Molecular Design of Multicomponent Polymer Systems. XII. Direct Observation of The Location of a Block Copolymer in Low-Density Polyethylene – Polystyrene Blends

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INTRODUCTION

The high surface activity of poly(hydrogenated butadiene-*b*-styrene) copolymers (HPB-*b*-PS) in the melt-blended low-density polyethylene/polystyrene (LDPE/PS) pair has been previously demonstrated.[1-3] As assessed by scanning electron microscopy, the addition of moderate amounts of HPB-*b*-PS copolymers triggers a finer and more homogeneous dispersion of LDPE and PS phases, and prevents them from segregating upon further thermal processing, i.e., compression and even injection molding. The examination of the polyblend morphology thus supports a significant decrease in the interfacial tension, whereas the substantial improvement in the mechanical properties of the modified blends agrees with a better interfacial adhesion.

In order to fully understand the role played by the block copolymer, our present knowledge must be complemented by the specific investigation of the interfacial region, and more precisely by the actual distribution of the copolymer between the interface and the pure phases. With this aim in view, a HPB-*b*-PS copolymer has been modified by the insertion of a short central polyisoprene (PIP) block. The selective staining of PIP provides an efficient means of locating the block copolymer in the modified LDPE/PS blends by transmission electron microscopy.[4] Polystyrene/poly(methyl methacrylate) (PS/PMMA) blends modified by a PS-*b*-PIP-*b*-PMMA copolymer have already been investigated through the same experimental approach.[5] In that case, the blends were prepared by solvent casting. To our best knowledge, a direct observation of blends prepared in the melt state has not yet been reported. This article aims at filling this gap.

EXPERIMENTAL

The HPB-*b* PIP-*b*-PS copolymer ($\overline{M}_n$ 65,000-15,000-50,000) was prepared by a classical three-step anionic polymerization of styrene, isoprene, and butadiene, respectively. The block copolymerization proceeded in toluene, using *s*. Bu-Li as initiator. Hydrogenation of the PB block was performed according to Falk's method,[6] under conditions which left the central PIP block essentially unmodified. 10 wt % of the block terpolymer were added into binary blends of a low-density polyethylene [Alkathene X DG 33 ($\overline{M}_n$ = 40, 000) from ICI] and a general purpose PS [polystyrol 158 K ($\overline{M}_n 10^5$) from BASF]. Blends containing 20 and 80 wt % LDPE, respectively, were prepared on a laboratory two-roll mill at 200°C for 5 min. The copolymer was milled with the minor component before the major one was added. The blends were then compression molded at 200°C for 5 min into sheets from which thin sections were microtomed.

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RESULTS AND DISCUSSION

Figure 1 reports transmission electron micrographs of LDPE/PS blends modified by the HPB-*b*-PIP-*b*-PS copolymer containing an OsO_4-stained central block. It is obvious that the block copolymer forms a continuous layer (dark zones) around the dispersed particles of either PS [Fig. l(a)] or PE [Fig. 1(b)]. Its thickness is rather regular, and is in the mean range of about 100 Å. This observation has to be considered while keeping in mind that the molecular weight of the stained block is 15,000. From the values proposed for the $r_o/M^{1/2}$ ratio of 100% *cis* (810×10^{-4}nm) and 100% *trans* (970×10^{-4}nm) polyisoprene,[7] the unperturbed end-to-end chain length r_o is in the range of 100–120 Å for a PIP chain of 15,000 molecular weight M. This order of magnitude is thus consistent with the thickness of the layer that the PIP central block forms around the dispersed LDPE or PS particles.

Furthermore, a more diffuse dark area seems to extend toward PE phases, whereas a part of the copolymer is dispersed in the LDPE phases to the exclusion of the PS ones, whatever the blend composition. The question is to know whether the dispersions observed into LDPE are of pure block copolymer or not. They could indeed contain a small part of PS, just as dispersed rubber particles with small PS inclusions are observed in high-impact polystyrene.[8]

It is worth noting that the block copolymer completely covers the interface, in sharp contrast to the situation reported for the solvent-cast ternary blends of PS (25 wt %), PMMA (50 wt %), and OsO_4-stained PS-*b*-PIP-*b*-PMMA terpolymer (25 wt %). In that case, although the block copolymer is also located at the PS/PMMA interface, the shell it forms around the dispersed PS particles is mostly discontinous. Among other parameters, blending conditions are likely to play a significant role in the modification of polyblends by such a polymeric emulsifier.

