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# Differential Scanning Calorimetry Studies of Ethylene–Propylene Copolymers

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ABSTRACT: A DSC examination of a series of ethylene–propylene copolymers together with their parent homopolymers has been made. Introduction of ethylene leads to a sudden drop in the glass transition temperature ($T_g$) of the polypropylene homopolymer (262 K) to values in the region of 214–222 K, depending on the overall composition. NMR analysis shows that the incorporation of ethylene and propylene into the copolymers is essentially random although the Al/Cr ratio in the catalyst does affect the tendency to block formation. Whereas only a few copolymers exhibit well-defined melting endotherms, the process of crystallization is observed in all samples. By cross correlation with NMR data, it is possible to assign the various exotherms to the crystallization of either ethylene or propylene blocks. The crystallization temperature ($T_c$) and the enthalpy of crystallization ($\Delta H_c$) decrease in step with the reduction in sequence length of the monomer blocks. A logarithmic plot of $\Delta H_c$ vs. either the mole fraction of ethylene or the mole fraction of ethylene triads is linear and indicates a minimum ethylene sequence length of between 9 and 10 for crystallization to occur.

## Introduction

Polyethylene and isotactic polypropylene are rigid plastics at normal temperatures due to the fact that the linear sequences of either type of unit have a strong tendency to crystallize. However, the two units are not able to cocrystallize satisfactorily in copolymers. Thus each type of unit is able to cause disruption in the crystallizability of the other, thereby increasing the inherent rotational flexibility of the two types of main-chain segments. This is manifested in the elastomeric character of the bulk material.

As the glass transition temperature ($T_g$) is a fundamental polymer characteristic and generally has a determining influence on the bulk properties of the material, the measurement of the $T_g$ of EP rubbers has attracted much attention over the years. Thus $T_g$ studies by techniques such as dilatometry,[1-4] coefficient of thermal expansibility,[5-7] NMR,[8] differential thermal analysis,[9-11] and DSC[12] have been reported. While there is a great variation of $T_g$ with composition for copolymers containing more than 65 mol % propylene, most commercial EP rubbers contain 30–65 mol % propylene and tend to show a very small variation of $T_g$ over the composition range for copolymers of comparable molecular weights. Thus $T_g$ alone does not provide much information about the actual composition and monomer sequence distributions in the copolymers. Since the contrasting elastomeric properties of the copolymers as compared to the homopolymers have been attributed to reduced crystallinities, the melting and crystallization of the polymers have become the subjects of studies over the years.[12,13] The crystallinity of the polymers is very much dependent on the chain length and composition, as well as the sequence distribution of the two types of monomers. Correlation of the various literature results of density and X-ray crystallinity data produces rather scattered graphs.[12] This may in part stem from the failure to characterize the polymers with respect to both molecular weight and monomer sequence distribution. In light of the above, we now report the results of DSC measurements for a series of well-characterized EP copolymers.

## Experimental Section

Polyethylene, polypropylene, and the various EP copolymers were prepared with a chemically modified chromium catalyst in combination with $AlEt_2Cl$ at 40 °C as previously described.[14,15] All the samples, except the homopolymers, were prepared at the same temperature and total monomer pressure. The experimental conditions of copolymerization are summarized in Table I. The samples of series A were prepared at a constant Al/Cr ratio of 10, while the composition of the monomer mixture was varied progressively. The B series was designed to probe the effect of variation in Al/Cr ratio on copolymer composition at constant monomer ratio.

$^{13}C$ NMR spectra were recorded on a JEOL JNM PS-100 spectrometer, equipped with a PET-100 FT system, operating at 25.14 MHz with full proton noise decoupling. Spectra were recorded at a temperature of 120 °C with pulse at 13.5 μs, a repetition rate of 7.0 s, and a sweep width of 5000 Hz. The monomer sequence distributions in the copolymers were determined from NMR data by the method of Doi et al.[16]

The molecular weight distributions of polypropylene and the various copolymers were measured at 140 °C with a Showo Denko gel permeation chromatograph fitted with a Shodex 80M column (ASOM/SX2), using 1,2-dichlorobenzene as solvent. The polyethylene sample was not soluble in this solvent and could not be measured.

