Notes

Effect of Polymers on the Crystallization of *n*-Alkanes from Solution. 3. Preparation and Investigation of a Spin-Labeled Ethylene−Vinyl Acetate Copolymer

Iain G. Davidson and G. Gordon Cameron*

Department of Chemistry, University of Aberdeen,
Aberdeen, AB9 2UE Scotland, U.K.

Received February 6, 1995
Revised Manuscript Received April 19, 1995

Introduction

The presence of certain polymeric materials is known to affect the crystallization of *n*-alkanes from solution. The interaction produces a lowering of the saturation temperature (cloud point) of the solution and changes the size and habit of the crystals formed.[1,2] Polymers which function as crystal modifiers in this manner always contain a combination of long methylene chains and polar groups. A good example of such polymers, which were the subject of our previous papers,[3,4] are the fumarate−vinyl acetate copolymers (FVA). In these materials the methylene sequences are in the side chain, which has to be of a suitable length for the polymer to be active. We studied the mode of action of FVAs containing C_{18} (octadecyl) ester groups by electron spin resonance (ESR) spectroscopy by incorporating a stable nitroxide group (a spin label) in the polymer.[3−5]

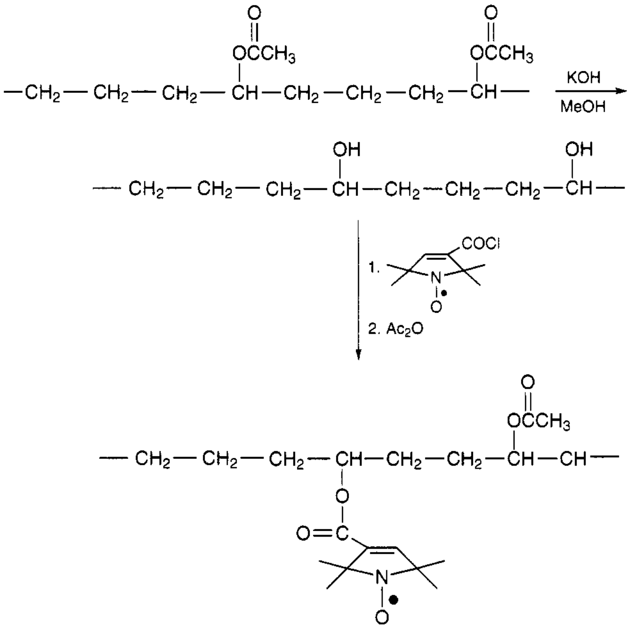
Another group of materials which are active in modifying crystals are copolymers of ethylene and vinyl acetate (EVAs). In these polymers the methylene sequences are part of the main chain which makes them structurally distinct from the FVAs. In this paper we describe the preparation of a spin-labeled version of an EVA copolymer and its interaction, as revealed by ESR spectroscopy, with crystals of dotriacontane ($C_{32}H_{66}$) growing from dodecane solutions. We were particularly interested in investigating whether the ESR technique would reveal any differences in the modes of action of the FVAs and EVAs and whether in the latter the spin-label experiment would show the existence of any precrystallization association between the *n*-alkane and the EVA copolymer.

Experiment and Theory

An EVA random copolymer containing 11 mol % VA was spin-labeled by the procedure shown in Scheme 1.

The acetate functions were first hydrolyzed by refluxing in methanolic potassium hydroxide for 2 h. On cooling, the solvent was decanted off, and the remaining solid was dissolved in chloroform and reprecipitated from methanol. The resulting ethylene−vinyl alcohol copolymer was then dissolved in toluene, 2 equiv of 3-(chloroformyl)-2,2,5,5-tetramethylpyrrolin-1-oxyl, prepared by the method of Rosantzev,[6] was added, and the mixture was stirred at room temperature overnight. Acetic anhydride was then added and the mixture refluxed for 3 h to reacetylate the remaining unreacted hydroxyl groups. The spin-labeled EVA, a sticky viscous gel, was purified by repeated reprecipitation from methanol. The infrared spectrum of the polymer showed no remaining free hydroxyl groups, while analysis by gel permeation chromatography (polystyrene standards) showed a single peak, M_n = 7500 and M_w = 15 900, with no low molecular weight material.

Scheme 1



ESR spectra were recorded on a Varian E-109 spectrometer fitted with a Varian E-257 variable-temperature accessory and interfaced with an Apple II-plus computer. The spin concentration, calculated as described previously,[3] was found to be about 1.5 spins/polymer chain.

