# Compatibilization of poly(methyl acrylate) with poly(methyl methacrylate) through charge transfer interactions

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**Summary**
Copolymers of methyl acrylate (MA) with an electron-donor comonomer (N-vinylcarbazole) (NVC) are mixed with copolymers of methyl methacrylate (MMA) with a electron-acceptor comonomer (2-(3,5-dinitrobenzoyl)oxyethyl methacrylate) (DNBM) such that 1:1 mol ratios of NVC:DNBM are present at all times. The blends obtained are phase separated up to an average of 27 mol% donor/acceptor structural unit in the copolymer. Above 27 mol% "perturbation", poly(MA) and poly(MMA) become compatible.

**Introduction**
Compatible polymer blends, defined as blends presenting a single phase which contains both components, are usually obtained when specific interactions take place between the components. Many types of nonbonding interactions have been investigated (1). We are interested in our laboratory in charge transfer interactions and recently have demonstrated that CP-MAS C-13 NMR spectroscopy can be successfully used to analyze the phase behavior of a polymer blend containing only interacting units (2). The useful parameter, indicating not only the phase structure but the "strength" of charge transfer interactions, is the proton spin-lattice relaxation time in the rotating frame $(T_{1\rho}H)$. It is interesting to investigate how this parameter is affected by the amount of interacting groups present in the system. To this end, we started the synthesis of a few series of copolymers containing various amounts of electron-donor and electron-acceptor groups and investigation of their blends.

The initial pair of polymers to be blended is chosen to be incompatible, so that introducing increasing amounts of interacting groups results in compatibilization. In a previous paper we reported compatibilization of poly(methyl acrylate) [poly(MA)] with polystyrene by introducing electron-donor groups in poly(MA) and electron-acceptor groups in polystyrene (3). The same paper contained a review of previous similar work reported in the literature. This paper presents the preliminary results of compatibilization of poly(MA) with poly(methyl methacrylate) [poly(MMA)] using as electron-donor comonomer N-

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vinylcarbazole (NVC) and as electron-acceptor comonomer 2-(3,5-dinitrobenzoyl)oxyethyl methacrylate (DNBM). The NMR investigation will be reported separately.
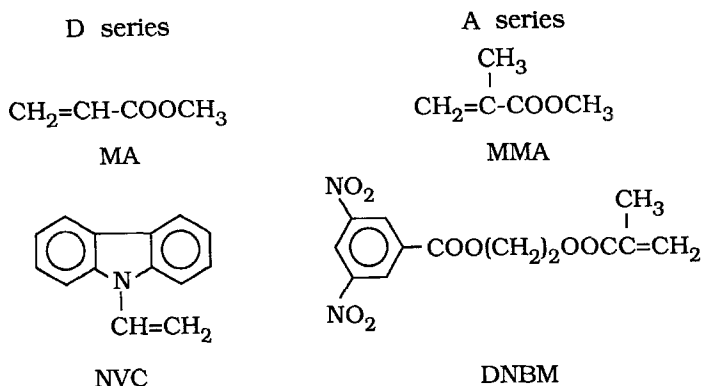
## Experimental

NVC (Aldrich) was used as received. DNBM was synthesized according to published procedures (4). MA and MMA (Aldrich) were vacuum distilled prior to use. Copolymerizations were performed in toluene at a total monomer concentrations of 1.5M with AIBN as initiator (1% of the total monomer weight). Details on copolymerization of MA with NVC will be published elsewhere (5). Copolymerization of MMA with DNBM was previously reported by another research group (6). Our procedure was similar, except that N-ethylcarbazole was added to the reaction mixture in a 1:1 mol ratio to DNBM to enhance the yield (3). The copolymer compositions are summarized for all samples in Table 1. The copolymers were isolated by precipitation in methanol and reprecipitated in a THF-methanol system. NMR spectra in $CDCl_3$ solutions were used to determine copolymer compositions and to confirm the absence of any residual monomer.

The chemical formulae for the monomers are given in Scheme 1. Blending was performed by mixing appropriate amounts of Dx and Ax to obtain the blend Bx. The amounts were calculated so that the donor:acceptor groups were in a ratio of 1:1. The copolymers were separately dissolved in THF, the solutions mixed together and the solvent slowly evaporated at room temperature. The blends were then dried in vacuo at 80°C for a few days. While all the copolymers were white or off-white powders, all blends were yellow-orange, due to the charge transfer interaction. The color was more intense as the content of interacting groups increased. The NMR spectra were obtained on a Bruker AC/F-200 spectrometer and the glass transitions were measured on a Mettler TA3000 DSC instruments with a TC10A processor. The glass transition (Tg) was measured on the second heating scan and was reproducible in subsequent scans.

