

Glass Transition Temperature of Mixtures of Poly(methyl methacrylate-*co*-ethyl acrylate)

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DSC thermogrammes of mixtures of poly(methyl methacrylate-*co*-ethyl acrylate), PMMA-EA, of different microstructure of macromolecular chains, exhibit two glass transition temperatures, T_g , indicating the presence of two phases. In one phase the copolymer chains are compatible with long blocks of ethyl acrylate and the second phase is very rich in long chains of methyl methacrylate. Based on the ^{13}C NMR results for compositional diads distribution and DSC data, a miscibility line can be drawn when the results are presented in a form of a triangular diagram.

Key words: poly(methyl methacrylate-*co*-ethyl acrylate), polymer blends, T_g , DSC, NMR

The aim of this work was to relate the miscibility phenomena of poly(methyl methacrylate-*co*-ethyl acrylate) mixtures with the microstructure of the copolymer chain. The two simplest criteria predicting compatibility of a pair of non-crystalline (co)polymers is the film transparency and the number of glass transition temperatures, T_g [1,2]. For a mixture of two homopolymers, A and B, the presence of two well separated glass transition temperatures, situated within the zone between the T_g values for pure homopolymers, corresponds to a biphasic system containing two amorphous phases, one rich in A, the second rich in B. The presence of only one large transition situated in the region between T_{gA} and T_{gB} indicates a limited miscibility between these two components. As a result, the truly homogeneous systems also exhibit only one glass temperature, T_{gAB} , but with a sharper transition, very similar to those for the pure homopolymers.

Since the miscibility properties are characterized by a formation of one homogeneous solution at the segmental level, it seems necessary to determine the distribution of comonomers along the macromolecular chain, at least at the diad level. We have already shown [3] that it is possible to determine from the ^{13}C NMR spectra of the PMMA-EA the distribution of compositional-configurational sequences up to pentads and relate this distribution with the glass transition temperature by introducing modifications to the equations of Barton and Johnston [4]. We have also observed a

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small difference in the fraction of the mixed sequences between the samples having the same global composition (close to 50/50), one synthesized at low conversion and the other at 100% conversion. In order to verify, if the sequence distribution really changes for different mixtures of the same global composition and to determine its eventual relations with T_g , we have modified the experimental mode of the copolymerization by introducing in the beginning of the synthesis the entire amount of one monomer, while the second monomer was divided into several portions and added gradually.

EXPERIMENTAL

Sample preparation: The PMMA-EA copolymer samples were synthesized at the Centre de Recherche Elf- Atochem in Carling, France by free radical polymerization method, as previously described [4]. The comonomers, taken in respective weight ratio, were poured into butan-2-one to obtain 40 wt % mixture and then placed in a double-coated reactor under nitrogen. The mixture was heated up to 78°C and azobisisobutyronitrile (AIBN) was added as radical initiator. In this work all the reactions were performed up to 100% conversion.

The samples were prepared in three different series denoted A, B and C, by varying the manner of the comonomer introduction. The mixtures of series A, featuring constant global composition (50/50), were obtained by introducing the total amount of ethyl acrylate and only a certain fraction of methyl methacrylate in the beginning of the reaction. The remaining amount of the second comonomer was divided into several identical portions and then introduced in regular time intervals. So the total number of moles of MMA was equal to that of EA and the copolymer obtained was equimolar since the reactions were carried out till 100% conversion (Table 1). For example, sample A7 was obtained by introducing MMA in two portions, first half at $t = 0$ (together with the catalyst) and the second one after 2 hours. In the case of sample A3 the amount of MMA was divided into six portions and introduced into the reaction mixture every twelve minutes during 1 hour. In practice, 100 g of ethyl acrylate and 280 g of methyl-ethylcetone (MEC) was introduced into the double coated reaction vessel and heated to 78°C. Then the first portion of MMA and 1 g of AIBN dissolved in 20 g of MEC were added. After introducing the last portion of MMA the reaction was continued for 3 hours, then 0.4 g of AIBN was added and reaction was continued for 1 hour to be sure that conversion had reached 100%. The polymer was precipitated from methanol/water mixture (3:2), dried at 80°C for one day, crushed and heated again at 100°C for 3 days.

