Glass-Transition Temperatures and Rheological Behavior of Methyl Methacrylate–Styrene Random Copolymers

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ABSTRACT: Poly(methyl methacrylate-*ran*-styrene) copolymers were synthesized under monomer-starved conditions by emulsion copolymerization. The glass-transition temperatures (T_g's) of the copolymers were measured by differential scanning calorimetry (DSC) and torsional braid analysis (TBA). The results showed that the methyl methacrylate–styrene random copolymers produced an asymmetric T_g versus composition curve, which could not even be interpreted by the Johnston equation with different contributions of dyads to the T_g of the copolymer considered. A new sequence distribution equation concerning different contributions of triads was introduced to predict the copolymer's T_g. The new equation fit the experimental data exactly. Also, the T_g determined by TBA (T_{gTBA}) was higher than the one determined by DSC (T_{gDSC}) and the difference was not constant. The rheological behavior of the copolymers was also studied. $T_{gTBA} - T_{gDSC}$ increased with increasing flow index of the melt of the copolymer, and the reason was interpreted. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2891–2896, 2003

Key words: glass transition; DSC; relaxation; T_g vs. composition; T_g determination

INTRODUCTION

Methyl methacrylate (MMA) and styrene (St) are two of the most widely used vinyl monomers in modern plastic industry. Methacrylic resins consisting of MMA and small amounts of St are widely used in optical applications, such as nonspherical optical lenses and optical disks, because of their excellent transparency and weatherability among synthetic resins.[1] MMA and St are also used to synthesize poly(methyl methacrylate)/polystyrene core–shell composites by seeded emulsion polymerization.[2,3] When grafted onto chlorinated polyethylene (CPE), MMA and St are widely used to make MCS engineering plastic.[4–6] The widely used proceeding and impact property modifier, acrylate core–shell resins (ACRs), can also be obtained from the grating copolymerization of MMA and St onto acrylates.[7,8] Random copolymers of MMA with St [poly(methyl methacrylate-*ran*-styrene); P(MMA-*ran*-St)] are also used as interface modifiers, for they are generally cheaper, easier to synthesize, and offer a larger degree of design flexibility than block and graft copolymers.[9] The molecular weight, free volume, strengthening, and other properties of P(MMA-*ran*-St) have been studied.[10–12] No doubt, the glass-transition temperatures (T_g's) and rheological behavior of the copolymers are also very important when they are used as modifiers or used to synthesize ACRs. In this study, P(MMA-*ran*-St) copolymers were synthesized by emulsion copolymerization with a semibatch method under monomer-starved conditions. The T_g's and rheological behavior of the copolymers were investigated.

EXPERIMENTAL

Materials

MMA, St, the emulsifying agent sodium lauryl sulfate (SLS), the initiator $K_2S_2O_8$, and $Al_2(SO_4)_3$ were all analytically pure and were supplied by Beijing Chemical Regent Corp. (Beijing, China). MMA and St were washed twice with a 5% solution of sodium hydroxide to eliminate any inhibitor and a few times with distilled water and were then dried over anhydrous calcium sulfate. Distilled deionized water was used in the experiments.

Emulsion copolymerization

P(MMA-*ran*-St) copolymers were synthesized by emulsion polymerization. SLS was used as an emulsifier and $K_2S_2O_8$ as initiator. A solution of SLS and partial $K_2S_2O_8$ was charged into a dried, clear, 100-mL four-necked flask equipped with a stirrer, a thermom-

eter, a condenser, and a nitrogen duct; the solution was then stirred for 15 min under nitrogen before the reaction vessel was heated to 85°C. Then, the mixture of MMA and St was added to the system gradually for about 0.5 h. Next, the residual $K_2S_2O_8$ was added in and the polymerization proceeded for another 0.5 h. All of the procedure was performed under a nitrogen atmosphere. The reaction was then stopped and precipitated with a 2% $Al_2(SO_4)_3$ solution. The copolymer was isolated by filtration and was washed a few times with hot water to remove the residual $K_2S_2O_8$ and SLS. The copolymer was then dried in a high-vacuum drying oven until it reached a constant weight. The conversion was measured gravimetrically and was always more than 95%.

The reactivity ratios of MMA and St in the copolymerization were 0.46 and 0.52, respectively. Both were smaller than 1, which meant they were likely to copolymerize with each other. The copolymerization proceeded under monomer-starved conditions, so they were not likely to form homopolymer or alter-copolymer but rather random copolymers.[13]

Copolymer analysis

Samples used were dried in a high-vacuum drying oven at 60°C for 24 h.

