Supermolecular Structure of Random Copolymers of Ethylene

M. D. Failla, J. C. Lucas, and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306

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ABSTRACT: The supermolecular structures developed after rapid crystallization from the melt of a series of ethylene–1-alkene copolymers has been investigated by small-angle light scattering. Copolymers with butene, hexene, octene, or 4-methylpentene as comonomers were studied over a wide range in molecular weights and copolymer compositions. It was generally found that for given co-unit content the structural order deteriorated with increasing molecular weight. When the molecular weight was fixed, the order deteriorated with increasing co-unit content. However, the level of superstructure organization was very dependent on the length of the side group. The supermolecular structure, for a given molecular weight and composition, was much better developed for the smaller side groups than the larger ones. Possible reasons are suggested for these structural differences.

Introduction

The arrangement of crystallites into higher levels of organization, termed supermolecular structures, is an inherent part of the morphology of crystalline polymers. It has been shown in homopolymers that the superstructures evolve in a systematic manner depending on molecular weight, distribution, and crystallization temperatures.[1–5] Although spherulite formation is the most commonly observed supermolecular form, it is not the universal mode of homopolymer crystallization.[1–5] For example, for linear polyethylene fractions, five distinctly different small-angle light scattering patterns, SALS (incoming beam vertically polarized, transmitted beam horizontally polarized), are observed.[2,6] The theoretical analyses of Kawai[7] and Stein[8] allow these patterns to be interpreted in terms of the supermolecular structures. Three of the patterns represent spherulites of deteriorating order, designated as "a", "b", and "c", respectively. Another pattern, which displays some azimuthal dependence of the scattering, is indicative of lamellae organized into thin rods or rodlike aggregates. Such structures are designated as "d". The fifth pattern, which does not display any angular dependence of the scattering can represent either sheetlike structures designated as "g" or randomly oriented lamellae designated as "h". Some form of microscopy needs to be used to distinguish between these latter two cases. All of the crystalline morphologies that are deduced from the light scattering patterns are directly confirmed by transmission electron microscopy using thin sectioning staining methods.[9]

Random ethylene copolymers also display supermolecular structures that depend on molecular weight, crystallization temperature, and an additional variable, the co-unit content. Detailed morphological studies have been reported for whole polymers and of fractions of long-chain branched polyethylenes,[10] a set of molecular weight fractions of hydrogenated poly(butadienes) having ca. 2.2 mol % branch points,[11] fractions of ethylene–butene copolymers,[12] and fractions of ethylene–octene copolymers.[13] The hydrogenated poly(butadienes) have randomly distributed ethyl branches and narrow molecular weight and composition distributions. From these results, certain generalizations on the role of molecular weight composition, and crystallization conditions were made.[11] Taking the formation of spherulites as a reference point, it is found that, at a fixed temperature, as the co-unit content increases, the molecular weight below which spherulites can form decreases. A molecular weight and co-unit content is reached, above which spherulitic structures cannot be developed. For a given co-unit content, as the molecular weight decreases, the temperature range for spherulite formation increases. For fixed molecular weight for linear polyethylene as well as for fixed molecular weight and co-unit content for copolymers, the superstructure becomes better developed and organized on slow cooling, or high crystallization temperatures, relative to rapid crystallization.[10–12]

In the present paper we investigate the superstructures formed by a series of random ethylene copolymers that have different chemical type branches. The main interest is to ascertain whether the chemical nature of the branch influences the supermolecular structure that is observed under comparable crystallization conditions. To this end, we have studied random ethylene–1-alkene copolymers with 1-butene, 1-hexene, 1-octene, and 4-methyl-1-pentene as comonomers. These copolymers have the same molecular constitution in that they possess most probable molecular weight and narrow composition distributions.[14] The crystallization behavior and phase structure of similarly constituted copolymers have been described in a series of reports.[14–16] Linear polyethylenes having the same molecular weight distribution and hydrogenated poly(butadienes) having a range in molecular weights and branch point concentrations equal to and greater than 2.2 mol % were used as references. Since our major interest here was to assess the role of copolymer composition and chemical type, emphasis was given to one set of crystallization conditions. For comparative purposes all the samples were rapidly crystallized, or quenched. Besides giving a uniform crystallization procedure for all the samples, the complications arising from isothermal or slow-cooling crystallizations are avoided. For random ethylene copolymers only very small amounts of crystallization are developed isothermally, or at high crystallization temperatures.[17–18] Consequently, for this type of crystallization the structures observed at room temperature result in great part from the details of the cooling process.[18]