Copolymer samples of series B were obtained in an analogous way, but for different global ratio between the comonomers. Samples for series C were obtained similarly, but the order of comonomer introduction was reversed, *i.e.* the total amount of EA was introduced in the beginning, while the respective amount of MMA was divided into several portions and added gradually at respective time intervals. Additional detailed description of the variations of the comonomer introduction mode, leading to more specific samples, is presented further in the text.

Determination of glass transition temperature: Polymer samples were kept *in vacuo* prior to the measurements and weighted (15–20 mg) into the aluminium DSC pans. They were held as liquids at 160°C for 10 min and cooled to the starting temperature, in order to minimize the differences in thermal history. The measurements were performed using three DSC apparatus: Mettler DSC 30 at the Centre de Recherche Elf-Atochem, Carling, France (under vacuum, without annealing and quenching); Setaram DSC 92 at Ecole Nationale des Industries Chimiques in Nancy, France (dry nitrogen used as purge gas, first measurement up to 160°C, annealing for 10 min, quenching in ice and then liquid nitrogen, second measurement); Du Pont 1090 at Polish Academy of Sciences (measurements were taken in the same conditions as for the Setaram apparatus). In all the cases the thermogrammes were obtained in the range from –50°C to 160°C at the heating rate of 20.0 K/min and the first cycle of heating was not taken into account. Regular calibration of the instruments was carried out using metal standards. For all the samples, the T_g represents a mean obtained from three measurements. The DSC curves recorded for different samples

were typical and the transients were rather symmetrical, so the T_g values were determined as the mid-point at the half-heights of the transitions.

Molecular weight determination: Number average molecular weights were measured by gel permeation chromatography, GPC, on a Knauer apparatus in THF (0.5 ml min^{-1} flow rate), using a differential refractometer with a mixed B column (internal diameter 7.5 mm, length 30 cm, pore size $10 \mu\text{m}$). Calibration of this system was carried out using 4 solutions of PMMA standards. The calibration curve was described by a third-order polynomial.

NMR spectroscopy: The 100 MHz ^{13}C NMR spectra of the PMMA-EA samples were recorded on a Bruker DRX 400 spectrometer for 5 wt % solutions in CDCl_3 at 40°C . A gated decoupling sequence was applied and a reasonable signal to noise ratio was obtained after 1200 scans. In order to obtain quantitative spectra the time delay between the pulses has to be at least five times greater than the longest relaxation time. Because $T_{1(\text{C}=\text{O})} \sim 3\text{--}6 \text{ sec}$, the delay was set to 30 sec. The quantitative nature of the spectra was verified by comparison of the intensities for the $\text{C}=\text{O}$ signal to the sum of those for $\alpha\text{-CH}_3$ (in the methyl methacrylate units) and OCH_2 (in the ethyl acrylate units) which yielded very good agreement. The composition of the copolymer, P(M), was calculated from the ratio between the intensity of the O-CH_3 signal of ethyl acrylate and intensity of the carbonyl signal. The diad probabilities were obtained from the $\beta\text{-CH}_2$ carbon signal region, from 35 to 55 ppm, as it was already described [5]. The diads of pure composition, P(MM) and P(EE), were calculated by integration of the extreme parts of this signal with subsequent subtraction of the lines of other carbons intervening in this region. The NMR spectra were simulated using our own special software written for Matlab, Math-Works Inc. environment. The simulated spectra were calculated at a given level of sequence length, applying a set of spectral parameters obtained for each sequence. Then the program compares an experimental NMR spectrum with the simulated one and the differential spectrum is used to modify the peak parameters within the experimental error and recalculate the spectrum to obtain the best fit.

