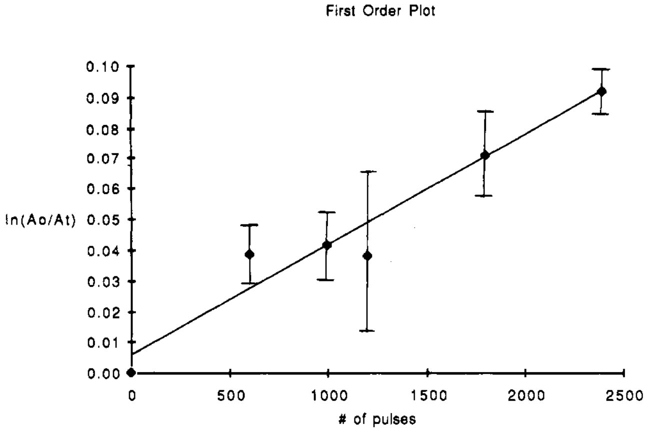

**Figure 3.** Fraction of PBD π-bonds reacted as a function of the number of laser pulses. Plotted as a first-order process.

formation of the films. The presence of chlorine at the surface of the polymer could be ascribed to the formation of fluorochlorocarbene in the photolysis of Freon 22; however, this source of chlorine is unlikely because fluorochlorocarbene is not produced when Freon 22 is photolyzed according to the experimental conditions described.[2-5]

The $^{19}F$ NMR spectra of reacted samples of PBD dissolved in chloroform had a single resonance of −128.6 ppm that indicates the presence of a geminal difluorocyclopropane. The chemical shifts for similar difluorocyclopropanes range from −121 to −135 ppm.[7,8] Additionally, the observed chemical shift is consistent with results obtained by Cais for difluorocarbene addition to *cis*- and *trans*-polybutadienes.[9] Reacted samples of PBD that were washed with solvents (e.g., methanol) prior to $^{19}F$ NMR experiments still exhibited the same resonances. This result indicates that the fluorine incorporated into the surface of the PBD is probably chemically bonded to the surface and not simply adsorbed by the polymer's surface.

The MIR-IR spectra of PBD exposed to difluorocarbene showed measurable changes relative to the MIR-IR spectra of unreacted PBD. For example, the intensity of the absorption associated with the π-bond at 1638 cm$^{-1}$ decreased with increasing exposure of the polymer to difluorocarbene. This result is consistent with the hypothesis that difluorocarbene is reacting with the π-bonds of PBD. The rate law for this reaction is

$$\text{rate} = k'[:CF_2][\pi\text{-bonds}]$$

However, since only ~1% of the Freon 22 in the volume subtended by the laser beam reacts with each laser pulse to yield difluorocarbene, the [:CF$_2$] is small and essentially constant for the conditions of these experiments. Therefore, the rate law for the reaction can be approximated as

$$\text{rate} = k[\pi\text{-bonds}] \quad \text{and} \quad k = k'[CF_2]$$

and the extent of this reaction can be described by an equation analogous to a first-order kinetic analysis; i.e., $A_0/A_n = e^{kn}$ in which $n$ is the number of laser pulses, $k$ is the fraction of the π-bonds of PBD reacted per pulse, and $A$ is the absorbance at 1638 cm$^{-1}$ at time zero (no pulses) and after $n$ pulses. This relationship is represented in Figure 3 (slope = $3.6 \times 10^{-5}$, $r = 0.97$). Similar results were obtained by analysis of other IR bands, e.g., the absorptions between 900 and 1000 cm$^{-1}$, which are assigned to the out-of-plane C–H motions of monosubstituted alkenes.

In a set of control experiments the laser was tuned to the R(20) line of the 001–020 transition (1078.6 cm$^{-1}$). The Freon 22 did not react to give difluorocarbene at this laser frequency. The PBD samples subjected to these control conditions showed no significant changes in the IR absorption bands associated with the π-bonds. Therefore, IR laser-induced decomposition of the Freon 22 is necessary to produce the observed changes in PBD. This observation is consistent with the ESCA results (vide supra), which indicated that simple exposure to Freon 22 did not alter the PBD.

