Charge-Transfer Interactions in Copolymer Blends. 3. Poly[(*N*-ethylcarbazol-3-yl)methyl methacrylate-*co*-styrene] Blended with Poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate-*co*-methyl methacrylate]

Mark C. Piton and Almeria Natansohn*

Department of Chemistry, Queen's University, Kingston, ON, K7L 3N6 Canada

Received July 20, 1994[⊗]

ABSTRACT: Polymer blends containing the title random copolymers were prepared in which the monomers (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM) and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBM) were introduced to induce compatibility between polystyrene (PS) and poly(methyl methacrylate) (PMMA) by providing charge-transfer (CT) interactions within the copolymer blends. NECMM to DNBM mole ratios were unity in all of the blends. The compatibilities of the blends were determined by differential scanning calorimetry (DSC). The closeness of the copolymer glass transition temperatures at low mole percentages of NECMM and DNBM prevents the determination of the minimum amounts of donor and acceptor groups necessary to compatibilize PS with PMMA using these copolymers. Consequently, blends containing 13 and 24 mol % donor and acceptor appeared to be thermodynamically compatible. Blends with more than 24 mol % are both kinetically and thermodynamically incompatible with the exception of two blends: samples with 28 and 60 mol % are kinetically compatible and phase separate upon heating past 200 °C. Blends with more than 28 mol % donor and acceptor exhibit endothermic transitions at approximately 195 °C in their DSC scans. The presence of these does not correlate with lower critical solution temperatures but is consistent with the relaxation of conformationally-constrained polymers within the blends.

Introduction

In the first two papers in this series,[1,2] we investigated the blending behavior of two random copolymers in which charge-transfer (CT) interactions had been introduced by using an electron donor (D), either (*N*-ethylcarbazol-3-yl)methyl methacrylate or acrylate (NECMM or NECMA) as one comonomer and an electron acceptor 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBM) as another comonomer. An interesting feature of these two monomers is that blends of homopolymers of NECMM and DNBM undergo phase separation at a lower critical solution temperature (LCST) of about 185 °C.[3,4] Microscopic evidence has also been presented that indicates that a LCST exists at around the same temperature for blends of poly(NECMA) and poly(DNBM).[5] This LCST behavior is believed to be initiated by the decomplexation of the donor–acceptor pair.[3,4] In some cases, our copolymer blends exhibited a similar behavior.[1,2]

In the first study,[1] we investigated copolymer blends containing poly(NECMM-*co*-MMA) as the donor copolymer, where MMA is methyl methacrylate, and poly(DNBM-*co*-MMA) as the acceptor copolymer. The "trivial" blending of MMA with MMA was chosen as a simplified system in which many intermolecular and intramolecular interactions cancel one another so that it is possible to determine more easily the effects of the copolymer composition and molecular weight of the components on blend compatibility. We found that with a sufficient mole fraction of donor and acceptor groups, one can actually render MMA thermodynamically incompatible with MMA if a small fraction of the molecular weight distribution of the acceptor copolymer exceeds some critical molecular weight. Furthermore, we postulated that the concomitant existence of endothermic absorptions at the decomplexation temperature and the absence of detectable phase separation within the sample were due to the reorganization and release of conformationally-constrained polymer chains and/or polymer segments once the CT pairs dissociated.[1]

In the second paper,[2] the structure of the donor copolymer was changed in two ways. First, poly(NECMM-*co*-MA)/poly(DNBM-*co*-MMA) blends were prepared, effectively replacing MMA with methyl acrylate (MA) in the donor copolymers, so that CT interactions would be used to compatibilize the incompatible pair PMA/PMMA. The compatibilities of the blends were also compared to those of poly(NECMA-*co*-MA)/poly(DNBM-*co*-MMA), blends in which NECMM was substituted by its acrylate analogue, (*N*-ethylcarbazol-3-yl)methyl acrylate (NECMA). We reported that, in the poly(NECMM-*co*-MA) blends, samples that had high donor and acceptor fractions were incompatible while there existed intermediate compositions that were compatible. Unfortunately, the closeness of the copolymer T_g's rendered the results of the poly(NECMA-*co*-MA)/poly(DNBM-*co*-MMA) blends inconclusive at high donor and acceptor compositions. However, both sets of copolymer blends were thermodynamically compatible at intermediate compositions but incompatible at low mole fractions. Since the poly(DNBM-*co*-MMA) copolymers were identical to those in the first set of studies,[1] the incompatibility at high mole fractions of NECMM in the poly(NECMM-*co*-MA) blends was attributed to the molecular weight distribution of the acceptor copolymers.

