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Influence of Charge-Transfer Interactions on Some Bulk Properties of Blends and Copolymers of (*N*-Ethylcarbazol-3-yl)methyl Acrylate and 2-[(3,5-Dinitrobenzoyl)oxy]ethyl Methacrylate

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ABSTRACT: Homopolymers, random copolymers, and polymer blends containing the electron-donor moiety (*N*-ethylcarbazol-3-yl)methyl acrylate (NECMA) and/or the electron-acceptor moiety 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBEM) were prepared. The effect of charge-transfer (CT) interactions was investigated by differential scanning calorimetry (DSC) and solid-state nuclear magnetic resonance (NMR) spectroscopy. Copolymers and blends have a single, composition-dependent glass transition temperature, T_g, elevated with respect to the weighted average of the components, reflecting restricted mobility and reduced free volume due to CT complex formation. Decomplexation occurs at about 170 °C, but phase separation cannot be detected by DSC because pNECMA and pDNBEM have the same T_g. Decomplexation was observed in a donor/acceptor copolymer for the first time. ^{13}C CPMAS/DD NMR showed that the homopolymers have very different rotating-frame spin–lattice relaxation time constants, $T_{1\rho}$(H)s. Blends and copolymers exhibit a single $T_{1\rho}$(H) lower than the weighted average of the components, due to increased proton density on CT complexation. Annealed blends possess two $T_{1\rho}$(H) values, confirming phase separation on decomplexation and demonstrating the superiority of solid-state NMR over thermal or mechanical analysis for the characterization of blends of polymers with coincident T_gs.

Introduction

Polymer blends continue to be the subject of a great deal of interest in both industrial and academic circles. From a practical point of view, the fact that materials with desirable properties can be obtained without the expense associated with the development of new monomers makes blends economically advantageous. However, most polymer pairs are not miscible. The negligible entropy of mixing of macromolecules requires a negative heat of mixing for miscibility. The fundamental scientific interest lies in elucidating the role of specific interactions on polymer/polymer miscibility and on the resulting morphology and physical properties of the blend.

Charge-transfer (CT) interactions are weak nonbonding interactions (10–30 kJ/mol)[1] that can occur between electron-donor and electron-acceptor groups. The incorporation of a small number of donor groups in one type of chain and acceptor groups in another has been used to improve the compatibility of poly(methyl methacrylate) and poly(butyl methacrylate),[2] poly(2,6-dimethyl-1,4-phenylene oxide) and poly(epichlorohydrin),[3] cellulose and polysiloxanes,[4] and poly(methyl acrylate) and poly(butyl acrylate).[5] Work in progress in our laboratory involves compatibilization of polystyrene with poly(methyl acrylate)[6] and of poly(methyl methacrylate) with poly(methyl acrylate).[7] CT interactions are a convenient subject for study because no self-association occurs in homopolymers, in contrast to polymers where ion–ion or hydrogen-bonding interactions are present. In addition, CT interactions play an important role in the self-organization of macromolecules in living systems.

Percec et al. have prepared copolymers[8] and blends of homopolymers[9,10] containing the electron donor (*N*-ethylcarbazol-3-yl)methyl methacrylate (NECMM) and the acceptor 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate (DNBEM). Percec et al. first used differential scanning calorimetry (DSC) to investigate CT interactions in pNECMM/pDNBEM blends,[9,10] and we applied DSC analysis to the NECMM/DNBEM copolymers.[11] Both NECMM/DNBEM copolymers and pNECMM/pDNBEM miscible blends have elevated glass transition temperatures, T_gs, with respect to the weighted average of the homopolymers, reflecting inter- and/or intramolecular CT interactions. Decomplexation occurs when miscible pNECMM/pDNBEM blends are heated above 185 °C, and a two-phase system is formed. Therefore, under the appropriate processing conditions either homogeneous or phase-separated systems with the same overall chemical composition can be obtained.

