Charge-Transfer Interactions in Copolymer Blends. 1. Poly[(*N*-ethylcarbazol-3-yl)methyl methacrylate-*co*-methyl methacrylate] Blended with Poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate-*co*-methyl methacrylate]

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Received July 20, 1994; Revised Manuscript Received November 15, 1994[®]

ABSTRACT: Polymer blends containing the title random copolymers, in which the monomers (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM) and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBM) were introduced to provide charge-transfer (CT) interactions within the copolymer blends, were prepared as a model system. This PMMA/PMMA based blend serves as a model for CT compatibilization of other, incompatible, blends. Poly(NECMM-*co*-MMA) copolymers were blended with poly(DNBM-*co*-MMA) copolymers containing similar acceptor mole fractions and with D–A ratios of unity. Single T_g's initially found for the blends (all compositons and molecular weights) indicated that all of the blends were compatible. Polymer blends which utilized acceptor copolymers which had peak molecular weights (versus PS standards) around 30 000 were thermodynamically compatible while similar blends prepared with acceptor copolymers with peak molecular weights 3 times larger were kinetically compatible but thermodynamically incompatible. These phase separated after being heated above 200 °C. Almost all of the blends exhibited endothermic transitions at this temperature, previously attributed to the decomplexation of the CT pairs, but only the blends containing high molecular weight components possessed LCSTs. These transitions are thus attributed to the "unlocking" of conformationally-constrained polymer segments at the so-called "decomplexation" temperature.

Introduction

Many of today's modern materials are inhomogeneous composites which possess complex structures on several different size scales ranging from microscopic (intimate molecular associations) to macroscopic (solid-in-solid emulsions). Their macroscopic properties, such as impact resistance, glass transition temperature, and optical clarity, depend on the interplay between the components, interplay that is being progressively well understood on the molecular level. Of particular interest to our group is the role that specific molecular interactions, particularly charge-transfer (CT) interactions,[1–7] play on the macroscopic properties of polymer blends. Other nonbonding interactions that have been exploited for this purpose include hydrogen bonding, ionic, dipole–dipole, ion–dipole, etc.

The thermodynamics of blending with such nonbonding interactions has attracted a great deal of attention.[8–11] Of the many models developed in an attempt to account for the complex behavior observed in polymer blends, perhaps the simplest is the Flory–Huggins mean-field approach.[8–10] In this model, the free energy of mixing for a pair of polymers, ΔG_m, is given by the usual expression

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

where T is the temperature and ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively. A necessary requirement for complete compatibility is that $\Delta G_m \leq 0$, although this alone is insufficient. In the simplest case, ΔS_m is considered a function of the molecular weight of the components according to

$$\Delta S_m = -R[N_1 \ln \phi_1 + N_2 \ln \phi_2] \tag{2}$$

where N_i and ϕ_i are the number of moles and volume fraction of polymer i and R is the gas constant. The enthalpy of mixing is given by

$$\Delta H_m = RT\chi_{12}N_1\phi_2 \tag{3}$$

where χ_{12} is an interaction parameter said to reflect the interaction energy between two dissimilar structural units. Large macromolecules will mix only when $\Delta G_m = \Delta H_m < 0$, since N_i, and consequently, ΔS_m, are diminutive.

Blending of copolymers of the type $A_aX_{(1-a)}$ with copolymers $D_\delta Y_{(1-\delta)}$, where A, D, X, and Y are "interacting groups", perhaps structural units, results in extremely complex interactions. If one assumes that only two-body interactions are important and can be considered independent of one another, the interaction parameter χ_{12} in (3) reflects both intramolecular and intermolecular interactions and may be expressed as the difference

$$\chi_{\text{blend}} = \sum_{ij} \chi_{ij}^{\text{intermol}} - \sum_{ij} \chi_{ij}^{\text{intramol}} \tag{4}$$

resulting in a total of six χ_{ij} terms. $\chi_{ij} < 0$ for strongly attractive pairs, such as those which possess CT interactions, $\chi_{ij} \geq 0$ for typical weak interactions between nonpolar, dissimilar polymer segments, and $\chi_{ij} \approx 0$ for identical polymer segments. It follows that favorable pairwise interactions can become extremely important in (4), thereby driving the mixing process. This approach cannot, of course, be applied to copolymer blends that possess any significant degree of microphase separation.[8] Several studies have appeared which have used the calorimetry of small-molecule analogues to gain a better understanding of the thermodynamics of blending.[12] Another possibility is to study the copolymer

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® Abstract published in *Advance ACS Abstracts,* January 15, 1995.

0024-9297/95/2228-1197$09.00/0

blends themselves,[1,2,13] a route we have chosen to follow for the current studies.