RESULTS AND DISCUSSION

Samples of equimolar global composition: For mixtures of miscible (co)polymers [6–8] the formulae relating T_g and composition are similar to that of DiMarzio-Gibbs [9] and Fox [10] taking into account individual copolymers. They contain an additional term when the experimental data deviate from linear relationship (non-ideal mixture), as is the case of equation of Jenkel-Heusch [11]:

$$T_g = w_A T_{gA} + w_B T_{gB} + qw_A w_B$$

or Gordon-Taylor [12]:

$$T_g = \frac{w_A T_{gA} + kw_B T_{gB}}{w_A + kw_B}$$

where T_{gA} , T_{gB} , are the glass transition temperatures of respective homopolymers, w_A and w_B are the weight fractions of comonomers A and B, respectively; q is the interaction parameter depending on rigidity of the chain, its free volume and cohesion energy; while k is another interaction parameter taking into account the intermolecular forces.

A real behaviour can lead to phase separation [13,14], so it is necessary to perform the thermal analysis measurements in well defined conditions and examine the thermogrammes in detail. Let us consider for example one of our samples, say A7, obtained from a synthesis performed for initial comonomer ratio of MMA/EA = 33.3/66.7. After 2 hours at 78°C the copolymerization is nearly completed and the initial amounts of both comonomers are almost consumed. So, when the second part of methyl methacrylate is added to the reaction mixture, the polymerization which follows is practically the formation of pure PMMA homopolymer chains. Such a mixture can, therefore, exhibit two Tg if the PMMA is not completely miscible in the copolymer. To a smaller extent the same situation takes place for sample A1, which can be considered as a mixture of six copolymer samples, where the last portion of MMA added to the reaction mixture after 1 hour contains only one sixth of the MMA amount.

All the thermogrammes for the samples of series A obtained with Mettler DSC apparatus without annealing and quenching in liquid nitrogen exhibit a principal Tg' transition, at about 10–20°C, and a small inflection at about 110°C only for sample A10. A series of measurements with annealing followed by quenching melts in liquid nitrogen, performed with Setaram DSC 92, revealed second transition, Tg'', at about 110–115°C (Figure 1) for all the samples, which is only 5–10°C lower than for pure PMMA. Such a small shift from the original Tg of pure PMMA indicates that the second phase is composed mainly of long MM-blocks, slightly intermingled with copolymer chains. The relative height of the second transition is much smaller than the first one and difficult to determine precisely, and therefore, to evaluate the fractions of the respective phases.

In order to confirm these results, we have repeated the measurements for several samples with another instrument, Du Pont 1090, significantly increasing the annealing time (4 h). Now, the second transition was clearly visible and the corresponding step of Δc_p was bigger with the increasing time interval of introduction of the last part of the second comonomer. In order to verify, if this phenomenon does not correspond to a delay of miscibility, a series of complementary experiments was accomplished. After 4 h of annealing at 160°C and subsequent quenching in liquid nitrogen, the sample was left for 48 h at ambient temperature before recording the DSC curve. We have still observed the presence of a second transition, Tg'', even after a slow cooling of the melts after the annealing at 160°C. Finally, to aid the phase separation, after the annealing of 4 h, the system was slowly cooled down to a temperature situated between Tg' and Tg''. In this case the second transition was revealed much more clearly. Therefore, these experiments indicate that the second phase is constituted of practically pure blocks of PMMA chains forming microdomains. Since the global composition of the system remains constant (50/50), it suggests that there is more and more of ethyl acrylate in the first phase when we change from A1 to A10 sample, because the Tg' value decreases continually.

