

Studies on Binary Copolymerization and Glass Transition Temperatures of Methyl Methacrylate with Ethyl Methacrylate and *n*-Butyl Methacrylate

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ABSTRACT: In this article, bulk copolymerization of methyl methacrylate (MMA) with ethyl methacrylate (EMA) and *n*-butyl methacrylate (*n*-BMA) was carried out at 60°C. The monomer reactivity ratios obtained by nonlinear fitting with Mayo-Lewis equation were as follows: $r_{\text{MMA}} = 0.93 \pm 0.03$, $r_{\text{EMA}} = 0.96 \pm 0.03$ for the MMA/EMA, and $r_{\text{MMA}} = 0.99 \pm 0.05$, $r_{\text{n-BMA}} = 1.11 \pm 0.06$ for the MMA/*n*-BMA series. A new equation proposed in view of bond rotation flexibility (Liu et al., J Phys Chem B 2008, 112, 93), which contains mole fractions of triads and T_g 's of corresponding periodic copolymers, was applied to describe the relation of T_g 's of MMA-EMA, MMA-*n*-BMA

copolymers with their compositions and sequence distribution. Excellent fitting results were obtained and T_g values of the assumed periodic copolymers were predicted by fitting the random copolymers. The influence of the substituent volume as well as substituent density on the T_g of poly(methyl methacrylate) (PMMA) was also tentatively predicted. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3939–3944, 2009

Key words: copolymer; glass transition temperature; structure-property relations; composition; substituent effect

INTRODUCTION

Copolymerization is one of the most important means to improve performance of polymers. Copolymers are extensively used in industrial processes, because of their physical properties, such as elasticity, permeability, glass transition temperature (T_g), and solvent diffusion kinetics can be varied within wide limits.¹ Among these, T_g is an important intrinsic characteristic that influences the material properties and potential applications of polymer. As well known, in most cases T_g 's of copolymers deviate from linear relations such as the Gordon-Taylor equation or Gibbs–DiMarzio (G–D) equation described below^{2,3}:

$$T_g = \frac{w_A T_{gA} + K w_B T_{gB}}{w_A + K w_B} \quad (1)$$

$$T_g = n_A T_{gA} + n_B T_{gB} \quad (2)$$

where T_g is the glass transition temperature of the copolymer; w_i and n_i are the weight fraction and molar fraction of the component i in the copolymer system, respectively; T_{gi} is the glass transition temperature of the homopolymer; K is model specific. Gordon and Taylor equation was proposed by assuming volume additivity of the repeating units in copolymer and G–D equation was based on the assumption that chain stiffness energy of the copolymer is additive. In the assumption of the Simha-Boyer rule, the Gordon–Taylor equation can be reformulated as the well known Fox relation^{4,5}:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad (3)$$

To interpret the deviations, sequence distribution effect was taken into account when the composition dependence of the copolymer T_g was investigated. Accounted for diad sequence contributions to the copolymers T_g 's, Johnston equation and Barton equation are mostly used^{6,7}:

$$\frac{1}{T_g} = \frac{w_A P_{AA}}{T_{gA}} + \frac{w_B P_{BB}}{T_{gB}} + \frac{w_A P_{AB} + w_B P_{BA}}{T_{gAB}} \quad (4)$$

$$T_g = n_{AA} T_{gAA} + n_{BB} T_{gBB} + n_{AB} T_{gAB} + n_{BA} T_{gBA} \quad (5)$$

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However, these expressions still cannot be adapted to describe the asymmetrical and even S-shaped T_g versus composition relation. In most cases, the agreement obtained by assuming the additivity of triad sequences is substantially improved over that of diad sequences.^{8–10} The triad equations were described as:

$$\frac{1}{T_g} = \frac{w_A P_{AAA}}{T_{gA}} + \frac{w_B P_{BBB}}{T_{gB}} + \frac{w_A P_{BAB} + w_B P_{ABA}}{T_{gABA}} + \frac{w_A P_{AAB} + w_B P_{BBA}}{T_{gAAB}} \quad (6)$$

$$T_g = n_{AAA} T_{gAAA} + n_{BBB} T_{gBBB} + n_{AAB} T_{gAAB} + n_{BAA} T_{gBAA} + n_{ABB} T_{gABB} + n_{BBA} T_{gBBA} + n_{ABA} T_{gABA} + n_{BAB} T_{gBAB} \quad (7)$$

