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

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ABSTRACT: NMR and DSC studies are used to investigate the compatibility of blends of random compolymers poly(NECMM-*co*-MA) and poly(DNBM-*co*-MMA) where NECMM is the electron donor (*N*-ethylcarbazol-3-yl)methyl methacrylate and DNBM is the electron acceptor 2-[(3,5-dinitrobenzoyl)oxy]-ethyl methacrylate. At least 14 mol % of NECMM and DNBM is needed to compatibilize PMA with PMMA. Similar blends are analyzed in which poly(NECMA-*co*-MA), where NECMA is the electron donor (*N*-ethylcarbazol-3-yl)methyl acrylate, was substituted for the NECMM-containing donor copolymer. Using NECMA, between 15 and 30 mol % donor and acceptor are required to compatibilize the blend. Blends which were prepared with high molecular weight acceptor copolymers were found to be both kinetically and thermodynamically incompatible. Almost all of the samples exhibited endothermic transitions at 200 °C but no accompanying phase changes. This is consistent with the interpretation of the so-called "decomplexation enthalpy" in terms of conformational relaxation in the copolymer chains within the blends.

Introduction

A great deal of attention has been given in recent years to the exploitation of specific interactions to induce miscibility in otherwise incompatible polymers. Most often this incompatibility is a consequence of the lack of significant entropic contributions to mixing in typical polymers. To overcome this, attractive intermolecular interactions (i.e. charge transfer (CT), ionic, hydrogen bonding, or dipole–dipole) between various polymeric units must be introduced.

In the preceding paper,[1] as part of a continuing project intended to better understand the effects of charge-transfer interactions on the compatibility of polymer blends, we reported the blending behavior of poly(DNBM-*co*-MMA) random copolymers with random copolymers of poly(NECMM-*co*-MMA), where DNBM is the electron acceptor 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate, NECMM is the electron donor (*N*-ethylcarbazol-3-yl)methyl methacrylate, and MMA is methyl methacrylate. In those blends, the thermodynamics of blending was simplified because the enthalpy of mixing, ΔH_m, which is proportional to the interaction parameter of the blend, χ_{blend}, expressed in terms of the intermolecular and intramolecular interactions as

$$\chi_{\text{blend}} = \sum_{ij}\chi_{ij}^{\text{intermol}} - \sum_{ij}\chi_{ij}^{\text{intramol}} \qquad (1)$$

where the subscripts refer to monomers i and j, reduced to terms involving only electron donor–acceptor (D–A) and MMA–MMA interactions. We reported that initially the blends were compatible, as expected, but that samples which possessed acceptor copolymers with peak molecular weights around 90 000 (versus polystyrene (PS) standards) phase separated upon heating over 200 °C. Virtually identical blends prepared with acceptor copolymers with peak molecular weights around 30 000 remained compatible. The criterion for incompatibility was based on the detection of two glass transition temperatures by differential scanning calorimetry (DSC). However, the limit to the resolution of this technique is approximately 100 Å. NMR relaxation techniques, such as $T_{1\varrho}(^1\text{H})$ measurements, provide another factor of 10 in "magnification", allowing for the resolution of phase domains with sizes on the order of 10 Å.

In this study, a detailed investigation into similar blends was undertaken, but with the important difference that MMA in the donor copolymers has been replaced with methyl acrylate (MA). It is known that PMA and PMMA form incompatible polymer blends. Recently, Russell *et al.* reported that compatible blends were formed when *N*-vinylcarbazole (NVC) was used as an electron donor in poly(NVC-*co*-MA)/poly(DNBM-*co*-MMA) blends that contained at least 27 mol % of the donor and acceptor groups.[2] One objective of the current work is to use both DSC and solid-state NMR techniques to determine the lowest amount of donor and acceptor groups needed to produce compatibility between PMA and PMMA. We also present the effects of the lower critical solution temperature (LCST), reported previously for poly(NECMM)/poly(DNBM) blends,[3,4] on the blending behavior of these copolymers.[1] Finally, blends containing copolymers of MA with the acrylate donor (*N*-ethylcarbazol-3-yl)methyl acrylate (NECMA) and some of the same acceptor copolymers were prepared and analyzed by DSC and the results compared to those for the methacrylate analogues.

Experimental Section

MA and MMA (Aldrich) were distilled under vacuum immediately prior to use. Monomers (*N*-ethylcarbazol-3-yl)-methyl methacrylate (NECMM),[1] (*N*-ethylcarbazol-3-yl)methyl acrylate (NECMA),[1] and 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBM)[5] and homopolymers[6] were synthesized according to literature procedures. The preparation and characterization of some of the poly(DNBM-*co*-MMA) copolymers used in this study have already been reported.[2] The same procedure was adopted in the preparation of additional samples with acceptor mole fractions of less than 10%, the results of which are summarized in Table 1.