In order to know the exact composition of the two copolymers contained in the mixture, at least in the simplest cases like A5, A7 or A10 when methyl methacrylate was added in two portions, we have determined by GC and HPLC techniques the con-

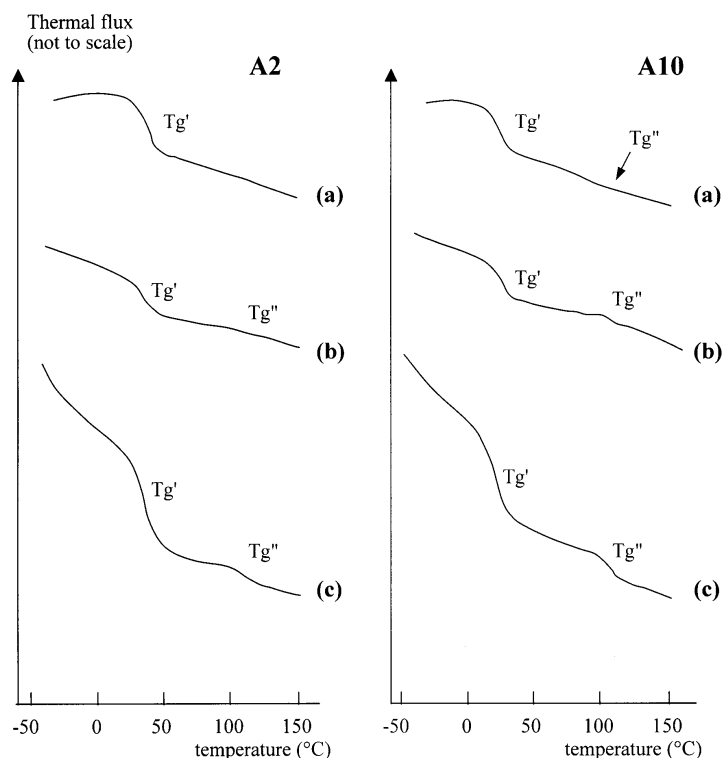


Figure 1. DSC curves for samples A2 and A10: (a) Mettler DSC 30 (b) Setaram DSC (c) Du Pont 1090.

centration of residual comonomers during the reaction for the initial MMA/EA concentration of 33.3/66.7. These analyses were performed for the filtrate obtained by precipitation of 10 g of the solution in 90 ml of methanol/water mixture (3:2). The results obtained show that after 1, 2, 3 and 4 hours of the polymerization, it remains respectively 1.4, 0.15, 0.04 and 0.02% of MMA in the reaction mixture and 10, 4.4, 2.6 and 1.9%, respectively, of EA. Therefore, it can be calculated that the global composition of the first copolymer is 34/66 and 96.1/3.9 for the second one. These two copolymers can be synthesized separately and blended in a proportion 3:1 to obtain an equimolar final mixture. The sample A10 will be therefore represented by the following blend:

$$A'10 \cong 3 \cdot \text{copo}(34/66) + 1 \cdot \text{copo}(96.1/3.9)$$

where, for example $3 \cdot \text{copo}(34/66)$ represents 3 parts of the PMMA-EA copolymer containing 34% of MMA and 66% of EA. Similar calculations show that the samples A7 and A5 can be represented as:

$$A'7 \cong 3 \cdot \text{copo}(34.4/65.6) + 1 \cdot \text{copo}(91.7/8.3); \quad A'5 \cong 2 \cdot \text{copo}(35.5/64.5) + 1 \cdot \text{copo}(82.8/17.2)$$

where each copolymer of a given composition was synthesized separately. Each blend was dissolved in methylethylcetone to obtain a homogeneous solution at 25°C, then dried, crushed and heated under vacuum for 72 h before the DSC measurements. Actually, two transitions were observed for each sample and the T_g values were comparable to those of A10, A7 and A5 samples, respectively (Table 1). In an additional experiment, when we replaced the second copolymer constituting the blend by pure PMMA, once again the second transition at 110°C was also observed.

Table 1. Values of T_g and \overline{M}_n of the PMMA-EA copolymer samples.