The meanings of the parameters are similar as described earlier. While defect exist in these equations is that the parameters have ambiguous physical meaning and/or are too many. In a previous article,¹¹ we proposed new equations which have less parameters with definite physical meaning in view of additivity of bond stiff energy. When triad sequence effect (accurately C₃ substituent effect) is concerned, the relation was described as:

$$T_g = n_{AAA} T_{gA} + n_{BBB} T_{gB} + 2(n_{ABA} - n_{AAB}) T_{g[AB]} + 3n_{AAB} T_{g[AAB]} + 3n_{BBA} T_{g[BBA]} \quad (8)$$

Where $T_{g[AB]}$, $T_{g[AAB]}$, 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. This equation has no intractable parameter and be quite suitable to describe copolymer T_g 's composition relations. Equation (8) has been applied to investigate the copolymers of methyl methacrylate with styrene (MMA-St), ethylene with methyl methacrylate (E-MMA), and ethylene with vinyl acetate (E-VAc). Excellent fitting results were obtained.

In this article, eq. (8) is applied to T_g versus composition relationship of methyl methacrylate-ethyl methacrylate (MMA-EMA) and methyl methacrylate-*n*-butyl methacrylate (MMA-*n*-BMA) copolymers because that MMA, EMA, and *n*-BMA are widely used monomers. One goal of this study is to verify the universal application of eq. (8), another one is to predict T_g values of corresponding periodic copolymers and to predict the substituent effect on polymer T_g at different substituent densities.

EXPERIMENTAL

Materials

MMA, EMA, *n*-BMA, the initiator azo-bis-isobutyronitrile (AIBN), the precipitating agents methanol,

and the solvent acetone are all analytically pure and were supplied by Tianjin Chemical Reagent (Tianjin, China). MMA was washed with 5% sodium hydroxide three times, and then washed with distilled water until neutral, dried over anhydrous sodium sulfate in refrigerator for more than 24 h. The monomer was distilled under reduced pressure before use. The refining methods of EMA and *n*-BMA were the same as MMA. AIBN was recrystallized twice by using methanol.

Copolymerization

Bulk polymerization of MMA with EMA and MMA with *n*-BMA were carried out in a water bath kept at a constant temperature of 60°C. AIBN was used as radical initiators. Monomers and AIBN was charged into a dried, clear, 100 mL four-necked flask equipped with a stirrer, a thermometer, a condenser, and a nitrogen duct. Monomer feed mole fractions were calculated from reactivity ratios in literature.¹² Then the system was heated to 60°C rapidly. The reaction was stopped at a conversion of less than 5% by controlling the reaction time. Copolymers were obtained by precipitating the reactant in excess anhydrous methanol. The precipitates were filtered and dried in vacuum at 50°C for 2 days. The samples were then dissolved in acetone and refined by excess anhydrous methanol. A series of copolymers with different compositions were prepared by similar method. All the obtained samples were dried in vacuum at 50°C for 48 h before the characterization and measurement.

Measurements

The copolymer compositions (monomer mole fractions) were determined by ¹NMR, which was recorded on a Bruker Avance-400 NMR spectrometer operating at 400 MHz. The detailed conditions of operation are as follows: temperature of the probe, 25°C; solvent, deuteriochloroform; pulse repetition time, 6 s. Copolymer molecular masses were measured using a Polymer Lab GPC 220. Tetrahydrofuran was used as flow phase. The column was calibrated by using commercially available narrow-distribution polystyrenes. The T_g of copolymer was determined on a Perkin-Elmer differential scanning calorimeter (DSC) under the following conditions: atmosphere, nitrogen; heating rate, 20°C/min; temperature range, -50 to 170°C. The glass transition temperature was 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 T_g was the average of several additional scans and reproducible to be ±0.5°C.

RESULTS AND DISCUSSION

Reactivity ratios determination

First, reactivity ratios must be solved out because that they are contained in eq. (8). Figure 1 shows $^1\text{H-NMR}$ spectra of an MMA-EMA and an MMA-*n*-BMA copolymer as examples to show the attribution of the peaks. The compositions of MMA-EMA and MMA-*n*-BMA copolymers were calculated from the ratio of peak area of hydrogen in methoxy to that of hydrogen in methyleneoxy. Table I tabulates the monomer feed mole fractions and the corresponding copolymer compositions. Nonlinear fittings (least square errors-in-variables methods, EVM) were used to the experimental data with using Mayo-Lewis equation. The theoretical composition curve obtained from the Mayo-Lewis equation using terminal model reactivity ratios along with the experimental data are shown in Figure 2.

