The Effect of Intrachain Order on Solid Solutions of Copolymers

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ABSTRACT: The theory of solid solution formation in binary systems for which mixing is ideal in both phases is generalized to include one-dimensional ordering. As such, the theory is most readily applicable to copolymeric systems. Calculations based upon the theory indicate that copolymers with a tendency for alternation would melt over a narrower, more intermediate range and would be less subject to compositional and sequence length fractionation than random or block copolymers. As the tendency to alternate is heightened a point of invariance is approached (at constant pressure) at a composition corresponding to equal numbers of the counits. The copolymers with a tendency to be ordered in blocks are predicted to display the broader melting ranges and undergo the greater compositional and sequence length fractionations. Theoretical equilibrium degree of crystallinity curves for block copolymers display fusion processes consisting of two distinct stages.

Isomorphic replacement of structural units in synthetic copolymers has been known since Edgar and Hill observed this phenomenon in copolyamides,[1] but theories describing the thermal behavior of such solid solutions have been lacking.

The thermal characteristics of copolymeric solid solutions can be strongly affected by nonideality of mixing, which in the solid phase may be associated with distortions, dimensional changes,[2–4] or structural transitions[2,3,5] (isodimorphism)[2,3] of the crystalline lattice as a function of composition. If mixing in both phases is ideal the equilibrium phase diagram may still display marked variations from system to system. It is this latter case that is treated theoretically in the present work.

In the case of solid solution equilibria involving ideal binary mixtures of low molecular weight substances Seltz derived equations relating equilibrium temperatures and composition in terms of the thermodynamic parameters of fusion of the pure components.[6] Although the values of these parameters may affect quantitative aspects of those phase diagrams their boundaries enclose lens-shaped areas in all cases. If deviations from Raoult's law occur which are similar for both phases the characteristic shape of the ideal mixing phase diagram will be preserved.[7]

In copolymers the chemical potential of each costructural unit species is dependent upon its sequence propagation probability.[8] Thus, any theory which treats solid solution formation in copolymers must include a description of the covariation of the sequence propagation probabilities as well as the thermodynamic parameters of fusion of the pure components, *i.e.*, homopolymers.

In this paper the effects of varying degrees of one-dimensional order in solid solution equilibria between binary mixtures will be examined. It will be shown that the equations for solid solution equilibria of ideal mixtures of low molecular weight substances are a special case of this treatment.

Theoretical

We consider a linear, infinite molecular weight, binary copolymer containing A and B units for which only nearest neighbor units influence the polymer sequence length distribution. It has been shown for such a copolymer whether formed by a kinetic or an equilibrium controlled process that[9]

$$\frac{P_{AA}P_{BB}}{P_{AB}P_{BA}} = Q \tag{1}$$

Here P_{IJ} (where I and J may be either A or B) is the conditional probability that an I unit selected at random will be followed by a J. Q describes the randomness of the copolymer. It is equivalent to both the reactivity ratio product for a kinetically generated copolymer and to the reciprocal of the equilibrium constant of the equilibrium copolymerization process defined by the reaction

$$\sim\!A\!-\!A\!\sim + \sim\!B\!-\!B\!\sim \rightleftarrows \sim\!A\!-\!B\!\sim + \sim\!B\!-\!A\!\sim \tag{2}$$

Thus, a value of Q which is less than, equal to, or greater than one, respectively characterizes arrangements of counits that tend to alternate, are random, or tend to be ordered in blocks.

If it is further stipulated that the enthalpy of mixing of the A with the B units is negligible one may write for any phase that[8]

$$\mu_A - \mu_A{}^0 = RT \ln P_{AA} \tag{3}$$

and

$$\mu_B - \mu_B{}^0 = RT \ln P_{BB} \tag{4}$$

where μ_I and $\mu_I{}^0$ are the chemical potentials of the I units in a copolymer and a homopolymer, respectively.

