Preparation of Poly(styrene-*co*-isobornyl methacrylate) Beads Having Controlled Glass Transition Temperature by Suspension Polymerization

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ABSTRACT: The styrene (St) and isobornyl methacrylate (IBMA) random copolymer beads with controlled glass transition temperature (T_g), in the range of 105–158°C, were successfully prepared by suspension polymerization. The influence of the ratios of IBMA in monomer feeds on the copolymerization yields, the molecular weights and molecular weight distributions of the produced copolymers, the copolymer compositions and the T_gs of these copolymers was investigated systematically. The monomer reactivity ratios were r_1 (St) = 0.57 and r_2 (IBMA) = 0.20 with benzyl peroxide as initiator at 90°C, respectively. As the mass fraction of IBMA in monomer feeds was about 40 wt %, it was observed that the monomer conversion could be up to 90 wt %. The fractions of IBMA unit in copolymers were in the range of 35–40 wt % and T_gs of the corresponding copolymers were in the range of 119.6–128°C while the monomer conversion increased from 0 to greater than 90 wt %. In addition, the effects of other factors, such as the dispersants, polymerization time and the initiator concentration on the copolymerization were also discussed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 113–120, 2013

INTRODUCTION

As a commonly used technique for polymerization of vinyl monomers, suspension polymerization has great advantages over other processes (bulk, solution, and emulsion), for example, easy heat removal, high conversion of monomer, high-molecular weight of product, and simple post polymerization process. Typically, the mixture of monomer and initiator is broken into small droplets (with diameters in the range of 0.45–5 mm) covered with a protective dispersant under vigorous stirring. The initiation and chain propagation take place predominantly in the droplets which play like minibulk reactors. In the early polymerization stage (monomer conversion less than 30 wt %), there is a dynamic equilibrium among the monomer droplets as illustrated in Scheme 1. When the conversion is higher than a critical value depending on the nature of monomer (for styrene, it is about 60–80 wt %), the size of the particles no longer changes significantly.[1] In general, ratio of water to oil, the kind and amount of dispersant and the degree of agitation are the major parameters having significant impacts on the suspension polymerization.

As a precursor of expanded polystyrene (EPS) foam, polystyrene bead is commonly produced by suspension polymerization. EPS foam has very unique and complex porous structure (exhibiting a double-scale porosity), which offers the EPS foam with excellent thermal and sound insulation, low density, and good cushioning characteristics.[2] Most importantly, EPS foam allows replicating very complicated shapes and structures by a simple molding process which is irreplaceable in somewhat by extruded styrene foam. Since its invention more than 50 years ago, EPS foam has been one of the most widely used thermal insulation materials in buildings for it offering the highest life cycle saving and lowest payback period compared to other foams, including extruded polystyrene, polyurethane, perlite, and polyvinyl chloride.[3–8] In addition, it has also been widely used in packaging.

However, in spite of the above advantages, EPS cannot meet some applications required higher servicing temperature because of its relatively low T_g (ca. 100°C). These applications includes packaging of warm or reheating foods in the microwave, heat insulation materials for hot fluid pipelines, tanks, etc. Therefore, it is of importance to improve the upper service temperature of EPS to compete with polyurethane, polypropylene and the other foams. For noncrystalline polymers like PS, the upper servicing temperature depends largely on its T_g. In other words, an

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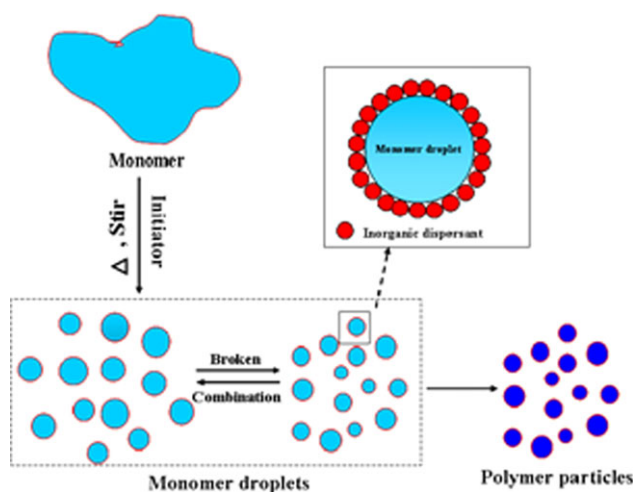
Scheme 1. Suspension polymerization process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increase in its T_g will lead to an improvement in its heat resistance. So far, a lot of efforts have been made to improve the servicing temperature (the T_g) of PS. The main strategies for this purpose could be classified into three categories. The first, also the most widely explored, is copolymerized with monomer(s) having polar, rigid or bulky substituents. The second is to control the isotacticity of the produced polymer, for example, melting point of s-PS is about 270°C and its vicat softening temperature is 254°C.[9,10] However, s-PS is a semicrystalline polymer which is not applicable for EPS. The last is to introduce appropriate crosslinking structure into polymer chains.[11] The crosslinking extent is extremely sensitive to the structure and amount of the crosslinker monomer.[12]