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Table 1. Results for the Copolymerizations of DNBM with MMA

sample	initial feed, mol % DNBM	conversion, %	composition, mol % DNBM
EL1	2.0	79	1.7
EL2	4.0	75	3.7
EL3	6.0	86	5.4
EL5	10	82	9.7

Table 2. Results for the Copolymerizations of NECMM with MA

sample	initial feed, mol % NECMM	conversion, %	composition, mol % NECMM
DL1	1.0	(low, ≤10%)	1.0
DL2	3.0		3.4
DL3	5.0		5.7
DL4	7.0		7.0
DL5	8.5		9.2
B1	10	41.1	14
B2	20	31.3	33
B3	30	72.8	37
B4	40	78.1	47
B5	50	80.2	57
B6	65	83.4	69
B7	75	82.9	78
B8	90	13.2	90

Table 3. Results for the Copolymerizations of NECMA with MA

sample	initial feed, mol % NECMA	conversion, %	composition, mol % NECMA
G1	14	71	13
G2	33	4.8	31
G3	57	39	58
G5	90	49	91

Two series of poly(NECMM-*co*-MA) copolymers were prepared by free-radical copolymerization in toluene at 60 °C. In the series DL (Table 2), which has <10% NECMM, several solutions were prepared which possessed varying mole fractions of NECMM and were 1.0 M in the total monomer concentration with 3% benzoyl peroxide (Aldrich) as initiator by weight. In series B (Table 2), total monomer concentrations were 0.5 M and the initiator (2,2′-azobis(2-methylpropionitrile), AIBN, Aldrich) was used at concentrations of 1% by weight relative to that of the monomer. The poly(NECMA-*co*-MA) copolymers (Table 3) were prepared in a similar manner using a total of 0.5 M monomer and 1% benzoyl peroxide in each ampule. 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 *ca.* 50% $CDCl_3$/50% DMSO-d_6 by volume (Isotech, 99.9 atom % D) at 360 K.

The determination of the molecular weight distributions was performed by gel permeation chromatography (GPC) in THF using PS standards.[1] The copolymer blends were prepared as before[1] by precipitation from 1–2% solutions in hot THF into at least a 10-fold excess of MeOH. The samples were then filtered or decanted (MeOH acted as a plasticizer for the copolymers with high concentrations of MA) 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 blend 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 230–250 °C (just 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 process involving the dissociation of the electron donor–acceptor complexes present in the blends which subsequently leads to separate donor-rich and acceptor-rich phases in the homopolymer blends.[4]) Two samples were used to obtain the T_g and ΔH_1 values. From the first, the T_g's before decomplexation and ΔH_1 values were obtained. Since the onset of decomposition has the potential of introducing oxidation products, a second set of samples was run to just prior to onset from which the T_g's after decomplexation were determined.

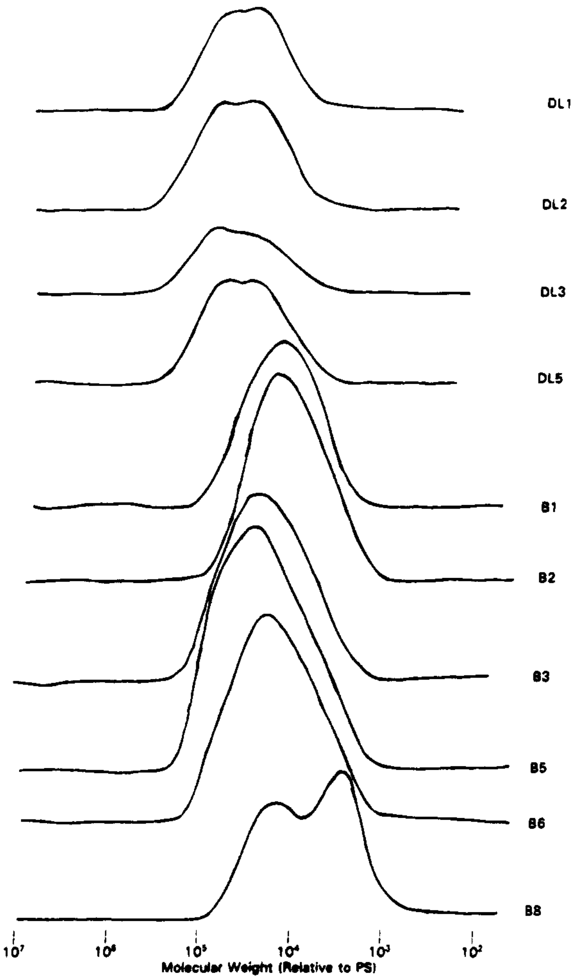

Figure 1. GPC distributions (versus PS) for the poly(NECMM-*co*-MA) copolymers.

Solid-state ^{13}C-NMR spectra were acquired on a Bruker CXP-200 spectrometer equipped with a Doty probe using cross-polarization (CP), magic-angle spinning (MAS), and dipolar decoupling (DD). Proton spin–lattice relaxation time constants in the rotating frame, $T_{1\varrho}(^1H)$, were obtained using a variable delay prior to a fixed contact time.[7] The experiments were carried out with a 90° pulse of 3.8 μs, variable delays between 1 μs and 30 ms, a fixed contact time of 1.5 ms, and a delay between pulses of 5 or 7.2 s. All spectra were obtained at room temperature. Samples AA2, AA3, and AA4 were also heated at 200 °C for 20 min and then analyzed for their $T_{1\varrho}(^1H)$ values.

Results and Discussion

Copolymers. The results for the poly(DNBM-*co*-MMA) copolymerizations with low acceptor content carried out for this work are reported in Table 1. The results for the poly(NECMM-*co*-MA) copolymerizations are summarized in Table 2. Analysis of the copolymerization results for the NECMM copolymers using the Kelen–Tüdös high-conversion method[8] yields reactivity ratios of $r_{NECMM} = 1.18$ and $r_{MA} = 0.25$. The data for the copolymerizations of NECMA with MA are presented in Table 3. Inspection of the limited data reveals that both reactivity ratios are close to unity.