TABLE 1. Copolymer compositions

| | MA copolymers | | MMA copolymers | |
|---|---|---|---|---|
| Blend | Sample | mol% NVC | Sample | mol% DNBM |
| B1 | D1 | 7.4 | A1 | 6.6 |
| B2 | D2 | 14.7 | A2 | 12.3 |
| B3 | D3 | 19.0 | A3 | 19.4 |
| B4 | D4 | 29.0 | A4 | 24.8 |
| B5 | D5 | 41.8 | A5 | 33.4 |
| B6 | D6 | 47.9 | A6 | 44.3 |

D series          A series

$CH_3$
|
$CH_2=CH-COOCH_3$      $CH_2=C-COOCH_3$

MA            MMA

$NO_2$

$CH_3$
|
$-COO(CH_2)_2OOCC=CH_2$

$NO_2$

|
$CH=CH_2$

NVC           DNBM

Scheme 1

## Results and Discussion

All copolymers were obtained at high conversions, their desired composition calculated from the literature reactivity ratios (5,6). The agreement between the calculated compositions and those actually obtained was fairly good, indicating that the terminal model describing these systems is acceptable.

There are a few equations in the literature which analyze copolymer glass transitions as a function of composition. They were recently critically reviewed (7). All equations use sequence distribution to explain deviation from additivity. In the system analyzed here, even if the terminal model seems to acceptably predict copolymer compositions, calculated sequence distributions would be too speculative. In a previous paper (8) we have demostrated that Kwei's equation (9) can be applied to a copolymer system. Figure 1 presents the dependence of Tg values on copolymer compositions for the two types of copolymers synthesized in this paper.

Both systems are of the type $k = 1$, $q \neq 0$ (10). While the meaning of k is still under discussion (10), the absence of any inflection points in the curves clearly indicates that $k = 1$. On the other hand, q is widely accepted as reflecting interactions between the two components of the blend. In our case q would reflect effects of unlike diads on the overall backbone stability. If q is positive, its contribution is to enhance the backbone stabilization, resulting in a better packed copolymer than either of the corresponding homopolymers. This is the case for poly(MMA-co-DNBM), the A copolymer series. If q is negative, interactions are still present, but the effect of bonding together of the two structural units is to lower the energy barriers of backbone rotation (10). This is the case for the other copolymer series (D), poly(MA-co-NVC). It is not surprising that these two comonomers do not produce a better packed copolymer than the corresponding homopolymers.
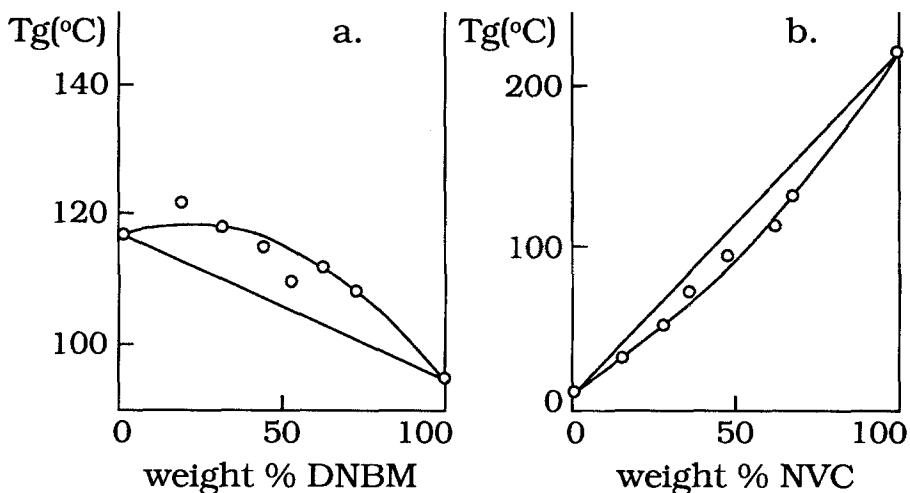
Figure 1. Tg as a function of copolymer composition (weight %). The points are experimentally determined, the curves are calculated using Kwei's equation (9) with k = 1 and q = +36 for poly(MMA-co-DNBM) (a) and q = -83 for poly(MA-co-NVC) (b).

