Polymer Vol. 36 No. 13, pp. 2559-2565, 1995
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0032-3861/95/$10.00+0.00

Studies of molecular motions in novel syndiotactic alternating ethylene-propylene crystalline copolymer by dynamic mechanical analysis and solid-state ^{13}C n.m.r.

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(Received 18 November 1994; revised 25 January 1995)

A syndiotactic alternating ethylene-propylene (SYN-ALT-EP) copolymer was synthesized. Two molecular relaxation processes (α and β relaxations) have been found below room temperature via dynamic mechanical analysis (d.m.a.): the α relaxation at -60°C and the β relaxation at -125°C. The apparent activation energy of the α relaxation is 285 kJ mol^{-1}, and the activation energy of the β relaxation is 43 kJ mol^{-1} based on the Arrhenius equation. Molecular motion in SYN-ALT-EP copolymer was probed by solid-state ^{13}C n.m.r. experiments. At temperatures above the glass transition temperature (T_g) there are two major molecular motions in this copolymer: a backbone motion (the rotational motion about single bonds) and a methyl side group rotation. The backbone motion is frozen below T_g, but there is still a methyl rotation. As the temperature is further decreased to about -175°C, well below the β-transition observed in d.m.a., the methyl side group rotation slows down, suggesting that the methyl rotation may be associated with the observed β relaxation process.

(Keywords: molecular relaxations; solid-state n.m.r.; ethylene-propylene copolymer)

INTRODUCTION

Polyolefins have served as an important class of commodity polymers for their desired physical properties and many applications[1-5]. The stereoregular isotactic and syndiotactic polypentadienes polymerized by Ziegler-Natta coordination catalysts have been studied and characterized by Natta and co-workers[6-8], Ciampelli and co-workers[9], Beebe and co-workers[10], Ellgert and Ritter[11], Gatti and Carbonaro[12], and Aubert and co-workers[13]. It is crucial that monomer isomeric purity be assured when a high degree of methyl side group tacticity is expected[14].

By taking advantage of the unique structural order and regularity of syndiotactic *cis*-1,4-polypentadiene (*cis*-PPD), we were able to convert this polymer into a novel syndiotactic alternating ethylene-propylene (SYN-ALT-EP) copolymer by a controlled hydrogenation scheme. This latter synthesis overcomes two major inherent difficulties in traditional methods of copolymerizing ethylene and propylene. First, there are no statistical runs of pure ethylene or pure propylene units. Second, the stereoregularity is ensured by the Ziegler-Natta coordination catalyst.

The synthesis of this copolymer has provided a well-defined, crystallizable SYN-ALT-EP copolymer with a melting temperature of 39°C. This copolymer can be crystallized at ambient temperatures and has a well-defined crystalline morphology. This report describes the local molecular motions and relaxations observed in the SYN-ALT-EP copolymer using both dynamic mechanical analysis (d.m.a.) and solid-state ^{13}C n.m.r. spectroscopy over a large range of temperature.

EXPERIMENTAL

Materials and sample preparation

The syndiotactic *cis*-PPD prepolymer was synthesized by using *trans*-1,3-pentadiene monomer in hexane with a triethylaluminium-nickel octanoate-boron trifluoride dibutyl etherate initiator[15,16]. Following the preparation of the *cis*-PPD prepolymer, the SYN-ALT-EP copolymer was synthesized by hydrogenation of *cis*-PPD prepolymer using the diimide reduction scheme[17-19]. *p*-Toluenesulfonhydrazide (TSH) was used as the source of a diimide reagent, and the hydrogenation process was conducted at 130°C in *p*-xylene for 9 h. Dilute solutions of SYN-ALT-EP were examined in 200 MHz proton n.m.r. experiments to check the extent of the hydrogenation reaction in the prepolymer. No unsaturation was detected in the double bond region (around 5.1-5.3 ppm). That is, >99% of the double bonds of *cis*-PPD prepolymer were saturated successfully. Furthermore, high resolution analytical ^{13}C n.m.r. spectra do not detect any resonance

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in the olefinic region (around 120–140 ppm) and provide additional evidence for a very successful hydrogenation reaction. The number-average molecular weight of SYN-ALT-EP was determined to be 4.6×10^4 g mol^{-1} by membrane osmometry at 37 ± 0.1°C in toluene. The weight-average molecular weight was also determined to be 1.88×10^5 by using g.p.c. with an on-line multi-angle laser light scattering (MALLS) detector at 30 ± 0.1°C in tetrahydrofuran (THF). The intrinsic viscosity was determined to be 1.69 dl g^{-1} by using a single bulb Ubbelohde capillary viscometer at 37 ± 0.1°C in toluene. The detailed steric sequence distribution and tacticity determinations, solution state characterization, the studies of both crystallization and melting behaviour, and morphology of SYN-ALT-EP copolymer will be reported elsewhere[20].

The SYN-ALT-EP copolymer was examined by wide-angle X-ray diffraction (WAXD), dynamic mechanical properties, and solid-state ^{13}C n.m.r. spectroscopy. Thin films of the copolymer were made by preheating the as-prepared copolymer directly to 80°C for 5 min. The samples were compression moulded at a pressure of 0.49 MPa for another 3 min. The thin films were then annealed at 24°C in a thermostat bath for 60 days to achieve nearly complete crystallization. Several thin films were cast from a 0.5% benzene solution to give a thickness of about 1 μm for polarized light microscopy (PLM) studies. Then, the films were annealed at 24°C in the microscope hot stage after the preheating treatment described in the next section.

