

MISCIBILITY IN COPOLYMER/HOMOPOLYMER BLENDS

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ABSTRACT

In order to study the miscibility of a copolymer with its corresponding homopolymers, varieties of multicomponent polymers including simple graft, multibranch, diblock, triblock and four-arm block copolymers and so-called ABCPs were synthesized and characterized. The morphologies of the blends comprising the copolymers and the corresponding homopolymers were examined by electron microscopy. It is concluded that besides molecular weight, architecture of a copolymers has apparent effect on the miscibility, i.e. the more complex is molecular architecture, the greater is conformation restriction in microdomain formation and the less is solubility of homopolymer in corresponding domains. In addition, a density gradient model is suggested for describing the segment distribution of the bound and free chains in block-homopolymer systems. Using this model, Helfand's theory is extended to the blends of copolymer and homopolymer predicting the miscibility which is in good agreement with the experimental results.

BACKGROUND

This article presents a brief review of a systematic study on miscibility in blends of homopolymer (Homo) and copolymer (Cop) consisting of long sequences of different components, which has been done in Fudan University since 1983, with emphasis on the architectural effect of copolymer on the miscibility^[1].

With regard to the miscibility between Homo chains (free) and the similar ones in copolymer (bound), it has been realized that they do not solubilize each other unconditionally in spite of their chemical identity because of the entropy loss in solubilization. In 1970's, attention in this research field was mainly paid on the effect of molecular weights (MW) of the component polymers on the miscibility. Based on morphological studies of blends comprising diblock copolymer of styrene and isoprene and homopolymers (PS and PI), Inoue et al.^[2] found that homopolymer chains can be solubilized into the domains of the same-type blocks provided that the MW of the former is the same as or less than that of the latter, while the free chains can not be incorporated into the domains and form their own phase separated from the copolymer if the MW of the Homo is apparently larger than that of the same type blocks (Fig.1). This conclusion was confirmed by some morphological data of diblock Cop/Homo blends reported later. However, Eastmond et al.^[3] have made a different conclusion based on their morphological studies on blends of so-called AB crosslinked copolymers (ABCPs, Fig.2c) and Homo A, i.e. the miscibility of Homo A chains in A domains of ABCP is very limited even they have the same MW . They suggested that multicomponent polymers are normally

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immiscible with homopolymers of the individual components arising from an unfavourable entropy of mixing associated with the conformation restriction of the blocks in formation of their microphase. In searching for the reasons for this discrepancy, in this laboratory, a series of copolymers with different chemical compositions and chain architectures including simple graft Cop^[4], multibranch graft Cop^[5], diblock, triblock, four-arm block Cops^[6] and ABCPs^[7] were synthesized and characterized (Fig.2). Electron microscopy (EM) was used to examine the morphologies of the solvent-casting blends of the individual copolymers and corresponding homopolymers. An argument about the chain-architectural effect of copolymer on the miscibility in

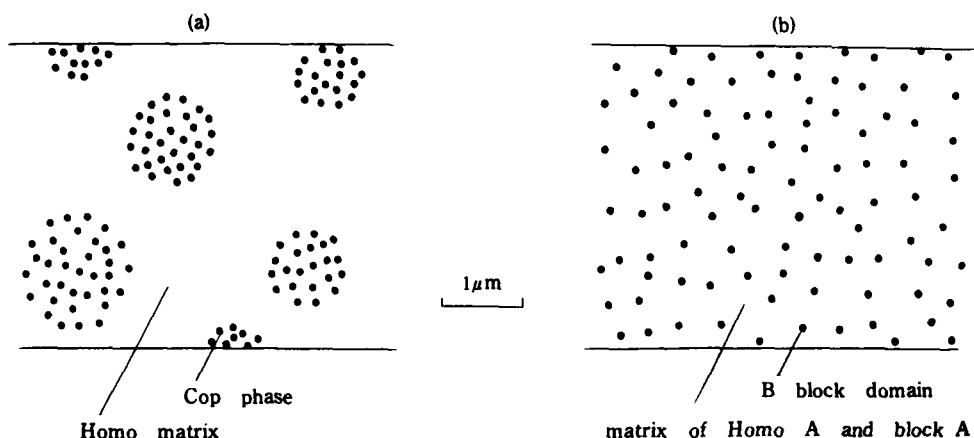


Fig.1 Schematic representation of morphologies in blend of homopolymer A (major component) and block copolymer AB (minor component) with characteristic structure of spherical microdomains (a) Cop and Homo are immiscible showing macroscopic Cop phase with microphase separation dispersed in Homo matrix; (b) Homo A and block A are miscible showing only microdomains of B blocks in A matrix.