Should the copolymer undergo a solid–liquid phase transition characterized by a latent heat and in which A and B units are found in both phases, then at equilibrium we may write that $\mu_A{}^{(c)} = \mu_A{}^{(a)}$ and $\mu_B{}^{(c)} = \mu_B{}^{(a)}$. The superscripts c and a denote the crystalline and the amorphous phase, respectively. Using these relation-

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[6] H. Seltz, *J. Amer. Chem. Soc.*, **56**, 304 (1934).
[7] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, Inc., New York, N. Y., 1964, Chapter 18.
[8] C. H. Baker and L. Mandelkern, *Polymer*, **7**, 7 (1966).
[9] M. H. Theil, *Macromolecules*, **2**, 137 (1969).

ships and eq 3 and 4 the equilibria between the two phases may be expressed in exponential form as

$$\frac{P_{AA}^{(c)}}{P_{AA}^{(a)}} = \exp[(\mu_A^{0,(a)} - \mu_A^{0,(c)})/RT] \tag{5}$$

and

$$\frac{P_{BB}^{(c)}}{P_{BB}^{(a)}} = \exp[(\mu_B^{0,(a)} - \mu_B^{0,(c)})/RT] \tag{6}$$

Fractionation as a consequence of phase equilibrium occurs by the selective inclusion in each of the phases, sequences which differ both in composition and in sequence length distribution from the copolymer as a whole. The sequence length distributions of the two phases may be interrelated by Q. Q, depending only upon the values of the different varieties of nearest neighbor intrachain interactions that determined the copolymer sequence length distribution, is independent of composition.[9] Then, the single value of Q which characterizes the whole copolymer as formed is preserved within each fractionated phase. Thus, from eq 1

$$\frac{P_{AA}^{(a)}P_{BB}^{(a)}}{(1 - P_{AA}^{(a)})(1 - P_{BB}^{(a)})} = Q = \frac{P_{AA}^{(c)}P_{BB}^{(c)}}{(1 - P_{AA}^{(c)})(1 - P_{BB}^{(c)})} \tag{7}$$

where P_{AB} and P_{BA} have been replaced by their equivalents in this system, $1 - P_{AA}$ and $1 - P_{BB}$, respectively. The system, eq 7, incorporates two independent equations which can be used in finding any of the four sequence propagation probabilities $P_{AA}^{(a)}$, $P_{BB}^{(a)}$, $P_{AA}^{(c)}$, or $P_{BB}^{(c)}$ in terms of the temperature and various parameters characteristic of the system.

We illustrate in detail the solution for $P_{AA}^{(a)}$. Equations 5 and 6 may be expressed in terms of the probabilities given on the right side of eq 7 and substituted for them giving

$$\frac{P_{AA}^{(a)}y_A P_{BB}^{(a)}y_B}{(1 - P_{AA}^{(a)}y_A)(1 - P_{BB}^{(a)}y_B)} = Q \tag{8}$$

where y_A and y_B are equal to the right sides of eq 5 and 6, respectively. The left side of eq 7 may be solved for $P_{BB}^{(a)}$ in terms of Q and $P_{AA}^{(a)}$ and that result substituted in eq 8. When the resulting equation is rearranged and terms are collected with respect to powers of $P_{AA}^{(a)}$ we obtain

$$P_{AA}^{(a)\,2}[(Q - 1)(1 - y_B)y_A] + P_{AA}^{(a)}[Q(y_A + 1)(y_B - 1) + 1 - y_Ay_B] + Q(1 - y_B) = 0 \tag{9}$$

The root of this equation which lies in the range zero to one inclusive is the physically significant value of $P_{AA}^{(a)}$. The composition of the melt is then obtained from[9]

$$X_A^{(a)} = \frac{1}{Q(1 - P_{AA}^{(a)})^2/P_{AA}^{(a)} - P_{AA}^{(a)} + 2} \tag{10}$$

where $X_A^{(a)}$ is the mole fraction of A units in the melt. The expression

$$P_{AA}^{(c)\,2}[(Q - 1)(1 - z_B)z_A] + P_{AA}^{(c)}[Q(z_A + 1)(z_B - 1) + 1 - z_Az_B] + Q(1 - z_B) = 0 \tag{11}$$

obtained in a similar manner is of the same form as that for $P_{AA}^{(a)}$ with y_I replaced by its reciprocal, z_I. Expressions for $P_{BB}^{(a)}$ and $P_{BB}^{(c)}$ correspond to those for $P_{AA}^{(a)}$ and $P_{AA}^{(c)}$, respectively, with all A and B subscripts interchanged. Alternatively $P_{BB}^{(a)}$ may be found by employing the results of eq 9 and 10 in the relationship[9]

$$P_{BB}^{(a)} = \frac{X_A^{(a)}}{X_B^{(a)}} P_{AA}^{(a)} + 1 - \frac{X_A^{(a)}}{X_B^{(a)}} \tag{12}$$

where $X_B^{(a)}$ is the mole fraction of B units in the melt, and $P_{BB}^{(c)}$ may be calculated *via* an analogous route.

