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Miscibility

Effect of Chemical and Configurational Sequence Distribution on the Miscibility of Polymer Blends

1. Blends of Monotactic Homopolymers

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Summary

Polymer blends of theoretical and practical interest frequently are comprised of copolymers, which contain sequences differing with respect to chemistry and / or to configuration. An approach is proposed, which may take into account the effect of configurational sequence distributions on the miscibility of blends. Blends of monotactic homopolymers with components of both identical and differing chemistry are treated first. Directional-specific intermolecular as well as repulsive intramolecular interactions are taken into account on a triad basis. The treatment will be expanded to blends with copolymer components, in which chemical and configurational sequences overlap.

Introduction

By mixing compatible polymers, new and favourable properties can be obtained, which differ from those of the individual components. This has been demonstrated, for example, by the dynamic mechanical properties of polystyrene - poly(vinylmethylether) blends 1). Partial thermodynamic compatibility plays a dominant role in two- or multiphase systems, because of force transfer between the phases.

Directional-specific intermolecular interactions have been assumed for quite some time to be the unique source of thermodynamic compatibility. The HILDEBRAND solubility parameter concept is based on this assumption. Experimentally it has been found, however, that many copolymers are miscible even if the homopolymer components are immiscible.

Although SIMHA 2) discussed the role of repulsive and of attractive interactions very early, within the context of copolymerization phenomena, those effects have only recently been taken into consideration with respect to polymer miscibility, by KAMBOUR et al. 3), PAUL and BARLOW 4), TEN BRINKE et al. 5), BALAZS et al. 6) 7) and HOWE and COLEMAN 8).

PAUL and BARLOW developed a binary interaction model for polymer blends containing copolymers, which explains the miscibility window in such systems. Both intermolecular and intramolecular interactions of component units are taken into account, with the consequence that repulsive intramolecular interaction may enhance miscibility. In a blend of a copolymer AB with a polymer C, the intermolecular AC and AB interactions are thus modified by the intramolecular repulsion between AB diads.

BALAZS et al. have refined this model by considering the sequence distribution using a triad approach. In the following, we compare both approaches with the conclusion that, in our opinion, BALAZS et al. have made some inconsistent approximations concerning triad influences.

Subsequently, we try to modify the polymer - copolymer approaches in order to make them applicable for blends of monotactic homopolymers, which are identical or non-identical with respect to their chemistry. Directional-specific intermolecular as well as repulsive type intramolecular interactions are taken into account. In a subsequent paper, blends containing copolymers with an overlapping of chemical and configurational sequence distributions will be treated with respect to their miscibility.

Background

For miscibility the free energy of mixing $\Delta G^m = \Delta H^m - T\Delta S^m$ has to be negative. In addition, it is required that $\partial^2 \Delta G^m / \partial \phi_i^2 > 0$, with ϕ_i the volume fraction of either component. The FLORY - HUGGINS model for polymer solutions has been extended for polymer - polymer mixtures. It is assumed that the only contribution to the entropy of mixing is the combinatorial one

$$\Delta S^m = -R(V_A + V_B)\,[\phi_A \ln\phi_A / \tilde{V}_A + \phi_B \ln\phi_B / \tilde{V}_B] \quad , \quad (1)$$

with $\tilde{V}_i$ the molar volume of component i and V_A and V_B the actual volumes of the components comprising the mixture. The enthalpy of mixing is assumed to be of VAN LAAR type

$$\Delta H^m = (V_A + V_B)\, B\, \phi_A \phi_B \quad . \quad (2)$$

The binary interaction energy density, B, is related to the interaction parameter χ by

$$B / RT = \chi_A / \tilde{V}_A = \chi_B / \tilde{V}_B = \tilde{\chi}_{AB} \quad . \quad (3)$$

While PAUL and BARLOW prefer B since its basis is always clearly a unit of mixture volume, we will apply the more familiar χ' s.