The experimental data are in good agreement with the theoretical ones, which indicates that the values

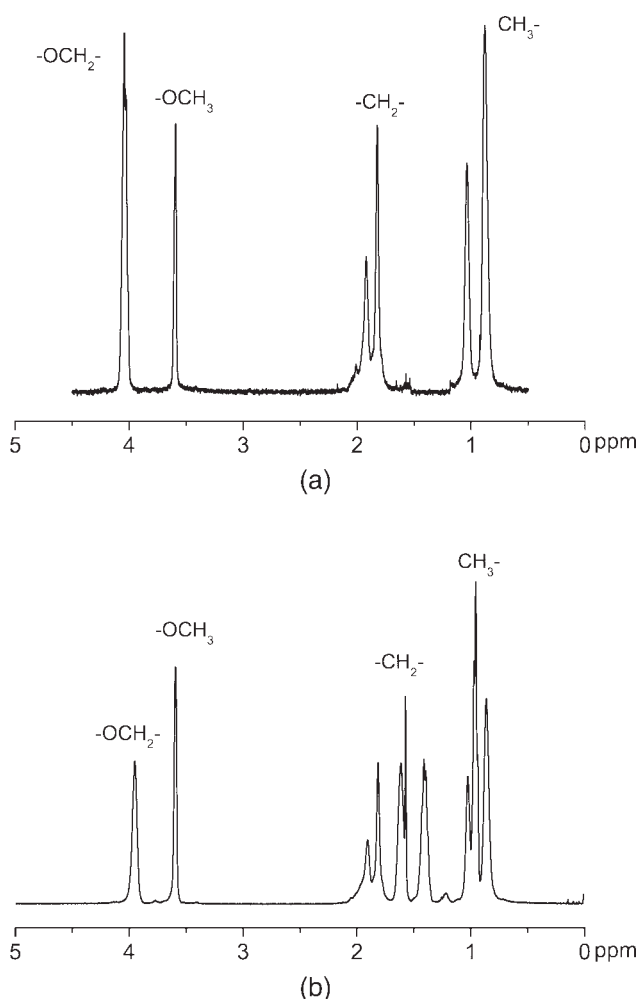


Figure 1 $^1\text{H-NMR}$ spectra (400 MHz) of (a) MMA-EMA copolymer ($F_{\text{MMA}} = 0.207$) and (b) MMA-*n*-BMA copolymer ($F_{\text{MMA}} = 0.389$).

TABLE I
Monomer Feed Mole Fractions and Copolymer Compositions in MMA/EMA and MMA/*n*-BMA Copolymerization

MMA/EMA		MMA/ <i>n</i> -BMA				
f_{MMA}	F_{MMA}	Conversion (wt %)	\bar{M}_n (10^3)	f_{MMA}	F_{MMA}	Conversion (wt %)
0	0	2.07	231.1	0	0	2.84
0.106	0.114	3.80	206.3	0.113	0.099	4.10
0.208	0.207	4.58	192.9	0.215	0.207	1.92
0.307	0.301	2.88	186.6	0.311	0.290	5.33
0.404	0.410	3.10	162.4	0.403	0.389	2.55
0.500	0.491	2.41	158.4	0.494	0.493	3.52
0.597	0.596	4.48	148.3	0.585	0.552	1.82
0.694	0.679	2.73	99.9	0.678	0.679	2.39
0.793	0.789	2.85	101.1	0.777	0.765	2.86
0.895	0.886	2.41	88.6	0.883	0.886	1.95
1	1	3.51	176.9	1	1	3.51

f 's are the monomer feed mole fractions and F 's are the monomer mole fractions in copolymers.

of reactivity ratios obtained from the copolymer compositions are reliable. The obtained reactivity ratios are summarized in Table II. It is found that the result is close to that of Musha.¹² The result also shows that there is little difference between reactivity ratios with considering monomer fraction change along the reaction (in other words, considering conversion) or not. This is due to that the reactivity ratios are close to 1 and monomer fraction changes little along with the copolymerization.