The *n*-alkane solution contained 0.1% (w/w) spin-labeled EVA and 2% dotriacontane in dodecane, and the control solution contained 0.1% spin-labeled EVA in dodecane.

Correlation times τ_c were calculated by the well-established line-width analysis[5,7] of the ESR spectra of the labeled polymer. An outline of the theory is given below; for a detailed account reference should be made to the more specialist literature.[7,8]

The dependence of the line widths (*W*) in a motionally-narrowed ESR spectrum of a nitroxide on m_I, the component of the nuclear spin along the direction of the applied field, is given by:

$$W(m_I) = A + Bm_I + Cm_I^2 \qquad (1)$$

where m_I has the allowed values +1, 0, and −1 corresponding to the low-, central-, and high-field lines, respectively. *A*, *B*, and *C* are parameters which depend on the magnetic tensors, the applied magnetic field, and the rotational correlation time, τ_c. Two values of the correlation time may be calculated

$$\tau_c(1) = \frac{4W_{(0)}}{b^2}(r_- + r_- - 2) \qquad (2a)$$

and

---

* Author to whom correspondence is addressed.

0024-9297/95/2228-5964$09.00/0

$$\tau_c(2) = \frac{15W_{(0)}}{8b\Delta\gamma H_0}(r_+ - r_-) \tag{2b}$$

where

$$b = \frac{4\pi}{3}\left[A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})\right] \tag{3}$$

and

$$\Delta\gamma = \frac{-|\beta|}{\hbar}\left[g_{zz} - \frac{1}{2}(g_{xx} + g_{yy})\right] \tag{4}$$

where A_{zz}, A_{xx}, A_{yy} and g_{zz}, g_{xx}, g_{yy} are the principal values of the **A** and **g** tensors, respectively (see Table 1) and $\hbar$ is Planck's constant divided by 2π.

H_0 is the applied magnetic field and β is the Bohr magneton. The parameters r_+ and r_- are given by

$$r_\pm = W_{\pm 1}/W_{(0)}$$

where $W_{(0)}$ is the peak-to-peak width of the central line ($m_{\rm I} = 0$) in the spectrum and $W_{\pm 1}$ represents the widths of the outer lines with $m_{\rm I} = \pm 1$.

As in earlier work involving this type of line-width analysis,[9] only $W_{(0)}$ was measured directly because the ratios $r_\pm$ are more conveniently and more accurately determined from the peak-to-peak intensities, Y, through the relationship:

$$r_\pm = \left[\frac{W_{\pm 1}}{W_{(0)}}\right] = \left[\frac{Y_{(0)}}{Y_{\pm 1}}\right]^{1/2}$$

Provided rotation of the nitroxide labels is isotropic, as assumed in the derivation of eqs 2a and 2b, values of $\tau_c(1)$ and $\tau_c(2)$ will be identical. Diverging values of $\tau_c(1)$ and $\tau_c(2)$ are therefore indicative of anisotropic motion.

The need to apply corrections for inhomogeneous broadening of the lines[9] is avoided if, as in the present work, the spectra are recorded in an air atmosphere. This is known as the method of "additional broadening".[10]

Results and Discussion

Addition of the EVA to the dotriacontane solution lowered the cloud point by 3–4 °C to 20 °C. The crystals which formed below this temperature were very small and irregular in shape in contrast to the large flat plates of the normal *n*-alkane crystals.

Above the cloud point a sharp fast-motion spectrum was observed (Figure 1). As the temperature was lowered, this type of spectrum remained, with the spectral lines broadening slightly with decreasing temperature. However, there was no obvious discrete change in the ESR spectrum as the temperature dropped below the cloud point. Thus, the steady buildup of a second, slow-motion component, such as was observed with the FVA in the same situation,[4] was not observed. A slow-motion component was just detectable in the spectrum at 15 °C, but this never exceeded 5% of the total even at temperatures as low as 4 °C. When the experiment was repeated with the control solution of 0.1% labeled EVA in pure dodecane, a sharp, fast-motion spectrum, broadening slightly with decreasing temperature, was seen at all temperatures above 0 °C.