The GPC distributions for all of the copolymers used in the blends are presented in Figures 1–3. The GPC

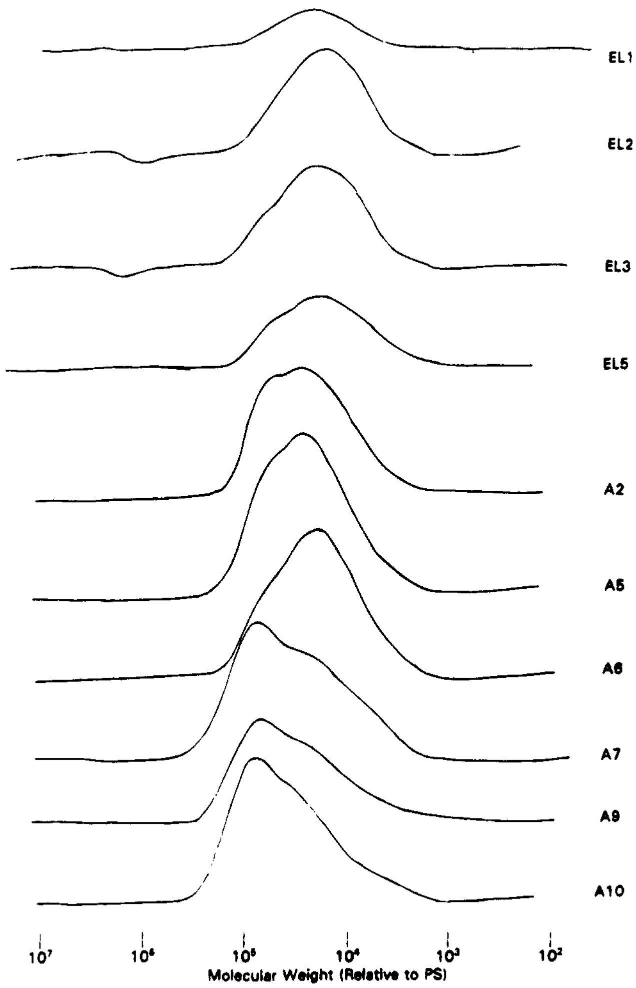

Figure 2. GPC distributions (versus PS) for the poly(DNBM-*co*-MMA) copolymers.

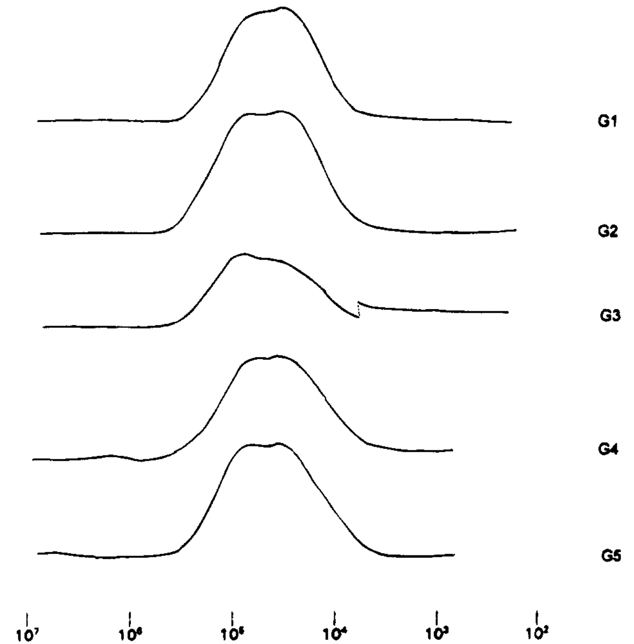

Figure 3. GPC distributions (versus PS) for the poly(NECMA-*co*-MA) copolymers.

curves for the NECMA copolymers are similar to those of their NECMM counterparts allowing for, at the very least, a qualitative comparison of the blend compatibilities. In the previous paper,[1] we demonstrated that relatively small differences in the molecular weight distributions could lead to drastically different degrees of compatibility in copolymer–copolymer blends.

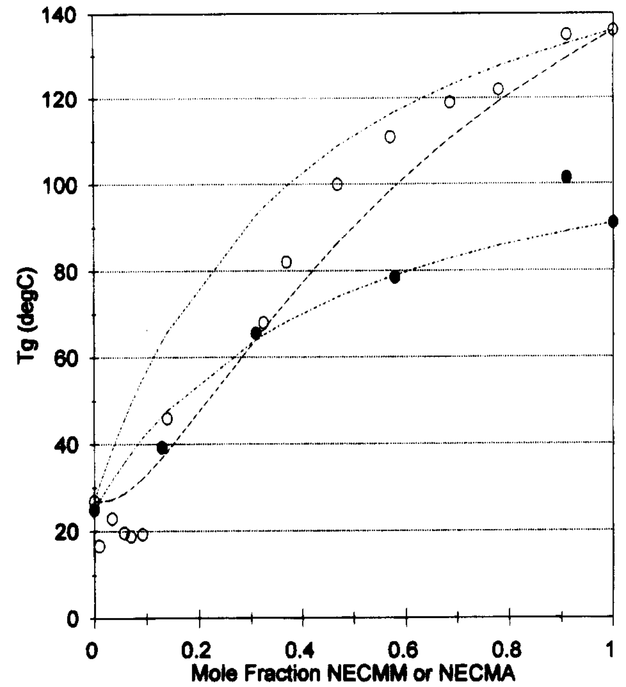

Figure 4. Dependence of T_g on the mole fraction of donor in the copolymers. Points are the experimentally-determined data for poly(NECMM-*co*-MA) (○) and poly(NECMA-*co*-MA) (●). The lines were calculated using eq 2 with $q = 0$ (– · –; both donors) and $q = -120$ (- - -; NECMM only) to demonstrate the deviation of the data from the weighted averages of the homopolymers.