 T_g 's of the copolymers

Figure 3 shows plots of T_g versus MMA mole fractions for MMA-EMA and MMA-*n*-BMA copolymers. As well known, polymer molar mass has great effect on its T_g when the polymerization degree is low. The number-average molar mass of MMA-EMA copolymers have been determined by GPC and tabulated in Table I. It is estimated that the difference between the MMA-EMA copolymer T_g 's is lower than 1.5 K by using $K = 2.1 \times 10^5$ of PMMA.¹³ This value could be negligible compared with the variety range of 39.9 K in the MMA-EMA series. Although not so remarkable, a S-shaped curve is characterized in the T_g versus composition of the copolymers, especially for MMA-EMA copolymers. This is different from that reported by Schneider,¹⁴ which may be caused by different copolymerization methods. The S-shaped curve indicates that diad equation could not interpret the T_g -composition relation perfectly and eq. (8) may exhibit its superiority. Diad compositions in eq. (5) (Barton equation) were calculated from feed compositions and reactivity ratios obtained earlier¹¹ and the fitting results with this equation was plotted in the same figure. It could be

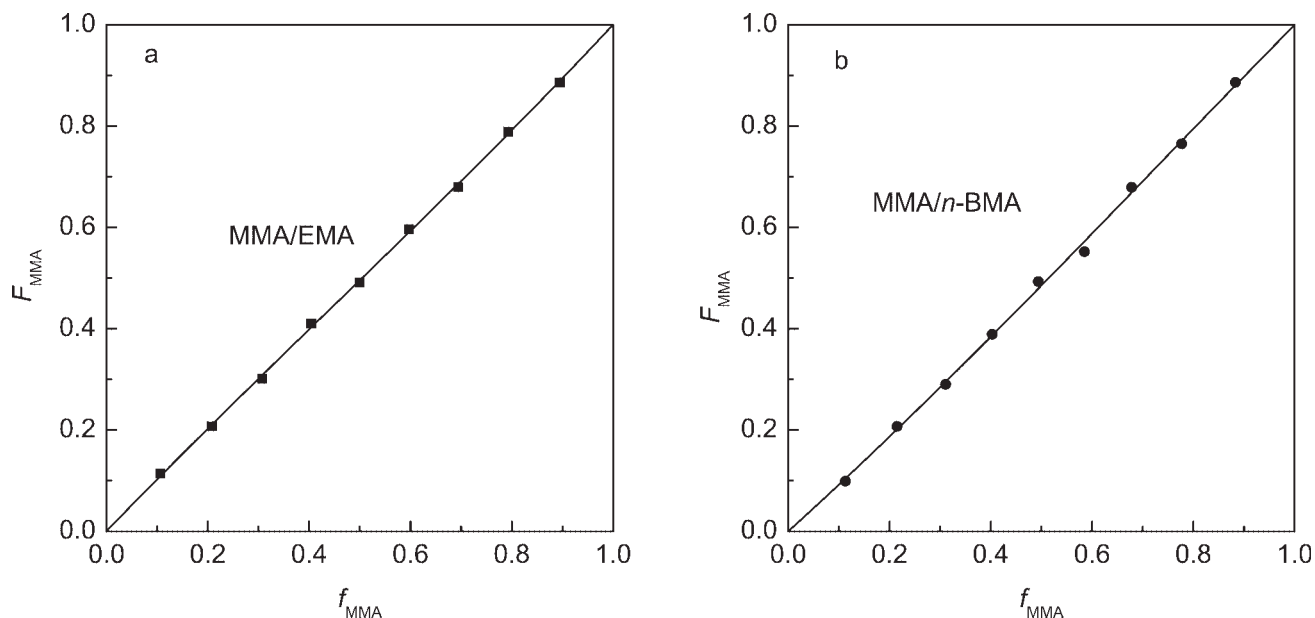


Figure 2 The mole fractions of MMA in (a) MMA-EMA and (b) MMA-*n*-BMA copolymers at different monomer feed mole fractions. (Lines: Mayo-Lewis equation).

found that system deviation instead of random deviation appears between the theoretical and experimental data. Also, it could be found that the differences between experimental data and fit values for MMA-EMA and MMA-*n*-BMA copolymers are much larger when using Barton equation compared with that using eq. (8). This pronounces that Barton equation (diad equation) is not suitable to describe the T_g -composition relation of MMA-EMA and MMA-*n*-BMA copolymers.

