

# Miscibility of Poly (acrylonitrile-co-Methyl Acrylate) with Some Thermoplastic Polymers

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## Synopsis

The phase behavior of binary mixtures of poly(acrylonitrile-co-methyl acrylate) (70 : 30) copolymer (B200) with various polymers including poly(N,N-dimethyl acrylamide) (PNNDA), poly(maleic anhydride) (PMA), poly(vinyl pyrrolidone) (PVP), poly(2-ethyl-2-oxazoline) (PEOX), poly(styrene-co-maleic anhydride) (50 : 50) copolymer (SMA), and poly( $\epsilon$ -caprolactone) (PCL) was examined by differential scanning calorimetry (DSC). Miscibility of B200 with some of these polymers was observed over a limited range of composition. Several equations existing in the literature (Fox, Gordon-Taylor, and Kwei) have been employed to describe the dependence of glass transition temperature of the miscible blends as a function of the blend composition. In most cases a deviation from the weight-average values of the experimental glass transition temperatures and of the values predicted by various equations was found. This has been attributed to specific interactions between the molecular constituents of the polymer pair.

## INTRODUCTION

The phase behavior of polymer blends plays a key role in determining their physical properties and subsequently their utility. Generally, from the thermodynamic description of polymer-polymer mixing:

$$\Delta G = \Delta H - T\Delta S$$

the compatibility of two polymers can be viewed as a balance between a free volume term ( $\Delta S$ ), and an interactional term ( $\Delta H$ ). Since the magnitude of entropy change on mixing of two polymers is very small, this term is generally negligible in regard to miscibility. On the other hand, if  $\Delta H$  is negative and overrides the free volume contribution at any given temperature, a miscible polymer blend is formed.

Such a system owes its miscibility to the presence of some specific favorable interactions between the two components. Some of the most common interactions are due to hydrogen bonding, donor-acceptor, ion-dipole or cation-anion interactions. At higher temperatures, the effect of favorable interaction is reduced while the unfavorable effect of the free volume change on mixing increases, eventually leading to phase separation above the lower critical solution temperature.

Aspects related to the intermolecular interactions occurring between different polymeric components are discussed in a number of papers published recently in the literature.<sup>1-12</sup> Hydrogen-bonding type of intermolecular interactions was for instance identified to involve the poly( $\epsilon$ -caprolactone) carbonyl group and

the hydroxyl groups of poly(hydroxy ether of Bisphenol A).<sup>6</sup> A quantitative measure of the fraction of hydrogen-bonded carbonyl groups as a function of temperature was performed on poly(vinyl phenol)/poly(vinyl acetate) and poly(vinyl acetate) copolymers.<sup>7</sup> Additional examples include the interactions involving the halogen groups of one polymer component and the carbonyl group of the other.<sup>8</sup>

Polyacrylonitrile and acrylonitrile copolymers are among the polymers which exhibit rather limited miscibility with any other polymer. Reports on blends of styrene-acrylonitrile copolymers with polymethacrylates indicate that such mixtures are miscible over a limited window of acrylonitrile content. They exhibit phase separation on mixing or lower critical solution temperature behavior.<sup>13-15</sup>

The overall objective of this study was to search for potential miscible polymer blends having as one of the components poly(acrylonitrile-co-methyl acrylate) (70 : 30) (experimental polymer of BP America commonly known as B200). Our work includes blends of B200 with PNNDA, PMA, PVP, PEOX, PCL, and SMA. In most cases, miscible blends were found for a limited range of composition as was evidenced by the existence of a single glass transition temperature.

The interpretation of the phase behavior of the B200 with these polymers is potentially complicated by the fact that in each system there are at least three sources of interactions. In addition, only the molar mass of one of the components in the blend (B200) was kept constant. The molar mass of the second component in each system varied in a rather large range (number average molar mass  $\bar{M}_n = 10,000$  to 50,000).