Instrumentation and experiments

D.s.c. measurements were carried out using a Dupont 9900 thermal analysis system. A sample weight of near 10 mg was used. The temperature and heat of transition scales were carefully calibrated at a heating rate of 10°C min^{-1}.

A reflection mode WAXD experiment was conducted using a Rigaku 12 kW rotating anode generator (Cu Kα) coupled with a diffractometer. The X-ray beam was monochromatized using a graphite crystal with a wavelength of 0.154 nm. The full 2θ angle was scanned from 8 to 30° with a scanning rate of 2° min^{-1}.

The dynamic mechanical experiments were performed on a Seiko DMS200 station. The thin film dimensions were measured to be $8.0 \times 6.5 \times 0.12$ mm ($l \times w \times d$). The temperature was scanned from −150 to 30°C at a heating rate of 2°C min^{-1}. The DMS200 tension module was used in a temperature sweeping mode in experiments over the frequency range 0.1–10 Hz.

The PLM experiments were carried out on an Olympus BH-2 optical microscope in conjunction with a Mettler hot stage (FP82) controlled by a Mettler FP90 central processor. The SYN-ALT-EP specimen was prepared by casting a drop of the 0.5% benzene solution, preheated in a sealed volumetric flask at 50°C for 30 min, on a glass slide. Following the preheating treatment, the film specimen was further dried in a vacuum oven for 5 min at 24°C, and then dried under vacuum for another 15 min at 75°C. Finally, the specimen was immediately transferred to the microscope hot stage at the desired temperature for isothermal crystallization.

The solid-state ^{13}C n.m.r. experiments were carried out on a Chemagnetics CMX200 spectrometer operating at 50 MHz for ^{13}C using a Doty 7 mm variable temperature magic angle spinning (MAS) probe. The 90° pulse widths for ^{1}H and ^{13}C are 6.0 and 8.0 μs, respectively. The sample spinning speed was regulated at 3 kHz for room temperature and at 2 kHz for −75°C and −175°C. Conventional single pulse excitation with decoupling of protons during acquisition (Bloch decay) and also cross-polarization (CP)-MAS were performed at room temperature, −75°C and −175°C. For the CP-MAS measurements, the contact time was chosen to be 1 ms. The variable contact time experiments were performed at 22°C ranging from 0.05 to 18 ms. For each contact time 100 data acquisitions were averaged. The ^{1}H spin-locked field was about 30 kHz. The ^{13}C spin-lattice relaxation times (T_1) were measured using conventional inversion–recovery at room temperature, and Torchia's method[21] at −75°C, and −175°C. The variable times ranged from 0.01 to 10 000 ms. The standard deviation for curve-fitting of the relaxation time data is about 10% and the correlation coefficient is >0.90. The concentration of structural defects (such as head-to-head structures) is estimated to be <5% from the observation of high-resolution liquid-state ^{13}C n.m.r. Therefore, the influence of defects on the motional behaviour discussed later will not be considered.

RESULTS AND DISCUSSION

Structure, morphology and thermal properties of SYN-ALT-EP copolymer crystals

From d.s.c. experiments this hydrogenated copolymer possesses a glass transition temperature (T_g) of −57°C and a melting temperature (T_m) of 39°C, as shown in *Figure 1*. In contrast, polyethylene (PE) has a T_g of −36°C and a T_m° of 142°C, and syndiotactic polypropylene (S-PP) has a T_g of 0°C and a T_m° of 160°C[22–24]. The equilibrium melting temperature depends upon both the enthalpy and entropy changes during crystal melting. The lower melting temperature of SYN-ALT-EP copolymer may be an indication of either loosened chain packing in the crystals (which leads to a small Δh_f°) or a long range rotational order in the crystals (which leads to a large ΔS_f°). We speculate that the former is responsible for this low melting temperature. *Figure 2* shows a WAXD pattern of the SYN-ALT-EP copolymer which was

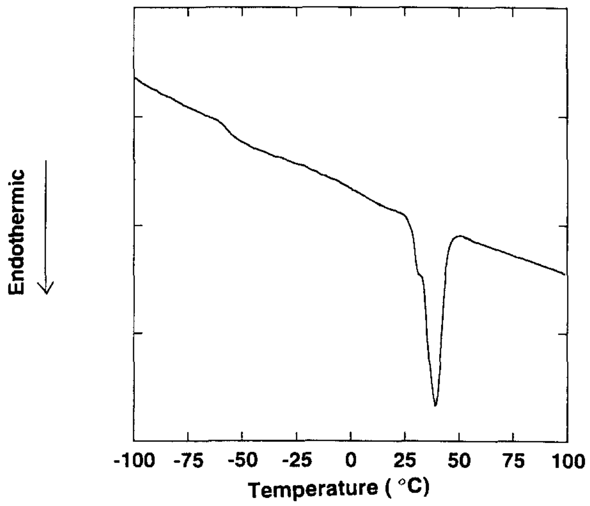

Figure 1 D.s.c. thermogram of as-prepared SYN-ALT-EP copolymer directly after the hydrogenation reaction and vacuum drying process. ($T_g = -57$°C; $T_m = 39$°C; $M_w = 1.88 \times 10^5$; heating rate = 10°C min^{-1})