There are two methods to fit copolymers T_g 's with eq. (8). First one is calculating $T_{g[AB]}$ by a diad equation [take C_2 substituent effect into consideration, i.e., eq. (9)]¹¹ and then solve $T_{g[AAB]}$ and $T_{g[BBA]}$ by curve fitting using eq. (8). The other is calculating the three parameters ($T_{g[AB]}$, $T_{g[AAB]}$, and $T_{g[BBA]}$) together by nonlinear fitting using eq. (8) at the same time.

$$T_g = n_{AA}T_{gA} + n_{BB}T_{gB} + 2n_{AB}T_{g[AB]} \quad (9)$$

In this article, we only introduce the first method because that the latter method usually give discrete

results with large errors. The formulas of calculating mole fractions of different diads and triads are as described before.¹¹

Figure 4 shows plots of $T_g - n_{AA}T_{gA} - n_{BB}T_{gB}$ versus $2n_{AB}$ for MMA-EMA and MMA-*n*-BMA copolymers (diad compositions were calculated from feed compositions and reactivity ratios). $T_{g[MMA-EMA]}$ was obtained to be 360.2 ± 2.2 K and $T_{g[MMA-n-BMA]}$ was obtained to be 337.5 ± 1.9 K with relatively small errors.

Triad (n_{AAA} , n_{BBB} , n_{AAB} , n_{ABA} , n_{ABB} , n_{BBA} , n_{BAB} , and n_{BAA}) compositions in eq. (8) were calculated from feed compositions and reactivity ratios obtained earlier.¹¹ By using the $T_{g[AB]}$ obtained, the fitting result of experimental data with eq. (8) is perfectly well, as shown in Figure 3. Experimental data randomly distributed in both sides of theoretical T_g 's versus composition curves of MMA-EMA and MMA-*n*-BMA copolymers. Therefore, eq. (8) gives an excellent fitting and shows its rationality and veracity. It gives 359.9 ± 2.8 K for $T_{g[MME]}$, 365.4 ± 2.7 K for $T_{g[EEM]}$, 346.9 ± 2.8 K for $T_{g[MMB]}$, and 329.3 ± 2.7 K for $T_{g[BBM]}$ at the same time.

TABLE II
Reactivity Ratios of MMA/EMA and MMA-*n*-BMA Copolymerization

M_A	M_B	Literature ¹²		r Without considering monomer fraction change		r With considering monomer fraction change	
		r_A	r_B	r_A	r_B	r_A	r_B
MMA	EMA	1.08	1.08	0.93 ± 0.03	0.96 ± 0.03	0.93 ± 0.03	0.96 ± 0.03
MMA	<i>n</i> -BMA	1.27	1.20	0.99 ± 0.05	1.10 ± 0.06	0.99 ± 0.05	1.11 ± 0.06

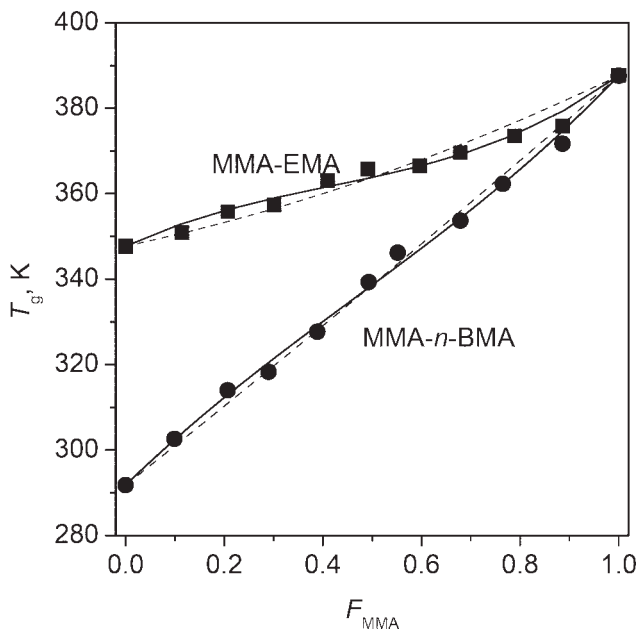


Figure 3 Experimental and predicted T_g 's of MMA-EMA and MMA-*n*-BMA copolymers. Solid squares and circles denote random copolymers and homopolymers. Solid lines: eq. (8). Dash lines: Barton equation [eq. (5)].