## EXPERIMENTAL

PNNDA ( $\bar{M}_w = 34,298$ ), PMA ( $\bar{M}_w = 23,000$ ), PVP ( $\bar{M}_w = 10,000$ ) and PEOX ( $\bar{M}_w = 50,000$ ) were obtained from Polysciences, Inc. SMA ( $\bar{M}_w = 350,000$ ) and PCL ( $\bar{M}_w = 40,000$ ) were purchased from Aldrich Chem. Co. B200 was synthesized at BP America Inc. ( $\bar{M}_n = 50,000$ ). All the polymers were used as received. The films of the blends prepared for thermal analysis measurements were cast from dimethylformamide (DMF) on glass plates heated at 80°C. After the majority of the solvent was evaporated, the films were transferred to a vacuum oven and heated to 80°C under vacuum for several days (6 to 10 days). The complete removal of residual DMF, which could act as an efficient plasticizer, was very difficult. Therefore, before performing any measurements, the films were analyzed by IR spectroscopy. Only the films found to be free of solvent were considered for thermal analysis.

The calorimetric studies were conducted on a Perkin-Elmer differential scanning calorimeter (DSC-4) coupled to a computerized data station. A heating rate of 20°C min<sup>-1</sup> was used in all experiments and the glass transition temperature was taken as the onset of the heat capacity change.

## RESULTS AND DISCUSSION

The concept of specific interactions generally evaluate the type of dissimilarities of the components. The systems under investigation in this study present

dissimilarities and similarities; therefore, the interactions which give rise to miscibility in some cases are as yet poorly understood. Several sites for the interaction on the acrylonitrile copolymer may be envisaged. The possible reactive sites involved in intermolecular interactions are summarized in Table I.

Weak hydrogen bonding can be assumed to occur when B200 is blended with some of the polymers shown in Table I. Generally, a hydrogen bond represents an interaction between a functional group A-H and an atom or group of atoms B in the same or different molecules. Besides oxygen, nitrogen, and fluorine as A or B, there is evidence reported in the literature that weaker hydrogen bonding exists in other systems.<sup>16</sup> For instance, hydrogen bonding where A is carbon has been identified.<sup>17,18</sup> In our systems, hydrogen bonding interactions are possible between the carbonyl group of one polymer component and an  $\alpha$ -hydrogen of the other. The nitrogen atom, that contains a lone pair of electrons, is an excellent site for potential hydrogen bonding to a labile proton. A direct dipole-dipole interaction between the carbonyl group and the cyano group is possible.

TABLE I  
Reactive Sites Potentially Involved in Interchain Interactions

No.	Polymer	Structure and reactive sites
1	B200	$\begin{array}{c} \text{C}=\text{N} \\   \\ \text{-(CH}_2\text{-CH)}_n\text{-CH}_2\text{-CH}_n\text{-} \\   \\ \text{COOCH}_3 \end{array}$
2	PNDA	$\begin{array}{c} \text{-(CH}_2\text{-CH)}_n\text{-} \\   \\ \text{C}=\text{O} \\   \\ \text{CH}_3\text{-N-CH}_3 \end{array}$
3	PMA	$\begin{array}{c} \text{-(CH-CH)}_n\text{-} \\   \quad   \\ \text{O}=\text{C} \quad \text{C}=\text{O} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{O} \end{array}$
4	PEOX	$\begin{array}{c} \text{-(N-CH}_2\text{-CH}_2\text{)}_n\text{-} \\   \\ \text{C}=\text{O} \\   \\ \text{CH}_2\text{-CH}_3 \end{array}$
5	PCL	$\text{-(CH}_2\text{)}_5\text{-C(=O)-O)}_n\text{-}$
6	PVP	$\begin{array}{c} \text{-(CH}_2\text{-CH)}_n\text{-} \\   \\ \text{N} \\   \\ \text{O} \end{array}$
7	SMA	$\begin{array}{c} \text{-(CH}_2\text{-CH-CH-CH)}_n\text{-} \\   \quad \quad \quad   \quad \quad \quad   \\ \text{C}_6\text{H}_5 \quad \quad \quad \text{O}=\text{C} \quad \quad \quad \text{C}=\text{O} \\ \quad \quad \quad \quad \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \quad \quad \quad \quad \text{O} \end{array}$

On the other hand, the involvement of these groups in nonbonding interactions may be retarded due to several reasons. First, the electron distribution in polymer segments and the mobility of the dipoles in macromolecular chains may be different from that of low molecular weight compounds. Second, the polymer conformation as well as the intra- and intermolecular bridges bring a certain amount of steric hindrance against free rotation, which differs from system to system. Finally, a contribution to miscibility in these systems may be simply the result of repulsive interaction between the two different units from which one of the blend's component (B200) is formed.

