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# Use of Azochromophoric Labels as a Molecular Probe of Physical Aging in Amorphous Polymers

When polymers are cooled from the rubbery state to the glassy state, they are in a nonequilibrium state with excess volume and enthalpy. They slowly reach an equilibrium state with concurrent loss of volume (densification) and enthalpy. This phenomenon, which is usually studied as a function of isothermal (sub-$T_g$) annealing time, is referred to as physical aging[1] as opposed to chemical aging. As well as densification, mechanical properties of polymers change as a consequence of physical aging; namely, the material becomes brittle. The current high level of research activity in this important area is directed at both experimental studies and theoretical studies.[2] Among the experimental studies, volume[3] or enthalpy relaxation,[4] mechanical[1c,5] or dielectrical,[6] and diffusion[7] measurements are often made. However, information obtained by these experimental measurements is macroscopic in nature rather than microscopic. It is well-known that physical aging is related to the loss of free volume, which has a certain distribution of sizes at a given temperature and time. It would be very desirable to have some information at the molecular level which can be related to the size distribution of free volume. Toward this goal, we have utilized one of the molecular labeling techniques by analyzing the kinetics of trans ⇄ cis photoisomerization of azochromophores covalently bonded to the main chain of amorphous polymers in small concentrations. As demonstrated by us,[8] such a molecular label, when properly designed in the polymer matrix, can be a sensitive molecular probe of the local environment surrounding the azo label. For example, in our most recent study,[9] we reported that as physical aging proceeds, photoisomerization of the azo label is progressively impeded, reflecting the disappearance of free volume above a certain size, since such isomerization would require free volume of a certain size in the immediate vicinity of the label.[10] We have now analyzed the kinetics of these photoisomerizations more fully. The results seem to provide information on the fraction of free volume above a critical size and its change as a function of temperature and aging time.

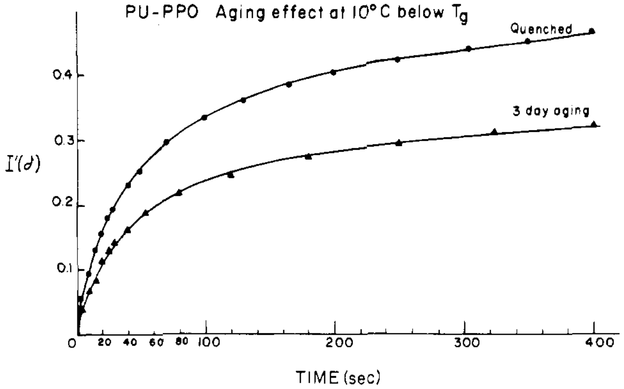
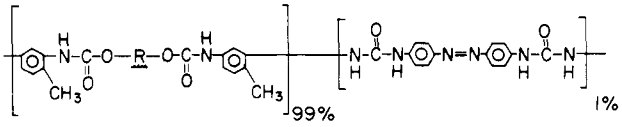


**Figure 1.** Course of the trans ⇄ cis photoisomerization of azobenzene residue in the main chain of PU–PPO at 10 °C below $T_g$ (at −2 °C) as a function of physical aging.

**Chart I**
**Chemical Structures and $T_g$'s of Amorphous Polyurethanes with a Small Concentration of Azo Label in the Main Chain**



| R | | $T_g$(°C) |
|---|---|---|
| $(CH_2)_4$ | PU-BD | 45 |
| $(CH_2)_{10}$ | PU-DD | 15 |
| $\left(\overset{CH_3}{\overset{\vert}{C}}H-CH_2-O\right)_7$ | PU-PPO | 8 |

Three amorphous, single-phase polyurethanes were studied, whose chemical structures are shown in Chart I. $T_g$ was measured by DSC. A description of general polymer syntheses and kinetic studies can be found in ref 8. Quenching of the samples was done from 10 to 12 °C above $T_g$ to their respective glassy temperatures, with the same cooling rate for all samples. This cooling rate in the DSC was 160 °C/min and in the kinetic studies was slower, about 4 °C/min. Therefore the quenched state in the kinetic studies actually corresponds to about 5–8 min of physical aging. Photoisomerization kinetics were always started with all-trans isomers, with similar radiation intensity.

