

Glass-Transition and Melting Behavior of Poly(ethylene terephthalate)/Poly(ethylene 2,6-naphthalate) Blends

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ABSTRACT: The glass-transition temperatures and melting behaviors of poly(ethylene terephthalate)/poly(ethylene 2,6-naphthalate) (PET/PEN) blends were studied. Two blend systems were used for this work, with PET and PEN of different grades. It was found that T_g increases almost linearly with blend composition. Both the Gibbs–DiMarzio equation and the Fox equation fit experimental data very well, indicating copolymer-like behavior of the blend systems. Multiple melting peaks were observed for all blend samples as well as for PET and PEN. The equilibrium melting point was obtained using the Hoffman–Weeks method. The melting points of PET and PEN were depressed as a result of the formation of miscible blends and copolymers. The Flory–Huggins theory was used to study the melting-point depression for the blend system, and the Nishi–Wang equation was used to calculate the interaction parameter (χ_{12}). The calculated χ_{12} is a small negative number, indicating the formation of thermodynamically stable, miscible blends. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 11–22, 2001

Key words: PET/PEN blend; Flory–Huggins theory; transesterification; compatibilizer; miscibility; glass-transition temperature

INTRODUCTION

Blends of poly(ethylene terephthalate) and poly(ethylene 2,6-naphthalate) (PET/PEN) have been attracting increasing interest because they combine the superior properties of PEN with the economy of PET.^{1–12} Both PET and PEN are polyesters.^{13–15} During melt processing of PET and PEN, a kind of reaction called the transesterification reaction may occur, resulting in the formation of PET and PEN copolymers (first block copolymers and then random copolymers). The transesterification reaction, which occurs in PET and PEN blends during melt processing, has been

studied by several authors.^{3–5,8–10} PET and PEN are intrinsically immiscible for most blend compositions.^{11–12} The copolymers formed during the melt mixing act as compatibilizers^{3–5} for the starting materials; thus, miscible blends of PET and PEN can be obtained through the formation of copolymers of PET and PEN. Studies in our laboratory¹⁶ showed that, after a certain transesterification level has been achieved, the thermal properties of the blends tend to stabilize and then level off with further increases in the transesterification levels (randomness levels). As further described below, the transesterification level is thus not a controlling factor for thermal properties, within the region investigated. The blend composition, however, seems to be the controlling factor for these properties. A study by Ihm¹⁰ and previous studies in our laboratory¹⁶ also showed that the sequence lengths of the blocks of terephtha-

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late and naphthalate units in the PET/PEN blends are much longer than those of random copolymers, yet the blends within such regions of transesterification levels show properties similar to those of random copolymers. Within this range, miscible blends of PET and PEN are formed and blend properties can be represented by any selected blend of the same composition, regardless of the transesterification level.

In the past two decades, a great number of miscible polymer pairs have been studied.^{17–27} Most of the systems investigated represent mixtures of two amorphous polymers or mixtures in which one of the components is semicrystalline.^{17–19,26} On the other hand, blends in which both components are semicrystalline polymers have received much less attention than have fully amorphous or amorphous/semicrystalline systems.^{20–27}

Both PET and PEN are crystallizable polymers. As the transesterification occurs, copolymer of PET and PEN form. As a result, the melting points (T_m) of the pure polymers are depressed. Flory²⁸ suggested that random copolymers that exhibit crystallinity consist of units of type A, which are capable of crystallizing, and units of type B, which do not crystallize under given conditions. Homopolymer sequences of crystallizable components, occurring by chance in random copolymer chains, are able to segregate and crystallize. Wunderlich²⁹ suggested that only nearest neighbors are capable of crystallizing without redistribution of sequences of like units, whereas the other types of units incorporated in the crystal are treated as defects. Windle et al.³⁰ suggested that the crystallinity in some random copolymers may result from the segregation and lateral matching of similar yet random sequences of the neighboring molecules. Lu and Windle³¹ studied the melting behavior of random copolymers of PEN and PET. The melting points of PEN/PET random copolymers were found to decrease with increasing PET content and reach a minimum at around 60 mol % PET, then increase as the PET content continued to increase. The lower melting points in the middle composition region were attributed to the statistical limitations of crystallite size, inherent in the sequence-matching models.³² In the composition range of 0–60 mol % PET, the X-ray patterns were quite similar to that of the PEN homopolymer, whereas the patterns for the copolymers with 80–100 mol % PET units were generally similar to each other, but distinct from those in the 0–60 mol % PET

range. Santa Cruz et al.³³ studied the crystalline structure of random copolymers of PET and PEN and distinguished the region in which PET or PEN crystallized, whereas the other component was ejected into the amorphous phase.

The melting behavior of PET has been extensively examined in the past two decades.^{34–64} Differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS)^{34–39} have been utilized to investigate the effects of crystallization conditions on the structure of semicrystalline PET. Most of these studies on crystallization and melting behavior of PET were conducted by crystallization from the melt.⁴⁰ The triple melting peaks of PET were clearly observed by Medellin-Rodriguez et al.⁴¹ as well as by Zhou and Clough.⁴² Qudah and Al-Raheil⁴³ investigated the multiple melting peaks of PET, annealed from the glassy state, and observed two melting peaks instead of three, found when samples were crystallized from the melt. As the chemical-structure analogue of PET, PEN also shows similar melting behavior to that of PET (i.e., the multiple melting peaks), which exist for many semicrystalline polymers.^{34,41–45} Cheng and Wunderlich⁴⁶ studied PEN crystallization extensively and reported the presence of the three melting peaks as a function of crystallization temperature.

At present, conflicting theories exist about the origin of the multiple fusion endotherms of isothermally crystallized PET and other semicrystalline polymers. Various morphological models have been proposed for these endotherms, the most popular of which is the recrystallization model, which was first proposed by Ikeda⁴⁷ and Jaffe and Wunderlich,⁴⁸ and further supported by Holdsworth,³⁹ Groeninckx,³⁶ Blundell and Osborn,^{49,50} and others.^{51–54} These authors suggested that the lamellae present initially melt and give rise to the lower temperature endotherm, but the melted material undergoes a continuous process of recrystallization into lamellae, which melt at higher temperatures. Ultimately, melting dominates recrystallization, giving rise to the observed higher temperature endotherm. Zhou and Clough⁴² studied the highest melting peak for pure PET and found that it was not originally present after the isothermal crystallization.