We have applied solid-state ^{13}C CPMAS/DD nuclear magnetic resonance (NMR) spectroscopy to the study of CT interactions in pNECMM/pDNBEM blends, NECMM/DNBEM copolymers, homopolymer/copolymer blends, and small-molecule analogues.[11-13] The proton rotating-frame spin–lattice relaxation time constant, $T_{1\rho}$(H), is a sensitive probe of the intimacy and homogeneity of mixing of polymer blends.[14] We found that NECMM/DNBEM copolymers and pNECMM/pDNBEM miscible blends exhibit a negative deviation from the weighted average of the homopolymer $T_{1\rho}$(H)s, reflecting the pulling together of donor and acceptor units due to CT interactions. Blends which were shown by thermal analysis to possess two T_gs were usually found to have separate $T_{1\rho}$(H) values for the donor and acceptor phases.[13]

The present paper is an investigation of CT interactions in copolymers and homopolymer blends containing the electron donor NECMA and the acceptor DNBEM described above. In the previously studied NECMM/DNBEM systems, there is greater than a 40 °C difference between the T_gs of the donor and acceptor homopolymers. However, pNECMA and pDNBEM have identical T_gs. This fact complicates the analysis of the NECMA/DNBEM system by thermal or mechanical techniques, so it has not been studied systematically yet. The NECMA/DNBEM system is, therefore, an excellent candidate for analysis by solid-state NMR. This work presents data obtained by a combination of DSC and ^{13}C CPMAS/DD NMR techniques and shows that observation of $T_{1\rho}$(H) complements the thermal analysis and even allows us to

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obtain information not otherwise available.

Experimental Section

NECMA and DNBEM were synthesized as described in the literature. NECMA was obtained by the reduction of (*N*-ethylcarbazol-3-yl)carboxaldehyde to (*N*-ethylcarbazol-3-yl)methanol and its subsequent reaction with acryloyl chloride.[15] DNBEM was made by the addition of ethylene glycol to 3,5-dinitrobenzoic acid to form 2-[(3,5-dinitrobenzoyl)oxy]ethanol, which reacts with methacryloyl chloride to give DNBEM.[16]

Homo- and copolymers were produced by free-radical polymerization of 0.5 M solutions of the monomers in toluene for several days at 60 °C with AIBN present at a level of 1% based on monomer weight. This resulted in high levels of monomer conversion in all cases. Polymers were isolated by two reprecipitations from THF into methanol and dried for several days in vacuo above 70 °C. Some of each sample was also heated to 185 °C in vacuo, maintained there for 10 min, and immediately quenched with liquid nitrogen. These samples are referred to herein as annealed or decomplexed.

The purity of all intermediate compounds and the monomers was confirmed by ^{1}H NMR in $CDCl_3$. The composition of the copolymers was determined by ^{1}H NMR in $CDCl_3$/DMSO-d_6 (50/50, v/v) at 100 °C.

Molecular weights of the homo- and copolymers were determined by gel permeation chromatography of 0.2 wt % THF solutions. A Waters Associates liquid chromatograph equipped with a Model 440 absorbance detector and a Model R401 differential refractometer was employed with a flow rate of 1 mL/min. Peak molecular weights were obtained by comparing retention times in μ-Styragel columns to those of polystyrene standards.

Thermal analysis of the samples was carried out on a Mettler TA3000 system equipped with a TC10A TA processor and a DSC30 head. Each sample was subjected to four heating scans with fast cooling to room temperature in between. Samples were heated twice from 30 to 150 °C and then twice from 30 to 200 °C at a rate of 20 °C/min. Heat flow vs temperature and first-derivative curves were obtained. The midpoint of the second-order transition is quoted as the T_g here.

Proton-decoupled solid-state ^{13}C NMR spectra were obtained at room temperature on a Bruker CXP-200 spectrometer operating at 50.307 MHz using cross polarization and magic angle spinning. $T_{1\rho}$(H) was obtained from the decay in ^{13}C magnetization at long contact time during matched spin-locked cross-polarization transfer experiments.[14] A $\pi/2$ pulse of 3.8 μs was used with a delay time between pulses of at least 5 s. Contact times ranged from 0.25 to 60 ms. Around 700 FIDs were required for each spectrum.

Results and Discussion

GPC indicated that all samples were high molecular weight polymers. Peak molecular weights of pDNBEM and NECMA/DNBEM copolymers ranged from 12 000 to 19 000, and the pNECMA had a peak molecular weight of 76 000.