Calorimetric measurements were made with a Perkin-Elmer DSC-2C instrument equipped with a liquid nitrogen subambient accessory. The temperature scale was calibrated at 20 K/min against indium (429.78 K), water (273.15 K), and mercury (234.28 K). The heat of fusion of indium (6.80 cal/g) was used as a calorimetric calibration. Melting temperatures, crystallization temperatures, heats of fusion, and heats of crystallization were calculated with the Perkin-Elmer standard TADS program. Unless otherwise stated, all cooling and heating runs were carried out at a scan rate of 20 K/min on samples of 5–10 mg encapsulated in standard aluminum pans.

Melting and crystallization temperatures are quoted as the maximum and minimum values, respectively, and not as onset temperatures.

## Results and Discussion

**Molecular Weight Distribution.** The results of the GPC studies on the polymers are summarized in Table I. The molecular weight distribution as characterized by the

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**Table I**
**NMR and GPC Data of EP Copolymers**

| | sample no. | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A1 | A2 | A3 | A4 | A5 | A6 | A7 | A8 | A9 | B1 | B2 | B3 | B4 | B5 |
| Experimental Conditions: Composition of Monomer Mixture Used | | | | | | | | | | | | | | |
| %E | 0 | 17 | 27 | 38 | 49 | 61 | 69 | 78 | 100 | 38 | 38 | 38 | 38 | 38 |
| %P | 100 | 83 | 73 | 62 | 51 | 39 | 31 | 22 | 0 | 62 | 62 | 62 | 62 | 62 |
| Al/Cr | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 2 | 5 | 8 | 15 | 20 |
| Molecular Weight Distribution from GPC Data | | | | | | | | | | | | | | |
| $M_w/10^5$ | 2.5 | | | 0.66 | 1.5 | 2.1 | 2.8 | | na | 0.93 | 0.79 | 0.94 | 1.4 | 3.2 |
| $M_n/10^4$ | 3.5 | | | 3.2 | 4.9 | 5.7 | 5.6 | | na | 3.0 | 2.9 | 2.4 | 4.9 | 4.0 |
| $Q$ | 7.0 | | | 2.1 | 3.0 | 3.8 | 5.0 | | na | 3.1 | 2.7 | 3.9 | 2.8 | 7.9 |
| Copolymer Composition from $^{13}C$ NMR Data | | | | | | | | | | | | | | |
| %E | 0 | 21 | 42 | 52 | 61 | 73 | 76 | 81 | 100 | 50 | 51 | 51 | 57 | 60 |
| %P | 100 | 79 | 58 | 48 | 39 | 27 | 24 | 19 | 0 | 50 | 49 | 49 | 43 | 40 |
| Sequential Distribution of Copolymer from $^{13}C$ NMR Data | | | | | | | | | | | | | | |
| PP | 1.00 | 0.63 | 0.37 | 0.30 | 0.15 | 0.08 | 0.07 | 0.08 | 0.00 | 0.31 | 0.28 | 0.30 | 0.21 | 0.20 |
| PE | 0.00 | 0.09 | 0.46 | 0.46 | 0.42 | 0.37 | 0.36 | 0.26 | 0.00 | 0.40 | 0.44 | 0.42 | 0.42 | 0.41 |
| EE | 0.00 | 0.08 | 0.17 | 0.25 | 0.43 | 0.56 | 0.58 | 0.69 | 1.00 | 0.29 | 0.28 | 0.28 | 0.37 | 0.39 |
| PPP | 1.00 | 0.58 | 0.32 | 0.17 | 0.13 | 0.06 | 0.04 | 0.05 | 0.00 | 0.23 | 0.27 | 0.21 | 0.17 | 0.16 |
| PPE | 0.00 | 0.13 | 0.13 | 0.19 | 0.11 | 0.09 | 0.07 | 0.06 | 0.00 | 0.12 | 0.12 | 0.11 | 0.13 | 0.08 |
| EPE | 0.00 | 0.09 | 0.11 | 0.17 | 0.17 | 0.12 | 0.11 | 0.09 | 0.00 | 0.15 | 0.12 | 0.14 | 0.14 | 0.14 |
| PEP | 0.00 | 0.06 | 0.16 | 0.14 | 0.09 | 0.07 | 0.08 | 0.04 | 0.00 | 0.12 | 0.13 | 0.11 | 0.10 | 0.10 |
| PEE | 0.00 | 0.07 | 0.18 | 0.16 | 0.20 | 0.22 | 0.21 | 0.18 | 0.00 | 0.18 | 0.17 | 0.24 | 0.20 | 0.21 |
| EEE | 0.00 | 0.04 | 0.10 | 0.16 | 0.30 | 0.43 | 0.49 | 0.59 | 1.00 | 0.22 | 0.19 | 0.19 | 0.26 | 0.30 |