Sample/time intervals of MMA introduction	\overline{M}_n	T _g measured (°C)		
		Mettler*	Du Pont	Setaram
A1: 0; 12'; 24'; 36'; 48'; 60'	21000	32.0		33.5; 110.0
A2: 0; 15'; 30'; 45'; 60'	25000	33.1	35.8; 111.8	34.6; 108.0
A3: 0; 20'; 40'; 60'	26000	33.2		
A4: 0; 30'; 60'	24000	33.2		
A5: 0; 60'	26000	28.5		31.2; 107.2
A6: 0; 60'; 2 h	22000	24.3		
A7: 0; 2 h	24000	22.4	24.5; 107.0	26.1; 106.0
A8: 0; 1 h 30; 3 h	25000	16.3		
A9: 0; 30'; 3 h 30	22000	27.0	29.8; 110.8	28.5; 111.4
A10: 0; 4 h	22000	17.3	20.5; 112.2	19.3; 112.0
A'5	25000	29.5		30; 107
A'7	31000	22.9		23.7; 105
A'10	29000	17.6		18.6; 110

*The second T_g was not observed with this apparatus.

As expected, the global composition, verified by ¹³C NMR from the ratio between the intensities of the OCH₂ and α-CH₃ and carbonyl signals, was very close to 50/50 (Table 2) with slightly higher deviations for samples A8 and A10. If we examine the carbonyl signal of the ¹³C NMR spectra of the most heterogeneous samples, A10, we can clearly see (Figure 2) the pentad splittings in the MrMrM triad band (177.2–177.9 ppm) with visibly distinguished peak of purely racemic chain, *i.e.* MrMrMrMrM pentad at 177.4 ppm, superimposed with the rest of the MrMrM-centred pentads. Since the shape of this band is considerably different from that of a statistical copolymer, it confirms the presence of significant amount of PMMA homopolymer responsible for the formation of the second phase mentioned above. The simulation of this signal requires the knowledge of diad probabilities, which can be derived directly from β-CH₂ signals. Such simulations can be performed at the pentad level only for a copolymer synthesized at low conversion, when the respective statistics governing the sequence distribution can be precisely applied. Nevertheless, we have already shown that such a simulation can yield quite satisfactory results for a copolymer of 100%

conversion, but only at the triad level. The spectrum of this copolymer is very similar to those for samples A1 and A2, confirming the presence of only slight difference in heterogeneity between these samples. Figure 2b shows that such a simulation of carbonyl signal is quite satisfactory. This interpretation can be extended even for sample A10, since we can see that the simulation at the triad level still provides satisfactory agreement, while it gives significant discrepancies at the pentad level. As expected, the spectrum for the mixture A'10 is very similar to that of A10 also exhibiting a little lower probability of the heterodiad, ME, than the other systems. This result indicates that this probability decreases with increase of the heterogeneity of the mixture. When during the synthesis the second portion of MMA is added after longer interval, the probability of ME diads decreases since at this moment there is practically no EA in the reaction mixture. In such a case the mixed sequences are formed practically only during the first period of the copolymerization.

Table 2. Global composition and diad probabilities for the PMMA-EA samples.

Sample	P(MM)	P(ME)	P(EE)	P(M)	P(E)
A1	0.26	0.47	0.27	0.495	0.505
A2	0.27	0.48	0.25	0.510	0.490
A3	0.27	0.48	0.25	0.510	0.490
A4	0.27	0.48	0.25	0.510	0.490
A5	0.29	0.45	0.26	0.525	0.475
A6	0.27	0.42	0.31	0.480	0.520
A7	0.27	0.42	0.31	0.480	0.520
A8	0.28	0.37	0.35	0.465	0.535
A9	0.27	0.45	0.28	0.495	0.505
A10	0.27	0.37	0.36	0.455	0.545
A'10	0.30	0.36	0.34	0.480	0.520

