

Aliphatic chain motion in a poly(alkylene terephthalate)

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SUMMARY

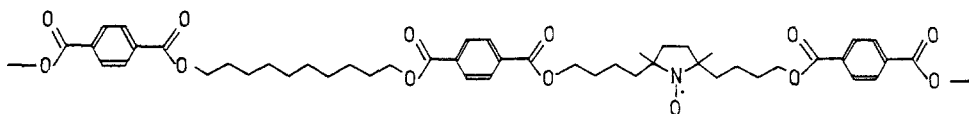
A spin labelled poly(decamethylene terephthalate) where the label is covalently bound into the aliphatic chain, has been studied by EPR spectroscopy. The motion of the label is strongly anisotropic at low temperatures, probably due to the extended all-trans conformation of the alkyl chain. The anisotropy of the label rotation decreases with increasing temperature. Two approaches to analyse the spectra at high temperatures are presented.

INTRODUCTION

Polyesters prepared from terephthalic acid and aliphatic diols are semicrystalline polymers whose glass transition temperature and melting temperature depend on the length of the alkyl chain connecting the terephthaloyl groups. It has been shown (1,2) that increasing the length of the alkyl chain decreases T_g and T_m but increases the degree of crystallinity of the polyesters. In poly(alkylene terephthalates), as well as in some liquid crystalline polyesters, (3,4) the flexible alkyl chain may adopt an extended all-trans conformation, thus giving rise to a relatively high degree of crystallinity. Changes in the crystal morphology, and indeed in the degree of crystallinity, may be induced by annealing the polymer at elevated temperature.

We have studied a spin-labelled poly(decamethylene terephthalate) where a small paramagnetic nitroxide label is rigidly bound into the polymer chain as a part of a flexible hydrocarbon chain. The polymer has been synthesised by polycondensing terephthaloyl dichloride with a mixture of diols; 20 % of the 1,10-decanediol was replaced with its labelled analogue. The product polymer thus has the following structure:

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EPR spectra of a freshly prepared solid polymer have been compared with those measured after prolonged standing (for several months) at room temperature. Information on the local dynamics of the long flexible alkyl chains has been obtained by studying the EPR spectra measured as a function of temperature.

EXPERIMENTAL

Synthesis. The spin-labelled copolymer was obtained by the polycondensation of terephthaloyl dichloride, 1,10-decanediol and 6-azetoxyl-1,11-undecanediol.

Monomers: Terephthaloyl dichloride and 1,10-decanediol were commercial products. 6-Azetoxyl-1,11-undecanediol was synthesised by the Grignard reaction of 2,5-dimethyl-1-pyrroline N-oxide with 4-chloro-1-butanol in several steps as described by Keana.(5) The product was an oily liquid, which was purified by chromatography. The structures of the intermediates and the final product were confirmed by mass spectrometry and infra-red spectroscopy. The geometric isomers of 6-azetoxyl-1,11-undecanediol (nitroxide diol) were not separated.

Polymerisation: The polymerisations were bulk polymerisations carried out in a small test tube reactor in an oil bath under nitrogen. The diols (mixture of 1,10-decanediol and nitroxide diol, 80%+20%) were heated in the reaction vessel to 80°C, and the terephthaloyl dichloride added in small portions over a period of 15 min. The hydrogen chloride was collected in aqueous ammonia. The mixture was then slowly heated to a maximum temperature of 130°C, and kept at this temperature 1 h. The vessel was then connected to a vacuum pump to remove hydrogen chloride. The dark brown solid product was powdered and purified by washing with diethyl ether.

Measurements. EPR spectra were recorded with a Varian E-109 spectrometer at temperatures varying from -150°C to 160°C. At high temperatures (>150°C), degradation of the nitroxide was observed. After measuring the sample which had been stored for months, another sample was heated to 120°C for five minutes. Then, the sample was allowed to cool at ambient

temperature for 30 minutes and the measurement was repeated. Calorimetric measurements were made with a Perkin Elmer DSC 2, in nitrogen atmosphere with a heating rate of $10^{\circ}/\text{min}$.

RESULTS AND DISCUSSION

The heating thermograms of the polymer are shown in Fig. 1. The glass transition at 13°C is weak and not shown in the figure. It is noteworthy that during the first run, the sample (kept several months at room temperature) shows a small endotherm at around 50°C . This endotherm (denoted by T_m') is not detected during repeated measurements, and it is supposed to be due to melting of slowly formed crystals. Close inspection of the thermogram obtained during the second heating shows that melting begins at about 70°C . T_m measured as shown in Fig. 1 is 107°C . By comparing the EPR spectra of a freshly prepared polymer with those recorded after several months, it may be concluded that the aliphatic chains take part in the slow crystallisation process. Figure 2 shows the width of the EPR spectra as a function of temperature. It can be seen that the decrease in the extrema separation - caused by increasing rate of the label motion - is gradual when measured right after the polymer synthesis. After the slow crystallisation the change is more distinct, starting between T_g and T_m' . A sample allowed to