Even less well understood are the effects of a lower critical solution temperature (LCST) on the blending behavior of copolymers. MacMaster[14] has interpreted a LCST in a polymer blend as an indication of a mismatch in the free volume in the respective polymers at elevated temperatures. This has the effect of introducing a temperature-dependent (entropic) contribution to the enthalpic parameter χ_{12} in (3).[14] To further complicate the phase separation process, it is well-known that the presence of a LCST depends on the molecular weights of the components. Often a blend is compatible if it is composed of low molecular weight polymers but may become incompatible if one or both of the components possesses a large molecular weight which exceeds some critical value.[9,10,14]

LCSTs have been reported for polymer blends which contain poly[(*N*-ethylcarbazol-3-yl)methyl methacrylate]-(poly(NECMM)) as an electron donor polymer and poly-(2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate) (poly-(DNBM)) as an electron acceptor homopolymer.[5,15] Initially, this blend is compatible due to CT interactions, but upon heating the material above approximately 185 °C it phase separates irreversibly into polydonor-rich and polyacceptor-rich domains, a process that is believed to be mediated by the decomplexation of the CT pairs at the LCST.[5]

It is apparent from this that such CT interactions may be taken advantage of to yield interesting materials with microscopic structures that lie somewhere between the limits of incompatibility and compatibility: at one extreme the electron donor–acceptor associations may have little or no effect in assisting the mixing of the two polymers and two discrete phases exist, whereas at the other extreme complete compatibility will be reflected in the intimate mixing of the polymers on the molecular level. Between these limits, partial miscibility may yield interesting morphologies. Using DSC, the lower limit of such discernible domain sizes is roughly 100 Å.

As part of our ongoing research into the CT effects in copolymer blends, we report the blending behavior of PMMA blended with PMMA "compatibilized" by CT interactions between NECMM and DNBM. In such a simple study, in principle many of the intermolecular and intramolecular interactions offset one another so that interactions between the NECMM and DNBM units should become the dominant forces in determining the stability and compatibility of the copolymer blends. To accomplish this, blends containing the random copolymers poly(NECMM-*co*-MMA) and poly(DNBM-*co*-MMA) were prepared and studied by DSC. We also report the effects of CT decomplexation and LCSTs, previously reported for poly(NECMM)/poly(DNBM) blends,[5,15] on the compatibility of the present copolymer blends as a function of their donor and acceptor content. The effects of the molecular weight of the acceptor copolymers on the compatibility of some of the blends are also reported.

There is one study in the literature reporting the effects of ionic interactions on the bulk properties of polymer blends in which both polymers possess the same structure (polybutadiene).[16] In a related study, Lu and Weiss prepared blends of poly(styrene-*co*-4-vinylpyridine) and partially-sulfonated polystyrene in dimethylformamide solutions in order to study the effects of ionic interactions in PS/PS blending.[17] Among other things, the authors reported that solution viscosities increased with decreasing solvent polarity, presumably due to the formation of tighter ion pairs. These results suggest that in the bulk polymer matrix Coulombic interactions will be at their strongest and will result in tight intermolecular interactions.

Experimental Section

MMA (Aldrich) was distilled under vacuum immediately prior to use. NECMM was prepared by starting with 9-ethyl-3-carbazolecarboxaldehyde (Aldrich) by reaction of its alcohol with methacryloyl chloride (Aldrich) in THF according to the procedure of Simionescu and Percec.[18] DNBM[19] and homopolymers[4] were synthesized according to literature procedures. Some of the poly(DNBM-*co*-MMA) copolymers were prepared by E. Russell,[1] A7–A10 were available in our laboratory, and F3–F5 were prepared for the current study according to the literature[1] procedures. Poly(NECMM-*co*-MMA) copolymers were prepared by free-radical copolymerization in toluene using benzoyl peroxide (Aldrich) as initiator. Solutions were prepared which possessed varying mole fractions of NECMM and were 1.0 M in the total monomer concentration. The solutions were degassed with nitrogen and then sealed in ampules which were heated at 60 °C for several days. Copolymer compositions were determined by solution ^{1}H-NMR using a Bruker AC/F-200 spectrometer either in $CDCl_3$ (Aldrich, 99.8 atom % D) at 298 K or in approximately 50% $CDCl_3$/50% DMSO-d_6 (by volume) (Isotech, 99.9 atom % D) at 360 K.

Peak polymer molecular weights were determined by size exclusion chromatography (GPC), relative to commercially-available PS standards (Polymer Laboratories), in THF using a Waters Associates HPLC apparatus fitted with a Model R401 differential refractive index detector, a Model 440 UV–visible detector (254 nm), U6K injector, and μ-Styragel columns. Sample solutions were 5–10 mg mL^{-1} prior to injection and elution rates were 1.0 mL min^{-1}.