According to the FLORY - HUGGINS approach, since the combinatorial entropy is negligible for high molecular weights, only a negative interaction parameter leads to polymer blend miscibility. Furthermore, demixing at elevated temperatures cannot be explained. Equation of state theories eliminate this shortcoming. Since they are also based on the concept of binary intermolecular interaction parameters, negative values of the interaction parameter are still necessary for miscibility.

BARLOW and PAUL successfully interpreted the mixing behaviour of blends containing copolymer components by appropriate consideration of both intermolecular and intramolecular interactions, with the consequence that polymers may be miscible if repulsive intramolecular interaction compensate non-favourable intermolecular contacts. As interaction parameter of a copolymer $\underline{AB}$ with a homopolymer C they derive

$$\chi_{\underline{AB};C} = \chi_{AC} f_A + \chi_{BC} f_B - \chi_{AB} f_A f_B \quad , \quad (4)$$

with f_A and f_B the mole fractions of the copolymer components, and χ_{AC} , χ_{BC} the intermolecular and χ_{AB} the repulsive intramolecular interaction parameters.

This model considers the intramolecular influence of the AB diad on the copolymer thermodynamic character. Assuming that both homopolymer pairs, AC and BC, are immiscible, their interaction parameters being positive, this can be outweighed by a large enough positive intramolecular repulsive interaction between A and B

$$\chi_{AB} > (\chi_{AC}^{1/2} + \chi_{BC}^{1/2})^2 \quad . \quad (5)$$

However, this model can describe only symmetrical curves for $\chi_{\underline{AB}}$ versus f_i.

BALAZS, SANCHEZ, EPSTEIN, KARASZ and MACKNIGHT [6)] have introduced, consequently, chemical triad sequence distributions into their approach. The repulsive type intramolecular interactions are supposed, however, equivalent with the average interaction parameter, $\bar{\chi}_{AB}$, in accordance with BARLOW and PAUL [4)]. The directional-specific intermolecular interactions are assumed to be dependant on the neighbours of the interacting groups. Consequently, the following A and B centered triads have been taken into account for a blend of a copolymer $\underline{AB}$ with a homopolymer C

BAB BAA AAB AAA - ABA ABB BBA BBB .

In order to reduce the number of parameters, the following simplifications are introduced by the authors

$$\bar{\chi}_{AC} = \chi_{BAB;C} = \chi_{AAB;C} = \chi_{BAA;C} \neq \chi_{AAA;C}$$

$$\bar{\chi}_{BC} = \chi_{ABA;C} = \chi_{ABB;C} = \chi_{BBA;C} \neq \chi_{BBB;C} \quad .$$

With these approximations the interaction between the blend components is

$$\chi_{\underline{AB};C} = \bar{\chi}_{AC} f_A + \bar{\chi}_{BC} f_B - \bar{\chi}_{AB} f_A f_B + \Delta\chi_A (f_{AA}^2/f_A) + \Delta\chi_B (f_{BB}^2/f_B) \quad , \quad (6)$$

with

$$\Delta\chi_A = \chi_{AAA;C} - \bar{\chi}_{AC} \qquad \Delta\chi_B = \chi_{BBB;C} - \bar{\chi}_{BC} \quad . \quad (7)$$

A negative $\Delta\chi_A$ means that AAA;C interactions are more favourable for miscibility than other interactions of A centered triads with C. Conversely, a positive $\Delta\chi_A$ implies that the interactions of mixed triads with C are more favourable than the AAA;C ones.

The authors then introduce a theta parameter that describes the sequence distribution within the polymer chain. The sequence distribution – blocky, alternating, or statistical – is determined in a convenient manner. For a fixed composition, an optimal range of sequence distributions – in terms of theta – exists for <u>AB</u>;C miscibility.

