Miscibility of Blends of Aliphatic Main-Chain Polyesters

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ABSTRACT: The phase behavior of binary blends of linear main-chain aliphatic polyesters and blends of poly(caprolactone) with caprolactam/caprolactone copolymers has been investigated both experimentally and theoretically within the terms of a binary interaction model. A relatively small and unfavorable value of the methylene–ester segmental interaction parameter, χ_{AD}, estimated previously from studies of polyamide/polyester blends allows for entropically driven miscibility of blend constituents possessing considerable chemical dissimilarity. Although a reasonable correlation between experiment and calculations has been obtained, the analysis also provides a discussion of how configuration, or the arrangement of chemical species or segments, may affect the parameters used.

Introduction

The phase behavior of binary blends involving aliphatic polyamides, aliphatic polyesters, and their copolymers[1,2] has been rationalized in terms of a binary interaction model.[3–5] Arguments were presented to show that miscibility in mixtures of the above can result exclusively when the unfavorable endothermic contribution to the free energy of mixing, ΔG, is overwhelmed by a favorable entropic contribution. Alternatively, it may be stated that homogeneous mixing occurs only if the chemical compositions of the blend constituents are not too dissimilar and their respective molecular mass is not excessively large. An outcome of the quantitative analysis also provided an estimation of the appropriate segmental interaction parameters, χ_{ij}, involved. Most interestingly, it was proposed that the relatively small value obtained for the methylene (A)/ester (D) interaction would lead to a situation whereby binary blends of linear main-chain aliphatic polyesters could tolerate relatively large differences in methylene content between the blend constituents before phase separation would occur. This would be particularly evident in view of the relatively low molecular mass usually encountered for this class of polymer. At the time of expressing these views, there was little experimental information from which to judge their validity; however, further studies performed in this laboratory, when examined in conjunction with recently published information,[6] allows for a closer inspection of this subject.

Experimental Section

Materials and Blends. All the polyesters used in this study were obtained from Scientific Polymer Products and subjected to purification by precipitation into diethyl ether from a solution in tetrahydrofuran (THF). A summary of the structure and properties is presented as Table 1. The blends (50:50 w/w) were also prepared from the polymers by precipitation from THF and dried in vacuum at ambient temperature for 24 h.

The copolyester–amides used are the same as those reported previously.[1] Blends of poly(caprolactone) (PCL) and the copolymers were prepared from a mixed solvent system as described above.

Procedures. The blends and pure polymers were characterized by differential scanning calorimetry (DSC), using a Perkin-Elmer Series 7 calorimeter, programmed at a heating rate of 20 °C/min. The blends were heated to an equilibrium liquid state and quench cooled in liquid nitrogen prior to analysis. Thus, the reported values of the glass transition temperature (T_g) are for vitrified materials. Molecular weight parameters were determined by size exclusion chromatography using a Waters Associates ALC chromatograph at 35 °C and THF as the solvent. Values of M_n and M_w are reported relative to polystyrene standards.

Optical microscopy was performed using a Nikon Microphot-FX equipped with a Mettler FP82 hot stage cell. The microscope was operated in transmitted light using crossed polarizers.

Results and Discussion

1. Binary Polyester Blends. The low melting point of all the polyesters necessitated only a low exposure temperature (90 °C) in order to establish a liquid–liquid equilibrium prior to analysis. Accordingly, it is assumed that transreaction in the melt will be negligible and that phase behavior has been determined in the absence of this phenomenon. A summary of the phase behavior of the blends is presented in Table 2. Representative thermograms illustrating the conclusions of miscibility or otherwise are shown for some of the blends as Figure 1. The miscible blends of PEA/PTA and PEA/PTG show quite clearly (thermograms B and D, respectively) a T_g intermediate between those of their respective pure constituents. The PBA/PEA blend, however, displays only partial miscibility when examined calorimetrically as shown in thermogram F. Although not shown here, the blend also displayed dual crystallization exotherms at temperatures above the T_g, which also suggests a heterogeneous blend. The two T_g's noted in the blend are also shifted considerably into the region bounded by the T_g's of the pure constituents. Further studies of this blend, involving optical microscopy, indicate a homogeneous blend, which implies that many of the contradictory calorimetric observations may be the result of partial crystallinity produced during the vitrifying step.