The results of the ESCA, MIR-IR, and $^{19}F$ NMR studies support the hypothesis that difluorocarbene generated by IR laser photolysis of Freon 22 reacts with 1,2-polybutadiene. Further studies on the effect of gas pressures and laser power on this reaction as well as on laser-induced reactions of other carbenes (e.g., dichlorocarbene[10] and difluorovinylidene[11]) with polybutadienes and other polymers (e.g. polystyrene and poly(ethylene glycol)) are in progress.

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**Registry No.** PBD, 9003-17-2; $F_2C^{2\bullet}$, 2154-59-8; $CHClF_2$, 75-45-6.

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# On a Controversy about Orientation Relaxation in Polystyrene Studied by Infrared Dichroism

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## Introduction

An understanding of polymer chain orientation in deformed melts is clearly of interest from the perspectives of both applied polymer processing and fundamental theory. It is now possible to follow the molecular response of a polymer melt subjected to a step strain by spectroscopic techniques, notably Fourier transform infrared (FTIR) dichroism. It is the purpose of this report to resolve an existing controversy based on FTIR measurements of uniaxially oriented polymer films.

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Independently, two research groups have reported FTIR measurements of the orientation relaxation in uniaxially drawn polystyrene films. Application of the same technique to the same polymer system apparently yields different experimental data sets, each one supporting a different model of polymer dynamics. Wool and Lee[1-3] report data which are consistent with the minor chain (MC) model,[4] while the results of Tassin and co-workers[5-8] support the model of Doi and Edwards (DE).[9,10] To resolve this controversy, we have reproduced both experiments with a high molecular weight polystyrene of relatively narrow molecular weight distribution and have made a critical comparison between the two data sets.

## Experimental Section

The polymer chosen for this comparison was an atactic polystyrene of weight-average molecular weight ($M_w = 1\,190\,000$) and polydispersity ($M_w/M_n = 1.40$). This high molecular weight was intentionally chosen so as to differentiate the two models more clearly. If the polymer exhibits more than one characteristic relaxation time, then these times should be the most clearly separated at high molecular weight. Polymer films were prepared by two techniques. Since the same material was used in both preparative techniques, any effect due to the molecular weight distribution will be equally present in both types of films.

The first technique was that described by Wool and Lee,[1] and the resulting films will hereafter be referred to as PS1. By this technique, films were prepared by dissolving the polymer in toluene and casting on a clean glass plate. After the films were air-dried, they were further dried at 100 °C under vacuum for 1 day.

The second technique corresponds to that of Tassin and coworkers, and the resulting films are designated PS2. In this preparative technique, the polystyrene was dissolved in benzene rather than toluene. After having been cast on glass and air-dried, the PS2 films were dried under vacuum at 150 °C for 3 days. For both PS1 and PS2, the films were dried on a reticulated plaque to give an irregular surface to the films and hence avoid interference fringes in the FTIR measurements.

Uniaxial extension of the films was performed in a new hydraulic apparatus designed in this laboratory. Its conception is similar to the one described in ref 11; improvements have been made on the strain rate ($10^{-4}$–1 $s^{-1}$) and temperature ranges (–50 to 250 °C). Elongation to a draw ratio of $\lambda = 4$ was performed at 115 ± 0.3 °C with a constant stretching rate of 0.1 $s^{-1}$. After stretching, the films were held at fixed strain and constant temperature for the desired aging time and then rapidly quenched to room temperature. This quench below the glass transition temperature ($T_g$) effectively freezes the residual orientation of the polymer and allows subsequent FTIR measurement of the partially oriented glass at ambient temperatures. For the two longest aging times of PS2, stretching was performed at 138 ± 0.4 °C, and the measured orientation was shifted by a standard WLF factor. Similar applications of time–temperature superposition are well established.[12] To check the presence of residual solvent in the films, the $T_g$ of unstretched material was determined by differential scanning calorimetry after various aging times. A Du Pont Instruments 1090 thermal analyzer was used with a scan rate of 20 °C/min.

Polarized infrared spectra are collected with a Nicolet 7199 FTIR spectrometer equipped with a SPECAC gold wire grid polarizer. For these measurements, the polarizer was kept in a fixed position and the samples were rotated. Each spectrum was based on 128 scans and had a resolution of 2 $cm^{-1}$. Dichroic ratios were calculated as $R = A_{\parallel}/A_{\perp}$ where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances parallel and perpendicular to the stretching direction, respectively. The orientation function $P_2(\cos\theta)$ was determined as

$$P_2(\cos\theta) = \frac{R-1}{R+2}\,\frac{R_0+2}{R_0-1}$$

where $R_0 = 2\cot^2\alpha$, where $\alpha$ is the angle between the dipole moment of the considered vibration and the chain axis and $\theta$ is the angle between the chain axis and the stretching direction. For this study, the absorption at 906 $cm^{-1}$ was selected since it is known to correspond to the out-of-plane $\nu_{17b}$ mode of the benzene ring, for which $\alpha = 35°$.