Pugh *et al.*[9] demonstrated that the miscibility of poly(NECMM)/poly(DNBM) blends depends strongly on the average molecular weight of the donor copolymer and that past a critical average molecular weight of approximately 5000 (relative to PS) the blends are only kinetically miscible and possess lower critical solution temperatures (LCSTs) at approximately 185 °C. Separate studies by Simmons and Natansohn have confirmed these results for 1:1 poly(NECMM)/poly(DNBM) blends using donor and acceptor homopolymers with peak molecular weights of 85 000 and 28 000, respectively.[3] While it appears as though the critical molecular weight which induces kinetic rather than thermodynamic compatibility is different for the copolymers[1] and homopolymers,[3,4] it is clear that the acceptor copolymers exhibit the same sort of effect as the homopolymers. Since we have utilized the same series of copolymers in this paper as we have in the previous one,[1] we anticipate the same sort of effect in the present set of experiments.

The T_g results for the copolymers used in this study are shown in Figure 4. The data for each copolymer series has been fitted to the Kwei equation[10]

$$T_g = \frac{W_1(T_{g1} - kT_{g2}) + kT_{g2}}{W_1(1 - k) + k} + q(w_1 - w_1^2) \qquad (2)$$

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. Large values of q are indicative of strong interactions, and the sign of q indicates the attractive ($q > 0$) or repulsive ($q < 0$) nature of the interactions. A value of $k \neq 1$ results in a point of inflection in a plot of T_g versus

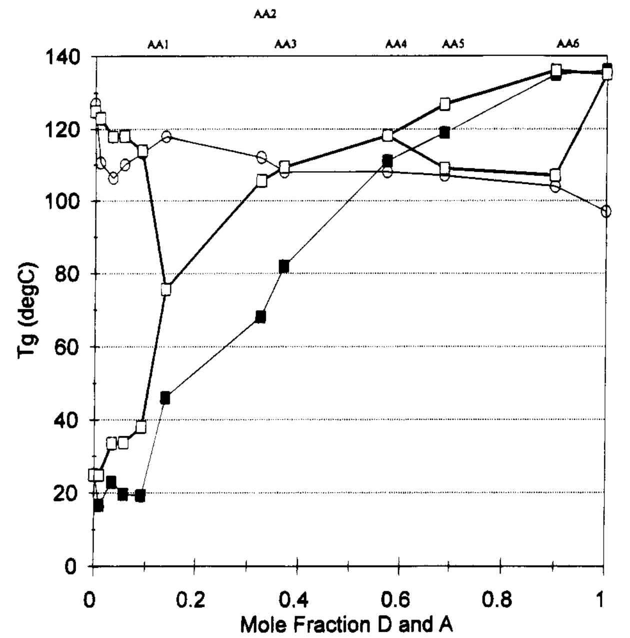

Figure 5. DSC data for poly(NECMM-*co*-MA) (■) and poly(DNBM-*co*-MMA) (○) copolymers plotted versus blend composition. Blend labels are presented along the top of the plot. DSC T_g data for the NECMM blends before heating past 200 °C (□). The T_g for a 1:1 poly(NECMM)/poly(DNBM) blend was used for the 100% D–A blend, and the datum was taken from ref 3.

w_i.[10] The fitting of the copolymer data was performed with k set to unity due to the absence of points of inflection in the experimental data curves. For poly(NECMM-*co*-MA), $q = -120$, indicating that fairly strong repulsive forces exist between the NECMM and MA units which result in a depression in the T_g's of the samples relative to the weighted average of the two homopolymers.

The T_g's for the poly(NECMA-*co*-MA) copolymers, also presented in Figure 4, are experimentally consistent with values calculated using eq 2 with $q = 0$. The T_g's for the poly(DNBM-*co*-MMA) copolymers are experimentally consistent with the data reported previously for which $q \approx 0$.[1] In both of these copolymer series, values of $q = 0$ imply that significant attractive or repulsive forces between unlike structural units within the copolymers are absent.

DSC Studies of the NECMM-Containing Blends. The glass transition temperatures for the donor and acceptor copolymers, plotted together as a function of the composition of each blend in Figure 5, are sufficiently well separated from one another (except at values close to the crossover at approximately 60 mol % D and A) to allow the analysis of blends containing similar mole fractions of D and A by DSC. The compositions of the NECMM copolymer blends are summarized in Table 4. The T_g data for the copolymer blends are also presented in Figure 5 and typical DSC second and third scans are shown in Figure 6. Two things are apparent in Figure 5. Initially, the samples exhibit several different compatibility regimes: copolymer blends which possess either low (≤14 mol %) or high (57 to >90 mol %) donor and acceptor percentages were both kinetically and thermodynamically incompatible, as indicated by two well-resolved T_g's in the DSC experiments. Samples containing intermediate mole fractions of D and A (between 14 and 57 mol % D and A) appeared to be compatible, although the result for the last blend in this region (AA4, 57 mol % D and A) is inconclusive since the donor and acceptor copolymers that comprise the blend have similar T_g's. Apart from a decrease in most of the T_g's after heating past 200 °C, the compatibility of the blends appeared to be little changed and the only sample in the series that underwent any significant morphological change was the 1:1 poly(NECMM)/poly(DNBM) homopolymer blend reported elsewhere[3,4] and included here.

