Polym. Bull. (2011) 67:1311–1323
DOI 10.1007/s00289-011-0528-6

ORIGINAL PAPER

Glass transition temperatures of copolymers from methyl methacrylate, styrene, and acrylonitrile: binary copolymers

**Liubin Fan · Dongmei Zhao · Ce Bian · Yanli Wang ·
Guodong Liu**

Received: 18 November 2010 / Revised: 7 May 2011 / Accepted: 30 May 2011 /

Abstract By using a new theoretical glass transition temperature (T_g)–composition equation, T_g's of statistic binary copolymers obtained from MMA, St and AN were investigated in this article. The copolymers were prepared by bulk copolymerization using azo-bis-isobutyronitrile (AIBN) as initiator. The compositions and T_g's were determined by NMR and DSC, respectively. The monomer reactivity ratios were obtained by nonlinear fitting with Mayo–Lewis equation. Excellent fitting results were obtained when relations of T_g's of MMA–St, MMA–AN, and St–AN copolymers with their compositions were investigated by using a new equation which assumed additivity of bond stiff energy (Liu et al. J Phys Chem B 112:93–99, 2008). This equation contains mole fractions of triads and T_g's of corresponding periodic copolymers. Compared with the widely used Johnston equation and Barton equation, the new equation showed its superiority. Meanwhile, T_g's of the assumed periodic copolymers that have not been acquired were tentatively predicted which may provide useful information.

Keywords Composition · Copolymer · Glass transition temperature · Monomers · Sequence

Introduction

Methyl methacrylate (MMA), styrene (St), and acrylonitrile (AN) are the most widely used monomers in the polymer industry not only in homopolymerization, but also in copolymerization. The binary copolymers among the three monomers are widely used in many applications, such as thermoplastics, optical materials,

L. Fan · D. Zhao · C. Bian · Y. Wang · G. Liu (✉)
Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China
e-mail: liugd@hebut.edu.cn

modifying agents and so on, due to their excellent chemical, thermal, mechanical, and optical properties [1–7]. The copolymerization characters determinate the structure of the formed copolymer, which in turn influences its properties and applications. The binary copolymerization behaviors among the three monomers under different conditions have been studied heretofore [8–16]. As an important intrinsic parameter, the glass transition temperature (T_g), greatly affects the properties and further applications of the copolymers. T_g–composition relations of the corresponding binary copolymers have been studied by several researchers, but usually only qualitative relationships were discussed [3, 17–23]. Although the quantitative relationships were also attempted to established, but large deviations from experimental data were found frequently because of the lacking of suitable T_g–composition equation [24–26].

As well known, copolymer T_g is mainly determined by T_g's of corresponding homopolymers, copolymer composition (F_i), sequence, etc., and so on. Large deviations from the experimental T_g's always appeared when T_g's were predicted by using the linear relations of Gordon–Taylor and Gibbs–DiMarzio (G–D) equations which only considered composition contribution [27, 28]:

$$T_g = \frac{w_A T_{gA} + K w_B T_{gB}}{w_A + K w_B} \tag{1}$$

$$T_g = n_A T_{gA} + n_B T_{gB} \tag{2}$$

where T_g is the glass transition temperature of the copolymer; w_i and n_i are the weight and molar fractions of the component i in the copolymer; T_{gi} is the glass transition temperature of the homopolymer; K is a parameter specified by the model. Gordon–Taylor equation was based on the assumption of the volume additivity of repeating units in copolymer, while G–D equation was on the additivity of the chain stiffness energy. In virtue of the assumption of the Simha–Boyer rule (αT_g = constant) [29] that the parameter K in Eq. 1 is equal to T_{gA}/T_{gB}, Eq. 1 can be reformulated as the well known Fox relation [30]:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \tag{3}$$

To interpret the deviations of experimental results from the linear equations, sequence distribution effect should be taken into account. Considering the effect of the diad sequence, Barton equation and Johnston equation are mostly used [31, 32]:

$$T_g = n_{AA} T_{gAA} + n_{BB} T_{gBB} + n_{AB} T_{gAB} + n_{BA} T_{gBA} \tag{4}$$

$$\frac{1}{T_g} = \frac{w_A P_{AA}}{T_{gA}} + \frac{w_B P_{BB}}{T_{gB}} + \frac{w_A P_{AB} + w_B P_{BA}}{T_{gAB}} \tag{5}$$

where T_{gij} is the additive temperature associated with diad sequence ij, n_{ij} and P_{ij} are the mole fraction and the probability of forming the respective diad ij from the end group of unit i, respectively. However, discrepancies between experimental data and theoretical results still exist when these equations are adapted to describe the asymmetrical and even S-shaped T_g versus composition relations. When triad sequence effect was taken into consideration, the fitting results of most copolymer T_g versus composition relations were obviously improved [33–35]. Ham extended Barton equation as:

$$\begin{aligned} T_g = {} & n_{AAA}T_{gAAA} + n_{BBB}T_{gBBB} + n_{AAB}T_{gAAB} + n_{BAA}T_{gBAA} \\ & + n_{ABB}T_{gABB} + n_{BBA}T_{gBBA} + n_{ABA}T_{gABA} + n_{BAB}T_{gBAB} \end{aligned} \tag{6}$$

where T_{gijk} and n_{ijk} are the additive temperature and mole fraction of triad sequence *ijk*. However, there are six unknown parameters in this equation. To reduce the number of intractable parameters, Ham arbitrarily assumed that T_{gABB}, T_{gBBA}, T_{gABA} and T_{gBAB} to be equal in effect.