Bassett et al.⁵⁵ first proposed a dual lamellar population model for poly(ether ether ketone) (PEEK), which was extended by Cebe and Hong⁵⁶ and other authors.^{57–62} The model suggests that

there exists a bimodal distribution of lamellar thicknesses within the semicrystalline polymers, with melting of thinner and thicker lamellae associated with the low- and high-temperature endotherms, respectively. The two variants of this model are the lamellar insertion model^{57–60} and the dual lamellar stack model.⁶¹

Recently, Medellín-Rodríguez and Phillips^{41,63} as well as Olley et al.⁶⁴ proposed a new hypothesis for the crystallization of PET and PEN based on morphological features perceived by new experimental techniques. They reported that, phenomenologically, the processes of crystallization and melting were morphologically reversed. Thus it is hypothesized that melting of PET and PEN occurs in three distinct steps, assuming that spherulites are composited of dominant lamellar and subsidiary branches. Al-Raheil^{43,65} and colleagues considered the lower and middle peaks of the triple peaks were attributed to two distributions of crystal perfection, even at early crystallization times, which eventually became two kinds of crystal morphologies. Eguiazabal et al.⁶⁶ studied the influence of the interchange reaction of PET/polyarylate (PAr) blends on the melting behavior of isothermally crystallized PET. They observed three melting endotherms in both pure PET and PET blends.

In our study, we assumed that in PET/PEN blends, one component was crystalline, whereas the other one was excluded from the crystalline phase, as is discussed later. This assumption is also supported by ongoing X-ray studies at our Polymer Institute laboratories. In a PET-rich blend, PET was assumed to be the crystalline component and PEN was rejected as defects or diluents, whereas in a PEN-rich blend, PEN was assumed to be the crystalline component and PET was rejected as defects or diluents. Because of the existence of the diluent or the defects, the melting points of the blends or the copolymers are depressed.^{67–68} The melting-point depression of the PET/PEN blends was thus calculated and the interactions between PET and PEN were studied.

EXPERIMENTAL

Materials

Two grades of PET and PEN were used to make the blends. PET 1 (Eastman Chemical Company, Kingsport, TN) is a homopolymer with an intrinsic viscosity (IV) of 0.72, corresponding to a num-

ber-average molecular weight (M_n) of 24,300. PET 2 (Shell Chemical, Akron, OH) is an isophthalic acid (IPA)-modified PET copolymer with an IV of 0.80 ($M_n = 28,400$). Both PEN 1 and PEN 2 are homopolymers (manufactured by Hoechst, Spartanburg, SC), with IVs of 0.57 ($M_n = 22,400$) and 0.63 ($M_n = 27,200$), respectively. The IV determination of PET was done at 25°C in 60/40 (wt/wt) phenol/tetrachloroethane solution, whereas the IV of PEN was determined at 30°C in the same solution. Two blend systems were formed by using PET 1 with PEN 1 as blend system A and PET 2 with PEN 2 as blend system B. Blend compositions investigated ranged from 100% PET to 100% PEN.

Extrusion

Amorphous films 26–41 mils (0.66–1.04 mm) thick were prepared using a Brabender single-screw extruder (Rochell Park, NJ) with a general-purpose screw [diameter of 0.75 in. (1.91 cm) and a length-to-diameter (L/D) ratio of 22/1]. Extrusion conditions were: screw speed of 80 rpm and extrusion temperature of 300°C. The polymers were dried at 120°C for 20 h in a Forma Scientific model 3237 vacuum oven (Marietta, OH) prior to extrusion. The polymers were then mixed and extruded. Multiple passes were run to achieve different transesterification levels. Before each subsequent extruder pass, the films were chopped, crystallized, and dried at 120°C for 20 h.

Differential Scanning Calorimetry (DSC)

A Perkin–Elmer DSC-2 instrument (Perkin–Elmer, Norwalk, CT) was used to study crystallization and melting behavior. All samples were dried in a vacuum oven at 40°C for 20 h prior to measurements. The calorimeter was operated with a stream of oxygen-free, dry nitrogen flowing over the sample and the reference. The glass-transition temperature (T_g) was calculated from the dynamic DSC scan of each amorphous sample. During the dynamic scanning mode, the temperatures in the sample and the reference holders of the DSC were increased at a pre-set rate. The thermal transitions were recorded as the temperature increased to a predetermined end point. The dynamic scanning was carried out from 40 to 320°C at a scanning rate of 20°C/min. The differential scanning calorimeter was used for measuring the following transitions occurring in the samples during the dynamic scanning: glass-transition temperature, crystallization peak tempera-

ture, and melting peak temperature. During an isothermal scan, the temperature of the sample was increased at 320°C/min to the desired crystallization temperature and kept at this temperature for a certain period of time. Samples isothermally crystallized at various temperatures were quickly cooled to 40°C and then reheated at 20°C/min from 40 to 320°C. The method used here was the same as for the dynamic DSC scan. After each scan, the multiple melting peaks of each sample were analyzed and recorded.

RESULTS AND DISCUSSION

Glass-Transition Temperature

The glass-transition temperature (T_g) may provide useful information on blend miscibility.⁶⁹ For an immiscible blend, two T_g 's generally appear on the DSC scan, whereas for miscible blends or copolymers, only one T_g is observed. Work from our laboratory¹⁶ shows that after a certain transesterification level has been achieved, the T_g value for the same composition blend system seems to stabilize and level off. Further increases in the randomness do not cause additional changes in T_g . For most blends, even at very low transesterification levels, only one T_g can be observed on the DSC scan, whereas at this transesterification level the blend is still hazy. This lack of clarity indicates that the blend obtained is still not completely miscible at the optical level. The reason only one T_g is observed on the DSC scan is that some compatibilization has occurred as a result of formation of PET and PEN copolymers, and thus the blends have become sufficiently compatible that the DSC is not sensitive enough to detect phase separation or the existence of two T_g 's.

Fried et al.⁷⁰ studied the blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with poly(styrene-co-4-chlorostyrene) and found that the width of the glass-transition region (ΔT_g) could be used as a measure of the miscibility of blends, in cases where only one T_g was observed in the DSC scan. They found that for homopolymers or miscible blends, ΔT_g values were less than 10°C, whereas for immiscible blends, the glass-transition regions were much wider, giving values of more than 30°C. Cakmak et al.⁷¹ used the same method in their study of PEN/poly(ether imide) (PEI) blends and found ΔT_g values were more than 30°C for the blends with PEI contents of

Table I ΔT_g Values for B Blend System (°C)

Number of Passes	PEN/PET		
	20/80 (17.7) ^a	40/60 (33.3) ^a	60/40 (53.9) ^a
1	17.1	17.3	49.1
2	11.9	16.6	13.1
3	10.7	11.5	8.7
4	6.7	6.9	11.7

^a NDC mol %.