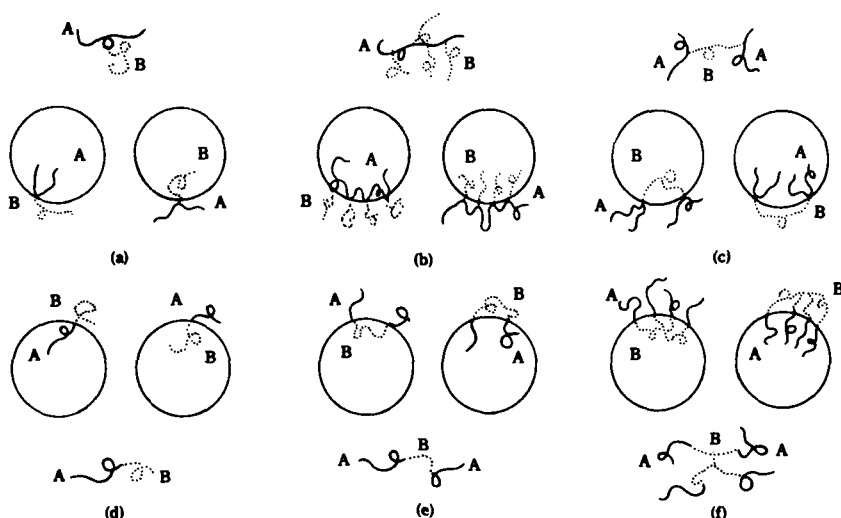


Fig.2 Schematic representation of chain architectures and microphase separation of various copolymers (a) simple graft Cop; (b) multibranch graft Cop; (c) ABCP (AB crosslinked Cop), only the simplest structure is shown; (d) diblock Cop; (e) triblock Cop and (f) four-arm star-type block Cop.

Cop/Homo systems was put forward and confirmed. Meanwhile, efforts were made to explore the nature of the miscibility in Cop/Homo blends through studies of statistical thermodynamics^[8,9]. In our theoretical treatment, a new gradient density model was used resulting in a miscibility prediction generally in agreement with experimental results reported in the literature.

SIMPLE GRAFT COPOLYMER^[4]

Simple graft copolymers (PB-g-PS) were prepared by free-radical polymerization of styrene in the presence of polybutadiene (PB) in a low monomer conversion range. The related characterization data showed that on average each PB backbone had only one PS graft. A series of blends of homo PS and the copolymer, as the major and minor components respectively, with different MW combinations, i.e. different values of the ratio of MW s of the former to the latter (M_H/M_g), were prepared. EM observations of the blends revealed a regular variation in the morphology with the MW ratio. When the MW of Homo is much larger than that of grafts, they are completely immiscible (Fig.3a). Solubilization increases as the MW of Homo becomes closer to that of the grafts (Fig.3b). The Homo can almost be solubilized with PS grafts when the MW of the former becomes less than that of the latter (Fig.3c). This experimental result is generally in accordance with that of Inoue et al. for diblock Cop/Homo blends^[2]. Besides, for the case that the average MW of Homo is larger than that of the grafts but an apparent overlap exists between their MW distributions, the morphology is more complex, i.e. coexistence of immiscibility and miscible trend—swelling of PS region in the Cop-rich phase by Homo PS and the presence of discrete PB microdomains in the PS matrix, is observed (Fig.3b). The inherent polydispersity of the MW s of both graft and free PS chains is supposed to be responsible for the complicated morphology of the blends.

