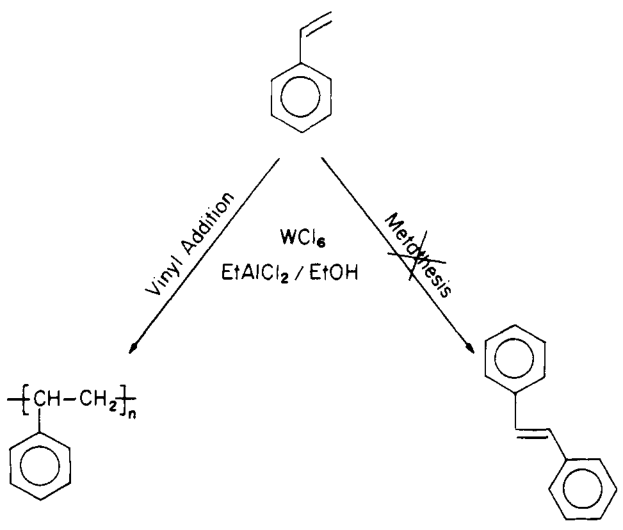

Figure 7. Styrene model compound reactions.

as a cocatalyst and even when tungsten hexachloride is used with no cocatalyst at all. Vinyl addition reactions are important "side" reactions, which indeed become the only reaction when the monomer favors cationic polymerization.

Obviously catalyst selection is important, and our research has turned to the synthesis of metathesis catalysts based on molybdenum and tungsten wherein no Lewis acid cocatalyst are present.[19] Our work on acyclic diene metathesis polymerization will continue since we feel the potential for this polymerization scheme is significant.

Acknowledgment. We thank the National Science Foundation–Solid State Chemistry (Grant DMR-8416511) for supporting M.L.-H., Dr. Dan Straus for his guidance in the initial experiments, and Dr. David S. Breslow for helpful discussions. We also thank DARPA (URI Navy Grant N00014-86-G-0224) for supporting K.B.W.

Registry No. 1 (homopolymer), 108793-14-2; 2 (homopolymer), 25067-96-3; 3, 28702-45-6; 4, 25038-44-2; WCl$_6$, 13283-01-7; EtAlCl$_2$, 563-43-9; C$_6$H$_5$CH=CH$_2$, 100-42-5.

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(12) See Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983; p 143. Self-metathesis was thought not to be possible "...presumably because the degenerate reaction is strongly favored". The author does note that cross metathesis of 1,5-hexadiene and cycloocta-1,5-diene has been observed (Pinazzi, C. P.; Campistron, I.; Reyx, D. *Revl. Trav. Chim. Pays-Bas* **1977**, *96*, M59). Other 1,5-hexadiene cross-metathesis reactions have been reported as well.
(13) The gas chromatograph used was an Aerograph Model 600-D, equipped with a 30-ft × $^1/_8$-in. column packed with 20% SE-30 on chromosorb P. The infrared spectrometer was a Perkin-Elmer Model 281. NMR spectra were obtained on a Nicolet NT-300 spectrometer operating at a field of 7 T.
(14) Degenerate metathesis of terminal olefins exchanges carbons and simply recreates the reactant, whereas productive metathesis produces a coupled product plus—in this case—ethylene. See: Tanaka, K.; Tanaka, K.; Miyahara, K. *J. Chem. Soc., Chem. Commun.* **1979**, 314.
(15) Polyoctenamer NMR and other data can be found in: Sato, H.; Okimoto, K.; Tanaka, Y. *J. Macromol. Sci.—Chem.* **1977**, *A11*, 767.
(16) To a certain extent this low number is not unexpected, since we used 98% pure 1,9-decadiene in these experiments. Assuming a stoichiometric imbalance ratio of 0.98 and 99% metathesis of the monomer in this step polymerization, calculations predict a number-average degree of polymerization of only 50, or a number-average molecular weight of 5500. Also, the monomer/catalyst ratio is also rather low in this work.
(17) Comparisons were made with the spectra of an authentic sample of polybutadiene obtained from Aldrich.
(18) In fact, if the polymerization is not terminated with methanol, the oil becomes insoluble in hexane after standing over a period of weeks, suggesting that slow vinyl addition reactions are continuing.
(19) At least one homogeneous metathesis catalyst free of Lewis Acids has been made. See: Schaverian, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

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Photochromic and Fluorescent Probe Studies in Glassy Polymer Matrices. 2. Isomerizable Planar Probe Molecules Lacking an Inversion Center of Symmetry

The extent of conversion of certain photochromic molecules which undergo trans–cis photoisomerization has been shown to be nearly always less in a rigid matrix such as a polymer glass (without significant sub-T_g relaxation taking place) than in nonviscous solutions.[1-5] This is consistent with the presence of two molecular environments in the rigid matrix: one which allows trans–cis isomerizations at rates comparable with those in solution, and another which blocks the isomerization. The blocking environment has been hypothesized to arise from insufficient local free volume to allow the isomerization at a molecular level.[2-5] In paper 1 of this series,[2] minimum local free volumes required by various trans–cis photochromic molecules to isomerize were calculated[2] based on van der Waals molecular volumes and known isomerization pathways. It was found that as the local free volume required for photoisomerization increases, the extent of isomerization at photoequilibrium achieved in polystyrene glass, divided by that achieved in toluene, decreases. This correlation amounts to a quantitative measurement of the distribution of local free volume in the polystyrene glass,[2] slightly increased by the local free volume added by the presence of small probe molecules.