Differential Scanning Calorimetry. The results of DSC analysis are listed in Table I. In general, an endotherm from removal of residual solvent was observed in the first heating run, so first-run data were not used. All samples showed a single T_g, reproducible to within 1 °C, during scans 2 and 3, which is quoted as T_{gi} in Table I. An endotherm was observed for some samples upon heating above about 170 °C, with a change in T_g in the following scan.

Table I
DSC Data for NECMA/DNBEM Copolymers and pNECMA/pDNBEM Blends[a]

NECMA, mol %	T_{gi}, °C	T_{gi} range, °C	ΔH_i, J/g	T_{gf}, °C	T_{gf} range, °C	ΔH_f, J/g
			(1) Homopolymers			
0	104	10.6		100	10.2	
100	104	10.8		104	10.5	
			(2) NECMA/DNBEM Copolymers			
32	115	10.8		112	10.2	
45	120	11.0		118	10.9	
58	120	11.0	1.1	118	10.6	
			(3) pNECMA/pDNBEM Blends			
30	115	14.1	2.4	103	11.2	
50	119	11.7	2.8	104	11.9	
70	115	13.0	2.3	109	15.6	2.6

[a] Values subscripted *i* refer to data collected before heating the sample to 200 °C; data collected after the sample was heated to 200 °C and cooled back to room temperature have the subscript *f*.

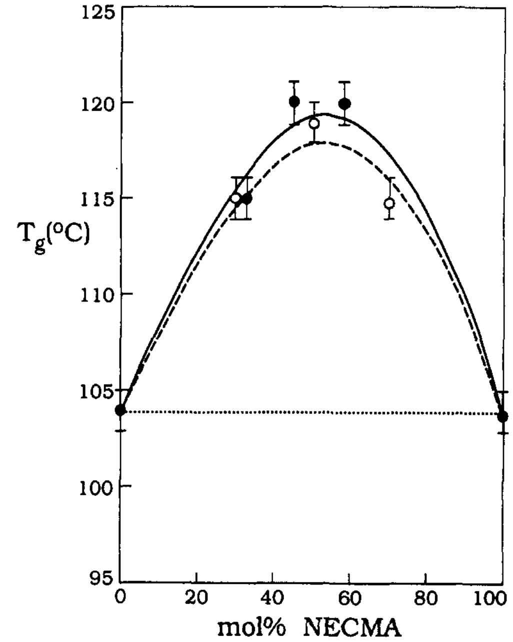

Figure 1. T_g vs composition for NECMA/DNBEM copolymers (●) and pNECMA/pDNBEM blends (○). The solid and dashed lines are generated from the Kwei equation with a *q* of 61.4 and 55.2, respectively.

Figure 1 shows the average of the second- and third-run T_gs for pNECMA, pDNBEM, NECMA/DNBEM copolymers, and pNECMA/pDNBEM blends. The copolymers and blends each exhibit a single T_g, elevated with respect to the weighted average of the homopolymers. The T_g elevation in copolymers and blends reflects a decrease in mobility or a reduced free volume due to CT complex formation between donor and acceptor units.[9,11,17] Kwei has developed an equation to fit T_g for miscible blends with strong intermolecular interactions[18]

$$T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) + qw_1w_2$$

where T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the blend and each of its components, w_1 and w_2 are the weight fractions of the components, and k and q are empirical parameters representing the shape of the T_g vs composition curve and strength of the interactions, respectively. Percec et al. have applied the Kwei equation to pNECMM/pDNBEM blends,[9] and we extended it to NECMM/DNBEM copolymers.[12] The q value obtained for those blends was 60.0 and that for the copolymers 69.4, suggesting that inter- and intramolecular interactions in the copolymers were more effective in stabilizing the backbone than the intramolecular interactions in the blends.

