Macromolecules **1989**, *22*, 481-483

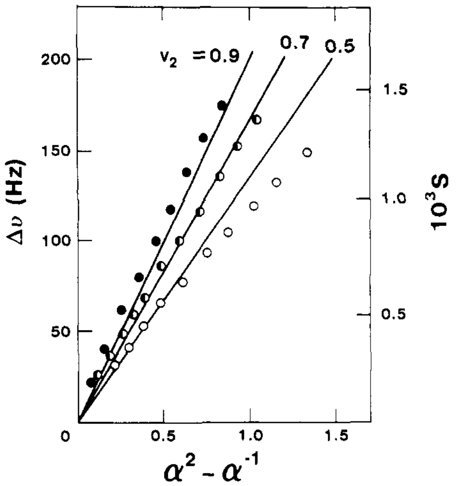

Figure 1. Quadrupolar splitting, $\Delta\nu$, and orientation function, S, for PDMS networks, shown plotted against the strain function ($\alpha^2 - \alpha^{-1}$).[7] The networks were prepared at the specified values of the volume fraction, v_{2C}, of polymer present during cross-linking and contained approximately 10 wt % $CDCl_3$ during the deuterium NMR measurements used to obtain $\Delta\nu$ and S. The experimental results are shown by the circles and the results calculated for phantom networks by the curves.[3,9]

constrained junction model.[3,9] This requires simply including the term $2B_x/\phi$ on the right-hand side of eq 4, where

$$B_x = (\lambda_x - 1)(\lambda_x + 1 - \zeta\lambda_x^2)/(1 + g_x)^2 \qquad (8)$$

with

$$g_x = \lambda_x^2[\kappa^{-1} + \zeta(\lambda_x - 1)] \qquad (9)$$

The two parameters κ and ζ characterize the severity of the constraints on the junctions and the nonaffineness of the transformations of the constraint domains, respectively.[3,9]

Results and Discussion

Typical experimental values of $\Delta\nu$ and S reported by Deloche et al.[7] for undeuterated polymer are shown by the circles in Figure 1. They are shown plotted against the strain function appearing in eq 7 for three representative values of v_{2C}. The curve from the phantom network theory can be fit to the data for $v_{2C} = 0.7$ and $v_2 = 0.90$ by the choice $D = 3.36 \times 10^{-3}$, as is shown in the figure. Recalculations of S from eq 7 for $v_{2C} = 0.9$ and 0.5 (with $v_2 = 0.90$) then give the other two curves. They are seen to give good representations of the two corresponding sets of experimental data, thus demonstrating that the observed dependence of S on v_{2C} can be simply accounted for by proper definition of the extension ratios. Explanations in terms of trapped entanglements[7] are thus clearly unnecessary, and in fact erroneous.

Although the issue involving reference volumes is of primary importance, the agreement is found to be even better if the same analysis is used with the constrained junction theory. The experimental data for $v_{2C} = 0.9$, 0.7, and 0.5 (with $v_2 = 0.90$) are fitted by $D = 2.37 \times 10^{-3}$ and the v_{2C}-dependent expression for PDMS[10]

$$\kappa = \kappa_0 v_{2C}^{4/3+m} \qquad (10)$$

with $m = 8/9$. Using these parameters and $\kappa_0 = 3$ and $\zeta = 0$ (the usual value)[3] in eq 9, 8, 4, 5, 6, and 3 then gives the curves shown in Figure 2. There is now nearly perfect agreement between experiment and theory. Similarly good agreement is obtained for the experimental results[7] reported for the deuterated polymer.

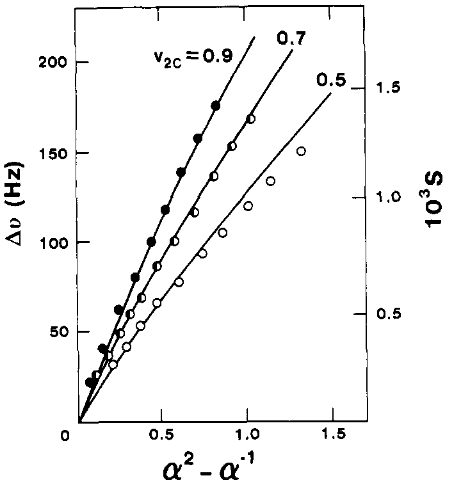

Figure 2. Same experimental results[7] as in Figure 1 but theoretical curves calculated from the constrained junction theory of elastomeric networks.[3,9]

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Infrared Laser-Induced Reactions of Difluorocarbene with 1,2-Polybutadiene

