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THE THERMODYNAMIC AND STRUCTURAL PROPERTIES OF METALLOCENE-TYPE RANDOM ETHYLENE COPOLYMERS



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The properties of a series of random ethylene copolymers prepared with the metallocene catalytic system $\text{rac-Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ were studied for a large variety of comonomer types. These include the classical 1-alkene type with length up to 10 carbons and those of the cyclic type such as cyclopentadiene and dicyclopentadiene. Under rapid crystallization, the melting temperatures of the newly synthesized copolymers followed the relation of model random copolymers indicating a behavior that conforms to that predicted by Flory's phase equilibrium theory. The molar entropy of fusion is not significantly altered by the comonomer type including the dicyclopentadiene type. All types of comonomers studied showed, for a fixed comonomer content, the same change in properties during annealing, except the ethylene 1-butenes. These latter copolymers and the hydrogenated polybutadienes showed a faster rate of change in thermal properties. This is consistent with a higher molecular diffusion for the butene comonomer than for the rest of comonomers analyzed. The properties of the interlamellar region were also studied as a function of comonomer type and content following the variation of the amorphous halo extracted from the WAXS diffractograms. The observed systematic decrease in the peak scattering angle with increasing comonomer content indicates a variation of the intermolecular liquid structure.

Introduction

The thermodynamic and structural properties of copolymers of ethylene and 1-alkene type comonomers have been previously reported (1-4). The melting temperature of model random ethylene-butene copolymers, such as hydrogenated polybutadienes and fractions from Ziegler linear low density polyethylenes were found to be independent of the chemical nature of the comonomer when the branch is longer than a methyl group. For 1-alkene type copolymers, properties such as melting temperature, density, enthalpy of fusion and the thickness of the crystallites were found to be very dependent on comonomer concentration, but essentially independent of the comonomer type (1,2). Recent reports have also analyzed thermal and structural properties of 1-octene copolymers under isothermal annealing. Changes with annealing time of the rate of heat flow upon melting were explained by a decrease of the molar conformational entropy in the non-crystalline regions (4). In this work we extend these studies to ethylene copolymers with comonomers of a significantly higher

molar volume than the 1-butene, 1-hexene, 1-octene studied previously. Comonomers of interest in this work include, 1-decene, 4-methyl-1-pentene and those of the cyclic type such as norbornene, cyclopentadiene (CP) and dicyclopentadiene (DCP) in concentrations below 20 mol%.

The properties of ethylene random copolymers are known to be a strong function of the chain microstructure. Thus, in an effort to maintain the same homogeneous microstructure within the different copolymers investigated, they were synthesized with the same metallocene-type catalyst. Our main interest is focused on investigating if these comonomers, which chemically differ significantly from the ethylene unit, effect the structure of the copolymer melt. A different entropy of the melt from that of the 1-alkene type would be reflected in the thermodynamic and structural properties of these copolymers and those that evolve upon annealing of these materials. Rapidly crystallized copolymers are analyzed in an effort to compare the new data with data previously reported in similarly based copolymers (1).

Experimental

The copolymers studied were synthesized with the metallocene catalytic system *rac*-Et[Ind]₂ZrCl₂/MAO in toluene at 30°C or 60°C. The polymers were precipitated in a 1.5 % mixture of HCl in methanol, washed with ethanol and water and further dried to constant weight. Films were prepared in a Carver press at 150°C and quenched in water at 23°C ± 1°C.

The molecular characterization was obtained by standard GPC and solution ¹³CNMR techniques. The NMR of the samples chosen for this study was free of diads, triads or other blocks from the comonomer indicating a predominantly random distribution of the ethylene sequences. Except for the ethylene-4 methyl-1-pentene copolymers, the weight average molecular weight of all the copolymers ranged from 50,000 g/mol to 130,000 g/mol. The molecular weight of the ethylene-4-methyl-1-pentenes ranged from 30,000 g/mol to 43,000 g/mol. The Mw/Mn of all the copolymers is ~2. Selected samples were subject to TREF analysis as a qualitative test for homogeneity in the comonomer composition among the different molecules of a given copolymer. The interchain composition distribution, as analyzed by TREF, was very narrow for the ethylene-decenes and increased in breadth for the CP and DCP copolymers.

The thermal behavior was analyzed by differential scanning calorimetry using a Perkin-Elmer DSC-7 under nitrogen and connected to an intracooler that allows subambient temperature control. The DSC was calibrated for static temperature and thermal lag effects with indium. The degree of crystallinity at 20°C was obtained from the heat capacities (6) data and also from measurements of the densities of the rapidly crystallized samples in a 2-propanol triethylene glycol density gradient column calibrated with glass floats. The densities were converted to a degree of crystallinity by the relationship given by Chiang and Flory (7).