Our miscibility study is based on the most widely used criterion—the existence of a single glass transition temperature of the polymer blend. From several equations available in the literature for correlating the dependence between the glass transition temperature of a miscible blend and its composition, we used the following:

*Gordon-Taylor equation*<sup>19</sup>:

$$T_g = \frac{W_1 T_{g1} + KW_2 T_{g2}}{W_1 + KW_2} \quad (1)$$

where  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are respectively, the glass transition temperatures of the blend, of polymer 1, and polymer 2;  $W_1$  and  $W_2$ —the corresponding weight fractions;  $K$ —ratio between the volume expansion coefficient of the polymers in the mixture.

*Fox equation*<sup>20</sup>:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (2)$$

where  $T_g$ ,  $T_{g1}$ ,  $T_{g2}$ ,  $W_1$  and  $W_2$  have the same meanings as in the Gordon-Taylor equation.

*Kwei equation*<sup>21</sup>:

$$T_g = \frac{W_1 T_{g1} + KW_2 T_{g2}}{W_1 + KW_2} + qW_1 W_2 \quad (3)$$

where  $T_g$ ,  $T_{g1}$ ,  $T_{g2}$ ,  $W_1$ ,  $W_2$ , and  $K$  have the same meaning as in eq. (1). Usually the  $K$  from the Gordon-Taylor equation<sup>7,8</sup> and  $q$  value from the Kwei equation<sup>21</sup> are used to estimate the strength of the interchain interaction. The values of the constant parameter  $K$  in Gordon-Taylor equation and  $K$  and  $q$  in the Kwei equation were determined by standard least-square procedures to obtain the best fit with the experimental points.

Equation (1) (Gordon-Taylor) introduces  $K$  as a fitting parameter. In a recent communication, Brekner et al.<sup>22</sup> have proposed an extended variation of eq. (1) which relates the fitting parameter  $K$  to the intensity of the polymer-polymer interaction and to the impact of the immediate surroundings. Accordingly, this modified eq. (1) suggests that constant  $K$  can be expressed in terms of the glass transition temperatures of the components by assuming the validity of the Simha-Boyer rule.<sup>23,24</sup>

$$K = \rho_1 T_{g1} / \rho_2 T_{g2} = K^1 T_{g1} / T_{g2} \quad (4)$$

where  $\rho_1$  and  $\rho_2$  are the densities of polymer 1 and polymer 2, respectively at the glass transition temperature of the blend. Introducing eq. (4) into eq. (1) results in Brekner et al. equation

$$T_g = (W_1 T_{g1} + K^1 (T_{g1} / T_{g2}) W_2 T_{g2}) / (W_1 + K^1 (T_{g1} / T_{g2}) W_2) \quad (5)$$

In this expression,  $K$  is no longer a fitting parameter.  $K^1$  is assumed to vary in a relatively small range (0.8 to 1.2) since polymers generally have close densities.

### B200/PNND A SYSTEM

The films prepared from binary blends of B200 and PNND A were optically transparent at room temperature. The DSC thermograms for this system exhibit single composition-dependent  $T_g$ 's as is shown in Table II.

The measured  $T_g$ 's as well as the values predicted by the various equations are illustrated in Figure 1. It is clear from Figure 1 that B200/PNND A blend system cannot be described by eq. (2). The best fit of the experimental results is given by eq. (1) with  $K = 0.17$  and eq. (3) with  $K = 5.1$  and  $q = -44.7$ .<sup>25-27</sup>

The negative deviation of the glass transition temperatures from the weight-average values may indicate weak interchain interactions which are not able to restrict the mobility of the nonparticipating segment or the entire macromolecule. Obviously, this observation does not agree with the relatively high value of  $K$  when the system is described by eq. (3). Therefore, we cannot count on this constant to judge the strength of the interchain interactions. No more information is gained by using the extended (Brekner et al.) eq. (5) since it reduces to simply additivity  $K = 1$  ( $\rho_{B200} = 1.15 \text{ g/cm}^3$ ,  $\rho_{PNND A} = 0.97 \text{ g/cm}^3$ ,  $T_{gB200} = 81.99$ ,  $T_{gPNND A} = 97.50 \text{ C}$ ).