To our best knowledge, copolymerization is one of the most practical and robust tools to modify PS with high T_g via conventional free radical mechanism. Kolayashi et al.[13] introduced a bulky and rigid adamantyl substituent into the side chain to obtain 4-(1-adamantyl) styrene (AdS). The adamantyl skeleton is particularly effective to enhance T_g value of the copolymer. Their result showed that the T_g of Poly(AdS) could be up to 234°C. The T_g values of random copolymers of AdS and styrene could be mediated between 100 and 234°C by changing the feed ratio of comonomers. However, AdS has not been put into mass production yet. The foam of styrene-maleic anhydride (SMA) copolymer could be prepared by extrusion process and the result showed that the heat distortion temperature of the foam is much higher than that of the styrene homopolymer. It was reported that an increase of about 1 wt % of maleic anhydride content in SMA copolymer would lead to about 1.48°C increase of the T_g.[14] The T_g of copolymer of styrene and N-phenyl maleimide (1 : 1) is about 165°C and it could be further improved by introducing crosslinking structure into polymer chain (the T_g of copolymer is as high as 175°C with addition of 2 mol % divinyl benzene).[15,16] However, maleic anhydride-based copolymers are poor in molding processability because of their poor fluidity.[15] In addition, the water soluble maleic anhydride monomer makes it difficult to prepare copolymer bead by direct aqueous suspension polymerization.[17] There is a very interesting

result that the multiblock copolymers of styrene and α-methylstyrene show a very high T_g (ca. 172–180°C) which is depended on both the molecular weight and composition.[18] However, the activity of α-methylstyrene in radical polymerization is too low because of its entropy (there is a polymerization–depolymerization equilibrium when the temperature greater than 61°C in radical polymerization process). It is difficult to prepare high-molecular weight styrene and α-methylstyrene copolymers which are incorporated high enough fraction of α-methylstyrene unit by a standard industrial EPS production process. Recently, Kharas et al.[19–25] investigated a series of trisubstituted styrenes with strong electrophilic groups on the α-position. These polymer products showed a considerable high T_g compared to the polystyrene homopolymer. Commercial resin of acrylonitrile and styrene copolymers also showed excellent heat resistance.[26] However, the low boiling point, health-hazard and fair water solubility of acrylonitrile monomer makes it impractical to produce styrene-acrylonitrile copolymer bead by a standard industrial EPS mass-production process. Methacrylic acid (MAA) and its alkyl esters are of importance as a comonomer to mediate the T_g of copolymers by free radical copolymerization. It has been reported that MAA modified PS having high heat resistance.[27] More importantly, a broad range of alkyl groups in ester of MAA offers a library of copolymers with different T_g. For example, T_gs of poly(cyclohexyl methacrylate), poly(isobornyl methacrylate), and poly(bornyl methacrylate) are about 110, 195, and 199°C, respectively.[28,29] Combined with the composition and sequential structure, it is possible to tailor the T_g of the copolymers.

As discussed above, the copolymerization is a practical pathway to improve the heat resistance of the styrene compolymers. Specifically, to meet the standard industrial EPS production process, the comonomer is expected to have the following features: (1) high activity and tendency to form homogenous copolymer with styrene in a wide range of monomer feed ratio; (2) miscible with styrene and the mixture is a good solvent for the produced copolymer; (3) no side reaction and low solubility in water at the temperature of EPS production; and (4) having mass production, environment benign, low vapor pressure and cost competitive. Obviously, styrene derivatives (such as α-methylstyrene, p-methylstyrene, tert-butyl styrene, and methoxy styrene) and alky methacrylates are two kinds of monomers which could be met the above requirements. However, styrene derivatives are not good candidates for improving T_g of polystyrene because α-methylstyrene has very low polymerization/copolymerization activity at the temperature of EPS polymerization and the other styrene derivatives are both ineffective in improving T_g of copolymers and lack competitive in cost. In this case, alkyl methacrylates seem to be a good alternative. In this article, IBMA was taken as a comonomer to improve the T_g of PS (the reaction is
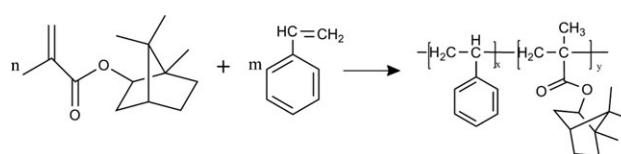
Scheme 2. The copolymerization process of styrene and IBMA.