The thermogram G (pure PBA) demonstrates a small change of heat capacity at T_g when compared to all the other polymers. This is believed to be caused by a competing crystallization exotherm on heating through the T_g. The PBA/PEZ blend, although concluded to be miscible, exhibits considerable transition broadening. Nevertheless, enthalpy recovery studies[7] did not indicate the multiple recovery peaks associated with phase separation.

Many of the inferences concerning phase behavior noted above are also corroborated by measurements of

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Table 1. Structure and Properties of Linear Aliphatic Polyesters

polymer	structure	CH_2/COO	vol frac of methylene groups[a]	T_g (°C)	T_m (°C)	M_w	M_n
poly(ethylene adipate) (PEA)	$[CO(CH_2)_4COO(CH_2)_2O]$	3	0.6673	−46	52	8500	6000
poly(trimethylene glutarate) (PTG)	$[CO(CH_2)_3COO(CH_2)_3O]$	3	0.6673	−56	40	7100	5500
poly(trimethylene adipate) (PTA)	$[CO(CH_2)_4COO(CH_2)_3O]$	3.5	0.7006	−59	52	5700	4800
poly(butylene adipate) (PBA)	$[CO(CH_2)_4COO(CH_2)_4O]$	4	0.7279	−64	na[b]	7400	5600
poly(ethylene azelate) (PEZ)	$[CO(CH_2)_7COO(CH_2)_2O]$	4.5	0.7506	−54	37	55500	29300
poly(caprolactone) (PCL)	$[(CH_2)_5COO]$	5	0.7698	−69	57	24900	16400

[a] Calculated using $v(CH_2) = 16.45$ cm³/mol, $v(COO) = 24.6$ cm³/mol.[8] [b] na = not available.

Table 2. Thermal Properties and Phase Behavior of the Blends

blend[a]	T_g (°C)	phase behavior	calcd χ_{blend}
PEA/PTG (−46, −56)	−51	M	0
PCL/PEZ (−69, −54)	−62	M	0.0008
PBA/PEZ (−64, −54)	−60	M	0.0012
PEA/PTA (−46, −59)	−51	M	0.0025
PEA/PBA (−46, −64)	−58, −50	(PM)	0.0082
PCL/PTG (−69, −56)	−68, −58	I	0.0235

[a] Values in parentheses are the T_g's of the pure polymers.

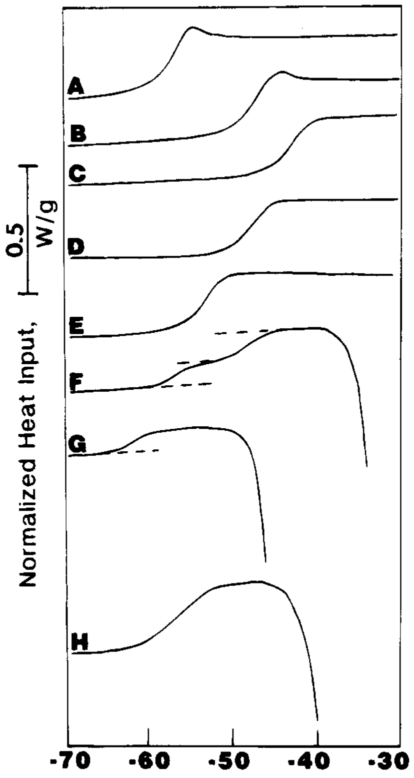

Figure 1. Representative thermograms of linear aliphatic polyesters and their blends: (A) PTA; (B) PEA/PTA (M); (C) PEA; (D) PEA/PTG (M); (E) PTG; (F) PBA/PEA (PM); (G) PBA; (H) PBA/PEZ (M).

the incremental change of heat capacity, ΔC_p, for the blend and qualitative evaluation of the position of the crystallization exotherm. An example of this can be provided by examining the PCL/PTG blend. The initial thermogram reveals a T_g at −68 °C (pure PCL), however, the T_g of the PTG is hidden under the crystallization exotherm. A ΔC_p of 0.3 J/g K indicates "missing" material (cf. ΔC_p of PCL and PTG as 0.42 and 0.72 J/g K, respectively).