In the system under consideration, k is equal to 1 because there is no inflection point in the T_g vs composition data[19] and $w_1 + w_2 = 1$. In addition, both homopolymers have a T_g of 104 °C, so the Kwei equation simplifies to

$$T_g = 104 + q w_1 w_2 \ (^\circ\mathrm{C})$$

An analysis of the T_gs we obtained gives an average q of 55.2 for the pNECMA/pDNBEM blends and a q of 61.4 for the NECMA-*co*-DNBEM copolymers. Figure 1 shows how the curves generated by the Kwei equation fit our data. Although the difference between the blends and copolymers is small, it appears significant, since the fit obtained by using an average value of q over all blends and copolymers combined was not good for either. Therefore, it seems that, for this system as well, the inter- and intramolecular interactions in the copolymers have a greater effect than do the intermolecular interactions in the blends. The q values for the NECMA/DNBEM samples are slightly lower than those for the NECMM/DNBEM system.[9,12] This may be because the more flexible acrylate backbone is not distorted as much by the CT interactions as the methacrylate in NECMM, so a smaller deviation from additive behavior is seen.

Schneider proposed that the decrease in free volume in compatible donor/acceptor blends is due to conformational rearrangements in the neighborhood of binary heterocontacts between pendant groups.[20] He has developed an equation to fit the T_g of miscible blends where attractive interactions are present,[20] but it appears to be unsuitable for the NECMA/DNBEM system, because both components have the same glass transition temperature. The presence of the term $(T_{g1} - T_{g2})$ in the denominator of Schneider's equation prevents its use to fit our data.

Table I shows that all the NECMA/DNBEM copolymers and blends possess a single T_g, indicating one-phase systems. Looking at the range over which the transition took place in different samples is also instructive. The T_g range in homopolymers is smallest, averaging about 10.7 deg. The T_g range in the copolymers is comparable to that in the homopolymers, at 10.9 deg, indicating almost the same degree of homogeneity. The T_g range is enlarged in the blends, although not uniformly for all compositions. This enlargement in the T_g range of miscible blends has been attributed to local composition fluctuations and so is an indirect measure of the mixing in the blend.[17] The 50/50 mol/mol pNECMA/pDNBEM blend, where one would expect the largest number of CT interactions, exhibit the most narrow transition range of the miscible blends. Although the present system does not show the two-phase behavior at low polydonor concentrations that was seen in the pNECMM/pDNBEM blends,[13] the T_g range of the 30 mol % NECMA blend is enlarged by 34%, suggesting a less homogeneous blend. The high-donor content blend shows an intermediate degree of T_g-range enlargement. These data suggest an asymmetry toward better mixing in samples with high polydonor content in comparison to those with the same proportion of polyacceptor. This resembles the trend toward phase separation we observed with increasing acceptor content in pNECMM/pDNBEM blends.

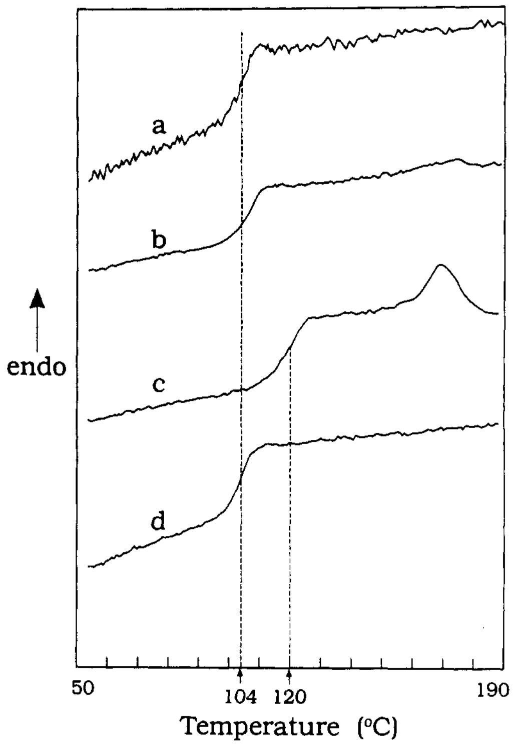

Figure 2. DSC data obtained on heating to 200 °C for (a) pNECMA, (b) pDNBEM, (c) a 50/50 mol/mol blend of pNECMA and pDNBEM, and (d) sample c after decomplexation by heating to 200 °C.

