Polymer 40 (1999) 4717–4721

polymer

Polymer Communication

Crystallization of ethylene–octene copolymers at high cooling rates

J. Wagner, S. Abu-Iqyas, K. Monar, P.J. Phillips*

Department of Materials Science & Engineering, University of Tennessee, Knoxville, TN 37996-2000, USA

Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

Received 13 November 1998; received in revised form 4 January 1999; accepted 10 January 1999

Abstract

The crystallization behavior of a series of ethylene–octene copolymers synthesized using metallocene catalysts was studied using the Ding–Spruiell method of rapid cooling. In conventional crystallization experiments it was found, as expected, that the spherulite growth rates varied with octene content and molecular weight. When studied at rapid cooling rates the polymers generate their own pseudo-isothermal crystallization temperatures, in agreement with Ding–Spruiell's studies on other systems, however, at the lowest temperatures of crystallization, the spherulite growth rates of all of the copolymers studied merge and are virtually indistinguishable. The results indicate that there is a major change of crystallization mechanism under these conditions, of considerable relevance to polymer processing operations. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Ethylene copolymer; Metallocene; Crystallization

1. Introduction

Linear low-density polyethylenes (LLDPE) are a commercially important class of polyethylenes, produced through the copolymerization of ethylene and comonomers such as hexene or octene, thereby producing butyl or hexyl branches, respectively. In order to separate the effects of copolymer content from molecular weight, a series of cross-fractionated copolymers has been investigated and reported in the recent past [1]. The copolymers which had been cross-fractionated for us by Dow Chemical had been synthesized using traditional Zeigler–Natta type catalysts, which are well known to produce molecules in which the copolymer content varies with molecular weight. What was not well known at that time, or even now, was the sequence length distributions of the octene and ethylene mers within each molecule. It has been assumed to be random in the absence of contradictory information. Our studies of random copolymers produced using metallocene catalysts showed that the crystallization behavior was very different from that of the Zeigler–Natta materials, a result which had to be a consequence of the ZM polymers being non-random within each molecule.

Quiescent crystallization is usually separated into its component parts of primary nucleation, linear spherulite (or lamellar) growth and secondary crystallization. In this article only the linear spherulite growth rates will be considered. Regime theory, which describes linear spherulite growth in flexible polymers, comprises two separate processes. The first process is the deposition of secondary nuclei on the growth face, usually denoted as occurring at a rate *i*, the second process being the subsequent growth along the face at the niches formed by the secondary nuclei, often referred to as the rate of surface spreading, and denoted by the rate *g*. The relative rates of these two processes determines the regime at which the crystallization occurs. The concept of transitions was first introduced in 1973 by Lauritzen and Hoffman [2] and has since been extensively evaluated by Phillips and others [3–6]. Studies of the cross-fractionated Zeigler–Natta ethylene–octene copolymers showed clearly that the effect of copolymerization was to reduce the linear growth rate. When analyzed further it was demonstrated that copolymerization reduced the rate of secondary nucleation in an exponential manner, whilst reducing the rate of surface spreading only in a somewhat linear manner. The net result was a depression of the regime-I–regime-II and regime-II–regime-III transitions to lower temperatures by a few degrees. The effect of increasing molecular weight was to negate the effect of increasing copolymer content as far as the transition temperature was concerned, but also to reduce the linear growth rate. Up until the present date, it has been generally assumed that regime

---

* Corresponding author. Tel.: +1-423-974-5304; fax: +1-423-974-4115.

E-mail address: pphillip@utk.edu (P.J. Phillips)