Copolymer blends were prepared as follows. Copolymers were selected which possessed similar mole fractions of donor or acceptor and small differences between the donor and acceptor copolymer compositions were corrected by varying the relative amounts of the acceptor copolymers to ensure a donor/acceptor mole ratio of unity. Blends were prepared by dissolving the desired masses of the copolymers in boiling THF or dichloromethane (1–2 wt % polymer) and then precipitating the solution in at least a 10-fold excess of MeOH. Solids were filtered and dried under vacuum at 25 °C for 2–3 days. Since the donor- and acceptor-containing copolymers are quite similar in their respective mole fractions of D and A, the composition of the blend has been designated as that of the donor copolymer for the sake of simplicity.

Glass transition temperatures, T_g, were determined by differential scanning calorimetry (DSC) on a Mettler TA3000 system. Samples ranging in mass between 9 and 17 mg were analyzed with scan rates of 20 °C min^{-1}. Three scans were performed on each sample: 0–170 °C, 0–T_{onset}, and 0–300 °C, where T_{onset} refers to the onset of decomposition for the particular sample, typically 220–250 °C. Glass transition temperatures before decomplexation were taken as the midpoints of the endothermic transitions in the second scans, and ΔH_1 were taken to be the integrals for the endothermic transitions around 190 °C in the second scans.[5,15] Values for ΔH_1 were particularly sensitive to how one selected the baseline and as such possess a large degree of uncertainty, typically 25–50%, even more for small values.

Results and Discussion

The data pertaining to the copolymers and blends are summarized in Tables 1 and 2. Reactivity ratios $r_{NECMM} = 0.95$ and $r_{MMA} = 0.91$ were calculated for the copolymerization of NECMM and MMA using the Kelen–Tüdős high-conversion method[20] and the data are summarized in Table 1, and are consistent with random copolymers. The pertinent data for the poly(DNBM-*co*-MMA) copolymers used in this study are summarized in Tables 1 and 2.

Table 1. Results for the Copolymerization of NECMM with MMA and DNBM and MMA

sample	feed mole fraction NECMM or DNBM	conversion (%)	copolymer NECMM or DNBM mole fraction
	Donor Copolymers		
D1	0.10	31	0.11
D2	0.20	25	0.20
D3	0.30	49	0.31
D4	0.40	51	0.40
D5	0.50	13	0.53
D6	0.65	72	0.63
D7	0.75	57	0.71
D8	0.90	80	0.91
	Acceptor Copolymers		
F3	0.50	60	0.46
F4	0.65	73	0.63
F5	0.81	85	0.80

Table 2. Composition of Each of the Copolymer Blends

	poly(NECMM-*co*-MMA)		poly(DNBM-*co*-MMA)	
blend	sample	mole fract D	sample	mole fract A
AD1	D1	0.11	A2	0.12
AD2	D2	0.20	A3	0.20
AD3	D3	0.31	A5	0.33
AD4	D4	0.40	A6	0.42
AD5	D5	0.53	A7	0.57
AD6	D6	0.63	A8	0.64
AD7	D7	0.71	A9	0.72
AD8	D8	0.91	A10	0.90
AF1	D5	0.53	F3	0.46
AF2	D6	0.63	F4	0.63
AF3	D7	0.71	F5	0.80

The molecular weight distributions of the poly(DNBM-*co*-MMA) and poly(NECMM-*co*-MMA) copolymers are shown in Figures 1–3. Assuming that a comparison with PS GPC standards allows one to interpret trends in the molecular-weight distributions of each copolymer series, several things are apparent in the figures. First, the distributions for the poly(DNBM-*co*-MMA) copolymers appear to be bimodal (trimodal in some cases). Also, there is a small change in the relative proportion of the major modes of these distributions. Most importantly, series F possesses lower peak molecular weights than samples in series A with similar compositions. Inspection of the molecular weight distributions in Figures 2 and 3 reveals that the peak molecular weights of samples A7–A10 lie at approximately 90 000 compared to those at approximately 30 000 for series F. The distributions in series F are similar to those of samples A1–A6. Furthermore, the molecular weights of the poly(DNBM-*co*-MMA) samples are independent of composition within each series (A1–A6, A7–A10, and F), a result which is somewhat unexpected since the nitro groups should act as inhibitors in the free–radical copolymerization mechanism. The poly(NECMM-*co*-MMA) copolymer molecular-weight distributions also show no trend with composition.