The copolymers' molecular weights were measured wtih an SN-01A gel permeation chromatography. The weight-average molecular weight was usually 1.5–3.0 $\times 10^5$.

The composition of the copolymers were measured with a PE-240 elemental analyzer. The results show that the copolymers' compositions were quite close to the monomer feed proportions. This was due to the copolymerization procedure as discussed previously.

The T_g's of the copolymers were measured with a TA-2000 component differential scanning calorimeter (DSC2910) with α-Al_2O_3 as a reference material at a heating rate of 20°C/min under nitrogen. The T_g's were obtained from the point of the half-change of the heat capacity in the differential scanning calorimetry (DSC) traces, which was given by the computer program. For a given sample, the glass-transition temperature determined by differential scanning calorimetry (T_{gDSC}) was the average of several additional scans and were reproducible to ±0.5°C.

The T_g's of the copolymers were also measured using a GDP-3 torsional braid analyzer at a heating rate of 2°C/min. The glass-transition temperature determined by torsional braid analysis (T_{gTBA}) was taken from the maximum of the logarithmic decrement in amplitude per cycle.

A KLY-II flow tester (Length/diameter = 40) was used to test the copolymers' rheological properties at 180°C at different shearing stresses. The shear rate, $\dot{\gamma}_\omega$, was improved for non-Newtonian.
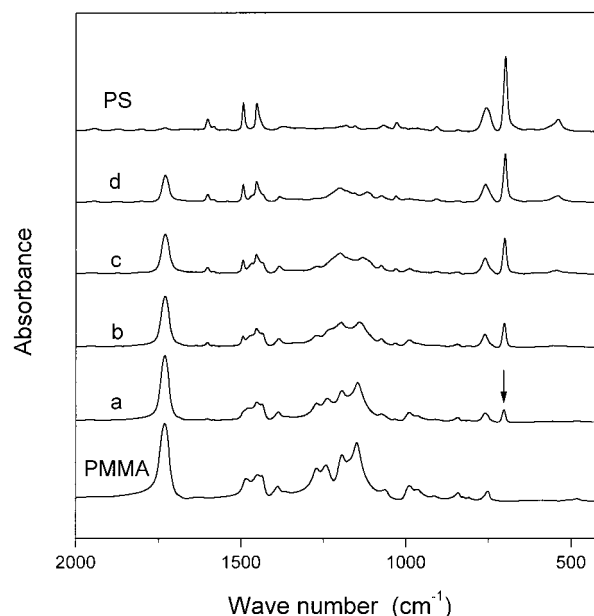

Figure 1 FTIR spectra of semibatch copolymers at St feed weight fractions of (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8.

RESULTS AND DISCUSSION

The copolymers' structure changes were investigated with a Bruker Vector22 FTIR spectrophotometer. The IR spectra of MMA–St copolymers at different monomer feed proportions are shown in Figure 1. With the incorportion of St, the most significant feature was the increase of the single-substituted benzene group absorption (marked by an arrow). The absorption peak of the single-substituted benzene group gradually increased with increasing St feed content. When there was no St fed, the absorption showed no peak because the lack of St segments. This indicated that the St content in the copolymer increased with increasing St feed content.

T_g's

A copolymer's T_g is a very important indication of its thermal properties. Usually, there are four methods for obtaining T_g values from a DSC curve: inflection, half-height, half-width, and half-extrapolated tangents. The T_g's obtained by the four methods from the DSC curves of one copolymer (MMA/St 6/4 w/w) are shown in Figure 2. Obviously, the half-height and half-width methods gave more steady and similar results. The other two ways gave unsteady results with large deviations. So in this article, all of the T_{gDSC} values are take from the half-height midpoint on the DSC curves.