Results and Discussion

Melting behavior

The melting temperature-comonomer composition relation for the rapidly crystallized copolymers is given in Fig. 1. The data of the new copolymers plotted as closed symbols, are compared in this plot with reference data for random ethylene-1-alkene copolymers taken from reference 1 and represented by the solid line. The open symbols are the data for hydrogenated polybutadienes that are model ethylene-butene copolymers with narrow molecular weight distribution and uniform interchain composition. It is of interest that, in spite of the large variety of comonomer types, the melting temperatures of most of the copolymers investigated fall in the same

reference line. Thus, the results recently obtained in ethylene-norbornene copolymers (8) are now confirmed with ethylene dicyclopentadiene, and ethylene cyclopentadiene. The insertion of the ring in the chain does not modify the chain conformation in the melt in any significant manner. The fact that comonomers as different as butene, 4-methyl-1-pentene, decene, CP and DCP show the same melting temperature-composition relation indicates a similar partitioning behavior of the comonomer between the crystalline and non-crystalline regions. Because of the large size variation in these side groups, they cannot enter the lattice to any meaningful extent in bulk crystallized systems. The crystallization of these copolymers follows the expectations from Flory's equilibrium theory formulated on the basis of phase equilibrium of two components, only one of them crystallizable.

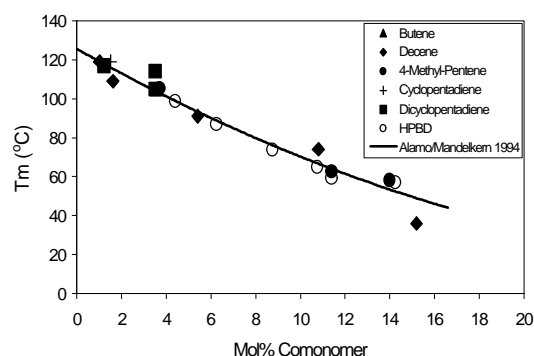


Figure 1 - Melting temperatures of rapidly crystallized ethylene copolymers as a function of comonomer composition

Degree of Crystallinity

The compositional dependence of the degree of crystallinity, normalized based on the mass fraction of ethylene and derived from heat of fusion of the rapidly crystallized samples, is shown in Fig 2. The data were obtained using a constant heat of fusion for the pure orthorhombic polyethylene crystal (290 J/mol). However, if the temperature dependence of the orthorhombic heat of fusion as listed in the ATHAS databank (237 J/mol at 20 °C) is used, the calculated crystallinity values will increase, but the trend with increasing comonomer content will be maintained. The solid line is the relation for the 1-alkene type copolymers extracted from reference 1. Substantial agreement is obtained between the degree of crystallinity of the new copolymers and the values for the hydrogenated polybutadienes and those of the 1-alkene type. The values of the 4-methyl-1-pentene copolymers are above the reference line due to the lower molecular weight of these copolymers compared to the rest (9). A lower molecular weight leads to less entanglements and, thus, less constraints to crystallization. The experimental values of Fig 2 are

much lower than those predicted by theory (1). First of all, the experimental crystallization conditions to obtain the data of Fig 2, are far from the equilibrium requirements and, second, kinetic factors control to a large extent the crystallization of these copolymers (10). Fig 2 indicates that the general trends followed by the 1-alkene copolymers are also followed by copolymers with bulkier structural irregularities. The levels of crystallinity vary from about 50% for copolymers with 1 mol% of comonomer to about 5% for a 16 mol% copolymer. The chemical nature of the structural irregularities has an insignificant influence on the crystallinity of rapidly crystallized samples.

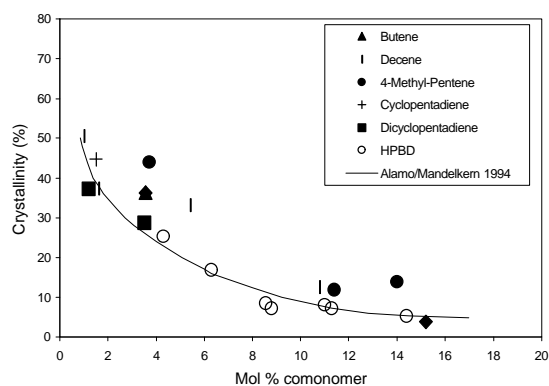


Figure 2 - Plot of degree of crystallinity calculated from heat of fusion as a function of comonomer composition

The levels of crystallinity determined from density measurements range from about 60% for 1 mol% comonomer to 40% for the 6 mol% in agreement with the data for the conventional 1-alkene type. However, these values are subject to possible variations of the specific volume of the amorphous (v_a) copolymer with comonomer type. The difference in (v_a) between ethylene 1-butene and ethylene dicyclopentadiene may not be negligible even at a low co-unit content.