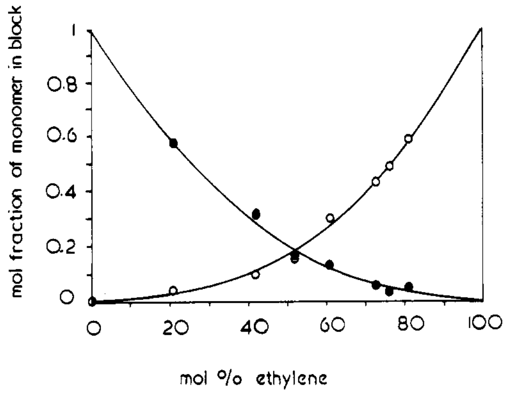

**Figure 1.** Variation of monomer triad sequences with overall copolymer composition: (○) EEE sequence; (●) PPP sequence.

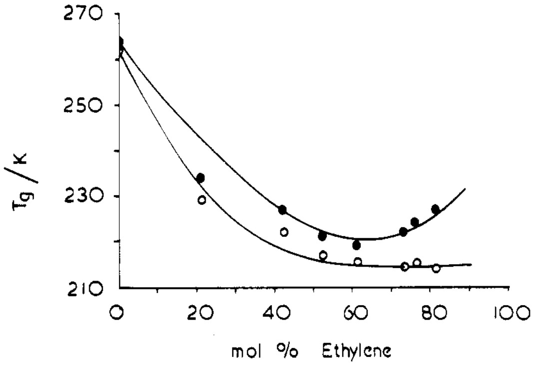

**Figure 2.** Dependence of $T_g$ on copolymer composition: (●) midpoint value; (○) onset value.

$Q$ value ($\bar{M}_w/\bar{M}_n$) varies with the copolymer composition. The lowest $Q$ value of 2.1 was observed with an ethylene content of 52%. Above this composition the $Q$ value increases with the ethylene content. However, the copolymer $Q$ values are all considerably smaller than the $Q$ value for polypropylene prepared under similar conditions. Varying the Al/Cr ratio affects both the copolymer composition and the molecular weight distribution. At Al/Cr ratios above 10, there is a significant increase of ethylene content of about 10%, together with a broadening of molecular weight distribution.

**NMR Characterization.** The NMR characterization of the polymers is summarized in Table I. Not unexpectedly, at constant Al/Cr ratio, the ethylene content of the copolymer increases with increasing amount of ethylene in the monomer feed. The copolymer composition was cross-checked by using the method of Randall[17] and was found to agree well within 1%. As can be seen from the sequence distribution, the monomers are distributed fairly randomly in the copolymers.