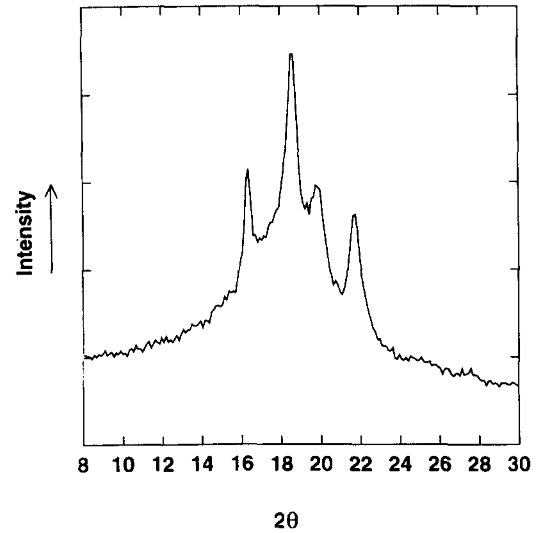

Figure 2 WAXD pattern of SYN-ALT-EP thin film crystallized at 24°C for 60 days

annealed at 24°C for 60 days. Four distinct diffraction peaks ($2\theta = 16.3$, 18.5, 19.8 and 21.7°) are detected, and they are different from both PE ($2\theta = 21.6$ and 23.9°) and S-PP ($2\theta = 12.2$, 15.8, 18.8 and 20.8°)[24,25]. These diffraction peaks indicate that crystallization of this copolymer is not hindered by any possible block sequences of PE or S-PP segments, and therefore, SYN-ALT-EP exhibits its own crystal unit cell symmetry and dimensions. By heating the sample up to 75°C, we are able to obtain the WAXD pattern of a totally amorphous SYN-ALT-EP copolymer. The weight per cent crystallinity (ω^c) has thus been determined to be 29%.

Earlier studies on ethylene–propylene copolymers[26] indicate that the crystallinity decreases from 90 to 40% by introducing only five to six methyl branches per 100 carbon atoms in a PE chain. A further increase of the number of the methyl branches to 18–20 branches per 100 carbon atoms of the backbone chain leads to a complete loss of crystallinity. In contrast, for SYN-ALT-EP copolymer there are 25 methyl branches per 100 carbon atoms of the backbone chain in which ethylene and propylene monomers are alternately arranged. Therefore, it is evident that a long range sequential steric order is present in the chain conformation of this copolymer. PLM observations on a solution-cast thin film show concentric banded spherulite patterns after crystallization at 24°C for 128 h (*Figure 3*). Such optical behaviour is characteristic of co-twisting lamellae during the spherulitic growth in this copolymer. A periodically varying orientation of the lamellae along the radial direction of spherulite is the origin of this banded texture which is similar to that of the PE spherulitic pattern; yet it is different from the axialitic pattern of S-PP.

Dynamic mechanical behaviour of SYN-ALT-EP copolymer

Two distinct relaxation processes can be identified below ambient temperatures based on the dynamic mechanical data (E', E'' and $\tan\delta$) at five different frequencies for annealed thin films of SYN-ALT-EP copolymer as shown in *Figures 4* and *5*. The α relaxation occurs around −59°C (at 1 Hz) and corresponds to the T_g observed in the d.s.c. thermogram in *Figure 1*. The β relaxation occurs around −125°C (at 1 Hz) and therefore, is a subglass relaxation process. For the α relaxation a simple Arrhenius relationship should not be used due to the involvement of co-operative motion in polymer chain segments which is not a single frequency relaxation. However, since the logarithmic frequency range used in the dynamic mechanical measurements is not larger than

