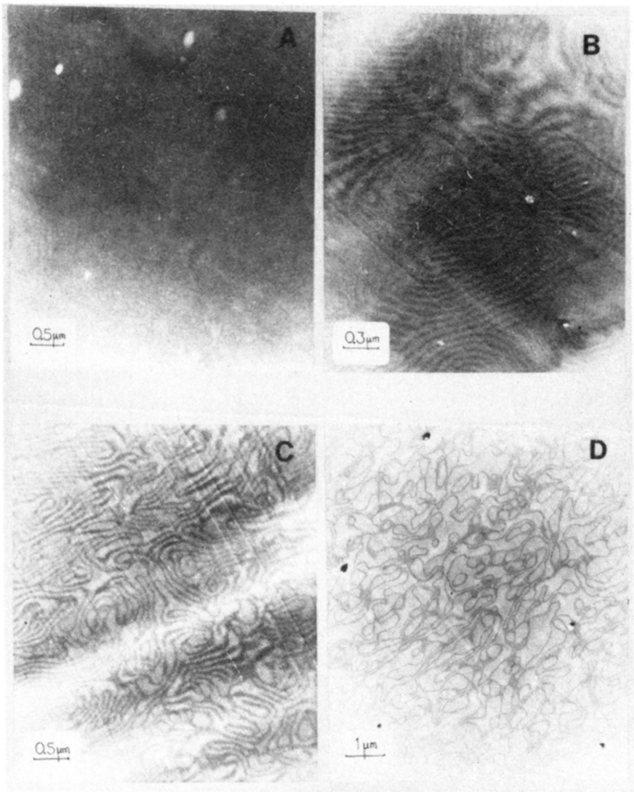

Figure 3. Transmission electron micrographs of (A) 30/100 copolymer; (B) blend of 75% 30/100 copolymer and 25% 30K 1,2B; (C) blend of 50% 30/100 copolymer and 50% 30K 1,2B; (D) blend of 25% 30/100 and 75% 30K, 1,2B.

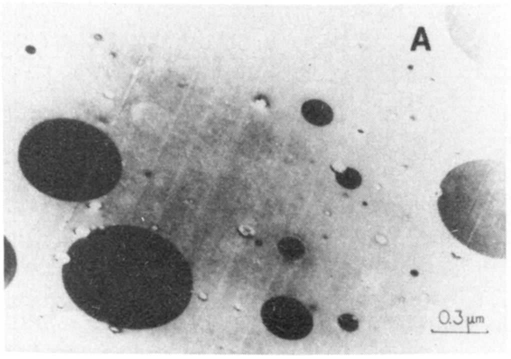

Figure 4. Transmission electron micrograph of a blend of 25% of the 30/100 copolymer and 75% of the high molecular weight 90K 1,2B.

electron micrographs of some of these blends are shown in Figure 3, showing clearly the homopolymer-induced microphase separation.

Although we have focused our attention here on the appearance of the heterogeneous morphology at low homopolymer contents, Hong and Noolandi[1] point out that continued addition of homopolymer should lead once again to homogeneous materials as the pure homopolymer composition is approached. At 75% homopolymer content this reversal had not yet occurred for the system examined here. We have no data at present in the region between 75 and 100% homopolymer. This region may be particularly interesting to study in the future since Leibler and co-workers[9] have predicted that phenomena similar to a critical micelle concentration should be seen in the region of very low diblock copolymer contents.

As a final point we note that the homopolymer-induced microphase separation documented above does not occur when the added homopolymer molecules are very much longer than the corresponding block of the copolymer. In this case two homogeneous phases are formed; the copolymer separates from the high molecular weight homopolymer but does not undergo microphase separation itself. Figure 4 shows an example of this type of behavior for a blend of the 30/100 copolymer with a 1,2-polybutadiene of molecular weight of 90 000; the proportion of copolymer is 25 wt %. Hong and Noolandi[1] point out the possibility of this type of phase separation into two homogeneous phases in some of the many phase diagrams which they are able to construct from their general theory.

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Registry No. Poly(butadiene) (homopolymer), 9003-17-2.

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Glass Transition of Poly(tetrafluoroethylene)

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The glass transition of poly(tetrafluoroethylene) has been a subject of long controversy. Figure 1 shows a histogram of the various reported glass transition temperatures.[1–41] The temperatures 400, 260, 230, and 170 K were cited most often. A similar histogram was prepared earlier for polyethylene by Davis and Eby.[42] The latter also showed a broad scatter, indicating that different relaxations can confuse the assignment of the glass transition. In the last years we have been collecting a data bank on heat capacities of linear macromolecules.[43] On the basis of these heat capacity data it was possible to resolve the question of the glass transition of polyethylene. Polyethylene has a specifically broad transition, reaching from about 120 to 250 K, with a temperature of half-freezing of 237 K.[44] For poly(tetrafluoroethylene), not enough data were available at that time to do a similar analysis.