The T_g's of copolymers' determined by DSC and torsional braid analysis (TBA) are shown in Figure 3. The results show that there was large deviation between the determined T_g and the theoretical T_g pre-
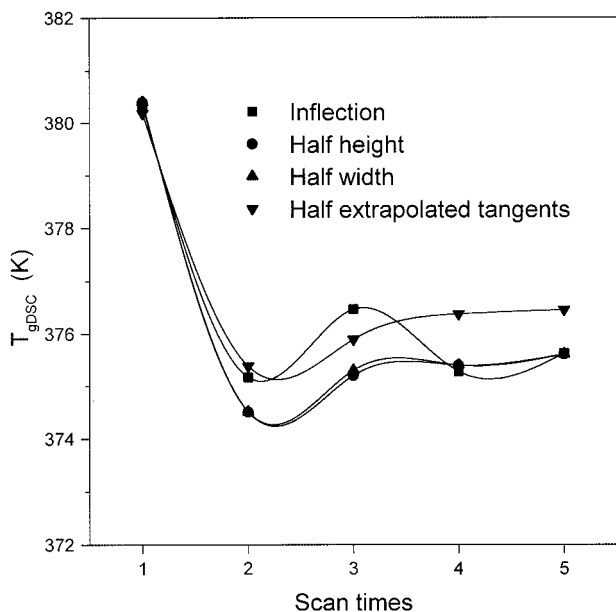
Figure 2 T_g's obtained with different T_g-determination methods at different scan times of the MMA–St copolymers (St feed weight fraction = 0.4).

dicted from the Fox equation, which is based on free volume concepts and is expressed as follows:[14]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \qquad (1)$$

where w_1 and w_2 are weight fractions of monomers 1 and 2, respectively, and T_{g1}, T_{g2}, and T_g are the glass-transition temperatures of homopolymers 1 and 2 and their copolymers, respectively.
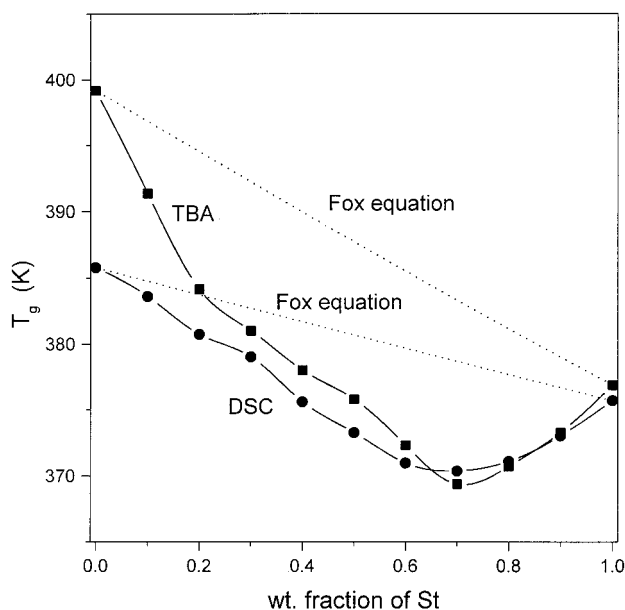

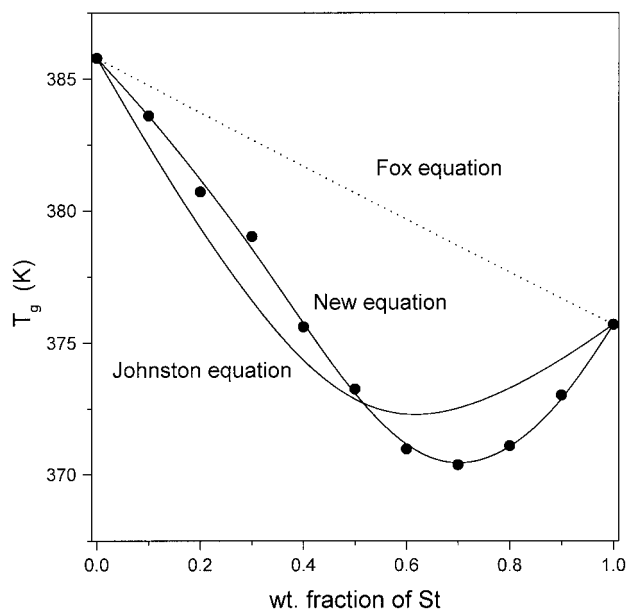**Figure 3** Effect of St feed content on the T_g of the copolymer.

Figure 4 T_g's versus St feed weight fractions predicted by the sequence distribution equation and Fox equation for MMA–St copolymers: St feed weight fractions: (a) 0.1, (b) 0.2, (c) 0.4, and (d) 0.7.

For the case in this study, the T_g versus composition curve may be interpreted by the modified Fox equation proposed by Johnston,[15] which takes the different contributions of the dyads to the T_g of the copolymer into consideration.

