers (Fig. 8) and makes the polymerization a controlled one under γ -irradiation. It is valuable to note that DPE concentration in monomer shows an influence on the conversion, MW and M_w/M_n . The conversion of MA increases with the decrease of DPE concentration at a certain absorbed dose (Fig. 2). The conversion data show nicely that DPE seems to act as a retarder in radical polymerization. When the conversion gets up to a little higher value (23%, DPE 0.1 mol %), the system becomes very sticky. It means that a gel effect must be taking place qualitatively with the increase of solution viscosity when the monomer conversion

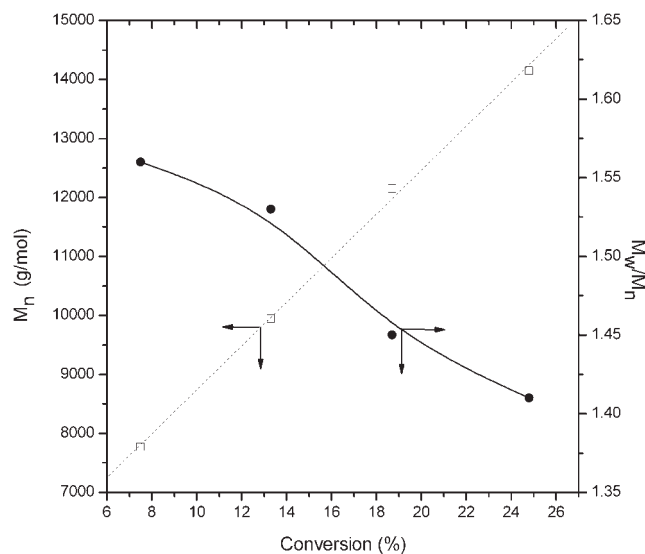


Figure 7 Evolution of molecular weight and polydispersity with conversion for the solution polymerization of MA in THF; DPE/(DPE + MA) mol % = 0.1.

reaches a certain value in the bulk polymerization system. From Table I, we can find that the presence of trace water is favorable to accelerate the polymerization and reform the molecular weight distribution for the polymerization of MA in bulk (comparing Sample 3 with 2), a probable explanation is that the trace water can sensitize radiation effect and increase the yield of radicals (H and OH), which initiate the polymerization and as the heads of the chains, every propagation chain is controlled to be growing at the "tails"; the MW and M_w/M_n are decreased with the increase of DPE concentration (from Sample 7 to 4); the MW increases and the M_w/M_n value firstly decreases with the increase of polymerization time (comparing Sample 3 with 7). However, the M_w/M_n value does not always decrease with the increase of

TABLE II
Copolymers of AA and BA Obtained with the DPE Method by γ -Irradiation

Entry	AA : BA (mol)	DPE (mol % comonomer)	Time (h)	Stabilization time of emulsion (h) ^a
A ₁	2 : 1	0.1	4	1.5
A ₂	1.5 : 1	0.1	4	2
A ₃	1 : 1	0.1	4	2
A ₄	1 : 1.5	0.1	4	10
A ₅	1 : 2	0.1	4	4
A ₆	1 : 1.5	0	0.5	0.5
A ₇	1 : 1.5	0.2	4	2
A ₈	1 : 1.5	0.3	4	1.5
A ₉	1 : 1.5	0.4	4	0.5
A ₁₀	1 : 1.5	0.5	4	0.2

Condition: dose rate = 97 Gy/min; polymerization was carried at room temperature.

^a denotes the emulsion of BA stabilized by the amphiphilic random copolymers.