The fractions of triad sequences are of particular interest since they reflect the amount of monomer blocks in three or more units in the copolymers. Figure 1 summarizes the variation of the copolymer triad content as the composition changes. As expected, under similar copolymerization conditions, copolymers with a higher mole percent of a particular monomer also contain a higher amount of the monomer in triad sequences. The total mole fraction of triads approaches a minimum when the copolymer contains 35–65% ethylene, which incidently is the composition range for most commercial EP rubbers.

By comparison of the sequence distributions of the samples in the B series with sample A4 of the A series, it is obvious that the variation of the Al/Cr ratio affects the composition as well as the length of the blocks in the copolymer, although the same composition of monomer mixture was used in the copolymerization. A low Al/Cr ratio tends to generated both longer ethylene and propylene blocks as can be seen in samples B1, B2, and B3, although the mole percent of each monomer is more or less the same. On the other hand, when the Al/Cr ratio is much higher than 10, the propylene content in the copolymer is reduced together with its triad sequence, as is evident in samples B4 and B5. When the conditions are changed from A4 to those of B5, the overall ethylene content increases by about 10% but the amount of ethylene triads is almost doubled. This may be due to the excess cocatalyst competing more effectively with propylene for adsorption at active sites.[18]

**DSC Analysis.** Figure 2 shows the dependence of $T_g$ on the copolymer composition. The variation of midpoint $T_g$ with composition is very similar to that reported by Baldwin et al.[12] Attempts to determine the $T_g$ of polypropylene (A1) by a quench-cooling method[19] proved unsuccessful. However, the procedure described by Wun-

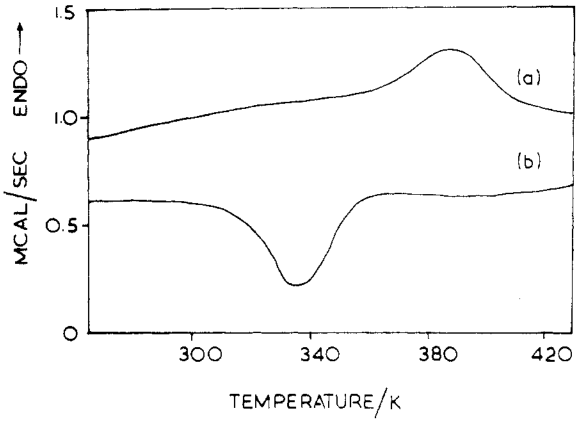

**Figure 3.** DSC scan of copolymer A2 containing 79% propylene: (a) heating; (b) cooling.

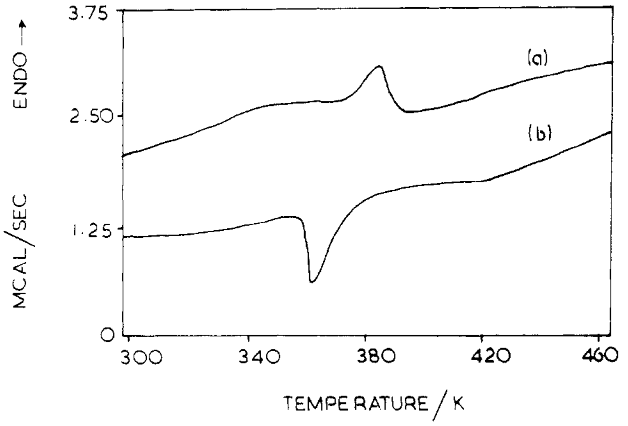

**Figure 4.** DSC scan of copolymer A8 containing 81% ethylene: (a) heating; (b) cooling.

derlich et al.,[20] whereby the sample was cooled at 0.5 K/min from the melting point and then heated at 50 K/min, enabled values of $T_g$ (midpoint) of 264 K and $T_g$ (onset) of 262 K to be recorded. The glass transition of polyethylene was not observable by any of these methods. Perhaps, as indicated in Figure 2, the difference between $T_g$(onset) and $T_g$(midpoint) increases tremendously as the composition approaches 100% ethylene. This causes the small change of heat capacity ($\Delta C_p$) at the transition point to spread over a wide temperature range, thus hindering the observation of the glass temperature in a DSC scan.

