

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

### 2. Homo- and Copolymer Blends

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#### Summary

A simple model is proposed to describe the miscibility of blends, which contain homo- and/or copolymers with tactic subunits. The directional-specific intermolecular interactions are assumed to be mediated by interactions caused by repulsive type intramolecular tacticity as well as chemical intersteps. Syndiotactic homopolymers are chosen as the reference state, for tactic as well as for mixed triads. The approximations developed in this paper include triad as well as diad treatment with respect to tacticity. Chemical intersteps are taken into account on a diad basis. Additive overlapping of tactic and chemical effects is assumed for mixed hetero- and isotactic triads.

Complex copolymer blends, including multi-component copolymers, are treatable in this way. The modification of tactic and chemical sequences in polymer blends with the aim of developing compatible, as well as phase separated, systems may be facilitated.

#### Introduction

As the rule, homopolymers with differing chemistry of their subunits are almost always immiscible. This is due to the fact that the increase of entropy is negligible for high molecular weight compounds, with the result that only exothermal systems are compatible in a thermodynamic sense. Until recently it was assumed that the unique source of such exothermal contributions are directional-specific interactions as found between polar groups. The reason of the common incompatibility has been believed to be caused by the dominant counteraction by dispersive type endothermic interactions. It has been observed however, that the miscibility of copolymers is much better, in many cases, than that of the corresponding homopolymers. Miscibility has been observed with copolymers even in cases, where the corresponding homopolymers are immiscible. KAMBOUR et al. <sup>1)</sup>, PAUL and BARLOW <sup>2)</sup>, TEN BRINKE et al. <sup>3)</sup>, BALAZS et al. <sup>4) 5)</sup>, and HOWE and COLEMAN <sup>6)</sup> have tried to interpret this phenomenon. The miscibility window in a polymer blend containing copolymers has been explained by PAUL and BARLOW by anticipating that intramolecular interactions within the copolymer chains may create a contribution to the interaction of unlike macromolecules, in addition to the specific intermolecular interaction.

Mixtures of low molecular weight compounds may be regarded as explanatory models. The mixture may be an ideal one, with no energetic interaction between the components, which are distributed at random in the system. There may be, on the other hand, a preference for dominant interaction between unlike molecules, when, for instance, one partner has donor and the other acceptor quality. Thus, unlike pair contacts dominate, resulting in an exothermic heat of mixing. Finally, the unlike contacts may be unfavourable, and the heat of mixing may be endothermic. Clusters of identical molecules may then be built up.

An example of the latter situation, which is relevant with respect to polymer solubility, is the solvent mixture of acetone and cyclohexane. Acetone exhibits a strong

clustering tendency and is a non-solvent for polystyrene, because of the dominant self-interaction. It has been found quantitatively - by light scattering and by swelling measurements - 7) 8) that with increasing addition of cyclohexane the self-association of acetone is diminished, and "single" acetone molecules become a thermodynamically excellent solvent for the polystyrene.

During a copolymerization the situation is more complex: The probability of a propagation step depends not only on the type of the monomers engaged, but also on the active end of the growing chain. Consequently, the probabilities of self-propagation or of chemical intersteps are different when compared with the affinity of the respective monomers in the non-activated state. Thus, the sequence length distribution is depending on the type of polyreaction. It is well known, for instance, that in anionic polymerizations the polarity of the solvent has a profound influence. Consequently, the copolymer chain is not in equilibrium with respect to repulsion or attraction between its subunits. This effect necessarily is temperature dependent.

A similar situation is given when homopolymerizing asymmetrically substituted vinyl monomers. It is well known that, during free-radical polymerization, the syndiotactic addition step usually has lower activation energy than the isotactic one. Consequently, the degree of syndiotacticity is increasing with decreasing polymerization temperature. Necessarily, again, the polymers will exhibit temperature-variable repulsions or attractions within the chain backbones.