Experimental Section

The ethylene copolymers studied in this work were prepared following the method of Kaminsky et al. using $(C_5H_5)ZrCl_2$ as catalyst.[19] The weight- and number-average molecular weights were obtained by gel permeation chromatography following

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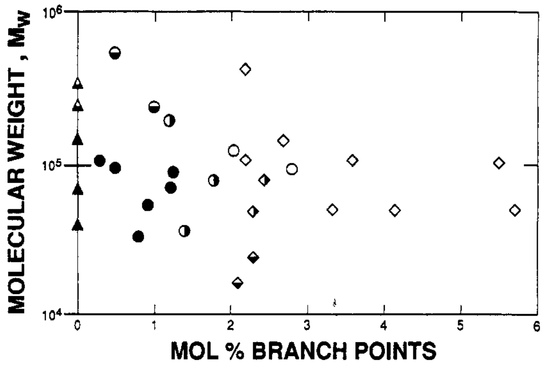

Figure 1. Morphological map of ethylene–butene copolymers and hydrogenated poly(butadienes). Plot of weight-average molecular weight against mole percent branch points. Supermolecular structures are designated as follows: for ethylene–butene, (a) ●, (b) ◑, (c) ⊖, (h) ○; for hydrogenated poly(butadiene), (a) ◆, (b) ⬗, (c) ⬘, (h) ◇. Triangles are for linear polyethylene.

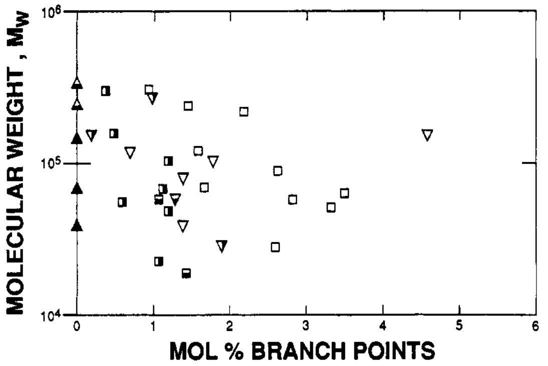

Figure 2. Morphological map of ethylene–hexene (rectangles) and ethylene–octene (inverted triangles) copolymers. Plot of weight-average molecular weight against mole percent branch points. Supermolecular structures are designated as in Figure 1.

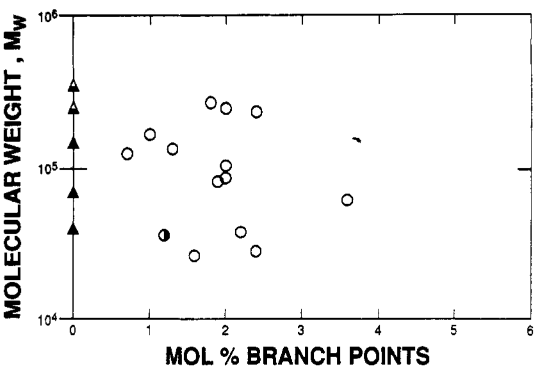

Figure 3. Morphological map of ethylene–4-methylpentene. Plot of weight-average molecular weight against mole percent branch points. Supermolecular structures are designated as in Figure 1.

conventional procedures.[20] The results show that this set of copolymers had most probable molecular weight distributions. The co-unit content was determined by high-resolution carbon-13 NMR of solutions following established methods.[21,22] These samples are also characterized by uniform composition distribution. The hydrogenated poly(butadienes) studied were used and described in previous reports.[11,14,15,23]

The H_v SALS patterns were obtained with a photometer similar to the one described by Stein.[24] The light scattering samples were in the form of thin films that were between 25 and 45 μm thick. The films were prepared by placing the polymer between two 20-μm-thick aluminum foils and pressing the specimen at ca. 160 °C between the plates of a Carver press. The pressure applied was between 5000 and 15 000 lb in.$^{-2}$. The film formed in this manner was rapidly cooled to room temperature. Then, while still between the aluminum foil, it was again rendered molten at 160 °C and then quickly plunged into an acetone–dry ice mixture. This refrigerant mixture served as the standard crystallization condition for all the quenched samples. To be able to discuss our results in terms of some literature reports, a selective set of copolymers were also slow cooled in the press.