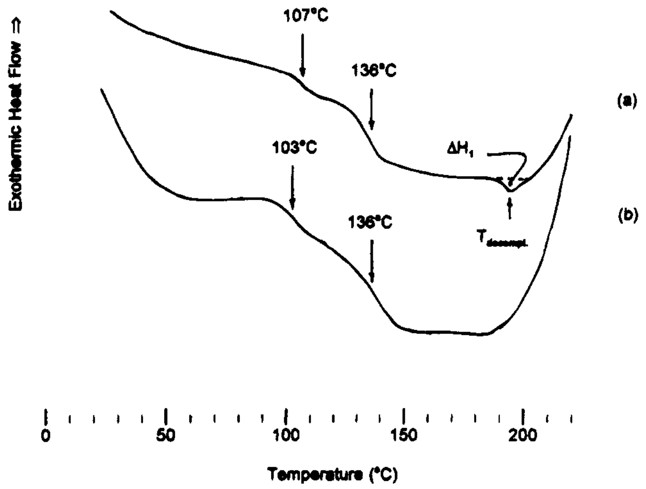

Figure 6. Typical DSC second (a) and third (b) scans taken from different DSC samples of blend AA6.

Table 4. Composition of Each of the NECMM Copolymer Blends

	poly(NECMM-*co*-MA)		poly(DNBM-*co*-MMA)	
blend	sample	mol % NECMM	sample	mol % DNBM
AC1	DL1	1.0	EL1	1.7
AC2	DL2	3.0	EL2	3.7
AC3	DL3	5.0	EL3	5.4
AC4	DL5	8.5	EL5	9.7
AA1	B1	14	A2	12
AA2	B2	33	A5	33
AA3	B3	37	A6	42
AA4	B5	57	A7	57
AA5	B6	69	A9	72
AA6	B8	90	A10	90

It is interesting to note that the incompatibility of the blends correlates once again with the molecular weights of the acceptor copolymers. In the previous case, the samples containing acceptor copolymers with higher average molecular weights were kinetically compatible but thermodynamically incompatible.[1] However, in these blends, samples AA5 and AA6 (and maybe AA4) are kinetically incompatible, presumably due to the elevated molecular weight of the acceptor copolymers. A similar effect exists in poly(NECMM)/poly(DNBM) blends. Rodriguez–Parada and Percec have reported that a blend containing 22 mol % poly(NECMM), in which the polydonor and polyacceptor had number-average molecular weights of 36 900 and 24 200, respectively, was compatible.[4] On the other hand, Simmons and Natansohn reported that blends containing 15 and 32 mol % poly(NECMM) were incompatible.[3] However, in these blends the peak molecular weight of the poly(NECMM) was 85 000 and of the poly(DNBM) was 28 000.[3] Despite the differences in how the molecular weights were reported (peak versus number-average) the differences in compatibility are quite clearly due, primarily, to the differences in the molecular weight of the donor homopolymer.[3]

Most of the copolymer blends exhibit the endothermic transitions in their second DSC scans around 195 °C

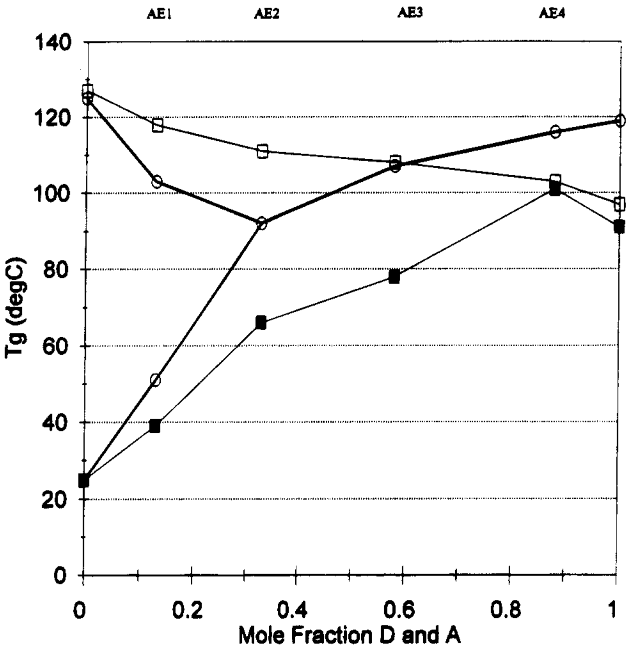

Figure 7. DSC data for poly(NECMA-*co*-MA) (■) and poly(DNBM-*co*-MM) (□) copolymers plotted versus blend composition. DSC T_g data for the poly(NECMA-*co*-MA) blends before heating past 200 °C (○). The T_g for a 1:1 poly(NECMA)/poly(DNBM) blend was used for the 100% D–A blend, and the datum was taken from ref 13.

previously interpreted to be due to the phase separation of the blends at their LCSTs.[3,4] The small endothermal transition at approximately 190 °C, evident in Figure 6 just prior to the onset of decomposition, is attributed to decomplexation. We have postulated that this endotherm is due to the release of conformational constrains which were formed when the polymer blend was precipitated.[1] Increasing ΔH_1 values reflect the increasing number of D–A interactions present as the donor and acceptor content in the blends increases. Samples AA4 and AA5 were the only samples in which there were small endothermic peaks (ΔH_2) in the third scans. In all of the other samples these were absent or below the detectable limit of our DSC instrument (0.1 J g^{-1}).