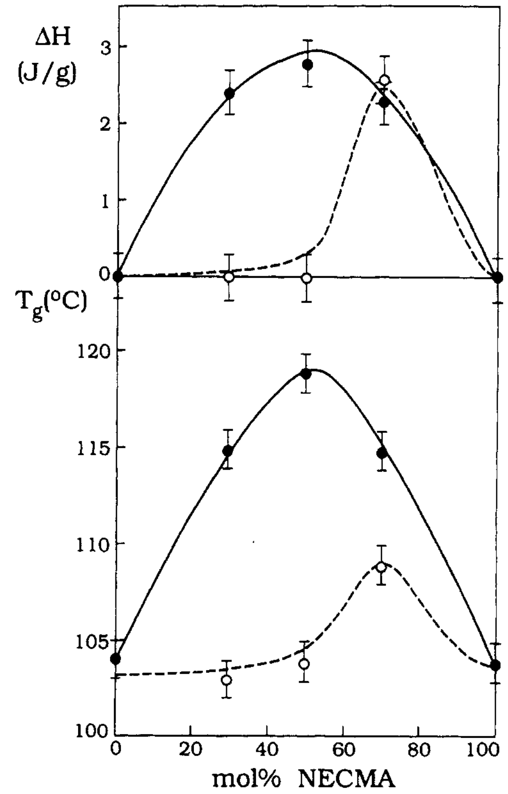

Figure 3. Bottom: T_g vs composition for pNECMA/pDNBEM blends before (●) and after (○) decomplexation. Top: ΔH of decomplexation vs composition for pNECMA/pDNBEM blends. First heating to 200 °C; (●) second heating to 200 °C (○).

The thermal behavior of pNECMA, pDNBEM, a miscible 50/50 mol/mol blend, and the same blend after decomplexation by heating to 200 °C is shown by the DSC data in Figure 2. An endotherm was observed when heating the pNECMA/pDNBEM blends above 170 °C. We believe this reflects the decomplexation process, in analogy with the behavior of pNECMM/pDNBEM blends.[9] This is supported by the observation of Uryu et al. that scanning electron microscopy of a pNECMA/pDNBEM film annealed at 190 °C for 2 min showed a phase-separated matrix-island structure.[21] Figure 3 shows the T_gs of pNECMA/pDNBEM blends before and after heating to 200 °C. For the blends containing 30 and 50 mol % polydonor, the T_g after heating to 200 °C is the same as that of the pure pNECMA and pDNBEM. This is consistent with the proposed decomplexation, but the two-phase nature of these blends cannot be confirmed by this method because both components have the same T_g. The blend containing 70 mol % pNECMA still has an elevated T_g after heating to 200 °C, suggesting that complete decomplexation did not occur or that CT complexes re-form very rapidly in this sample. The T_g range in this sample (Table I) is also broadened considerably after heating, perhaps reflecting some incipient phase separation. The T_g range data for the decomplexed 30 and 50 mol % pNECMA blends are misleading, however, because pNECMA and pDNBEM both have a T_g of 104 °C; in these samples we actually have the situation where the T_g range for a two-phase sample (after decomplexation) is narrower than that in a one-phase sample (miscible blend). This effect underscores the unsuitability of T_g measurement as a method to study the decomplexed blends. There is also no significant difference in the change in heat capacity (ΔC_p) at T_g for the homopolymers, copolymers, and miscible or two-phase decomplexed blends.

The ΔH associated with the endotherms is also plotted vs composition in Figure 3. For the pNECMM/pDNBEM blends, Percec suggested that the ΔH associated with the first heating above the decomplexation temperature is related to the dissociation of CT complexes in the blend, while the ΔH observed on the second heating originates in CT complexes at the interface of pure donor and acceptor phases.[9] Figure 3 shows that the first enthalpy of decomplexation follows the same pattern as the T_g of the miscible blends, with a maximum around a 1/1 mol/mol ratio of donor to acceptor units. The second ΔH does not follow this pattern; there is no measurable endotherm for the samples containing 50 mol % pNECMA or less, whereas, in the 70 mol % pNECMA blend, the ΔH on heating above the decomplexation temperature a second time is as big as the first. However, the T_g of the blend containing 70 mol % pNECMA does decrease on decomplexation but not to the T_g of the homopolymers. This may indicate the formation of smaller domains and therefore a greater interfacial area in this sample, or it may reflect some physical property of the CT complex in the presence of excess donor which makes it easier to re-form.