The phase behavior of the blends noted in Table 2 has been combined (Figure 2) with recently published data[6] involving a wider range of aliphatic polyesters, synthesized from the condensation of the respective diol and diacid chloride. Little information concerning the polyesters in the latter study has been presented other than the fact that they were all relatively low molecular mass polymers. It is evident from Figure 2 that there is a region of miscibility given approximately by $(x - y) \leq 0.05$, where x and y are the respective volume fraction of methylene groups of the polymers. This significance of this observation will be discussed below.

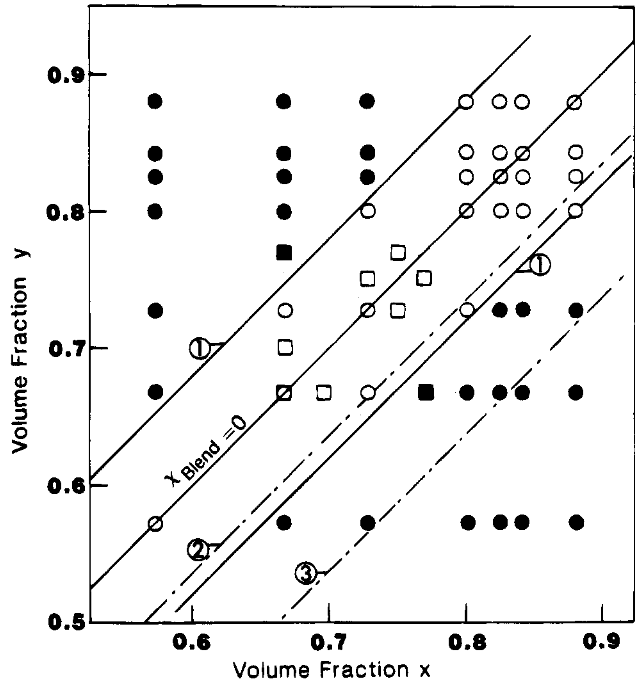

Figure 2. Summary of phase behavior of binary aliphatic polyester blends A_xD_{1-x}/A_yD_{1-y}: (○) miscible, (●) immiscible (ref 6); (□) miscible; (■) immiscible (from Table 2). Lines drawn are the loci of points where $\chi_{blend} = 0.0145$ ($N_1 = N_2 \approx 138$) calculated for the following cases: (1) $\chi_{\overline{AD}} = 2.233$; (2) $\chi_{AAA:ADA} = 2.233$; $\chi_{AAD:ADA} = 1.0$; (3) $\chi_{AAA:ADA} = 2.233$; $\chi_{AAD:ADA} = 3.5$.

Binary aliphatic polyester blends will conform to behavior identical to that proposed previously for their aliphatic polyamide analogues.[2] For both types of blend, the free energy of mixing, ΔG_m, is given by eq 1.

$$\frac{\Delta G_m}{RT} = \left(\frac{\Phi_1 \ln \Phi_1}{N_1} + \frac{\Phi_2 \ln \Phi_2}{N_2}\right) + \chi_{blend}\Phi_1\Phi_2 \qquad (1)$$

Φ is the volume fraction of polymer 1 and 2, and N is the weight-average degree of polymerization. For a blend of polymers denoted as A_xD_{1-x}/A_yD_{1-y}, where A and D represent methylene and ester groups, respectively, the quantity χ_{blend} is given by eq 2.[1,2]

$$\chi_{blend} = (x - y)^2\chi_{AD} \qquad (2)$$

$(x - y)$ is the difference in methylene content of the blend constituents, quantities which are easily calcu-