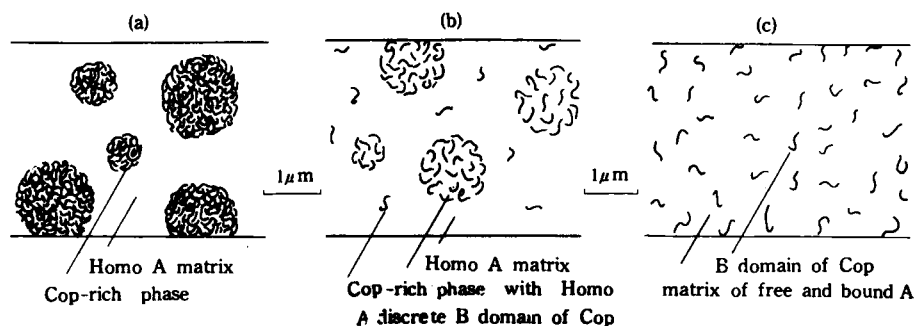


Fig.3 Schematic representation of morphologies in blend of graft copolymer AB (minor component) and homopolymer A (major component), both of which have molecular weight polydispersity (a) Homo and Cop are completely immiscible showing macrophase separation between Cop phase and Homo matrix; (b) Homo and Cop are immiscible but with a certain mixing trend between the Homo and Cop; (c) Homo and Cop are miscible showing only B microdomains in A matrix.

MULTI-BRANCH GRAFT COPOLYMER^[5]

PI-g-PS graft copolymers having polyisoprene (PI) backbone and PS branches were prepared by metallating prepolymer PI and anionically initiating styrene in cyclohexane. The compositions of the Cops and the MW s of PS branches, were adjusted by changing the polymerization conditions.

The solvent-casting blends of the Cops and Homo PI with different MW combinations M_H/M_b (M_b — MW of PI backbone in Cop) were examined by EM. For the case that the MW of Homo PI is equal to that of PI backbone of the Cop, the Homo PI is separated from the Cop phase with the characteristic morphology of the pure Cop which indicates complete immiscibility between the free and bound PI chains. The main morphological feature of the blends, i.e. macrophase separation between the Cop and Homo does not change when M_H/M_b decreases. Even for the extreme case that the average MW of Homo PI (6,500) is less than that of PI segments (9300) between neighbouring junction points in the backbones, the miscibility of the low MW Homo PI in PI microdomains is still limited. Therefore, it concludes that the miscibility in multibranch graft Cop/Homo blends is much less than that in the simple graft Cop/Homo blends.

For the multibranch graft copolymer, there are several junction points along each PI backbone and they have to be located at the interface area between the phases. Thus, this brings about more chain conformation restriction in PI domain formation (Fig.2b). Apparently, this restriction is larger than that in the simple graft copolymers. This argument implies that the chain architecture complexity of the multibranch graft copolymer might be responsible for the limited miscibility in the Cop/Homo systems.

ABCPs^[7]

With regard to Eastmond's results on ABCP/Homo A system, a question has arisen about the estimation of the effective length of A-chain in ABCP. Since A-B junctions must be located in the area of the interface and each junction point divides side chain A into two segments (Fig. 2c), the effective chain length of A, which determines its domain size and the miscibility with Homo A, should be shorter than that of prepolymer A, which was used to make the blends as the Homo component. In order to explore the miscibility in ABCP/Homo blends without this ambiguity, a series of blends of ABCP and Homo B rather than Homo A were studied. The ABCPs used in this study were prepared by photo-initiating styrene monomer (B) at some active sites of CCl_3 in the chains of prepolymer polycarbonate (A). All the blends of the ABCPs and Homo PS covering a broad range of MW combination characterized by the ratio of MW of Homo PS to that of the PS crosslinks in the Cop (M_H/M_g from 0.2 to 20) present a common character—macrophase separation between the ABCP and PS Homo. As far as the chain architecture is concerned, it is noticed that the structure of ABCPs shown in Fig.2c is only the major and simplest one among the species in ABCP. Actually it has a distribution of molecular structure of different complexity. In comparison with the cases of the simple graft Cop and diblock Cop, ABCP obviously has more complicated chain architecture which may be responsible for its low miscibility with the homopolymers.

