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Morphology and thermal analysis of poly(ethylene-b-vinylacetate) copolymers

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Summary

Studies of crystallization kinetics and morphological analysis on three samples of poly(ethylene-b-vinylacetate) multiblock copolymers have been performed. The copolymers contain 28% by weight of vinylacetate and their macromolecules are builted up by different numbers of blocks, whose lengths are constant in all cases. An original method of staining puts into evidence the segregation of the polyethylenic blocks in crystalline domains, whose dimensions are less than 50 Å, in good agreement with the molecular characteristics. A structural model, involving fringed micellae for the rigid segments, is suggested and supported by values of the Avrami index, less than 2. The crystallization rates are also discussed as functions of the molecular weights of the samples.

Introduction

The foundamental papers on poly(ethylene-b-vinylacetate) multiblock copolymers concern molecular structure and solution physical properties relationships (1-4);many investigations have shown the possibility to get blends with several polymers, mainly poly(vinylchloride) (5-13) and polyamide (14-15). Less attention has been devoted to the morphology in the solid state of the pure copolymer, which this short paper deals with.

Materials

Three samples of poly (ethylene-b-vinylacetate) multiblock copolymers, in the following indicated with the commercial label of EVA 25/28, EVA 7/28 and EVA 3/28, were used in our studies. They correspond to the general formula $(A_nB_m)_z$; the ethylenic

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repeating units A generate crystallizable blocks, which are connected by soft segments of vinylacetate, and supply physical crosslinks, so that a thermoelastic behaviour can be observed.

Our samples contain the same amount of vinylacetate (28% by weight), but their molecular weights scatter over a large range of values, as indicated by the first figure of the label, which refers to the melt index. Since the copolymerization reaction leads to sequences whose block lengt depends only on the composition, it must be inferred that, in our case, the macromolecules are built up by different numbers of similar blocks, i.e. z changes, n and m remaining constant, according to Salyer and Kenyon (1),the most probable length of the ethylenic blocks is about 20 repeating units, the maximum reaching 145.

Techniques and Measurements

Morphological observations were performed by scanning and transmission electron microscopy.

For TEM analysis a Siemens Elmiscope 102 apparatus was used. Thin sections (600-1000 Å) were cut with a diamond knife from embedded specimens, using a Reichert OmU2 ultramicrotome, equipped with the Shandon FC 150 device to freeze specimen and blade; the most suitable temperatures were found to be -110°C and -60°C , respectively.

The copolymer microstructure can be shown off only by staining. Kato's procedure is not applicable to EVA because the copolymer is not susceptible to OsO_4 (16). In our experience phosphotungstic acid proved itself to be the most efficient agent; the chemical treatment consists of a partial hydrolysis of the polyvinylacetate blocks with a 10% by weight solution of NaOH in water (1 hr) followed by 1h of wetting with a standard solution of acid. Our technique seems to be more practical and efficacious than the method suggested by Matsuo et al. (6), since the whole treatment can be carried out directly on sections and it is able to put into evidence the finest morphology of the copolymer.

Scanning microscopy was performed with a Cambridge Stereoscan 250 MK2 apparatus on fracture surfaces, obtained at the liquid nitrogen temperature.

Thermal scanning and isothermal crystallization were followed with a Perkin Elmer DSC 2 calorimeter, equipped with the mod.3600 Data Station. Heating rate of 20 K/min and cooling rate of 10 K/min were used; the isothermal crystallizations were carried out by melting the copolymer at 147°C for 5 mins and rapidly cooling the specimen at the selected temperature.

Results and Discussion

Data of rate constant K and Avrami index n at several temperatures , elaborated according to the Avrami equation, are collected in Table 1.

TABLE 1
Kinetic data of isothermal crystallization of EVA copolymer.

T,°C	EVA 3/28		EVA 7/28		EVA 25/28	
	n	K,min^{-n}	n	K,min^{-n}	n	K,min^{-n}
61	-	-	-	-	1.6	0.10
63	-	-	-	-	1.5	0.05
65	-	-	1.3	0.40	-	-
67	1.65	0.20	-	-	-	-
69	1.8	0.09	1.6	0.12	-	-
71	1.7	0.05	-	-	-	-

As for as the values of n, it must be underlined that they are always less than 2. In addition both to the macromolecular structure, where hard and soft blocks alternate each other, and the peculiar block lengths, this result points toward the conclusion that the crystalline domains correspond to the fringed micellae rather than to the folded lamellae model. It means (figure 1) that the crystalline regions originate from the aggregation of polyethylene segments mainly belonging to different chains, each macromolecule crossing several hard domains. It is well known that similar structures have been previously proposed for other semicrystalline multiblock copolymers, such as poly(etherester)s (17), and are the fundamentals for the thermoelastic properties of materials.

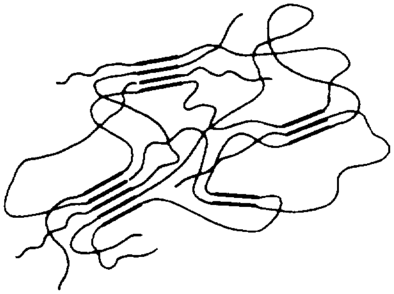

Figure 1. Two-phase structure of EVA copolymer.

The deduction fits the morphological observations. SEM does not produce any evidence of definite morphology and rough fracture surfaces are generally observed (figure 2). However, the TEM analysis leads to the conclusion that the polyethylenic blocks segregate in crystalline domains whose dimension is less than 50 Å (figure 3). The microstructure does not change with the molecular weight of the sample.