30–70%, although only one T_g was seen in the DSC scans for these blends.

In PET/PEN blends, as the transesterification continues, the blends become more miscible. The ΔT_g value, if it is a measure of miscibility as pointed out by Fried et al.,⁷⁰ should decrease with the increase of reaction time or the blending time. The measured ΔT_g values for B blend systems are shown in Table I. It is obvious that as a general trend, ΔT_g decreases with increased blending time for all the blend compositions. After the third pass through the extruder, there is not much difference in ΔT_g values and the value of ΔT_g is generally less than 10°C. This is in good agreement with our observation of blend haze. All ΔT_g values are less than 30°C, except for the first-pass values of the 60% (wt/wt) PEN composition blends. According to the definition by Fried et al.,⁷⁰ a ΔT_g value of more than 30°C indicates the blend is immiscible. Thus the 60% PEN composition blend, passed once through the extruder, is immiscible. This is reasonable because, for 60% PEN blends, the mole percentages of terephthalate and naphthalate units are almost equal. The immiscibility factor reaches the maximum, and thus we would expect either two T_g 's on the DSC scan (if the DSC is sensitive enough) or one very wide transition region (ΔT), as was observed at this composition.

Previous work done in our laboratory^{16,72} showed not only that after a certain transesterification level has been achieved, thermal properties depend only on blend composition, but also that the degree of randomness is not a controlling factor. This critical level of transesterification (randomness) that must be reached is generally indicated by optical clarity and a single narrow ΔT_g of about 10°C or less. For these experiments, it has been achieved within three passes through the single-screw extruder. Details of transesterifi-

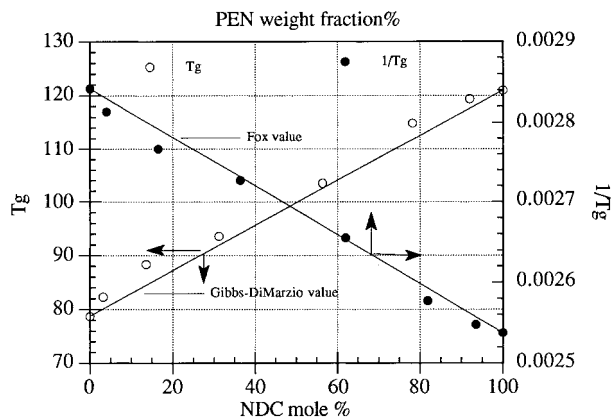


Figure 1 T_g values for A blends.

cation reaction kinetics and degree of randomness are reported in a previous study.⁷² As shown, additional passes yield increased percentage transesterification; however, no additional changes are noted for optical clarity, the glass-transition temperature, or melting behavior. It should be noted that processing conditions required to attain complete randomization would include longer processing time and/or higher processing temperatures. Either of these conditions could cause severe degradation, which would overcome the transesterification process. The thermal properties, described in the following sections, all represent values obtained after critical transesterification has been achieved, as demonstrated by optical clarity and a narrow ΔT_g , as described by Fried et al.⁷⁰

The glass-transition temperatures for both the A and the B blend systems were plotted as functions of blend compositions or dimethyl-2,6-naphthalene dicarboxylate (NDC) contents, as shown in Figures 1 and 2. NDC mol % concentration was determined using NMR, as described in the previous study that addressed the transesterification reaction kinetics of the blends.⁷² It is seen that T_g increases almost linearly with NDC content. In the case of miscible blends of polymers or random copolymers, the T_g of the blend or copolymer can be expressed by the widely used empirical Fox equation^{73,74}:

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

where W_1 and W_2 are the weight fractions of components 1 and 2 with T_{g1} and T_{g2} , respectively. More complicated equations are also available.⁷⁵ Using the Fox equation, we calculated T_g

values for both of the previously described blend systems. These calculated values are shown as the solid lines in Figures 1 and 2, where it is seen that the Fox equation gives very good fits to the experimental T_g values, indicating the formation of miscible blends or random copolymers of PET and PEN.

As mentioned earlier, as a result of the transesterification reaction, PET and PEN blends behave in a manner similar to that of random copolymers. For random copolymer data, the Gibbs–DiMarzio theory⁷⁶ gives a good fit. This equation gives the resultant T_g as a function of the T_g 's of the two component polymers. Using the universal value of $\epsilon/KT = 2.26$, the Gibbs–DiMarzio equation can be described by eq. (2)⁷⁶:

$$T_g = X_1 T_{g1} + X_2 T_{g2} \quad (2)$$

where T_{g1} and T_{g2} are the glass-transition temperatures of component polymers 1 and 2, with mole fractions X_1 and X_2 , respectively.

T_g values for both blend systems were also calculated, using the Gibbs–DiMarzio equation, by assuming random copolymer formation. The theoretically calculated T_g values as well as the experimental points were plotted, as shown in Figures 1 and 2. These plots show that T_g values calculated from the Gibbs–DiMarzio equation fit the experimental data for all the blend compositions and for both blend systems. These figures also show that both the Gibbs–DiMarzio equation and the Fox equation fit the experimental data very well. The blend system is therefore seen to behave more like a random copolymer than like a miscible polymer–polymer blend. This is in agreement with our experimental observation that the

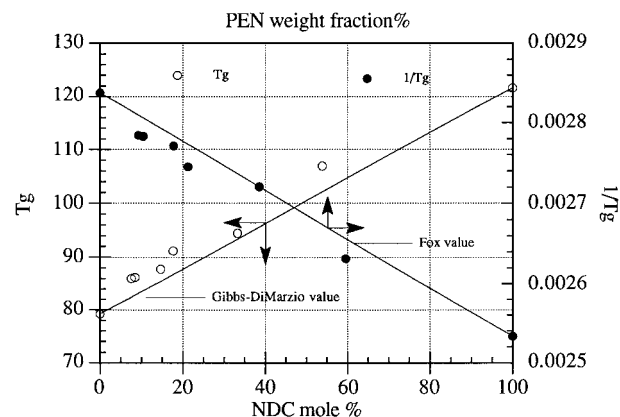


Figure 2 T_g values for B blends.

degree of randomness does not seem to affect the T_g value after a certain value has been achieved. After a certain degree of randomness values have been reached, blends assume T_g values of the random copolymers of PET and PEN. In another way, we can say that there is not much difference in T_g values between random copolymers of PET and PEN and PET/PEN blends, once certain transesterification levels have been achieved. The T_g value for a copolymer of PET and PEN, with 92 mol % NDC content, was also measured and plotted in Figure 1. It falls exactly on the straight line plotted using blend T_g data.