In contrast with our previous findings for unattached photoisomerizable probe molecules,[2] and those of Sung et al.[4] for polymers having covalently attached azobenzene labels, Priest and Sifain[1] found that 4-ethoxyazobenzene had the same extent of isomerization at photoequilibrium

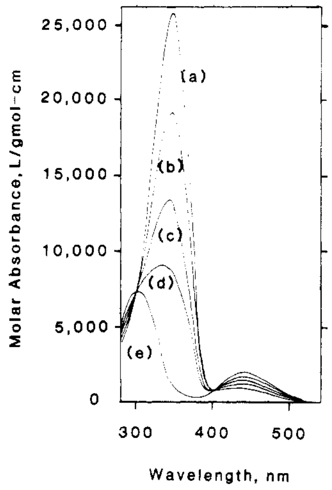
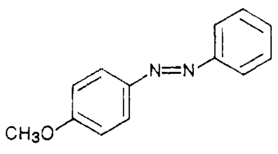
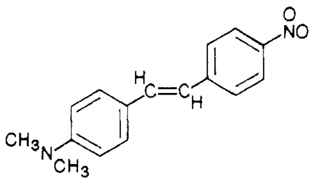


Figure 1. UV absorbance spectrum of 4-methoxyazobenzene in toluene following irradiation at 365 nm for fixed lengths of time: (a) all-trans isomer, (b) 1 min, (c) 2 min, (d) 3 min, (e) 9 min and longer.

in unannealed polystyrene glass as in butylbenzene solution. *trans*-4-Ethoxyazobenzene can photoisomerize to the cis form by an "inversion" pathway, similar to azobenzene.[6] Unlike azobenzene, the "inverting" groups, 4-ethoxyphenyl or phenyl, do not require an equivalent amount of local free volume to isomerize. 4-Ethoxyazobenzene is thus one of a class of photochromic molecules with planar trans isomers that photoisomerize to cis isomers by segments that cannot be superimposed through an inversion center of symmetry. We examined the photoisomerization of two other such molecular species, 4-methoxyazobenzene and 4-(dimethylamino)-4′-nitrostilbene (DANS), to see if any general conclusions could be reached regarding their suitability as probes of local free volume in polymer glasses.



4-methoxyazobenzene



DANS

trans-4-Methoxyazobenzene and *trans*-DANS, shown below, were used as received from Fluka Chemical Co. and Eastman Kodak Chemical Co., respectively. The solvent *tert*-butyl acetate, a model compound for poly(methyl methacrylate) (PMMA), was purchased from Fluka Chemical Co. Polystyrene and PMMA with narrow molar weight distributions were from Pressure Chemical Co., having molar weights of 670000 and 188200, respectively.

Film preparation, other chemicals and solvents, and details of the experimental procedure and UV absorbance measurements have been described elsewhere.[2] Films were unannealed: they were kept at 120 °C (above their glass transition temperature) for 10–15 min in vacuum and then quenched rapidly to ambient temperature in another vacuum oven, with photoisomerization carried out immediately after the films had cooled. Photoisomerizations were completed within several tens of minutes from the films being quenched. Photoisomerizations were done by using equipment described elsewhere,[2] except that a 150-W xenon lamp with a continuous UV emission spectrum was used instead of a mercury lamp, to allow greater flexibility in the choice of wavelength used to irradiate films and solutions. The nominal wavelength of irradiation had a bandwidth of 16 nm. Relatively small changes in temperature affected the extent of photoisomerization of DANS so that experiments with this probe were carried out at 25.0 ± 0.4 °C. Experiments with other probe molecules were carried out at 23–25 °C.