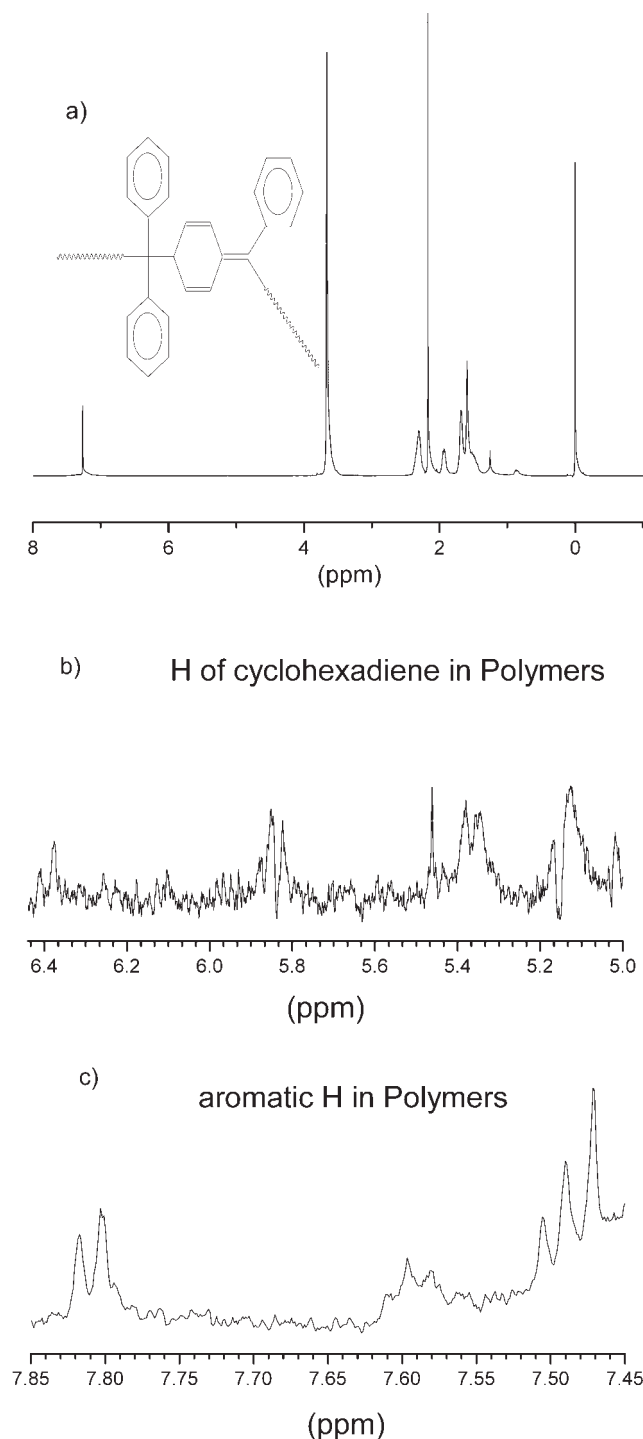


Figure 8 (a) ¹H NMR spectra of DPE-MA copolymers; (b, c) magnification and peak assignment.

absorbed dose, in company with the gelation appearing during the polymerization, M_w/M_n will go up in the bulk polymerization system, just as shown in Figure 1.

To avoid the gel effect in the polymerization system, solution system has been adopted to carry out the DPE controlled radiation polymerizations.

Solution polymerization of MA by the DPE-method

Solution polymerizations of MA were studied in THF. It can be found that the polymerization rates in solution are much larger than that in bulk system (Figs. 2 and 3); no obvious gelation is observed even for high MA concentration at high conversion [Fig. 3(a)]; but the M_w/M_n values still increase with the conversion in a certain higher conversion region (Fig. 4). For the lower MA concentration system [Fig. 3(b)] (30.0 g of MA and 0.07 g of DPE in 100.5 g of THF), however, the M_w/M_n values show the ideal variation (Fig. 5). In the case of bulk or high monomer concentration solution, when the monomer conversion reaches at a little higher level, the viscosity of system becomes very high, it makes the radiation grafting and crosslinking of inborn polymer chains easier. Although the yield of grafting and crosslinking could be very small, it is enough to result in the increasing M_w/M_n value with the increase of conversion in bulk or solution with high monomer concentration.

To explain that the polymerization rates in solution are much larger than that in bulk system, it is valuable to make a simple comparison between curve B in Figure 3 and the curve with 0.1 mol % of DPE in Figure 2. Although the DPE/(DPE+MA) mol % values in both cases are the same (0.1), however, the concentration of DPE in the solution system (Fig. 3) is only 0.02 mol %, much smaller than that of the sample with 0.1 mol % of DPE in Figure 2. From

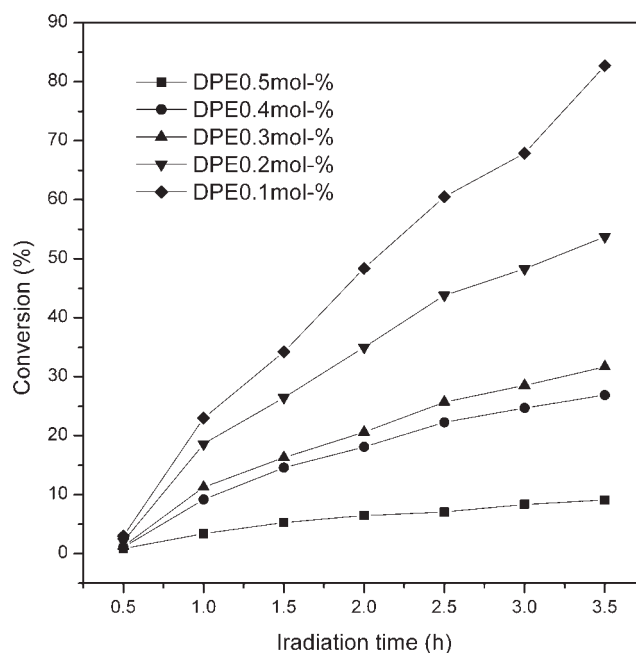


Figure 9 Variation of conversion versus time in the solution polymerization of AA and BA in the presence of DPE; dose rate: 97 Gy/min.