PII: S0032-3861(99)00077-4

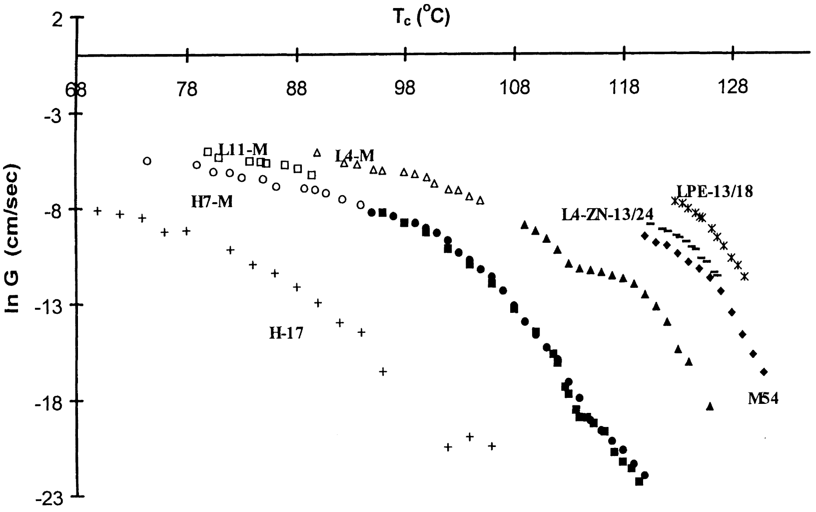

Fig. 1. Logarithm of radial growth rate versus crystallization temperature for the polymers, as indicated.

theory can describe all known crystallization behavior in polyolefins.

Similar copolymers have been produced using metallocene catalysts, which are believed to produce random copolymers because of the nature of catalytic process. Whether or not there is a non-random distribution present cannot be evaluated because of the lack of a technique to measure sequence lengths, however there are no reasons to suspect a major source of non-randomness, which is well-established for the Zeigler–Natta polymers. There is always the possibility of chain scission occurring near a branch point, which may result in a dependence of molecular weight on comonomer content, however there are as yet no reports in the literature of such an occurrence for these copolymers. So, it is not yet known whether cross-fractionation of metallocene copolymers will assist in studies such as these. It appears at the present time that radial growth rate of spherulites is the property most sensitive to sequence length distributions.

Dow Chemical synthesized for us metallocene copolymers with molecular characteristics, as near as possible, identical to those of the cross-fractionated samples. Prior studies of the melting point—lamellar thickness relations have shown that the equilibrium melting points are depressed by a factor greater than that predicted by the Flory equation [7,8]. It was shown that for one of these copolymers the linear growth is depressed much more than that in the equivalent fraction of a Zeigler–Natta polymer, the regime-I–regime-II transition temperature being depressed much more, and regime-III appears [9]. The conclusion resulting was that the fractions of the Zeigler–Natta polymer contained non-random inclusion of the octene mers and that this study generated a very important new variable for crystallization studies, namely the sequence length distribution.

In the study reported here, the studies of the metallocene copolymers have been extended to the very high supercoolings characteristic of commercial processing operations. It will be demonstrated that, under such conditions, the polymer behavior changes dramatically and no longer is dependent on comonomer content and, apparently, on molecular weight also. This process is envisioned as being similar to a congealing process in which the copolymer molecules wiggle into place as the growing crystal sweeps through them, the hexyl branches being included in the metastable crystals. Presumably, these crystals anneal and perfect through a variety of subsequent processes, in which some of the hexyl branches are ejected from the crystals. It is suggested that these later events control the final mechanical and physical properties, rather than the effective crystallization temperature.

2. Experimental

LLDPE fractions, copolymers synthesized using metallocene catalysts and linear fractions were supplied and characterized by the Dow Chemical Co. All copolymers contain octene as the comonomer. The fractions have been described previously [1,2], and also the metallocene copolymers [8–10]. In sample designation L and H refer to low molecular weight and high molecular weight respectively ($M_w \sim 50$ k, $M_n \sim 25$ k and $M_w \sim 98$ k, $M_n \sim 48$ k). The suffix M refers to materials synthesized using metallocene catalysts and ZN to materials synthesized using Zeigler–Natta catalysts (the latter are all fractions). The numbers following the letters refer to the number of hexyl branches per 1000 carbon atoms. Samples denoted by LPE are linear samples, the numbers following the LPE referring to the molecular weights in 1000s.

