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ORIGINAL CONTRIBUTION

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Miscibility as a function of copolymer composition in blends of a random copolymer and a homopolymer

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Abstract Random copolymers of *n*-butyl acrylate (BA) and cyclohexyl acrylate (CHA) were synthesized by solution polymerization in cyclohexane. Blends of polystyrene with the poly(CHA-*stat*-BA) copolymers were prepared by solvent casting and coprecipitation. The miscibility of the blends was characterized by means of differential scanning calorimetry. While blends with a low content of CHA in the copolymer showed two characteristic glass-transition temperatures of the corresponding blend components, those with a CHA content higher than 70% presented good compatibility. Phase separation of the miscible blends took place after annealing at 200 °C for 1 h, which implies an upper miscibility gap (lower critical solution temperature).

Keywords Blend · Random copolymer · Glass-transition temperature · Compatibility · Differential scanning calorimetry

Introduction

Polymer blends show the phase behavior of an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST), which depend on the chemical structure, the segmental interactions and the molecular weight of the mixed polymer pairs [1, 2, 3]. Although two homopolymers may be incompatible with each other, compatible blends can be achieved from their copolymer pairs [2]. For example, despite the fact that miscible blends of high molecular weight polymers cannot be obtained from any two of these four homopolymers, polybutadiene, polystyrene (PS), poly(vinyl chloride) and poly(vinyl acetate), compatibility has been observed in a blend consisting of poly(butadiene-*co*-styrene) and poly(vinyl chloride-*co*-vinyl acetate). This has been interpreted as the ''repulsion effect'' amongst the comonomers in the same polymer chains. It is this repulsive interaction that favors the mixing of polymer segments with the segments of the other blend component.

Another way is to design blend systems with adjustable segmental interactions via random copolymerization of compatible and incompatible monomers (with

respect to the second polymer). Using the blend system of PS and poly(cyclohexyl acrylate-*stat*-butyl methacrylate) [poly(CHA-*stat*-BMA)], the Flory–Huggins χ parameter and its temperature dependence were determined by neutron scattering techniques, and furthermore with respect to the composition of the random copolymerLCST or UCST behavior could be predicted [4]. The spinodal decomposition of the same blend system by temperature-jump experiments was investigated later [5].

It is known that poly(CHA) is miscible with PS over a large range of temperature and composition [4] and their blends show an UCST. Poly(butyl acrylate) Poly(BA)) shows miscibility with PS only when the degree of polymerization is very low. We were interested in investigating the phase behavior of PS with random copolymers of CHA and BA as a function of the copolymer composition. Through a systematic change of the repulsive segments, the compatibility of the blend partners is affected. As a probe for miscibility the glass transition was investigated by means of differential scanning calorimetry (DSC).

Experimental

Methods

Differential scanning calorimetry

DSC measurements were performed with a PerkinElmerDSC 7 thermoanalyser. The block temperature was kept at −110 °C. Calibration was done according to standard procedures. For each sample of blends and individual copolymers three scans at heating rates 40, 30 and 20 °C min^{-1} were measured from −75 to 145 °C. The transition temperatures were values extrapolated to the heating rate at 0 °C min^{-1}.

Size-exclusion chromatography

The molecular weights and the polydispersity index of the homopolymers and the copolymers were determined by size-exclusion chromatography (SEC) in tretrahydrofuran (THF) at 40 °C. All measurements were done on an instrument equipped with PLGel columns (Bischoff). The refractive index and UV absorption were monitored with a differential refractometer and a UV detector (Waters). Calibration was done with PS.

^{1}H NMR spectroscopy

The measurements were carried out using a BrukerAC-200 spectrometer and $CDCl_3$ solutions.

Fourier transform IR spectroscopy

Fourier transform (FT)-IR spectroscopy was used to characterize the CHA synthesized at a resolution of 4 cm^{-1} using a Bruker IFS 48 spectrometer.

Preparation procedures

Materials

AIBN butyl acrylate, acrylic acid chloride and cyclohexanol were products of Fluka, Germany. PS with $M_n = 100{,}000$ was obtained by anionic polymerization in THF using *s*-butyl lithium as the initiator.