Table I
Ratio of Molar Absorption Coefficients, $\epsilon_{cis}/\epsilon_{trans}$, Found at the Principal UV Absorbance Peak Used To Measure the Extent of Isomerization

photochromic species	solvent	wavelength, λ, nm	$\epsilon_{cis}/\epsilon_{trans}$ at λ
azobenzene	toluene	320	0.050
	tert-butyl acetate	317	0.047
4-methoxyazobenzene	toluene	348	0.028
	tert-butyl acetate	344	0.034
4,4′-dinitrostilbene	toluene	358	0.250
	tert-butyl acetate	354	0.233
DANS	toluene	430	0.37
	tert-butyl acetate	425	0.432

Table II
Extent of Photoisomerization of Azobenzene, 4-Methoxyazobenzene, 4,4′-Dinitrostilbene, and DANS in Films[15] and Solutions at 25 °C

photochromic species	film/soln	irradiation wavelength, nm	Y_{cis}(film)/Y_{cis}(soln) at photoequilibrium
azobenzene	polystyrene/toluene	440/438	0.153/0.171 = 0.89[14]
	polystyrene/toluene	322/320	0.757/0.864 = 0.876
azobenzene	PMMA/*tert*-butyl acetate	444/442	0.167/0.185 = 0.90
4-methoxyazobenzene	polystyrene/toluene	440/438	0.247/0.263 = 0.94
	PMMA/*tert*-butyl acetate	440/438	0.242/0.253 = 0.96
4,4′-dinitrostilbene	polystyrene/toluene	360/358	0.579/0.808 = 0.717
	PMMA/*tert*-butyl acetate	359/354	0.580/0.823 = 0.705
DANS	polystyrene/toluene	438/430	0.126/0.177 = 0.71
	PMMA/*tert*-butyl acetate	435/425	0.083/0.022 = >1

Figure 1 shows a typical UV absorbance spectrum of 4-methoxyazobenzene in toluene solution after successive intervals of irradiation to photoequilibrium. The isobestic points are preserved for an extent of photoisomerization of *trans* to cis exceeding 98%. The method of Fischer[7] was used to determine the ratio of molar absorption coefficients of cis-to-trans isomers at the wavelength of peak UV absorbance of the trans isomer for the 4-methoxyazobenzene and other photochromic species examined. For DANS in *tert*-butyl acetate, the method of Blanc[8] was used to find the ratio. Table I gives the ratios found. The ratio was assumed to be the same in the polymer film as in the model solvent for the polymer. This ratio, inserted in eq 1, gives

$$Y_{cis} = \frac{1 - A_{eq}/A_{trans}}{1 - \epsilon_{cis}/\epsilon_{trans}} \qquad (1)$$

the cis-isomer fraction, Y_{cis}, at photoequilibrium, where A_{eq} is the absorbance at photoequilibrium at wavelength λ, A_{trans} is the initial (trans-isomer) absorbance at λ, and $\epsilon_{cis}/\epsilon_{trans}$ is the ratio of molar absorption coefficients of cis-to-trans isomers at λ.

Results of photoisomerizing azobenzene, 4-methoxyazobenzene, 4,4′-dinitrostilbene, and DANS in polymer films and model compound solutions are given in Table II. The wavelengths of peak absorbance are red-shifted from model compound solutions to polymer films because of a difference in the index of refraction arising from the greater polymer film density. Provided that the isomerizing wavelength is changed between model compound and film by an amount equal to the red shift, the extent of photoisomerization of 4-methoxyazobenzene in glassy polymers is less than that in model compounds. This is consistent with the idea that, at a molecular level, part of the polymer is too tightly packed about the 4-methoxyazobenzene to allow isomerization from a trans isomer to a cis isomer. We believe that similar results would have been obtained by Priest and Sifain[1] with 4-ethoxyazobenzene if they had been able to use a continuous UV source and adjusted the isomerization wavelength a few nanometers (the red shift) between solution and film.

One of the isomerizable segments of *trans*-4-methoxyazobenzene has a minimum local free volume requirement for isomerization similar to that of half an azobenzene molecule, assuming equal bond lengths and geometry. The other segment has a minimum local free volume requirement larger than that of half a *m*-azotoluene molecule. We showed[2] that probe molecules requiring larger local free volume to isomerize, such as *m*-azotoluene, photoisomerize to a smaller extent in polystyrene, normalized by that in toluene, than probe molecules requiring smaller local free volume, such as azobenzene. Thus, one might expect the extent of photoisomerization of 4-methoxyazobenzene in film, divided by the extent of photoisomerization in solution, to be less than that of azobenzene. However, our experimental results show just the opposite. This is the case for both polystyrene films and PMMA films. Although the extent of isomerization in film divided by that in solution is not identical for the two types of polymers, it is interesting to note that the extent of isomerization of 4-methoxyazobenzene in film divided by that in model compound is 5–6% higher than that of azobenzene regardless of the type of polymer. (A complete discussion comparing isomerization of photochromic probes in PMMA to that in polystyrene is the subject of another publication.[9])

The reason for the higher extent of isomerization of 4-methoxyazobenzene in film divided by that in solution may be that in the film, some of the probe molecules lie in space that allows the isomerization of the larger 4-methoxyazophenyl segment but blocks the isomerization of the smaller azophenyl segment. In solution, a molecule isomerizes from an excited state with a radiationless relaxation rate proportional to the moment of inertia of the isomerizing segment and inversely proportional to the segment's frictional resistance.[10] This means that 4-methoxyazobenzene photoisomerizes in solution mostly by its smaller azophenyl segment, like azobenzene. The presence of space in the film which only allows the larger 4-methoxyazophenyl segment to isomerize will increase the extent of isomerization, divided by that in solution, beyond the azobenzene value. This situation cannot arise with azobenzene because the azophenyl segments can be superimposed through an inversion center of symmetry so that in solution either segment is equally likely to isomerize.