Empirical equations were also found to be convenient to describe copolymer T_g–compostion relations. Schneider extended the Gordon–Taylor equation as [36]:

$$\frac{T_g - T_{gA}}{T_{gB} - T_{gA}} = (1 + K_1)w_{Bc} - (K_1 + K_2)w_{Bc}^2 + K_2 w_{Bc}^3 \tag{7}$$

The notations w_{Bc} is:

$$w_{Bc} = 1 - w_{Ac} = \frac{K w_B}{w_A + K w_B} \tag{8}$$

K_1 and K_2 are fitting parameters. Good fitting results were obtained, but Schneider pointed out that no relationships between the fitting parameters and physical characteristics of the copolymer components were available. Recently, Brostow proposed an equation for the dependence of T_g on composition in blends as well as in copolymers as [37]:

$$\begin{aligned} T_g = {} & w_A T_{gA} + w_B T_{gB} + w_A w_B [a_0 + a_1(w_A - w_B) + a_2(w_A - w_B)^2 \\ & + a_3(w_A - w_B)^3] \end{aligned} \tag{9}$$

where a_0, a_1, a_2, and a_3 are fitting parameters. For the copolymer or blend with higher complexity, the new equation shown better fitting results with the experimental data compared with Fox, Gordon–Taylor, and Kwei equations. a_0, a_1, a_2 and a_3 are just fitting parameters without explicit physical meaning.

In a previous article [38], we proposed a copolymer T_g–composition equation by assuming additivity of bond stiff energy. When the effect of triad sequence distribution (accurately C_3 substituent effect) on copolymer T_g was considered, the equation was described as:

$$\begin{aligned} T_g = {} & n_{AAA}T_{gA} + n_{BBB}T_{gB} + 2(n_{ABA} - n_{AAB})T_{g[AB]} \\ & + 3n_{AAB}T_{g[AAB]} + 3n_{BBA}T_{g[BBA]} \end{aligned} \tag{10}$$

where n_{ijk} is the mole fraction of the triad *ijk*, $T_{g[AB]}$, $T_{g[AAB]}$ and $T_{g[BBA]}$ are T_g's of periodic copolymers poly[AB], poly[AAB] and poly[BBA] (normally poly[AB] is called alternating copolymer), respectively. The mole fractions of triads can be calculated from the reactivity ratios and feed compositions of the monomers and those T_g contributions of periodic copolymers can be determined experimentally or solved out by data regression. Excellent fitting results have been obtained when it was applied to copolymers of ethylene with methyl methacrylate (E-MMA), ethylene with vinyl acetate (E-VAc), methyl methacrylate with ethyl methacrylate (MMA-EMA) and methyl methacrylate with *n*-butyl methacrylate (MMA-*n*-BMA) [38, 39]. Simultaneously, the equation can also provide the effect of substitution on bond rotation flexibility [39] as well as the T_g's of periodic copolymers that have not been synthesized yet.

In this article, Eq. 10 is applied to investigate the T_g versus composition relationships of MMA–St, MMA–AN, and St–AN statistic binary copolymers. From this article, two objects are to be carried out, one is the certification of the universal application of the equation, the other is the acquisition of quantitative results for MMA–St, MMA–AN, and St–AN binary copolymers.

Experimental

Materials

MMA, St, AN, the initiator azo-bis-isobutyronitrile (AIBN), the precipitating agents methanol, and the solvent *N*,*N*-dimethylfomamide (DMF) were all analytically pure and supplied by Tianjin Chemical Reagent Co. (Tianjin, China). MMA and St were washed thrice with 5 wt% sodium hydroxide to remove inhibitor followed by distilled water until neutral and dried for 24 h over anhydrous sodium sulfate and anhydrous calcium chloride, respectively. Then they were distilled under reduced pressure. AN was firstly distilled under normal pressure, then followed with fractional distillation under normal pressure. AIBN was recrystallized twice from methanol, dried in a vacuum oven at room temperature. Then all the products were stored in the refrigerator before use.