Preparation of CHA via acylation

To a 250-ml three-necked flask equipped with a stirrer, a thermometer, an ice–salt bath and a dropping funnel was added a solution of 0.25 mol acrylic acid chloride and 50 ml toluene and a small spoonful of Cu_2Cl_2 as the inhibitor for radical polymerization. An equimolar amount of cyclohexanol (0.25 mol) was added over 2 h from the funnel into the flask. The temperature was kept below 0 °C by controlling the speed of dropping. The reaction solution was maintained at the bath temperature for an additional 2 h after the addition and then at room temperature for 6 h. The reaction mixture was poured into distilled water to wash away HCl and then distilled under vacuum. A colorless liquid with a boiling point at 70–72 °C/15 mbar was obtained. The chemical structure (Scheme 1) was confirmed by FT-IR at 1,618 and 1,632 cm^{-1} for $\nu_{C=C}$ and 1,706 cm^{-1} for $\nu_{C=O}$, respectively, and ^{1}H NMR at 1.5–2.0 (10H^a, m), 4.68 (1H*, m), 5.74–6.54 (3H^b, m).

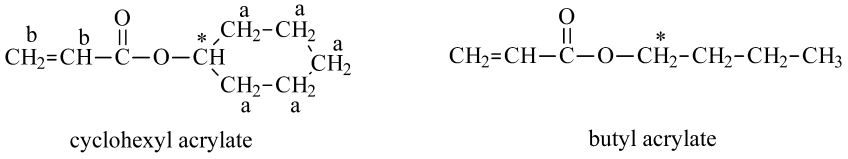
Solution polymerization/copolymerization of BA and CHA

Solution polymerization was used to copolymerize CHA with BA. AIBN was used as the initiator and cyclohexane as the solvent. The monomer content amounted to 20 wt% in the solution. The solution of the initiator and monomers in cyclohexane was added to a round-bottomed flask which was bathed in oil and equipped with a reflux condenser, an inlet of nitrogen gas and a magnetic stirrer. The reaction mixture was flushed with nitrogen gas for 5 min before heating. The reaction temperature was kept at 65 °C. After 7–8 h the polymers were precipitated from the reaction solution by methanol and then purified by dissolving and precipitating several times. The polymers were finally freed from solvent at 60 °C under vacuum for 8 h and were characterized by SEC.

Kinetics of copolymerization

Because the purpose of the present study was to investigate the segmental interactions through characterization of the phase behavior, it was essential that the copolymers be random, i.e., the monomer ratio in the copolymer should be identical throughout the polymerization reaction.

Scheme 1



In a copolymerization, the reactivity ratios of radicals of different monomers (r_1,r_2) determine the composition of the copolymer. For an ideal copolymerization of two different kinds of monomers ($r_1 = 1/r_2$), the propagating radicals show the same preference for adding one of the monomers over the other. In the special case of $r_1 = r_2$ the composition of the resulting copolymer, F, has the same ratio of monomer units as the feed ratio of the monomers, f. Only in this case random copolymers with the same composition are formed through the whole conversion. In this case the f–F plot appears as the diagonal. For other cases such as $r_1 > 1, r_2 > 1$, or $r_1 < 1, r_2 < 1$, the composition of the resulting copolymer has different values as the polymerization proceeds, unless the so-called azeotropic point is chosen, at which the f–F curve crosses the diagonal. When the feed ratio corresponds exactly to the azeotropic point, the copolymer composition will be equal to the monomer feed ratio. Otherwise, different copolymer compositions are expected at different conversions during the copolymerization.

In the NMR spectra, the signals of the two protons of BA (labeled with an asterisk in Scheme 1) and the single proton in CHA appear apart from each other. The former is a triplet at 4.02 ppm and the latter a multiplet centered at 4.68 ppm. Their ratio represents the relative amount of the monomer units in the copolymer. The monomer ratio of BA to CHA in the copolymer was calculated by area integration.

The feed molar ratio of CHA to BA was selected as 2:1. This corresponds to the ratio 1:1 of the integrated area at 4.02 and 4.68, respectively. The polymerization reaction was carried out at a bath temperature of 65 °C. Sampling of a 2 ml solution took place every 15 min, with the first sampling 35 min after the flask had been dipped into the bath. The samples were then precipitated into methanol and dried for NMR measurement. Conversion as a function of polymerization time is plotted in Fig. 1.