In the present work, blends are presented which contain random copolymers of poly(NECMM-*co*-S), where S is styrene, and poly(DNBM-*co*-MMA) to study the compatibilization of PS with PMMA. The effects of blend composition and decomplexation of the CT pairs on the compatibilization are reported.

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* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, February 1, 1995.

0024-9297/95/2228-1605$09.00/0

Table 1. Results for the Copolymerizations of NECMM With Styrene

sample	initial feed, mol % NECMM	conversion, %	composition, mol % NECMM
C1	10	54	13
C2	20	63	24
C3	30	68	28
C4	40	70	38
C5	50	57	47
C6	65	57	60
C7	75	86	73
C8	90	50	80

Experimental Section

Styrene (Aldrich) was distilled under vacuum immediately prior to use. Monomers (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM)[1] and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBM)[6] and homopolymers[7] were synthesized according to literature procedures. The preparation and characterization of the poly(DNBM-*co*-MMA) copolymers used in this study have already been reported.[2,8] The poly(NECMM-*co*-S) copolymers were prepared by free-radical copolymerization as previously described.[1,2] Total monomer concentrations were 0.5 M and the initiator AIBN (2,2′-azobis(2-methylpropionitrile), Aldrich) was used at concentrations of 1% by weight relative to that of monomer. The solutions were degassed with nitrogen and then sealed in ampules which were heated at 70 °C for several days. Copolymers compositions were determined by solution ^{1}H-NMR using a Bruker AC/F-200 spectrometer in $CDCl_3$ (Aldrich, 99.8 atom % D) at 298 K.

The determination of the molecular weight distributions was performed by gel permeation chromatography (GPC) in THF at room temperature using polystyrene standards.[1] The copolymer blends were prepared as before[1] by precipitation from 2–5% solutions in hot THF into at least a 10-fold excess of MeOH. The samples were then filtered and dried for 48 h at room temperature under reduced pressure. All of the blend samples had D/A mole ratios of unity. For the sake of convenience, references to the mole fractions of the donor and acceptor in each sample are to those of the donor. For each blend sample, three DSC scans were performed at a scanning rate of 20 °C min^{-1}: 0–170 °C, 0 to approximately 240 °C (prior to the onset of decomposition), and 0–280 °C. T_g's before decomplexation and enthalpies of decomplexation, ΔH_1, were determined from the second scans and T_g's after decomplexation were determined from the third scans. (Decomplexation is the dissociation of the electron donor–acceptor complexes present in the blends which leads to separate donor-rich and acceptor-rich phases.[4])

Results and Discussion

The results for the copolymerizations are summarized in Table 1. Analysis of the data using the high-conversion Kelen–Tüdös method[9] gives $r_{NECMM} = 0.35$ and $r_S = 0.58$. The GPC molecular weight distributions of the donor copolymers are presented in Figure 1. The distributions are similar to one another and to the ones for the poly(NECMM-*co*-MMA)[1] and poly(NECMM-*co*-MA)[2] copolymers. The compatibility of homopolymer[3,10] and copolymer[2,3] blends involving CT interactions between NECMM and DNBM has been shown to depend on the molecular weight of the components. However, since the molecular weights of the present donor copolymers are similar to those in the previous studies, and since the acceptor copolymers are identical, it is appropriate to compare the present blend studies to those already reported.[1,2]