The kinetics of reversible trans ⇄ cis photoisomerization were analyzed based on the following equations,[11] since thermal reaction is negligible at the temperatures we studied:

$$I(\delta) \equiv \left(1 + \frac{D_\infty}{2} + \frac{D_\infty{}^2}{12}\right) \ln |\delta| - \left(\frac{1}{2} + \frac{D_\infty}{6}\right)\delta + \frac{\delta^2}{24}$$

$$I(\delta) = At + \text{constant}$$

where $A = -I_0\phi_t\epsilon_t/y_\infty$, $D_\infty$ and $D$ are optical densities at the photostationary state and at time $t$, respectively, $\delta \equiv D_\infty - D$, $I_0$ is the radiation intensity, $\phi_t$ is the quantum efficiency, $\epsilon_t$ is the molar extinction coefficient, and $y_\infty$ is the cis fraction at the photostationary state. In dilute solutions, the $I(\delta)$ vs. $t$ plot gives a series of almost parallel straight lines up to 90% conversion in the ±20 °C range near $T_g$, meaning that the rate of photoisomerization is almost independent of temperature in this range. But in solid films there is a certain extent of relatively fast reaction followed by much slower reaction. Thus the plot of $I(\delta)$ vs. $t$ results in a curvature if $y_\infty$ is assumed to be 90%. In Figure 1, $I'(\delta)$ is plotted vs. time for convenience, where $I'(\delta)$ is $I(\delta)$ minus the intercept at $t = 0$. When

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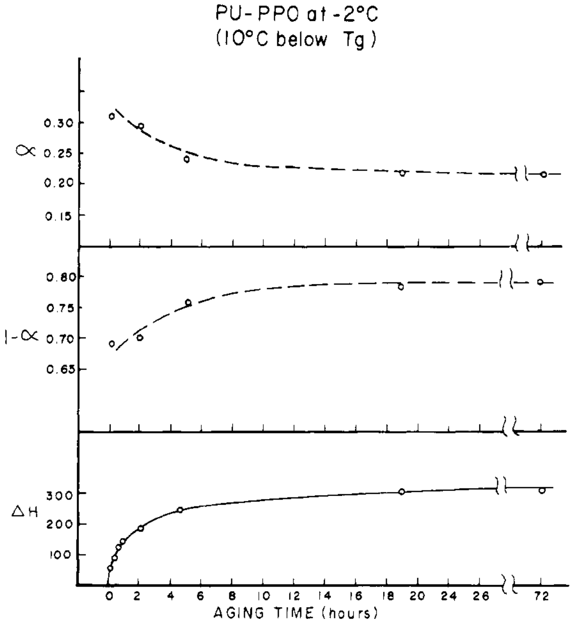

**Figure 2.** Changes of fast rate fraction ($\alpha$), slow rate fraction ($1 - \alpha$), and $\Delta H$ as a function of isothermal (10 °C below $T_g$) aging time.

PU-PPO is quenched from the rubbery state to 10 °C below $T_g$, its photoisomerization proceeds along the upper curve. If the sample is aged (annealed at 10 °C below $T_g$) in the dark prior to irradiation, photoisomerization becomes progressively more sluggish as shown by the lower curve, which corresponds to 3-day aging and which appears to be near equilibrium because a further increase in aging time does not change the curve. Intermediate aging time gives curves in between these two curves. A kinetic profile of this type can be best analyzed by a biphasic process as follows:

$$e^{-I'(\delta)} = \alpha e^{-k_1 t} + (1 - \alpha)e^{-k_2 t}$$

where $k_1$, $k_2$, and $\alpha$ can be graphically estimated. The slower rate, $k_2$, turned out to be about $2 \times 10^{-4}$ s$^{-1}$, while $k_1$ was about $2 \times 10^{-2}$ s$^{-1}$ (100 times faster than $k_2$), regardless of aging time. This fast rate is similar to the rate in dilute solution. The only variable as a function of aging time was $\alpha$, the fraction which is characterized by the faster rate constant ($k_1$). When the sample is quenched, $\alpha$ is about 0.31, which gradually decreases with aging time to about 0.22, with a subsequent increase in the fraction of slower rate ($1 - \alpha$), as shown in Figure 2. Enthalpy relaxation was followed on the same sample as shown in the bottom curve. The $\Delta H$ value corresponds to the graphic area measured from DSC traces by subtracting the DSC trace of the quenched sample, as Petrie[4a] and Uhlmann[4b] have done. It is clear from Figure 2 that both $\alpha$ and enthalpy relaxation reach equilibrium after a similar time period (about 1 day). This rate compares well with the physical aging rate of polystyrene at 10 °C below its $T_g$ as measured by Petrie[5] by mechanical and enthalpy relaxation.