A part of the HPB-*b*-PIP-*b*-PS copolymer added into the LDPE/PS blends is thus dispersed in the PE phase. This means that the copolymer molecules are in an apparent equilibrium between their own domains in LDPE (200–300 Å in size) and the blend interface. It is noteworthy indeed that the copolymer inclusion in the LDPE phase is independent of blending conditions. This situation is observed even though the copolymer is mixed with PS before the addition of LDPE. It is also meaningful that the block copolymer is much more easily dispersed into LDPE than into PS. The ternary blends appear therefore as a micro-three-phase system similar to an oil-in-water emulsion with the emulsifier molecules at the oil–water interface as well as in micelles dispersed in the water phase. Quite similarly, block copolymers containing highly immiscible components tend to form stable microdomains, and the driving force to domain formation competes with the propensity of the copolymer to disperse at the blend interface. Heikens et al. forecast such a situation from the modulus of LDPE/PS blends modified with HPB-*b*-PS copolymers.[9] It is expected that the block copolymer used in this investigation tends to phase separate, with the formation of a continuous HPB phase accounting for its micellar dispersion in LDPE and not in PS. The morphology of the pure block copolymer has, however, to be characterized in order to support the proposed mechanism of phase segregation.

As the electron micrographs show that the interface should be saturated by the block copolymer, it is interesting to evaluate the surface occupied, on the average, by the copolymer at the interface (a), using the equation derived by Paul:[10]

$$a = 3\phi_A M / RNW$$

ϕ_A is the volume fraction of polymer A dispersed as spherical particles of radius R, N is Avogadro's number, W is the weight percentage of the added block copolymer, and M is its molecular weight. As $M = 1.3 \times 10^5$, $\phi_A = 0.2$, $R = 0.5$ μm (i.e., the approximate average size of the dispersed particles), and $W = 10$ wt %, an interfacial area per copolymer molecule of about 260 Å^2 is calculated. As a part of the 10 wt % added copolymer is not located at the LDPE/PS interface, this means that this interface is still homogeneously covered at an even lower occupation density than estimated above ($a > 260$ Å^2). The calculated value of a is much higher than the possible 50-Å^2 minimum value suggested by Paul for a diblock copolymer completely penetrating the two phases.[10] Nevertheless, an interfacial area of a few hundred Å^2 can be supported by experimental results relative to the structural parameters of mesomorphic structures that poly(styrene-*b*-isoprene) copolymers form in the presence of a selective solvent of PS.[11,12] For instance, a PS-*b*-PIP copolymer with a PIP block of practically the same molecular weight as in this study ($\overline{M}_n$ PIP 17,500, $\overline{M}_n$ PS 23,000) exhibits a lamellar structure in the presence of acetone (up to 40 wt %), a selective solvent of PS.[12] The thickness of the layers formed by the insoluble PIP blocks ranges from about 130 down to 90 Å as the solvent content grows up to 40%. At the same time, the area occupied by the block copolymer at the interface increases from 470 (no solvent) up to 700 Å^2 (40% acetone). The central PIP block of the HPB-*b*-PIP-*b*-PS copolymer is immiscible with the other components of the ternary LDPE/PS/copolymer blend. Furthermore, it is atttached to a PS block which is diluted with a selective solvent, i.e., the homopolystyrene. As a first approximation, the PIP block is in a situation comparable to that observed in the mesomorphic structure analyzed by Mayer.[12] Of course, the block copolymer content is much smaller (10%) in the present study, and the an-

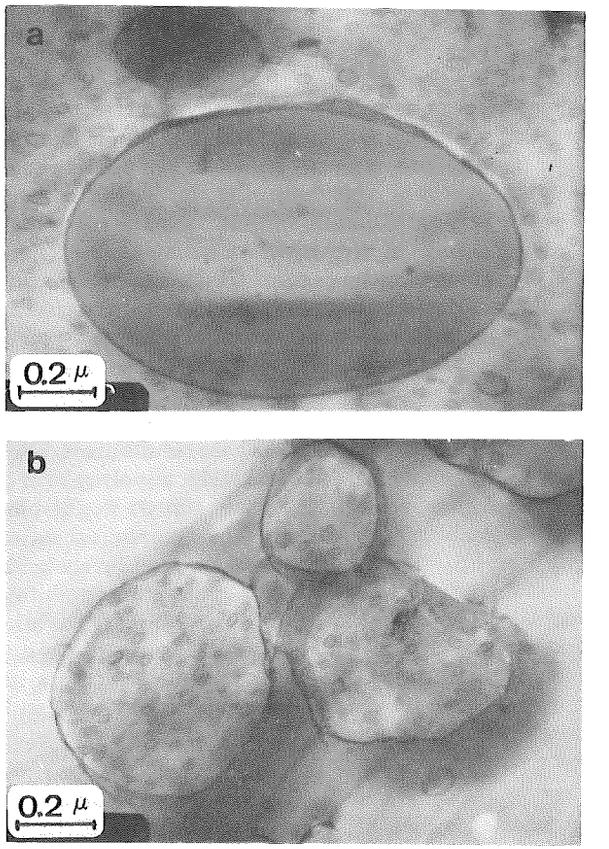

Fig. 1. Transmission electron micrographs of LDPE/PS blends with 10 wt % HPB-*b*-PIP-*b*-PS copolymer: (a) 80 wt % LDPE, 20 wt % PS; (b) 20 wt % LDPE and 80 wt % PS.