TABLE II  
Glass Transition Temperatures of B200/PNND A Blends

$W_2^a$	$T_g$ (°C)	Observations
0.00	81.99	Optically clear film
0.05	82.32	Optically clear film
0.10	82.91	Optically clear film
0.20	83.99	Optically clear film
0.25	84.20	Optically clear film
0.50	84.63	Optically clear film
0.60	85.16	Optically clear film
0.80	87.58	Optically clear film
1.00	97.55	Optically clear film

<sup>a</sup> Weight fraction of PNND A.

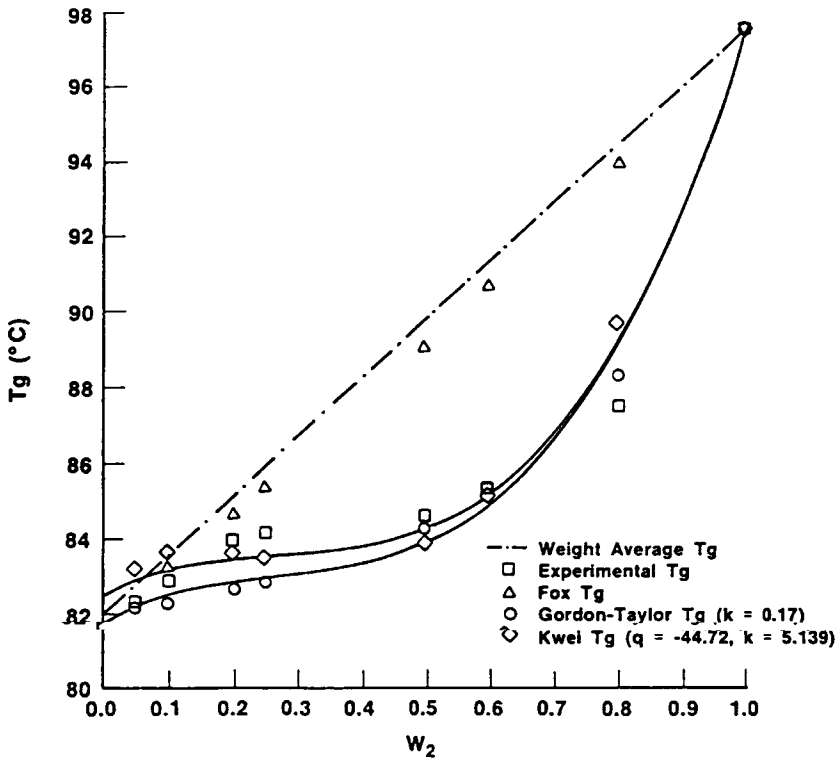


Fig. 1. The experimental  $T_g$  values of B200/PNND blend system and theoretical curves predicted by different equations.

### B200/PMA SYSTEM

The blend composition for this system as well as the measured  $T_g$  values are shown in Table III. The miscibility of the two polymers was proved by the existence of a single glass transition temperature intermediate between those of the parent polymers (Fig. 2). As in the case of B200/PNND system, the

TABLE III  
Glass Transition Temperatures of B200/PMA System

$W_2^a$	$T_g$ (°C)	Observations
0.00	81.99	Optically clear film
0.05	81.30	Optically clear film
0.10	74.63	Optically clear film
0.20	73.40	Optically clear film
0.25	71.02	Optically clear film
0.50	70.30	Optically clear film
0.75	69.90	Optically clear film
1.00	69.15	Optically clear film

<sup>a</sup> Weight fraction of PMA.