In order to understand the influence of repulsive or attractive interaction between the subunits within a copolymer or within a tactic homopolymer on the compatibility with another component, let us discuss first a blend of a copolymer with a homopolymer. When the copolymer subunits repel each other, the tendency for a self-association of segments of the copolymer will be diminished. The consequence is a relative improvement to the copolymer (AB) - homopolymer (C) interaction. This can be expressed in a favourable contribution to the interaction parameter depending on the copolymer composition. Thus, in a straightforward approach the effective interaction parameter splits up into two types of terms, the positive sign directional-specific intermolecular interactions,  $\chi_{A;C}$  and  $\chi_{B;C}$ , and the negative sign repulsion type intramolecular interaction,  $\chi_{A;B}$ . With  $f_A$ ,  $f_B$  and  $f_C$  the mole fractions of the components, we may write for the interaction parameter

$$\chi_{AB;C} = \chi_{A;C} f_A + \chi_{B;C} f_B - \chi_{A;B} f_A f_B \quad (1)$$

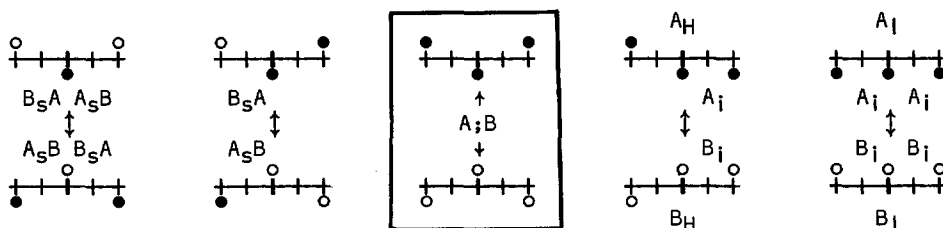
This PAUL-BARLOW approach 2) does not take into account, however, the influence of adjacent groups on the effective intermolecular interaction between two groups. BALAZS et. al 4) 5) have considered those neighbourhood influences in copolymer blends by a triad treatment. It was necessary, however, to introduce severe approximations, because of the large number of possible homo- and heterochain interactions. In our opinion these approximations are partly inconsistent 9).

The influence of tacticity, however, has been treated only in a very recent approach, which takes into account the effect of configurational sequence distributions. This tacticity effect has been realized experimentally in a number of cases, with blends of chemically identical syndiotactic and isotactic homopolymers, respectively. In this recent approach, blends of monotactic homopolymers with components of both identical and different chemistry have been treated. Different directional-specific intermolecular interactions have been attributed to chemically identical groups within isotactic (I), heterotactic (H) and syndiotactic (S) triads. In this way, for blends of chemically identical homopolymers which differ in tacticity, and for blends of two chemically different homopolymers, with optional tacticity, the interaction parameters have been derived by considering heterochain and homochain contacts 9).

For blends of copolymers, which are built up from tactic subunits, this approach appears too complex. In the following a simplified model is proposed, which makes allowances for tacticity as well as for chemical sequences within an unified treatment.

### The Model

In contrast to the model discussed above, the directional-specific intermolecular interaction parameters are assumed to be determined only by the chemical nature of the interacting groups, regardless of their chemical and configurational environment within the respective triads. The next neighbour effects are coordinated with intramolecular repulsion type interaction terms. Syndiotactic homopolymers are chosen as



the reference state, for homo-tactic as well as for mixed triads. Above - for asymmetrically substituted vinyl polymers - the interactions according to this model are shown for triads containing A (●) and B (○) groups, which are chemically different.

All A centered triads exhibit intermolecular directional-specific interaction with the parameter  $\chi_{A;B}$ , irrespective of their next neighbours (see †). Their net interaction is mediated by tacticity and chemistry-induced intramolecular contributions due to their neighbour groups, when they differ from the syndiotactic homo-triad reference state.

In the following, we introduce effective interaction parameters for all inter- as well as intramolecular interactions, which include the accompanying mole fractions of the components. Thus, the contributions only have to be added up in order to obtain the effective interaction parameter of the respective blend. We may explain this for a blend consisting of an optional tacticity copolymer  $A^*B^*$  and a homopolymer  $C^*$ , which is also built up by variable tactic subunits. The star signifies an optional tacticity component. For the directional-specific intermolecular interaction between groups A and C we write

$$\chi_{A\ddagger C} = \chi_{A;C} f_A f_C \quad . \quad (2)$$

With  $C^*$  being a homopolymer,  $f_C$  equals 1.  $\chi_{A;B}$  is the concentration independent interaction parameter, and the sign † indicates an intermolecular contact between unlike types of polymers. Analogously, we write for the AB self-contact directional-specific interaction

$$\chi_{A\ddagger B} = \chi_{A;B} f_A f_B \quad , \quad (3)$$

with †† the sign for directional-specific self-contacts between identical types of macromolecules. It must be kept in mind that both types of interactions, eqn. (2) and (3), are defined to be independent of the chemistry or configuration of the adjacent groups.