NVC is a very bulky structural unit, its bulkiness coming very close to the backbone. Unless a parallel stacked structure of carbazole rings can be formed, as in poly(NVC), which has a Tg of 220°C, the effect of introducing NVC into almost any copolymer would be backbone destabilization.

The Tg values measured for the blends are presented in Figure 2 as a function of the average "perturbation" introduced into the poly(MA)-poly(MMA) blend by incorporating the comonomers. As expected, at relatively low concentrations of interacting groups, two glass transitions are exibited by the blend. This indicates the phase separated nature of such blends, due to the tendency of poly(MA) and poly(MMA) to form two different phases when mixed. At higher content of interacting groups, the Tg values come closer to each other. Table 2 summarizes the Tg values of the copolymers and blends.

The differences in the Tg for the phase separated blends as compared to the individual copolymers are not very high. The only tendency seems to be a decrease of the Tg of the stiffer copolymer (A1-3), while the more flexible copolymer (D1-3) doesn't change much. By 27 mol% of interacting groups in the copolymer (B4), the two glass transitions merge into one and higher perturbations generate only compatible blends. It is

worth noting that the Tg of the compatible blends is equal to or lower than the Tg of either component. In terms of Kwei's equation this means that the charge transfer interactions bring about an unfavorable packing of the two copolymers in the blend.

There is an important difference in the amount of perturbation necessary to compatibilize poly(MA) with poly(MMA) (27 mol%) as compared to the previous system (3) (ca. 12 mol%). The interacting groups introduced in both cases are identical. One possible explanation is related to the sign of q found for the two copolymer series. In the previous paper, both copolymers had Tgs below the weighted average. The resulting blends also had consistent negative q values. The system analyzed in this paper has a copolymer with positive q and the other with negative q. The resulting blend probably has a negative interaction parameter. It appears that more energy is necessary to overcome the repulsive forces in a system where the copolymers to be mixed are dissimilar than in the previous case.



Tg(°C)

100

50

20    40    60
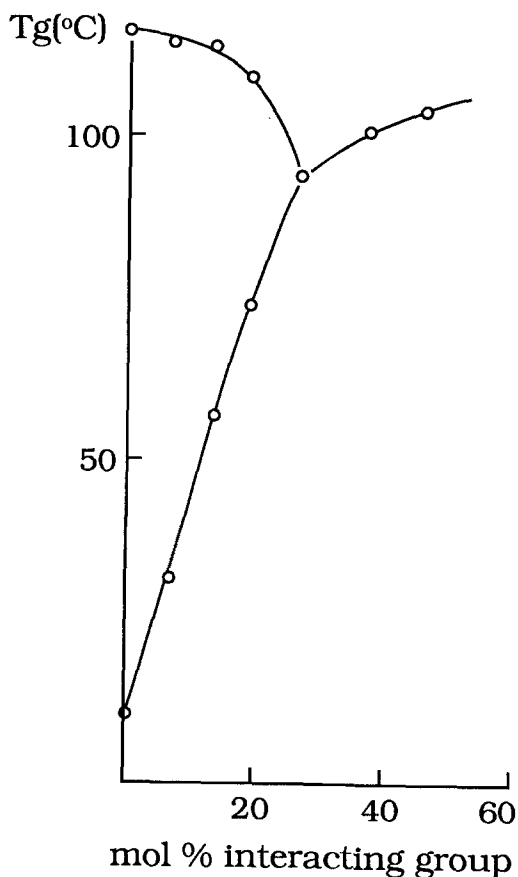
mol % interacting group

Figure 2. Glass transition temperatures of the blends as a function of average molar percent of interacting groups.

TABLE 2. Glass transition temperatures ($^O$C)

| Blend | Tg1 | Tg2 | Tg | Poly(MA-co-NVC) | Poly(MMA-co-DNBM) |
|-------|-----|-----|-----|-----------------|-------------------|
| B1 | 32 | 115 |     | 32 | 122 |
| B2 | 57 | 114 |     | 52 | 118 |
| B3 | 74 | 109 |     | 74 | 115 |
| B4 |    |     | 94  | 93 | 110 |
| B5 |    |     | 101 | 114 | 112 |
| B6 |    |     | 109 | 130 | 108 |

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