Table I. Summary of the Experiments[a]

Sample	IBMA (wt %)	Yield (%)	$M_n \times 10^{4b}$	T_g (°C)[c]
1	0	83.6	10.1	103
2	5	84.9	10.2	106
3	10	89.3	7.72	108
4	15	88.5	7.53	110
5	20	93.6	10.1	112
6	30	93.7	9.51	114
7	40	91.1	9.17	119
8	50	97.7	8.92	136
9	60	88.9	15.9	159
10	80	88.0	16.7	–

[a]Copolymerizations were carried out in 100-mL deionized water with 0.4 wt % BPO (to monomer), 0.4 wt % TCP (to water) at 90°C, [b]Determined by GPC, THF as eluent, [c]Determined by DSC, 20°C/min.

shown in Scheme 2). The bulky isobornyl group can not only provide the copolymer with high T_g (ca. 195°C) but also offer the copolymer a good solubility in the mixture of styrene and IBMA.

EXPERIMENTAL

Materials

Styrene, Tianjin Fuchen Chemical Reagent Factory (China) (98%, purity) and isobornyl methacrylate (IBMA) (J&K Chemical, 98%) were purified with a short column filled with inhibitor removal resin (CAS 9003-70-7, Alfa Aesar). Tetrahydrofuran (THF) and ethanol (Beijing Modern Oriental Fine Chemical Co.), benzoyl peroxide (BPO, Alfa Aesar, 97%) was used as received. Hydroxyapatite (TCP) was kindly donated by Wuxi Xingda Foam Plastic Materials Co. The deionized (DI) water was supplied by a Direct-Q™ water purification system of Millipore.

Determination of Monomer Reactivity Ratios

The copolymerization of St and IBMA was carried out by bulk copolymerization using BPO as initiator at 90°C. The molar fraction of IBMA monomer in feed was varied from 0.06 to 0.76. The polymerizations were terminated at low conversion (<10 wt %) by pouring the reaction mixture into a large amount of cold methanol. Then the precipitate was filtered and washed with methanol. After being dried, the solid polymer was purified by repeating precipitation with methanol from solution of THF for five times and finally dried under vacuum at 50°C.

Suspension Polymerization of Styrene with IBMA

TCP and water were added into a three-necked flask equipped with a nitrogen gas supply, a mechanical stirrer and a condenser. Then, the flask was heated to the set temperature by an oil bath under stirring and gentle nitrogen purging. After the temperature was ready, the mixture of styrene, IBMA and BPO was introduced into the flask. Keeping the polymerization at set temperature for about 6 h, then heating was stopped and the reactant was cooled to room temperature under stirring. The reactant was filtered, washed with diluted HCl and DI water. The obtained polymer beads were dried under vacuum at 50°C to constant weight. The overall monomer conversion was deter-

mined gravimetrically. The experimental formula and results were summarized in Table I.

Characterization

FTIR spectra of the copolymers were recorded by a Nicolet Nexus-670 FTIR spectrometer using KBr pellets. Molecular weights and molecular weight distributions of the copolymers were determined by a Waters 515-2410 gel permeation chromatography (GPC) with THF as eluent and universal calibration with polystyrene standard. ^{1}H-NMR spectra were collected with a Bruker av600 (600 Hz) spectrometer at room temperature with deuterated chloroform (CDCl$_3$) as solvent and TMS as internal standard, respectively. T_gs of polymers were measured with a DSC 204F1. The thermal scan was performed in the range of 20–200°C at a heating rate of 20°C/min. All the polymer samples used for measurement were dissolved in THF and precipitated in methanol for three times. The precipitate was dried under vacuum at 50°C to constant weight finally.

RESULTS AND DISCUSSION

The Reactivity Ratios of St and IBMA

For conventional free radical copolymerization, the reactivity ratios of monomers are mainly dependent on their chemical structures and slightly affected by polymerization temperature. The composition, sequential structure, and thus the properties of the copolymers are largely dependent on the reactivity ratios of monomers. There is some difference in data of the reactivity ratios of styrene with IBMA from literatures. For example, in *Polymer Handbook* of 1975 Edition $r_1 = 0.70$, $r_2 = 0.32$ which were determined at 60°C with AIBN as initiator, and in Polymer Handbook of 1999 Edition, $r_1 = 0.61$, $r_2 = 0.20$ without the details specified.[30,31,32] It is well known that the typical temperature for industrial EPS bead production is about 90°C for lower temperature stage (monomer conversion up to about 90 wt %). To determine the reactivity ratios of St and IBMA at this temperature is helpful to get better understanding of the suspension copolymerization of styrene and IBMA. For convenience, the copolymerization for determining the reactivity ratios was carried out in bulk. The monomer conversions were controlled to be less than 10 wt % to analyze the copolymer composition.[33] The values of reactivity ratios were calculated by Mayo–Lewis method.[34] Equation (1) shows the relationship between feed composition and copolymer composition.