Linear spherulitic growth kinetics experiments were performed using an Olympus polarizing microscope with an attached 35-mm camera and temperature controlled hot stage. The change in the morphological size was measured by taking photographs as a function of time. Samples were

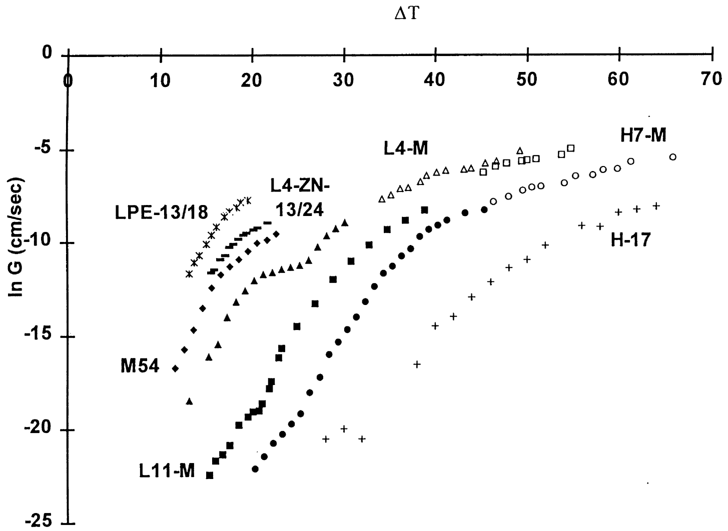

Fig. 2. Logarithm of radial growth rate versus supercooling, using established equilibrium melting points of each individual copolymer.

held at the melt temperature of 150°C for 5 min and then rapidly quenched to the crystallization temperature. Crystallization experiments at high supercoolings were carried out in the original Ding–Spruiell rapid cooling equipment [11,12] using a video camera.

3. Results and discussion

The variation of linear growth rate with temperature is shown in Fig. 1 for several different materials, where the filled symbols represent points obtained in conventional isothermal crystallization experiments. The open symbols represent data points obtained in rapid cooling experiments, where the polymer generates its own pseudo-isothermal crystallization temperature. It can be seen clearly that as high supercoolings are approached the curves of all the copolymers are tending to merge into a single curve, regardless of comonomer content or molecular weight. It has to be remembered that the equilibrium melting point is dependent