The glass transition temperatures (T_g's) of the copolymers and blends were determined by DSC. The composition of each of the blends is summarized in Table 2. Figure 2 shows the variation in T_g with donor and acceptor content. Analysis of the T_g data for the donor copolymers using the Kwei equation,[11]

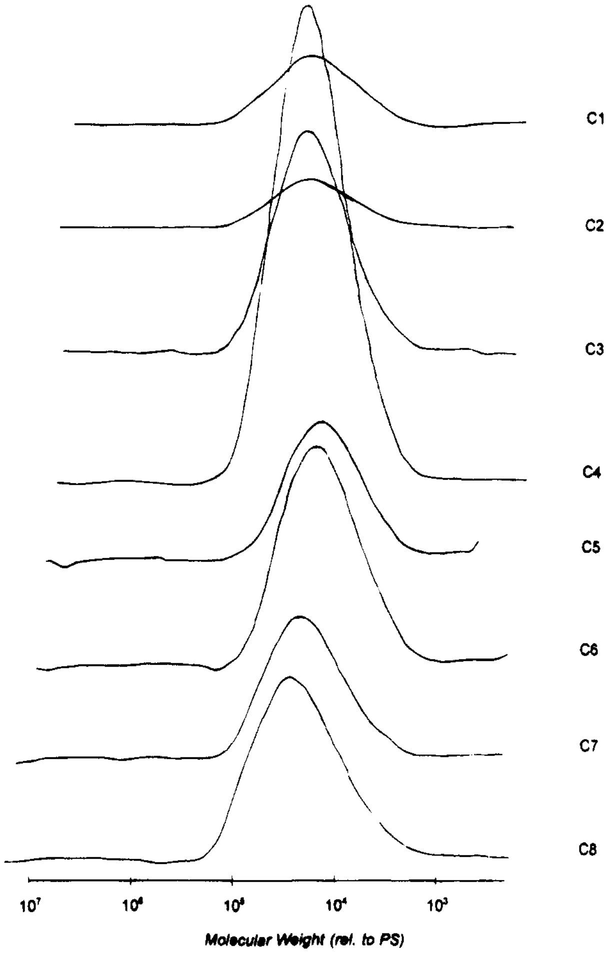

Figure 1. GPC distributions for poly(NECMM-*co*-S) copolymers. The molecular weights on the *x*-axis are for PS.

Table 2. Composition of Each of the Copolymer Blends

	poly(NECMM-*co*-S)		poly(DNBM-*co*-MMA)	
blend	sample	mol % NECMM	sample	mol % DNBM
AB1	C1	13	A2	12
AB2	C2	24	A4	27
AB3	C3	28	A4	27
AB4	C4	38	A6	42
AB5	C6	60	A7	57
AB6	C7	73	A9	72
AB7	C8	80	A10	90

$$T_g = \frac{w_1(T_{g1} - kT_{g2}) + kT_{g2}}{w_1(1 - k) + k} + q(w_1 - w_1^2) \quad (1)$$

where T_{gi} is the glass transition temperature for homopolymer *i*, w_1 is the weight fraction of structural unit 1 in the copolymer, and *q* and *k* are fitting parameters, shows that the data are consistent with the trivial case $q = 0$ and $k = 1$. Since the T_g data are simply the weighted average of the homopolymer T_g's, one can conclude that repulsions or attractions between NECMM and styrene, if they exist, are exceedingly small.[11] Previously, we reported that $q \approx 0$ for the acceptor copolymers[1] as well, so that significant intramolecular forces are absent in both copolymer series.