## Theoretical Section

Since the MC and DE theories have already been developed in previous papers,[1,7] we will only recall their specific predictions. The MC theory describes orientation relaxation in terms of a single relaxation time $T_r$ through a reptation process. This time corresponds to the rearrangement of the chain conformation to about 70% of its initial value by curvilinear diffusion along its contour. For times $t < T_r$, the orientation $F(t)$ is predicted to vary as

$$F(t) \simeq 1 - (4/\pi^{3/2})(t/T_r)^{1/2}$$

Hence a plot of $F(t)$ vs $t^{1/2}$ should be linear with a negative slope of $4/(\pi^{3/2}T_r^{1/2})$.

In contrast to the MC model, the DE model describes the dynamics of relaxing polymer chains by three characteristic times: $\tau_A$, the time for Rouse motion of chain subsections between entanglements; $\tau_B$, the time for retraction of the deformed chain inside its deformed tube to recover its equilibrium curvilinear length (this motion is only important for large deformations); and $\tau_C$, the time for reptation of the chain through its deformed tube.

Though originally devised to describe the motion of a free chain through a net of fixed obstacles, this model can be made self-consistent to account for the motion of the surrounding chains.

The relaxation of orientation for a single chain in a fixed network is predicted to be the product of three relaxation functions related to each of these processes. Self-consistency effects can be easily taken into account. Mathematical expressions of the relaxation functions have been already given in ref 7. Theoretical scaling predictions exist which interrelate the three relaxation times $\tau_A$, $\tau_B$, and $\tau_C$. Hence, once $\tau_A$ is determined, the other parameters are fixed.

Although the two models are equivalent at long times when reptation is the dominant mechanism, their predictions are very different at short and intermediate times.

## Results and Discussion

The essential difference between the two data sets is the technique used to prepare the films. To compare the orientation relaxation in PS1 and PS2, we have plotted $P_2(t)$ vs $t^{1/2}$ in Figure 1. As is readily apparent, the PS1 data fall on a straight line as previously reported by Wool and Lee. However, the $T_g$ does not remain constant with time. This implies the presence of residual solvent, which gradually leaves the polymer film during aging at 115 °C. This point has been further checked by multiple DSC runs, the sample being held at 140 °C for 15 min after each run. A $T_g$ shift of 15 °C has been noted after the first run together with a 4% weight loss. On further runs, smaller shifts have been noted until $T_g$ reaches 102 °C. Unfortunately, similar measurements of $T_g$ were not reported in previous preparations[1] of films spanning a range of molecular weights. Nonetheless, our present data on a single molecular weight are unequivocable. When the technique of Wool and Lee is used to prepare films of this molecular weight, residual solvent is present which plasticizes the chains and alters the $T_g$. The presence of residual solvent reduces the relaxation times at a given temperature. Therefore, the time regimes for Rouse motion and retraction may pass too rapidly to be seen experimentally. This would explain why the samples appear to follow a single long-time relaxation. Due to this

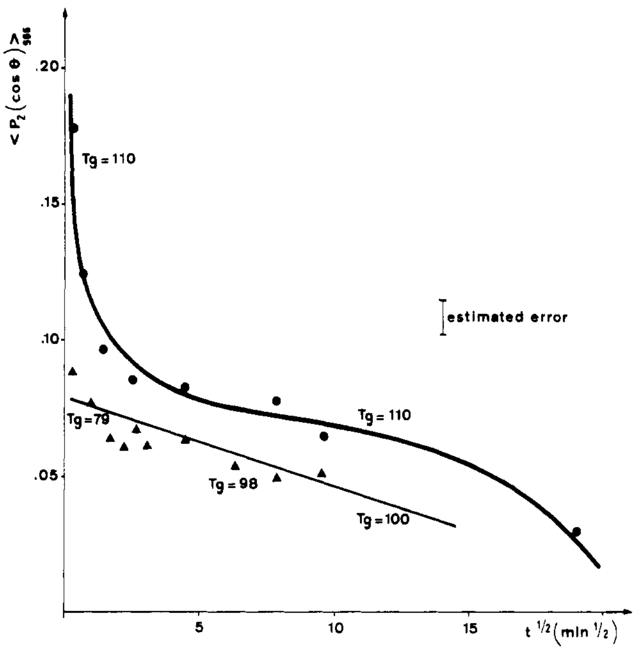

**Figure 1.** Orientation function and glass transition temperature as a function of time for polystyrene (▲, PS1; ●, PS2).

changing glass transition temperature, the determination of a relaxation time seems ambiguous.