Presented in Figure 4 are the glass transition data for each copolymer series. The data for each copolymer series has been fitted to the Kwei equation[21]

$$T_g = \frac{w_1(T_{g1} - kT_{g2}) + kT_{g2}}{w_1(1-k) + k} + q(w_1 - w_1^2) \qquad (5)$$

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 the fitting parameters. The sign and magnitude of *q* are said to be indications of the type of intramolecular interactions present between the unlike structural units in the copolymer. Values of $q > 0$ indicate attractive interactions while $q < 0$ reflects repulsive interactions; large values of *q* are indicative of strong such interactions. A value of $k \neq 1$ results in a point of inflection in a plot of T_g versus w_i.[21] Here, *k* is taken as a fitting parameter which at times has been ascribed to state properties of the polymers by other research groups.[22,23]

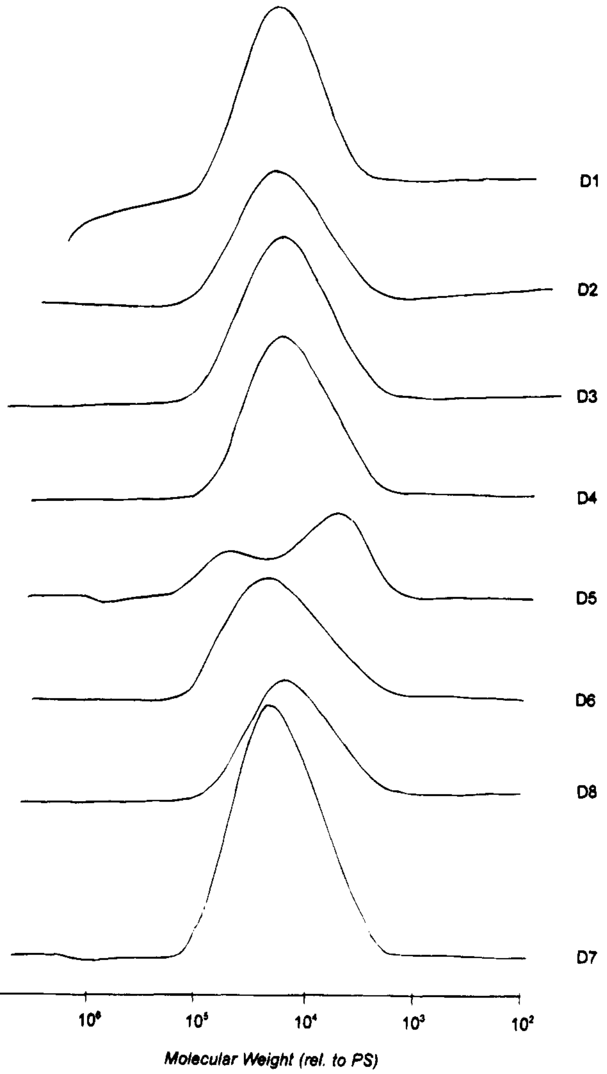

Figure 1. GPC distributions for the poly(NECMM-*co*-MMA) copolymers.

The fitting of the copolymer data was performed with *k* set to unity due to the absence of points of inflection in both curves in Figure 4. For both copolymer series, *q* is close to zero. The value of *q* should be at least 20 in order to show a significant influence on the T_g's. For poly(NECMM-*co*-MMA), $q = -6$, indicating that weak repulsive forces, probably dipolar as well as electrostatic in nature, exist between the NECMM and MMA units which result in a slight depression in the T_g's of the samples relative to the weighted average of the two homopolymers.

The glass transition temperatures for the two copolymer series are well separated as a function of donor and acceptor content (Figure 4). Two series of blends composed of the donor and acceptor copolymers were prepared and analyzed by DSC. Typical second and third DSC scans are shown in Figure 5 for sample AD6 which phase separates upon heating. In the upper trace