Samples of variable global composition, diagram Tg-diad distribution: In order to vary the global composition of the blends, we have synthesized two new copolymer samples B1 and B2 containing respectively 20 and 81% of MAM. During these syntheses MAM was added in two portions with time interval of 2 h as in the case of A7, studied previously. A third sample, B3, containing 30% MMA was prepared in a similar manner, but the second introduction of MMA was performed after 4 hours, as for sample A10. The DSC curves for these samples exhibit also two glass transitions especially distinguishable for B2 and B3, being very heterogeneous (Table 3). At the same time in the carbonyl signal of its ^{13}C NMR spectrum we can observe an intense line of the MrMrMrMrM pentad, characteristic for chains of pure syndiotactic PMMA.

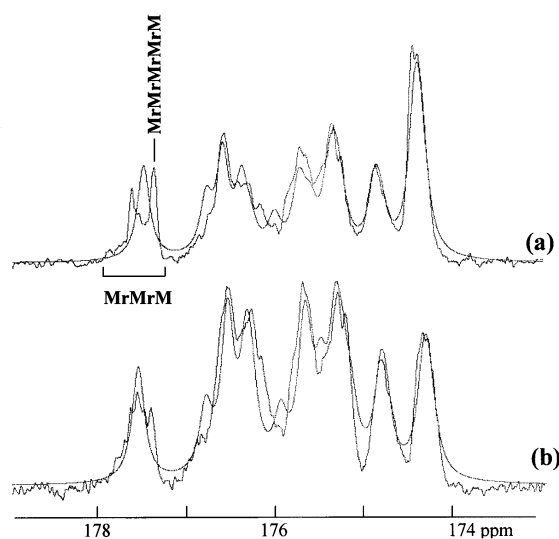


Figure 2. Simulation at the triad level of the carbonyl signal of the 100 MHz ^{13}C NMR spectra of PMMA-EA for samples A10 (a) and A2 (b).

Table 3. Diad probabilities and Tg of mixtures of the PMMA-EA samples.

Mixture	P(MM)	P(ME)	P(EE)	P(M)	Tg' and Tg'' (°C)		
					Mettler	Setaram	Du Pont
B1	0.06	0.25	0.69	0.19	-4.3	-1.0; 98.7	-1.3; 110.0
B2	0.64	0.32	0.04	0.80	82.0	80.8; 112.6	86.4; 115.0
B3	0.16	0.24	0.60	0.29	-2.4	3.2; 102.0	0.3; 110.0
C1	0.06	0.27	0.67	0.20	4.2	5.1	1.7
C2	0.33	0.37	0.30	0.51	53.4 ¹	~30; ~60 ²	0-80 ¹
C3	0.68	0.27	0.05	0.80	91.8	92.9	89.0
C4	0.32	0.34	0.34	0.49	61.2 ¹	~20; ~60 ²	0-80 ¹

1 – very large step, difficult to resolve into two transitions;

2 – two very large overlapping transitions (description in the text).

Finally, three other samples, C1, C2 and C3, containing 20, 50 and 81% of MMA, respectively, were prepared in an inverse manner, *i.e.* by introducing initially the total amount of MMA and half of EA, while the second portion of EA was added after 2 hours. A fourth sample, C4, containing 50% MMA was synthesized in an analogous way except that the second portion of EA was added after 4 hours. For such a method of preparation the copolymer chains are formed during the first stage of reaction, up to nearly complete consumption of the comonomers, therefore, the addition of the second portion of EA can lead to formation of the PEA homopolymer chains. As a result,