One final aspect of the thermal analysis of the NECMA/DNBEM system concerns the possibility of observing decomplexation in the copolymers. In principle, copolymers should form both inter- and intramolecular CT complexes in the solid state. One would expect that upon heating the intermolecular complexes could be decomplexed, while the intramolecular ones, particularly complexes formed between adjacent donor and acceptor units bonded together during polymerization, would be more difficult to separate. Nevertheless, to our knowledge, decomplexation has never been observed in donor/acceptor copolymers. It is not known whether this is simply because the number of intermolecular CT complexes formed is too small to produce a measurable ΔH of decomplexation. The NECMA/DNBEM copolymers containing 32 and 45 mol % NECMA both decomposed on heating to 180 °C, so we could not look for decomplexation in these samples. However, Table I shows that we have observed decomplexation in the copolymer containing 70 mol % NECMA and that its magnitude is less than half of that in the corresponding blend sample. This decomplexation endotherm was the same shape as that in the blends and was entirely reproducible in position and intensity over several replicates. Observation of decomplexation in this copolymer appears consistent with the observation that intermolecular CT complex formation seems particularly easy in blends containing excess donor.

Table II
Solid-State Relaxation Data for NECMA/DNBEM Copolymers and pNECMA/pDNBEM Blends

NECMA, mol %	$T_{1\rho}$(H), ms before decomplexn	$T_{1\rho}$(H), ms after decomplexn
	(1) Homopolymers	
0	17	
100	76	
	(2) NECMA/DNBEM Copolymers	
32	19	
45	24	
58	26	
	(3) pNECMA/pDNBEM Blends	
30	19	16, 26
50	25	16, 39
70	30	17, 39

Solid-State NMR. ^{13}C CPMAS/DD NMR of pNECMA, pDNBEM, blends, and copolymers gave well-resolved spectra which were assigned by comparison to the NECMM/DNBEM system.[12,13] $T_{1\rho}$(H)s for the NECMA component and the DNBEM component were calculated individually using two resonances from each, as described in ref 12.

$T_{1\rho}$(H) is a measure of the efficiency of spin diffusion between portons in a sample. It is, therefore, sensitive to both the homogeneity and the intimacy of mixing in a blend or copolymer.[14] The presence of a single $T_{1\rho}$(H) is evidence that spin diffusion takes place throughout the sample unimpeded by phase boundaries and indicates homogeneity. The inverse sixth-power dependence of the rate of spin diffusion on interproton distance means that its magnitude is strongly related to proton density, and any change in the relaxation of one component due to the presence of a second component implies some close (molecular level) contact between them. These properties have made $T_{1\rho}$(H) a parameter of choice when using solid-state NMR to analyze polymer mixtures, and a list of systems investigated to date appears elsewhere.[13]

Table II lists the room-temperature $T_{1\rho}$(H)s of the samples studied. It turns out that the NECMA/DNBEM system is very amenable to $T_{1\rho}$(H) analysis for measuring mixing: although pNECMA and pDNBEM have identical T_gs, their $T_{1\rho}$(H)s differ by nearly a factor of 5, 76 and 17 ms, respectively. Figure 4 shows the $T_{1\rho}$(H) values of NECMA/DNBEM copolymers and pNECMA/pDNBEM blends as a function of composition. All the samples have a lower $T_{1\rho}$(H) than the weighted average of the pNECMA and pDNBEM, so spin diffusion is more efficient than expected. Although $T_{1\rho}$(H) can show some sensitivity to molecular mobility,[14] we feel that interproton distance is the dominant factor in these samples. The formation of CT complexes when both DNBEM and NECMA units are present increases the efficiency of spin diffusion because it pulls the chains closer together. Thus the decreased $T_{1\rho}$(H) is a manifestation of the reduction of free volume upon the formation of heterocontacts discussed earlier.