While the visual inspection of the ESR spectrum of the polymer reveals no evidence of an interaction between the polymer and the crystallizing alkane, the dramatic change in crystal habit of the dotriacontane when crystallized in the presence of the EVA provides unequivocal evidence that there is indeed an interaction. The nature of this interaction must be such that the rotation of the spin labels is not greatly restricted. Such unhindered motion of the label suggests that most of the polymer is associated with the surface of the dotriacontane crystals rather than being locked within the interior of the crystals. In that sense, the results with EVA are similar to those from our earlier work with FVA copolymers[4] and are consistent with the view that crystal modifiers, in general, function by being selectively adsorbed on developing crystals at specific faces where further growth is blocked.[11]

Table 1. Principal Values for the g and A Tensors of Spin-labeled EVA

	g	A/Gauss
x	2.00841	4.95
y	2.00641	4.45
z	2.00210	32.6
iso	2.00564	14.0

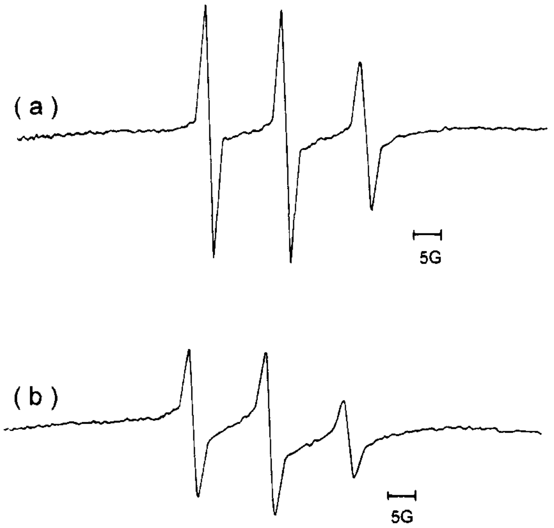


Figure 1. ESR spectra of a spin-labeled EVA copolymer (0.1%) with *n*-dotriacontane (2%) in a dodecane solution at (a) 30 and (b) 15 °C (cloud point 20 °C).

To examine the interplay of polymer and crystallizing *n*-alkane more closely, the rotational correlation times $\tau_c(1)$ and $\tau_c(2)$ of the spin labels, in both the presence and absence of dotriacontane, were calculated by analyzing the ESR spectra (see the Experiment and Theory section).

Figure 2 shows Arrhenius plots for the control solution and for the solution containing both labeled EVA copolymer and dotriacontane. For the former, the two values of τ_c at a given temperature are very close, indicating near-isotropic rotation of the label, and over the temperature range studied lie on a smooth line with no obvious discontinuities.

The corresponding data for the solution containing dotriacontane show markedly different behavior. At temperatures well above the cloud point (20 °C) the curve is virtually coincident with that of the control solution. Below the cloud point, the two curves deviate strongly, the one from the dotriacontane solution falling well below the control curve. Furthermore, the marked separation between corresponding values of $\tau_c(1)$ and $\tau_c(2)$ for the dotriacontane solution as the temperature decreases progressively below the cloud point shows that the motion of the label becomes increasingly anisotropic as the temperature is lowered. Thus, Figure 2 provides clear evidence of an interaction between the polymer and the crystallizing *n*-alkane, the latter imposing restrictions on both the rate and mode of rotation of the polymer.

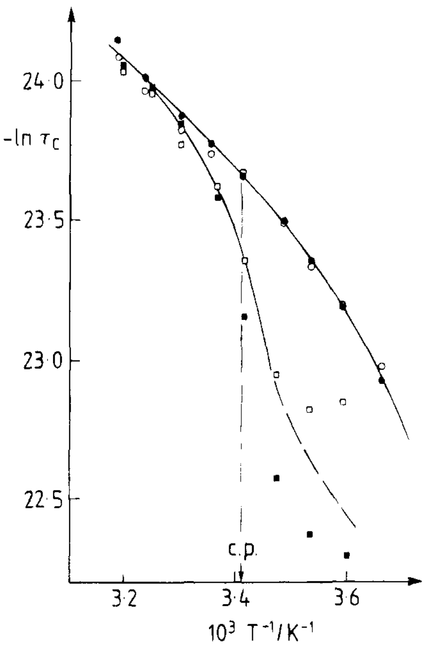


Figure 2. Arrhenius plot of correlation time τ_c of spin-labeled EVA: (○) τ_c (1) and (●) τ_c(2) for 0.1% EVA in dodecane (control solution); (□) τ_c(1) and (■) τ_c(2) for 0.1% EVA with 2% dotriacontane in dodecane (c.p. = cloud point).