this group of samples should be very heterogeneous and contains the copolymer chains intermixed with relatively long chains of the PEA homopolymer. Moreover, formation of long MM-blocks should be significantly reduced in this case. For samples C1 and C3, containing predominant fraction of one monomer (80% of EA in sample C1 and 80% of MMA in sample C3), only one distinct glass transition is observed at about 3°C for C1 and at about 90°C for C3. In the case of nearly equimolar copolymer samples, C2 and C4, a very large transition is observed covering the zone 0–80°C. However, for both the samples, using the Setaram apparatus, it is possible to distinguish an inflection of the heat drop in the middle of this region, therefore, it can be regarded as two very large overlapping transitions of comparable heights. We can only estimate the position of the first transition, T_g' , at about 20°C, while the second one, T_g'' , is situated at about 60°C. Therefore, it indicates that the copolymer chains exhibit limited miscibility over very large zone of temperatures and separation into two phases, being in comparable amounts, is observed. For this series of copolymer samples, formation of long EE blocks is favoured but we do not observe a separate transition near the glass transition for pure PEA homopolymer, *i.e.* about –20°C. It also indicates that PEA is well soluble in the PMMA-EA copolymer phase, while the phase separation is due to the presence of longer MM-blocks, which are not compatible with the copolymer chains. Therefore, when the copolymer is synthesized in such a manner that longer blocks of MMA can be obtained it leads to separation of a second phase very rich in long MM segments, incompatible with the copolymer chains.

Allen and Fisher [15] have already presented the fractions of isotactic, syndiotactic and atactic diads in the form of a triangular diagram to study the structure of PMMA in various solvents. In a similar way we would like to present the relation between the compositional diads of the copolymer and the number of T_g observed, *i.e.* heterogeneity of the mixture (Figure 3). If we place in this diagram the points for a series of PMMA-EA samples synthesized at low and 100% conversion, described in our previous work [3,4] and exhibiting only one T_g , we can see that the points for the 100% conversion samples are situated below the respective points for the analogous samples synthesized at low conversion. Moreover, the mixtures studied in this work are also situated below those points due to smaller content of the ME diads, hence higher homogeneity. It would be possible to decrease the probabilities of the mixed diad by decreasing gradually the initial amount of MMA added. The limit $P(\text{ME}) = 0$ can be achieved for a mixture of the two relevant homopolymers, practically equivalent to a dibloc copolymer, exhibiting two distinguished T_g , which was reported for similar system, *i.e.* copolymer of methyl methacrylate and ethyl methacrylate, PMMA-EMM [16]. The respective point would be situated in the middle between the points $P(\text{MM}) = 0$ and $P(\text{EE}) = 0$ at the base of the triangle. The other limit, $P(\text{ME}) = 1$, represents the perfectly alternating copolymer exhibiting obviously one T_g . Therefore, the line drawn between the points for the samples of 100% conversion constitutes the miscibility limit between the samples exhibiting one (above) and two T_g (below the line).

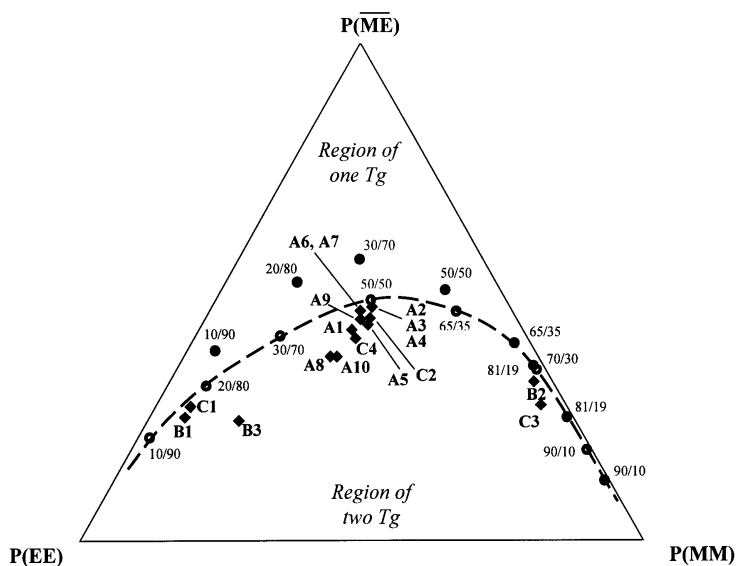


Figure 3. Diagram of diad probabilities for mixtures of PMMA-EA. The dots represent the data for samples of different initial monomer composition [3]; • – ~10% conversion; ○ – 100% conversion.