Figure 3 shows the DSC scan of one of the copolymers. Both the melting and crystallization peaks are small but distinctively observable. This particular sample contains 58 mol % propylene in blocks of three or longer units. The difference between the values of the crystallization temperature ($T_c$) and the melting temperature ($T_m$) is 50 K, which is similar magnitude to the difference between $T_c$ and $T_m$ of the propylene homopolymer (44 K). Thus the observed crystallization in this sample may be assigned to the presence of propylene blocks. On the other hand, Figure 4 shows the DSC scan of an ethylene-rich copolymer (43 mol % ethylene in blocks of three or longer units). The difference between the values of $T_c$ and $T_m$ is only 29 K, which is similar to the corresponding value for polyethylene (24 K). The crystallinity of the copolymer is attributed to the presence of ethylene blocks.

Table II summarizes the results of the DSC studies on the series of copolymers described in Table I. Although only 5 copolymers display distinctive melting peaks on heating, all of the 13 samples showed crystallization exotherms during the cooling cycles. In fact a few of them displayed more than one crystallization exotherm due to the presence of multiple types of blocks. The failure to observe melting endotherms is probably a consequence of a very broad melting range, which reduces the sensitivity of detection. Thus it appears that monitoring the crystallization process is more discerning in the characterization of such polymers since the polymer blocks crystallize over fairly narrow ranges independently of one another.

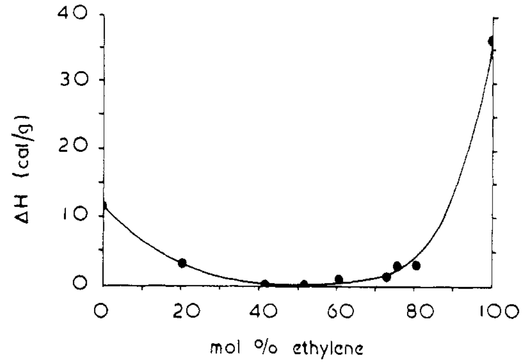

**Figure 5.** Dependence of crystallization enthalpy on overall copolymer composition.

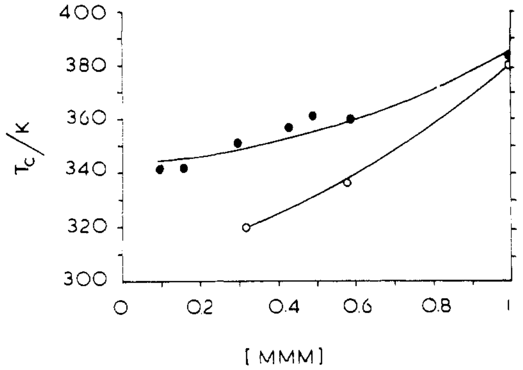

**Figure 6.** Variation of crystallization temperature with triad content: (●) EEE sequences; (○) PPP sequences.

While $T_c$ is dependent on both the type and length of the monomer block, the enthalpy of crystallization ($\Delta H_c$) would reflect the amount of such blocks in the polymers that are able to crystallize. The polypropylene sample A1 has a molecular weight similar to that of the copolymers. It exhibits a $T_c$ of 380 K with $\Delta H_c$ of −11.6 cal/g. Isotactic polypropylene of higher stereoregularity is known to have a higher $T_c$ and larger $\Delta H_c$ due to more extensive crystallinity.[21] Polyethylene (sample A9) exhibits a $T_c$ of 384 K with $\Delta H_c$ of −37.1 cal/g. The higher value of $-\Delta H_c$ and smaller difference between $T_c$ and $T_m$ of polyethylene as compared with those of polypropylene can be attributed to the fact that polyethylene crystallizes more readily than polypropylene, forming polymer crystallites of greater stability. In comparison, the values of $-\Delta H_c$ for the propylene blocks in copolymers of the A series range from 2% to 28% of the value for polypropylene. On the other hand, ethylene blocks exhibit $-\Delta H_c$ values in the range 0.1–8% of that of the parent homopolymer.

