Table I
Packing Density: Polyethylene vs. Poly(propylene oxide)[a]

	ρ_A at room temp	M	Vw	ρ^*
polyethylene	0.855	28	20.46	0.625
poly(propylene oxide)	0.998	58	34.38	0.592

[a] ρ^* (packing density) = $\rho_A Vw/M$, where ρ_A is amorphous density.

molecular theory of physical aging based on rotation around short segments of the polymer main chain, suggested that the initial fast volume relaxation is due to relaxing molecular rearrangements in regions of particularly high free volume produced by thermal fluctuations. As physical aging proceeds, α decreases, reflecting the collapse of such large free volume. This suggests that free volume distribution is skewed toward smaller sizes after aging.

As to the effect of diol structure on α, our results indicate that there is more free volume above a critical size in PU-PPO than in PU-BD, probably because of the poor chain packing efficiency in PU-PPO due to the bulky CH_3 group. We may compare packing densities[12] of amorphous polyethylene and poly(propylene oxide) since the difference between the two polyurethanes is butylene vs. propylene oxide. Based on literature values of the amorphous density of polyethylene[13] and poly(propylene oxide)[14] at 25 °C and estimating the molar volume (Vw) following Bondi's method,[15] a packing density of 0.625 for polyethylene and 0.592 for poly(propylene oxide) is obtained as shown in Table I. This indicates that there will be more free volume in poly(propylene oxide) than in polyethylene at the rubbery state of 25 °C. However, packing density values are not easily available, either at their respective T_g or in the glassy state, for the two polymers. As an approximation, assuming the T_g of polyethylene to be lower than -70 °C[16] (which is close to the T_g of poly(propylene oxide)[17]) and also assuming that the thermal expansion coefficient in the rubbery region is similar in both polymers, the same tendency in packing density would hold for the two polymers even at T_g and probably in the glassy state, which supports our results. Preliminary results with PU-DD indicate that it is close to PU-BD in α values at their respective glassy temperatures.

To the best of our knowledge, this is the first demonstration of the use of molecular labels in a study at the molecular level of the physical aging phenomenon, by which we can estimate a fraction of free volume above a critical size at a given temperature and time of aging. This provides more information about the distribution of free volume and its change with aging.

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Tilting Phenomena in Forms II and III of Poly(vinylidene fluoride): Evidence for Monoclinic Structures

We reported the crystal structures of forms II and III of poly(vinylidene fluoride).[1,2] Recently, Lando et al.[3,4] proposed crystal structures of forms II and III different from ours, both of which belong to the orthorhombic system (form II, $P2cm$; form III, $C2cm$), in contrast to our monoclinic structures (form II, $P2_1/c$; form III, Cc). We surmise that the conclusions of Lando et al.[3,4] were reached because they were unaware of the tilting phenomena of forms II and III. By utilizing these phenomena, Bunn was able to analyze the crystal structure of poly(ethylene terephthalate).[5] X-ray diffraction patterns of the tilt samples of forms II and III clearly show that the crystal structures belong to the monoclinic system. Here, we describe and interpret the tilting phenomena.

First the fiber specimen of form II was prepared by crystallizing through the elongation of the melt (KF-1100, Kureha Chemical Co., Ltd.). The tilt sample of form II was prepared by annealing the fiber specimen at about 150 °C with the ends free. The tilt sample of form III was accidentally obtained during heat treatment at ca. 175 °C with the ends fixed. Figure 1 shows X-ray diffraction patterns and their schematic representations for the tilt samples of forms II and III.

All the reflections observed in the X-ray diffraction pattern shown in Figure 1A can be indexed by the unit cell of form II (a = 4.96 Å, b = 9.64 Å, c (fiber period) = 4.62

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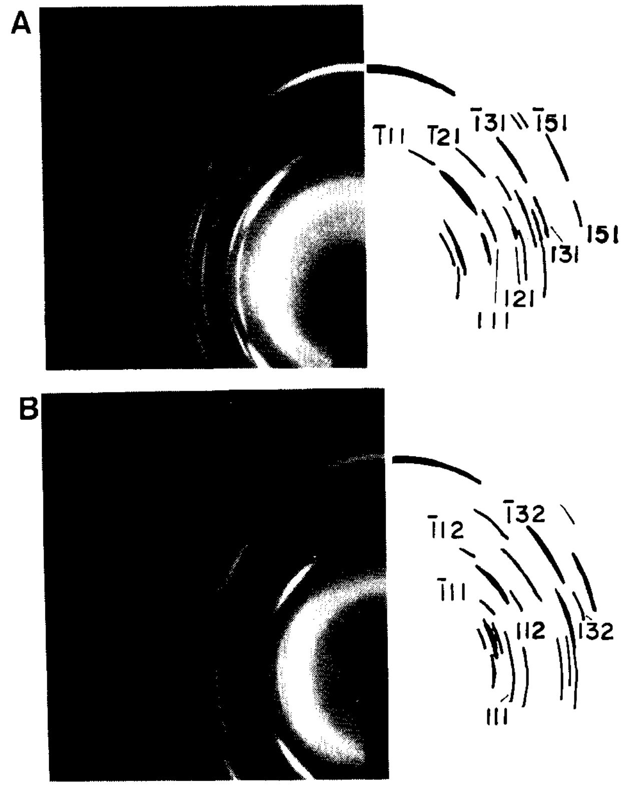