Percec and co-workers have attributed these thermal absorptions (ΔH_2) in "decomplexed" samples to the enthalpy associated with CT complexes formed at the interface between donor-rich and acceptor-rich phases.[4] Relatively large values are said to indicate large regions of overlap between donor and acceptor phases and hence partial compatibility within the samples.[3,4] On the basis of this interpretation, AA4 appears to be compatible while AA5 and AA6 appear to be partially incompatible. It is quite probable that polymer chains from the higher molecular weight fraction of the GPC distributions comprise the DNBM-rich incompatible phase while the lower molecular weight fraction resides in the interfacial regions. As with the poly(NECMM-*co*-MMA)/poly(DNBM-*co*-MMA) blends,[1] almost all of the samples have non-zero ΔH_1 values despite the absence of phase changes (LCST). Clearly, the endotherms must reflect more than the decomplexation process alone and, at more than 50 °C above the T_g of the blends, probably involve the reorganization of the polymer chains themselves.

DSC Studies of the NECMA-Containing Blends. The T_g results for the NECMA copolymers used in blend series AE are shown in Figure 7 as a function of blend composition. Except at high D and A contents, blends prepared using these copolymers are amenable to analysis by DSC given the wide separation in the T_g's for the donor and acceptor copolymers over most of the composition range. The compositions of the NECMA copolymer blends are summarized in Table 5. There are single T_g's for blends AE2, AE3, and AE4 but two T_g's for sample AE1, suggesting that a composition with somewhere between 15 and 30 mol % NECMA and DNBM is required to compatibilize PMA and PMMA using these particular interacting groups.

Table 5. Composition of Each of the NECMA Copolymer Blends

	poly(NECMA-*co*-MA)		poly(DNBM-*co*-MMA)	
blend	sample	mol % NECMA	sample	mol % DNBM
AE1	G1	13	A2	12
AE2	G2	31	A5	33
AE3	G3	58	A7	57
AE4	G5	91	A10	90

Table 6. Homopolymer $T_{1\rho}(^1H)$ Values

homopolymer	$T_{1\rho}(^1H)$, in ms	ref
PMA	10	14
PMMA	18	14
poly(NECMM)	47	3
poly(DNBM)	20	3

The T_g results at intermediate compositions are qualitatively similar to those of the NECMM-containing blends. However, at 13–14 mol % donor and acceptor, blend AA1 is thermodynamically compatible while AE1 is incompatible. At approximately 90 mol % donor and acceptor the converse is true: AA6 is incompatible while AE4 appears thermodynamically compatible despite the use of the high molecular weight acceptor copolymer. This apparent compatibility may be due to the closeness of the copolymer T_g's at high donor and acceptor compositions. The use of NECMA rather than NECMM has the effect of shifting the "compatibility scale" to higher donor and acceptor contents. The compatibility of sample AE3 (and maybe AE4) shows that the critical molecular weight which induces this blend system to become kinetically compatible at the very least is higher than 90 000, higher than was observed for the PMMA/PMMA blends[1] and for the NECMM-containing PMA/PMMA blends.

ΔH_1 values for the AE blend series show an increase with donor and acceptor content, but all are smaller than the corresponding NECMM ones. Values of ΔH_2 were zero or close to zero for all of the blends. The reason for lower ΔH_1 values than the corresponding ones for the NECMM blends, as well as the other differences in compatibility, is unclear.

$T_{1\rho}(^1H)$ Measurements of the NECMM-Containing Blends. $T_{1\rho}(^1H)$ experiments were performed to ascertain if the blends, which appear to be compatible by DSC, also appear so by NMR which is sensitive to sizes of phases about 1 order of magnitude smaller than those determined by DSC. Figure 8 shows the CP-MAS ^{13}C-NMR spectra for donor copolymer B5 (57 mol % NECMM) and acceptor copolymer A7 (57 mol % DNBM). The assignments are also presented in the figure. Peaks labeled *d1* at 146 ppm and *d2* at 117 ppm are assigned to carbons 8a and 9a and carbons 1 and 8, respectively, from the NECMM rings. The DNBM aromatic carbons labeled *a1* at 169 ppm and *a2* at 156 ppm are assigned to carbon 1 and carbons 3 and 5, respectively.