If we now consider the PS2 data set in Figure 1, it is seen that this preparative technique effectively removes all solvent from the films since a constant $T_g$ is observed. The PS2 data cannot be described by a single relaxation time. Hence, for this polystyrene at 115 °C and $\lambda = 4$, the MC model does not accurately describe the relaxation of orientation in this time range.

We now consider the second model, that of Doi and Edwards. In order to calculate the relaxation predicted by the DE model, several parameters must be known. The Rouse relaxation time $\tau_A$ has been shown to be 5.6 s for polystyrene at 120 °C.[6,7] We have shifted this value to our experimental temperature of 115 °C by the well-known WLF relation and obtained a value of $\tau_A(115\ °C) = 28$ s. Knowing $\tau_A$, the other relaxation times have been calculated by scaling laws. The predicted values are $\tau_B = N^2\tau_A$ (since a limited number of Rouse subchains have to be considered, which modifies the numerical prefactor in the scaling law[7]) and $\tau_C = 3N\tau_B$, where $N$ is the number of entanglements per chain. The value of $N$ is obtained from the molecular weight between entanglements (18 000 for polystyrene).

The resulting predictions of the DE model are compared with the experimental data in Figure 2. The agreement with the model is quite reasonable. As already observed for other molecular weights, a slight divergence can still be noted at short times. Self-consistent corrections for the motions of the surrounding chains improve the agreement at long times.

## Conclusions

Previous discrepancies in FTIR dichroism studies of chain relaxation are shown to arise from sample preparation artifacts, namely, plasticization of the melt by residual solvent. When measurements are made with consistently prepared samples, stretched close to the glass transition temperature, the relaxation of a high molecular weight polystyrene melt cannot be described by the reptation process alone. Additional relaxations at short and intermediate times are seen. Quite reasonable agreement is observed with the predictions of the DE model, especially when allowance is made for the self-consistent motion of the surrounding chains.

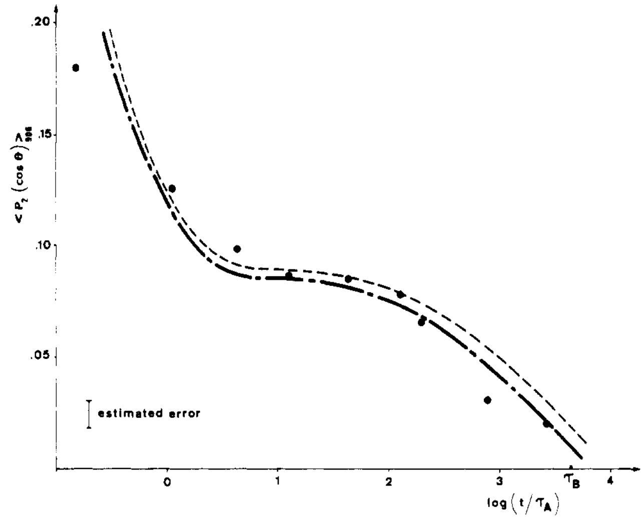

**Figure 2.** Orientation function vs time for polystyrene PS2 compared with theoretical predictions (- - -, free chain in a fixed network; —·—, self-consistent treatment).

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**Registry No.** PS, 9003-53-6.

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# Permeation of Aqueous KBr through Langmuir–Blodgett Films of Singly and Doubly Polymeric Monolayers

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We describe herein the permeation experiment of aqueous KBr across Langmuir–Blodgett (LB) films deposited on a porous polymer film. The gas permeation characteristics of the LB films have been examined by several groups, because of their unique structures as very thin films of ordered molecules. Rose and Quinn[2] showed in their pioneering study that the rate of gas permeation was reduced by a built-up multilayer film of stearic acid.

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