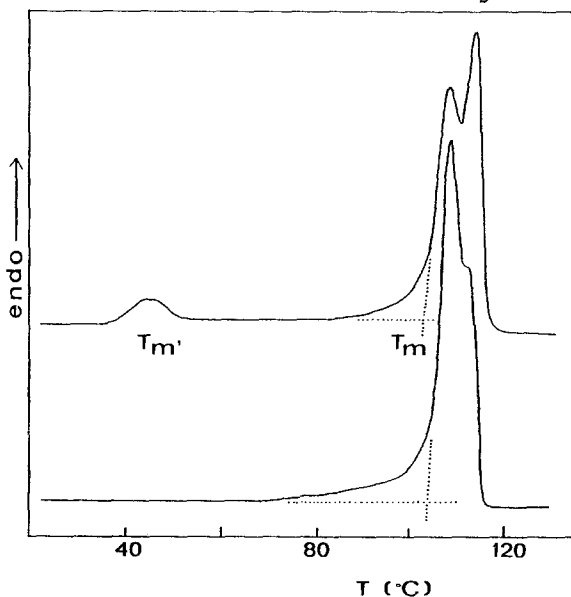


Figure 1.

Heating thermograms of the polymer, after standing at room temperature for several months. Upper curve: first scan, lower curve: second scan.

Sample mass 6 mg.

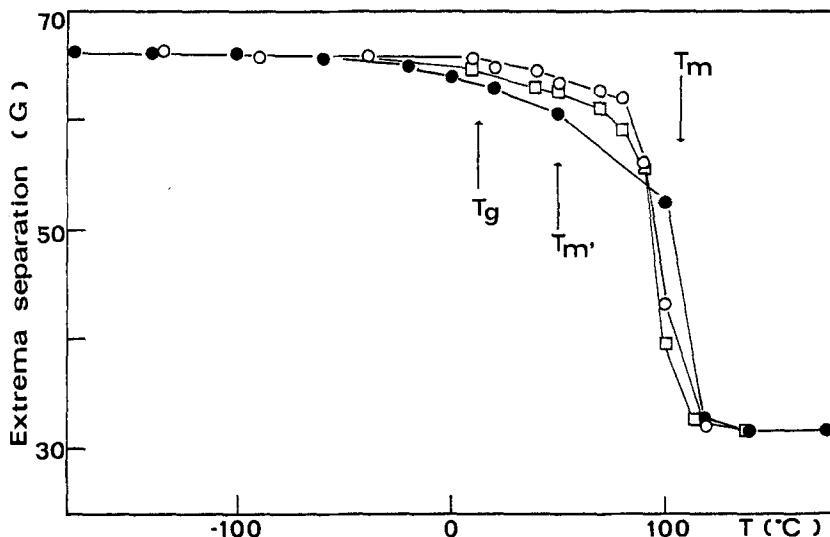


Figure 2. The width of the EPR spectra against temperature. Filled circles: sample measured after the synthesis. Open circles: measured after slow crystallisation. Squares: sample quickly melted prior to measurement.

crystallise for several months and then melted prior to the measurement is an intermediate case, cf. Fig. 2. Although it is improbable that the label would be located in the crystalline region, data in Fig. 2 shows that the nitroxide detects changes not only in the amorphous but also in the crystalline parts of the polymer. The temperature range where the spectra change from slow motional ones to narrow three line spectra typical for rapidly rotating nitroxide, is close to the melting temperature detected by DSC.

EPR spectra of the polymer at various temperatures are shown in Fig. 3. The spectra were simulated using the program published by Freed.(6) The magnetic parameters which gave the best fit for the rigid limit spectrum (registered at -140°C) are: $A_{xx} = 5.35$ G, $A_{yy} = 4.00$ G, $A_{zz} = 33.5$ G, and $g_{xx} = 2.0085$, $g_{yy} = 2.0054$, $g_{zz} = 2.0021$. To simulate the slow motional spectra it was assumed that the label rotates anisotropically, the principal axis of rotation being the nitroxide fixed y axis, i.e. the axis along the extended alkyl chain. The logarithmic rotational correlation times ($\log \tau_R$) obtained from the simulations are shown in Fig. 4 against inverse absolute temperature.