Annealing effects

Compression molded films of the copolymers were initially prepared by quenching the melts (150°C) to 23°C in a water bath. They were further annealed at 20°C in the DSC cell for times up to about 1,000 min or annealed at room temperature (22-25°C) for the times that exceeded 1,000 min. We focus on the analysis, as a function of the comonomer type, of the time dependence of the low temperature endotherm that develops during annealing. The peak value of this endotherm for ethylene 1-butene ethylene-1 decene, ethylene 4-methyl-1-pentene and ethylene dicyclopentadiene follows a linear dependence with log time in agreement with the results obtained in ethylene-octenes (5). The values of the slopes and intercepts for a constant content of comonomer of ~3.6

mol% are given in Table 1. It is interesting that the values of the slope, which reflect the rate of change of structure or dynamics of the system during annealing, are basically identical for the 1-decene, 4-methyl 1-pentene and DCP comonomers. They are also very similar to the value reported for ethylene 1-octene of similar comonomer content. A slope of 1.25 was reported for a 3.4 mol % octene (5). However, the change of the melting temperature with time for 1-butene is significantly faster, as indicated by the higher value of the slope.

One could initially associate the difference in the slope of the 1-butene to compositional differences of the non crystalline region of this sample and the rest of the copolymers. This hypothesis is ruled out for two reasons, the partitioning of the comonomer in the different regions is the same for all the copolymers studied and there is no appreciable difference in the degree of crystallinity of the quenched samples before annealing. Therefore, we deduce that the average comonomer composition in the non-crystalline region of the quenched samples, is the same for all the copolymers, including the 1-butene. In this region the average comonomer content must be significantly higher than the overall copolymer composition. It is also unlikely that the non-crystalline regions of ethylene butenes develop higher constraints than those of the ethylene dicyclopentadienes. The higher rate of change in the 1-butene could be associated with a higher molecular diffusion in the non-crystalline regions.

Table I Time dependence parameters of low temperature endotherm (T_{m2}) of ethylene copolymers on annealing at 20 °C. According to the relation $T_{m2} = k + m \ln t$

Comonomer type	mol % comonomer	m	k
1-butene	3.56	1.53	23.0
1-decene	3.7*	1.20*	24.8*
4MP	3.7	1.22	26.4
DCP	3.5	1.18	24.6

Interpolated values

WAXS diffractograms of quenched and annealed copolymers showed insignificant differences as seen in Figure 3. However, the angular position of the amorphous halo scales linearly and in inverse proportion with the concentration of comonomer in the copolymer reflecting the increase of the average backbone carbon-carbon intermolecular distance associated with the interlammellar region (11).

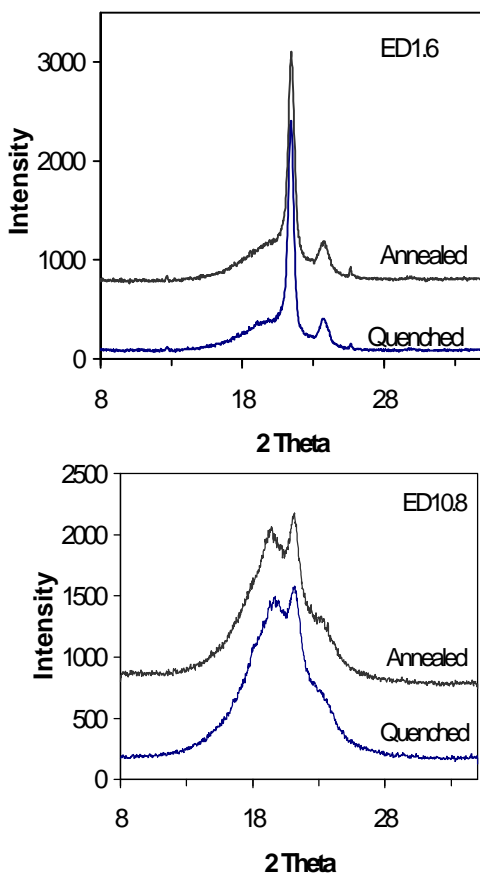


Figure 3.- WAXS diffractograms for quenched and annealed ethylene 1-decene (1.6 mol%) and ethylene 1-decene (10.8 mol%). Diffractograms of annealed samples are displaced in the y axis to facilitate distinction with those of the quenched samples

Conclusion

In summary the thermodynamic and structural behavior of rapidly crystallized ethylene copolymers with a large variety of comonomer types, including the 1-alkenes longer than propene and those of the cyclic type, can be explained on the basis of Flory's phase equilibrium theory. The observed melting temperatures are independent of the chemical nature of the comonomer. The molar entropy of fusion does not seem to be significantly affected by the copolymer

type. Significant differences in the annealing behavior are also not found between ethylene 1-decene, ethylene 4 methyl-1-pentene or ethylene dicyclopentadiene. Further evolution of the crystallinity during annealing is only a function of the fractional content of ethylene sequences of sufficient length to participate in crystallites that are stable at the annealing temperature. A higher rate of increase in the low melting temperature, which is associated with the isothermal annealing process, is found only for the ethylene butene copolymer studied.

Acknowledgements

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