Johnston extended the Fox equation as

$$\frac{1}{T_g} = \frac{w_1 P_{11}}{T_{g1}} + \frac{w_2 P_{22}}{T_{g2}} + \frac{w_1 P_{12} + w_2 P_{21}}{T_{g12}}, \qquad (2)$$

where P_{ij} are the probabilities of formation of the respective dyads, depending on the conditions of copolymerization, that is, on the monomer feed composition and the monomer reactivity ratios of the copolymerization reaction:

$$P_{11} = \frac{r_1[1]}{r_1[1] + [2]} \quad P_{12} = \frac{[2]}{r_1[1] + [2]} \quad P_{11} + P_{12} = 1,$$

where r_1 is the reactivity ratio of monomer 1. This equation was applied to the T_g's of the copolymers of acrylonitrile–MMA copolymer and α-methyl St–MMA–acrylonitrile terpolymer, and excellent fitting was obtained.

A multiple-regression analysis computer program was used to solve eq. (2) for a T_{g12} value. The T_g's of the random MMA–St copolymers were then predicted with eq. (2) with a T_{g12} value of 369.1 K. Figure 4 compares the experimental T_g's with values predicted with the dyad distribution–T_g relationship and those predicted with the Fox equation. Although the deviation became smaller than the difference between the

TABLE I
T_g's of Different Dyads and Triads in MMA–St Copolymers

Dyad or Triad	T_g
MMA–MMA	385.8
St–St	375.7
MMA–St	369.1
MMA–MMA*–MMA	385.8
St–St*–St	375.7
MMA–MMA*–St	382.4
St–St*–MMA	362.5
St–MMA*–St	371.9
MMA–St*–MMA	371.9

The data used were obtained by DSC.

experimental T_g's with the ones predicted with the Fox equation, unfortunately the deviation was still very large. This indicates that the T_g's of the random copolymers could not be predicted well with the Johnston equation.

In fact, in a majority of the cases, for a given monomer unit 1, it will contribute different T_g's to the copolymer when it is in different triads such as 11 * 1, 11 * 2, or 21 * 2. Therefore, it will have three different T_g's: T_{g1}, T_{g112}, and T_{g212}. When $T_{g121} = T_{g212}$ (both indicate the alter-copolymers) is assumed, the relationship between the T_g of a random copolymer with its composition and the T_g's of the two homopolymers should be described with the following:[16]

$$\frac{1}{T_g} = \frac{w_1 P_{111}}{T_{g1}} + \frac{w_2 P_{222}}{T_{g2}} + \frac{w_1 P_{212} + w_2 P_{121}}{T_{g121}}$$
$$+ \frac{w_1 P_{112}}{T_{g112}} + \frac{w_2 P_{221}}{T_{g221}}, \quad (3)$$

where P_{111}, P_{112}, and P_{212} represent the probabilities of monomer unit 1 in the different triads 11 * 1, 11 * 2, and 21 * 2 and T_{g1}, T_{g112}, and T_{g212} represent the T_g's of monomer unit 1 at the respective conditions. The probabilities of different linkages (P_{111}, P_{112}, P_{212}) can be calculated from the monomer compositions in the polymerization system and the monomer reactivity ratios:

$$P_{111} = \left(\frac{r_1[1]}{r_1[1] + [2]}\right)^2, \quad P_{112} = 2\frac{r_1[1][2]}{(r_1[1] + [2])^2},$$

$$P_{212} = \left(\frac{[2]}{r_1[1] + [2]}\right)^2$$

$P_{111} + P_{112} + P_{212} = 1$.

If P_{111} and P_{222} tend to be 1, that is, the homopolymerization becomes dominant, eq. (3) will give the Fox equation.

Also, eq. (3) can be solved with a computer program. The obtained T_{g112}, T_{g121} (T_{g212}), and T_{g221} values of MMA–St random copolymer are shown in Table I, and the predicted copolymer T_g's compared with the experimental data are shown in Figure 4. As shown in Figure 4, the new equation fit the experimental data exactly. This indicates that the new equation was very suitable for predicting the random copolymers' T_g's. We also found that T_{g121} (or T_{g212}) value, which represents the T_g of the alter-copolymer of MMA–St, was very close to the T_{g12} obtained from the Johnston equation.

An interesting fact can also be observed in Figure 3: the T_{gTBA} was always higher than the T_{gDSC} for the same sample in most cases. This was due to the different test frequencies of the two different methods for obtaining T_g. As is known, the test frequency of DSC, a static method, is about 10^{-3} Hz, which is much lower than 0.5 Hz, the test frequency of TBA, a dynamic method.[17]

Rheological behavior

The copolymers' apparent viscosities (η_a's) at different shear rates are shown in Figure 5. As shown in the figure, the copolymers' η_a's decreased with increasing shear rate, which demonstrated a pseudoplastic flow behavior in the melt. The flow index (n) and ln K (K is a constant) of the Ostwald–De Waele equation ($\eta_a = K\dot{\gamma}^{n-1}$) of the copolymers were calculated and are shown in Table II.