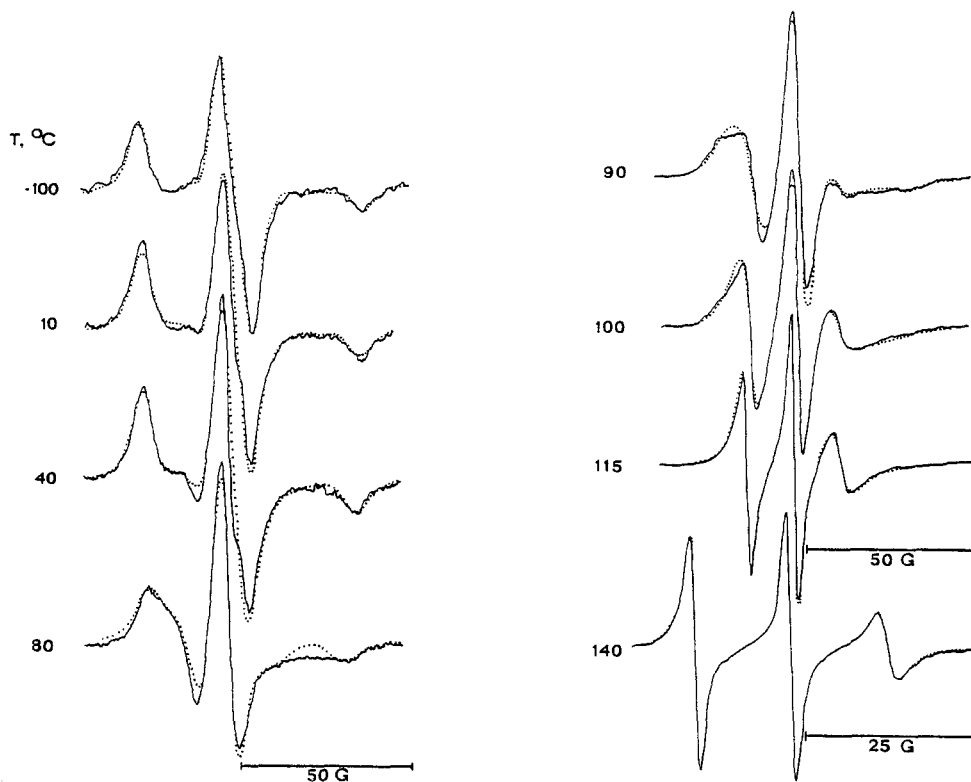


Figure 3. Experimental (solid line) and simulated (dotted line) EPR spectra at various temperatures.

Two regions where $\log \tau_R$ changes linearly with $1/T$ are separated by a transition region. The points at both ends of the transition region are seen to be close to the calorimetrically measured transition temperatures T_g and T_m' . Temperature where the melting of the polymer was observed to begin during the second heating in DSC is also shown; it is also close to the upper transition point. T_m (as defined in Fig. 1) is not detected as a discontinuity in the curve, however.

The degree of anisotropy of the label motion is described by $N = R_{\parallel}/R_{\perp}$, where R_{\parallel} is the rate of rotational diffusion around the principal axis of rotation and R_{\perp} , the rate of rotation around axes perpendicular to the main axis. The values of N are inset in Fig. 4. At low temperatures the label rotation is strongly anisotropic; the nitroxide rotates much faster around the axis parallel to the extended alkyl chain than

around the axes perpendicular to that direction. This is a strong evidence supporting the proposed all-trans conformation of the alkyl chain at temperatures below T_g . With increasing temperature N decreases and around T_m the label rotates isotropically. This finding emphasises the high flexibility of the alkyl spacer between the terephthaloyl groups.

At high temperatures it is possible to analyse the EPR spectra using an alternative model developed for nitroxide labels bound to macromolecules.(7-10) It is assumed that the label is involved in two types of motion: fast anisotropic reorientation relative to the polymer segment, and slow diffusional rotation of the segment. In this model, the spatial limitation for the label rotation is described by a parameter $S = (\overline{A_{\parallel}} - a)/(A_{\parallel} - a)$, where a is the hyperfine coupling constant. For details, see references (7)-(10). Assume that the fast reorientation of the label takes place in a cone having the opening equal to 2α . Then S is related to the amplitude of the fast reorientation of the label by $S = 1/2(\cos^2\alpha + \cos\alpha)$. Thus, $S = 1$ ($\alpha = 0^\circ$) indicates that the label rotates together with the