The T_g's of the blends before heating above 200 °C are shown in Figure 3 as a function of the donor and acceptor content of each blend. Each of these was

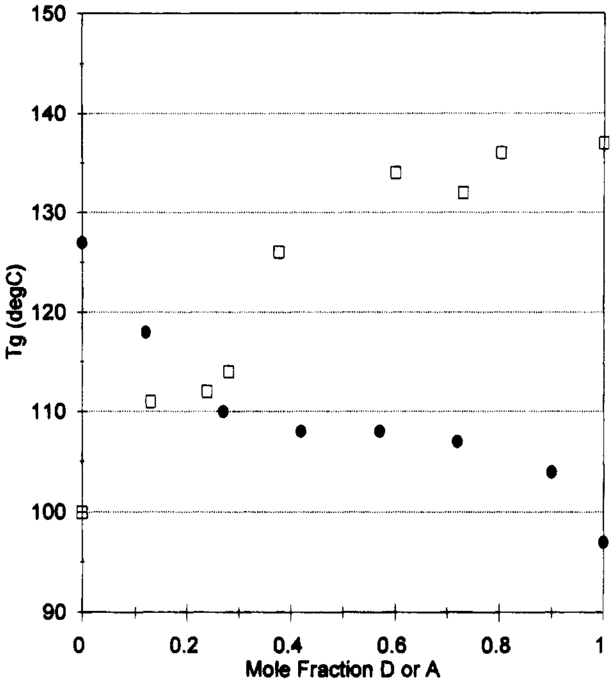

Figure 2. T_g's of the donor (□) and acceptor (●) copolymers plotted versus composition for the copolymers.

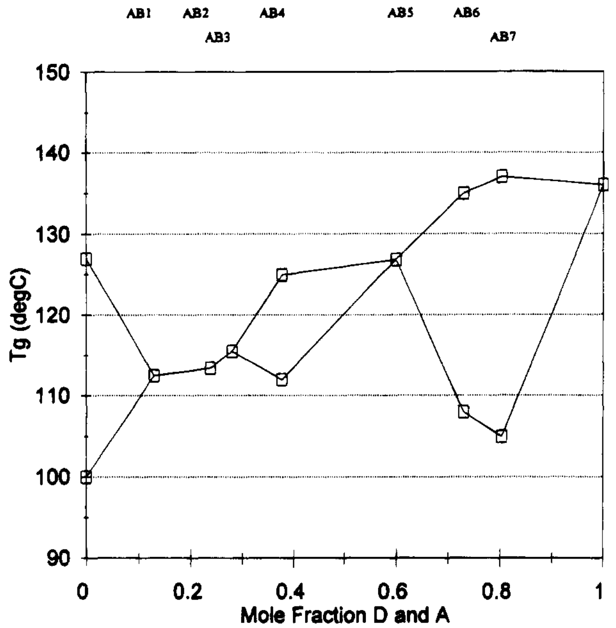

Figure 3. T_g's of the blends *vs* composition for the blends *before* heating above 200 °C.

determined from each of the second DSC scans. Examples of the DSC scans are shown in Figure 4. An inspection of the data in Figure 3 reveals some interesting features. Blends AB1, AB2, and AB3 appear to be compatible since each sample possesses a single T_g. A comparison of the T_g's with those of the copolymers (Figure 2) shows that the crossover in the curves in Figure 2 occurs at approximately the same composition in these blends. Consequently, their compatibility is unclear by DSC. AB4, AB6, and AB7 are clearly incompatible since each blend displays two T_g's. Most interesting is the compatibility of blend sample AB5, which is flanked by incompatible blends at both lower and higher donor and acceptor mole fractions.

Many other NECMM/DNBM-containing polymer blends reported in the literature exhibit endothermic transitions attributed to LCSTs at around 185–200 °C,[1,2,4,7] behavior believed to be initiated by the decomplexation of the D–A pairs in the polymer blend.[4] In Figure 4, this type of behavior can be seen quite clearly. The sample (AB5) exhibits a single T_g and an endothermic transition around 195 °C in scan (a). The presence of two T_g's in the subsequent scan (b) shows that the sample has phase separated. Also, there is no thermal absorption around 195 °C in scan (b) as there is in (a). While samples AB3 and AB5 were the only samples to exhibit this type of LCST behavior, all of the samples with more than 28 mol % donor and acceptor exhibited thermal absorptions around 200 °C similar to those in Figure 4a.