BLOCK COPOLYMERS^[6]

As block copolymers prepared living-anionically possess MW monodispersity, well-defined and desired structures, they are suitable for examining the chain-architectural effect on the miscibility with the relevant homopolymers. Thus, diblock, triblock and four-arm star block copolymers of styrene and isoprene were prepared and characterized. In the triblock and star block Cop, PI is the central block. EM observations of the blends of the Cops and relevant Homos presented regularity in the miscibility variation of the blends with the molecular structures of the Cops. For the blends of diblock Cop/Homo PI, the same conclusion as that given by Inoue et al.^[12]

has been made. However, the blends of triblock Cop/Homo PI show much less miscibility, i.e. macrophase separation occurs when the MW of Homo PI is only about one half of the MW of the central block PI in the copolymers. Among the blends consisting of four-arm star block Cop covering a broad range of MW combinations (M_H/M_b from 0.07 to 1.4, M_b-MW of PI blocks) apparent solubilization of Homo PI in the PI block domains without macrophase separation only occurs in the blend in which M_H/M_b is 0.07 while clear macrophase separation happens for the blend with M_H/M_b 0.23. These results clearly show that the miscibility varies in the sequence of diblock > triblock > Four-arm star copolymers. Apparently, this sequence is just in the opposite direction to the variation of the architectural complexity of the copolymers.

CHAIN-ARCHITECTURAL EFFECT^[10]

Our experimental studies on the morphologies of Cop/Homo blends mentioned above lead to and confirm that the miscibility between the free and bound chains in Cop/Homo blends depends on the chain-architecture of the Cop, i.e. the more complex is molecular architecture, the less is miscibility of Homo in corresponding domains of block Cop. Simple consideration of statistical thermodynamics gives clear explanation of the effect. In the process of solubilization between Homo and Cop, the combinatorial entropy, which is always positive, is the main driving force and the enthalpy of mixing for the free and bound chains is negligible. Thus the only unfavourable factor for solubilization is the entropy loss of the bound and free chains in the process. For simplicity, we discuss the cases of block Cops. As shown in Fig.2d for diblock Cop, any block chains in the domains have a junction point in the interface region while the other end is free. The thermodynamic requirement of uniform density in the domains can be satisfied if the chains assume some unfavourable conformations that entail entropy loss. In the case of triblock Cop (Fig.3e), each central block has two junction points in the interface region, which results in more conformation restriction and more entropy loss because of the requirement of uniform segment density. As for the central blocks of four-arm star block Cop (Fig.2f), besides the restriction of keeping the A-B junction points in the interface region, the common junction for the four central blocks results in a complicated structure that entails even more entropy loss for keeping uniform density in the domains. The essence of the conditional solubilization of Homo and like chains in Cop is associated with the unfavourable environment in the domains of corresponding blocks, i.e. the solubilized Homo chains have to assume unfavourable conformations that entail more entropy loss. Qualitatively, it appears that this extra entropy loss is significant if the blocks in the domains have more conformation restriction. Therefore, a fair inference from this idea is that the complexity of chain architecture of Cop leads to less miscibility of it with Homos. However, since the limitation for the miscibility is caused by the conformation restriction of blocks in copolymer, for the case that Homo is the same chain as the blocks with less conformation restriction in the domain formation, for example, the side blocks forming continuous phase in four-arm Cop, there would not be apparent architectural effect.

STATISTICAL THERMODYNAMICS^[8,9]

It is noticed that Meier's statistical theory^[11], which explores the essence of the conditional miscibility in Cop/Homo blend, i.e. the entropy loss of the free and bound chains in solubilization, predicts low miscibility, about one order of magnitude less than that found experimentally. In the

theory, Meier assumed that in the whole block domains where the Homo is solubilized the segment densities of both the free and bound chains are constant. This assumption can be realized only if the bound chains adopt some very improbable conformations for filling the domain centres that entail high entropy loss and then lead to low miscibility. Instead, in our statistical study, a density gradient model is proposed—maintaining a constant total reduced density of the segments in the whole domains solubilized with Homo chains, the blocks form a distribution of segment density decreasing from the boundary to the centre of the domains while the segment density of Homo decreases from the centre to the interface of the domains. Based on this model and Helfand's^[12] statistical procedure dealing with microphase separation of block Cop, we calculated the miscibility in Cop/Homo systems for both cases of Cop having characteristic lamellar^[8] and spherical^[9] morphologies. The predicted miscibility and its dependence on the MW ratio of Homo to block is in general in good agreement with the main known experimental results.

Keywords:

Polymer blend; Morphology; Miscibility; Chain-architectural effect

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