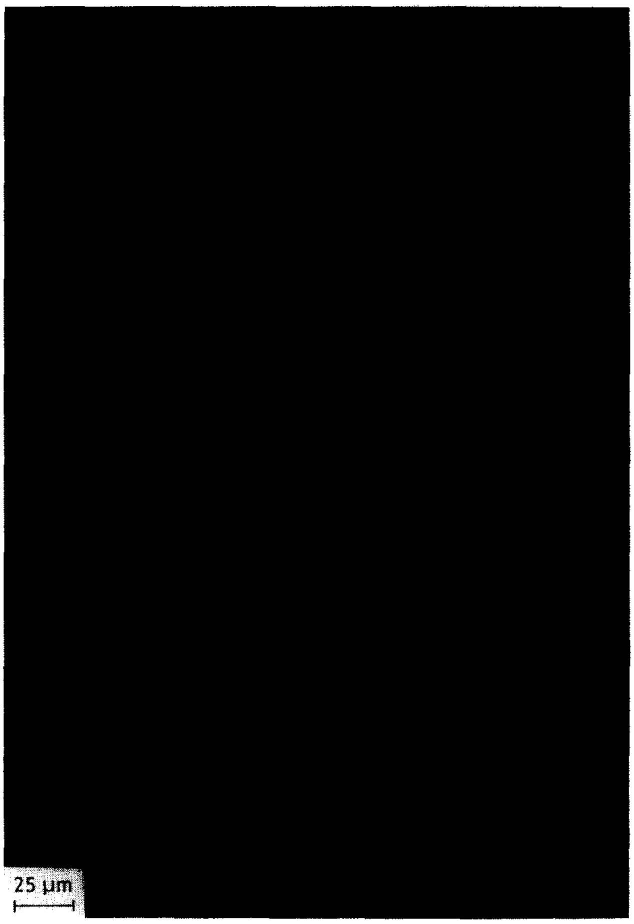

Figure 3 Typical spherulite pattern from PLM of SYN-ALT-EP copolymer crystallized at 24°C for 7663 min

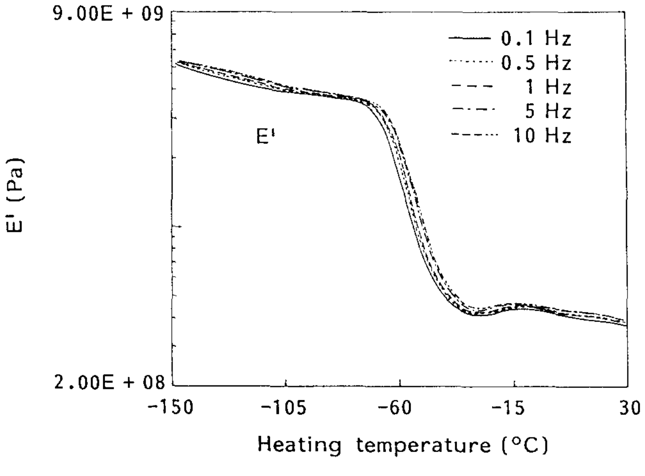

Figure 4 Dynamic mechanical spectra showing the storage modulus (E') for SYN-ALT-EP *versus* temperature at five different frequencies using the Seiko DMS200

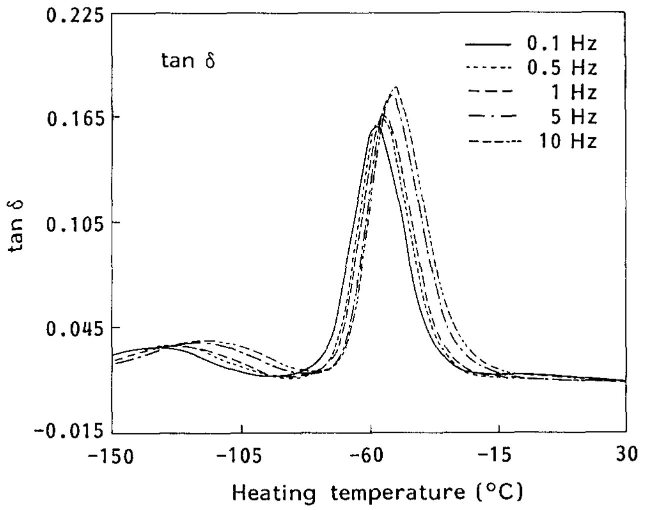

Figure 5 Dynamic mechanical spectra showing the tan δ for SYN-ALT-EP *versus* temperature at five different frequencies using the Seiko DMS200

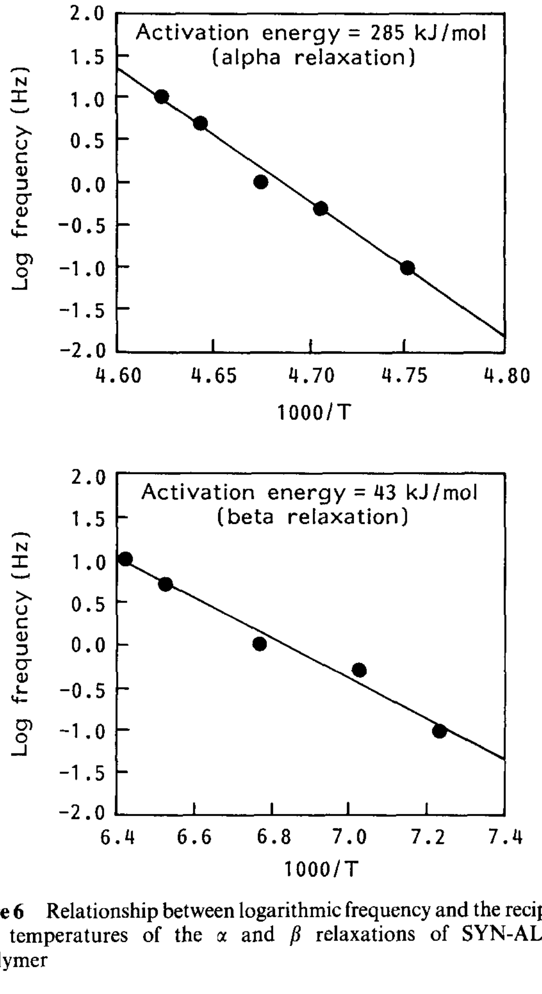

Figure 6 Relationship between logarithmic frequency and the reciprocal peak temperatures of the α and β relaxations of SYN-ALT-EP copolymer

three orders of magnitude (0.1–10 Hz), a linear relationship can be approximated based on the Arrhenius relationship between the reciprocal of the peak temperatures of loss modulus (E'') and the frequencies as shown in *Figure 6*. The apparent activation energy, $E_a(\alpha)$, is calculated to be 285 kJ mol^{-1}. From the frequency-dependent dynamic mechanical data the Arrhenius relationship can also be plotted for the β relaxation (*Figure 6*). The activation energy, $E_a(\beta)$, is calculated to be 43 kJ mol^{-1}, which may be attributed to the rather isolated methyl side group rotation in the SYN-ALT-EP copolymer.