Copolymerization

Free radical polymerization of MMA with St, MMA with AN, and St with AN were performed in the presence of AIBN as radical initiator at 60 °C in a water bath. The initial mixtures of monomers and AIBN were added entirely into a 100 mL four-necked flask which was equipped with stirrer, thermometer, condenser, and a nitrogen gas introducing tube. The initial mixtures consisted necessary mole fractions of corresponding monomers and approximately 2.5×10^{-2} mol L^{-1} AIBN. The polymerizations were stopped at low conversion (less than 5 wt%) to ensure the compositional homogeneity of prepared copolymers by cooling the system to room temperature and dripping the products slowly into a beaker filled with tenfold volume of cold anhydrous methanol. The post-precipitation mixtures were left in the anhydrous methanol overnight by stirring it and then filtered through a sintered funnel. The products were further purified by a repeated dissolution/precipitation procedure, using DMF and anhydrous methanol as a solvent/non-solvent pair. The powdered copolymer samples were finally dried to constant mass under vacuum at 50 °C for a week before the characterization and measurement.

Measurements

The compositions of copolymers were determined experimentally by quantitative ^{1}H-NMR spectra which were recorded with a Bruker Avance-400 NMR spectrometer operated at 400 MHz and 25 °C using deuteronchloroform ($CDCl_3$) or (dimethyl sulfoxide)-d_6 (DMSO-d_6) as solvent. 16 scans were accumulated for each sample. The pulse delay is 6 s and the concentration was about 5% (w/v, g mL^{-1}).

Glass transition temperatures were measured by using a Perkin-Elmer Diamond differential scanning calorimeter (DSC). The sample weight was about 10 mg. All the samples were scanned several times in the temperature range from −20 °C to 50–60 °C after the glass transition. After each heating scan the sample was annealed for 10 min to erase the thermal history memory. The DSC traces were recorded in the heating scans except the first one. T_g was estimated from the point of the half-change of the heat capacity. For a given sample, the T_g was the average of all the scans and reproducible to be ±0.5 °C.

Results and discussion

Copolymer of methyl methacrylate with styrene

First of all, reactivity ratios (r_i) must be solved out because that the they are necessary for the calculation of triad concentration in Eq. 10. ^{1}H-NMR spectra of a MMA–St copolymer is shown in Fig. 1 as an example to illuminate the attributions of the diverse peaks. The compositions of MMA–St copolymers were calculated from the ratio of the peak area of hydrogen in phenyl to that of hydrogen in methyl.

Fig. 1 ^{1}H-NMR spectra (400 MHz) of MMA–St copolymer ($F_{St} = 0.104$) in $CDCl_3$ at 25 °C

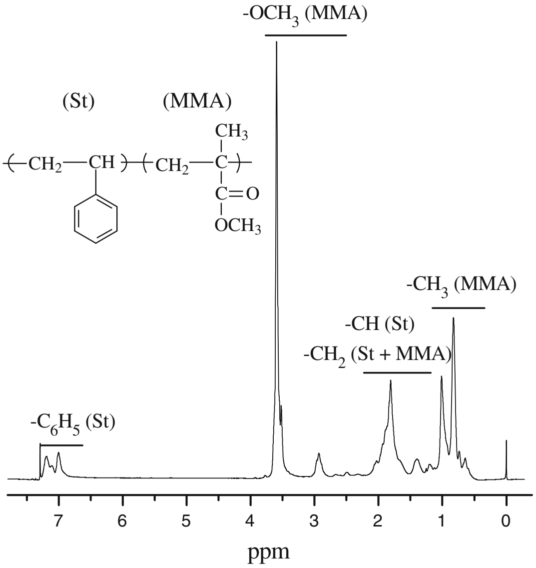

Table 1 Average monomer feed mole fractions and copolymer compositions in MMA/St copolymerization

f_{St}	F_{St}	Conversion (wt%)
0	0	4.48
0.053	0.104	3.51
0.121	0.205	1.53
0.217	0.295	2.63
0.337	0.393	3.55
0.484	0.501	2.99
0.630	0.597	2.76
0.760	0.705	2.89
0.868	0.802	2.50
0.939	0.895	3.03
1	1	2.84

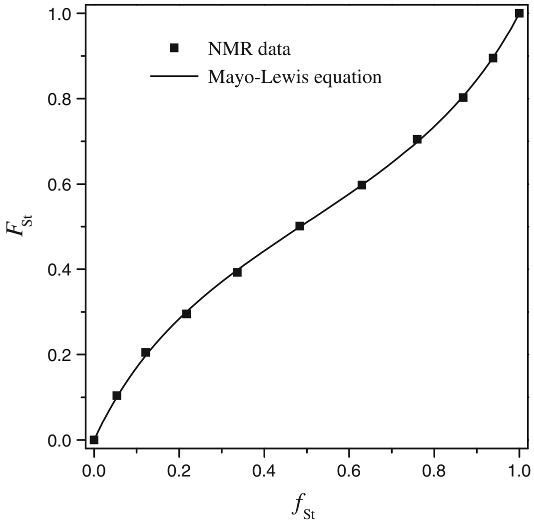

Fig. 2 The mole fractions of St in MMA–St copolymers versus average monomer feed compositions

Table 1 tabulates the monomer feed mole fractions (f_i), which are the average of the initial and final ones in the copolymerization, and the corresponding copolymer compositions. A nonlinear least square method (NLLS) was utilized to fit the experimental data with Mayo–Lewis equation [40, 41]. The experimental data as well as the theoretical results are shown in Fig. 2.