McGee et al.⁴ also found that the T_g of PET/PEN blends changed almost linearly with NDC content. Because of the formation of copolymer during the transesterification reaction, blend properties resemble those of copolymers of PET and PEN. From our previous study,^{16,72} we found that the blend transesterification level is much less than that of totally random (100%) materials and, thus, the sequence length of the naphthalate or terephthalate units in blends is much longer than that in random copolymers. It seems that T_g values are not very different for random copolymers and short-block copolymers. Once a certain degree of randomness has been achieved, these values seem insensitive to further changes of the sequence length (block length).

Multiple Melting Peaks

As pointed out earlier in the introduction, when isothermally crystallized PET and PEN samples were reheated with the DSC, multiple melting peaks were observed.^{41,42,46} This phenomenon of multiple melting peaks is common for many rigid semicrystalline polymers such as PEEK, PET, and PEN. Some authors^{47–53} have attributed these peaks to primary and secondary crystallization.

In our experiments, we found three melting peaks for each sample annealed within a certain crystallization temperature range, including PET, PEN, and blend samples with various compositions. An example of such a multiple melting behavior is shown in Figure 3 with the lower melting peak T_{mI} , the intermediate melting peak T_{mII} , and the main melting peak T_{mIII} . Similar triple melting peaks were observed for both PET and PEN as well as for blends in certain crystallization temperature ranges. The range for which the triple melting peaks appear is different for different blend compositions. Below this range, only two melting peaks

were observed in the DSC scan, the lower melting peak T_{mI} and the main melting peak T_{mIII} . Above this range, the three melting peaks seemed to merge and finally only one melting peak was seen in the DSC scan. The observation of multiple melting peaks is very similar to that observed by Cheng.⁴⁶

Various melting peak temperatures were plotted as functions of crystallization temperature. Figure 4 gives an example of the change of these melting points with the crystallization temperature (T_c) for PET 2, whereas Figure 5 gives an example of the change of those melting points with T_c for one composition blend, 20/80 PEN/PET B sample. As can be seen in these figures, the lowest temperature melting peak (T_{mI}) occurs about 10 to 15°C above the crystallization temperature. It increases linearly with crystallization temperature with a slope of almost 1. T_{mIII} remains almost unchanged with T_c for a given blend system. T_{mII} , relatively small compared to T_{mIII} , first appears as a shoulder to the main melting peak and increases linearly with a crystallization temperature with a smaller slope than that of T_{mI} . The multiple melting points for all the other samples have similar behavior. The averaged T_{mIII} values for blend samples are listed in Tables II and III for the two blend systems. Using the Hoffman–Weeks method,⁶⁷ the equilibrium melting point T_m^0 was obtained by extrapolating the straight line of T_{mII} against T_c to the intersection of the straight line drawn to give equal T_m and T_c , as shown in Figures 4 and 5. Thus calculated T_m^0 values for all samples are also listed in Tables II and III for the two blend systems. Measurements were performed on blends that had reached previously described critical transesterification levels.

The slopes of Hoffman–Weeks plots (straight line of T_{mII} against T_c) assume values between 0 and 1 and can be regarded as a measure of the stability (i.e., the lamellar thickness) of the crystals undergoing the melting process.⁶⁷ A value of 0 implies that the crystals are perfectly stable, whereas a value of 1 reflects inherently unstable crystals. The slopes of the straight lines of T_{mII} versus T_c are between 0.3 and 0.4 for all the samples. They change with blend composition as well as with the PET and PEN used. These values are similar to those obtained by Eguiazabal et al.⁶⁶ for their PET/PAr blends. The values they reported are around 0.38 to 0.39 for both pure PET and PET/PAr blends.⁶⁶ The slope values reported for crystalline polymers in polymer blends also yield similar results.^{19,68,77}

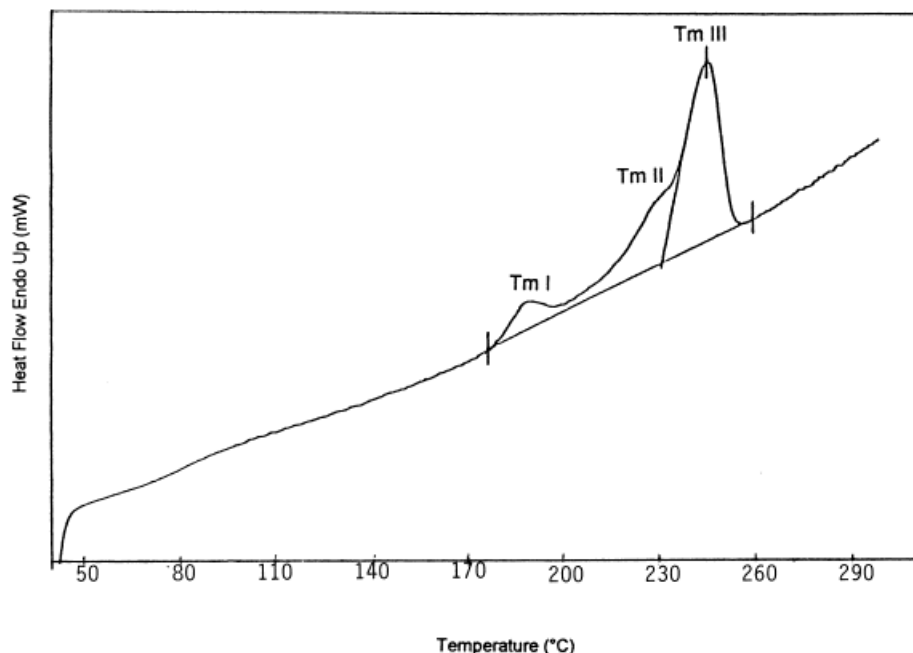


Figure 3 Example of multiple melting peaks in DSC scan.