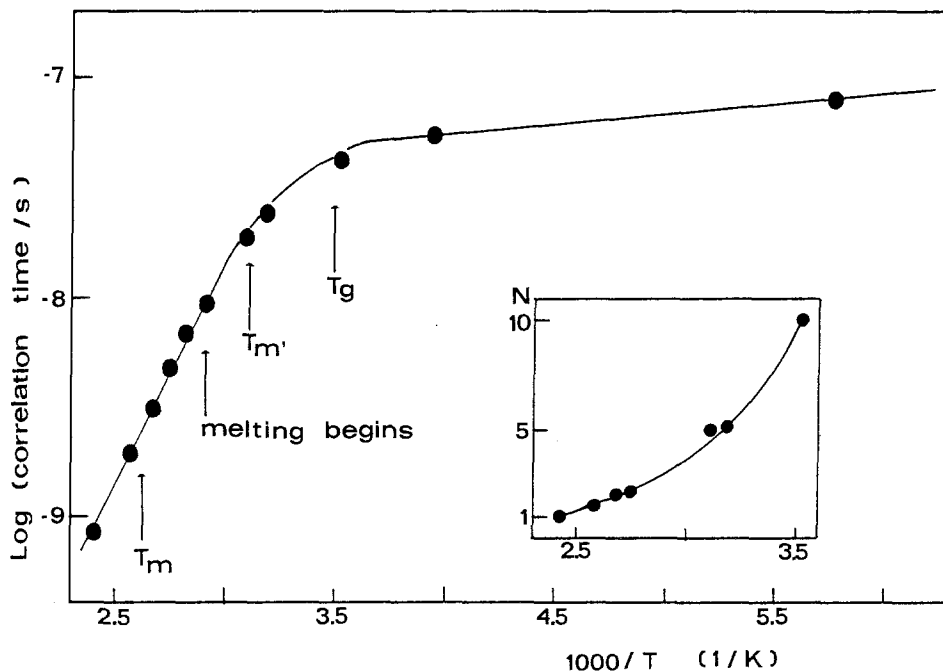


Figure 4. Log τ_R against $1/T$. Arrows indicate phase transitions observed by DSC. Inset shows the values of N vs. $1/T$.

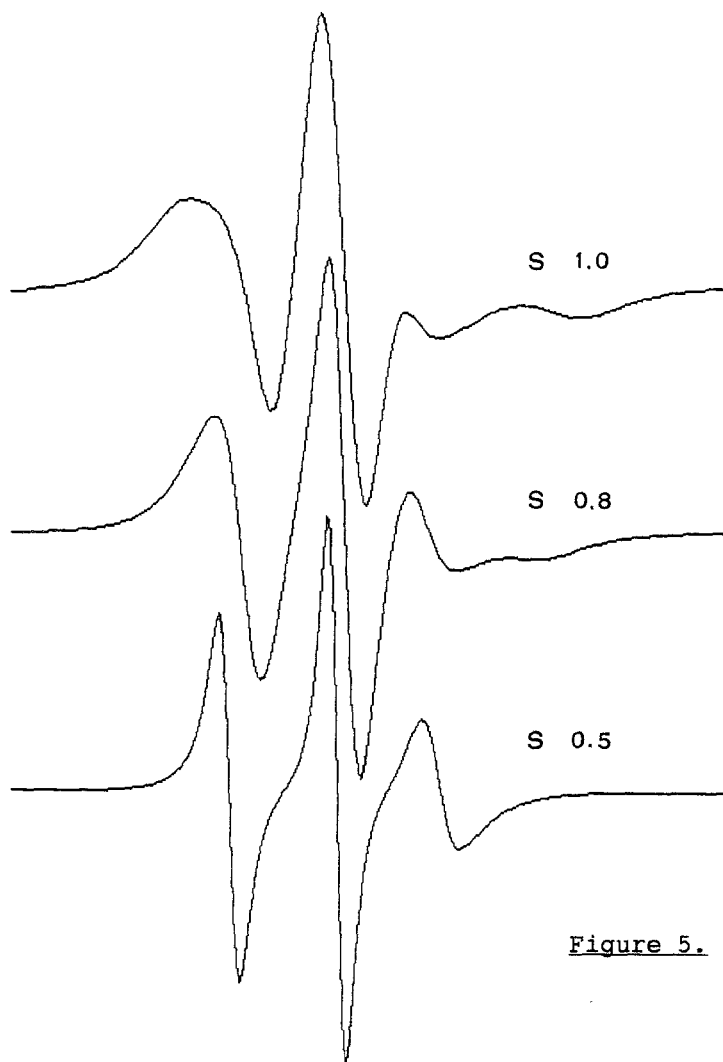


Figure 5.

polymer segment, whereas S equals zero ($\alpha=90^\circ$) for a freely rotating nitroxide probe. With increasing temperature the conformation of the alkyl chain changes from extended all-trans; rapid fluctuations of the dihedral angles, occurring near T_m give a considerable motional freedom for the nitroxide label.

The EPR spectrum registered at 90°C was taken as a starting point for further simulations; at this temperature τ_R is 5 ns. Fig. 5 shows three calculated spectra, all with $\tau_R=5$ ns but with varying value of S . In Fig. 5, with decreasing value of S , the value of α changes from 0° to 50° . As can be seen, the spectra at temperatures $>90^\circ\text{C}$ may very well be simulated without any large changes in the average rotational correlation

time. This is reasonable because in a viscous polymer melt there certainly is a limiting value for the rate of tumbling of the covalently bound label.

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