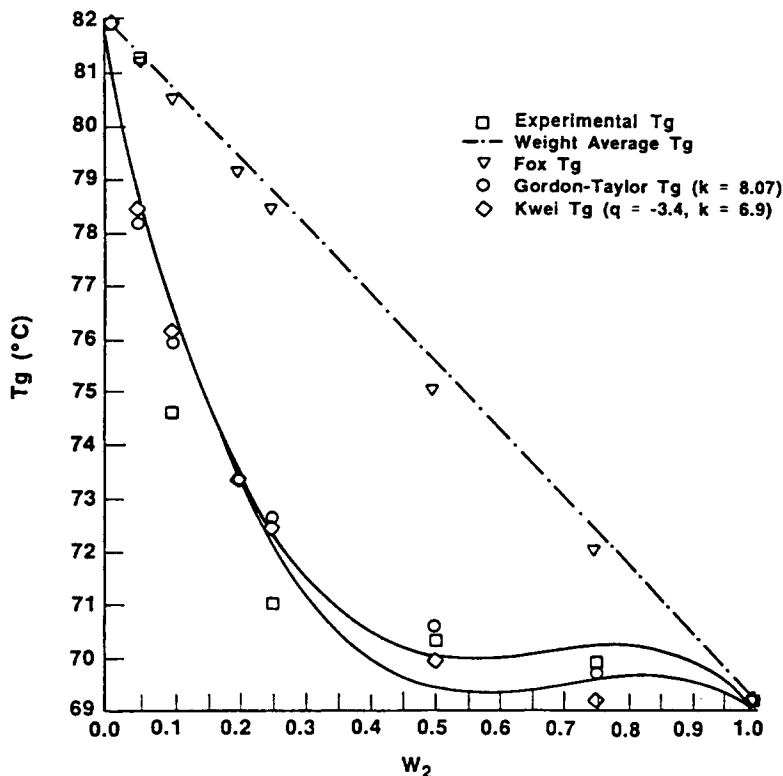


Fig. 2. The experimental  $T_g$  values of B200/PMA blend system and theoretical curves as described by different equations.

best fit of the experimental data is obtained with eq. (3) when  $K = 6.9$  and  $q = -3.4$ .

The estimation of this system by eq. (1) gives an optimum fit with  $K = 8.07$ . Again the physical meaning (if any) of the values obtained for these constants cannot be ascribed with our present data.

### B200/PVP SYSTEM

The composition range studied for this system and the  $T_g$  values measured for several compositions are given in Table IV. Miscibility was observed over the whole composition studied. This was proved by the formation of transparent films and the existence of a single glass transition temperature. Figure 3 presents the experimentally observed glass transition temperatures of this system as well as the values predicted by different equations.

Both eqs. (1) and (3) adequately describe the system. The computed optimum fit with experimental points is obtained with  $K = 0.716$  [eq. (1)] and  $K = 0.95$ ,  $q = 1.64$  [eq. (3)]. The deviation of the experimental data and of predicted  $T_g$  values from the weight average line is positive. This might be an indication of strong interchain interactions which decrease the mobility of the polymer chains.

TABLE IV  
Glass Transition Temperatures of B200/PVP System

$W_2^a$	$T_g$ (°C)	Observations
0.00	81.99	Optically clear film
0.05	81.80	Optically clear film
0.10	81.51	Optically clear film
0.20	81.30	Optically clear film
0.25	81.10	Optically clear film
0.60	79.20	Optically clear film
0.75	78.00	Optically clear film
1.00	76.50	Optically clear film

<sup>a</sup> Weight fraction of PVP.