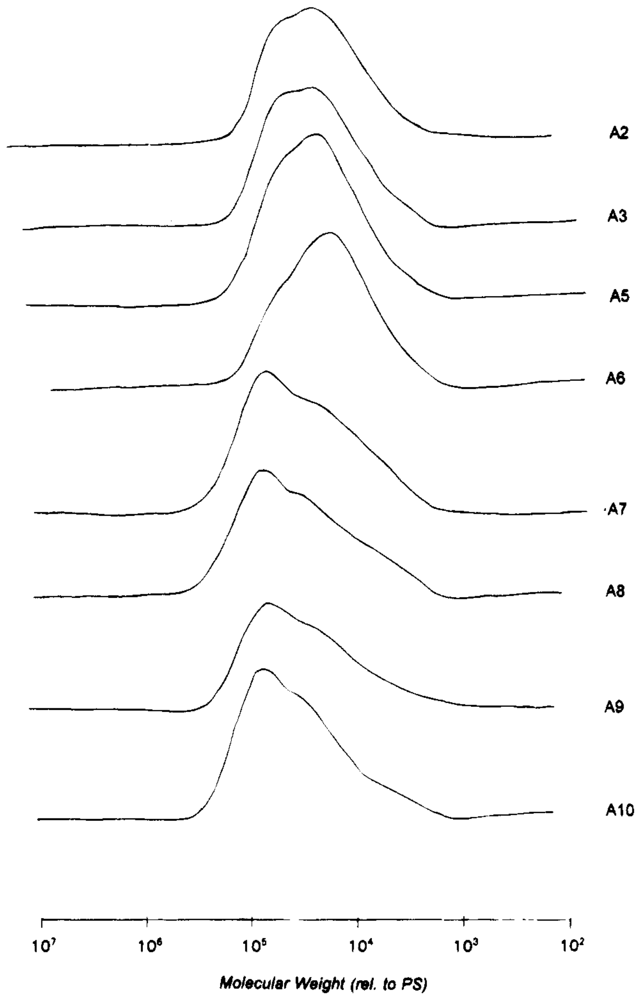

Figure 2. GPC distributions for the poly(DNBM-*co*-MMA) copolymers, series A.

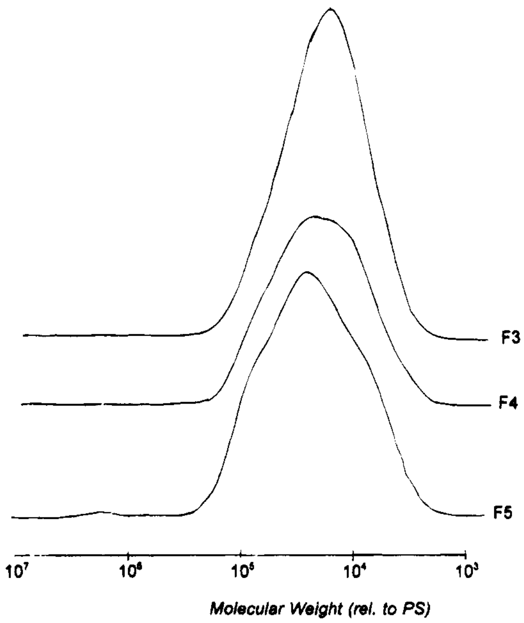

Figure 3. GPC distributions for the poly(DNBM-*co*-MMA) copolymers, series F.

(a), only a single T_g is evident in the scan, as is a relatively large thermal absorption peak at approximately 200 °C. In the subsequent scan shown in the figure (b), two T_g's exist, showing that the sample has phase separated upon heating. There is no endothermal absorption at 200 °C in this scan.

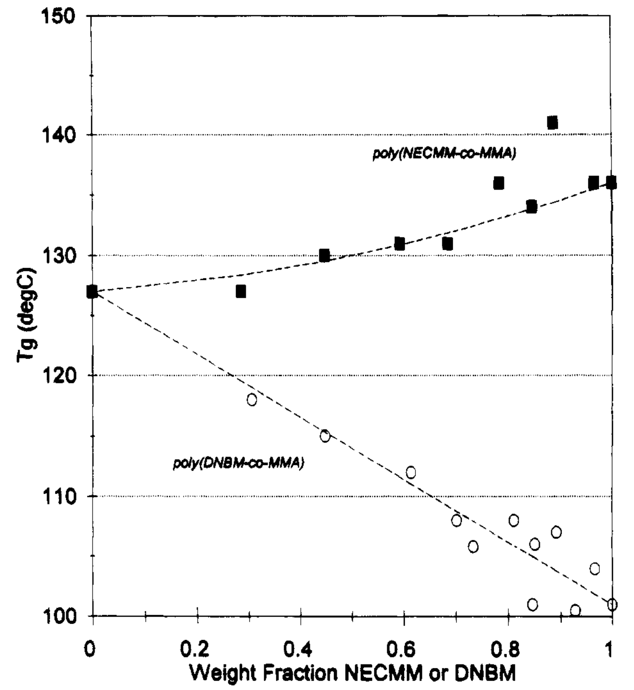

Figure 4. Kwei plots for the poly(NECMM-*co*-MMA) and poly(DNBM-*co*-MMA) copolymers. Dotted curves are shown for the best fit to eq 5 with $k = 1$ ($q = -6$ for the donor copolymers and $q = 0$ for the acceptor copolymers). T_g for poly(DNBM) taken from ref 5.