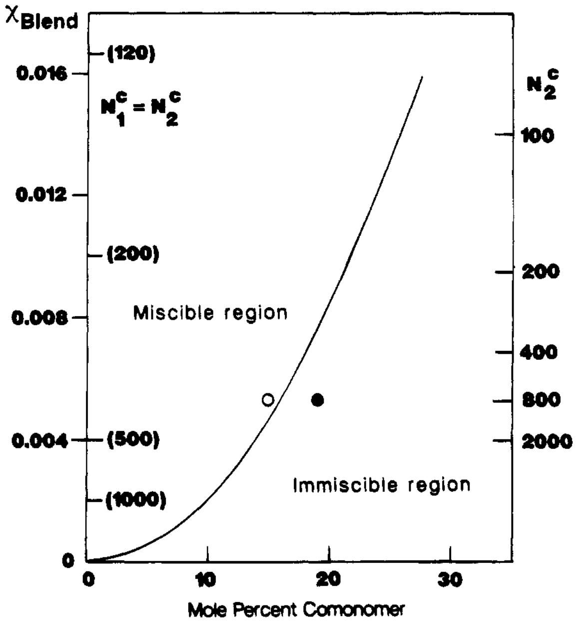

Figure 3. Calculated value of χ_{blend} (and associated values of $N_1^c = N_2^c$) for a binary blend of either poly(caprolactone) or nylon 6 with a copolyester–amide of caprolactam and caprolactone as a function of comonomer content. The right-hand axis represents N_2^c for a copolyester–amide in a blend of poly(caprolactone) $N_1^c = 220$.

lable using group contributions tabulated by Van Krevelen.[8] A value of $\chi_{AD} = 2.233$ has been obtained previously,[1] providing the simple result that χ_{blend} is always positive and therefore unfavorable for homogeneous mixing. Within a Flory–Huggins mean-field treatment, miscibility or homogeneous mixing may occur if χ_{blend} is less than a critical value, χ_{crit}, which can be estimated using eq 3.

$$\chi_{crit} = (N_1^{-1/2} + N_2^{-1/2})^2/2 \tag{3}$$

This provides the argument that entropically driven miscibility can result for relatively large values of $(x - y)$. This occurs because χ_{AD} is relatively small; cf. the methylene–amide interaction parameter $\chi_{AB} = 8.534$[1] for binary aliphatic polyamide blends. A casual comparison of the segmental interaction parameters used here with those reported by other workers suggests that they are, in fact, relatively large. This occurs because the parameters noted above reflect the interaction of chains composed exclusively of ester or amide groups with a polymethylene chain. Nevertheless, the values obtained lead to sensible values of χ_{blend}.[1,2]

The information contained in Figure 2 summarizes the conclusions presented in Table 2 and those in ref 6. The general agreement between the two sets of data is good, except for the blend PEA/PBA. Investigations here have determined that this blend may be partially miscible, whereas other workers[6] concluded that the blend was completely miscible. Partial miscibility is also in contradiction to a calculated $\chi_{blend} = 0.008$ which is below an estimated value of $\chi_{crit} \approx 0.028$. Nevertheless, the general trend of χ_{blend} and phase behavior, noted in Table 2, is as expected. As χ_{blend}, i.e., chemical dissimilarity, increases, the blends progress from miscible to partially miscible and then phase separated.

Also noted on Figure 2 is the locus of points for $\chi_{blend} = 0$, the athermal condition, and the loci of points for $\chi_{blend} = 0.0145$. These have been calculated using eq 2 and $\chi_{AD} = 2.233$. When $\chi_{crit} = \chi_{blend}$, the latter represents values for the symmetrical case of $N_1 = N_2 \approx 140$ and was chosen to fit all the data. This represents polymers with a relatively low molecular mass, and although $\chi_{blend} < \chi_{crit}$, for most of the data points shown, there are several exceptions. For example, the blend where $y = 0.824$ and $x = 0.8803$, which was reported[6] as miscible, has a calculated value of $\chi_{blend} = 0.007$; this contrasts with an estimated $\chi_{crit} = 0.005$. The latter is based on the measured molecular mass of each polymer. Although the difference between χ_{crit} and χ_{blend} is relatively small, these calculations predict a heterogeneous blend. This observation, as well as other considerations, makes it difficult to place too much emphasis on the accuracy of the correlation presented in Figure 2. The reasons for this are discussed below.