According to Starkweather's theory[27], a lower limit for the activation energies of internal motions in polymers can be defined by a relationship that leads to a zero activation entropy. Therefore, a linear relationship can be applied by plotting the Arrhenius activation energies as a function of the relaxation temperatures. This relationship has been found to be followed by several polymer motions such as the side group relaxations of the main-chain methyl groups in several methacrylate polymers, such as poly(methyl methacrylate), poly(ethyl methacrylate) and poly(butyl methacrylate) and those of the methyl side groups in polypropylene and polyisobutylene. The β relaxation in SYN-ALT-EP copolymer at 1 Hz conforms closely to the likely conditions for a zero activation entropy within the experimental errors. That is, a non-cooperative motion characteristic of the methyl side groups exists in SYN-ALT-EP copolymer.

Molecular motions associated with the α and β relaxations

Figure 7 shows the ^{13}C n.m.r. spectra of SYN-ALT-EP copolymer at different temperatures. *Figure 7A* is a Bloch decay spectrum obtained at room temperature. There are four major chemical shifts, and their assignments are: 20 ppm (-CH_3, the methyl); 33 ppm (-CH, the methine); 38 ppm (-$CH_2CH(CH_3)$, the α-carbon, i.e. the methylene next to the methine); and 25 ppm (-CH_2–CH_2–CH_2 $CH(CH_3)$, the β-carbon, i.e. the central methylene). *Figures 7B, C* and *D* show the CP-MAS spectra at room temperature, −75°C and −175°C, respectively.

As the temperature is decreased to −75°C, which is below the glass transition ($T_g = -57$°C), a dramatic change is observed in the CP-MAS spectrum (*Figure 7C*). The sharp peaks at 38, 33 and 25 ppm that are observed at room temperature become rather broad and exhibit serious overlapping. Since the resonances show broader lines in the glassy state than those in the crystalline state, the observed line-broadening reflects the fact that 71% of the material becomes glassy at −75°C (crystallinity = 29% from WAXD). *Figure 8* shows the inversion–recovery measurements as a function of variable time (τ) on the ^{13}C T_1 at room temperature. The inversion–recovery data can be fitted with the following empirical equation:

$$I = I_0(1 - k\,e^{-\tau/T_1}) \qquad (1)$$

where I is the signal intensity at τ, I_0 is the signal intensity at $\tau = \infty$ and k is a constant close to 2 (in this case it is 1.60) and is used to compensate for the imperfection of radio frequency pulses. The values of the fitting parameters are listed in *Table 1*.

Figures 9 and *10* are the spectra for the measured ^{13}C T_1 values using Torchia's method at low temperatures, namely at −75°C and −175°C, respectively. In these two cases the data can be fitted to the single exponent decay of equation (2):

$$I = I_0\,e^{-\tau/T_1} \qquad (2)$$

where I_0 is the signal intensity at $\tau = 0$. As shown in *Figure 7*, at low temperatures the signals from the backbone atoms become so broad that they overlap.