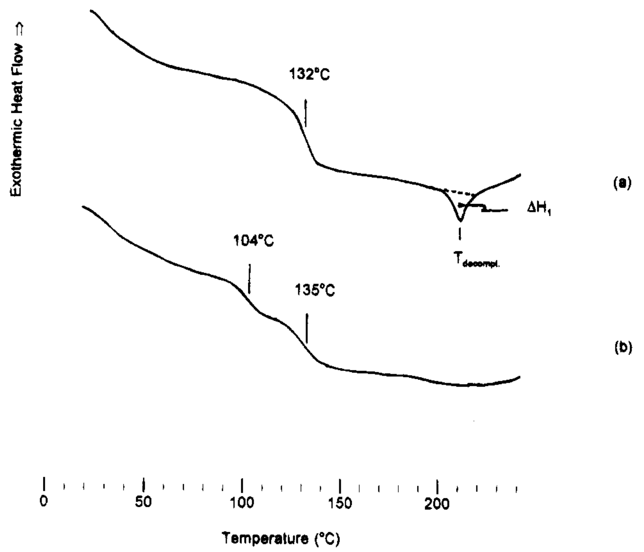

Figure 5. Typical DSC traces for blend AD6 (a) before (scan 2 in Experimental Section), and (b) after decomplexation (scan 3). The dotted line indicates the baseline used for integration and determination of ΔH_1. Note that this endotherm is absent from curve b.

The results for the two blends series prior to heating the samples past 200 °C are shown in Figure 6. Initially, all of the blends are compatible. It is a little surprising that the glass transition temperatures of the blends are very close to those of the donor copolymers and not higher, which would be expected because of the presence of specific interactions. However, it has been demonstrated that in blends of poly(NECMM) and poly(DNBM) the T_g of the blend reached a maximum at intermediate mole fractions, well above the weighted average of the homopolymer T_g's, but at approximately the same temperature as the donor homopolymer.[5,15] In the present blends most of the blend T_g's also lie above the averages of the copolymer ones.

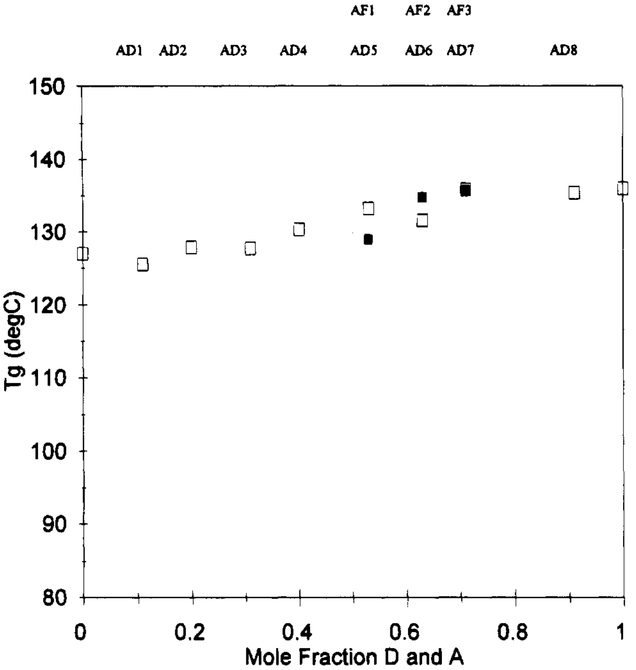

Figure 6. Blend T_g's before heating above 200 °C. The T_g for a 1:1 poly(NECMM)/poly(DNBM) blend was used for the 100% D–A blend, and the datum was taken from ref 5. Unfilled symbols are those of blend series AD; filled are for AF.

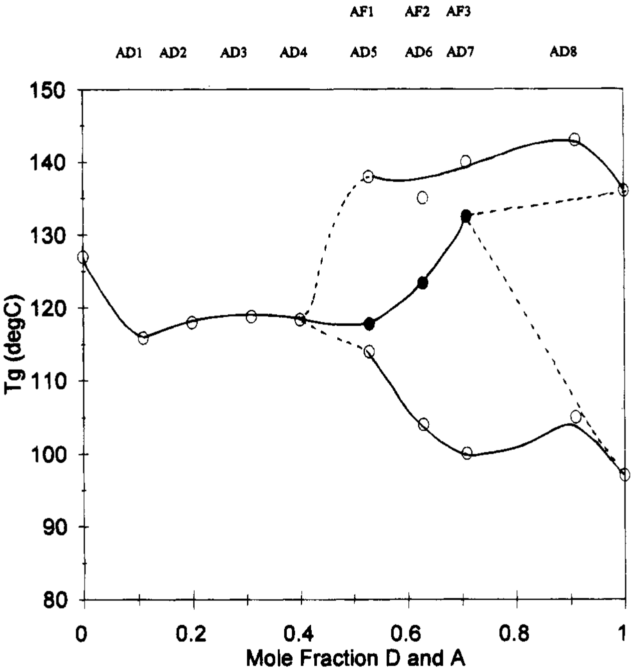

Figure 7. Blend T_g's after heating above 200 °C. The T_g for a 1:1 poly(NECMM)/poly(DNBM) blend was used for the 100% D–A blend, and the data were taken from ref 5. Unfilled symbols are those of blend series AD; filled are for AF.