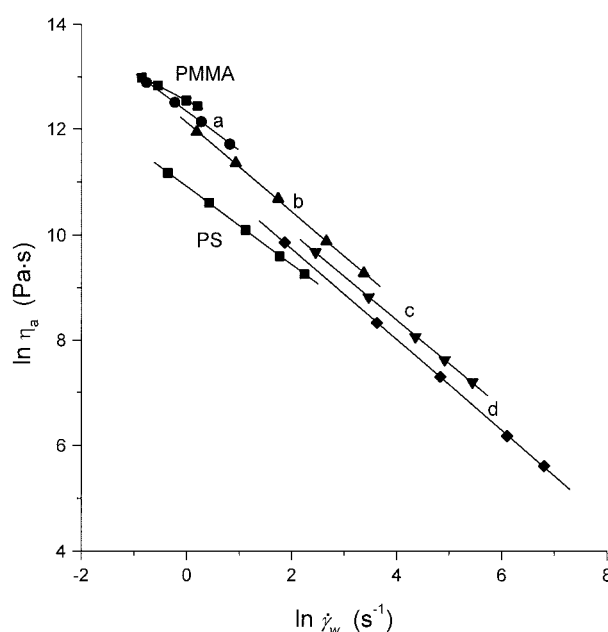Figure 5 and Table II show that the copolymer η_a decreased with increasing St feed content. This was

Figure 5 Copolymers' η's at different St feed contents; (a) 0.1, (b) 0.2, (c) 0.4, (d) 0.7.

TABLE II
Effect of St Feed Content on Copolymer Viscosity

St feed content (wt %)	0	10	20	40	70	100
n	0.478	0.257	0.157	0.169	0.138	0.263
$\ln K$	12.54	12.33	12.11	11.69	11.45	10.90

mainly because of the lower polarities of St segments that minimized the intermolecular forces in the polymers. Also, the copolymers' n decreased largely with increasing St feed content because of the low polar structure of St, which facilitated the rotation of the macromolecule and decreased the chain's stiffness.

Also, the difference value (ΔT_g) between $T_{g\text{TBA}}$ and $T_{g\text{DSC}}$ of the copolymers was not a constant (Fig. 3). ΔT_g decreased with increasing St feed content. A plot of ΔT_g versus n of the copolymers at different St feed contents is given in Figure 6. Obviously, at a higher n, a higher ΔT_g was observed.

In the determination of a polymer's glass transition, which is a relaxation, there is a relationship among observed time (t), relaxation time (τ), and viscosity (η):[17]

$$\frac{t_1}{t_2} = \frac{\tau_1}{\tau_2} = \frac{\eta(T_1)}{\eta(T_2)},$$

where T is the test temperature.

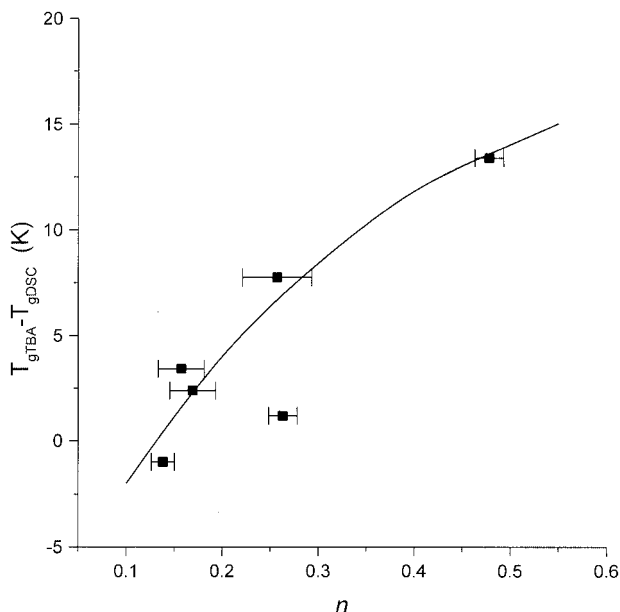Let f be the test frequency because when $t \propto (1/f)$, we have

Figure 6 ΔT_g versus the copolymer's n at different St feed contents.

$$\frac{f_1}{f_2} = \frac{t_2}{t_1} = \frac{\eta(T_2)}{\eta(T_1)}$$

$$\because \eta = K\dot{\gamma}^{n-1}$$

$$\therefore \frac{f_1}{f_2} = \frac{K_2\dot{\gamma}_2^{n_2-1}}{K_1\dot{\gamma}_1^{n_1-1}},$$

where $\dot{\gamma}$ is the shear rate.