We report here about T_g of a low CF_2–CF_3 content copolymer as a model of poly(tetrafluoroethylene). DSC experiments at low temperature are described and interpreted together with literature data on crystalline poly(tetrafluoroethylene). It will be shown that the glass transition is quite broad. It reaches from about 160 to 240 K, with a midpoint of about 200 K. This agrees with most calorimetry data in Figure 1 and covers the suggested 170 and 230 K T_g's.

The measurements were carried out with a Standard Mettler TA 2000B low-temperature differential scanning calorimeter in the temperature range from 110 to 350 K at a heating rate of 10 K/min. The sample mass was about 30 mg. Calibration of the amplitude was done with aluminum oxide (sapphire). The sample was a slightly copolymerized poly(tetrafluoroethylene) [poly(tetrafluoro-

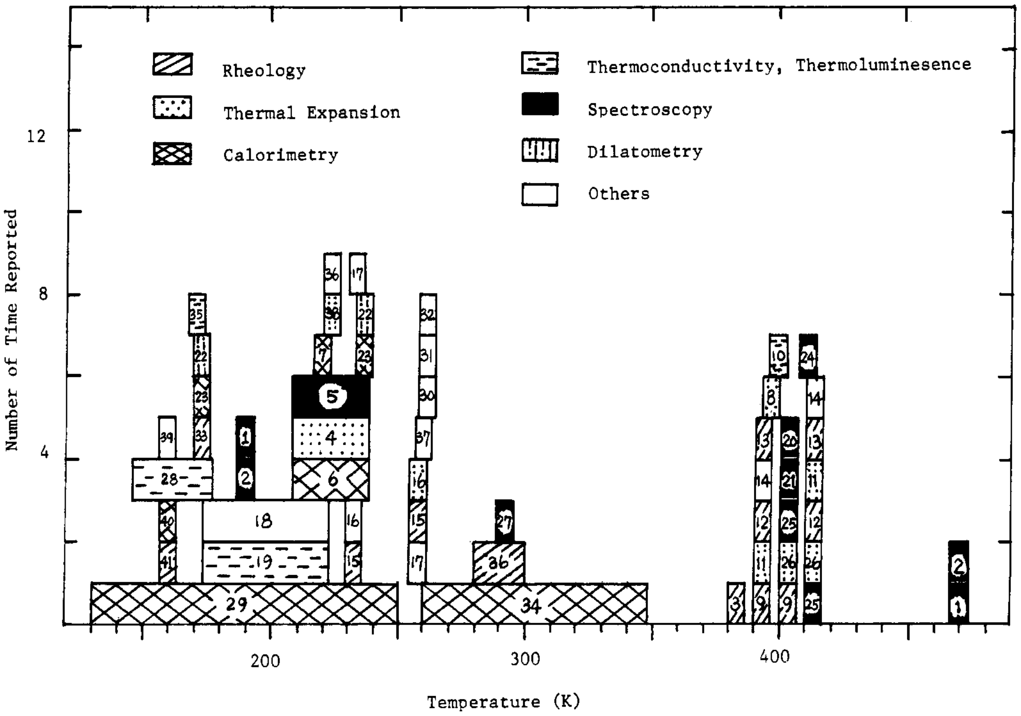

Figure 1. Histogram of reported glass transition temperatures of poly(tetrafluoroethylenes). Numbers refer to the reference list at the end of the paper.

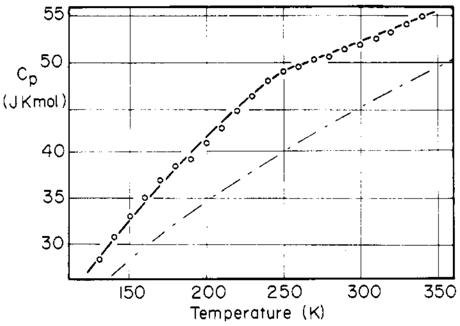

Figure 2. Heat capacity of 17% crystalline poly(tetrafluoroethylene). The dashed line represents the data of 100% crystalline poly(tetrafluoroethylene) as presented in ref 45.

ethylene-*co*-hexafluoropropylene), 10–14 wt % HFP, about 4–5 CF_3 branches per 100 backbone carbon atoms, sample T110V (Teflon 110 FEP, Du Pont)]. Its remaining crystallinity of 17% was found by measurement of the heat of fusion.[45] The sample was used as received. For measurement the calorimeter was cooled from room temperature at a rate of 10 K/min. Figure 2 shows a plot of the resulting heat capacity on heating.

By itself the heat capacity plot is of little informative value. On the low-temperature side, however, the heat capacity is close to the well-established heat capacity of crystalline poly(tetrafluoroethylene) [28 J/(K mol) at 130 K, match to within 12%, estimated error ±10% because of low heat capacity of the sapphire used for calibration]. On the high-temperature side, the heat capacity is close to the heat capacity established for 17% crystalline poly(tetrafluoroethylene) from extrapolation of the heat capacity as a function of crystallinity[45] [52 J/(K mol) at 300 K, match to within 2%, estimated error of the determination ±3%]. Since no sharp step occurs over the whole temperature range, we must assume that for poly(tetrafluoroethylene), as for polyethylene, the glass transition is rather broad. Using 200 K as an approximate midpoint for the glass transition gives a ΔC_p of 9.4 J/(K mol) for completely amorphous poly(tetrafluoroethylene), which is acceptable in the light of the rule of constant ΔC_p per mobile bead [11.3 J/(K mol)] which was found empirically for many macromolecules.[46] [ΔC_p varies from 11.8 J/(K mol) at 160 K to 7.8 J/(K mol) at 240 K.]