Figure 5 shows the result of plotting $-\Delta H_c$ vs. the copolymer composition. The smallest crystallization exotherms occur in the composition range of 35–65% ethylene, which as shown by the NMR data earlier, corresponds to the smallest amount of triad sequences.

Based on $T_c$, $\Delta H_c$, the mole fraction of triads, and in some cases $T_m$ and $\Delta H_m$, it is possible to assign each crystallization peak of polymer samples A1–A9 in Table II to either propylene or ethylene blocks. The results are summarized in Figure 6. The crystallization temperature due to propylene blocks is depressed from a value of 380

**Table II**
**DSC Studies of EP Copolymers**

| | polym comp | | blocky fraction[a] | | $T_g$, K | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| sample code | % E | % P | EEE | PPP | onset | midpt | $-\Delta H_c$, cal/g | $T_c$(min), K | $\Delta H_m$, cal/g | $T_m$(max), K | note[b] |
| Copolymers Prepared at Constant Al/Cr but Different E/P | | | | | | | | | | | |
| A1 | 0 | 100 | 0 | 1 | 262 | 263 | 11.6 | 380 | 11.6 | 424 | p |
| A2 | 21 | 79 | 0.04 | 0.58 | 229 | 234 | 3.2 | 336 | 3.42 | 386 | p |
| A3 | 42 | 58 | 0.1 | 0.32 | 222 | 227 | 0.17 | 320 | | | p |
| | | | | | | | 0.04 | 342 | | | e |
| A4 | 52 | 48 | 0.16 | 0.17 | 217 | 221 | 0.09 | 342 | | | e |
| A5 | 61 | 39 | 0.3 | 0.13 | 215 | 219 | 0.74 | 351 | | | e |
| A6 | 73 | 27 | 0.43 | 0.06 | 214 | 222 | 1.3 | 357 | 0.98 | 386 | e |
| A7 | 76 | 24 | 0.49 | 0.04 | 215 | 224 | 2.8 | 361 | | | e |
| A8 | 81 | 19 | 0.59 | 0.05 | 214 | 227 | 3 | 360 | 2.21 | 384 | e |
| A9 | 100 | 0 | 1 | 0 | na | na | 37.1 | 384 | 48.7 | 488 | e |
| Copolymers Prepared at Different Al/Cr but Constant E/P | | | | | | | | | | | |
| B1 | 50 | 50 | 0.22 | 0.23 | 216 | 221 | 1.13 | 367 | 0.21 | 386 | e |
| B2 | 49 | 51 | 0.19 | 0.27 | 215 | 223 | 0.18 | 332 | | | p |
| | | | | | | | 0.06 | 361 | | | e |
| B3 | 51 | 49 | 0.19 | 0.21 | 217 | 221 | 0.11 | 360 | | | p |
| | | | | | | | 0.05 | 334 | | | p |
| | | | | | | | 0.03 | 343 | | | e |
| B4 | 57 | 43 | 0.26 | 0.17 | 215 | 222 | 0.31 | 352 | | | e |
| B5 | 60 | 40 | 0.3 | 0.16 | 217 | 224 | 0.93 | 356 | 0.59 | 388 | e |

[a] PPP indicates mole fraction of propylene triads in copolymer and EEE indicates mol fraction of ethylene triads in copolymer. [b] p indicates crystallinity peak due to propylene units and e indicates crystallinity peak due to ethylene units.