Figure 4 shows that all the blends and copolymers have a single $T_{1\rho}$(H), indicating that they are homogeneous. The $T_{1\rho}$(H) values of NECMA/DNBEM copolymers and pNECMA/pDNBEM blends lie on the same curve, suggesting a similar rate of spin diffusion in a copolymer and blend of the same composition. The T_gs, on the other hand, suggested a slightly greater effect of CT complexation in the copolymers. One possible explanation for this is that the actual interproton distance in the CT

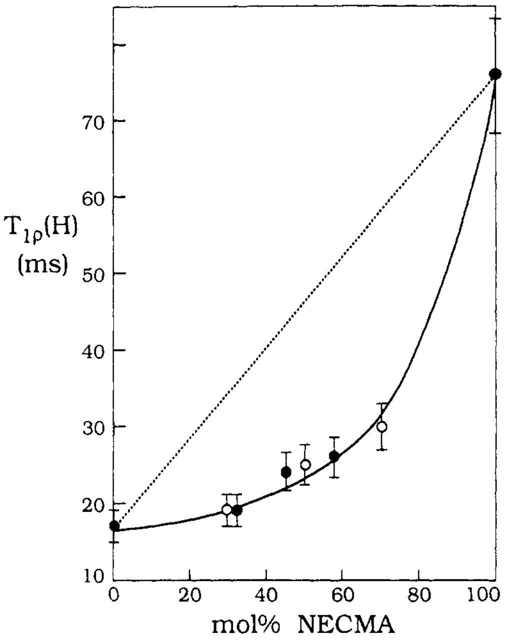

Figure 4. $T_{1\rho}$(H) vs composition for NECMA/DNBEM copolymers (●) and pNECMA/pDNBEM blends (○).

complex is the same in the blends and copolymers but that the effect of complexation on the motion of the backbone measured by T_g is different in copolymers and blends.

Blends annealed at high temperature and quenched are analogous to those decomplexed during the DSC scan to 200 °C. Clearly, it is difficult to assure that the 0.5-g sample prepared for solid-state NMR analysis is identical to a 10-mg sample decomplexed in the calorimeter, due in part to the slightly longer time required for the large sample to attain a temperature of 185 °C and the associated possibility of decomposition. In fact, all copolymers showed signs of decomposition after annealing, so they were not subjected to further $T_{1\rho}$(H) analysis. On the other hand, a single DSC scan to 200 °C of each annealed blend sample was similar to the data observed for small thermal analysis samples, so we feel a comparison is appropriate.

Figure 5 shows the $T_{1\rho}$(H) behavior for blends dried at 70 °C and those annealed above the decomplexation temperature. Although only one T_g could be detected for the decomplexed samples, they clearly exhibit two $T_{1\rho}$(H) values, confirming that phase separation occurs upon heating. The decomplexed blends possess one $T_{1\rho}$(H) close to that of pure pDNBEM and one higher one, the magnitude of which depends on the composition. It appears that CT complexation at the interface of pNECMA and pDNBEM domains is sufficient to increase the rate of spin diffusion compared to that in pure pNECMA, since the $T_{1\rho}$(H) of pure pNECMA is never reached in the decomplexed blends.

The difference in the effect of blending and decomplexation on the $T_{1\rho}$(H) of pNECMA and on that of pDNBEM can be rationalized. Because protons are abundant nuclei, spin diffusion averages the relaxation rate over a whole phase, so the relaxation rate of a given phase is that of the fastest relaxing nuclei in that phase. In the homopolymers, pDNBEM relaxes much more quickly than pNECMA. When pDNBEM is diluted with pNECMA in a miscible blend, its relaxation rate decreases. However, upon decomplexation, there must be many DNBEM/DNBEM contacts in the polyacceptor phase, so it relaxes as quickly as the pure pDNBEM in spite of some interfacial NECMA/DNBEM contacts, because the relaxation is dominated by the fast-relaxing nuclei.