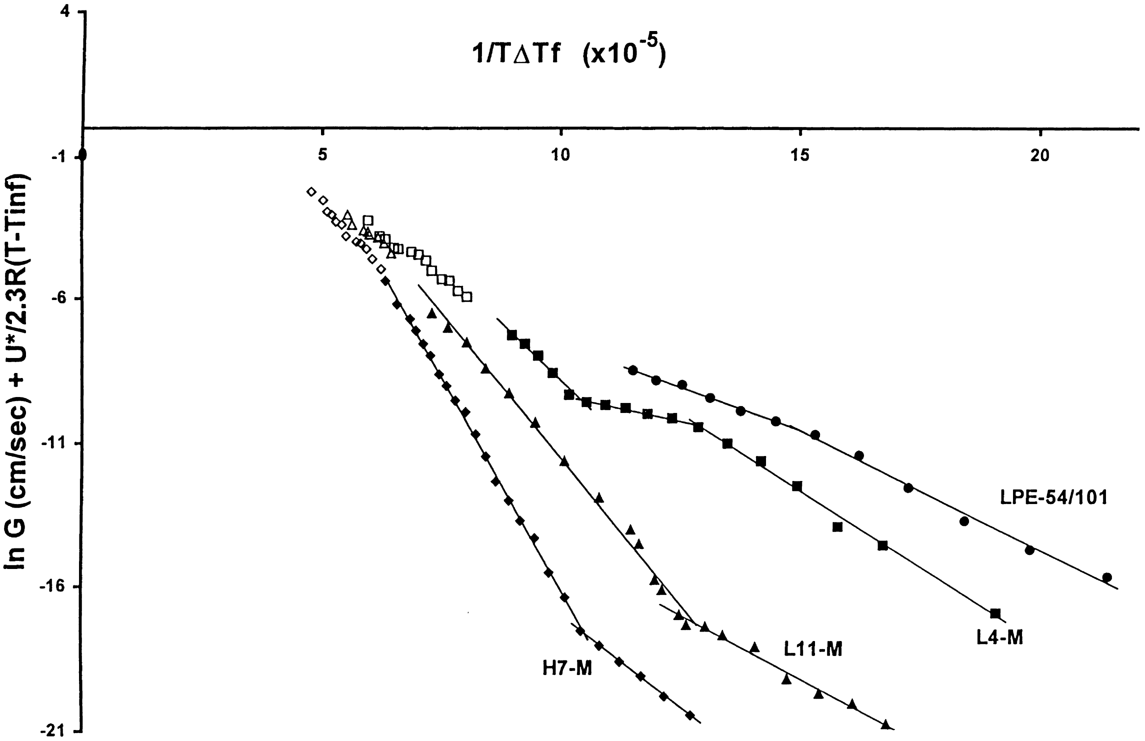

Fig. 3. Secondary nucleation plot for the copolymers indicated (filled symbols are isothermal crystallizations; open symbols are pseudo-isothermal crystallizations obtained from rapid cooling experiments).

on molecular weight and comonomer content and the data should be corrected for that variable using the supercooling, relative to the equilibrium melting point of each copolymer. When the data are plotted as a function of supercooling (Fig. 2), the same merging phenomenon can be seen, perhaps even more clearly. The third type of plot normally made is the secondary nucleation, or regime, plot in which the logarithm of the growth rate, less a mobility term, is plotted against the reciprocal of supercooling. It is this plot that permits the different regimes to be identified and is, in many ways, the defining plot for the crystallization behavior of a polymer. Such a plot is shown in Fig. 3.

The entire crystallization behavior of the copolymers can now be analyzed. First, the filled points, indicative of conventional isothermal studies, show the expected decrease in crystallization rate as comonomer content is increased (e.g. compare L4 with L11). Also apparent is the decrease of crystallization rate with increasing molecular weight (e.g. H7 is slower than L11). Also shown are the data for the Zeigler–Natta fraction, (L4-ZN), which crystallizes much more rapidly than for the comparable metallocene copolymer L4-M. When the open symbols, indicative of rapid cooling experiments, are considered, it can be seen that initially they continue on the same lines as the filled points. This is a very important observation, as it tells us that there is no significant difference between an experiment carried out isothermally and one that is carried out dynamically in a rapid manner, and in which the polymer generates its own pseudo-isothermal crystallization condition. It is, however, clear that as the experiments proceed to successively higher and higher cooling rates that there is a slow downward change in the slope for all the copolymers. Ultimately, the copolymers are attaining the same growth rates. This cannot occur if the normal selection rules of copolymer crystallization, based on exclusion of the comonomer units, continue to apply. Nor can the merging of the curves to a common line, regardless of molecular weight, occur unless there is essentially a lack of long range movement of the polymer chains during the crystallization process. In other words, the copolymer molecules, essentially, must freeze into place without the exclusion of molecular defects. This is a new form of crystallization, quite different from the one occurring at higher temperatures, where the molecules have time to reject the comonomer species and to diffuse in a way which is dependent on their molecular weights.

It can also be noticed that in the isothermal regions (filled points) that the slopes of the lines are increasing as the comonomer content increases. From the equations governing regime theory, this can only be a result of two possible changes. The first is an increase in the fold surface free energy, which appears in the numerator of the slope, probably caused by crowding of the rejected side branches in the interfacial regions. Secondly, there may be a reduction in the latent heat of fusion, which appears in the denominator, caused by incorporation of hexyl branches in the crystal. Although this might seem unlikely, studies of the equilibrium melting points of these copolymers crystallized isothermally at relatively low supercoolings have already shown major diversion from the Flory equation and conformation to the Sanchez Eby equation for partial incorporation of comonomers in the crystals [7,8]. Calculations of defect energies are consistent with those predicted for incorporation of methyl or ethyl groups. Presumably this is because the hexyl group is long enough for several of its methylene units to enter crystallographic register, leaving basically a branch point and a methyl group as the defects. The equilibrium melting point of the copolymers will be decreased if there exists a substantial incorporation of defects, and so the equilibrium melting points of the copolymers may be progressively decreasing as crystallization temperature decreases. If this is the case, then our estimates of effective supercooling used in Figs. 2 and 3 will be high. This in itself could be responsible for the decreasing slope found at very high supercoolings (open symbols). Additionally, if large amounts of hexyl branches are incorporated in the crystals, rather than being excluded, then the crystal will expand, lowering the latent heat of fusion. At the same time, the crowding in the interfacial regions will be reduced, thereby causing a reduction of the fold surface free energy. All of these effects would result in a decrease in the slope. The effects are likely to be occurring simultaneously. It should also be noted that expansion of the crystal lattice, through incorporation of defects, will reduce the surface free energy by allowing more surface area per emerging chain in the fold surfaces.