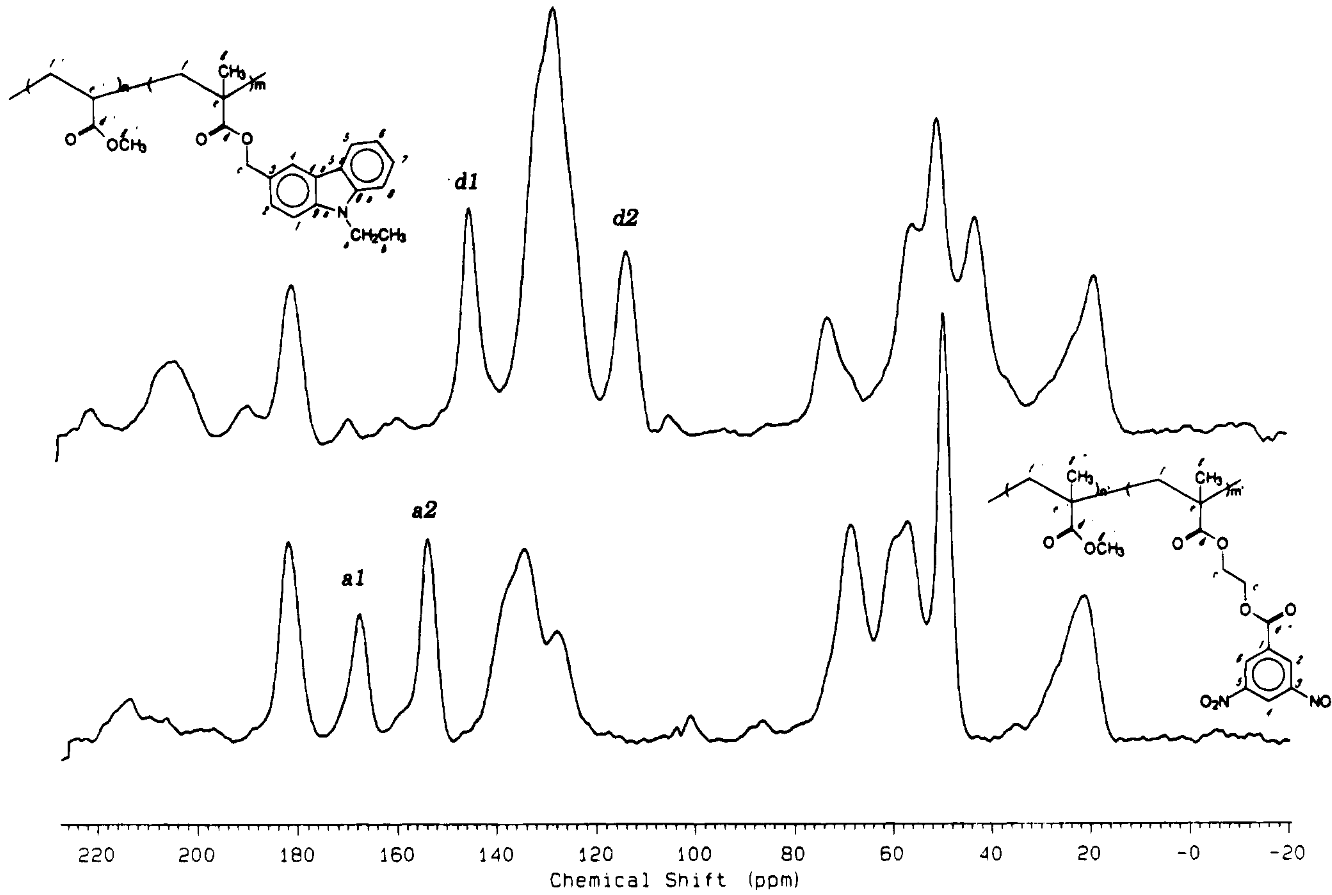

Figure 8. ^{13}C CP-MAS NMR spectra for copolymers A7 and B5.

$T_{1\varrho}(^1H)$ values were determined from plots of the natural logarithm of the peak intensities versus delay times for the signals *a1*, *a2*, *d1*, and *d2*. All plots were exponential. Values were obtained for the copolymers with ≥14 mol % of interacting groups and the results are shown in Figure 9. (The blend series AC was not analyzed by NMR since the DSC already demonstrated incompatibility within the samples.) Also shown in Figure 9 are the $T_{1\varrho}(^1H)$ values calculated using eq 3,[11]

$$\frac{1}{T_{1\varrho}(^1\mathrm{H})} = \frac{N_1}{N_{\mathrm{total}}}\frac{f_1}{T_{1\varrho}(^1\mathrm{H})_1} + \frac{N_2}{N_{\mathrm{total}}}\frac{(1-f_1)}{T_{1\varrho}(^1\mathrm{H})_2} \qquad (3)$$

where N_i, $T_{1\varrho}(^1H)_i$, and f_i are the number of protons in structural unit *i*, $T_{1\varrho}(^1H)$, and mole fraction of structural unit *i*, respectively, and N_{total} is given by

$$N_{\mathrm{total}} = N_1 f_1 + N_2(1 - f_1) \qquad (4)$$

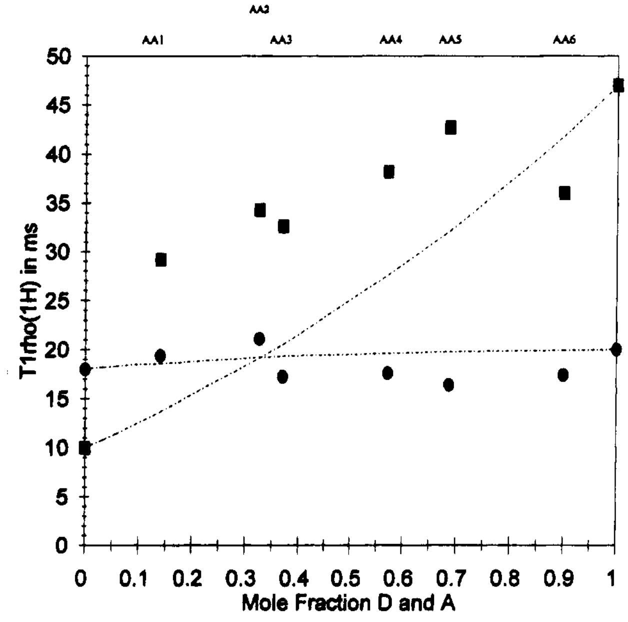

Figure 9. $T_{1\varrho}(^1H)$ values for poly(NECMM-*co*-MA) (■) and poly(DNBM-*co*-MMA) (●) copolymers.

With the exception of a single point, the data for the donor copolymers are consistently higher than those calculated on the basis of the simple weighted averages. The relaxation times for the acceptor copolymers are quite close to the calculated ones. If *q* is negative in eq 2, this reflects poor packing with an increase in the distance between structural units, a consequent increase in the free volume, and a depression of T_g from the calculated average. An increase of free volume due to poor packing of the side groups has as a consequence a decrease in proton density, which in turn could produce the increase in $T_{1\varrho}(^1H)$.[3] For poly(DNBM) blended with poly(NECMM), attractive CT interactions increased the proton density with a concomitant increase in T_g and decrease in $T_{1\varrho}(^1H)$.[3] It has been demonstrated for that system that T_g and $T_{1\varrho}(^1H)$ were directly related because motion had a relatively minor influence on $T_{1\varrho}(^1H)$.[12] The DSC and NMR results for the poly(NECMM-*co*-MA) copolymers illustrate that repulsions between NECMM and MA units result in reduced T_g's and elevated $T_{1\varrho}(^1H)$ values relative to the weighted average of those for the homopolymers, probably also due to increased intergroup distances.