Suppose $\dot{\gamma} \propto f$, then

$$K_1 f_1^{n_1} = K_2 f_2^{n_2}.$$

If there is little deviation in the n value of polymer in the test temperature range, that is, $n_1 \approx n_2 = n$, then

$$K_1 f_1^{n} = K_2 f_2^{n}$$

$$n \log\frac{f_1}{f_2} = \log\frac{K_2}{K_1}.$$

Suppose K_1 and K_2 are related to the Williams–Landel–Ferry (WLF) equation, so:

$$n \log\frac{f_1}{f_2} = \log\frac{K_2}{K_1} = \frac{-C_1(T_2 - T_1)}{C_2 + (T_2 - T_1)}$$

$$T_2 - T_1 = \frac{-C_2 n \log\frac{f_1}{f_2}}{n \log\frac{f_1}{f_2} + C_1},$$

where C_1 and C_2 are WLF constants. This formula shows that the determined result of polymer's T_g not only increases with the increasing f but also increases with the increasing polymer's n when the two f's are fixed. From this equation, $T_{g\text{TBA}} - T_{g\text{DSC}}$ should have been zero if polymer's n was zero, although the T_g's were tested at different test frequencies. However, this was not the case; this was because of the different tests and T_g-determination methods.

CONCLUSIONS

A combined static and dynamic method was a more effective way to detect the glass transition and reflect the movement of the molecular chain and stiffness for

the MMA–St copolymers. The difference between $T_{g\mathrm{TBA}}$ and $T_{g\mathrm{DSC}}$ was not only related to f but was also affected by the polymer's n. The higher the n, the higher was the $T_{g\mathrm{TBA}} - T_{g\mathrm{DSC}}$ value.

References

1. Takaki, A.; Yanazaki, K.; Narisawa, I. Polym Eng Sci 2000, 40, 398.
2. Lee, C. F. Polymer 2000, 41, 1337.
3. Young, J. L.; Spontak, R. J.; Desimone, J. M. Polym Prepr 1998, 39, 437.
4. Yang, L. T.; Zhang, C. M.; Gao, J. G. Gaofenzi Cailiao Kexue Yu Gongcheng 1997, 13, 40.
5. Gao, J. G.; Yu, C. X.; An, Q. F.; Yang, L. T.; Liu, G. D. Int J Polym Mater 2001, 48, 447.
6. Li, D.; Guo, W. H.; Tang, S. C.; Xu, Z. D. Huadong Ligong Daxue Xuebao 1999, 25, 584.
7. Huo, D. X.; Liu, D. Z.; Sun, P. Q. Acta Polym Sinica 2000, 55.
8. Kan, C. Y.; Li, H. H.; Sun, J.; Yuan, Q.; Kang, X. Z. Acta Polym Sinica 1999, 199.
9. Pellegrini, N. N.; Sikka, M.; Satija, S. K.; Winey, K. I. Polymer 2000, 41, 2701.
10. Xu, L. Shiyou Huagong Gaodeng Xuexiao Xuebao 1998, 11, 12.
11. Qi, C. Z.; Zhang, S. H.; Wu, Y. J.; Li, H. M.; Wang, G.; Gao, H.; Wang, T. M.; Ma, J. T. J Polym Sci Part B: Polym Phys 1999, 37, 465.
12. Kulasekere, R.; Kaiser, H.; Ankner, J. F.; et al. Macromolecules 1996, 29, 5493.
13. Liu, G. D.; Li, X. C.; Zhang, L. C.; et al. J Appl Polym Sci 2002, 83, 417.
14. Fox, T. G. Bull Am Phys Soc 1956, 1, 123.
15. Johnston, N. W. Appl Polym Symp 1974, 25, 19.
16. Liu, G. D.; Cui, W. Z.; Yang, L. T.; et al. 2000 National Conference on Molecular Characterization of Polymers, Nanjing, People's Republic of China, 2000; p 58.
17. He, M. J.; Chen, W. X.; Dong, X. X. Polymeric Physics; Fudan University Press: Shanghai, China, 1990.