Effect of substituent length and density on $T_{g[PMMA]}$

$T_{g[EMME]} = 359.9$ and $T_{g[EEM]} = 365.4$ K means that T_g of PMMA will decrease 27.7 K and 22.2 K when one third or two third methyl in the ester side group was substituted by ethyl in the same interval along the chain, respectively. Outwardly, the T_g of poly [EMA-EMA-MMA] should be lower than that of poly[MMA-MMA-EMA] because poly[MMA-MMA-EMA] contains less flexible EMA units. This may be the case because the periodic copolymers usually have quite different glass transition characters in comparison with statistical copolymers. Yokota reported that the T_g of poly[MCA-Pr] (alternating copolymer of methyl α -chloroacrylate with propylene) increased from 56 to 76°C when the propylene unit was substituted by more flexible units of EE (poly [MCA-E-E]).^{15,16} For statistical copolymers, it has also been reported that introducing a more flexible unit of vinylidene chloride could increase the T_g of poly(methyl acrylate) as much as 32.5°C.¹⁷ Fitting by assuming poly[EMA-EMA-MMA] with a lower T_g (e.g., 350 K) has also been attempted and shows large deviations. When one third or two third methyl was substituted by *n*-butyl, T_g of PMMA may decrease 40.6 and 58.2 K respectively, according to the results mentioned earlier.

Additivity of bond stiff energy is the basis of eq. (8), then if the substituent on carbon farther than C₃ from the objective bond is not considered, one may expect to predict T_g 's of other period copolymers beside poly[AB], poly[AAB], and poly[BBA]. As

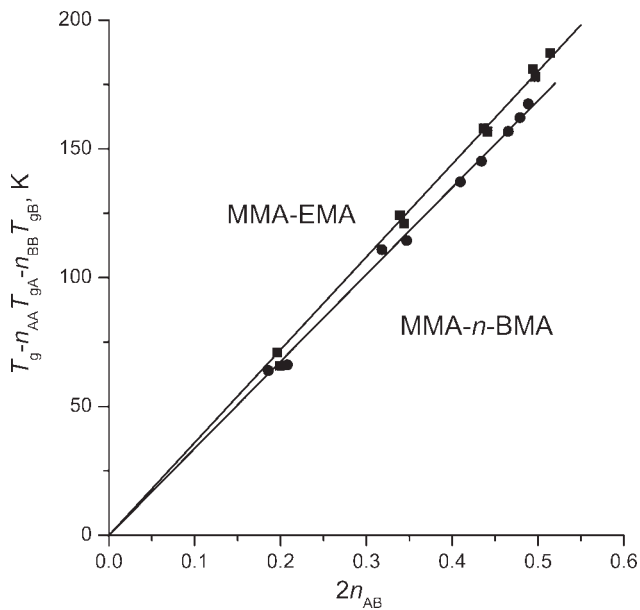


Figure 4 Plots according to eq. (9) for MMA-EMA and MMA-*n*-BMA random copolymers. Lines: eq. (9).

described in the previous article,¹¹ poly[AAB] is composed of bonds b_{ABA} , b_{AAB} , and b_{BAA} in equal mole fractions. Whereas poly[AAAB] is composed of bonds b_{ABA} , b_{AAA} , b_{AAB} , and b_{BAA} in equal mole fractions, as shown in Figure 5. Then, we can predict T_g of poly[AAAB] by the assumption of additivity of bond stiff energy based on the thermodynamic theory of glass transition as:

$$T_{g[AAAB]} = \frac{1}{4} [T_{g^{b_{ABA}}} + T_{g^{b_{AAB}}} + T_{g^{b_{AAA}}} + T_{g^{b_{BAA}}}] = \frac{3}{4} T_{g[AAB]} + \frac{1}{4} T_{gA} \quad (10)$$

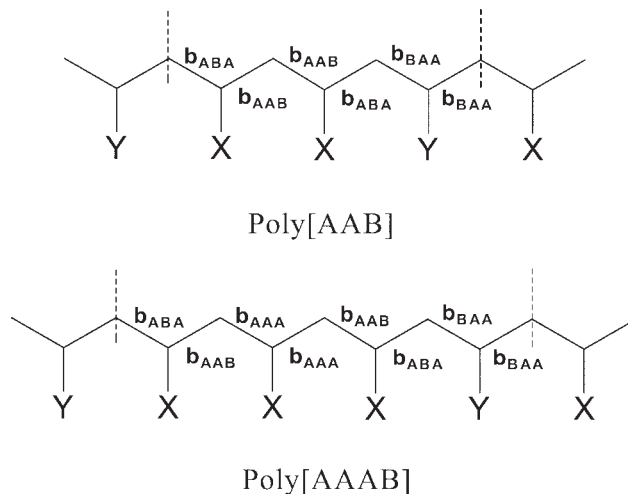


Figure 5 Illustration of bond composition of periodic copolymers.