As shown in Fig. 2, the agreement of theoretical results with experimental data is excellent, which indicates that the obtained reactivity ratios are reliable, which are summarized in Table 2. The results of $r_{MMA} = 0.463$ and $r_{St} = 0.523$ are approximately equal to that reported by Brar [42], O'Driscoll [43], and Hirooka [44] for bulk copolymerization and Lewis [40] for solution copolymerization.

The T_g's determined by DSC versus St mole fractions for MMA–St copolymers are shown in Fig. 3. It illuminates that the copolymer T_g decreases sharply with the increasing content of St in and shows a minimum, which is similar to the literatures

Table 2 Reactivity ratios among MMA, St and AN

M_1	M_2	Fitting results		Literature data		Reference
		r_1	r_2	r_1	r_2	
MMA	St	0.463 ± 0.010	0.523 ± 0.011	0.47	0.52	42
MMA	AN	1.364 ± 0.029	0.165 ± 0.003	1.45	0.17	47
St	AN	0.491 ± 0.012	0.056 ± 0.001	0.40	0.04	54

[32, 35, 36]. It is also known that the glass transition temperature changes with molecular weight of the polymer but remains relatively constant when the molecular weight is large enough. The number-average molar masses of the obtained MMA–St copolymers were in the range of 4.0–7.0 × 10^4 determined by GPC. Using $K = 1.9 \times 10^5$ for the average of PMMA and PS[45, 46], the variety of T_g will be smaller than 2.0 K, which could be ignored comparing with the range of 26.1 K in the MMA–St series. Also the regularity of the T_g change indicates that the deviation of the T_g caused by molecular weight change has little influence on the T_g–composition relation.

Firstly, Barton equation (Eq. 4) and Johnston equation (Eq. 5) were applied to explain the experimental data. Diad compositions in these equations were calculated from monomer feed compositions and reactivity ratios. The fitting results are also plotted in Fig. 3. The results show that there are large system deviations instead of random ones between the predicted and the experimental T_g's. This indicates that the T_g–composition relation of the MMA–St statistical copolymers can't be predicted perfectly with the diad equations.

Meanwhile, Eq. 10 was also adapted to interpret the experimental data. The mole fractions of different triads were calculated by using the feed compositions and reactivity ratios, as described before [38]. The three parameters ($T_{g[AB]}$, $T_{g[AAB]}$, and

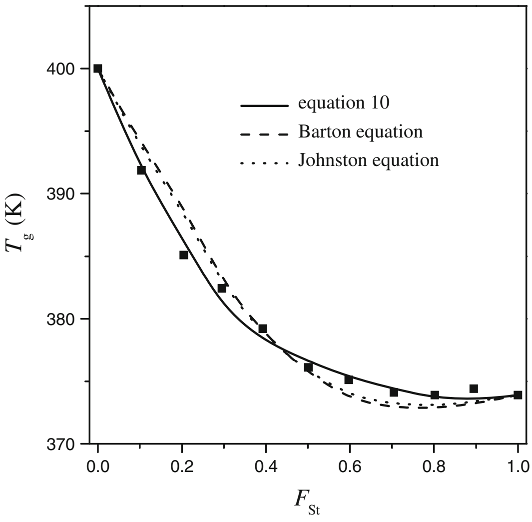

Fig. 3 Experimental and predicted T_g's of MMA–St copolymers. *Solid squares* denote statistical copolymers and homopolymers. *Solid line* Equation 10, *dash line* Barton equation (Eq. 4), *Dot line* Johnston equation (Eq. 5)

$T_{g[BBA]}$) were regressed simultaneously by nonlinear fitting the experimental data with Eq. 10. As shown in Fig. 3, the fitting result is perfectly well and the experimental data distribute in both sides of the theoretical T_g–composition curve randomly. That is to say that Eq. 10 is more suitable for predicting the T_g–composition relation of MMA–St statistical copolymers comparing with Johnston and Barton equations. Besides, Eq. 10 also gives 384.8, 372.1, and 372.2 K for $T_{g[MS]}$, $T_{g[MMS]}$, and $T_{g[SSM]}$, respectively. Although large deviation can be found for the predicted $T_{g[MS]}$ from 364.2 K reported by Hirooka. While the difference between $T_{g[MS]}$ with T_{gPMMA}, 15.2 K, is close to that of 11.0 K obtained by Hirooka [44].

Copolymer of methyl methacrylate with acrylonitrile

The compositions of MMA–AN copolymers obtained from ^{1}H-NMR spectra by calculating the ratio of peak area of hydrogen in methine to that of hydrogen in methoxy are tabulated in Table 3. The average monomer feed mole fractions are also enumerated in the same table. The corresponding reactivity ratios of MMA/AN copolymerization were acquired by fitting the experimental data with the same method mentioned above and also listed in Table 2. The results of $r_{MMA} = 1.364$ and $r_{AN} = 0.165$ are close to that of $r_{MMA} = 1.45$ and $r_{AN} = 0.17$ obtained by Brar [47] and the results obtained by other researchers [6, 48–51].