The value of χ_{AD} is derived from studies involving a reference temperature of approximately 510 K. Interaction parameters and hence χ_{ij} will vary as a function of temperature; however, the exact dependence for blends of the type discussed here is unknown. In general, $\chi_{blend} \sim 1/T$, and therefore a potentially larger value of χ_{AD} may be anticipated when investigating aliphatic polyester blends at approximately 360 K. In addition to the above, the value of χ_{AD} is really an average $(\overline{\chi_{AD}})$ of segmental interactions of the type noted below and was obtained from investigating behavior of blends of copolyester–amides, where B represents an amide group.

$$\chi_{AAA:ADA}; \quad \chi_{AAB:ADA}; \quad \chi_{AAD:ADA}$$

The notation above is directed, as usual, only to interacting A and D groups but takes into account their nearest neighbors. Even by applying the assumption that $\chi_{AAA:AAB} = \chi_{AAA:AAD} = 0$ the value of χ_{AD} is obtained as an average and may be slightly in error when applied to blends containing only polyesters. The influence of configuration of chemical species, or sequence effects, has been discussed extensively[9–12] within the context of phase behavior of blends involving random addition copolymers. In principle, the same arguments and considerations are equally applicable to the polymers in question here.

Some model calculations to illustrate the influence of assigning different values to the interactions noted above have been explored. This is an instructive exercise for binary polyester blends because it involves the permutation of only one parameter. The equation for χ_{blend} is obtained in the manner described previously,[1] and the exact proportions of the two types of triads, AAA and AAD, can be easily calculated for the polyesters in question. For example, if $\chi_{AAA:ADA}$ is assigned a value of 2.233, the "average" value referred to previously, and $\chi_{AAD:ADA}$ is increased or decreased arbitrarily from this value it is found that the loci of $\chi_{blend} = 0.0145$ simply contract or expand the region of miscibility. The symmetry remains constant; i.e., the loci are parallel to χ_{blend}. These calculations have been included, in part, in Figure 2 so that the magnitude of the effects can be seen in relation to the known behavior. Thus it is not really possible to separate this effect from errors that can be introduced as discussed previously. It is unlikely that the magnitude of the difference between the two types of interactions would be as extreme as noted in Figure 2. In order to obtain unsymmetrical loci of equal values of χ_{blend}, additional configurations, e.g., ADD, which do not occur in these polymers, need to be present. The different possibilities which may be encountered have been discussed with