The supermolecular structure was determined from the light scattering patterns and given the letter designation described in the Introduction.

Results and Discussion

All of the experimental results are presented as morphological maps in Figures 1–3, Here, since the quenching temperature is fixed, the molecular weight is plotted against the mole percent of branch points. The different structural forms are given by the symbols defined in the legends. Figure 1 represents the results for the hydrogenated poly(butadienes) and the ethylene–butenes, Figure 2 gives the results for the ethylene–hexenes and the ethylene–octenes, and Figure 3 is for the ethylene–4-methylpentene copolymers.

We take the data for the ethyl-branched copolymers as a reference and examine the influence of co-unit content at fixed molecular weight and of molecular weight at fixed co-unit content. The hydrogenated poly(butadienes) at 2 mol % branch points display b type spherulitic structures at the low molecular weights. The superstructural organization progressively deteriorates from b to c type spherulites with increasing molecular weight at this co-unit content. Eventually, only random structures develop for $M \geq 10^5$. A similar deterioration in the superstructure occurs in the ethylene–butene copolymers at 1 mol % branch points. At this copolymer composition well-organized a type spherulites are observed at the low molecular weight. At this composition, the change in superstructure parallels that of linear polyethylene having the same molecular weight distribution. No organized superstructures are observed for any molecular weight when the branch content is greater than 2.2%. Thin-section electron microscopy indicates that the crystallites that exist in the range of co-unit contents equal to or greater than 3 mol % are not very well organized.[25]

If the molecular weight is fixed, a decrease in structural order takes place as the branch content is increased. For example, for molecular weights of the order of 1 × 10^5 and less, well-developed a type spherulites, typical of the linear polymer, are maintained to ca. 1 mol % branch points. With a further increase in co-unit content there is a progressive decrease in order, culminating in random structures when the composition exceeds 2 mol % branch points. At the higher molecular weights, where the linear polyethylene initially displays b type spherulites, the copolymers change from c type spherulites to random lamellae as the co-unit content increases.

The results for the ethylene–hexene and ethylene–octene copolymers, given in Figure 2, display similar general trends, with molecular weight and composition, as the ethyl-branched copolymers. However, for these copolymers, with longer alkyl side groups, the supermolecular structures are not as well organized. For example, no well-developed a type spherulites are observed for this group of copolymers. Even b type spherulites are relatively rare. At ca. 1.4 mol % branch points and greater, only random lamellae develop for all molecular weights. This results is to be compared with the fact that for the ethyl-branched copolymer random lamellae do not form at all molecular weights until 2.2 mol % branch points are reached (Figure 1). At the lower co-unit contents the order progressively decreases with molecular weight. Poorly developed spher-

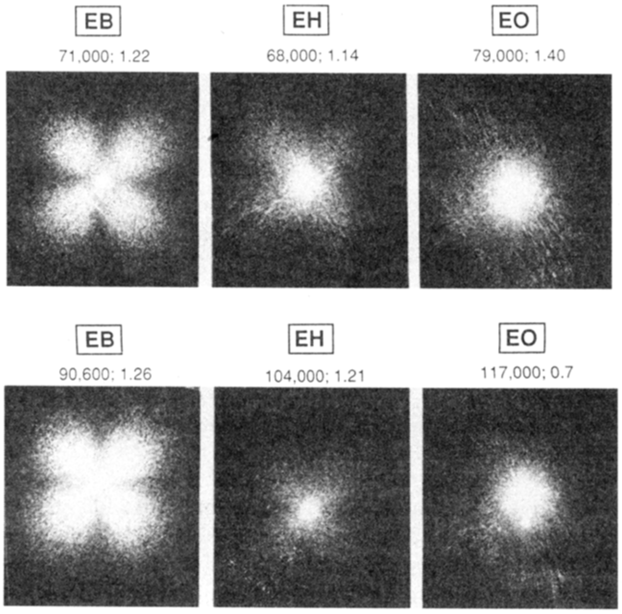

Figure 4. Small-angle light scattering patterns, H_v, for ethylene–butene, ethylene–hexane, and ethylene–octene copolymers. Weight-average molecular weights and mole percent branch points are indicated in the figure.

ulites of the c type predominate. At fixed molecular weight c type spherulites are observed with the initial introduction of co-units. Depending on molecular weight, this is to be compared with the a and b types of the corresponding linear polyethylenes and the ethylene–butene copolymers. When the region in the vicinity of 1 mol % branch points is examined in detail, small differences can be found between the ethylene–hexene and ethylene–octene copolymers. The latter copolymers develop much poorer ordered superstructures under comparable conditions. The SALS patterns for the 4-methylpentene copolymers that have been studied (Figure 3) show virtually no elements of organized superstructures. Since there is a paucity of data in the range of 0–1 mol % branch points, 5×10^4–1×10^5 molecular weight, a more definite generalization cannot be made for this copolymer.