NMR spectra were obtained for each sample; however, for the first two samples no spectra could be obtained owing to the small amounts. For samples 3–8 an identical ratio of the signals for BA and CHA, i.e., 1:1 from their NMR spectra was obtained. This indicates that the composition of the copolymer was the same as that of the feed ratio throughout the polymerization. From this we conclude that a random polymerization mechanism is most probable, because it is very unlikely to have chosen the azeotropic composition of a nonideal system. The molecular characteristics of the homopolymer of BA and its copolymers with CHA are listed in Table 1.

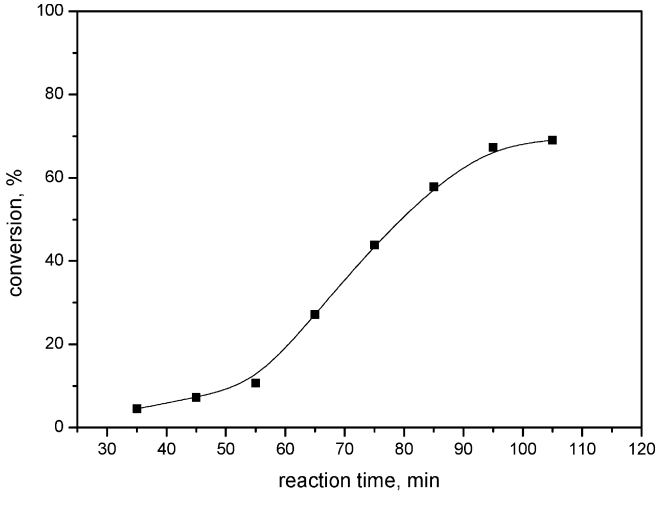


Fig. 1 Sample weight at different times of reaction

Table 1 Molecular characteristics of the copolymers

Polymer	Cyclohexyl acrylate molar content (%)	*n*-Butyl acrylate molar content (%)	M_w	M_w/M_n
CHA-BA00	0	100	68,288	1.363
CHA-BA15	15	85	80,017	1.632
CHA-BA30	30	70	86,524	1.735
CHA-BA50	50	50	67,158	1.828
CHA-BA60	60	40	60,425	2.006
CHA-BA70	70	30	81,426	3.455
CHA-BA80	80	20	78,699	1.870
CHA-BA90	90	10	75,922	1.909
CHA-BA100	100	0	35,651	1.440

Preparation of polymer blends

Toluene was used as the solvent in this study. Copolymer of acrylates (0.5 g) and PS (0.5 g) were dissolved in 15 ml toluene and cast into a Teflon petri dish. A diaphragm pump was used first to strip the solvent, as toluene evaporates very slowly at room temperature owing to its high boiling point. After 72 h the dishes were put into a vacuum oven at 60 °C for 60 h. The films obtained were then used for DSC measurement.

For blends B-1, B-2 and B-3 no proper solvent was found to obtain a homogeneous film. They were prepared by coprecipitation. For that purpose 0.5 g copolymer and 0.5 g PS were dissolved in THF. Excessive water was then added to the polymer solution from a dropping funnel. The precipitate was dried with a diaphragm pump at 60 °C for 60 h and then placed in a vacuum oven at 60 °C for 60 h. The polymer blend was isolated as a white fibrous solid.

DSC results and discussion

Glass-transition temperatures of copolymers

The glass-transition temperatures, T_g, of the copolymers are presented in Table 2. The T_g of PS was obtained from Ref. [6]. The T_g values of the copolymers were in good agreement with those calculated using Fox's equation [7] (Eq. 1) and increased with CHA content (Fig. 2).

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \tag{1}$$

where w_1 and w_2 represent the weight fractions of the respective polymer components. Note that the Fox equation is a special case of the Gordon–Taylor equation [8]

$$T_g = \frac{(w_1 T_{g1} + K w_2 T_{g2})}{(w_1 + K w_2)}, \tag{2}$$

with $K = 1$.