Many theories have been proposed to explain the multiple melting peaks, although the most popular one among them is recrystallization theory.⁴⁷⁻⁵³ Lin and Koenig⁵³ thought that the lowest melting peak indicates small and/or imperfect crystals resulting from the secondary crystallization process, whereas the higher melting peak T_{mII} results from the melting of the crystalline structure formed near the crystallization temperature. The main melting peak T_{mIII} was believed to be formed by fusion of crystals grown and perfected during the DSC scan itself⁵³ and does not represent the melting of crystals grown during the isothermal crystallization process. The recrystallization theory also seems to apply to the blend samples as well as to pure PET and PEN. In our experiments all samples showed the same changing trend for the three melting peaks. The absolute values varied with composition. The results we obtained in our study are similar to those Eguiazabal et al.⁶⁶ obtained in their study of PET/PAr blends, in which they reported multiple melting endotherms for both pure PET and the PET blends. T_{mII} showed a linear relationship with crystallization temperature for both pure PET and its blends.

The equilibrium melting points and the averaged T_{mIII} values were plotted against NDC content, as shown in Figures 6 and 7. It is clear that

they all show the same changing trends. All melting points decrease with NDC mole percentage until they pass through a minimum at NDC mol % around 33%, then increase with a further increase in NDC content, up to a 100% PEN value. In other words, from both pure PET and PEN, the melting point starts decreasing by addition of the second monomer (PEN or PET). The lowered melting point in the intermediate NDC range indicates the disruption of crystalline structure by the addition of the other monomer and has been attributed to the statistical limitations of crystallite size inherent in the sequence-matching model.³² The addition of one polymer to the other disrupts the symmetry of the crystal structure of the crystalline component. The degree of disruption increases with increases in the second monomer content until it reaches a maximum. Thus, adding PET to PEN or PEN to PET will hinder the crystallization of either the PEN-rich or PET-rich phases and depress the melting point. Eguiazabal et al.⁶⁶ reported T_{mIII} was lower in blends compared to that of pure PET and the equilibrium melting point was reported to be 268.85°C for pure PET and 264.85°C for PET/PAr blends. The depression of melting point in miscible blends has been studied for a long time and has provided a method for calculating the polymer interaction parameters.^{69,78}

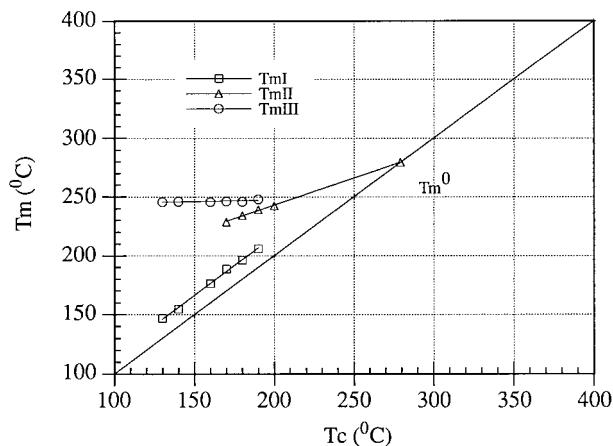


Figure 4 Melting points versus T_c for PET 2.

Melting-Point Depression: Theoretical Background

For miscible blends, the melting point of the crystalline component is usually lowered with respect to the pure polymer, as a result of thermodynamically favorable interactions. The extent of the melting-point depression in such systems provides a measure of the interaction between polymers, as described by the Flory–Huggins theory,⁷⁸ according to which, under thermodynamic equilibrium, the melting-point depression can be expressed as follows⁷⁸:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \times \left[\frac{\ln \nu_2}{x_2} + \left(\frac{1}{x_2} - \frac{1}{x_1} \right) (1 - \nu_2) + \chi_{12} (1 - \nu_2)^2 \right] \quad (3)$$

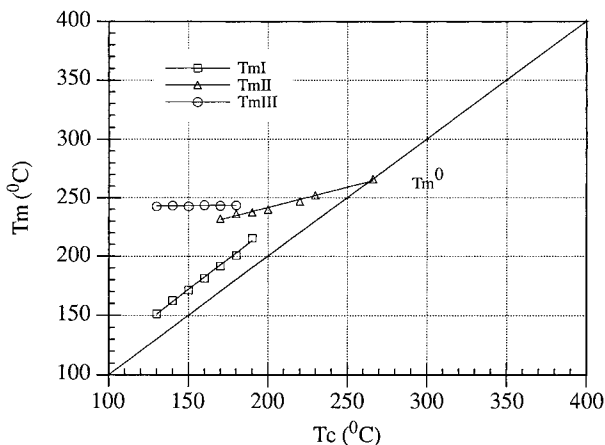


Figure 5 Melting points versus T_c for 20/80 PEN/PET B blends.

Table II Melting Points for A Blends

NDC (mol %)	T_m^0 (°C)	Average T_{mIII} (°C)
0	275.9	251.3
13.6	271.8	242.6
31.2	251.6	227.7
56.3	269.2	234.4
78.2	291.0	252.1
92.0	300.9	254.7
100	305.8	270.3

where T_m^0 and T_m are the equilibrium melting points of the crystallizable polymers in the bulk and in the blends, respectively. Subscript 1 is identified with the amorphous polymer and subscript 2 with the crystalline polymer; ν represents the volume fraction; V is the molar volume of the repeat units; x is the degree of polymerization; ΔH_2 is the heat of fusion per mole of crystalline units; R is the gas constant; and χ_{12} is the Flory–Huggins interaction parameter. In polymer blends, both x_1 and x_2 are very large compared to unity, and thus eq. (3) can be reduced to the Nishi–Wang equation^{68,78}

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_2}{\Delta H_2 V_1} \chi_{12} (1 - \nu_2)^2 \quad (4)$$

Here the equilibrium melting point of the polymer is used instead of the measured melting point from the DSC scan. This is because the melting point of a polymer is, in general, affected not only by thermodynamic factors but also by morphological parameters such as the crystal thickness. To separate morphological from thermodynamic effects in analysis of melting-point depression, the equilibrium melting point data are used. In the miscible polymer blends, χ_{12} is usually negative and small.^{19,68,79}

Table III Melting Points for B Blends

NDC (mol %)	T_m^0 (°C)	Average T_{mIII} (°C)
0	279.3	246.3
17.7	266.1	243.1
33.3	256.3	229.9
53.9	272.6	247.2
100	307.1	262.6

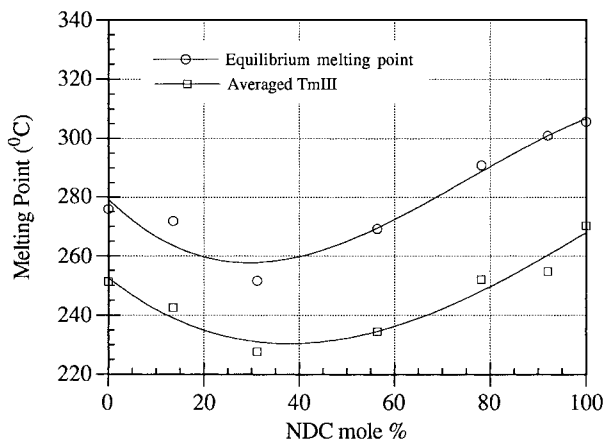


Figure 6 Melting points versus NDC content for A blends.