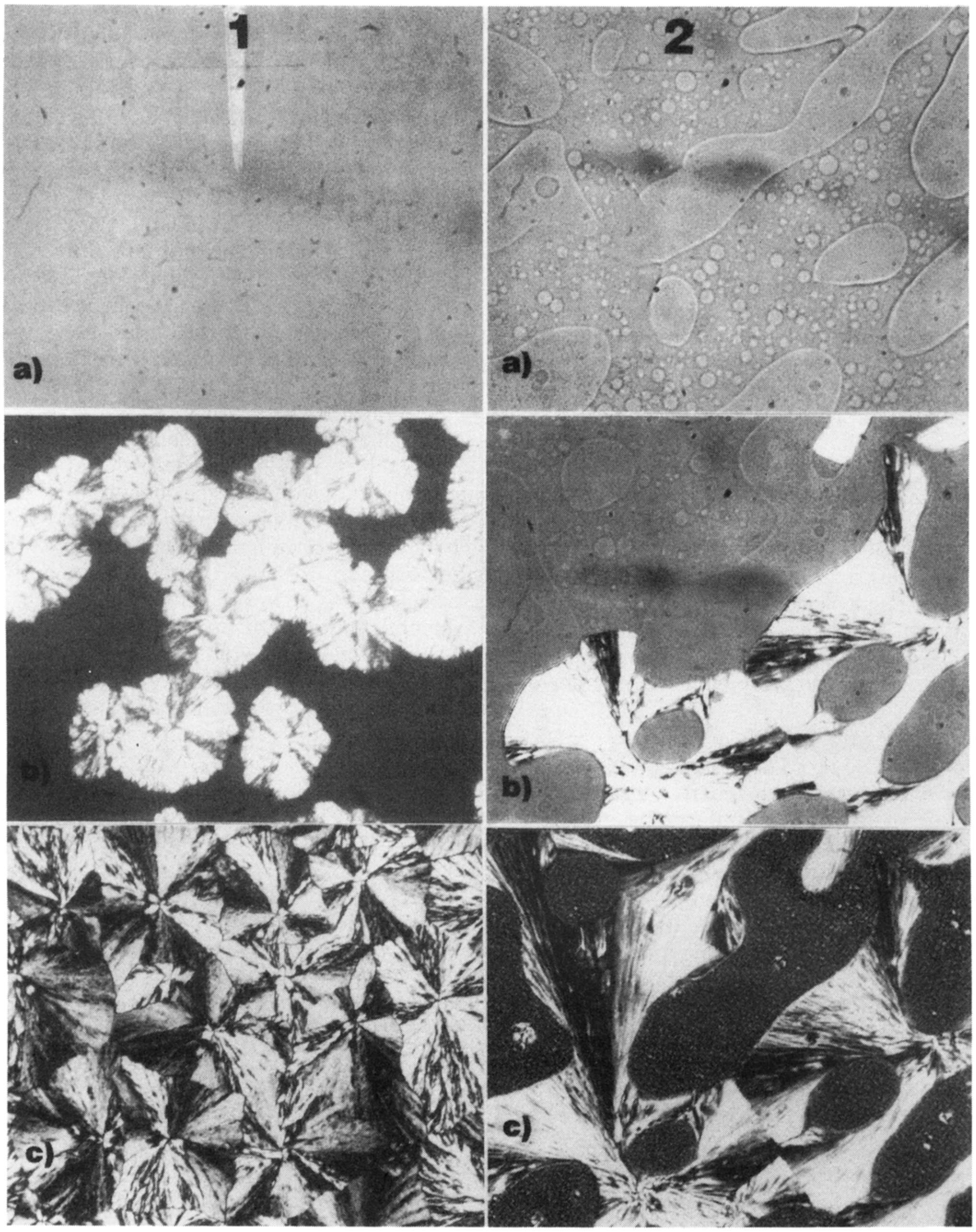

Figure 4. Optical micrographs recorded as a function of time of blends containing PCL and caprolactam/caprolactone copolymers melted at 100 °C for 4 min and crystallized isothermally at 46 °C (series 1) and 42 °C (series 2), respectively. Series 1 contains a copolymer with 15 mol % lactam, and series 2 contains a copolymer with 19 mol % lactam. (a) Melt; (b) partially crystallized; (c) fully crystallized.

reference to random addition copolymers, where in practice these different configurations will exist.

2. Polyester/Copolyester–Amide Blends. The question of configuration as an influence on interactions can be examined from a different perspective by considering the critical lactam content required to induce phase separation in a blend PCL with a caprolactone/caprolactam copolymer. Figure 3 shows calculations ($\chi_{AB} = 8.534$, $\chi_{BD} = 3.880$, ref 1) indicating how χ_{blend} varies as a comonomer is added to either PCL or nylon 6 in a blend of the respective pure polymer. Note that the curve is identical for either case because χ_{AB} and χ_{AD} are unaffected by polymer microstructure. If molecular weights are equal in all the blends, then the figure states that the same quantity of comonomer, lactam or lactone, will cause phase separation with the respective homopolymer. The figure also indicates on the left-hand side critical values of $N_1^c = N_2^c$ which defines a miscible and immiscible region. Thus, for example, for a blend where $\chi_{blend} = 0.004$ (approximately 14 mol % of comonomer) and both components possess $N_1^c = N_2^c < 500$ miscibility should be anticipated. The converse is true for higher molecular weight constituents.

Studies[1] have shown that nylon 6 ($N \approx 300$) in a blend with a copolymer of caprolactam containing approximately 16 mol % lactone and a molecular mass $N > 470$ forms a heterogeneous mixture ($\chi_{blend} > \chi_{crit}$). This agrees with the information in Figure 3. A similar result should be obtained in a blend of PCL with the respective copolymer. Studies by DSC on blends chosen to probe this question were compromised owing to a small separation of T_g between the components and difficulty in obtaining completely vitrified samples for analysis. DSC was able, however, to show that PCL in a blend with copolymer containing 30 mol % lactam was phase separated. Optical microscopy was applied to examine blends with copolymers containing smaller quantities of the lactam.