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Laser-induced gas–solid heterogeneous reactions are important because they provide insight into mechanisms of heterogeneous processes and hold promise of technical innovations for practical applications.[1] Most work has involved metal and metal oxide surfaces (e.g., Pt, Zn, TiO_2, ZnO) or non-metal and non-metal oxide surfaces (e.g., Si, Ge, SiO_2); however, little effort has been expended to study the analogous reactions involving polymers. Alterations of polymer surfaces without affecting the bulk of the

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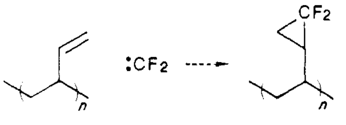
polymer have potential for producing low-cost polymers for specialty applications. We have investigated the infrared laser-induced reactions of difluorocarbene with 1,2-polybutadiene (PBD) and herein report our findings.

When chlorodifluoromethane (Freon 22) is irradiated by the focused output of a pulsed CO_2 TEA laser, it absorbs energy and decomposes to difluorocarbene and HCl (reaction 1).[2-4] Once formed, the carbene can migrate to the surface of a PBD film and react with π-bonds to form difluorocyclopropanes.[5] However, two known reactions could compete with this process (reactions 2 and 3). The reaction of difluorocarbene with HCl to reform Freon 22 is a very slow reaction[2,3] and therefore should not successfully compete with the desired reaction. Since the dimerization of difluorocarbene has a relatively small rate constant,[2] and since the concentration of the carbene at any time is low, this bimolecular process should not compete with the reaction of carbene with PBD. Thus, the difluorocarbene generated in the presence of PBD may react with the π-bonds to form geminal difluorocyclopropanes at the surface of the polymer (reaction 4).

$$HCClF_2 \rightarrow :CF_2 + HCl \qquad (1)$$

$$:CF_2 + HCl \rightarrow HCClF_2 \qquad (2)$$

$$2(:CF_2) \rightarrow CF_2{=}CF_2 \qquad (3)$$



(4)

Experimental Section

The experiments were performed with a grating-tuned Lumonics TEA 101 CO_2 laser which was operated at 0.5 Hz and was tuned to the R(36) line of the 001–020 transition (1087.9 cm^{-1}). The laser beam was collimated by using ZnSe lenses in order to obtain qualitatively reproducible beam profiles, which were checked by using thermally sensitive paper. In all cases the laser fluence was 0.9 ± 0.1 J/cm^2. The power was monitored with a Scientech Model 362 power–energy meter. Frequencies were determined by using an Optical Engineering 16A CO_2 spectrum analyzer.

The photolysis cell was a 250-mL round-bottomed flask modified with gas inlet ports and fitted with KCl or NaCl windows. The PBD films were mounted on a glass plate (1.8 cm × 8.0 cm) affixed to a rotatable stopcock at the center of the cell. The cell was filled with 1.0 ± 0.1 Torr of Freon 22 on a vacuum line equipped with a Granville-Phillips Model 275 convectron gauge.

Reactions were performed by positioning the cell within the laser beam path so that the parallel geometric relationship of PBD film to the beam was constant. Typically, between 600 and 2400 pulses were delivered to a given sample prior to analysis of the reacted PBD. The PBD was analyzed with multiple internal reflectance infrared spectroscopy (MIR-IR) performed on a Perkin-Elmer Model 983. Changes in IR absorbances of the PBD were determined by standard spectral subtraction techniques.[6] Nuclear magnetic resonance experiments (^{19}F NMR) were performed with a JEOL FX-90Q spectrometer operated at 84.25 MHz with a spectral width of 50 kHz and hexafluorobenzene as the reference ($\delta = -163$). Typically, 8000 transients were acquired from ~10% polymer solutions in $CDCl_3$ in a 5-mm sample tube at ambient temperature. ESCA experiments were done by an independent laboratory in the University of Missouri–Rolla.

The chlorodifluoromethane (Freon 22, Matheson) was used without further purification. However, the sample was always subjected to freeze–pump–thaw cycles before use in an experiment. The 1,2-polybutadiene films were prepared from solutions of the polymer (Scientific Polymer Products, Inc.) in distilled chloroform. The solutions were poured over smooth, level pieces of aluminum foil, and the solvent was allowed to evaporate. Samples of the polymer film (1.5 cm × 2.0 cm) were then cut and used with the aluminum backing. The foil backing facilitated handling of the PBD films.