The participation of ideal binary mixtures of small molecules in solid solution equilibria is a special case of the present development. This random arrangement of small molecules corresponds to the entirely random arrangement of costructural units in this system that occurs when $Q = 1$. At this point eq 9 reduces to the monomeric case,[6] $X_A^{(a)} = (y_B - 1)/(y_B - y_A)$, since, according to eq 10, $P_{AA}^{(a)} = X_A^{(a)}$ when $Q = 1$. Similarly, $X_A^{(c)} = y_A(y_B - 1)/(y_B - y_A)$ for the random case.

Results and Discussion

The implications of the effects of copolymer order upon solid solution equilibria as represented by equations of the form of eq 9 and 11 are best demonstrated by specific illustration. The literature lacks evidence of adequate characterization of thermodynamic parameters of the pure components for copolymers which display solid solution formation, and lacks documentation of ideal solid solution formation in nonrandom copolymers. Consequently we choose a set of hypothetical parameters for these illustrations. In doing so we make use of the approximations that, at temperature T in the range of interest $(\mu_A^{0,(a)} - \mu_A^{0,(c)}) = \Delta H_{u,A}(1 - T/T_{m,A}^0)$ and $(\mu_B^{0,(a)} - \mu_B^{0,(c)}) = \Delta H_{u,B}(1 - T/T_{m,B}^0)$. Here $\Delta H_{u,I}$ is the heat of fusion per mole of I structural units and $T_{m,I}^0$ is the equilibrium melting point of the infinite molecular weight homopolymer of I units. The values of the parameters which are consistent among all of the examples of this paper are $\Delta H_{u,A} = 6000$ cal/mol of structural units, $T_{m,A}^0 = 500$°K, $\Delta H_{u,B} = 8000$ cal/mol of structural units and $T_{m,B}^0 = 400$°K. These chosen values are close to those of many known polyesters and polyamides. While the selection of other sets of parameters would affect the quantitative results of the examples that follow, the qualitative implications of the theory would be consistently retained in the illustrations.

We first give constant pressure equilibrium diagrams of temperature *vs.* composition for systems characterized by these parameters and by different levels of copolymer order. In these cases it proved convenient to calculate the solidus and liquidus temperatures as functions of composition rather than by the converse approach suggested by eq 9 and 10. For this purpose P_{AA} was calculated from given values of composition and randomness by[9]

$$\left[\frac{X_A}{X_B}(1 - Q)\right]P_{AA}^2 + \left[1 - \frac{X_A}{X_B}(1 - 2Q)\right]P_{AA} - \frac{X_A}{X_B}Q = 0 \tag{13}$$

and eq 9 and 11 were solved for the liquidus and solidus

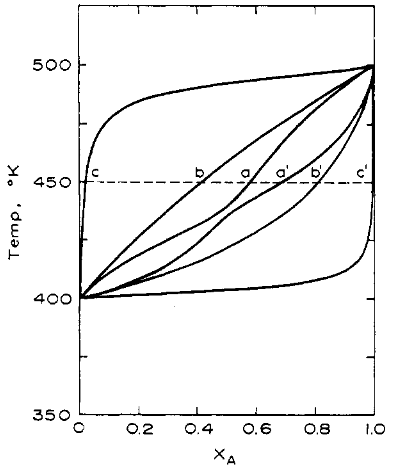

Figure 1. Solid solution equilibria in copolymers of different degrees of intrachain order. Temperature *vs.* mole fraction of A units for copolymers described by parameters given in text. Liquidus and solidus curves are denoted by unprimed and primed symbols, respectively. Curves *a* and *a'*, Q = 0.01; curves *b* and *b'*, Q = 1; curves *c* and *c'*, Q = 100.

temperatures as functions of P_{AA} by the Newton–Raphson method, an iterative numerical technique.[10]