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) \tag{1}$$

where $[M_1]$ and $[M_2]$ are the molar fraction of monomer St and IBMA in feed, $d[M_1]$ and $d[M_2]$ are the instantaneous composition of St and IBMA structural unites in copolymer (mol). Assuming $a = \frac{[M_1]}{[M_2]}$, $b = \frac{d[M_1]}{d[M_2]}$, then eq. (1) can be rewritten as:

$$a = b \cdot \frac{r_1 b + 1}{r_2 + b} \tag{2}$$

Equation (2) could also be expressed:

$$\frac{a(b-1)}{b} = r_1 \cdot \frac{a^2}{b} - r_2 \tag{3}$$

Plot of $\frac{a(b-1)}{b}$ against $\frac{a^2}{b}$, a straight line will be obtained with r_1 as slope and r_2 as intercept.
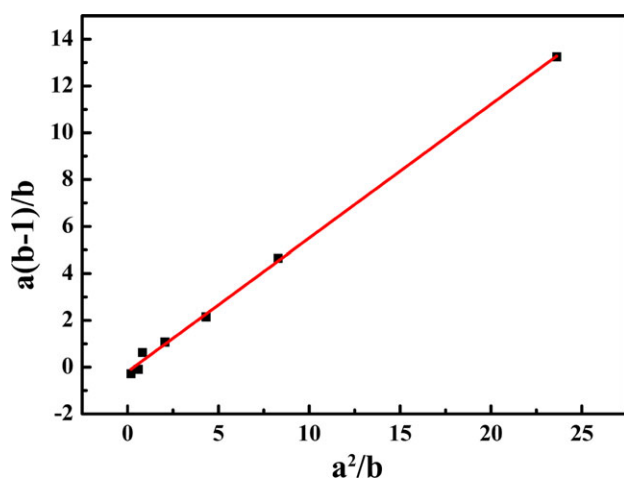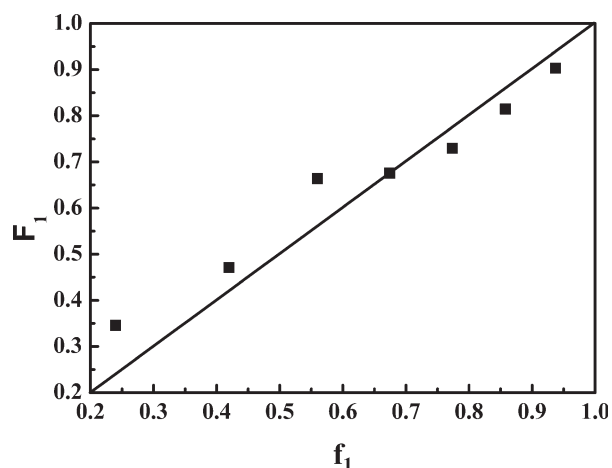
Figure 1. Plot of $a(b - 1)/b$ against a^2/b for poly(St-*co*-IBMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Mayo–Lewis plot for poly(St-*co*-IBMA) is shown in Figure 1 and the calculated r_1(St) and r_2 (IBMA) are 0.57 and 0.20, respectively. This result is close to the data in Polymer Handbook of 1999 Edition.[30] What is more, both the value of r_1 and r_2 are <1, so that the copolymerization system has an azeotropic polymerization point. From Figure 2, we can see that the azeotropic molar fraction of St is about 67.9%. According to Price–Alfrey method, the value of Q (IBMA) and e (IBMA) are 5.63 and −2.27, respectively.

Effect of Dispersant

The dispersants used in suspension polymerization could be divided into two categories: (1) water-soluble polymers and (2) nonsoluble inorganic fine powders. For example, poly(vinyl alcohol), neutralized copolymer of SMA, and hydroxyethylcellulose are the most common organic suspension stabilizers.[35] TCP is one of the most efficient and widely used dispersants in industrial EPS production. As shown in Scheme 1, TCP par-