Theoretical Considerations Concerning the Effect of Chemical and Configurational Sequence Distribution on the Miscibility of Polymer Blends

In our opinion, the approximations concerning the triad effects on miscibility, as given above, are inconsistent. To make this evident, we notice that it is assumed that it is irrelevant whether an AB diad within an A centered triad is neighboured by an A or a B unit. Analogously for the B centered triads, the same assumptions have been made. The situation is visualized on the left. Consequently, it is not established that $\bar{\chi}_{AC}$ and $\bar{\chi}_{BC}$ have different values. As the consequence of these approximations, $\bar{\chi}_{AC}$ becomes identical with $\bar{\chi}_{BC}$. Furthermore it is not discerned that $\chi_{AAA;C} \neq \chi_{AAB;C}$, if $\chi_{AAB;C} = \chi_{BAB;C}$. In both cases an A is substituted by a B. The consequence is $\chi_{AAA;C} - \bar{\chi}_{AC} = \chi_{BBB;C} - \bar{\chi}_{BC} = \Delta\chi_A = \Delta\chi_B = 0$.

BAB	ABA
AAB	ABB
BAA	BBA
AAA	BBB

If this is true, the triad approach collapses because the sequence distribution is not taken into account, and the equation for $\chi_{\underline{AB};C}$ is governed by the diad contributions in the repulsive term only. Thus, it becomes identical to that of BARLOW and PAUL.

A modified assumption, however, may be justifiable. The difference in interaction between AAA;C and AAB;C may be assumed to be identical with that of AAB;C and BAB;C. The corresponding assumption may be made for the interaction of the B centered triads with C. Changing neighbours within a triad may be weighted then in an appropriate way. Thus, we define

$$\Delta\chi_A = \chi_{AAA;C} - \chi_{AAB;C} = \chi_{AAB;C} - \chi_{BAB;C} \quad (8)$$

$$\Delta\chi_B = \chi_{BBB;C} - \chi_{BBA;C} = \chi_{BBA;C} - \chi_{ABA;C} \quad . \quad (9)$$

The conclusions of BALAZS et al. concerning miscibility windows in polymer-copolymer blends will remain valid, however.

We like to propose, however, an alternative approach, which takes into account the role of the transitions between blocky and alternating sequences in a consequent way, for chemical as well as for configurational copolymers.

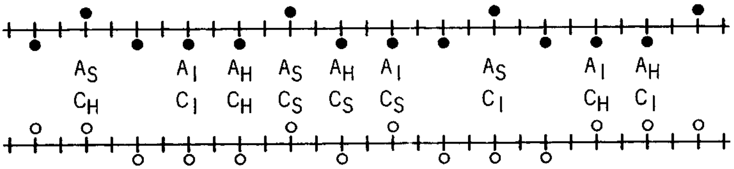
In order to interprete the influence of the configuration on miscibility we first discuss a blend of two chemically identical homopolymers, A* and A*', which differ in tacticity. We regard isotactic (I), syndiotactic (S) and heterotactic (H) triads as separate units. Inter- and intramolecular interactions are assumed to depend on the neighbour groups. The interaction parameter may be written

$$\chi_{A^*A^{*\prime}} = \chi_{A_IA_S}(f_{A_I} - f_{A'_I})\cdot(f_{A'_S} - f_{A_S}) + \chi_{A_IA_H}(f_{A_I} - f_{A'_I})\cdot(f_{A'_H} - f_{A_H})$$
$$+ \chi_{A_SA_H}(f_{A_S} - f_{A'_S})\cdot(f_{A'_H} - f_{A_H}) \quad . \qquad (10)$$

As the next system the blend of A* with non-tactic C, e. g. polyvinylchloride and polyvinylidenchloride, may be discussed. The interaction parameter is

$$\chi_{A^*C} = \chi_{A_IC}\, f_{A_I} + \chi_{A_HC}\, f_{A_H} + \chi_{A_SC}\, f_{A_S}$$
$$- \chi_{A_IA_S}\, f_{A_I}f_{A_S} - \chi_{A_IA_H}\, f_{A_I}f_{A_H} - \chi_{A_SA_H}\, f_{A_S}f_{A_H} \quad . \qquad (11)$$