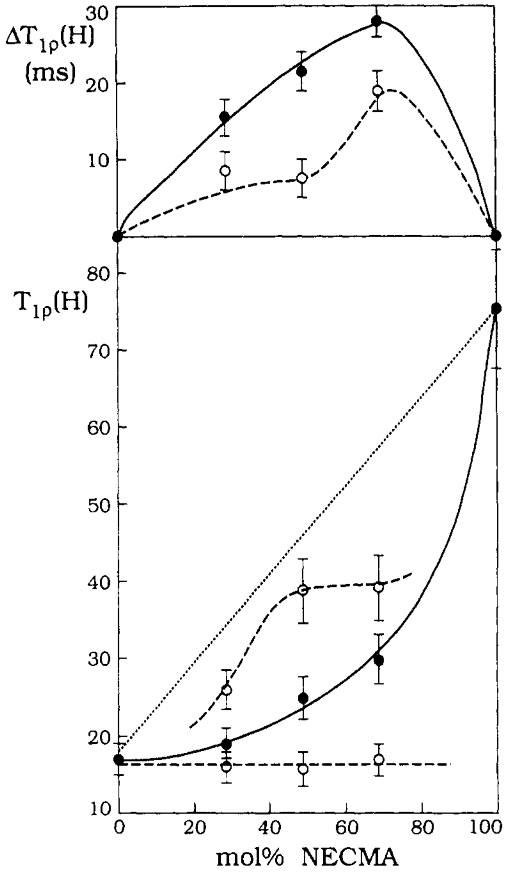

Figure 5. Bottom: $T_{1\rho}$(H) vs composition for pNECMA/pDNBEM blends before decomplexation (●) and after decomplexation (○). Top: [Expected $T_{1\rho}$(H) − observed $T_{1\rho}$(H)] for pNECMA in blends before (●) and after (○) decomplexation vs composition.

The situation for pNECMA is different, and it shows that the relaxation rate of the more slowly relaxing component is a good measure of the extent of CT interactions present. As pDNBEM is added to pNECMA, the chains are pulled together and the pNECMA relaxes more quickly. Upon decomplexation the relaxation of the pNECMA in the polydonor phase is dominated by the relaxation of NECMA units at the interface, so its relaxation is more efficient than expected. The upper part of Figure 5 is a plot of the difference between the expected (weighted average) $T_{1\rho}$(H) and the observed $T_{1\rho}$(H) of pNECMA in miscible and decomplexed blends vs composition. The similarity in shape between this graph and that of the heat of decomplexation or the T_g shown in Figure 3 is convincing evidence that the relaxation rate of pNECMA in the blends is a measure of the intermolecular CT interactions.

Conclusions

We have studied the effect of CT interactions in blends and random copolymers containing the electron donor NECMA and the electron acceptor DNBEM. DSC showed that the NECMA homopolymer and the DNBEM homopolymer both have a T_g of 104 °C, precluding investigation of phase-separated systems by thermal analysis. Blends and copolymers possess a single T_g, elevated with respect to the weighted average of the components, reflecting restricted mobility and reduced free volume due to the formation of inter- and/or intramolecular CT complexes. The Kwei interaction parameter, q, and the decomplexation temperature are lower than those of the pNECMM/pDNBEM system, suggesting weaker interactions. Recomplexation is unusually rapid in samples containing an excess of pNECMA. In addition, decomplexation was observed in a NECMA/DNBEM copolymer containing 58 mol % NECMA. We believe this to be the first time decomplexation has been detected in a donor–acceptor copolymer.

We found that pNECMA and pDNBEM have sufficiently different $T_{1\rho}$(H) values for the investigation of mixing by changes in relaxation rates. Before decomplexation, blends and copolymers have a single $T_{1\rho}$(H), indicating a homogeneous system. The negative deviation in $T_{1\rho}$(H) from the weighted average of the components was attributed to an increased proton density on the formation of CT complexes. Phase separation was confirmed by the presence of two $T_{1\rho}$(H) values in decomplexed blends. Some interfacial CT complexation is still present in decomplexed blends, as evidenced by reduced values of $T_{1\rho}$(H) for the more slowly relaxing component, pNECMA, in decomplexed blends.

This investigation demonstrates the limited utility of thermal analysis for the characterization of the NECMA/DNBEM system, particularly after phase separation. It clearly establishes solid-state NMR, in particular measurement of spin diffusion efficiency via $T_{1\rho}$(H), as a viable alternative, and even the preferred analytical method in systems of polymers with coincident T_gs.

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