Figure 2. Fraction of styrene structural unit in copolymer versus styrene in monomer feed (the composition of copolymers was determined by ^{1}H-NMR).
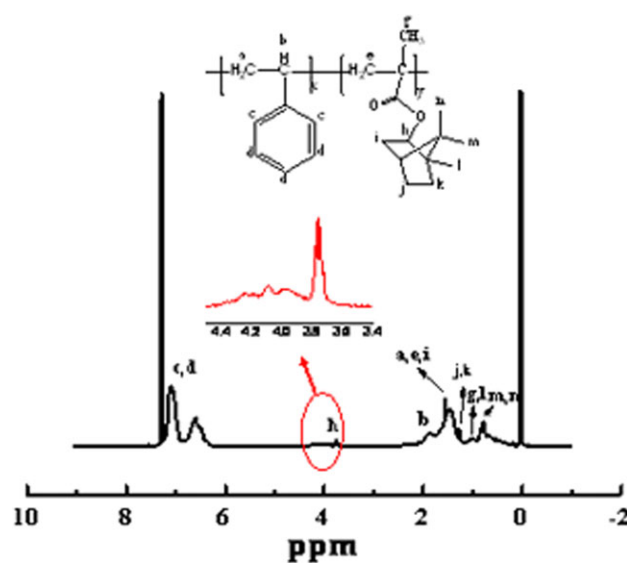
Figure 3. ^{1}H-NMR spectrum of poly(St-*co*-PIBMA) (produced at 25 wt % of in monomer feed). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ticles are absorbed onto the surface of monomer droplet to form a protective layer to keep the droplets from aggregating.

With the introduction of the comonomer IBMA, it is necessary to check if TCP is still an efficient dispersant during the copolymerization. A series of experiments with different TCP/monomer ratios, 1, 1.5, 2, 2.5, and 2.8 wt %, were carried out at the similar water–oil ratio, molar fraction in monomer feed, initiator concentration, reaction temperature and stirring speed. It was observed that the droplets/particles tended to aggregate during copolymerization when the dispersant amount is less than 2 wt %, and as a result there were no discrete polymer beads formed. As the dispersant amount was greater than 2 wt %, nearly perfect spherical polymer particles were produced and diameters of these copolymer beads decreased with the increase of dispersant concentration.

Synthesis of Poly(St-*co*-IBMA) Beads by Suspension Polymerization

Figure 3 presents the ^{1}H-NMR spectrum of the Poly(St-*co*-IBMA) with CDCl$_3$ as solvent. The chemical shifts between 6.66 and 7.12 ppm (c,d) are assigned to the protons of benzene ring of styrene and the signal at 4.24 ppm (h) is attributed to the O—CH< of the IBMA unit. The methylene group of the polymer backbone shows a broad signal between $\delta = 1.28$ and $\delta = 1.61$ ppm (a,e,i,k) due to tacticity. The peaks at around $\delta = 0.795$–0.989 (g,l,m,n) are assigned to the protons of CH_3—C—. Two chemical shifts at $\delta = 5.54$ and $\delta = 6.09$ related to =CH_2 have disappeared.
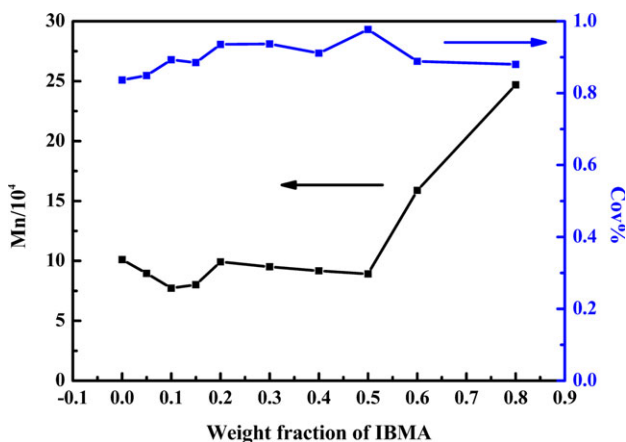
Figure 4 shows FTIR spectra of PS, PIBMA and Poly(St-*co*-IBMA), respectively. The characteristic absorption bands of ester carbonyl groups of the copolymer are observed at 1723 cm^{-1}. The signal around 1150 cm^{-1} is assigned to the C—O of the ester group. The band at 3030 cm^{-1} is ascribed to the C—H of the benzene ring. The three signals around 1451, 1492, and 1600 cm^{-1} are assigned to the stretching vibration of C=C
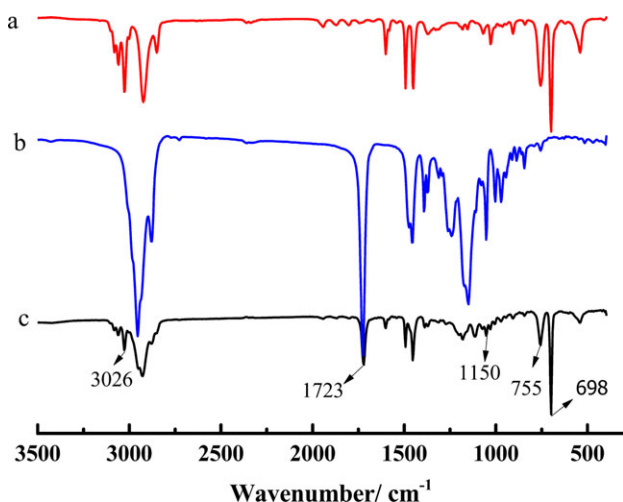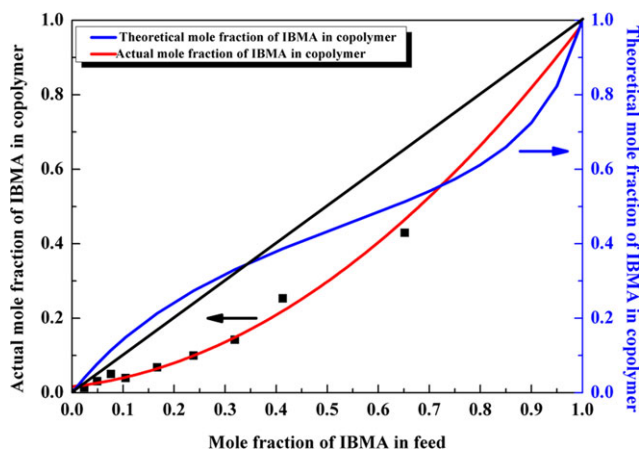
Figure 4. FTIR spectra of (a) PSt, (b) PIBMA, and (c) poly(St-*co*-IBMA) (produced at the 30 wt % of IBMA in monomer feed). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]