TABLE III
The Predicted T_g 's of Periodic Copolymers

Substituent	Substituent density								
	0	0.2	0.25	0.333	0.5	0.667	0.75	0.8	1.0
—COOCH ₃	387.6	387.6	387.6	387.6	387.6	387.6	387.6	387.6	387.6
—COOC ₂ H ₅	387.6	371.0	366.8	359.9	360.2	365.4	361.1	358.3	347.7
—COOC ₄ H ₉	387.6	363.2	357.2	347.0	337.5	329.4	320.0	314.4	291.8

Similarly, we can obtain:

$$T_{g[\text{BBBA}]} = \frac{3}{4}T_{g[\text{BBA}]} + \frac{1}{4}T_{g\text{B}} \quad (11)$$

Then the glass transition temperatures of PMMA with different substituent size at different substituent densities (regular substituent) could be predicted. Thereupon, we can not only get the substituent effect on polymer T_g reported in textbook or literatures,¹⁸ but also concern the substituent density at the same time. The predicted results are shown in Table III. It can be found that the substituent effect on T_g at lower substituent densities are similar to the case of fully substituent. T_g of PMMA substituted by ethyl is higher than that substituted by *n*-butyl at all the substituent densities. It is attributed to the length of *n*-butyl, this is in line with the glass transition theory. Furthermore, it could be found that the decrease of $T_{g\text{PMMA}}$ generally depressed along with the decreasing substituent density for the substituent with same size. One could found that T_g s of PMMA regularly substituted with low fraction ethyl and *n*-butyl ester groups are lower than the linear addition law. This may be due to the fact the incorporation of side group will increase the molecule distance and introduce more free volumes. Also, it could be found that the substituent of *n*-butyl ester group deviate little from the linear addition law than that of ethyl ester group. It may be attributed to that *n*-butyl ester are flexible than ethyl ester and could fill in the space through conformation rearrangement and decrease the excess free volume. In turn, this lead to T_g increase compared with that extrapolated from the ethyl ester substituent.

CONCLUSIONS

MMA-EMA and MMA-*n*-BMA copolymers with different compositions were synthesized by bulk polymerization with AIBN as initiator. The reactivity ratios of the copolymerization are $r_{\text{MMA}} = 0.93 \pm 0.03$ and $r_{\text{EMA}} = 0.96 \pm 0.03$ for MMA with EMA, $r_{\text{MMA}} = 0.99 \pm 0.05$ and $r_{\text{n-BMA}} = 1.11 \pm 0.06$ for

MMA with *n*-BMA. T_g 's versus copolymer compositions were studied by using a bond rotation equation proposed earlier and there are little deviations between the experimental data and theoretically predicted T_g 's. This indicates that the new equation is feasible for the T_g composition relation investigation of MMA-EMA and MMA-*n*-BMA binary copolymers. T_g 's of alternating copolymers and periodic copolymers of MMA with EMA or *n*-BMA have also been evaluated as: $T_{g[\text{ME}]} = 360.2 \pm 2.2$ K, $T_{g[\text{MME}]} = 359.9 \pm 2.8$ K, $T_{g[\text{EEM}]} = 365.4 \pm 2.7$ K, $T_{g[\text{MB}]} = 337.5 \pm 1.9$ K, $T_{g[\text{MMB}]} = 346.9 \pm 2.8$ K, and $T_{g[\text{BBM}]} = 329.3 \pm 2.7$ K. Furthermore, the substituent effect on T_g of PMMA at different substituent density was tentatively predicted. It could be found that T_g of PMMA substituted by ethyl is higher than that substituted by *n*-butyl at all the substituent densities. The decrease of $T_{g\text{PMMA}}$ generally depressed along with the decreasing substituent density for the substituent with same size.

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