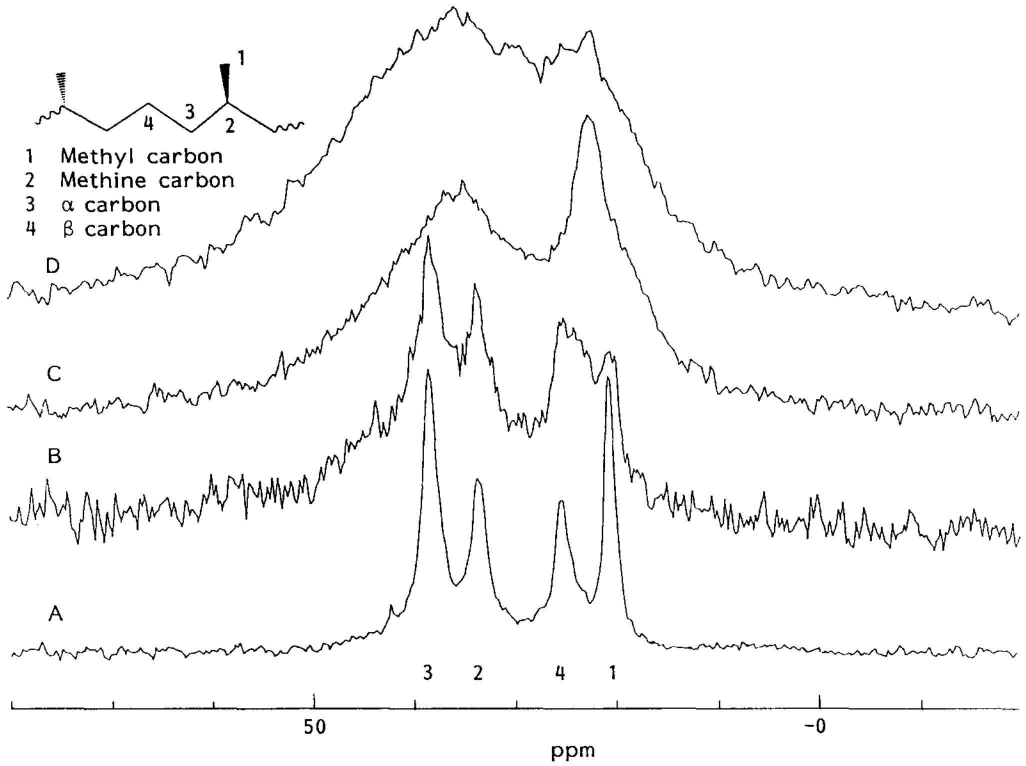

Figure 7 50 MHz solid-state ^{13}C MAS n.m.r. spectra of SYN-ALT-EP copolymer: (A) Bloch decay spectrum at room temperature; (B) CP spectrum at room temperature with contact time of 1 ms; (C) CP spectrum at −75°C; (D) CP spectrum at −175°C

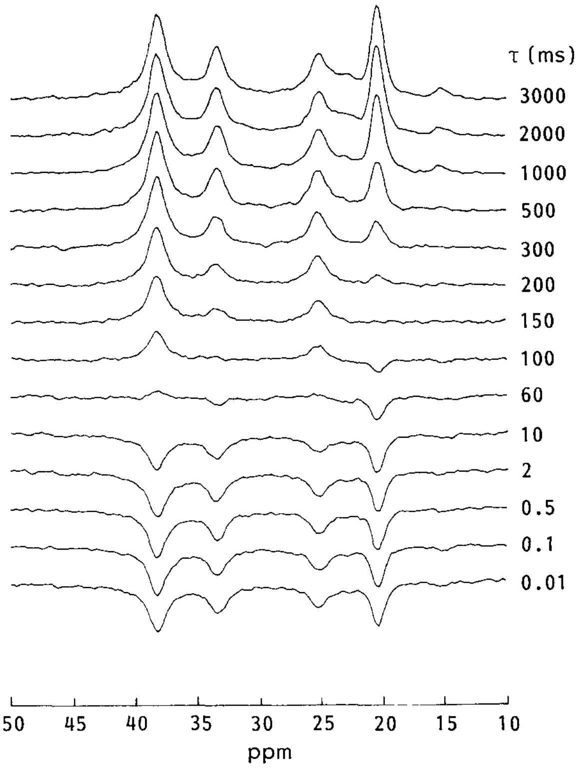

Figure 8 ^{13}C T_1 measurements using the inversion–recovery method at room temperature, where τ is the variable time

Table 1 ^{13}C T_1 (inversion–recovery) data at room temperature

	ppm	I_0	k	T_1 (ms)	r^2
α carbon	38	25.3±0.2	1.59±0.01	114±2	0.99965
Methine	33	15.4±0.2	1.58±0.01	203±6	0.99877
β carbon	25	13.6±0.2	1.56±0.01	130±4	0.99868
Methyl	20	28.5±0.3	1.45±0.01	415±8	0.99954

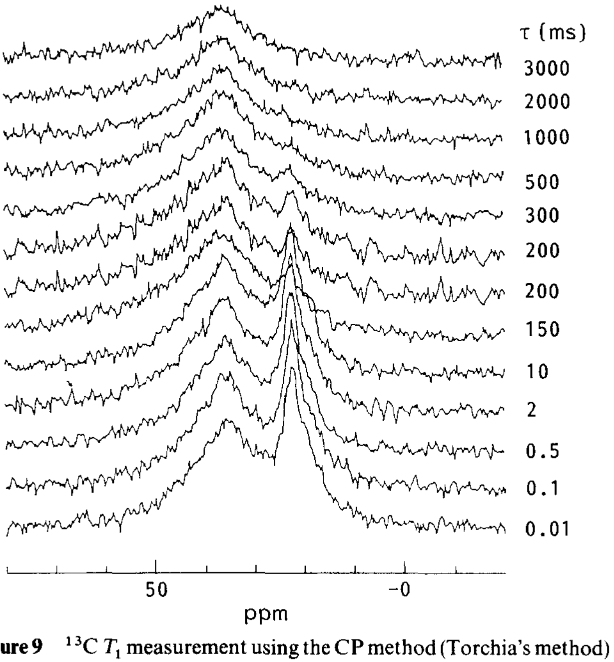

Figure 9 ^{13}C T_1 measurement using the CP method (Torchia's method) at −75°C, where τ is the variable time

Thus, only a single average time constant can be determined for all the backbone atoms. The resulting values of ^{13}C T_1 are listed in *Table 2* for all three temperatures. The apparent mean values of T_1 for the broad feature is >2 s as shown in *Table 2*, suggesting that the backbone is largely frozen. The methyl carbon shows, however, a relatively sharp and intense peak observable at about 21 ppm. As indicated in *Table 2*, the ^{13}C T_1 (209 ms) at −75°C is an order of magnitude faster than that of the backbone atoms. It may be concluded that the α transition involves the freezing of the backbone motion, while leaving the methyl rotation intact.

