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The supermolecular structure of ethylene-vinyl acetate copolymers

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Summary

The supermolecular structures, as measured by small-angle light scattering, were determined as a function of branching content and quenching temperature for a series of ethylene-vinyl acetate copolymers. The morphological pattern that evolved was similar to that of random ethylene-1-alkene copolymers and long-chain branched polyethylenes. The structure of the lamellar crystallites determines whether spherulites develop and how well they are organized.

Introduction

Spherulitic type supermolecular structures are ubiquitous to polymer crystallization. However, spherulite formation is not a universal mode of polymer crystallization. Its development depends on the crystallization temperatures(1,2), molecular weight(1,2), distribution(3,4), long chain branching(1,5-7), and comonomer concentration(2,8). The chemical nature of the co-unit also plays a decisive role in determining whether spherulitic structures form and organize(8). With the influence of molecular constitution, it is of interest to examine the role of other types of comonomers, particularly polar ones. We have, thus studied superstructure formation in a set of ethylene-vinyl acetate copolymers of similar molecular weight, but varying comonomer content.

Experimental

The ethylene-vinyl acetate copolymers used were obtained from commercial sources. They were prepared by conventional, high pressure, free-radical polymerization. Thus, in addition to comonomer, long chain and short chain alkyl branches are incorporated in the chain. The molecular characteristics of these copolymers are given in Table I. The molecular weights were obtained by conventional GPC, using differential refractive index. The chain microstructure was determined by ^{13}C NMR(9,10). The mole fraction of acetate and long chain alkyl branch points are given in the last two columns of the Table.

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Table I. Molecular Characteristics of Ethylene-Vinyl Acetate Copolymers

Sample Designation	$M_w \times 10^{-3}$	M_w/M_n	Mole percent acetate branches	Mole percent total branches
EVA 2	128	5.1	0.3	1.7
EVA 4.8	130	5.4	0.9	2.3
EVA 9	144	7.2	1.6	2.9
EVA 18	103	4.0	4.7	5.1
EVA 28	88	3.6	5.7	6.1
EVA 40	87	3.2	8.8	9.7

The specimens studied were compression molded in a Carver press at about 150°C and then quickly transferred to thermostatic baths set at one of four temperatures, -78°C, 0°C, 50°C, and 100°C. They were crystallized at these temperatures for ca. 5 minutes and then allowed to reach room temperature. The bath temperatures do not correspond to the actual crystallization temperatures since the major part of the crystallization undoubtedly occurred during the cooling. Thus, it is the different cooling rates that cause the difference in properties that are observed for a given copolymer.

Differential scanning calorimetry measurements were carried out with a Perkin-Elmer DSC-2B calibrated using indium. The melting endotherms were obtained at scanning rates of 10K/min. over the temperature range of 320-420K. In one set of experiments heating was initiated at 280K after quenching in an ice/water mixture. The melting temperature, T_m, is defined as the temperature at which the peak of the melting curve occurs. The measured enthalpy of fusion was converted to a degree of crystallinity, $(1-\lambda)_{\Delta H}$, by taking 69 cal/g as the enthalpy of fusion of a perfect polyethylene crystal(11).

Small-angle light scattering (SALS) patterns were obtained using an apparatus previously described(1). Polyethylenes display five distinguishable light-scattering patterns that are \associated with six different morphologies. These patterns have been described and defined previously(1, 12). Of concern in the present work are the four-fold symmetric SALS patterns designated as a, b, and c, corresponding to spherulitic structures labeled in the same manner. The spherulitic order deteriorates in the progression a to c(1, 12). Also of interest is the h-type scattering pattern that does not show any angular dependent scattering and is indicative of no defined superstructure.

Results and Discussion

As a background to the morphological studies, we consider the DSC results. All of the thermograms showed only one endothermic peak except for EVA2 quenched at 100°C, which gave three melting endotherms reflecting the slower cooling rate. The observed melting temperatures, T_m, are plotted against the mole fraction of total branch points in Fig. 1.