Figure 4 shows the plots of experimental T_g's versus AN mole fractions for MMA–AN copolymers. It is found that the incorporation of both AN to MMA or MMA to AN causes decrease of T_g and minimum T_g appears in the middle composition. This result is same to that reported by Johnston [52] and other researchers [34, 36]. Barton equation, Johnston equation, and Eq. 10 were adopted to fit the experimental data and the fitting curves with these equations are also plotted in Fig. 4. During the course of the data processing, the diad compositions as well as the triad compositions were calculated from the average monomer feed mole fractions and reactivity ratios [38].

Table 3 Average monomer feed mole fractions and copolymer compositions in MMA/AN copolymerization

f_{AN}	F_{AN}	Conversion (wt.%)
0	0	4.48
0.137	0.088	2.57
0.287	0.198	3.76
0.447	0.302	3.74
0.604	0.394	3.97
0.750	0.509	2.40
0.853	0.611	2.49
0.911	0.699	3.19
0.952	0.800	2.80
0.975	0.884	1.73
1	1	2.56

Fig. 4 Experimental and predicted T_g's of MMA–AN copolymers. *Solid squares* statistical copolymers and homopolymers, *solid line* Eq. 10, *dash line* Barton equation (Eq. 4), *dot line* Johnston equation (Eq. 5)

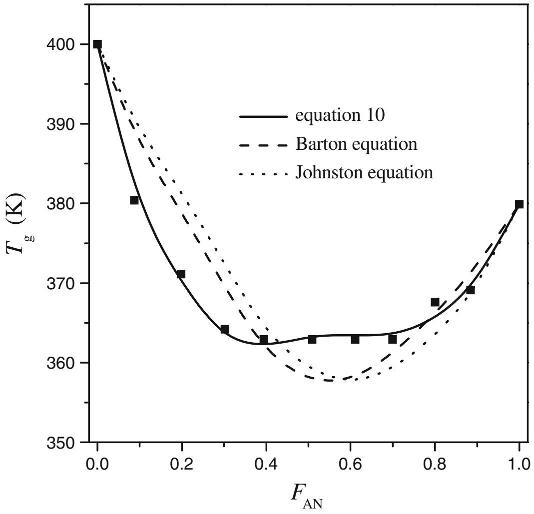

Figure 4 demonstrates that not only large but also system deviations appear between the theoretical T_g's predicted by Barton and Johnston equations with the experimental data for MMA–AN copolymers. On the contrary, outstanding consistency as well as random deviation was observed when Eq. 10 was used instead. This indicates that when the T_g–composition relation of MMA–AN copolymers is studied, Eq. 10 also shows its superiority over Johnston and Barton equations. Apart from these, the data fitting also affords 419.6, 331.8, and 345.4 K for $T_{g[MA]}$, $T_{g[MMA]}$, and $T_{g[AAM]}$, respectively. It seems that the result of $T_{g[MA]}$ is comparatively high comparing with that of 352.2 K predicted by Johnston [53], but the deviations will increase greatly if the $T_{g[MA]}$ deviates little from 419.6 K. The phenomena also appeared in the fitting of T_g's of MMA–St–AN terpolymers which will be described in a later paper. This conforms the reliability of the fitting result although the validation of the T_g of poly[MMA–AN] remains unknown because that the alternative copolymer has not been acquired up to now.

Copolymer of styrene with acrylonitrile

The compositions of St–AN copolymers were also obtained from the ^{1}H-NMR spectra by reckoning the ratio of peak area of hydrogen in phenyl to that of hydrogen in methine. The obtained average monomer feed mole fractions and copolymer compositions are tabulated in Table 4. The NLLS fitting gives the results of $r_{St} = 0.491$ and $r_{AN} = 0.056$ (as shown in Table 2) which are highly close to that of $r_{St} = 0.4$ and $r_{AN} = 0.04$ acquired by Doak [54] and the results reported by Schmidt-Naake [55], Arsac [56], and Brar [42].

Figure 5 shows the relation of T_g's determined by DSC with copolymer compositions for St–AN copolymers. Maximum T_g appears in the middle composition as reported by other researchers [3, 44, 52]. This may attribute to the increase of the chain stiffness of the macromolecule. The experimental data

Table 4 Average monomer feed mole fractions and copolymer compositions in St/AN copolymerization

f_{AN}	F_{AN}	Conversion (wt%)
0	0	2.84
0.048	0.091	4.01
0.118	0.181	4.55
0.228	0.273	2.92
0.424	0.379	2.93
0.756	0.504	2.30
0.926	0.630	2.24
0.967	0.714	2.61
0.983	0.807	1.2
0.993	0.897	0.87
1	1	2.56

were also dealt with Barton equation, Johnston equation, and Eq. 10, respectively. The method used in fitting was same as used in MMA–St copolymers.