Table 2 Glass-transition temperatures, T_g, of the copolymers

Copolymer	Cyclohexyl acrylate molar content (%)	Cyclohexyl acrylate content (wt%)	T_g calculated (°C)	T_g found (°C)
CHA-BA00	0	0	−54.0	−47
CHA-BA15	15	17.5	−44.0	−43
CHA-BA30	30	34.0	−33.7	−35
CHA-BA50	50	54.6	−19.4	−19
CHA-BA60	60	64.3	−12.1	−14
CHA-BA70	70	73.7	−4.5	−4
CHA-BA80	80	82.8	3.2	1
CHA-BA90	90	91.5	11.0	12
CHA	100	100	19.0	20

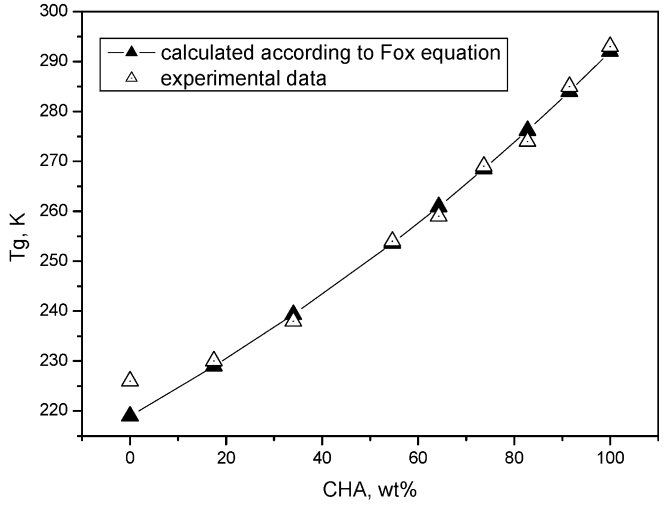


Fig. 2 Dependence of glass-transition temperature dependence on cyclohexyl acrylate (*CHA*) composition

Compatibility of blends

The T_g values of the blends obtained by DSC together with the T_g values calculated according to Eq. (1) for the blends showing only one T_g during the first scan are presented in Table 3. The DSC traces of B-1, B-2 and B-3 showed two characteristic T_gs of the corresponding blend components CHA-BA00, CHA-BA15, CHA-BA30 and PS during the first scan. However, by carefully examining the two T_gs, it was noticeable that the differences between the two T_gs were becoming smaller. The blend of poly(-BA) with PS (i.e., CHA-BA00 + PS, B-1) gave two T_gs of the characteristic blended components of poly(BA) at −49 °C and PS at 102 °C, respectively, showing phase separation. For the first T_gs of B-2 and B-3 at lower temperatures, the values were obviously higher than those of pure random copolymers, though the T_g of PS remained almost unchanged. This may indicate that some PS is mixed in the CHA-BA phase.

Table 3 Composition and T_g of the blends

Blend	Composition	T_g(°C)	T_g calculated results (°C)
B-1[a]	CHA-BA00 + PS	−49, 102	–
B-2[a]	CHA-BA15 + PS	−38, 106	–
B-3[a]	CHA-BA30 + PS	−28, 100	–
B-4[a]	CHA-BA50 + PS	46	28.9
B-5[a]	CHA-BA60 + PS	45	34.0
B-6	CHA-BA70 + PS	34	39.2
B-7	CHA-BA80 + PS	36	44.4
B-8	CHA-BA90 + PS	38	49.5
	PS	–	100.0

[a] T_g at heating rate 40 °C min^{-1}

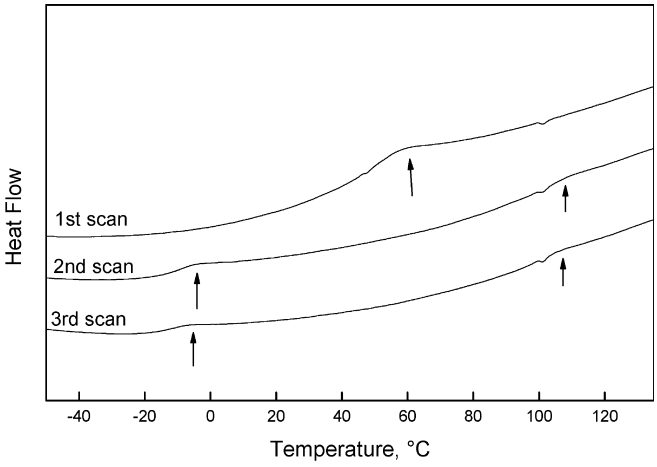


Fig. 3 Differential scanning calorimetry (*DSC*) traces for B-4: first scan at 40 °C min^{-1}, second scan at 30 °C min^{-1} and third scan at 20 °C min^{-1}. *Arrows* represent the glass transition