Figure 6. The theoretical and the actual mole fraction of IBMA in copolymer versus molar fraction of IBMA in monomer feed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the benzene skeleton. The peaks at 755 cm^{-1} and 698 cm^{-1} are attributed to the backbone vibration of substituted aromatic ring.

Figure 5 shows the conversion of monomers and molecular weight of the copolymers for copolymerization with different weight fraction of IBMA in the monomer feeds. The conversions of the copolymerization were almost greater than 85 wt % The molecular weights of these copolymers are in the range of 80,000–100,000 with the weight fraction of IBMA in feed less than 50 wt %. However, the molecular weights of copolymers increased significantly with the increment of the fraction of IBMA when the IBMA concentration is more than 50 wt %. The root cause of this change is not clear at present. It might be related to the change of the copolymer chain structure. As the IBMA fraction in feed increased, the IBMA unit in copolymer also increased. When the content of bulky IBMA unit is

greater than a certain value, the copolymer chain flexibility changed greatly. This change would dramatically reduce the mobility of the copolymer chain free radicals and increase the dynamic volume of the copolymer chains in good solvent. The former extended the life time of chain free radicals which led to high-molecular weight copolymer, and the later gave a high apparent molecular weight as it was based on the universal calibration with polystyrene standard. It should be emphasized that direct comparison of the molecular weight (determined by GPC with universal calibration) of the copolymers with different composition should be careful.

Figure 6 presents the dependence of copolymer composition on molar fraction of IBMA in monomer feed. As a whole, the contents of IBMA unit in copolymers increased steadily with the increase of IBMA fraction in monomer feed. However, the IBMA fraction in copolymers is lower than that of the corresponding IBMA in monomer feeds. This is due to the relatively lower copolymerization reactivity of IBMA indicated by r_2 (IBMA) = 0.20 and r_1 (St) = 0.57. In Figure 6, it was also given the theoretical line of F_1 (the molar fraction of styrene unit in copolymer) versus f_1 (the corresponding molar fraction of styrene in monomer feed) which was calculated from the r_1 and r_2 by using eq. (4). It was clearly that there was obvious difference between predicted and experimental data, and this is easy to be understood because the assumptions in Mayo–Lewis method are not guaranteed at high monomer conversion.

Figure 5. Molecular weights of copolymers and monomer conversions versus the IBMA in the monomer feeds (copolymerizations were carried out in 100-mL deionized water with 0.4 wt % BPO (to monomer), 0.4 wt % TCP (to water) at 90°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{4}$$