K for the homopolymer to only 320 K for a copolymer containing 32% propylene triads. At lower propylene block concentration no crystallization is detectable. On the other hand, $T_c$ due to ethylene blocks ranges from 385 to 342 K, and crystallization exotherms were observed even when the mole fraction of ethylene triads is as low as 0.1. As expected, at similar levels of triad content, the ethylene blocks crystallize more effectively than their propylene counterparts, resulting in a higher enthalpy change and a narrower crystallization temperature range.

As discussed earlier, based on the $^{13}$C NMR data, the use of low Al/Cr ratios results in higher amounts of both propylene and ethylene blocks (samples B1, B2, and B3) as compared with the control sample (A4), prepared with an Al/Cr ratio of 10 and the same monomer feed. This is confirmed by the higher crystallinity of these samples (Table II). In fact, both samples B2 and B3 show crystallization of propylene blocks besides having larger crystallization exotherms for ethylene blocks. The $T_c$ of the ethylene blocks is as high as 360 K even though it contains only 19% ethylene triad. Similarly $T_c$ of propylene blocks was observable even when samples contain only 21% propylene triads.

On the other hand, copolymers B4 and B5, which were prepared with higher Al/Cr ratios, display values of $-\Delta H_c$ due to ethylene blocks which are 3–10 times that of the control value. This again is in good agreement with the conclusion from NMR studies that high Al/Cr ratios reduced the propylene content and increase the length of ethylene blocks in the copolymers.

Recently,[22] in DSC studies of linear low-density polyethylenes, it was shown that the enthalpy of fusion of the ethylene segments of the copolymers was a function of the ethylene sequence length. Consequently, it was of some interest to see whether similar dependencies would hold for these EP copolymers where the ethylene contents are spread over a much wider range. By the assumption that only uninterrupted ethylene sequences undergo crystallization, it is to be anticipated that

$$\Delta H_c = kP_E^{\,n} \tag{1}$$

where $k$ is a constant that may be dependent on parameters such as molecular weight and $Q$, $P_E$ is the mole fraction of ethylene in the copolymer, and $n$ represents the minimum sequence length for crystallization to occur.

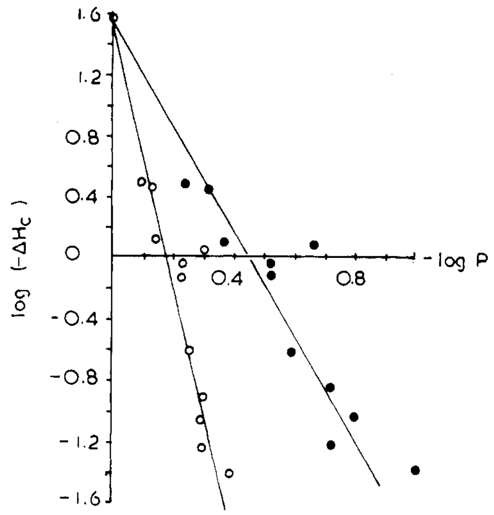

**Figure 7.** Logarithmic plot of $\Delta H_c$ vs. ethylene content: (○) mole fraction $P_E$; (●) triad fraction $P_{EEE}$.

In the present work the NMR analysis permits the evaluation of both $P_E$ and the mole fraction of ethylene triads ($P_{EEE}$). If the ethylene distribution in the copolymer is random, as described by Bernoullian statistics, then $P_{EEE} = P_E^{\,3}$. If this relationship does not hold, then the crystallization enthalpy should fit more closely the equation

$$\Delta H_c = kP_{EEE}^{\,n/3} \tag{2}$$

Figure 7 illustrates logarithmic plots of $\Delta H_c$ vs. the ethylene content for both the functions $P_e$ and $P_{EEE}$. It is apparent that the plot derived from the ethylene mole fraction is an equally good fit as that from the triad content. This suggests that the incorporation of ethylene into the copolymer may be treated as random to a first approximation. Values of $n$ derived from the slopes of the two plots are 10 (triad curve) and 9 (mole fraction curve), respectively. These values are somewhat lower than the value of $n = 14$ derived from enthalpy of fusion data on LLDPE sample.[22]

**Registry No.** (Ethylene)·(propylene) (copolymer), 9010-79-1; polyethylene (homopolymer), 9002-88-4; polypropylene (homopolymer, 9003-07-0.