When the samples were heated past approximately 200 °C, several of the blends phase separated (Figure 7). An examination of the copolymer molecular-weight distributions reveals that all of the blends that phase separated were composed of acceptor copolymers which had average (peak) molecular weights higher than those in blends which remained compatible. This is particularly true for blends AD5, AD6, and AD7 which shared the same donor copolymers as the compatible ones AF1, AF2, and AF3, respectively. Since only minor differences exist in the acceptor copolymer compositions, the only major difference between these three compatible blends and their incompatible counterparts lies in their molecular weight distributions. From this we conclude that the primary driving force for compatibility in these blends is one of molecular weight.

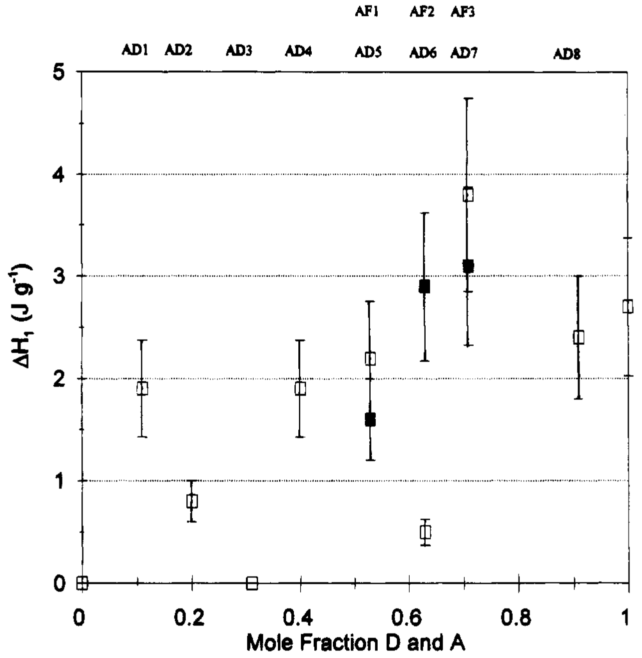

Figure 8. Experimentally-determined values of ΔH_1, the enthalpy of decomplexation for each blend. Results for a 1:1 poly(NECMM)/poly(DNBM) blend were taken from ref 5. Unfilled symbols are those of blend series AD; filled are for AF. (Error bars represent a nominal ±25% uncertainty.)

All of the blend samples except AD3 exhibit endothermic transitions around 185–200 °C which are similar to those reported for poly(NECMM)/poly(DNBM) homopolymer blends.[5,15] Consequently, we also attribute these to the decomplexation process and refer to their integrals as enthalpies of decomplexation, ΔH_1. The values for ΔH_1 are presented in Figure 8 as a function of the donor and acceptor content in the blends and do not seem to differ according to the compatibility of the blend. Unlike previous blends which employed the homopolymers,[5,15] the ΔH_1 values in Figure 8 do not simply correlate with the LCST. Clearly the endothermic transitions characterized by ΔH_1 must be indicative of a different phenomenon, presumably connected with the decomplexation of the CT pairs.

In the simplest case, a thermodynamically compatible blend will have a single T_g both before and after "decomplexation" and hence possesses fully reversible CT pairings. In this case, the magnitude of ΔH_1 will then simply reflect the degree of association that all of the donor moieties have with the acceptors if ΔH_1 is due solely to the interaction energy between the associated donor and acceptor pairs. Only in the best possible cases will every donor be associated with an acceptor. Another consequence of complete reversibility would be that enthalpies similar to ΔH_1 should be seen in subsequent DSC scans if the transition is due to the decomplexation process alone. However, if the absorption of thermal energy is dominated by a relaxation of conformationally unfavorable pairings that were formed in the kinetic pairing of donor and acceptor groups (i.e. that decomplexation allows donor groups within the polymer to sample several different acceptors until the system is in a more conformationally relaxed arrangement), then upon cooling the stress associated with such pairs will be relieved and the system will return to a single phase. Although subsequent DSC scans will exceed the decomplexation temperature, there will be no decomplexation enthalpies. This interpretation is consistent with the concomitant absence of LCSTs and the presence of non-zero ΔH_1 values. So, while the ΔH_1 values are referred to as "enthalpies of decomplexation", the process entails more than just decomplexation and might be more appropriately referred to as an enthalpy of disentanglement or conformational relaxation assisted by decomplexation.

Copolymer samples A7–A10 possess a more pronounced shoulder at molecular weights around 90 000 than do the A1–A6 samples and the F series of copolymers. Since GPC detectors are sensitive to the molecular weight of each chain as well as the number of chains present in the sample, the large molecular-weight end of the scale is exaggerated relative to the lower molecular-weight end of the distribution. This difference in area, which might account for 5–10% between samples A6 and A7 in the weight-sensitive distributions shown in Figure 1, appears larger than it would in a number distribution curve. However, even this small fraction of the sample may serve to nucleate phase separation if the molecular weight is larger than the entropically critical molecular weight. Despite the differences in compatibility, the ΔH_1 values appear to be independent of molecular weight (over the rather limited range) and of blend compatibility and are consistent with the interpretation that some sort of reorganization involving the polymer chains themselves occurs above the "decomplexation" temperature.