As IBMA concentration in monomer feed increased from 0 to 70 wt %, the copolymer beads with almost spherical shape were obtained (as shown in Figure 7). The size of poly(St-*co*-IBMA) beads was roughly in the range of 0.6–1.0 mm. It is well-known that the size of beads is greatly affected by the ratio of monomer to water, the ratio of dispersant to water, the stirring speed and configuration of the reactor. Obviously, this topic is not objective of this article. So far, our experiments demonstrated
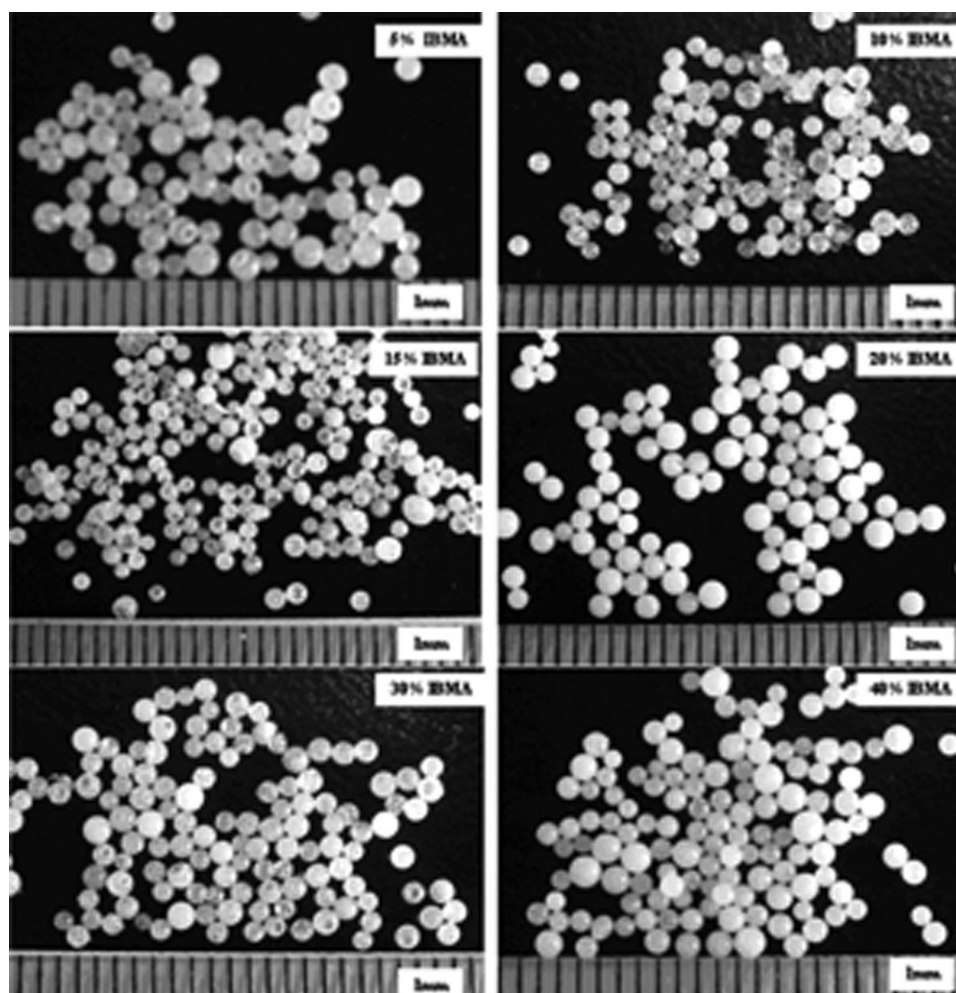
Figure 7. Digital photographs of poly(St-*co*-IBMA) beads with different IBMA fraction (wt %) in monomer feed.

that the copolymer beads of IBMA and styrene could be prepared by suspension polymerization with a similar process of the EPS production. That is to say, the EPS production line could be switched to copolymer beads of IBMA and styrene without making any major modification.

The T_g of Poly(St-*co*-IBMA)

The T_g of copolymers with different monomer feed ratios was shown in Figure 8. All these copolymers exhibited a single T_g which demonstrated that the product was a random copolymer of styrene with IBMA rather than a mixture of two homopolymers. As expected, the T_g of copolymers increased with the increase of IBMA unit in the copolymers. When the copolymer contained about 9.93 mol % of IBMA unit, the T_g of the copolymer was 120°C. Keep increasing the content of IBMA unit in the copolymer to 42.9 mol %, the T_g of the copolymer went up to 158°C which was nearly 55°C higher than the T_g of PS ($T_g = 100$°C).

The Fox equation [eq. (5)] established for random copolymers is applied for poly(St-*co*-IBMA).[36]

$$1 \Big/ T_g = W_A \Big/ T_{g_A} + W_B \Big/ T_{g_B} \qquad (5)$$

where T_g indicates the glass transition temperature of the copolymers; W_A *and* W_B are the mass fraction of monomer A

and B, respectively; T_{g_A} and T_{g_B} are the glass transition temperature of the homopolymers of A and B, respectively.