Figure 1 shows that at a given composition the larger the value of Q, the more extended are the upper and lower temperature limits over which equilibrium conditions prevail. Similarly the intersection of the dashed tie line with the set of curves indicate that the solid solutions in equilibrium with their melts characterized by the higher values of Q undergo the more marked compositional fractionation. The 450°K tie line connects $X_A^{(a)}$ = 0.575 with $X_A^{(c)}$ = 0.687 when Q = 0.01 and $X_A^{(a)}$ = 0.020 with $X_A^{(c)}$ = 0.993 when Q = 100. Thus, a copolymer which contains equal numbers of each kind of unit and is characterized by a value of Q of 100 may yield separate, though not necessarily cleanly partitioned, phases having compositions approaching those of the reference homopolymers. The zone between curves *a* and *a'* is constricted at X_A = 0.5. This departure from the classical solid solution phase diagram is increasingly manifested as values assigned to Q diminish from one toward zero, and the liquidus and solidus curves approach coincidence at this over-all composition. The aproach to coincidence at this point satisfies the requirements of the phase rule. As Q nears zero at X_A = 0.5 the arrangement of copolymer structural units approaches perfect alternation. At the limit of perfect alternation the copolymer is, in fact, a homopolymer; just as the copolymer of adipic acid and hexamethylenediamine is nylon-6,6, and a perfectly alternating stereoregular arrangement of methylene and ethylidene may be isotactic polypropylene. Containing one component, the system is invariant at constant pressure; the equilibrium temperature range becomes a melting point, and compositional fractionation is eliminated.

A binary alternating copolymer which forms solid solutions is somewhat analogous to a binary low molecular weight mixture which forms 1:1 compounds as well as solid solutions. Thus, the system, bromine-iodine which forms the compound IBr[7,11] and solid solutions over the entire composition range, exhibits a temperature *vs.* composition diagram closely resembling that of Figure 1, curves *a* and *a'*.[7,12]

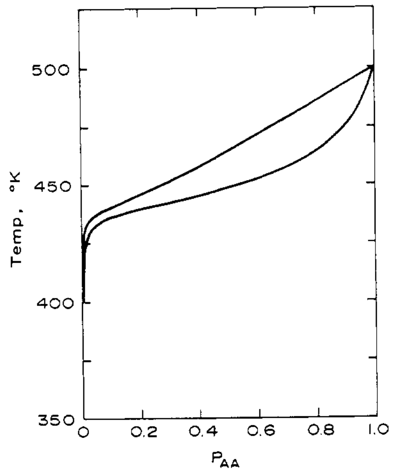

Figure 2. Solid solution equilibria in copolymers described by parameters given in text and for which Q = 0.01. Temperature *vs.* the sequence propagation probability P_{AA}. Upper curve is the solidus, lower curve is the liquidus.

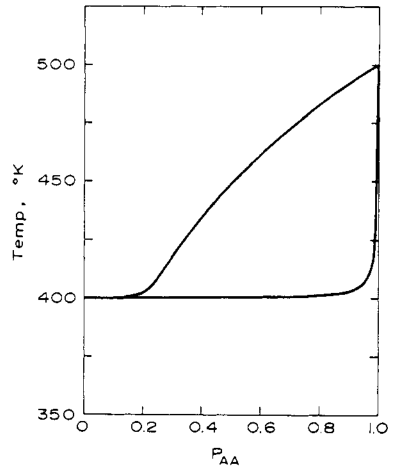

Figure 3. Solid solution equilibria in copolymers described by parameters given in text and for which Q = 100. Temperature *vs.* the sequence propagation probability P_{AA}. Upper curve is the solidus, lower curve is the liquidus.

Solidus and liquidus temperatures of these copolymers plotted as functions of their sequence propagation probabilities give direct information about the sequence length distributions in the two phases. Calculations for such plots were performed by solution of eq 9 and 11 for temperature at uniform increments of P_{AA}, again using the Newton–Raphson method. These calculations are plotted for the case in which Q = 0.01 in Figure 2 and for which Q = 100 in Figure 3. Since P_{AA} = X_A when Q = 1, the T *vs.* P_{AA} plots for the random copolymer are identical with curves *b* and *b'* in Figure 1. The plots for T *vs.* P_{AA} indicate that the longer sequences of the higher melting component re-

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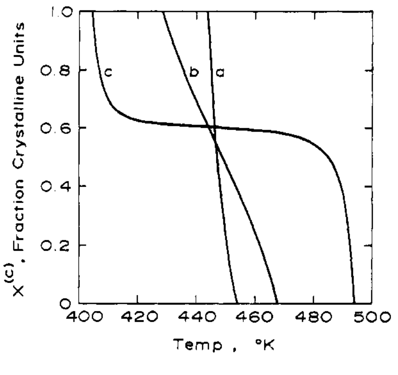