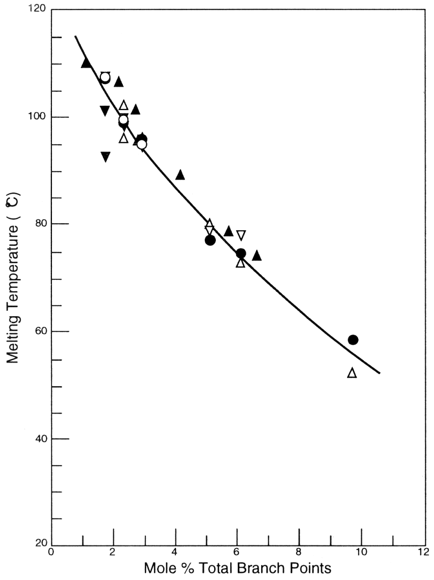

Fig. 1. Plot of observed melting temperature against mole percent of total branch points for different quenching temperatures. Quenched at -78°C ○; quenched at 0°C ●; quenched at 50°C ▽; quenched at 100°C ▼; quenched at 0°C with heating initiated at 10°C △; previous work from ref. (13) ▲. Multiple T_m's correspond to multiple peaks.

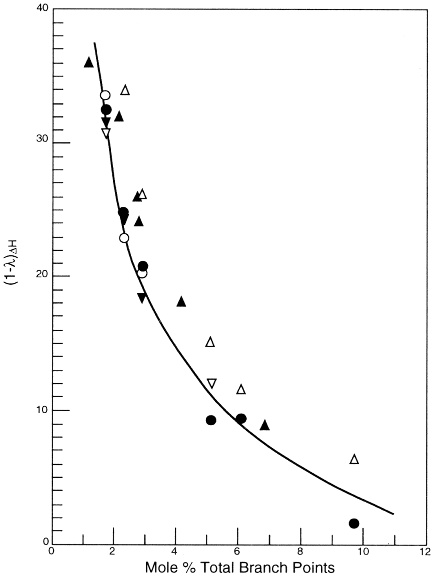

Fig. 2 Plot of degree of crystallinity obtained from enthalpy of fusion $(1-\lambda)_{\Delta H}$ against mole percent of total branch points. Same symbols as in Fig. 1 for quenching and heating conditions.

There is a smooth decrease in T_m with branch point concentration, as would be expected. Also plotted in this figure are results reported previously for ethylene-vinyl acetate fractions(13). The agreement between the data sets is quite good. The melting temperatures do not depend in any significant manner on the cooling rate indicating that the size of the thin crystallites formed do not vary with the crystallization conditions.

The degree of crystallinity, $(1\text{-}\lambda)_{\Delta H}$, is plotted against the mole fraction of total branch points in Fig. 2 for the five coolings rates. There is a monotonic decrease of $(1\text{-}\lambda)_{\Delta H}$ with increasing concentration of branch points and good agreement between the present work and an earlier study with ethylene-vinyl acetate fractions(13). The samples that were heated over the range 280-420K gave slightly higher crystallinity levels. Heating of the other samples was initiated at 320K, where a portion of the initial crystallite population has already melted and does not contribute to $(1\text{-}\lambda)_{\Delta H}$. The crystallinity level for the copolymer with the lowest branching content is about 35% and is reduced to about 3% for 9.7 mole percent of branch points. An extrapolation indicates that at about 12-13 mole percent of branches the copolymer would be completely amorphous.

Two sets of typical SALS patterns are shown in Fig. 3. In Fig. 3a, the copolymer composition is held constant at 2.9 mole percent branch points and the quenching temperature is varied. In Fig. 3b the quenching temperature is held constant at 50°C, and the copolymer composition is varied. Significant changes are observed in the scattering patterns with either of the two paths. In Fig. 3a, the circular symmetric patterns observed at low quenching temperatures are indicative of the lack of superstructure. As the quenching temperature is increased, poorly organized c-type spherulites are observed, as indicated by the development of azimuthal scattering at the higher temperatures. At 100°C better developed b-type spherulites are formed. In Fig. 3b a progressive deterioration of the supermolecular structure takes place as the concentration of branch points increases. Starting with b-type spherulites formed by the copolymers that contain 1.7 mole % branch points, there is a continuous decrease in the order with increasing branching. Spherulites of the c-type are observed for the 2.3 and 2.9 mole percent branch point copolymers. At higher contents of structural irregularities superstructures are no longer observed.