Similar to the results shown above, large deviations of theoretical values predicted by both Johnston and Barton equations from experimental data for St–AN copolymers were observed. In contrast, excellent agreement of theoretical values with experimental data was obtained when Eq. 10 was employed. Meanwhile, the fitting result of Eq. 10 shows a random deviation, instead of system deviations of Barton equation and Johnston equation, between the theoretical and experimental data, as shown in Fig. 5. This indicates that Eq. 10 is more appropriate to interpret the relation of T_g's versus compositions of St–AN statistical copolymers compared with Barton and Johnston equations. The excellent fitting results shows the dependability and applicability of Eq. 10. In addition, T_g values of the assumed periodic copolymers are provided as follow: $T_{g[SA]} = 382.4$ K, $T_{g[SSA]} = 384.8$ K

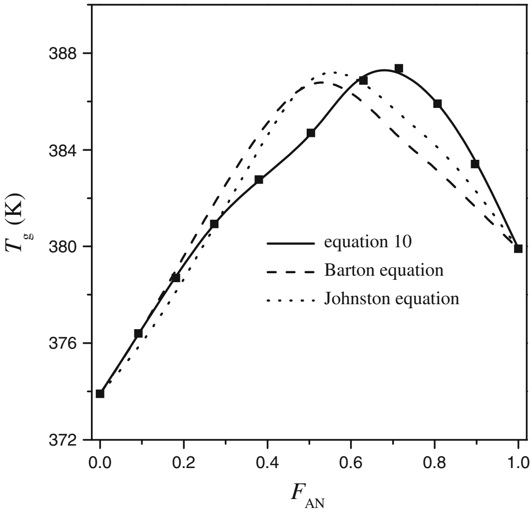

Fig. 5 Experimental and predicted T_g's of St–AN copolymers. Solid squares denote statistical copolymers and homopolymers. *Solid line* Eq. 10, *dash line* Barton equation (Eq. 4), *dot line* Johnston equation (Eq. 5)

and $T_{g[AAS]} = 393.0$ K. It is significant to note that the fitting result of 382.4 K for $T_{g[SA]}$ is highly close to the experimental result of 384.7 K obtained by Johnston [52]. This illuminates that the obtained periodic copolymer T_g's from the Eq. 10 are rather trustworthy.

Conclusions

For the bulk copolymerization of MMA/St, MMA/AN and St/AN systems, the reactivity ratios were obtained as $r_{MMA} = 0.463$ and $r_{St} = 0.523$ for MMA with St; $r_{MMA} = 1.364$ and $r_{AN} = 0.165$ for MMA with AN; $r_{St} = 0.491$ and $r_{AN} = 0.056$ for St with AN. When the T_g–composition relationships of the three series binary copolymers were investigated, both Barton equation and Johnston equation showed large deviations. Whereas Eq. 10 which assuming the additivity of bond stiff energy gave outstanding consistencies for all the three series of copolymers. Also the predicted values showed random deviations, instead of system deviations, from the experimental data when Eq. 10 was employed. Therefore, Eq. 10 is feasible and veracious for the T_g–composition relation investigation of MMA–St, MMA–AN and St–AN binary copolymers. T_g's of periodic copolymers among MMA, St, and AN were also rationally evaluated as: $T_{g[MS]} = 384.8$ K, $T_{g[MMS]} = 372.1$ K, $T_{g[SSM]} = 372.2$ K, $T_{g[MA]} = 419.6$ K, $T_{g[MMA]} = 331.8$ K, $T_{g[AAM]} = 345.4$ K, $T_{g[SA]} = 382.4$ K, $T_{g[SSA]} = 384.8$ K and $T_{g[AAS]} = 393.0$ K.

Acknowledgments This work is supported by the National Natural Science Foundation of China (20804013) and the Natural Science Foundation of Hebei Province (B2007000019).

References

1. Andreis M, Rakvin B, Veksli Z, Rogosic M, Mencer HJ (1999) An electron spin resonance study of molecular dynamics and heterogeneity in the styrene-acrylonitrile copolymers. Polymer 40:1955–1960
2. Saby-Dubreuil AC, Guerrier B, Allain C, Johannsmann D (2000) Glass transition induced by solvent desorption for statistical MMA/nBMA copolymers-influence of copolymer composition. Polymer 42:1383–1391
3. Li D, Gao J, An Q, Liu G, Yang L (2001) Thermal analysis of poly(AN-co-St) and poly(AN-St-MMA). J Therm Anal Calorim 63:69–74
4. Shi Y, Wu Y, Hao J, Li G (2005) Kinetics of microemulsion copolymerization of styrene and acrylonitrile in the presence of cosurfactant. Colloids Surf A 262:191–197
5. Khesareh R, Mcmanus NT, Penlidis A (2006) High temperature bulk copolymerization of methyl methacrylate and acrylonitrile: II. Full conversion range experiments. J Macromol Sci A 43:23–37
6. Khesareh R, Mcmanus NT, Penlidis A (2006) High temperature bulk copolymerization of methyl methacrylate and acrylonitrile. I. Reactivity ratio estimation. J Appl Polym Sci 100:843–851
7. Hameed N, Sreekumar PA, Francis B, Yang W, Thomas S (2007) Morphology, dynamic mechanical and thermal studies on poly(styrene-co-acrylonitrile) modified epoxy resin/glass fibre composites. Compos Part A 38:2422–2432
8. Aerdts AM, de Haan JW, German AL (1991) Characterization of intramolecular microstructure of styrene-methyl methacrylate copolymers: new ^{1}H NMR assignments supported by 2D-NOESY NMR. Macromolecules 24:1473–1479
9. Aerdts AM, de Haan JW, German AL (1993) Proton and carbon NMR spectra of alternating and statistical styrene-methyl methacrylate copolymers revisited. Macromolecules 26:1965–1971