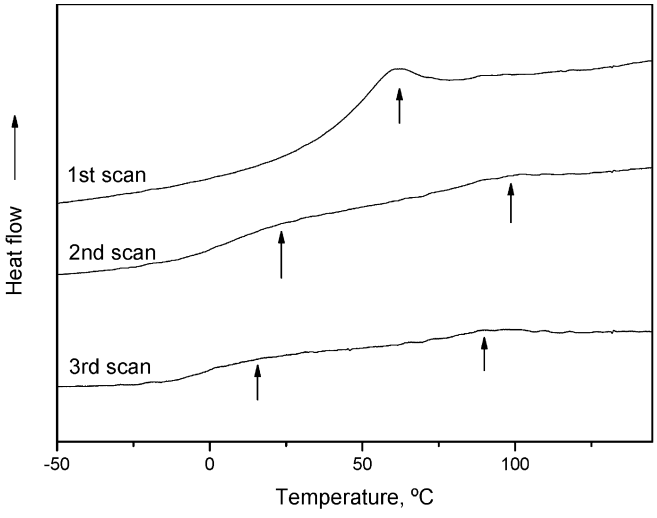


Fig. 4 DSC of B-5: first scan at 40 °C min^{-1}, second scan at 30 °C min^{-1} and third scan at 20 °C min^{-1}. *Arrows* represent the glass transition

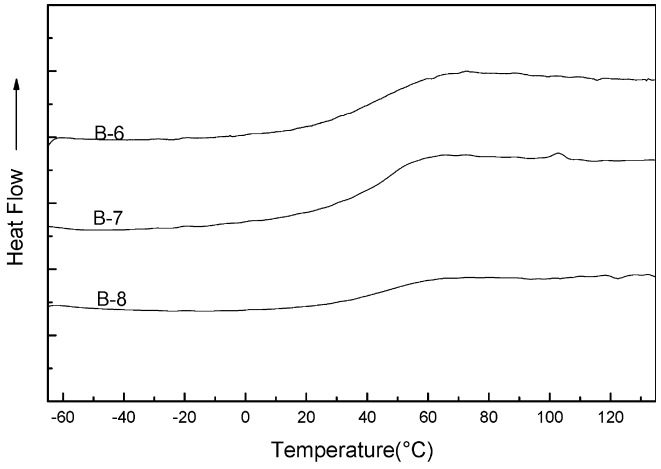


Fig. 5 DSC traces of B-6, B-7 and B-8 at a heating rate of 30 °C min^{-1}

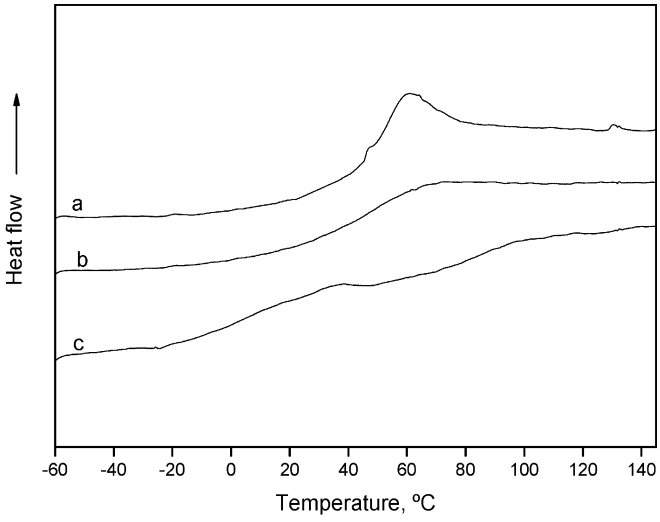


Fig. 6 DSC traces for B-6 at 40 °C min^{-1}. First scan (*a*); after 1 h at 145 °C (*b*); after 1 h at 200 °C (*c*)