A complete morphological map, containing the results for all the copolymers and cooling rates, is given in Fig. 4. Superstructures are not observed for any copolymers containing 5.1% or more branch points, irrespective of the quenching temperature. For copolymers in the intermediate composition range, 2.3 and 2.9 mole percent, the superstructures are dependent on the quenching temperature. Superstructures are not observed at the lowest temperatures. As the quenching temperature is increased, poorly developed c-type spherulites form. Eventually, at the highest crystallization temperature studied better developed b-type spherulites are observed. Spherulites of the b-type are observed at all temperatures for the copolymers containing the lowest branch point content, 1.7%. We have not, with this set of copolymers and range of quenching temperatures, found well developed a-type spherulites. The crystallinity level remains essentially constant with quenching temperature. Therefore, for the copolymers that contain 2.3 and 2.9 mole percent branch points different supermolecular structures, as well as a lack thereof, are observed at a constant crystallinity level. A similar situation has also been found in linear polyethylene(1,2). For the homopolymer, at a constant molecular weight and crystallinity level, significant changes occurred in the supermolecular structure as the crystallization temperature varied. These results are relevant to studies of properties that depend on supermolecular structure and crystallinity level.

The trends displayed by the morphological map of ethylene-vinyl acetate copolymers are similiar to those reported for random ethylene-1-alkene copolymers(2) and long-chain branched (low density) polyethylenes(5). A common finding among these systems is that for a fixed molecular weight and crystallization (quenching) temperature the supermolecular structural order deteriorates with increasing branch content. Another common feature of ethylene copolymers is that at a fixed branch content the structural order becomes enhanced as the quenching temperature is raised.

The present and previous results make clear that a range in supermolecular structures can be developed in both homopolymers and copolymers. There are also well-defined situations where superstructures are not formed. In favorable cases the changes in structure that occur