Neglecting the entropic contribution,¹⁹ we can write χ_{12} as

$$\chi_{12} = \frac{BV_1}{RT} \quad (5)$$

where B is the interaction energy density characteristic of the polymer–polymer pairs. Inserting eq. (5) into eq. (4) at the melting point, we have

$$\frac{1}{\nu_1} \left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) = - \frac{BV_2}{\Delta H_2} \left(\frac{\nu_1}{T_m} \right) \quad (6)$$

Thus, a plot of the left-hand side of eq. (6) versus ν_1/T_m should give a straight line, and the interaction energy density B can be obtained from the slope of this straight line.

From eq. (4), the depression of melting point is possible only when χ_{12} is negative, which is in agreement with the Scott’s condition for the miscibility of the two polymers⁷⁹:

$$\chi_{12} < \frac{1}{2} \left[\frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}} \right]^2 \quad (7)$$

which requires χ_{12} to be near zero or negative for the polymer–polymer pair whose x_1 and x_2 values are much greater than 1.

Equation (6) was used to plot the melting-point depression and to give the interaction energy density value. The equilibrium melting points were obtained using the Hoffman–Week’s method as described previously and shown in Tables II and III. In construction of the plots using eq. (6), we assume that for blends with NDC contents of less

than 40%, the melting-point depression is the result of the addition of naphthalate units to the terephthalate chain (PET). For NDC contents of more than 40%, the melting-point depression was thought to be attributed to the addition of terephthalate units to the naphthalate chain (PEN). This assumption means that for PET-rich blends, PET is considered to be the crystalline component, whereas PEN is considered to be the amorphous component rejected from the crystalline phase. In PEN-rich blends, PEN is considered to be the crystalline component and PET is excluded from the crystalline phase to the amorphous phase. Santa Cruz et al.³³ studied random copolymers of PET and PEN. They found that for samples containing 0–30 mol % PEN, the PET sequences crystallized, whereas the PEN sequences remained in the amorphous region. For samples containing 80 mol % PEN, the PEN sequences crystallized in the α -form, whereas the PET sequences were excluded in the noncrystalline region. In the case of 50 and 60 mol % PEN composition random copolymers, they found the PEN did not crystallize. This finding is in agreement with our assumptions. Equation (6), which was derived to describe the thermodynamics of miscible crystalline–amorphous polymer–polymer blends, can thus be used here. The following values were used with eq. (6): for PET, $\Delta H_2 = 121.34$ J/g, $V_{\text{PET}} = 144$ cm³/mol; for PEN, $\Delta H_2 = 103.34$ J/g, $V_{\text{PEN}} = 182.4$ cm³/mol. The density of amorphous PET is 1.333 g/cm³,¹⁵ and that of amorphous PEN is 1.327 g/cm³.⁸⁰ Results are shown in Figures 8 and 9. Figure 8 shows the plot of eq. (6) for the A blend system, assuming the melting point of PEN was depressed by the addition of

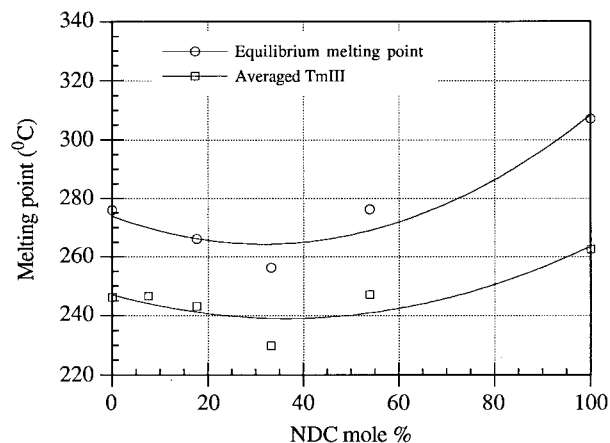


Figure 7 Melting points versus NDC content for B blends.

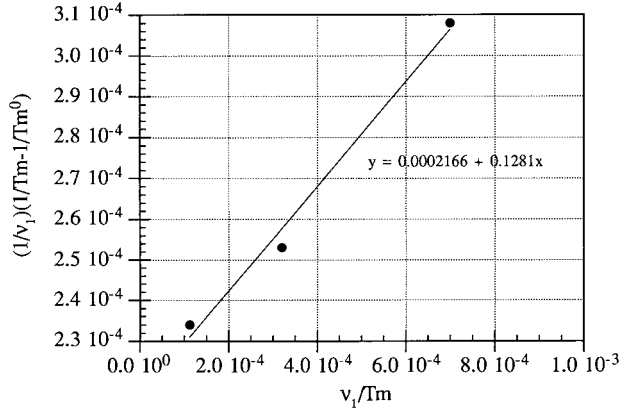


Figure 8 Plot of eq. (6) for A blends.