In a crude sense, for sufficiently large polymer chains, the addition of CT interactions between NECMM and DNBM has made PMMA incompatible with PMMA. The results are probably more aptly viewed in terms of the amount of PMMA required to make poly(NECMM)/poly(DNBM) thermodynamically compatible. At intermediate compositions, the intermolecular and intramolecular terms in eq 6 cancel one another so that χ_{blend} reduces to the sum of $\chi_{\mathrm{NECMM/DNBM}}$ and $\chi_{\mathrm{MMA/MMA}}$. Under these conditions, the thermal behavior of the blend is dominated primarily by the intermolecular interactions between the NECMM and DNBM units and the molecular weights of the copolymers. Initially, these interactions are favorable. However, upon heating the blend beyond the decomplexation temperature of the D–A pairs, mixing becomes unfavorable for the samples with relatively large molecular weights and phase separation takes place.

From this "trivial" blend study, we conclude that some, if not all, of the samples are *kinetically* compatible but *thermodynamically* incompatible, as poly(NECMM)/poly(DNBM) blends have been shown to behave.[5] That is to say, in the precipitation process the compatible blends form kinetically due to the rapid collapse of the polymer chains in the nonsolvent. This rapid collapse is accompanied by rapid reorganization and pairing of the donor and acceptor groups due to CT interactions. However, upon heating past the decomplexation temperature of approximately 200 °C, some of the samples which have sufficiently large molecular weights undergo phase separation irreversibly, thereby producing thermodynamically stable, but incompatible, blends.

To the best of our knowledge, this is the first reported evidence for LCSTs in copolymer blends involving CT interactions, particularly in which the molecular weight of one of the components determines the final compatibility of the material. This behavior raises the possibility of using combinations of temperature, molecular weight and copolymer composition to control the compatibility of a copolymer blend, and hence ultimately control the final properties of the material.

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

References and Notes

(1) Russell, E.; Crone, G.; Natansohn, A. *Polym. Bull.* **1991**, *27*, 67.
(2) Crone, G.; Natansohn, A. *Polym. Bull.* **1991**, *27*, 73.
(3) Natansohn, A.; Simmons, A. *Macromolecules* **1989**, *22*, 4426.
(4) Simmons, A.; Natansohn, A. *Macromolecules* **1990**, *23*, 5127.
(5) Simmons, A.; Natansohn, A. *Macromolecules* **1991**, *24*, 3651.
(6) Simmons, A.; Natansohn, A. *Macromolecules* **1992**, *25*, 3881.
(7) Simmons, A.; Natansohn, A. *Macromolecules* **1992**, *25*, 1287.
(8) For example, see: Walsh, D. A. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Ser. Eds.; Polymer Properties; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 2, Chapter 5.
(9) Huggins, M. L. *J. Am. Chem. Soc.* **1942**, *64*, 1712.
(10) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(11) Hino, T.; Lambert, S. M.; Soane, D. S.; Prausnitz, J. M. *Polymer* **1993**, *34*, 4756.
(12) For instance, see: Landry, C. J. T.; Teegarden, D. M. *J. Polym. Sci., Polym. Phys.* **1994**, *32*, 1285 and references therein.
(13) Cowie, J. M. G.; Demaude, A. *Polym. Adv. Technol.* **1994**, *5*, 178.
(14) MacMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(15) Rodriguez–Parada, J. M.; Percec, V. *Macromolecules* **1986**, *19*, 55.
(16) Otocka, E. P.; Eirich, F. R. *J. Polym. Sci., Polym. Phys. Ed.* **19686**, 921.
(17) Lu, X.; Weiss, R. A. *Macromolecules* **1991**, *24*, 5763.
(18) Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2287.
(19) Simionescu, C. I.; Percec, V.; Natansohn, A. *Polym. Bull.* **1980**, *3*, 535.
(20) Tüdös, F.; Kelen, T. Goldes-Berezsnich; Turcsanyi, B. *J. Macromol. Sci., Chem.* **1976**, *A10*, 1513.
(21) Lin, A. A.; Kwei, T. K.; Reiser, A. *Macromolecules* **1989**, *22*, 4112.
(22) Cowie, J. M. G.; Reilly, A. A. N. *J. Appl. Polym. Sci.* **1992**, *33*, 4814.
(23) Lu, X.; Weiss, R. A. *Macromolecules* **1992**, *25*, 3246.

MA941171P