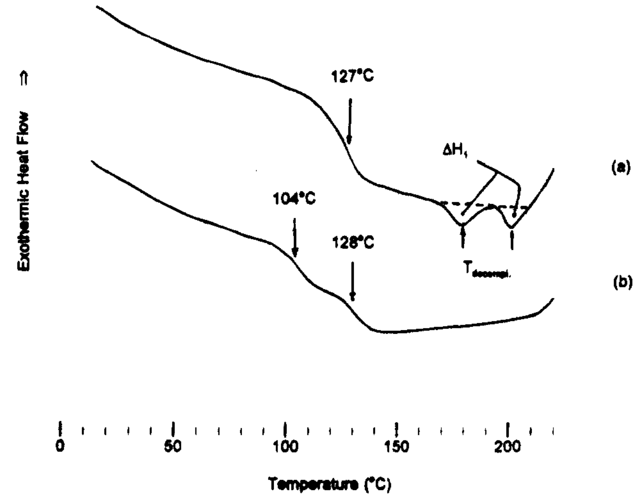

Figure 4. Second (a) and third (b) DSC scans for sample AB5. The presence of a single T_g in (a), prior to heating above 200 °C, and two T_g's after heating above 200 °C (b) is indicated.

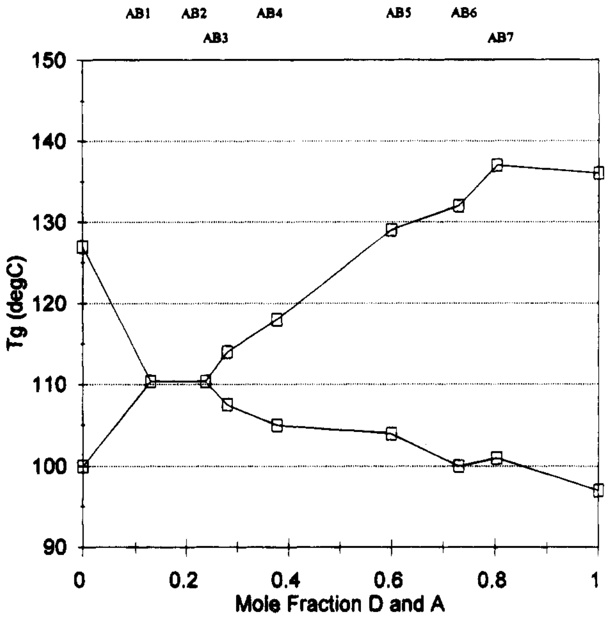

Figure 5. T_g *vs* composition for the blends *after* heating above 200 °C.

Figure 5 shows the T_g results taken from the third scan. After heating past 200 °C, only two samples phase separated: AB3 and AB5. These samples are therefore compatible kinetically but not thermodynamically.[10] The result of this is that only samples AB1 and AB2 appear to be compatible and that beyond 13–24 mol % D and A all are thermodynamically incompatible.

Unlike previous blend series,[1,2] the endothermic transitions attributed to the decomplexation process in

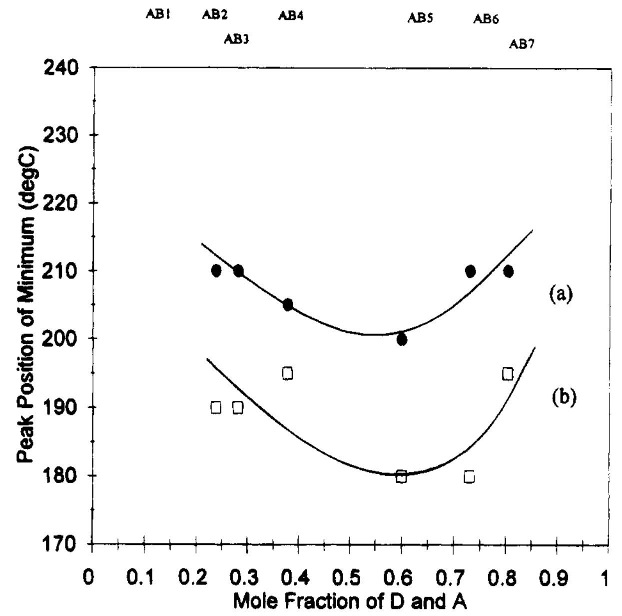

Figure 6. Temperature of the endotherms from the second scans versus composition for the blends. Only the endotherms that were easily identified have been plotted.