Figure 4. Solid solution equilibria in copolymers of different degrees of intrachain order. Over-all fraction of crystalline units *vs.* temperature for copolymers described by parameters given in text and for which $X_A = 0.6$. Curve *a*, $Q = 0.01$; curve *b*, $Q = 1$; curve *c*, $Q = 100$.

main in the solid phase during equilibrium, and fractionation with respect to sequence length is more pronounced in polymers characterized by the highest value of Q. Accordingly it is predicted that the polymer with $Q = 100$ will undergo a marked fractionation with respect to sequence lengths of A units, particularly at the lower end of the equilibrium temperature range. In the system with the high tendency to alternate, fractionation of A unit sequence lengths are nearly absent at values of P_{AA} corresponding to $X_A < 0.5$, a composition range in which A unit sequence lengths greater than one are uncommon.

Figure 4 demonstrates the effect of variations in the extent of copolymer randomness on the theoretical equilibrium degree of crystallinity curves of copolymers, each of which is characterized by an over-all composition $X_A = 0.6$. The plots are in terms of $X^{(c)}$ the over-all fraction of crystalline A and B units, *vs.* T. $X^{(c)}$ is given by

$$X^{(c)} = \frac{X_A - X_A^{(a)}}{X_A^{(c)} - X_A^{(a)}} \tag{14}$$

since $X_A = (1 - X^{(c)})X_A^{(a)} + X^{(c)}X_A^{(c)}$. $X_A^{(a)}$ and $X_A^{(c)}$ were calculated as functions of T by the procedure outlined in the presentation of eq 9–11. A qualitative change in the fusion process accompanies the broadening of its temperature range as larger values of Q are encountered. As progressively higher values of Q characterize the polymer, the fusion curve becomes markedly sigmoidal; the broad range of the entire melting process contains two distinct sharp intervals which encompass most of the fusion. Thus, portions of the fusion curve of an ordered block copolymer may be more abrupt than any part of the fusion curve of a random copolymer. It is evident from the appropriate curves of Figures 1, 3, and 4 that the material melting in the lower temperature portion of curve *c* in Figure 4 consists of long sequences of B structural units between which very short A sequences are embedded. After a temperature interval in which very little fusion is observed the fusion of conversely arranged sequences of A and B units occurs at temperatures approaching $T_{m,A}{}^0$.

The curves plotted in Figure 4 depict a situation in which equilibrium and perfection of sharply demarcated phases is maintained during the entire fusion process. The predictions of finite melting ranges for these substances is solely a function of their two-component nature.

Up to this point Q has been treated as a parameter characterizing a given copolymeric system in any state. It is not unusual, however, for certain copolymers to equilibrate to other than their original values of Q at temperatures at which they would undergo phase transitions.[13] For situations in which Q can vary with temperature we may write $Q = \exp(2\Delta\epsilon_{AB}/RT)$.[9] Here $2\Delta\epsilon_{AB}$ is the standard state free energy for the reaction as written in eq 2. If $\Delta\epsilon_{AB}$ should equal zero, as it often does, then a random copolymer would result at equilibrium, and the phase relationship expected would be identical with those for monomeric mixtures as previously discussed. If $\Delta\epsilon_{AB}$ should be other than zero the resulting phase diagrams would be modified versions of those for the nonrandom copolymers already outlined. Because of the greater randomness of these copolymers at higher temperatures, such phase diagrams should more nearly resemble those for nonrandom copolymers in the lower rather than the upper portions of their temperature ranges. It is likely, however, that concomitant with any appreciable values of $\Delta\epsilon_{AB}$ there would be interactions between A and B units not covalently bonded to one another leading to nonideality of mixing.

This model, by featuring ideality of mixing in both phases and lacking the specification of a strained interfacial zone between the liquid and solid phases,[14] is an oversimplification which may, nevertheless, lead to the identification of departures from ideality and equilibrium in real systems. The simplicity of the model heightens our understanding of the substantial effects that one-dimensional ordering may exert upon these phase equilibria.

While the development thus far has been described in terms of a solid–liquid transition it should be recognized that no stipulations have been made with respect to the structure within either phase with the exception of the sequence length distribution of the chain and ideality of mixing. Phase morphology and chain configuration remain unspecified. Thus both phases involved could be solid. The foregoing development is then sufficiently general to include any phase transition for a copolymer-like system that is characterized by latent heats and described by the assumptions and restrictions previously listed.

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