Accepting 200 K as the glass transition temperature and assuming that the glassy heat capacity is not much different from the crystalline heat capacity, it is also possible to evaluate the entropy of the glass at absolute zero. The result is 3.38 J/(K mol), close to the value observed for polyethylene [2.59 J/(K mol)].[43]

To summarize the results, heat capacity measurements strongly support a low and broad transition for poly(tetrafluoroethylene). ΔC_p at T_g and S_0^a are of the order of magnitude expected.

This is the third polymer analyzed that has a relatively smooth chain structure, the others being polyethylene[43,44] and selenium.[43,47] All three showed abnormally broad glass transitions. Most likely, this broadening is due to local chain mobility which is unhindered by side groups. Further possible examples of such polymers are the polyoxides of which poly(trimethylene oxide)[43] seems also to have a broad glass transition. Work on poly(oxymethylene) and poly(ethylene oxide) is in progress.[48]

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Communications to the Editor

Structure of Peroxy Radicals of Isotactic Polypropylene

A number of studies[1,2] of the electron spin resonance (ESR) of peroxy radicals of isotactic polypropylene (it-PP) have been reported. However, there have been few studies of the structure of the peroxy radicals,[3] and there is little geometrical information about the internal rotation angle around the C–O bond, ϕ, and the bond angle ∠COO. Iwasaki et al.[4] and Hori et al.[5] concluded that the COO group lay in the plane perpendicular to the polymer main chain axis, as shown in Figure 1, the polymer chain having a planar zigzag conformation (like polyethylene) or a slightly distorted planar zigzag structure (like poly(tetrafluoroethylene)). However, it is hard to decide whether the orientation of the O–O bond is gauche ($\phi = 60°$) or skew ($\phi = -120°$) to the adjacent C–C bond, as shown in Figure 1. It is well-known that the chain structure of crystalline isotactic polypropylene is a 3_1 helix, and thus very different from a planar zigzag conformation, as shown in Figure 2. In this report we study the structure of stable peroxy radicals trapped in the crystalline regions of it-PP, affected by the helical conformation. In order to estimate the angles λ_1 and λ_3 between the principal directions of the **g** tensor and the polymer chain axis, the angular dependence of the ESR spectrum of the peroxy radicals with respect to the external magnetic field must be analyzed.

An isotactic polypropylene, Noblen MA-4 (product of Mitsubishi Petrochemical Co. Ltd., $M_v = 40 \times 10^4$), was heated and pressed into a film which was subsequently stretched at 393 K to obtain a stretch ratio of 6 (stretch ratio is defined to be the ratio of the film length after stretching to the original length). This elongated film was then cut into a narrow strip which was placed in a Spectrosil sample tube. The sample was prepared with the stretching direction perpendicular to the axis of the sample tube. The sample was evacuated to 10^{-5} torr and then irradiated at ambient temperature with ^{60}Co γ rays for a total dose of ca. 4.25 Mrd. After the irradiated sample was annealed at 318 K for 2 h, only the tertiary alkyl radicals of polypropylene ($\sim CH_2-\dot{C}(Me)-CH_2\sim$) were trapped. Oxygen molecules at a pressure of 200 torr were introduced into the sample tube, and peroxy radicals were produced by reaction of the alkyl radicals with oxygen at 263 K for 33 h. The ESR spectra of the peroxy radicals are composed of two spectra arising from the chemically identical peroxy radicals but having different mobilities.[1,6] In order to observe the ESR spectra of the rigid peroxy radicals trapped in crystalline regions, the sample was annealed at 313 K for 40 h.

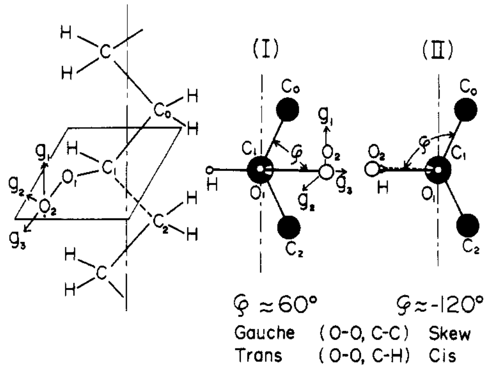

Figure 1. Schematic illustration of peroxy radicals of polyethylene and possible orientations of the O–O group to the adjacent C–C bond around the C–O bond, gauche (I) and skew (II).

The ESR spectrum of the rigid peroxy radicals showed a very marked angular dependence, as illustrated in Figure 3. With the external magnetic field along the stretching

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