choring of the second PIP chain end to a HPB block is expected to modify, and probably to decrease, the area that PIP occupies at the interface. By analogy with well-defined and carefully characterized heterophase systems, it is thus possible to account for the accommodation of PIP into the investigated ternary blends, and to foresee an important penetration and entanglement of the HPB and PS blocks within the corresponding homopolymers (i.e., a situation comparable to that of the PIP block of PIP-*b*-PS into acetone). This feature is also supported by the physico-mechanical properties of LDPE/PS blends, in particular the molecular weight dependence of phase adhesion and the very high elongation at break, in the presence of a tapered HPB-*b*-PS,[3] for which the present triblock is a good model.

A more systematic and comparative study would be helpful to establish the smallest amount of copolymer necessary to saturate the interfacial region in relation to the molecular features of the additive. This point is of great significance as previous experiments have shown that 2 wt % of carefully tailored HPB-*b*-PS copolymers were sufficient to reach asymptotically the optimum improvement in the physico-mechanical properties of LDPE/PS blends.[13] These results are again in disagreement with those recorded with the PS-*b*-PIP-*b*-PMMA copolymer in the PS/PMMA blends.[5] In that case, even when used at a rate of 25 wt %, the block copolymer is essentially located at the blend interface in a discontinuous manner. Furthermore, the morphology of the PS/PMMA blends is unchanged by the addition of 2 wt % copolymer; at least 5 wt % of the additive is required, to maintain homogeneous dispersions. Accordingly, it would also be of interest to study the micellar dispersion of block copolymers with respect to their chemical composition, molecular characteristics, and blending conditions. Whatever the issue of future investigations on these challenging questions, the original observations reported in this paper demonstrate that melt blending is a very efficient technique to disperse a polymeric emulsifier at the interface of hydrocarbonated polyblends.

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On the Isomorphism of Ethylene/α-Olefin Copolymers

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INTRODUCTION

The crystallization behavior of random copolymers has been the focus of a good deal of investigations on the phenomenon of isomorphism, i.e., the inclusion of comonomer units within the crystal lattice of the prevalent species. In this connection, in studies concerned with ethylene/α-olefin copolymers, there has been a great deal of disagreement about the different types of co-units that may or may not be incorporated within the polyethylene (PE) crystal lattice and also about the way the crystallizable co-units can fit in the lattice.[1-19] Nonetheless, the general trend emerging from these works is that the rate of inclusion of the olefinic co-units depends mainly on the size of the side group: the bulkier the side group, the weaker its capability of accomodation within the crystal lattice.

The purpose of the present paper is to contribute to the understanding of the phenomenon that rules the accomodation or rejection of the side groups.

THE INTERSTITIAL MODEL OF ACCOMODATION

First and foremost, it must be emphasized that any kind of branching on a PE chain is likely to interrupt, or at least disturb, the crystallization process because the most probable conformation of the chain next to the branch is *gauche* instead of *trans*, as required for the crystallization of PE chains in the orthorhombic stable form. However, conformational chain defects may be introduced within the PE crystal lattice as point defects in the form of kinks or jogs.[20,21] The presence of *gauche* conformations in such defects involves a distortion of the chain with respect to its main axis and a local displacement of the methylene units from their normal crystallographic positions. In the case of short displacements, the chain is able to get back to the right location owing to a slight bending on both sides of the defect, so that the lattice distortion falls off gradually with distance. For large displacements, the chain may take the place of a neighboring chain. In this latter case, the kink is called a jog.

The most abundant conformational chain defect in a PE crystal is the $2g1$ kink characterized by a gtg^- conformation sequence of three C-C bonds, where t is a *trans* conformation between two *gauche* conformations g and g^- of opposite signs. A $2g1$ kink is sketched in Figure 1, according to Scherr et al.[20] It can be seen in this figure that the defective chain is inclined with respect to the surrouding chains having all *trans* conformations and that the latter are shifted from their original positions so that the lattice becomes slightly expanded around the defect.

Starting from the concept of kinks conformers to account for the defective crystalline state of polymers, Baltà-Calleja et al.[16,17] have proposed an attractive model for the incorporation of structural chain defects within the crystal lattice of PE at interstitial positions that relies on the formation of $2g1$ kinks that expand the lattice. Unfortunately, this model takes no account of the nature of the structural defect, namely chain ends, unsaturations, long branches, and different types of short branches.

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