10. Hatada K, Kitayama T, Terawaki Y, Sato H, Chujo R, Tanaka Y, Kitamaru R, Ando I, Hikichi K, Horii F (1995) NMR measurement of identical polymer samples by round robin method. IV. Analysis of composition and monomer sequence distribution in poly(methyl methacrylate-co-acrylonitrile) leading to determinations of monomer reactivity ratios. Polym J 27:1104–1112
11. Lee KC, Gan LM, Chew CH (1995) Copolymerization of styrene and acrylonitrile in ternary oil-in-water microemulsions. Polymer 36:3719–3725
12. Sanghvi PG, Patel AC, Gopalkrishman KS, Devi S (2000) Reactivity ratios and sequence distribution of styrene-acrylonitrile copolymers synthesized in microemulsion medium. Eur Polym J 36:2275–2283
13. Reddy GVR, Babu YPP, Reddy NSR (2002) Microemulsion and conventional emulsion copolymerizations of methyl methacrylate with acrylonitrile. J Appl Polym Sci 8:1503–1510
14. Miura Y, Nakamura N, Taniguchi I, Ichikawa A (2003) Radical polymerization of butyl acrylate and random copolymerization of styrene and butyl acrylate and styrene and methyl methacrylate mediated by monospiro- and dispiropiperidinyl-*N*-oxyl radicals. Polymer 44:3461–3467
15. Brar AS, Pradhan DR (2003) Investigation of microstructure of the acrylonitrile-styrene-glycidyl methacrylate terpolymers by 1D and 2D NMR spectroscopy. J Appl Polym Sci 89:1779–1790
16. Stretz HA, Paul DR (2006) Properties and morphology of nanocomposites based on styrenic polymers. Part I: styrene-acrylonitrile copolymers. Polymer 47:8123–8136
17. Beevers RB, White EFT (1960) Physical properties of vinyl polymers. Part 2. The glass transition temperature of block and random acrylonitrile + methyl methacrylate copolymers. Trans Faraday Soc 56:1529–1534
18. Beevers RB (1962) Physical properties of vinyl polymers. Part 4. Glass-transition temperature of methyl methacrylate + styrene copolymers. Trans Faraday Soc 58:1465–1472
19. Beevers RB, White EFT (1963) A note on the glass-transition temperatures of acrylonitrile + styrene copolymers. J Polym Sci Part B 1:171–176
20. Parker MS, Krasnansky VJ, Achhammer BG (1964) Effects of composition and irradiation on the glass transition temperature of methyl methacrylate-styrene copolymers. J Appl Polym Sci 8:1825–1838
21. Ahuja SK (1979) Structure and rheology of styrene methyl methacrylate copolymers. Rheol Acta 18:374–381
22. Penzel E, Rieger J, Schneider HA (1997) The glass transition temperature of random copolymers: 1. Experimental data and the Gordon-Taylor equation. Polymer 38:325–337
23. Tusi OKC, Russell TP, Hawker CJ (2001) Effect of interfacial interactions on the glass transition of polymer thin films. Macromolecules 34:5535–5539
24. Wood LA (1958) Glass transition temperatures of copolymers. J Polym Sci 28:319–330
25. Illers KH (1966) Glasige Erstarrung und Relaxationsverhalten von amorphen Copolymeren im festen Zustand. Ber Bunsenges Phys Chem 70:353–375
26. Fevotte G, Mckenna TF, Santos AM (1998) Modelling of the glass transition temperature of free radical copolymers: An approach for control purposes. Chem Eng Sci 53:2241–2256
27. Gordon M, Taylor JS (1952) Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. J Appl Chem 2:493–500
28. Dimarzio EA, Gibbs JH (1959) Glass temperature of copolymers. J Polym Sci 40:121–131
29. Simha R, Boyer RF (1962) On a general relation involving the glass temperature and coefficients of expansion of polymers. J Chem Phys 37:1003–1007
30. Fox TG (1956) Influence of diluent and of copolymer composition on the glass temperature of a polymer system. Bull Am Phys Soc 1:123–135
31. Barton JM (1970) Relation of glass transition temperature to molecular structure of addition copolymers. J Polym Sci Part C 30:573–597
32. Johnston NW (1973) Sequence distribution-glass transition effects. III. α-methylstyrene-acrylonitrile copolymers. Macromolecules 6:453–456
33. Uematsu I, Honda K (1965) Rep Prog Polym Phys Jpn 8:111–112
34. Ham GE (1975) Role of triad concentration in glass transition temperatures of copolymers. J Macromol Sci Part A A9:461–467
35. Liu GD, Zhang LC, Yao YM, Yang LT, Gao JG (2003) Glass-transition temperatures and rheological behavior of methyl methacrylate-styrene random copolymers. J Appl Polym Sci 88:2891–2896
36. Schneider HA, Rieger J, Penzel E (1997) The glass transition temperature of random copolymers: 2. Extension of the Gordon-Taylor equation for asymmetric Tg vs composition curves. Polymer 38:1323–1337