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# Quantitative Measurement of Chain Folding in 1,4-*trans*-Polyisoprene Crystals by Carbon-13 NMR Spectroscopy

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ABSTRACT: The amorphous fraction of solution-grown crystals of 1,4-*trans*-polyisoprene (TPI) is considered to be at the surface of the crystals and contains two components, chain folds and noncrystallizing chain ends or cilia. We report the development of an analytical method for the quantitative measurement of the average surface fold and crystal stem lengths in addition to the degree of crystallinity for TPI. This method uses the combination of selective epoxidation of the double bonds in the surface folds and carbon-13 solution NMR measurements. The crystals were suspended in amyl acetate and reacted with *m*-chloroperbenzoic acid at 0 °C until the rate diminished to zero. It was expected that the fold material would react completely and that the crystal stems would not react at all, producing a block copolymer structure. The carbon-13 NMR spectra of the resultant copolymer were analyzed with the aid of TPI and squalene epoxidized in homogeneous solution to several levels of reaction. The NMR data indicate that epoxidation preserves the stereochemistry of the double bonds, producing only the trans oxirane rings. The TPI preparation examined in this study is found to have an average surface fold length of 7.4 monomer units and an average stem length of 4.92 nm. The degree of crystallinity is observed to be 58.9%. The measure of fold length is in good agreement with an earlier estimate based on the lamellar thickness given by electron microscopy for this same TPI sample. The results of this work indicate that the method of nondestructive chemical transformation of the surface folds followed by NMR analysis provides a detailed picture of the morphology of TPI solution-grown crystals.

## Introduction

The nature of the noncrystalline material at the surface of polymer crystals has been of interest to polymer scientists for many years.[1,2] Of particular concern are the length of the surface folds and the extent of adjacent reentry. However, most physical methods used to evaluate the amorphous fraction of polymer samples measure the total noncrystalline content and provide little detail as to the nature of the chains in the surface folds. Using a chemical modification technique, Williams et al.[3] found a high degree of adjacent reentry in the chain folding of solution-grown crystals of polyethylene. A similar study[4] using oxidative degradation followed by GPC measurements on melt-crystallized samples of polyethylene indicated the presence of at least some adjacent reentry. Other studies[5] indicate that the crystal surface is rough and that there is some disordered material at the surface. In previous work[6] we combined the technique of epoxidation at the crystal surface with solution NMR analysis to examine in a quantitative fashion the nature of the chain folds in solution-grown crystals of 1,4-*trans*-polybutadiene (TPBD). Values for the average fold length uncorrected for the presence of cilia varied from 3.0 to 5.6 monomer units, suggesting that adjacent reentry predominates. In a subsequent analysis[7] we used solid-state NMR experiments to examine the motion of the surface folds before and after epoxidation of the polymer. We found that the presence of oxirane rings significantly reduces the motion of the fold as compared with that of the unreacted chain fold, although the motion remains more rapid than that of the crystal stems.

In the present work the combination of selective epoxidation of the double bonds in the surface folds followed by solution NMR measurements is developed for the study of the noncrystalline fraction of solution-grown crystals of 1,4-*trans*-polyisoprene (TPI). The amorphous fraction is considered to be at the surface of the crystal and contains two components, chain folds and the noncrystallizing chain ends or cilia. The selective epoxidation of the double bonds in the fold region is accomplished with the use of *m*-chloroperbenzoic acid (MCPBA), a mild, quantitative, but highly selective reagent.