Next we interprete the miscibility of two monotactic vinyl polymers, A* and C*, which are different with respect to their chemical structure, e. g. polyvinylchloride and poly(methylmethacrylate). Both the partners contain isotactic (I), syndiotactic (S) and heterotactic (H) triads, which determine the configurational sequence distribution within the chain. Below, A (●) and C (o) chain sectors are visualized. They include all



the triads, which may perform intermolecular interaction, with $\chi_{A_IC_I}$, $\chi_{A_IC_S}$, $\chi_{A_IC_H}$, $\chi_{A_SC_I}$, $\chi_{A_SC_S}$, $\chi_{A_SC_H}$, $\chi_{A_HC_I}$, $\chi_{A_HC_S}$, and $\chi_{A_HC_H}$. We introduce the approximations $\chi_{A_IC_S} = \chi_{A_SC_I}$, $\chi_{A_IC_H} = \chi_{A_HC_I}$, $\chi_{A_SC_H} = \chi_{A_HC_S}$, $\chi_{A_HC_H} = (\chi_{A_IC_H} + \chi_{A_SC_H})/2$. Further, we consider the self-interaction parameters $\chi_{A_IA_S}$, $\chi_{A_IA_H}$, $\chi_{A_SA_H}$, $\chi_{C_IC_S}$, $\chi_{C_IC_H}$, and $\chi_{C_SC_H}$. They may take into account also the effect of conformational transitions between I and S triads, as a consequence of those from prefered helical to prefered zig - zag conformation. Under these premises the interaction parameter between the monotactic polymers A* and C* becomes

$$\chi_{A^*C^*} = \chi_{A_IC_I}\, f_{A_I}f_{C_I} + \chi_{A_SC_S}\, f_{A_S}f_{C_S} + \chi_{A_IC_S}(f_{A_I}f_{C_S} + f_{A_S}f_{C_I}) + \chi_{A_IC_H}(f_{A_I}f_{C_H}$$
$$+ f_{A_H}f_{C_I} + f_{A_H}f_{C_H}/2) + \chi_{A_SC_H}(f_{A_S}f_{C_H} + f_{A_H}f_{C_S} + f_{A_H}f_{C_H}/2) - \chi_{A_IA_S}\, f_{A_I}f_{A_S}$$
$$- \chi_{A_IA_H}\, f_{A_I}f_{A_H} - \chi_{A_SA_H}\, f_{A_S}f_{A_H} - \chi_{C_IC_S}\, f_{C_I}f_{C_S} - \chi_{C_IC_H}\, f_{C_I}f_{C_H} - \chi_{C_SC_H}\, f_{C_S}f_{C_H} \qquad (12)$$

The enthalpies of mixing for the A*C* and the A*A*' blends are

$$\Delta H^m_{A^*C^*} = \chi_{A^*C^*}\,\phi_A\,\phi_C \qquad \Delta H^m_{A^*A^{*\prime}} = \chi_{A^*A^{*\prime}}\,\phi_A\,\phi_{A'} \quad . \qquad (13)$$

The experimental determination of the intermolecular and of the intramolecular interaction parameters may be performed with blends of the A*A*', the C*C*' and the A*C* type, with variable tacticity. Simplifications may be introduced with respect to the effect of H triads. Their intermolecular effect may be taken into account by delegating their action half to the I and half to the S triads. The analysis of the miscibility behaviour of tactic blends would be weakened, however, by this attempt.

Polymer blends of theoretical and practical interest frequently are comprised of copolymers, which contain sequences differing with respect to chemistry and / or to configuration. Their physical and applicational properties are strongly governed by sequence distributions within the macromolecular chains. The proposed evaluation may help to develop a better understanding of the molecular basis of polymer compatibility.

In a subsequent paper miscibility of copolymer blends of the types <u>A*B*</u> ; A*' , <u>A*B*</u> ; C* , <u>A*B*</u> ; <u>A*'D*</u> , and <u>A*B*</u> ; <u>C*D*</u> will be discussed, in which overlapping effects of chemical and configurational sequence distribution may be seen.

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