37. Brostow W, Chiu R, Kogeras IM, Vassilikou-Dova A (2008) Prediction of glass transition temperatures: binary blends and copolymers. Mater Lett 62:3152–3155
38. Liu GD, Meng ZY, Wang W, Zhou YL, Zhang LC (2008) Sequence distribution effects on glass transition temperatures of copolymers: An extended Gibbs-DiMarzio equation in view of bond rotation flexibility. J Phys Chem B 112:93–99
39. Liu GD, Zhang LY, Wang YL, Zhao P (2009) Studies on binary copolymerization and glass transition temperatures of methyl methacrylate with ethyl methacrylate and *n*-butyl methacrylate. J Appl Polym Sci 114:3939–3944
40. Lewis FM, Walling C, Cummings W (1948) Copolymerization. IV. Effects of temperature and solvents on monomer reactivity ratios. J Am Chem Soc 70:1519–1523
41. Joshi RM, Kapur SL (1954) A modified method of deriving the reactivity constants r1 and r2 in copolymerization. J Polym Sci 14:508–510
42. Brar AS, Hekmatyar SK (1999) Microstructure determination of the acrylonitrile-styrene-methyl methacrylate terpolymers by NMR spectroscopy. J Appl Polym Sci 74:3026–3032
43. O'Driscoll KF, Kale LT (1984) Applicability of the Mayo-Lewis equation to high-conversion copolymerization of styrene and methylmethacrylate. J Polym Sci 22:2777–2788
44. Hirooka M, Kato T (1974) Glass transition temperature and sequential structure of equimolar copolymers. J Polym Sci Part B 12:31–37
45. Beevers RB, White EFT (1960) Physical properties of vinyl polymers, Part 1. Dependence of the glass-transition temperature of polymethylmethacrylate on molecular weight. Trans Faraday Soc 56:744–752
46. Fox TG, Flory PJ (1950) Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight. J Appl Phys 21:581–591
47. Brar AS, Dutta K, Hekmatyar SK (1998) Stereochemical and compositional assignment of acrylonitrile/methyl methacrylate copolymers by DEPT and inverse HETCOR NMR spectroscopy. J Polym Sci A 36:1081–1092
48. Kapur GS, Brar AS (1991) Determination of compositional and configurational sequence distribution of acrylonitrile-methyl methacrylate copolymers by ^{13}C n.m.r. spectroscopy. Polymer 32:1112–1118
49. Grassie N, Beattie SR (1984) The thermal degradation of polysiloxanes: Part 6—products of degradation of poly(tetramethyl-*p*-silphenylene siloxane) and copolymers with dimethylsiloxane. Polym Degrad Stab 7:231–250
50. Steinfatt I, Schmidt-Naake G (2001) Free radical co- and terpolymerization reactions of methyl methacrylate, acrylonitrile, 4-vinylpyridine, and styrene in microemulsion. Macromol Chem Phys 202:3198–3204
51. Simionescu C, Asandei N, Liga A (1967) Research in the field of terpolymers I. Copolymerization of acrylonitrile/methacrylic acid/methyl methacrylate. Makromol Chem 110:278–290
52. Johnston NW (1976) Sequence distribution-glass transition effects. J Macromol Sci Part C 14: 215–250
53. Johnston NW (1974) Sequence distribution-glass transition effects. 5. Acrylonitrile Co- and terpolymers. Appl Polym Symp 25:19–26
54. Doak KW (1950) Copolymerization. XV.1 Copolymerization of acetylene derivatives with olefins. Retardation by radicals from acetylenes. J Am Chem Soc 72:4681–4686
55. Schmidt-Naake G, Schmidt H, Litauszki B, Schmutzler H (1989) Copolymerization behavior of donor and acceptor monomers - a comparison. Wiss Z Tech Univ Dresden 38:131–138
56. Arsac A, Zerroukhi A, Ainser A, Carrot C (2000) Rheological characterization of styrene acrylonitrile copolymers. J Appl Polym Sci 77:1316–1321