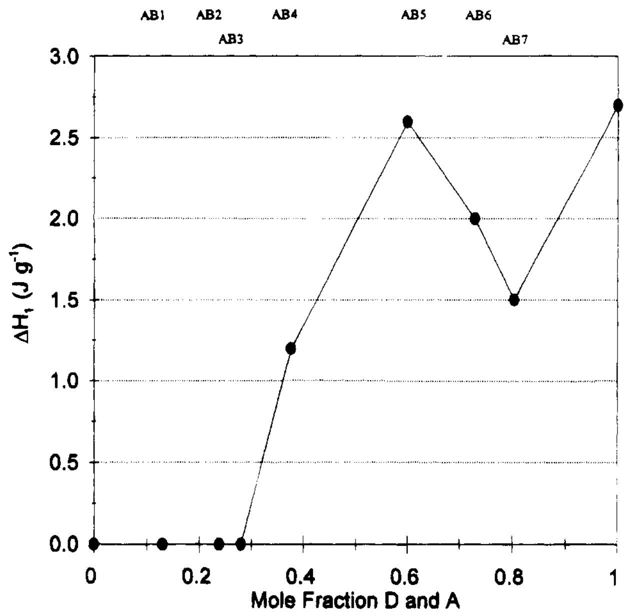

Figure 7. Decomplexation enthalpies ΔH_1 for the blends, determined from the second DSC scans. Each point has a nominal uncertainty of ±25%.

the second scans appear to consist of two overlapping transitions. This would seem to indicate that two decomplexation mechanisms may be at work although we have no further evidence for this other than the consistent appearance of the double-peaked endotherms. This is quite apparent in Figure 4a where minima lie at approximately 180 and 200 °C. The temperature dependence of these minima is presented in Figure 6. The two sets of data each possess a minimum at approximately 60 mol % donor and acceptor. This lies, perhaps serendipitously, at a composition close to that of sample AB5 which possesses an LCST. However, since only one other sample exhibited an LCST (AB3), and since there may be two or more mechanisms at work here, it is difficult to draw any significant conclusions regarding the temperature dependence(s) shown in the figure.

The integrals containing both endothermic transitions have been taken to be the enthalpy of decomplexation, ΔH_1. The results are presented in Figure 7 as a function of the composition of the blends. As before,[1,2] ΔH_1 increases with donor and acceptor content in the blends. Also, the magnitudes of the transitions are comparable to those previously reported.[1,2] The appearance of nonzero values for ΔH_1 which do not correlate with phase changes is consistent with the interpretation that constrained conformations are created when the polymer chains associate with one another in the blending process or, in our case, during the precipitation process.[1] Once the CT pairs have been disrupted, the polymer chains are free to move independently of one another. Upon cooling, the chains are free to move as the CT pairs re-form, but this time, since the re-complexations occur above the T_g of the copolymers, there are many fewer unfavorable chain conformations. The subsequent DSC scan will then contain the T_g for a truely annealed sample.

In summary, blends have been prepared that utilize CT interactions between NECMM and DNBM to compatibilize blends of PS and PMMA. As little as 13 mol % of donor and acceptor groups may be needed to accomplish this, although this number may be misleading due to the overalp of the copolymer T_g's in this composition region. However, unlike the previous cases reported in ref 1 and 2, the CT interactions produce a very complicated dependence of compatibility on composition. One blend, AB5 (60% donor and acceptor), is particularly unusual since it is kinetically compatible but phase separates after heating the sample beyond its LCST. Sample AB3 also exhibits this behavior, but there is some uncertainty in the interpretation due to the closeness of the T_g's of the copolymers that make up the blend.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support for this work and NSERC Canada. We also thank G. Crone and E. Russell for the preparation of the acceptor copolymers.

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MA941216M