In order to consider the influence of these adjacent groups on the overall interaction parameter, we introduce effective chemical interstep (°) and tacticity (\*) interaction parameters,  $\chi_{AB}^\circ$ ,  $\chi_{A^*}$ ,  $\chi_{B^*}$ , and  $\chi_{C^*}$  for the blend  $A^*B^*;C^*$ . Thus, the total interaction parameter is

$$\chi_{A^*B^*;C^*} = \chi_{A\ddagger C} + \chi_{B\ddagger C} - \chi_{A\ddagger B} - \chi_{AB}^\circ - \chi_{A^*} - \chi_{B^*} - \chi_{C^*} \quad . \quad (4)$$

For a blend  $A^*B^*;C^*D^*$ , which consists of two binary copolymers with tactic subunits,  $A^*B^*$  and  $C^*D^*$ , the terms for the unlike molecules intermolecular contacts,  $A\ddagger D$  and  $B\ddagger D$ , as well as  $C\ddagger D$  for the self-contacts, and for mediation due to  $CD^\circ$  intersteps and due to  $D^*$  tacticity must be added

$$\chi_{A^*B^*;C^*D^*} = \quad (5)$$

$$\chi_{A\ddagger C} + \chi_{A\ddagger D} + \chi_{B\ddagger C} + \chi_{B\ddagger D} - \chi_{A\ddagger B} - \chi_{C\ddagger D} - \chi_{AB}^\circ - \chi_{CD}^\circ - \chi_{A^*} - \chi_{B^*} - \chi_{C^*} - \chi_{D^*}$$

Note that two types of AB and CD interactions exist: those by self-contacts within identical polymer chains, and those terms effected by direct neighbour influence.

The meaning of the repulsion type intramolecular tactic and chemical interstep terms must be explained. In the sketch, on the right of the homopolymer S triads, one finds the heterotactic triads (H) first, which are formed by changing one syndiotactic diad (s) to an isotactic (i) one. An interchange of both neighbours from s to i yields the isotactic triads (I). The repulsive or attractive intramolecular interaction within a H triad, relative to the reference S triad, is  $\chi_{A_H;A_S}$  for the A triad, and  $\chi_{B_H;B_S}$  for the B triad. The contributions of the I triads can be taken into account on a triad or on a diad basis. On the diad basis the effect arising from an I triad is assumed to have double the H value,  $2\chi_{A_i;A_S}$ , and  $2\chi_{B_i;B_S}$ , resp. Introducing the index d for diad, and t for triad treatment, we conclude for the interaction of the arbitrary tacticity homopolymer,  $A^*$ , relative to the syndiotactic one,  $A_S$ ,

$$\begin{aligned} \chi_{A^*d} &= \chi_{A_i;A_S} (f_{A_H} + 2f_{A_I}) \\ \chi_{A^*t} &= \chi_{A_H;A_S} f_{A_H} + \chi_{A_I;A_S} f_{A_I} \end{aligned} \quad . \quad (6)$$

The triad approach may be favourable for homopolymers and for copolymers with one predominate component. In the interaction equations we omit the suffixes t and d.

On the left of the homopolymer S triads syndiotactic mixed triads are shown, which are formed by the chemical interchange of one or two neighbours to the central group. Thus, AB diads are formed in both types of triads, the A and the B centered ones. It is proposed that the mediating influence of chemical intersteps is treated on a diad basis, for syndiotactic enchainment only. Since two groups, A and B, are engaged in the interstep, we assume  $A \leftrightarrow B$ , the average between  $A_S$  and  $B_S$ , as the reference state. We write

$$\chi_{AB^*} = \chi_{A_S B; A \leftrightarrow B} f_{AB} \quad . \quad (7)$$

Since both types of intramolecular terms include the triad composition, they give the direct measure for the mediation of the intermolecular terms. We restrict the chemical sequence treatment to diads for the following reasons: Eight different A and B centered triads would have to be considered, two S, four H and two I type. At this time, such triads are quite unanalyzable by spectroscopic methods. Even chemical diad intersteps mostly can not be analyzed with respect to their configuration. From copolymerization data only chemical sequences may be obtained, irrespective of their tacticity

We anticipate, however, that the effect of mixed triads of arbitrary tacticity can be taken into account by an additive overlapping of the effects. The tacticity effect in mixed triads is assumed to be approximated by those of the homopolymers.