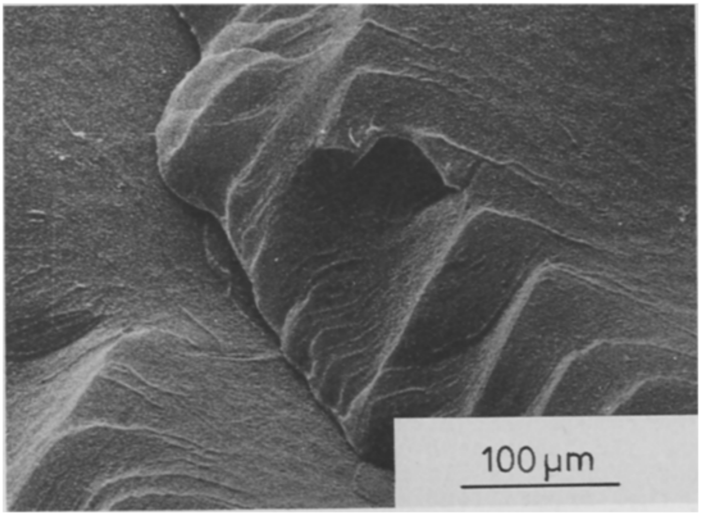

Figure 2. Scanning electron micrograph of a fracture surface of EVA 7/28.

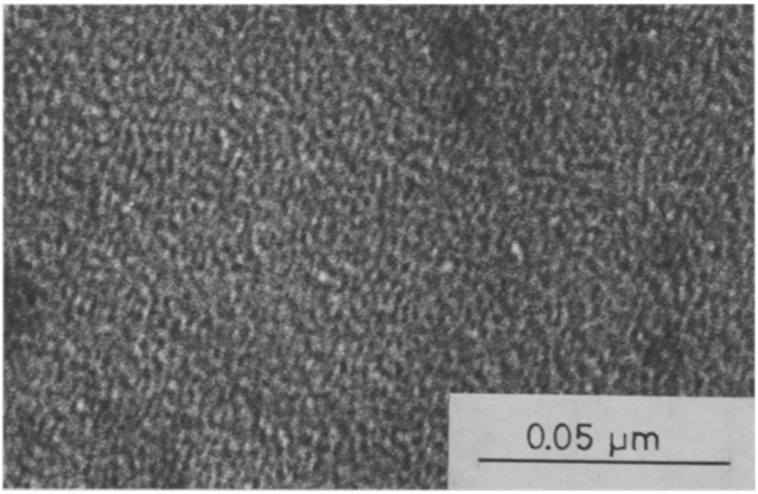

Figure 3. Transmission electron micrograph of a thin section of EVA 3/28.

This is in good agreement with the structure of the multiblock macromolecules previously discussed. Making reference to the general formula, the block lengths (i.e. the values of n and m) depend only on the relative amounts of A and B and different chain dimensions originate from dissimilar values of z. Therefore no difference between the crystal sizes of our three samples has to be expected. On the other side the crystal thickness of about 50 Å corresponds to the most probable length of the polyethylenic blocks (≈ 20 ethylenic sequences) indicated by Salyer and Kenyon (1).

As for as the crystallization rate constants, they decrease with temperature (figura 4) being in the region where the supercooling is rather small.

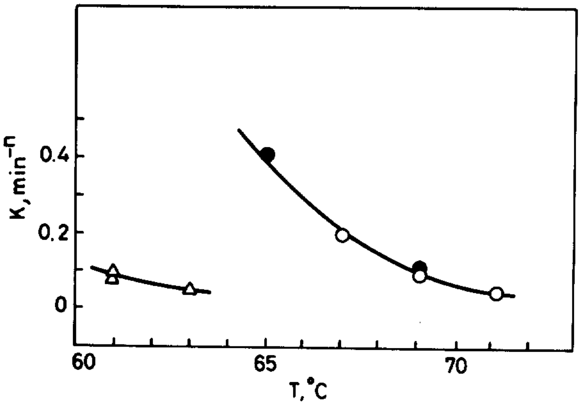

Figure 4. Thermal dependence of the crystallization rate constant for samples of EVA with different chain lenght. Δ , EVA 25/28; ● , EVA 7/28; ○ , EVA 3/28.

According to the copolymer structure and the morphological observations, we would expect small differences, if any in the melting and crystallization behaviour of the three samples. This actually occurs for EVA 3/28 and EVA 7/28. EVA 25/28 exhibites slower crystallization rates and the phase transition can be followed with accuracy only below 63°C.

It is not possible to give definite figures of the thermodynamic melting temperatures since the melting curves (figure 5) are very broad and complicated, no matter what thermal history has been followed to prepare the specimen. However the EVA 25/28 $T°_m$ should be largely less than in the other two cases, following the increased number of chain ends which supply higher mobility to the amorphous regions.

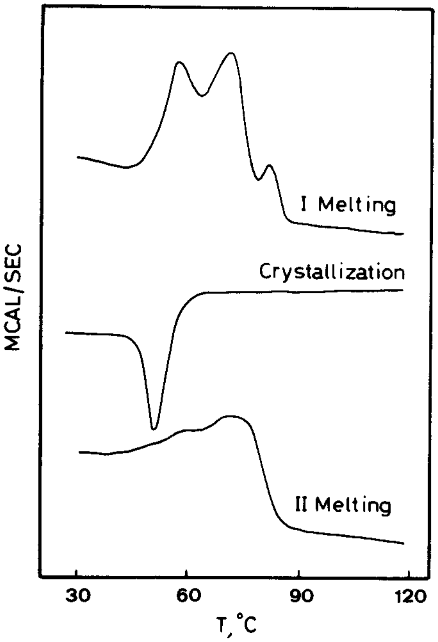

Figure 5. Melting and crystallization behaviour of EVA 7/28 by thermal scanning.

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