Optical micrographs, shown in Figure 4, reveal the progress of crystallization in a phase-separated blend of PCL ($N \approx 220$) and a copolymer ($N \approx 800$) containing approximately 19 mol % of caprolactam ($\chi_{\text{blend}} = 0.0077$). In contrast, the micrographs of a blend containing a copolymer ($N \approx 800$) possessing 15 mol % lactam ($\chi_{\text{blend}} = 0.0048$) show spherulites growing in an isotropic liquid. The micrographs obtained for the latter duplicate those obtained for pure PCL (not shown) and support the conclusion of a homogeneous liquid in the melt. These observations are also represented schematically in Figure 3 by the two data points shown. The right-hand ordinate indicates the critical degree of polymerization (N_2^c) for the copolymer in a blend of PCL where $N_1^c = 220$. For both blends χ_{crit} is the same (≈ 0.0053); hence the departure of the data point from the calculated value of χ_{blend} is consistent with the experimental data. For the 19 mol % blend $\chi_{\text{blend}} > \chi_{\text{crit}}$ and the converse is true for the blend containing 15 mol % of comonomer. It is obviously rather difficult to pinpoint the critical comonomer content more accurately; however, 16 mol % of lactam appears to approximate the behavior reasonably well for polymer of similar molar mass.

At first glance, the results provide evidence to support the application of the model to these systems and the validity of the parameters employed in the analysis. However, there are several factors that must be weighed against these conclusions. For example, the measurements of copolymer composition and molecular mass are vitally important. For the PCL used in this study, Figure 3 indicates that only 5 mol % of comonomer corresponds to a change of critical molecular mass, $200 < N < 800$, of the copolymer. Additionally, if the configuration of the species influences the segmental interaction parameters, then the calculations in Figure 3 should include the parameters below where

$$\chi_{\text{AAA:ABA}} \neq \chi_{\text{AAA:ADA}} \neq \chi_{\text{AAB:ABA}} \neq \chi_{\text{AAB:ADA}} \neq \chi_{\text{AAD:ABA}} \neq \chi_{\text{AAD}} \neq \chi_{\text{ADA}}$$

There is insufficient information to judge if the relationship given above is correct. Moreover, without an estimation of each of these parameters, it is not possible to evaluate exactly how the curve in Figure 3 is affected. Notwithstanding the uncertainties noted above, the value of χ_{AD} applied throughout these calculations appear to give a reasonable approximation of the observed behavior.

Conclusions

It has been shown both experimentally and theoretically that binary blends of linear main-chain aliphatic polyesters will form homogeneous or miscible mixtures only when the entropic contribution to the free energy of mixing overcomes an unfavorable interaction between the components. This result mirrors that encountered for blends involving aliphatic polyamides; however, the most important feature of the analysis is the confirmation that a relatively small value of the methylene–ester segmental interaction parameter appears to model the behavior with reasonable accuracy. Consequently, it has been found that for low to moderate molecular mass polyesters, homogeneous mixing can be obtained with a relatively large dissimilarity of alkyl content between the constituents. The experimental data forming the basis of this conclusion have been garnered from a recent publication, involving polyesters with a CH_2/COO ratio in the range 2:1–11:1 and separate studies conducted in this laboratory.

An alternative approach for evaluating the accuracy of χ_{AD} has involved a determination of the critical caprolactam content, in a copolymer with caprolactone, required to induce phase separation in a blend with poly(caprolactone). A lactam content in excess of approximately 15 mol % appears to be sufficient to effect this process; however, the exact composition will also depend upon the molecular mass of the constituents. Calculations have shown this result to reflect favorably on the values of the parameters used in the application of the model to the data. Part of the discussion has centered on how miscibility will be affected by the configuration, i.e., arrangement, of chemical species; however, at this stage, other factors, such as the temperature dependence of interaction parameters, cannot be distinguished quantitatively from these effects.

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