### B200/PEOX SYSTEM

The blend composition and the measured  $T_g$  values are presented in Table V. The two polymers are not miscible in all proportions but only in a limited composition range. Beyond 20% they are immiscible and separate into two

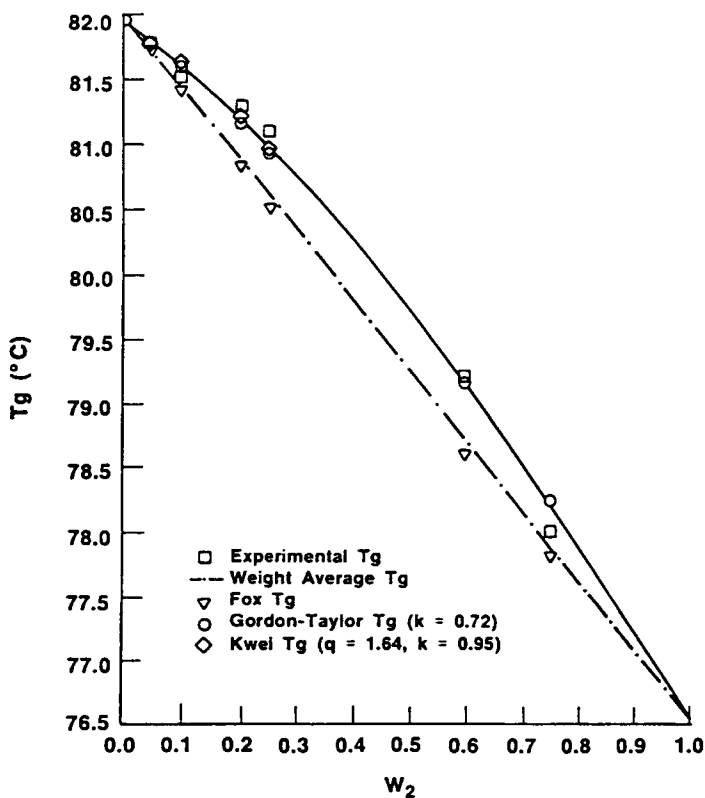


Fig. 3. The experimental  $T_g$  values of B200/PVP blend system and theoretical curves as described by different equations.



TABLE V  
Glass Transition Temperatures of B200/PEOX System

$W_2^a$	$T_{g1}$ (°C)	$T_{g2}$ (°C)	Observations
0.00	81.99	—	Optically clear film
0.05	81.84	—	Optically clear film
0.10	80.30	—	Optically clear film
0.20	81.90	57.0	Cloudy film
0.25	81.83	56.7	Cloudy film
0.50	81.90	56.9	Cloudy film
1.00	56.62	—	Optically clear film

<sup>a</sup> Weight fraction of PEOX.

distinct phases. The solution cast films were cloudy at room temperature and exhibited two glass transition temperatures occurring at essentially the same temperature as for the pure components (Fig. 4).

### B200/PCL SYSTEM

The binary blends of B200 and PCL formed cloudy solutions when PCL was present in more than 10%. Their cast films were opaque indicating their het-