On the basis of our model we give further interaction parameters of various blend compositions. For the blend of an optional tacticity homopolymer  $A^*$  with syndiotactic  $A_S$  we write

$$\chi_{A^*;A_S} = - \chi_{A^*} \quad , \quad (8)$$

for a blend of different tacticity chemically identical homopolymers,  $A^*$  and  $A^{*1}$ ,

$$\chi_{A^*;A^{*1}} = - \chi_{A^*} - \chi_{A^{*1}} \quad . \quad (9)$$

The blend of the two homopolymers  $A^*$  and  $C^*$ , which are built up by tactic subunits, has the interaction

$$\chi_{A^*;C^*} = \chi_{A^* \uparrow C} - \chi_{A^*} - \chi_{C^*} \quad , \quad (10)$$

the corresponding blend with the syndiotactic homopolymer  $C_S$

$$\chi_{A^*;C_S} = \chi_{A^* \uparrow C} - \chi_{A^*} \quad . \quad (11)$$

A blend with a non-tactic homopolymer C yields the identical interaction parameter

$$\chi_{A^*;C} = \chi_{A\uparrow C} - \chi_{A^*} \quad . \quad (12)$$

The blend of the copolymer A\*B\* with the homopolymer built up by one of its tactic components, A\*, has the interaction parameter

$$\chi_{A^*B^*;A^*} = \chi_{A'\uparrow B} - \chi_{A\uparrow B} - \chi_{AB^*} - \chi_{A^*} - \chi_{A^*} - \chi_{B^*} \quad , \quad (13)$$

the A\*B\*; A\*B\* blend of two copolymers with different composition (14)

$$\chi_{A^*B^*;A^*B^*} = \chi_{A\uparrow B'} + \chi_{A'\uparrow B} - \chi_{A\uparrow B} - \chi_{A'\uparrow B'} - \chi_{AB^*} - \chi_{A'B^*} - \chi_{A^*} - \chi_{A^*} - \chi_{B^*} - \chi_{B^*}$$

Blends with terpolymer components can also be treated easily. The interaction parameter of the blend A\*B\*C\*; D\*E\*, with tactic subunits exclusively, is

$$\chi_{A^*B^*C^*;D^*E^*} = \chi_{A\uparrow D} + \chi_{A\uparrow E} + \chi_{B\uparrow D} + \chi_{B\uparrow E} + \chi_{C\uparrow D} + \chi_{C\uparrow E} - \chi_{A\uparrow B} - \chi_{B\uparrow C} - \chi_{A\uparrow C} - \chi_{D\uparrow E} - \chi_{AB^*} - \chi_{BC^*} - \chi_{AC^*} - \chi_{DE^*} - \chi_{A^*} - \chi_{B^*} - \chi_{C^*} - \chi_{D^*} - \chi_{E^*} \quad . \quad (15)$$

As an example, the enthalpy of mixing for A\*B\*C\*; D\*E\* is given by

$$\Delta H^m_{A^*B^*C^*;D^*E^*} = RT \chi_{A^*B^*C^*;D^*E^*} \phi_{ABC} \phi_{DE} \quad . \quad (16)$$

The combinatorial part of the free energy of mixing takes into account the influence of the molecular weight on blend miscibility. Again, for the example presented, and degree of polymerization N we find

$$\Delta H^m_{A^*B^*C^*;D^*E^*} + RT [(\phi_{ABC}/N_{ABC}) \ln \phi_{ABC} + (\phi_{DE}/N_{DE}) \ln \phi_{DE}] \quad . \quad (17)$$

The influence of the molecular weight distribution may be taken into account in the combinatorial terms only, when the polydispersity is relatively small. For broader molecular weight distributions the molecular weight dependence of the interaction parameters must also be considered.