Figure 8 shows the theoretical and actual T_g versus weight percent of IBMA unit in the copolymer. It can be seen that there
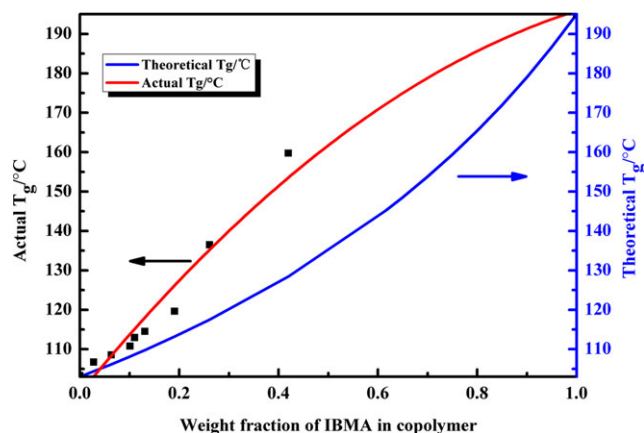
Figure 8. The theoretical and actual T_g of copolymers versus the copolymer composition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
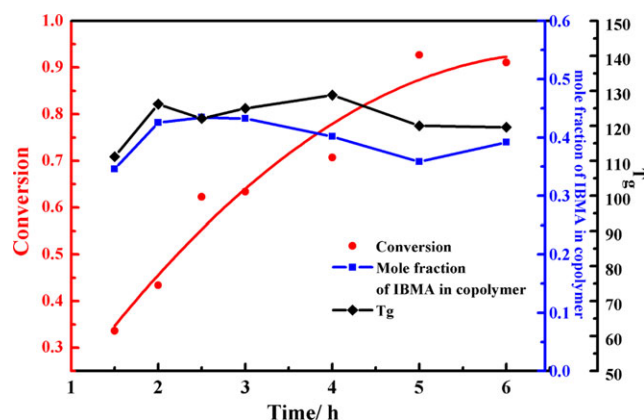
Figure 9. Monomer conversion, copolymer composition, and T_g of poly(St-*co*-IBMA) versus the time of suspension copolymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

are obvious difference between predicted values and experimental data. The actual T_g of copolymers and the polymer compositions do not fit well with the Fox equation. This indicates that bulky isobornyl group makes the molecular chain hard to move, thus, the T_g of the copolymers are improved dramatically. Moore et al.[37,38] reported that the T_g of styrene and *N*-phenyl maleimide copolymers with 30 wt % *N*-phenyl maleimide are 193°C measured by DTA. With the *N*-phenyl maleimide contents increased from 30 to 40 wt %, "service" temperatures of the copolymer increased linearly from 193 to 204°C accordingly. Compared with Moore's results, the relationship between T_g and copolymer composition is nonlinear for poly(St-*co*-IBMA) in our research. This positive deviation from the predicted data of Fox equation is due to the fact that the bicycle isobornyl group is much more bulky and rigid than benzene ring. As the content of IBMA unit in copolymers increased from 0 to 47 mol %, the value of the deviation is also increased.

Evolution of IBMA and Styrene Copolymerization

When the weight fraction of IBMA is up to 40%, the T_g of the resulted copolymer is about 120°C, which is high enough for applications such as reheating food packaging and hot water insulation.[14] Another concern is whether the variation of the copolymer compositions and corresponding T_gs is small enough at different copolymerization times and/or monomer conversions. To address this point, the influence of monomer conversion on copolymer composition and T_g of the copolymers was monitored, and the results are presented in Figure 9. It could be seen that the monomer conversion increased steadily up to about 90 wt % with the proceeding of the copolymerization without observable "gel effects." The copolymerization proceeded rapidly in the first 4 h (the conversion reached up to about 70 wt %) and then the rate of copolymerization leveled off. The contents of IBMA unit in copolymers were in the range of 35–40 wt % and the variation was very small during the copolymerization process. With changing of the polymerization time the T_g of the produced copolymer also did not showed significant variation except in the early stage. In the very early phase of polymerization (within 1 h), there were some low mo-

lecular weight copolymers due to the induction period of the free radical polymerization (presented in Supporting Information Figure S2). When the polymerization time was greater than 1 h, the T_gs of the copolymers were in the range of 119.6–128°C, with a small variation of 8.4°C.

The reason for the small variation of the copolymer composition, T_g and molecular weight of the copolymers might be related to the fact that the monomer feed ratio was close to the azeotropic point of this monomer pair. These results are advantages for proposed application.

CONCLUSION

The poly(St-*co*-IBMA) beads with controlled T_g were successfully prepared by suspension polymerization. The monomer conversion could be nearly up to 90% and the molecular weight of copolymers is in the range of 80,000–100,000. The monomer reactivity ratios were r_1 (St) = 0.57 and r_2 (IBMA) = 0.20, respectively, determined by the Mayo–Lewis method at the 90°C, which is the typical temperature for EPS production. The T_g of the copolymers could be controlled in the range from 105 to 158°C by simply adjusting the fraction of IBMA in monomer feed. As the weight fraction of IBMA in monomer feed was about 40 wt %, the fraction of IBMA structural unit in compolymers was in the range of 10–14 mol % and T_g of the corresponding copolymers was in the range of 119.6–128°C, during the entire polymerization process with the monomer conversion increased from 0 to greater than 90 wt %.

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