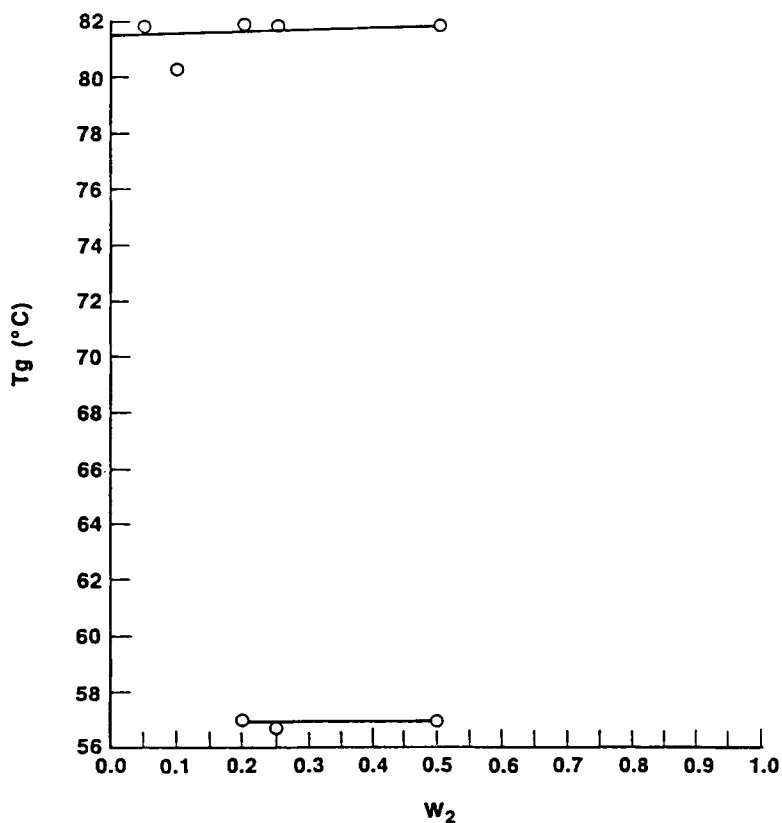


Fig. 4. Glass transition temperatures of B200/PEOX blend system.

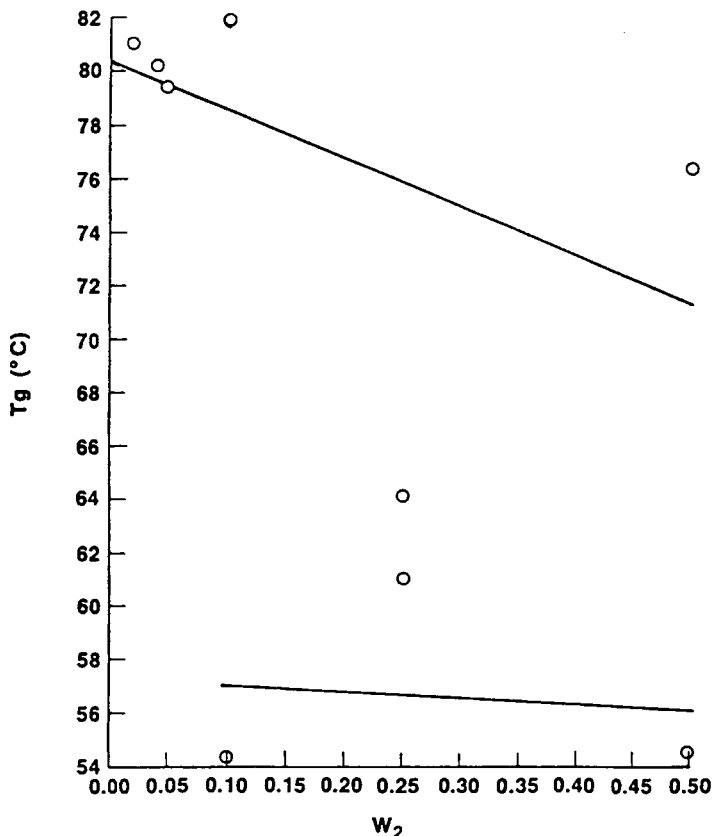


Fig. 5. Glass transition temperatures and melting behavior of B200/PCL blend system.

erogeneous nature. The limited miscibility of this system was further confirmed by DSC measurements.

The glass transition temperatures and the melting behavior of different compositions of B200/PCL blends can be seen in Figure 5 and Table VI. The

TABLE VI  
Glass Transition Temperatures and Melting Behavior of B200/PCL System

W <sub>2</sub> <sup>a</sup>	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)		Observations
		First heat	Second heat	
0.00	81.99	—	—	Optically clear film
0.02	81.00	—	—	Optically clear film
0.04	80.20	—	—	Optically clear film
0.05	79.40	56.04	—	Cloudy film
0.10	81.90	56.29	56.68	Cloudy film
0.25	67.73	59.75	55.38	Cloudy film
0.50	76.41	62.00	60.22	Cloudy film
1.00	—	58.88	61.38	Cloudy film

<sup>a</sup> Weight fraction of PCL.

blends containing PCL are different from the other systems in that this component is readily crystallizable. At low concentrations of PCL (10 to 50%), the crystallizable fraction melts at slightly lower temperatures than that of the pure component (Table VI). However, the melting point depression data are not sufficient to calculate the interaction parameter and based on it to show conclusions regarding the miscibility of the blend. The  $T_g$  values of the amorphous fraction are also lower than for pure B200 which may be an indication of the partial miscibility of such a system.