## Discussion

With the simple model introduced we have tried to interpret the peculiar mixing behaviour of tactic copolymer blends. It has been assumed that the intermolecular directional-specific interactions and the negative sign competing action of self-contacts of identical type macromolecules are mediated by the influence of adjacent groups, which may be different with respect to constitution and to configuration. Consequently, these three effects may improve the miscibility of blends: self-interaction, and mediation due to chemistry and/or tacticity. The well-known observation that copolymers are oftenly miscible even in cases, where the corresponding homopolymers are incompatible, may be interpreted more precisely in this manner.

Experimental evidence will show how far the simple approach will hold. Two examples may be discussed briefly, where tacticity influences are evident. First, stereo-complexes are well-known in solutions of iso- and syndiotactic poly(methylmethacrylate)s. According to eqn. (8), with the triad treatment of eqn. (6),  $\chi_{A_1;A_2}$  should be positive. That means that the ester groups do not interact favourably in an isotactic position. Thus, attraction between iso- and syndiotactic groups occurs. Second, the fact that the compatibility of atactic polyvinylchloride is strongly dependent on the tacticity of poly(methylmethacrylate) as the second component, may be interpreted again by the mediation of the interaction of the latter component by tacticity.

A remark may be made concerning the fact that polymer blends have a dominant tendency for phase separation at elevated temperature, when compared with polymers

in solution. It must be noted that the experimental interaction parameters for polymer blends are much lower than those of the corresponding solutions of one of the blend components in a solvent whose structure is analogous to that of the second polymer component. It is evident that, from topological reasons, groups within unlike macromolecular chains only can form limited interactions with each other. This has been shown, for example, by FTIR measurements<sup>10)</sup>. Thus, the measured interaction parameters effectively are the product of the contact probability with the "real" interaction parameter. Evidently, with increasing temperature the probability of unlike contacts has a tendency to decrease at the cost of self-contacts of identical chains. Equation of state theories take into account these effects. Their capability to predict the mixing behaviour of polymer blends is limited up to now, however, because the mediating influences due to the configuration and the constitution of adjacent groups have not been taken into account.

The reasons for the choice of the syndiotactic reference state for our model can be discussed briefly. In most of the cases, highly syndiotactic homopolymers are most easily obtained. From blends with chemically identical copolymers with different tacticity the tactic term may be obtained. For blends which contain copolymers, the data for the chemical terms may be obtained, by comparing the interactions of the copolymer blends with those of their respective copolymers. Again, it must be noted that the intramolecular effect due to chemically mixed sequences is related to syndiotactic steps. It is assumed that the tacticity influence within hetero- and syndiotactic mixed triads is taken into account by the intramolecular tacticity parameters of the respective homopolymers. In a special case this can be checked experimentally. KLES-  
PER et al.<sup>11)</sup> have investigated cotactic copolymers, starting with syndiotactic and isotactic poly(methyl methacrylate)s, respectively. By partial saponification and subsequent polymer analogous reaction they obtained cotactic samples. Here, the assumption of additivity of tacticity and chemistry effect can be tested critically.

In principle, another reference state would be applicable. By epimerization polymers could be obtained which are free of positive or negative neighbourhood influences, because they depict thermodynamic equilibrium. This would be valid only, however, at a distinct temperature. Syndiotactic polymers as the reference cancel this problem. Furthermore, they are mostly accessible.

The principal advantage of the proposed approach is given by the fact that even very complex blend systems are treatable in an uncomplicated way. The reduced mediating term gives direct information among its actual influence in a specific blend system. Even ternary copolymers with tactic subunits, copolymers containing macromolecules of differing gross composition and polymolecular systems are analyzable. Head-to-head vinyl polymers and polydiene cis-trans isomerism may also be treated.

The proposed approach may be useful, when searching for thermodynamically compatible polymer blends. Combinations of miscible and immiscible components may be accessible too, in order to obtain two- or multiphase systems of technological interest.

In subsequent publications the reliability of the proposed approach will be checked critically with experimental data, and the temperature dependence of polymer miscibility will be discussed.

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