TABLE III
Recipe of BA and St for Emulsion Polymerization

Copolymer	Copolymer amount (g)	Water (g)	Monomer		Particle diameter (nm)	Coagulum (wt %)
			St	BA		
A ₃	2	56	42	0	260 ^a	0.9
A ₄	2	58	0	40	200 ^b	0.1
A ₄	2	56	42	0	250 ^a	0.2
A ₅	2	56	42	0	225 ^a	0.8
A ₆	2	56	42	0	200 ^a	4

Condition: dose rate = 97 Gy/min; polymerization was carried at room temperature.

^a Cumulant average particle size determined by TEM.

^b Cumulant average particle size determined by DLS.

this comparison it becomes obvious that not only the ratio DPE/(monomer + DPE) but also the absolute concentration of DPE effects molar masses, M_w/M_n and rate of polymerization. It means although the system is diluted synchronously for monomer and DPE, the effect on them can be different for the diffusion controlled radical polymerization process: the larger the molecule is, the slower diffusion must be, as a result DPE gets much larger effect from the system dilution than the monomer (MA) does.

Controlled character of polymerization

The controlled nature of polymerization in the presence of DPE is indicated by a linear increase in molecular weights with the increase of conversion and the narrower distribution of the polymers produced (Figs. 6 and 7), while the M_n -conversion lines do not pass the origin but cross the y -axis at certain M_n values. Maybe this is a normal problem for all of the living free radical polymerization, but it was always ignored. A probable explanation can be made as follows: at the primary period of polymerization process, once a chain reaction is initiated by an active radical, the molecular chain should be growing continuously until the active chain radical is terminated by another radical or by certain special molecule-like DPE. For the former case (radical to radical combination), a dead polymer molecule is produced, the molecular weight is quite high even at the primary period of polymerization (at very low conversion) and not changed much with the increase of monomer conversion; while for the latter case, a mediated molecule which can be reinitiated is produced, so that the molecule chain can be growing step by step and the molecular weight increased with the increase of the conversion, the M_n at very low conversion depends on the "step" reaction period and can be very low (if the "step" period is very short) but not to zero, so the so called origin point is nonsensical in the M_n -conversion relation. The fact in Figure 7 shows the higher controlled character compared with that in Figure 6. It means that a solution system

with a suitable monomer concentration is better than a bulk system for carrying out a controlled radical polymerization initiated by γ -irradiation with DPE as the controlling reagent.

Copolymers of AA and BA prepared by the DPE-method

Solution polymerizations of AA and BA were carried out in EtOH by the DPE-method under γ -irradiation. As seen in Table II, a series of different ratio between AA and BA in the presence of different DPE concentration were studied. Table II indicates that when the ratio between AA and BA is 1 : 1.5 and DPE concentration was 0.1 mol % of comonomers, the amphiphilic copolymers prepared by this method were proved to be powerful electrosteric stabilizers in free radical emulsion polymerization. The emulsion stabilized by A₃ can be kept for 10 h. In Figure 9, it can be seen that DPE concentration in AA and BA shows an influence on the conversion of

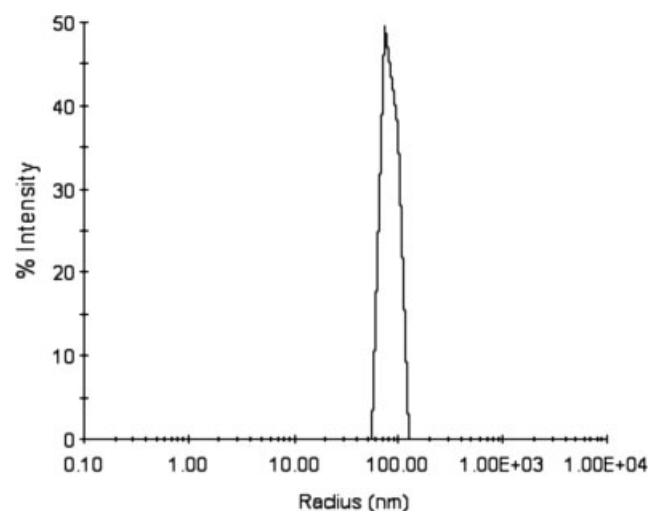


Figure 10 Particle size distribution of PBA latices measured by DLS.