### B200/SMA SYSTEM

Blends of B200 with SMA show single glass transitions located at temperatures intermediate between those of the parent polymers when the second component does not exceed 15% (Table VII). Two transitions at temperatures close to those of pure polymers have been found for blends containing more than 50% SMA component. Evidently as Figure 6 shows, there are not enough data to comment on the miscibility behavior of this system when SMA varies in concentration from 15 to 50%.

### CONCLUSIONS

Experimental information regarding the miscibility of B200 with various polymers have been accumulated. B200 is miscible with PNND, PMA, and PVP over their entire range of composition. Films cast from solution exhibit distinctive single  $T_g$ 's which are intermediate between those exhibited by the pure components. The experimental values of the glass transition temperatures are consistent with those predicted for a miscible blend by classical equations available in the literature. The deviation from the weight average values of the experimentally observed glass transition temperatures and of those predicted by various equations are accounted to intermolecular interactions involved. A negative deviation indicating weak intermolecular interactions characterizes B200/PNND and B200/PMA blend systems. On the other hand, the  $T_g$  of the B200/PVP blends falls above the linear relationship suggesting that strong interchain interactions are present. In the case of B200/PEOX and B200/PCL

TABLE VII  
Glass Transition Temperatures of B200/SMA System

$W_2^a$	$T_{g_1}$ (°C)	$T_{g_2}$ (°C)	Observation
0.00	81.99	—	Optically clear films
0.05	82.30	—	Optically clear films
0.10	83.70	—	Optically clear films
0.15	84.90	—	Optically clear films
0.50	81.99	133.00	Cloudy film
0.80	81.99	133.00	Cloudy film
1.00	133.00	—	Optically clear film

<sup>a</sup> Weight fraction of SMA.

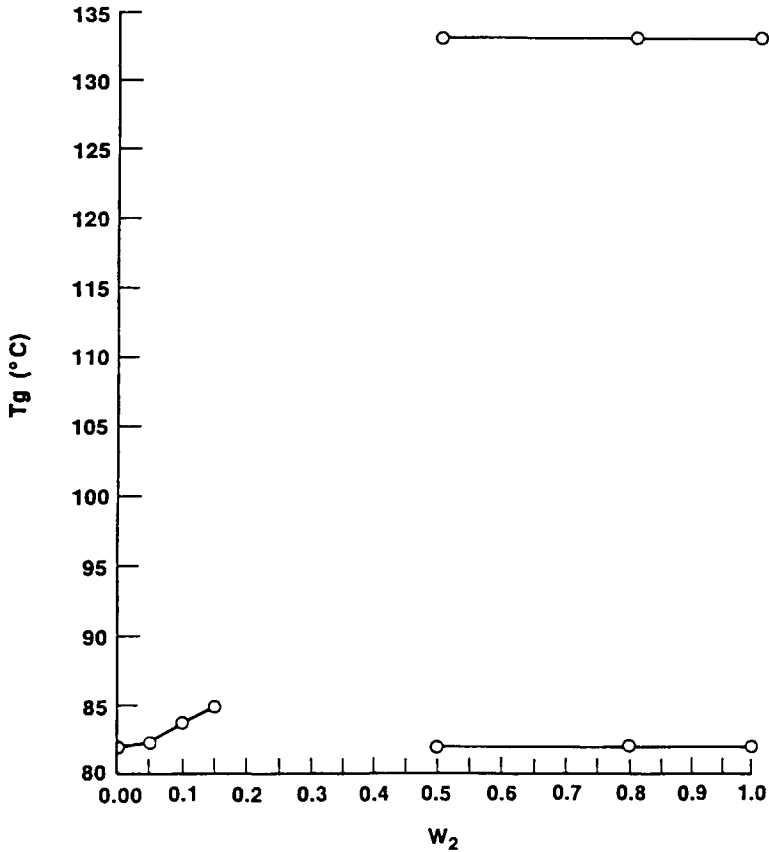


Fig. 6. Glass transition temperatures of B200/SMA blend system.

systems, miscibility was limited beyond 15% and 10% of the second polymer, respectively. Additional information is required for developing an understanding of the relationships between the phase behavior of these blend systems and the molecular structure of their components.

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