PET, whereas Figure 9 shows the plot for the B blend system, where the depression of melting point for both PET and PEN were plotted on the same figure. Because of material limitations, only a few compositions were studied. In spite of these limitations, the data give us a basic idea as to the miscibility of the blend systems and the interaction parameter ranges in this blend system. The slopes of these straight lines give $-(BV_2/\Delta H_2)$, and the interaction parameters χ_{12} can be calculated from eq. (5). The calculated parameters are as follows:

For the A blend system the interaction energy density characteristic (B) is

$B = -17.6 \text{ J/cm}^3$, calculated from the melting-point depression of PEN

For the B blend system

$B = -10.2 \text{ J/cm}^3$, calculated from the melting-point depression of PEN

$B = -10.6 \text{ J/cm}^3$, calculated from the melting-point depression of PET

Equation (5) also shows that the Flory–Huggins interaction parameter (χ_{12}) is temperature dependent. Here we chose the processing temperature of 300°C for the calculation of χ_{12} . At this temperature, the interaction parameters for these two blend systems are determined to be as follows:

For the A blend system

$\chi_{12} = -0.531$, calculated from the melting-point depression of PEN

For the B blend system

$\chi_{12} = -0.309$, calculated from the melting-point-depression of PEN

$\chi_{12} = -0.407$, calculated from the melting-point-depression of PET

The calculated χ_{12} values are small negative numbers. This is expected because for a miscible polymer blend, χ_{12} usually is negative and small.^{19,68} Similar values of -0.2 and -0.3 have been reported for other blend systems.^{68,77,81} These small negative χ_{12} values indicate that the blend system can form a thermodynamically stable, compatible mixture at temperatures above the melting point (the temperature at which χ_{12} was determined). As a result of the formation of short-block copolymers,¹⁶ the blends of PET/PEN form mixtures at the molecular level (or short repeating unit sequence level).

For the B blend system, the χ_{12} values calculated from the melting-point depression of both PET and PEN are very close to each other. This is also expected because χ_{12} is a measure of interaction between terephthalate and naphthalate units or PET and PEN molecules. Thus it should remain the same whether we calculated from the effect of addition of PEN to PET or from the effect of addition of PET to PEN. The interaction will remain the same. This interaction is related to the polymer structure and inherent to polymer pairs. The variance in the absolute values of χ_{12} for the B blend system, calculated from the melting-point depression of both unblended PET and PEN, can be considered as the experimental error in view of the limited numbers of experimental data points. This variance might also be attributed to the simplified

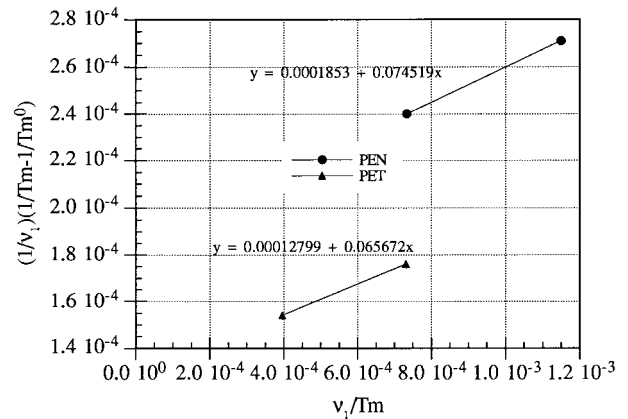


Figure 9 Plot of eq. (6) for B blends.

assumptions we used in constructing eq. (6). The Flory–Huggins interaction parameter χ_{12} for the two blends is slightly different, which might be attributed to the fact that the PET and PEN materials we selected for making the two blend systems are different. PET 1 is a homopolymer of PET. PET 2 is a copolymer of PET with small amounts of other comonomers. The synthesis methods for the two PET materials used are different, and thus the polymerization catalyst systems are also different, causing differences in the structures of the two PETs. The differences in χ_{12} values for both blend systems, however, are not very substantial and might also be caused by experimental error and the simplified assumptions for the calculation of eq. (6).

CONCLUSIONS

Blends that have achieved miscibility, as indicated by optical clarity and a single narrow glass-transition region, show no further changes in these properties after additional processing and increased levels of transesterification. The glass-transition temperatures of PET/PEN blends that have achieved this critical level of randomness follow both the Fox equation and the Gibbs–DiMarzio equation very well, indicating that they behave in a manner similar to that of random copolymers. Multiple melting peaks were observed for both PET and PEN as well as for blend samples within a certain crystallization temperature range. This multiple melting peak behavior is considered to be partially the result of the recrystallization of polymers during the DSC scan. Melting points of both PET and PEN were depressed because of the formation of miscible blends and copolymers. The depression of the melting point increases with the increased content of the other component. For PET-rich blends, PET is considered to be the crystalline component, whereas PEN is considered to be the amorphous component rejected from the crystalline phase. In PEN-rich blends, PET is thought to be excluded from the crystalline phase as defects or diluents. The interaction parameters were calculated for PET/PEN blends using the Flory–Huggins theory. The calculated interaction parameter (χ_{12}) value is a small negative number, which indicates the formation of thermodynamically stable, miscible blends.

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REFERENCES

1. Shepherd, F. A.; Ronald, R. L. (to Eastman Kodak Co.) U.S. Pat. 5,006,613, 1991.
2. Sherman, L. M. *Plast Technol* 1995, May, 55.
3. Jenkins, S. D. in *Proceedings of the Specialty Polyesters '95 Conference*, Munich, 1995; p. 197.
4. McGee, T. M.; Jones, A. S. in *The Effect of Processing Parameters on Physical Properties of PET/PEN Blends for Bottle Applications*, *Proceedings of the SPE 11th Annual High-Performance Blow-Molding Conference*, Cleveland, OH, October 1995; pp. 91–106.
5. Stewart, M. E.; Cox, A. J.; Taylor, D. M. *Polymer* 1993, 34, 4060.
6. Callunder, D.; Sisson, E. *Bev-Pak, America'94*, Ft Lauderdale, FL, 1994.
7. Naitove, M. H. *Plast Technol* 1989, September, 33.
8. Hoffman, D. C.; Caldwell, J. K. in *Proceedings of the Specialty Polyesters '95 Conference*, Munich, 1995; pp. 223–242.
9. Heisey, C. L.; Hoffman, D. C.; Zawada, J. A. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1996, 231.
10. Ihm, D. W.; Park, S. Y.; Chang, C. G.; Kim, Y. S.; Lee, H. K. *J Polym Sci Part A Polym Chem* 1996, 34, 2841.
11. Kern, C. L. in *Plastics Blow Molding Today and Tomorrow—Pushing the Process Limits*, Cherry Hill, NJ, 1989.
12. French, R. N.; Walsh, J. M. *Shell Internal Research Communication*, 1993.
13. Cook, J. G.; Hugill, H. P. W.; Lowe, A. R. *Brit. Pat.* 604 073, 1948.
14. Wang, C. C.; Sun, Y. M. *J Polym Sci Part A Polym Chem* 1994, 32, 1305.
15. Jabarin, S. A. *PET Technology Seminar*, University of Toledo, 1996.
16. Shi, Y. Ph.D. Dissertation, Polymer Institute, The University of Toledo, 1998.
17. Utracki, L. A. *Polymer Alloys and Blends*; Hanser Publishers: Munich, 1989.
18. Jonza, J. M.; Porter, R. S. *Macromolecules* 1986, 19, 1946.
19. Hsiao, B. S.; Sauer, B. B. *J Polym Sci Part B Polym Phys* 1993, 31, 901.
20. Roerdink, E.; Challa, G. *Polymer* 1978, 19, 173.
21. Eshuis, A.; Roerdink, E.; Challa, G. *Polymer* 1982, 23, 735.
22. Avella, M.; Martucelli, E. *Polymer* 1988, 29, 1731.
23. Edie, S. L.; Marand, H. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1991, 32, 329.
24. Cheung, Y. W.; Stein, R. S. *Macromolecules* 1994, 27, 2512.
25. Cheung, Y. M.; Stein, R. S.; Lin, J. S.; Wignall, G. D. *Macromolecules* 1994, 27, 2520.
26. Penning, J. P.; Manley, R. S. J. *Macromolecules* 1996, 29, 77.