A better understanding of the influence of the different branch lengths on the supermolecular structures can be obtained by comparing specimens where molecular weights and branch contents are matched as closely as possible. In Figure 4 the SALS patterns are given for two series of copolymers, one with molecular weight ca. 7×10^4 and the other ca. 1×10^5; in each series the branch point concentrations are very similar. In each series the well-developed spherulites formed by the ethylene–butenes are readily apparent. Their SALS patterns are distinctly different from those of the other copolymers. The highly ordered a type spherulitic structure is no longer observed in the ethylene–hexenes although some remnants of the spherulitic form remain. The ethylene–octenes give essentially random type structures. This particular compilation and method of presentation accentuates the differences in the supermolecular structures for the copolymers with different side groups. A direct comparison with the ethylene–4-methylpentene copolymers could not be made because of the unavailability of appropriate samples. However, from the morphological map of Figure 3 we can surmise that the pattern will show the same type of disorder as displayed by the ethylene–octene copolymers. We can also deduce from the report of Flory and Jackson[26] that copolymers with methyl groups directly bonded to the main chain give better developed supermolecular structures. In this case, however, it is known that the side group is partially incorporated into the lattice.

For reasons described above, we have for comparative purposes limited the crystallization to rapid quenching. This does not mean that other superstructures cannot be developed in the same sample by adopting other crystallization procedures. As was pointed out earlier, more highly organized superstructures result from isothermal crystallization or by slow cooling from the melt.[18] Similar changes have also been found for the copolymers studied here. For example, the ethylene–hexene copolymers of high branch content which were studied here did not develop any ordered superstructure on rapid cooling. However, on slow cooling, poorly developed spherulitic strucures could be formed. Similar observations were also made with the ethylene–4 methylpentene copolymers. The ethylene–octene copolymers behaved in a similar manner. A better developed spherulite could be observed for the very low co-unit content copolymers on slow cooling. However, the influence of branch type can be observed even on slow cooling. An ethylene–butene copolymer ($M_w = 1.25 \times 10^5$, 2.05 mol % branch points) gave a random structure on quenching (Figure 1). However, on slow cooling, well-developed a type spherulites are observed.

Hosada et al. have studied by SALS the supermolecular structures of ethylene–butene fractions that were slowly cooled from the melt.[12] The results were comparable to those observed here and to those previously reported for hydrogenated poly(butadienes).[11] Defoor et al. have reported the results of similar experiments with fractions of ethylene–octene.[13] The ratios of the weight- to number-average molecular weights of these fractions were generally greater than those of the samples with most probable molecular weight distributions. The slow-cooling crystallizations induced spherulitic structures of varying degrees of order, in contrast to the results in Figure 2. However, as we have noted, slow cooling of our ethylene–octene samples also allows for development of well-ordered superstructures.

The question then arises as to why the length of the side group under controlled crystallization conditions causes such major differences in the supermolecular structure of these copolymers. Although a definitive answer cannot be given at present to this question, there are several possibilities that can be sorted out. Studies have shown that, except for the directly methyl bound copolymers, the other alkane type side groups do not enter the crystal lattice. The copolymers studied here have the same melting temperature and crystallization conditions.[14–16] However, the thickness and relative amount of the interphase of the ethylene–octene copolymers are slightly higher than the others.[16] These results imply that the interfacial structure changes with the branch length of the co-unit. It would then be expected, as has been theoretically confirmed, that the branches are preferentially located in the anisotropic interfacial region.[27–29] The changing interfacial structure would then affect the surface density of chains at the crystallite basal plane. In turn, the probability of chain reentry would be altered.[30,31] These changes, caused by the different interfacial structures, could play a role in influencing the resulting morphology. If, in contrast, attention is focused away from the properties of the crystalline state, the possibility also exists that the differences observed in the supermolecular structure could be caused by changes in the initial melt structure and thus in the noncrystalline regions. The validity of this conjecture would require detailed, comparative studies of the isotropic, pure melt. The results of such studies are not as yet available.

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