Using the peaks indicated in Figure 8, the $T_{1\varrho}(^1H)$ values were determined for all of the blends (Figure 10).

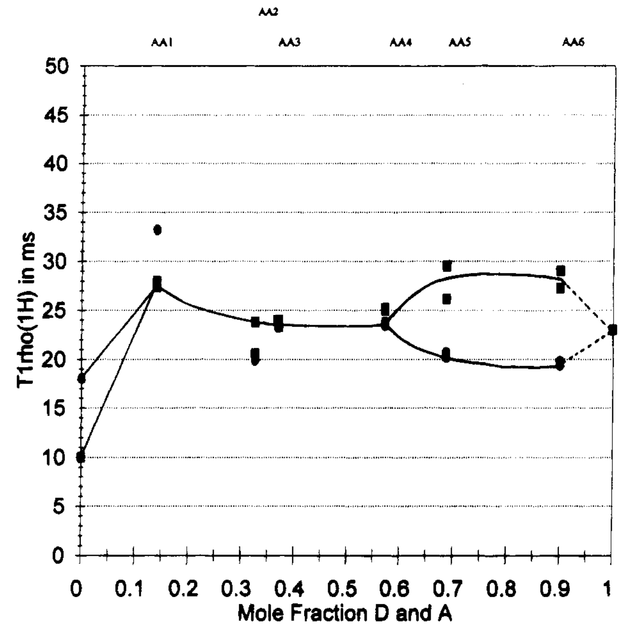

Figure 10. $T_{1\varrho}(^1H)$ values for blend series AA: donor (■) and acceptor (●) peaks.

Except at very low D and A mole fractions (for instance, some of the AC blends which are not presented here), where signal intensities were difficult to determine reliably, the separation of the D and A aromatic carbon signals were sufficient to allow for the independent determination of the $T_{1\varrho}(^1H)$ values for the donor and acceptor. In general, the compatibilities of the blends as studied by CP-MAS NMR relaxation studies are identical to the results obtained by DSC. Furthermore, the compatibility of blend AA4, which was uncertain by DSC due to the overlap of the donor and acceptor copolymer T_g's, is confirmed by NMR. AA5 and AA6 exhibit two $T_{1\varrho}(^1H)$'s and are incompatible: the lower $T_{1\varrho}(^1H)$ values (for the acceptor copolymers) are slightly higher while the higher $T_{1\varrho}(^1H)$ values (for the donor copolymers) are slightly lower compared to those of the copolymers alone. These deviations suggest that there is some degree of mixing within the samples.

To check for the presence of a LCST for the compatibility of samples AA2–AA4 by NMR, they were heated above 200 °C and then their $T_{1\varrho}(^1H)$'s determined again. Phase separation within these samples, if it indeed occurred, went undetected by DSC so that the domains must be less than 100 Å or so in size if they exist. The NMR results showed no change after heating. These results provide further support for the conclusions that AA4 is truely (both thermodynamically and kinetically) compatible while AA5 and AA6 appear to be incompatible.

Conclusions

NMR and DSC studies have been used to investigate the compatibility of blends of random compolymers poly(NECMM-*co*-MA) and poly(DNBM-*co*-MMA). It was found that at least 14 mol % of NECMM and DNBM was needed to compatibilize PMA with PMMA. Blend compositions below 14 mol % and above 57 mol % were both thermodynamically and kinetically incompatible, although ΔH_1 and NMR $T_{1\varrho}(^1H)$ results are consistent with partial compatibility within the samples with >57 mol % donor and acceptor.

Several blends similar in composition to the NECMM-containing ones were prepared in which poly(NECMA-*co*-MA) was substituted for the NECMM donor copolymer. Using NECMA, between 15% and 30% donor and acceptor were required to compatibilize the blend, more than for NECMM. It has been proposed elsewhere[2] that the values of q may provide an indication as to why different amounts of donor and acceptor are needed to compatibilize incompatible polymers. Since it is reasonable to assume that the inclusion of a methyl group does little to affect the oxidation potential of donor and hence the driving force of CT complex formation, NECMA and NECMM are essentially identical to one another as far as the strength of the CT interaction is concerned. However, $q = -120$ for the poly(NECMM-*co*-MA) copolymer indicates that strong repulsions are present in the copolymer (intermolecular and intramolecular) which will act to contribute a compatibilizing effect to the overall interaction parameter of the blend (eq 1). These repulsions are absent in the poly(NECMA-*co*-MA) copolymers, since $q = 0$, so that more attractive interactions must be introduced to induce compatibility. It is interesting to note that the omission of a relatively small methyl unit (usually associated with weak intermolecular forces) on the large donor structural unit sufficiently affects the blend so that the number of CT interactions may have to be as much as doubled to overcome the minor structural change.

Blends which were prepared with high molecular weight acceptor copolymers (blends AE3 and AE4) were found to be both kinetically and thermodynamically compatible although the compatibility of blend AE4 is uncertain due to the closeness of the copolymer T_g's. As in the previous study,[1] almost all of the samples exhibited endothermic transitions at 200 °C but no accompanying phase changes. This is consistent with the interpretation of the so-called "decomplexation enthalpy" in terms of conformational relaxation in the copolymer chains within the blends.

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