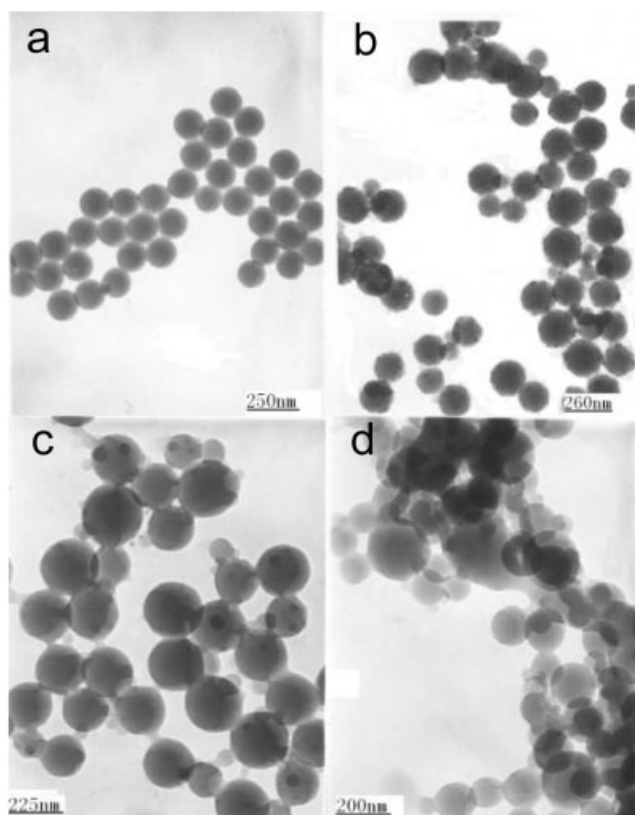


Figure 11 TEM micrographs of PS latices prepared by γ -irradiation; (a) PS latex particles stabilized by A_4 , (b) PS latex particles stabilized by A_3 , (c) PS latex particles stabilized by A_5 , (d) PS latex particles stabilized by A_6 .

monomers, which increases with the decrease of DPE concentration at a certain radiation dose.

Emulsion polymerization stabilized by the amphiphilic copolymers

The basic recipe of emulsion polymerization in the presence of the amphiphilic copolymer is given in Table III. Figure 10 shows the DLS particle size distribution of PBA latex prepared by the emulsion polymerization with 38% solids content. The particle diameters are reasonably uniform, and the level of coagulum is acceptable at higher solids content. Sample A_4 was proved to be most effective for the emulsion polymerization of BA. Figure 11 shows the TEM images of PS latices prepared with 40% solids content. The PS latex prepared, using A_4 as emulsifier, is also monodispersed and lower coagulated. On the contrary, when the emulsion polymerization of St is stabilized by A_3 or A_5 (the ratio between AA and BA is 1 : 1 or 1 : 2), the particle size distribution of latex is more polydispersed. Furthermore, when different copolymer is employed, apparent difference appears in the morphology of the particles. From the study, it can be found that A_4 is the most effective emulsifier among the prepared amphiphilic copoly-

mers for the emulsion polymerization of BA and St, which results in the lower coagulum and higher mechanic stability than A_3 , A_5 . However, when the amphiphilic copolymer prepared with the same monomers ratio as A_4 in the absence of DPE (A_6 in Table III) used as the emulsifier, the resulted particle diameter of PS is very polydispersed and the level of coagulum is very high. The experiments indicate that DPE and the molar ratio AA to BA determine the stabilizing properties of the copolymers in emulsion polymerization.

CONCLUSIONS

Polymerizations of MA in bulk and solution were successfully obtained by γ -irradiation in the presence of DPE. Higher conversion and better controllable character were obtained in solution polymerization compared with bulk polymerization. Although the M_w/M_n of the products cannot compete with that obtained by the known methods for controlled free radical polymerization (such as ATRP, RAFT, etc.), the products are colorless, odorless, and free from toxic additives. Especially, the products are more pure by γ -irradiation method than by traditional chemical method because no chemical initiator is needed. The amphiphilic copolymers of AA and BA were successfully prepared by the DPE-method and applied in emulsion polymerization to obtain monodispersed emulsion latices with relatively high solids content. So the method presented here is significant for application in industry.

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