For the region of noncompatibility, below the miscibility line, the presence of two glass transition temperatures, T_g' and T_g'' , indicates the existence of two phases. This is comparable to the properties of a blend of two partially miscible polymers, as described for example by Kovačić [17], who studied miscibility of poly(vinyl chloride) with terpoly(α -methylstyrene-acrylonitrile-methyl methacrylate). In such a case, for samples very rich in one component, one observes only one T_g (shifted from the original T_g for this pure component towards the T_g of the second component), while for a certain region of composition the system exhibits two T_g . Since we deal here with a copolymer and not the mixture of two homopolymers, such phenomenon can be attributed rather to the presence of macromolecular segments, rich in MM and EE blocks, respectively, than to the chains of pure homopolymers. For the samples of A and B series the first glass transition, T_g' , can be attributed to the phase rich in EE diads, while the second one, T_g'' , at about 100–110°C, to the phase rich in MM diads. The minimum average length of the –MM– blocks required to observe the phase separation could be calculated from the NMR spectra, however, since we deal here with a mixtures of copolymer of varying composition mixed with chains of respective homopolymers this parameter could only be roughly related with the real –MM– block length in the copolymer responsible for phase separation. Nevertheless, it is possible to determine the composition of both the phases. The “apparent” mass fraction, w'_{EE} , of PEA homopolymer in the phase rich in EE diads can be calculated by applying the equation of Fox:

$$w_{EE}' = \frac{T_{g_{EE}}(T_{g'} - T_{g_{MM}})}{T_{g'}(T_{g_{EE}} - T_{g_{MM}})}$$

where $T_{g'}$ is the glass transition temperature of the phase rich in EE diads, $T_{g_{EE}} = -24^{\circ}\text{C}$ for PEA and $T_{g_{MM}} = 120^{\circ}\text{C}$ for PMMA. In an analogous way, the apparent mass fraction of PMMA in the second phase, rich in MM diads, can be calculated from equation:

$$w_{MM}'' = \frac{T_{g_{MM}}(T_{g''} - T_{g_{EE}})}{T_{g''}(T_{g_{MM}} - T_{g_{EE}})}$$

where $T_{g''}$ is the glass transition temperature of the phase rich in MM diads.

It can be seen from the data for the samples of series A (Table 1) that $T_{g'}$ values range from 16.3 to 33.2°C, which corresponds to the PEA mass fraction in the first phase, *i.e.* rich in EE diads, ranging from 0.62 to 0.49. The heat drop of the second transition, $T_{g''}$, for the phase rich in MM diads, is much smaller and less visible, even though it occupies narrower region of temperatures from 100 to 112°C, corresponding to apparent mass fraction of PMMA in the phase rich in MM diads ranging between 0.91 and 0.96.

CONCLUSIONS

The samples of PMMA-EA copolymer can exhibit two T_g transitions. The copolymers of the same global composition can exhibit different miscibility properties, due to different distribution of the comonomers along the macromolecular chains. The separation of the second phase is mainly due to the small miscibility of long MM blocks with the copolymer chains, while the long EE segments are well miscible with the copolymer. So, when the copolymer is synthesized in such a way that formation of long MM segments is possible, it can exhibit a second T_g . A triangular diagram can be used to visualise the existence of a relation between the number of observed transition temperatures and probabilities of compositional diads, especially the heterodiad, ME. NMR data on the distribution of compositional sequences in the copolymer can, therefore, provide complementary information to the DSC technique in the studies of polymer miscibility.

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