It would seem unlikely that the metastable crystals formed at the growth front would retain their initial structure and condition. They would be expected to try to reduce their free energy by annealing processes, which would result in the ejection of substantial numbers of hexyl branches to the fold surfaces, or even the lateral surfaces, of the crystals. Such processes could be occurring immediately after the crystals are formed, if there is adequate molecular mobility, or perhaps later during storage at ambient temperature, or both. The stabilization processes could occur so rapidly that they would not be detected in normal characterization experiments, or they might require some form of thermal activation and hence could be studied independently. The type and character of the stabilization processes will be controlled to some extent by the detailed structure of the folded surface. Presumably, this crystallization process is very similar to the Flory switchboard model, there being many tie-molecules. Also the number of adjacent reentry folds will be very restricted. Under these conditions, there would be very little molecular mobility as the ability of the molecules to move through the crystal would be very much inhibited. If this were the case the restricted molecular mobility could result in the potential annealing processes, outlined earlier, occurring quite slowly, or not at all. These restrictions would lead to very complex morphological structures on a micro-scale, as the crystals stabilize, involving the crystals, the interfacial regions and the interlamellar material. They would also lead to complex molecular trajectories and hence network structures. It would be these morphological–molecular features that would interact to control the resultant mechanical and physical properties. The ultimate properties, such as strain to failure and fracture toughness might be affected most by these features.

4. Conclusions

The random copolymers show up to three different ranges of radial growth rate in the isothermal temperature range studied, assigned to all three regimes of growth. Increasing branch content shifts regimes from the I–II transition to II–III transition and reduces the growth rate significantly.

When studies are extended to rapid cooling experiments, in which the polymer generates its own pseudo-isothermal crystallization temperature, the applicable existing regime-III region is continued for a restricted range of temperature. When very high supercoolings are approached a new form of crystallization occurs, in which the comonomer units are no longer excluded and molecular weight dependencies appear to be eliminated. The copolymers become indistinguishable from one another on the basis of their spherulite growth rates.

Acknowledgements

This research was supported by the Polymers Program of the National Science Foundation under grants DMR9408678 and DMR 9711986 and by the Center of Excellence in Materials Processing at the University of Tennessee.

References

[1] Lambert WS, Phillips PJ. Macromolecules 1994;27:3537.
[2] Lauritzen JI, Hoffman JD. J Appl Phys 1973;44:4340.
[3] Phillips PJ. Polym Prepr (Am Chem Soc Div Polym Chem) 1979;20:438.
[4] Hoffman JD. Polymer 1983;24:3.
[5] Hoffman JD, Miller RL. Polymer 1997;38:3151.
[6] Phillips PJ, Lambert WS. Macromolecules 1990;23:2075.
[7] Kim M-H. PhD Dissertation, University of Tennessee, 1996.
[8] Kim M-H, Phillips PJ, Lin JS. Submitted for publication.
[9] Wagner JE, Abu-Iqyas S, Monar K, Phillips PJ. Proc. ANTEC 98, Society of Plastics Engineers, 1998.
[10] Kim M-H, Phillips PJ. J Appl Polym Sci 1998;70:1893.
[11] Ding Z, Spruiell JE. J Polym Sci B Polym Phys Ed 1996;34:2783.
[12] Supaphol P, Sprueill JE. J Polym Sci B Polym Phys Ed 1998;36:681.