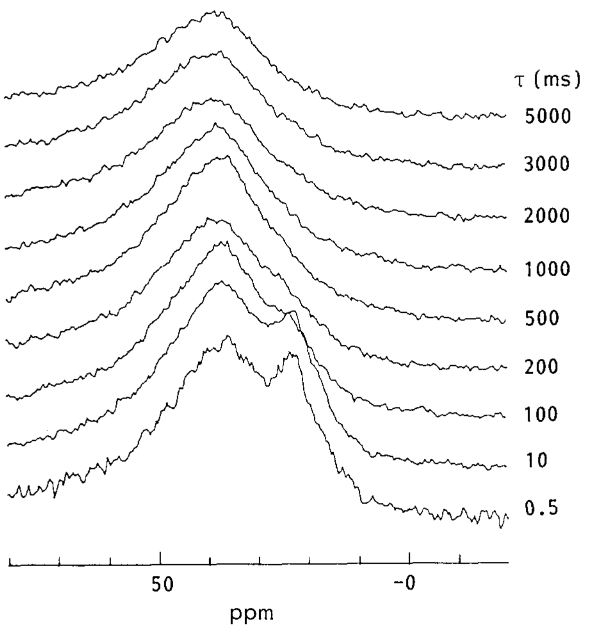

Figure 10 ^{13}C T_1 measurement using the CP method (Torchia's method) at −175°C, where τ is the variable time

Table 2 ^{13}C T_1 (in ms) data at various temperatures

	Side group	Backbone		
Temperature (°C)	Methyl 20 ppm	Methine 33 ppm	α carbon 38 ppm	β carbon 25 ppm
24	415±8	203±6	114±2	130±4
−75	209±17		2454±210	
−175	57±8		2579±253	

As the temperature is decreased to −175°C, which is below the β transition ($T_\beta = -125$°C at 1 Hz by dynamic mechanical measurements), the most prominent change is in the line-shape and the ^{13}C T_1 value found for the methyl carbon, as indicated by the CP-MAS spectrum (*Figure 7D*) and *Table 2*. The peak becomes rather broad in linewidth and weak in intensity. The same trend is observed for the backbone atoms during the glass transition. The spectra of the backbone atoms, thereafter, show further broadening in linewidth, but the spectra do not show a qualitative difference. The ^{13}C T_1 data listed in *Table 2* show that in going through the β transition the mobility of the backbone carbons undergoes little change. The trend of the spectral line-shape and ^{13}C T_1 numerical values for the backbone atoms correlate well. The lack of change is due to the fact that the large-amplitude conformational motion about the backbone is already frozen at the glass transition. On the other hand, the T_1 for the methyl carbon decreases to about 60 ms, and suggests a significant decrease in its rate of motion. The line broadening of the methyl resonance has been noted to be a general phenomenon for polymers having either rapidly reorienting side groups or main-chain carbons that are forced to move in an applied force field. A decrease in the rotational motion of a methyl group has been found for a 90% isotactic polypropylene having 70% crystallinity[28]. In the latter polymer, the methyl carbon resonance as a function of decreasing temperature is similar to that shown in *Figure 7*. There is a slowing-down of the methyl rotation that causes progressive line-broadening. The broadening in the 90% isotactic polypropylene case becomes visible even at −80°C and reaches a maximum at −170°C when the methyl signal vanishes completely. Other examples of a broadening of the methyl resonance as a result of a slowing of motion have been seen in polycarbonate, poly(methyl methacrylate) and epoxy polymers[29].

Possible molecular motions and their correlation with three different temperature regimes at room temperature ($<T_m$)*, below* T_g (< -60°C) *and below* β *transition* (< -125°C)

The material is rather rubbery because the observation temperature (room temperature) is much higher than the observed T_g ($T_g = -57$°C from d.s.c.) and the crystallinity is low (29%). *Figure 11* shows the measured variable contact time spectra. The relation between the signal intensity and spin-contact time, τ, in a CP experiment can be fitted to equation (3):

$$I = I_0 e^{-\tau/T_{1\rho H}}(1 - e^{-\tau/T_{CH}}) \qquad (3)$$

where τ is the contact time, I_0 is the maximum attainable signal intensity, T_{CH} is the cross-polarization time constant and $T_{1\rho H}$ is the ^1H spin-lattice relaxation time in the rotating frame. The fitted parameters, T_{CH} and $T_{1\rho H}$, are listed in *Table 3*. At the molecular level the characteristic motions in the sample are characterizable by $T_{1\rho H}$ and ^{13}C T_1. The times are listed in *Tables 3* and *2*, respectively. The $T_{1\rho H}$ values for all of the backbone atoms show basically the same value (7 ms) within

Table 3 T_{CH} and $T_{1\rho H}$ (variable contact time) data at room temperature