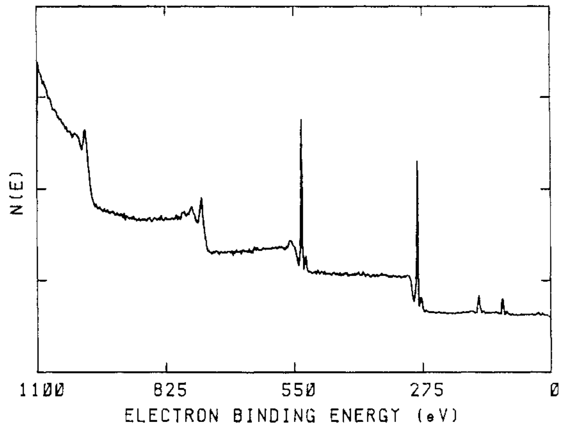


Figure 1. ESCA profile for unreacted PBD film.

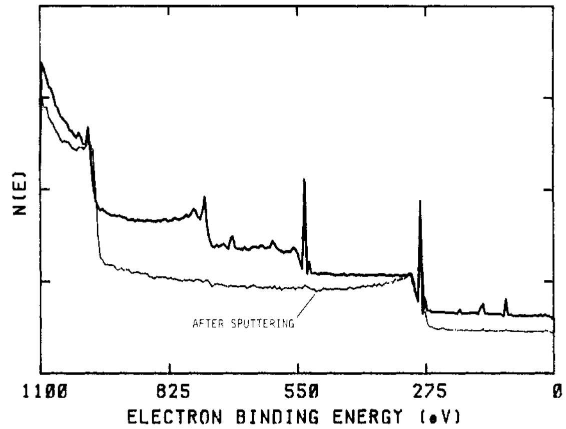


Figure 2. ESCA profile for PBD film reacted with difluorocarbene.

Results and Discussion

The ESCA profiles of various PBD films are provided in Figures 1 and 2. The profile of the unreacted PBD film (Figure 1) shows peaks that correspond to carbon (289 and 1008 eV), oxygen (537 and 756 eV), and silicon (105 and 156 eV). The use of silicon grease on the glassware used to distill chloroform and to prepare polymer solutions accounts for the silicon and oxygen. Additionally, some oxygen may be attributed to the slow oxidation of the PBD samples. The profile for a reacted PBD film (Figure 2, upper curve) possesses these same peaks and a new peak at 691 eV, which indicates the presence of fluorine. When ~30 Å of the PBD surface is removed by sputtering, the fluorine peak disappears (Figure 2, lower curve). This result indicates that fluorine is only at the surface of the PBD film. The incorporation of fluorine into the PBD surface is rationalized by the reaction of difluorocarbene with the polymer (reaction 4). The fluorine in the reacted PBD samples cannot be attributed to absorption of Freon 22 by the polymer. The ESCA profile of PBD subjected to all experimental conditions except laser photolysis (i.e., mounting in the photolysis cell, evacuation, and exposure to Freon at 1.0 Torr for 90 min) does not exhibit a peak at 691 eV. Indeed, the ESCA results for the polymer simply exposed to Freon 22 are identical with those results obtained for completely untreated PBD.

The ESCA peak at 203 eV, which is evident in Figure 2, is assigned to chlorine. Sputtering experiments indicate that the chlorine is occasionally present in the bulk of the polymer, and therefore its presence is probably an artifact associated with occlusion of chloroform by PBD during the

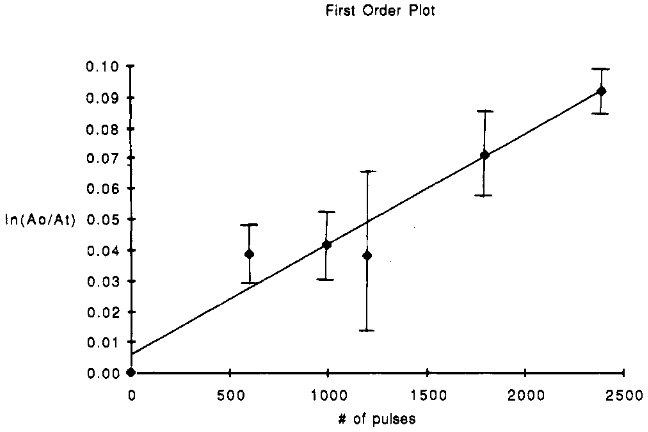


Figure 3. Fraction of PBD π-bonds reacted as a function of the number of laser pulses. Plotted as a first-order process.

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

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

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

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

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 = 3.6×10^{-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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