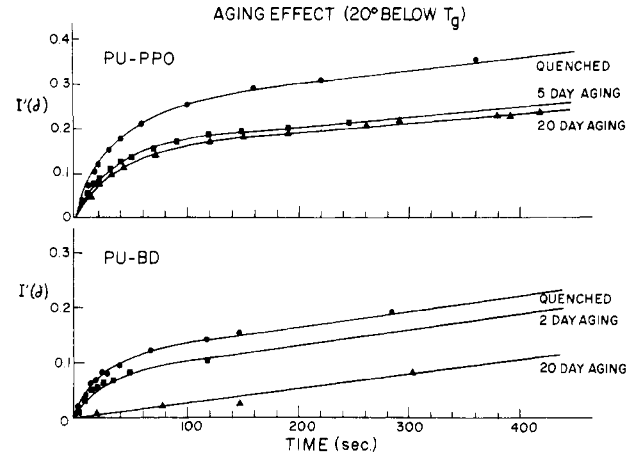

**Figure 3.** Course of the trans ⇄ cis photoisomerization of azobenzene residue in the main chain of PU-PPO and in PU-BD at 20 °C below $T_g$ as a function of physical aging.

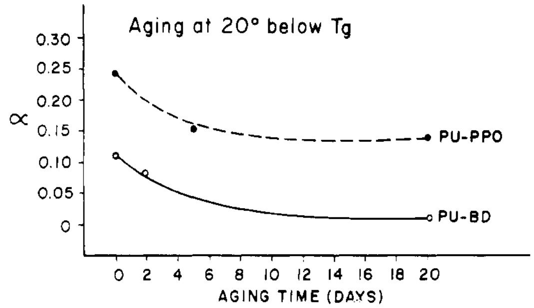

**Figure 4.** Changes of fast rate ($k_1$) fraction ($\alpha$) as a function of isothermal (20 °C below respective $T_g$) aging time for PU-PPO and PU-BD.

At 20 °C below $T_g$, the kinetic profile is of a similar biphasic nature, except that the physical aging process is much slower as shown in Figure 3, taking at least several days to reach an equilibrium. It is also noted in Figure 3 that the extent of photoisomerization is influenced by the choice of diol used in the amorphous polyurethane matrix. In PU-PPO, both in the quenched state and after physical aging, photoisomerization proceeds to a greater extent than in PU-BD. From the near-parallelism of the slower portions of kinetic profiles as shown in Figure 3, it is obvious that similar $k_2$ values can be used to fit these data in biphasic analyses for both PU-PPO and PU-BD. Furthermore, $k_1$ and $k_2$ values from these data turned out to be similar to the values from Figure 1. The error in $k_1$ ($(2.0 \pm 0.3) \times 10^{-2}$) in curve fitting is smaller than in $k_2$ ($(2.0 \pm 1.0) \times 10^{-4}$). In other words, $k_1$ appears to be independent of the extent of physical aging, of whether the matrix is PU-PPO or PU-BD, and of the temperature, while $k_2$ may have a small temperature dependence which contributes to the error. The available data do not permit accurate assessment of temperature dependence in $k_2$ at the present time, but future work will address this problem. If we assume $k_1$ and $k_2$ to be $2 \times 10^{-2}$ and $2 \times 10^{-4}$, respectively, we can nevertheless obtain the plot of $\alpha$ as a function of physical aging at 20 °C below $T_g$ for both polymers as shown in Figure 4. For PU-PPO in the quenched state at 20 °C below $T_g$, $\alpha$ is lower than at 10 °C below $T_g$ but much greater than that for PU-BD at the equivalent temperature. There is a progressive decrease in $\alpha$ for both PU-PPO and PU-BD over a period of 20 days, but even after 20 days, $\alpha$ for PU-PPO is greater than for PU-BD. In fact, for PU-BD, $\alpha$ approaches zero after 20 days or, as shown in Figure 3, if the film is cast and slowly dried at 25 °C (20 °C below $T_g$).

In view of the results discussed above and the fact that $\alpha$ approaches unity at temperatures well above $T_g$, we propose to interpret $\alpha$ as reflecting the fraction of free volume above a certain critical size which is necessary for the azo label to isomerize. In regions of this high free volume, photoisomerization seems to occur without much difficulty, since $k_1$ is similar to the rate observed in dilute solution. It is interesting to note that Robertson,[2b] in his

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

| | $\rho_A$ at room temp | $M$ | $Vw$ | $\rho^*$ |
|---|---|---|---|---|
| polyethylene | 0.855 | 28 | 20.46 | 0.625 |
| poly(propylene oxide) | 0.998 | 58 | 34.38 | 0.592 |

[a] $\rho^*$ (packing density) = $\rho_A Vw/M$, where $\rho_A$ 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, $\alpha$ 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 $\alpha$, 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 $\alpha$ 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