For blends B-4 and B-5 there was only one glass transition in the first scan (heating rate 40 °C min^{-1}). In the second and third scan two glass transitions appeared in the thermograms (Figs. 3, 4). This indicated that phase separation was induced by increasing the temperature during the DSC measurements. For blends B-6, B-7 and B-8 there was only one transition temperature throughout the three scans. shows The DSC curves at a scan rate of 30 °C min^{-1} for B-6, B-7 and B-8 are shown in Fig. 5. In order to check if the blends are compatible at higher temperatures, B-6, B-7 and B-8 were then kept for 1 h at the final temperature of 145 °C after the third scan and were measured once more. Still only one glass transition at the same temperature in the DSC traces was observed for the three samples B-6, B-7 and B-8 as during the first scan. This indicated that stable blends of PS with poly(CHA-*stat*-BA) can be achieved and the compatibility remained even at temperatures well above the T_g of the blend components, when the content of CHA in the random copolymers exceeded 70%. After B-6, B-7 and B-8 were annealed at 200 °C for 1 h, all the three samples showed two T_gs (Fig. 6). Thus B-4, B-5, B-6, B-7 and B-8 may be systems showing LCST behavior.

Taking the random copolymers of CHA and BA as "homopolymers" and calculating the T_g for the miscible blends B-6, B-7 and B-8 using Eq. (1), which was originally developed for pure random copolymers and not for blends (Table 3), the calculated values were higher than those found by DSC measurement. This means there was a negative deviation from the heterocontact formation of the additivity of the T_gs. Such a negative deviation from the additivity rule has also been described by Kanig [9] using a thermodynamic treatment for the influence of plasticizers on the T_g. Following Kanig's theory, which, by the way, was also used for random copolymers and includes the Fox and Gordon–Taylor equations as special cases [10], a negative deviation from a linear composition dependence as expressed by the Fox–Flory equation occurs when the different blend partners have less favorable energetic interactions with each other. This means that the energy of a heterocontact, E_{AB}, is less than the arithmetic mean of the corresponding pair of homocontacts, E_{AA}, E_{BB}:

$$E_{AB} < \frac{E_{AA} + E_{BB}}{2}. \tag{3}$$

According to Schneider's findings [11], the experimental T_g versus composition data of miscible polymer blends can be accounted for by two parameters: K_1 and $K_2.K_1$ accounts for energetic interaction effects and is correlated with the difference of the solubility parameters of the blended components, and K_2 is related to changes in the conformational entropy:

$$\begin{aligned}\Delta T_g &= T_{g\,\text{blend}} - T_{g\,\text{Fox}} \\ &= \left(T_{g1} - T_{g2}\right)\left[K w_{2c} - (K_1 + K_2) w_{2c}^2 + K_2 w_{2c}^3\right],\end{aligned} \tag{4}$$

where T_{g2} is the glass temperature of the component with the higher T_g and w_{2c} is the weight fraction of that component which is corrected for additivity of the T_gs, $w_{2c} = w_2 T_{g1}/(w_1 T_{g2} + w_2 T_{g1})$.

Equation (4) can be reformulated to

$$\Delta T_g / \left(T_{g2} - T_{g2}\right) = w_{2c}(1 - w_{2c})(K_1 - w_{2c} K_2). \tag{5}$$

Since $w_{2c} < 1$, for the negative deviation, i.e., $\Delta T < 0$, it follows that $K_1 < K_2$. This means that the energetic contributions of the conformational mixing

entropy caused by conformational rearrangements are larger than the difference between interaction energies of the heterocontacts and homocontacts [11]. Furthermore, there may exist a positive difference of the solubility parameters between the blend component with higher T_g(PS) and that with lower T_g(poly(CHA-*stat*-BA), i.e., $(\delta_{PS}-\delta_{CHA\text{-}stat\text{-}BA})>0$, according to Schneider's prediction. For blends B-4 and B-5, it seems that a positive deviation of measured T_gs from the calculated ones existed. However, the T_gs in Table 3 for B-4 and B-5 were obtained from the first scan. They were phase-separated during the second scan. This means that the initially measured single T_g corresponds to a kinetically frozen-in, but thermodynamically unstable, single phase. Therefore a comparison between the calculated and measured T_gs for B-4 and B-5 is not reasonable.

Conclusions

The copolymerization of CHA with BA obeys a random mechanism. Blends of PS with poly(CHA-*stat*-BA) were stable even at 145 °C, when CHA units in the random copolymers exceeded 70%. At 200 °C phase decomposition occurred in all the blends, implying that this blend system shows LCST behavior. The negative deviation of the glass temperatures for the miscible blends from the additivity indicates that there may be attractive interactions and favorable sterical factors between PS segments and those of the random copolymers.

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