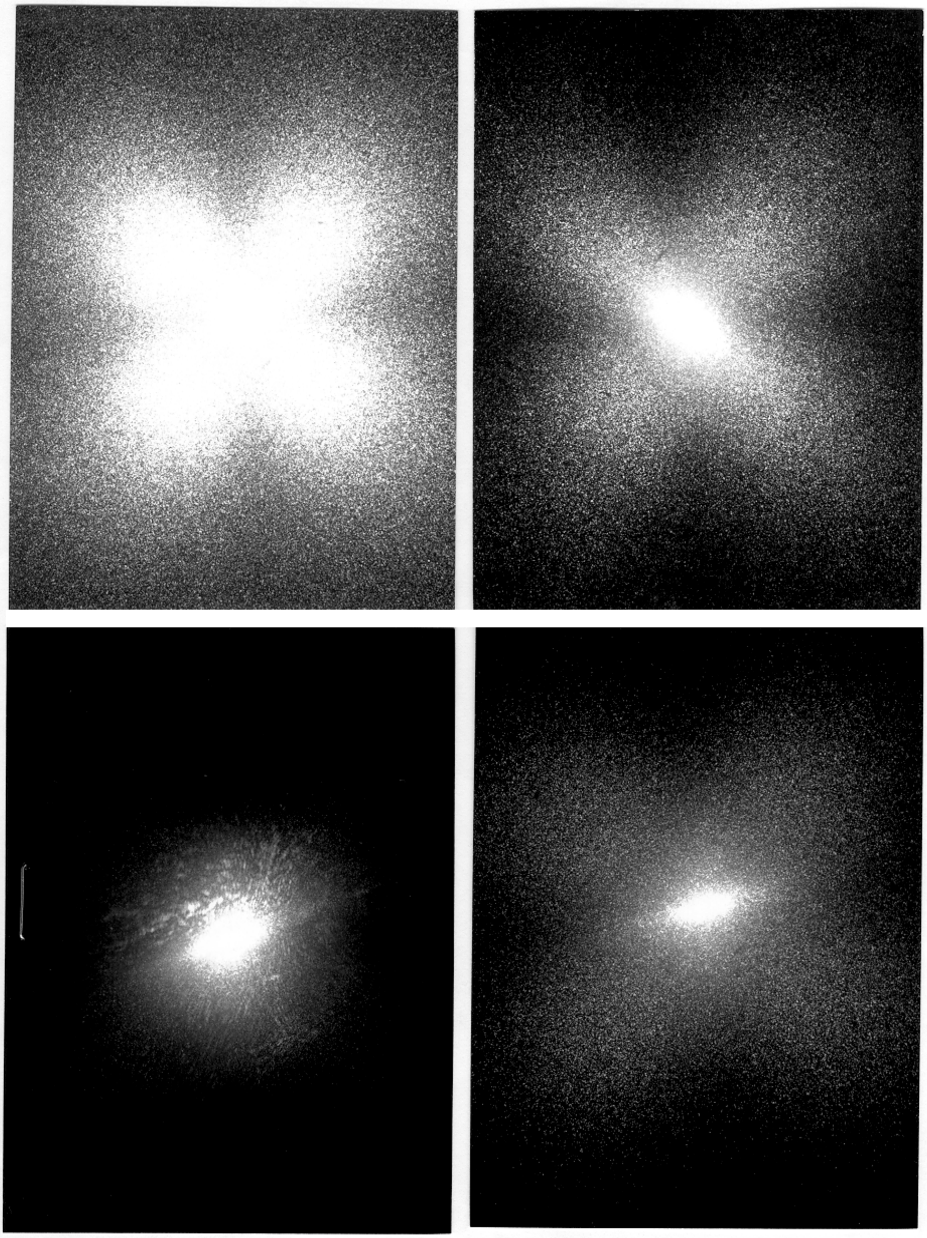

Fig. 3a. SALS patterns, H_v, for ethylene vinyl acetate copolymer EVA9 quenched at (clockwise from top left) 100 °C, 50 °C, 0 °C and -78 °C.

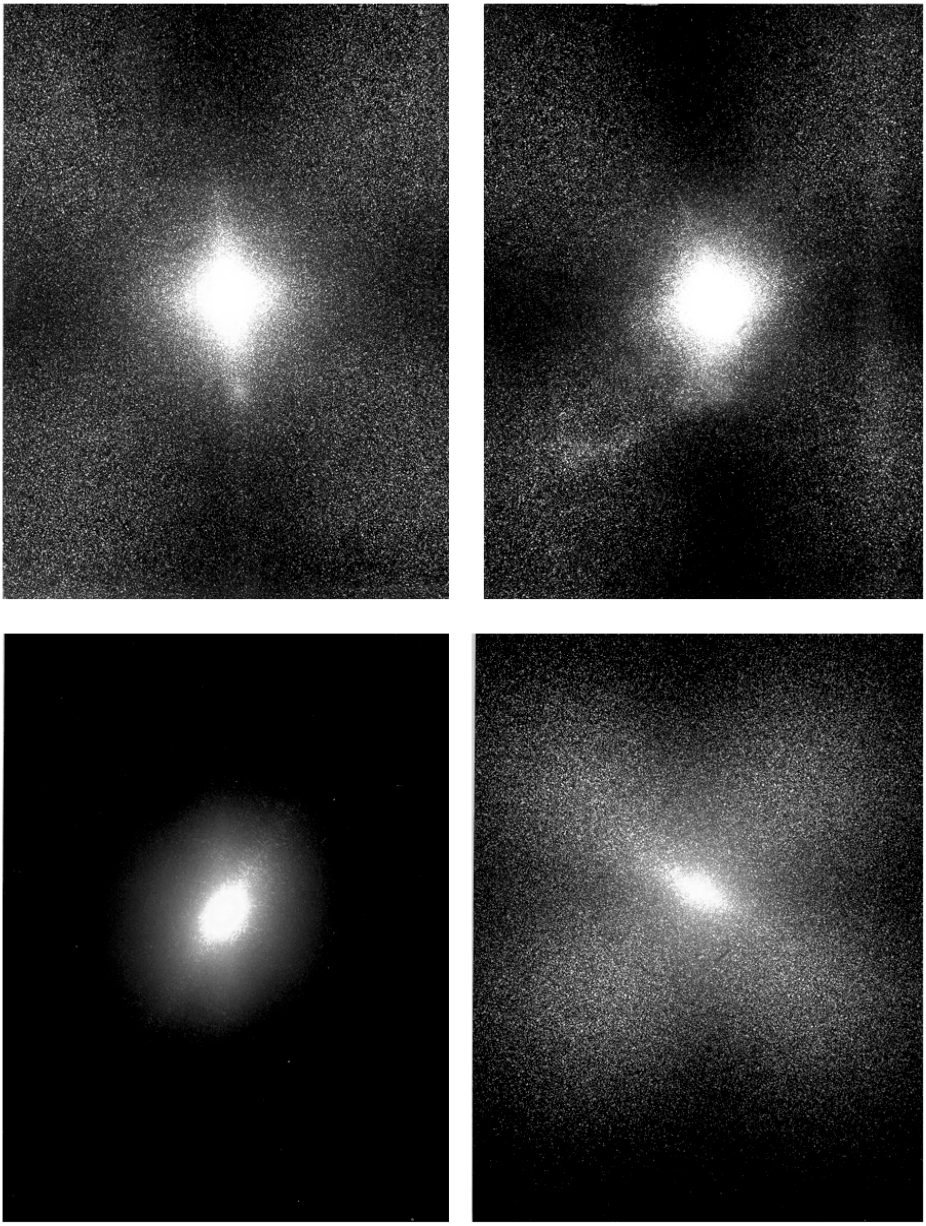

Fig. 3b. SALS patterns, H_v, for ethylene vinyl acetate copolymers quenched at 50°C with composition (clockwise from top left) 1.7, 2.3, 2.9 and 5.1 mole percent branches.

can be observed for polymers having the same crystallinity level. It is a matter of interest to inquire if there are any underlying features that govern the evolution of superstructures.