	Side group	Backbone		
	Methyl 20 ppm	Methine 33 ppm	α carbon 38 ppm	β carbon 25 ppm
T_{CH} (μs)	258±53	167±25	191±24	170±32
$T_{1\rho H}$ (ms)	28.6±4.2	8.4±0.7	6.5±0.5	6.8±0.7

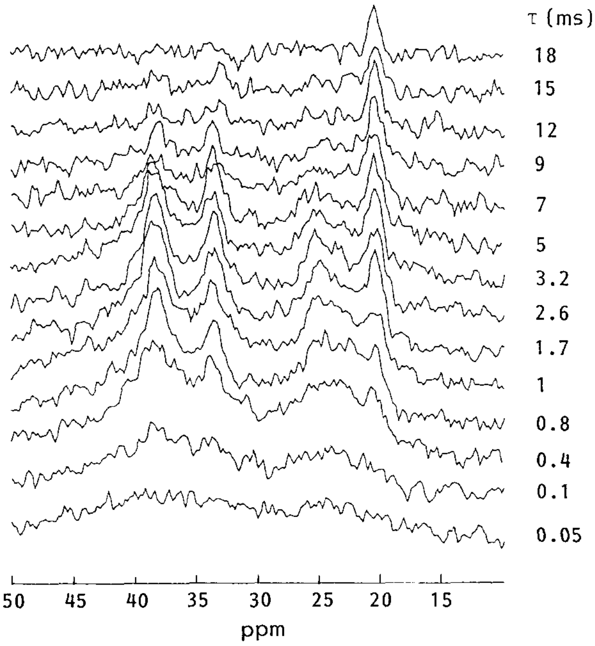

Figure 11 Variable contact time spectra at room temperature from solid-state ^{13}C n.m.r. where τ is the contact time

experimental error. Such a value indicates that the kHz range backbone motion is somewhat coupled throughout the polymer backbone. However, the $T_{1\rho H}$, as detected from the CH_3 peak, shows a much larger value (about 30 ms) from that of the backbone. Such a distinct difference suggests that the motion of the CH_3 group is decoupled from the backbone. This decoupling is due to the fact that the CH_3 group has a rapid rotation about its C_3-axis that quenches the proton spin diffusion between the side group and the backbone.

In the MHz range the motion associated with individual carbon atoms can be studied by the ^{13}C T_1 values shown in *Table 2.* At room temperature the methyl carbon has the largest T_1 value, indicating the fastest motion. Along the backbone the methine carbon has the shortest T_1 value of only 203 ms/2 = 102 ms indicating the slowest motion. In order to make a direct comparison with the methylene carbons, the factor of 2 accounts for the fact that there is only one directly attached proton. The T_1 value increases in going from the methine to the central methylene unit (the β carbon). The successive increase indicates that the mobility of each carbon atom increases along the chain as one moves toward the central carbon atom (the β carbon). This stepwise increase in mobility from the methine carbon to the α carbon and finally to the β carbon suggests the existence of other conformational motions. For example, there are rotations between the methine carbon and the α carbon, and also rotations between the α carbon and the β carbon.

Figures 7A and *B* show a comparison of the Bloch decay and CP-MAS spectra, respectively, and indicates the semicrystalline behaviour of the polymer. In the CP experiment the resonances from the carbon atoms in the relatively rigid component (crystalline phase) are preferentially detected. For the same number of acquisitions the signal-to-noise ratio in the CP-MAS is relatively low compared to the signal-to-noise ratio of the Bloch decay spectrum. The Bloch decay measurements detect preferentially the mobile, amorphous phase and reflect the low crystallinity (about 29% by WAXD) of the material at $T_c = 24°C$. It is rather interesting to see that in the CP-MAS spectrum (*Figure 7B*), the β carbon atom (the central methylene) shows a significant broad distribution in the chemical shift to the extent that there is a partial overlap with the resonance of the methyl carbon. Using the reasoning for the existence of a γ-*gauche* effect[30], the broadening of the resonance of the β carbon indicates that there must be a distribution of conformations available for the bond between the α carbon and the methine carbon. Therefore, the rigid phase of the material is conformationally disordered with respect to the bond between the α carbon and the methine carbon.

CONCLUSIONS

SYN-ALT-EP copolymer can be synthesized by hydrogenation of syndiotactic *cis*-PPD. This novel copolymer can be crystallized at ambient temperatures. It exhibits a T_g of $-57°C$ and has a T_m of 39°C. The spherulite morphology shows a distinct concentric banded pattern. Such behaviour indicates the co-twisting nature of lamellae during the spherulite growth of this copolymer. Two relaxation processes below ambient temperatures (the α and β relaxations) can be found. Two types of molecular motion may be ascribed to these relaxation processes: (1) the rotations about single bonds in the backbone (conformational motion); and (2) the rotation of the methyl side group. The α transition (around $-60°C$) involves freezing of the backbone motion and corresponds to the glass transition of this copolymer. The β transition (with an onset around $-80°C$) is linked to the decrease of the frequency of the methyl side group rotation of this copolymer at successively lower temperatures.

ACKNOWLEDGEMENT

The authors would like to thank Professor Stephen Z. D. Cheng for many helpful discussions. This work was supported by British Petroleum Incorporated, America.

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