The values of τ_c below the cloud point in the presence of dotriacontane should be regarded as relative rather than absolute, for two reasons. First, the line-width analysis becomes less reliable as the degree of anisotropy of rotation increases. Second, the theory underlying the calculations of τ_c assumes the existence of a single correlation time,[7] while, in reality, below the cloud point there must be at least two distinct populations of spin labels—those attached to polymer segments in solution (or remote from the crystal) and those attached to polymer segments on or near the crystal surface.

The evidence from the comparative spin-label studies of the FVA and EVA copolymers suggests that the former tend to be more tightly bound to the alkane crystal, though precisely why this should be so is unclear at present.

It is interesting to note in Figure 2 that the curve for the dotriacontane-containing solutions begins to decline below that of the control solution at temperatures just *above* the cloud point. In other words, in the alkane solution there is an increase in τ_c *in anticipation* of crystallization. This is what one would expect if crystallization is preceeded by an association between the alkane and polymer molecules. The spin-label experiment with the EVA appears to be more sensitive in this respect than that with the FVA where no precrystallization aggregation was detectable.[3]

The extent of aggregation can be calculated very approximately in the following manner. It is assumed that rotation of the label is dominated by whole-molecule rotation in solution; in view of the low molar mass of the EVA copolymers, this is not unreasonable.[9] The rotational correlation time τ_c is therefore given by the relationship[12]

$$\tau_c = \frac{K[\eta]\eta_0}{3RT}M$$

where M is the polymer molecular weight, $[\eta]$ the limiting viscosity number of the polymer solution, η_0 the solvent viscosity, and K a constant that depends on whether the polymer is a free-draining or nondraining coil.

At 24 °C τ_c in pure dodecane and in the 2% dotriacontane solutions are 4.9×10^{-11} and 5.7×10^{-11} s, respectively. Assuming that the higher value of τ_c at 24 °C in the presence of 2% dotriocontane is due only to association of the polymer with the n-alkane (i.e., the dotriacontane does not affect K, $[\eta]$, or η_0), the effective molecular weight M of the aggregate is given by:

$$M \approx \frac{7500 \times 5.7}{4.9} = 8724$$

The molecular weight of the aggregate at 24 °C is therefore equivalent to about three molecules of dotriacontane (MW 450) per molecule of polymer. Because of the fairly sweeping approximations involved in the above calculation, the absolute composition of the material aggregating at 24 °C is uncertain. We can assert, however, that the spin-label experiment is sensitive to the early stages of molecular association in advance of the actual crystallization.

Conclusions

The results of this study are consistent with the view that crystal modification of n-alkanes by EVA copolymers is a consequence of selective adsorption of the polymer at growing crystal faces.

The ESR experiment is capable of detecting association of the n-alkane and the EVA, i.e., precrystallization aggregation, at temperatures above the cloud point.

Acknowledgment. We thank Exxon Chemicals for financial support, including a research fellowship to I.G.D. We are grateful to Dr. M. Y. Qureshi for GPC analyses.

References and Notes

(1) Lewtas, K.; Tack, R. D.; Beiny, D. H. M.; Mullin, J. W. In *Advances in Industrial Crystallization*; Garside, J., Davey, R., Jones, A., Eds.; Butterworth-Heinemann: London, 1991; p 161.
(2) Holder, G. A.; Macaulay, D. *Polym. Int.* **1992**, *28*, 47.
(3) Davidson, I. G.; Cameron, G. G. *Polym. Int.* **1994**, *34*, 443.
(4) Davidson, I. G.; Cameron, G. G. *Polym. Int.* **1994**, *34*, 449.
(5) Cameron, G. G. In *Comprehensive Polymer Chemistry*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, 1989; Vol. 1, p 517.
(6) Rosantsev, E. G. *Free Nitroxyl Radicals*; Plenum Press: London, 1970.
(7) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1107.
(8) Hudson, A.; Luckhurst, G. R. *Chem. Rev.* **1969**, *69*, 191.
(9) Bullock, A. T.; Cameron, G. G.; Smith, P. M. *J. Phys. Chem.* **1973**, *77*, 1635.
(10) Kuznetsov, A. N.; Kolkov, A. Y.; Livshits, V. A.; Mirzoin, A. T. *Chem. Phys. Lett.* **1974**, *26*, 369.
(11) Weissbuch, I.; Shimon, L. J. W.; Landau, E. M.; Popovitz-Biro, R.; Berkovitch-Yellin, Z.; Addadi, L.; Lahav, M.; Leiserowitz, L. *Pure Appl. Chem.* **1986**, *58*, 947.
(12) Zimm, B. H. *J. Phys. Chem.* **1956**, *24*, 269.

MA950141Z