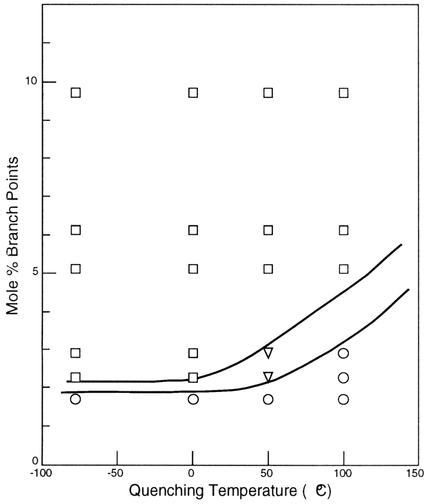

Fig. 4. Morphological map of ethylene-vinyl acetate copolymers as function of mole percent branch points and quenching temperatures. ○ b-type spherulites; ▽ c-type spherulites; □ no supermolecular structure

For linear polyethylene fractions the observed superstructures depend on molecular weight and the crystallization temperature(1,2). Sheet-like structures are formed with very low molecular weight polymers. As the molecular weight is increased, spherulitic structures form whose internal order deteriorates as the chain length increases. Eventually, for the high molecular weights, no organized superstructures are observed. Thin section electron microscopy studies show systematic variations in the structure of the lamellar crystallites that correlate quite well with the observed changes in supermolecular structure(14). At the low and moderate molecular weights, well developed lamellae that are straight and long are observed leading to well organized supermolecular structures. With an increase in the molecular weight the lamellae become curved and shorter, while the spherulitic structure continually deteriorates. At high molecular weights, ~10^6 and greater, the lamellae become highly segmented and there is no evidence of any organized superstructure, only randomly arranged lamellae.

Random ethylene copolymers also show a similar correlation between of superstructure evolution and thin section electron microscopy studies(15). A detailed study of hydrogenated poly(butadiene) shows that very small non-lamellar crystallites are found in the high co-unit content copolymers. Concomitantly spherulitic structures are not observed(2). However, as the co-unit content decreases, longer curved lamellae develop. At the same time spherulitic structures are observed whose internal structures become better organized in the low co-unit content copolymers that have the better developed lamellar crystallites. A similar pattern is found with ethylene-vinyl acetate copolymers(15). For example, for a copolymer that contains 1.12 mole% branch points, straight lamellae of medium length are formed after slow crystallization. However, after rapid crystallization, the lamellae that are formed are curved, segmented, and much shorter, and the spherulitic character is altered accordingly. At the other extreme, a copolymer that contains 6.06 mole% branch points yields only very small, non-lamellar crystallites. As found here, supermolecular structures are not observed with copolymers that have this composition. Copolymers with co-unit contents between the two extremes give intermediate lamellar structures. A similar correlation between lamellar and supermolecular structure was found by Bensason *et al*(16) in their study of ethylene-octene copolymers.

Low density polyethylenes, which contain long-chain branches, show a similar relation between the lamellar crystallites and supermolecular structures. Electron microscopy studies have shown that as the concentration of long-chain branches increases the lamellar character of the crystallites progressively deteriorates(6,7). At the same time, the superstructure becomes less well-defined. Eventually, no supermolecular structure is observed(5). When the molecular weight is varied, at a fixed long-chain branching content, the pattern of structures that evolves is similar to that found for linear polyethylene(6,7).

The electron microscopy results demonstrate that for different types of molecular architecture there is a strong correlation between the lamellar structure and the type and organization of the superstructures that develop. The structure of the lamellar crystallites is the key feature that controls morphology. The lamellar structure is controlled by molecular weight, structural regularity of the chain and the crystallization temperature. Studies of the properties of crystalline polymers, as they relate to morphology, should, therefore, be directed to the key role that is played by the lamellar crystallites.

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