27. Song, H. H.; Stein, R. S.; Chu, B.; Wu, G. *Macromolecules* 1994, 27, 3589.
28. Flory, P. J. *J Chem Phys* 1947, 15, 684.
29. Wunderlich, B. *J Chem Phys* 1958, 29, 1395.
30. Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss Chem Soc* 1985, 79, 55.
31. Lu, X.; Windle, A. H. *Polymer* 1995, 36, 451.
32. Hanna, S.; Windle, A. H. *Polymer* 1988, 29, 207.
33. Santa Cruz, C.; Balta Calleja, F. J.; Zachmann, H. G.; Chen, D. *J Mater Sci* 1992, 27, 2161.
34. Roberts, R. C. *Polymer* 1969, 10, 117.
35. Groeninck, S. G.; Reynaers, H.; Berghmans, H.; Smets, G. *J Polym Sci Polym Phys Ed* 1980, 18, 1311.
36. Groeninck, G.; Reynaers, H. *J Polym Sci Polym Phys Ed* 1980, 18, 1325.
37. Fakirov, S.; Fischer, E. W.; Hoffman, R.; Smidt, G. F. *Polymer* 1977, 18, 1121.
38. Roberts, R. C. *J Polym Lett* 1980, 8, 1311.
39. Holdsworth, P. J.; Turner-Jones, A. *Polymer* 1971, 12, 195.
40. Medellin-Rodriguez, F. J.; Phillips, P. J. *ANTEC* 1991, 37, 893.
41. Medellin-Rodriguez, F. J.; Phillips, P. J.; Lin, J. S. *Macromolecules* 1996, 26, 7491.
42. Zhou, C.; Clough, S. B. *Polym Eng Sci* 1988, 28, 65.
43. Qudah, A. M. A.; Al-Raheil, I. A. *Polym Int* 1995, 38, 367.
44. Verma, R.; Marand, H.; Hsiao, B. *Macromolecules* 1996, 29, 7767.
45. Harris, I. R. *Polymer* 1985, 26, 3.
46. Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* 1988, 21, 789.
47. Ikeda, M. *Chem Abstr* 1968, 69, 19666.
48. Jaffe, M.; Wunderlich, B. *Kolloid Z Z Polym* 1967, 216, 203.
49. Blundell, D. J.; Osborn, B. *Polymer* 1983, 24, 953.
50. Blundell, D. J. *Polymer* 1987, 28, 2248.
51. Lee, Y.; Porter, R. S. *Macromolecules* 1987, 20, 1336.
52. Alfonso, G. C.; Pedemonte, E.; Ponzetti, L. *Polymer* 1979, 20, 104.
53. Lin, S. B.; Koenig, J. L. *J Polym Sci Polym Symp* 1984, 71, 121.
54. Roberts, R. C. *J Polym Sci Polym Lett Ed* 1970, 8, 381.
55. Bassett, D. C.; Olley, R. H.; Raheil, I. A. M. *Polymer* 1988, 29, 1745.
56. Cebe, P.; Hong, S. D. *Polymer* 1986, 27, 1183.
57. Kruger, K.-N.; Zachmann, H. G. *Macromolecules* 1993, 26, 5202.
58. Wang, J.; Alvarez, M.; Zhang, W.; Wu, Z.; Li, Y.; Chu, B. *Macromolecules* 1992, 25, 6943.
59. Hsiao, B. S.; Gardner, K. H.; Wu, D. Q.; Chu, B. *Polymer* 1993, 34, 3986.
60. Hsiao, B. S.; Gardner, K. H.; Wu, D. Q.; Chu, B. *Polymer* 1993, 34, 3996.
61. Lattimer, M. P.; Hobbs, J. K.; Hill, M. J.; Barham, P. J. *Polymer* 1992, 33, 3971.
62. Santa Cruz, C.; Stribeck, N.; Zachmann, H. G.; Balta Calleja, F. J. *Macromolecules* 1991, 24, 5980.
63. Medellin-Rodriguez, F. J.; Phillips, P. J. *ANTEC* 1991, 37, 89364.
64. Olley, R. H.; Bassett, D. C.; Blundell, D. J. *Polymer* 1986, 27, 344.
65. Al-Raheil, I. A. *Polym Int* 1994, 35, 189.
66. Eguiazabal, J. I.; Cortazar, M.; Iruin, J. J. *J Appl Polym Sci* 1991, 42, 489.
67. Hoffman, J. D.; Weeks, J. J. *J Res Natl Bur Stand (A)*, 1962, 66, 13.
68. Nishi, T.; Wang, T. T. *Macromolecules* 1975, 8, 909.
69. Porter, R. S. *Polymer* 1992, 33, 2019.
70. Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1978, 11, 150.
71. Kim, J. C.; Cakmak, M.; Geil, P. H. *ANTEC* 1997, 1572.
72. Shi, Y.; Jabarin, S. A. *J Appl Polym Sci* 2001, 80, 2422.
73. Fox, T. G.; Loshaek, S. *J Polym Sci* 1955, 15, 371.
74. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
75. Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979.
76. Gibbs, J. H.; DiMarzio, E. A. *J Chem Phys* 1958, 28, 373, 807.
77. Morra, B. S.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1982, 20, 2243.
78. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
79. Scott, R. L. *J Chem Phys* 1949, 17, 279.
80. Buchner, S.; Wiswe, D.; Zachmann, H. G. *Polymer* 1989, 30, 480.
81. Rim, P. B.; Runt, J. P. *Macromolecules* 1984, 17, 1520.