Figure 1. X-ray diffraction patterns and their schematic representations for the tilt samples of (A) form II and (B) form III.

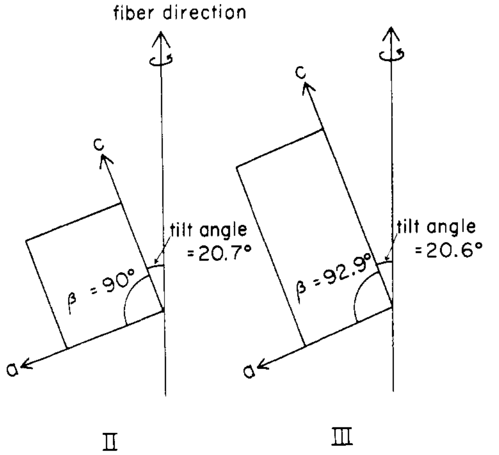

Figure 2. Orientation of the crystallites in the tilt samples of forms II and III.

Å, $\alpha = \beta = \gamma = 90°$)[1] and the reflections in Figure 1B can be indexed by the unit cell of form III (a = 4.96 Å, b = 9.58 Å, c (fiber period) = 9.23 Å, β = 92.9°, $\alpha = \gamma$ = 90°). In both samples, the c axes of the crystallites tilt about 20° around the b axes from the fiber axis of the sample and the crystallites are equally distributed over all angles around the fiber axis (Figure 2). In the case of the form II, it was found that the tilt angle depends on the heat treatment temperature, and the sample with the angle about 45° is obtained by annealing at 175 °C.

On the diffraction pattern of form III, it is observed that the arc of the 132 reflection is located outside the arc of $\bar{1}32$. This suggests that the β unit cell parameter deviates from 90° (β = 92.9°). Lovinger also observed this deviation by electron diffraction.[6] In both cases of forms II and III, hkl and $\bar{h}kl$ reflections have different intensities. This clearly shows that the crystal structures of forms II and III should belong not to the orthorhombic system but to the monoclinic system. Tables I and II give observed intensities and calculated structure factors for some pairs of hkl and $\bar{h}kl$ reflections of forms II and III, respectively. Here, the structure factors were calculated on the basis of the reported crystal structures.[1,2] The tables showed good agreement between observed and calculated values. This suggests that our monoclinic structures are correct. In form II, a slight discrepancy between observed and calculated intensities can be found.[1] This should be interpreted by a kind of disorder contained in the crystallite of form II. A study of structure and disorder of form II is now in progress and the results will be published soon.

Table I
Intensities of hkl and $\bar{h}kl$ Pairs of Reflections by the Tilt Sample of Form II

index	rel intens[a]	$\lvert F_c \rvert$
111	m	22.2
$\bar{1}11$	w	11.3
121	vw	10.6
$\bar{1}21$	w	18.1
131	vw	7.9
$\bar{1}31$	w	23.4
141	vw	10.6
$\bar{1}41$	w	29.1

[a] m = medium, w = weak, vw = very weak, vvw = very very weak.

Table II
Intensities of hkl and $\bar{h}kl$ Pairs of Reflections by the Tilt Sample of Form III

index	rel intens[a]	$\lvert F_c \rvert$
111	w	42.0
$\bar{1}11$	vvw	15.6
112	vw	29.2
$\bar{1}12$	vvw	16.8
131	vw	32.4
$\bar{1}31$	vvw	22.9
132	vw	24.7
$\bar{1}32$	m	68.5
151	vw	27.6
$\bar{1}51$	vw	34.2

[a] See footnote of Table I.

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Iodide-Specific Formation of κ-Carrageenan Single Helices. ^{127}I NMR Spectroscopic Evidence for Selective Site Binding of Iodide Anions in the Ordered Conformation

The carrageenans are sulfated D-galactans extracted from certain marine red algae and characterized by al-

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