DANS is a drastic test of the use of photoisomerizable probes in rigid polymer matrices. It is a polar molecule with an excited state having one of the largest dipole moments known.[11] Solvent polarity affects the extent of isomerization[12] so that while 18% photoisomerizes in toluene, only 2% photoisomerizes in the 6 times more polar *tert*-butyl acetate. Although accurate bond lengths and geometry are not available, the DANS segments appear to have only slightly different volume requirements for isomerization. By the reasoning given in the preceding paragraph, the extent of photoisomerization of DANS in polystyrene, divided by that in toluene, should be similar to that of 4,4′-dinitrostilbene, which agrees with the experimental results. However, DANS photoisomerizes in PMMA to a greater extent than in *tert*-butyl acetate. This is probably because the mobile polar solvent molecules stabilize the polar DANS transition state[12] so that the trans–cis quantum yield is less than that in the nonblocking film environment. This result underscores our statement made previously[2] that caution needs to be exercised when interpreting the extent of photoisomerization of molecules with significant dipole moments in films and solvents.

Clearly, when making use of photochromic probe molecules to investigate quantitatively the size distribution of local free volume in glassy polymers, probe molecules possessing an inversion center of symmetry are superior to other types of probes. With the use of probe molecules possessing an inversion center of symmetry, complications associated with polarity effects and different isomerizing segments on the same probe being sensitive to different sizes of local free volume may be minimized.

A second important point to be made from this study is revealed in Table II. When azobenzene was photoisomerized at its primary (π,π^*) transition (about 320 nm), the same extent of isomerization in polystyrene film normalized to that in solution was obtained as when the photoisomerization occurred at its secondary (n,π^*) transition (about 440 nm). Rau and Luddecke[13] had speculated that some of the photoisomerization at 320 nm occurred by a rotation pathway even though photoisomerization at 440 nm occurred by an inversion pathway. As a rotational pathway would require substantially more local free volume (90 Å^3 more) for isomerization of azobenzene than an inversion pathway, and as an increase in required local free volume should result in a decrease in the normalized extent of isomerization of the probe,[2] the nearly identical normalized extents of isomerization at photoequilibrium suggest that photoisomerization takes place via the same inversion pathway at both transitions.

Acknowledgment. Financial support for this work came from the Materials Research Center (NSF Grant DMR 82-16972), the Northwestern University Research Grants Committee, and 3M Company (nontenured faculty research initiation grant to J.M.T.).

Registry No. DANS, 2844-15-7; PMMA, 9011-14-7; 4-$H_3COC_6H_4N{=}NC_6H_4$, 2396-60-3; $C_6H_5N_2C_6H_5$, 103-33-0; 4,4′-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, 2501-02-2; $C_6H_5CH{=}CH_2$, 9003-53-6.

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(14) It should be noted that the value of the normalized extent of photoisomerization for azobenzene is slightly smaller and that for 4,4′-dinitrostilbene is slightly larger than the ones we previously reported.[2] In the present study, we were able to compensate for the red shift in films by altering the photoisomerizing wavelength. This changed the normalized extent of photoisomerization values slightly.

(15) These films had undergone no physical aging prior to photoisomerization. A publication is in preparation that gives experimental findings on the effect of physical aging on the extent of isomerization of photochromic probes.

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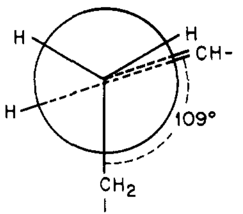
Variable-Temperature, High-Resolution Solid-State Carbon-13 NMR Study of 1,4-*trans*-Polybutadiene

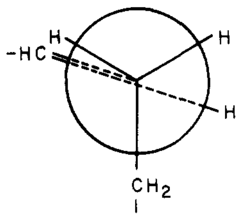
It has long been known[1] that 1,4-*trans*-polybutadiene (TPBD) exists in two crystalline polymorphs. At room temperature, the chain conformation of form I is as follows:[1,2]

$$\begin{array}{c} \mathrm{E} \quad \mathrm{s}^{\pm} \quad \mathrm{t} \quad \mathrm{s}^{\mp} \quad \mathrm{E} \\ \cdots-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-\mathrm{CH_2}-\cdots \end{array}$$

where the double bond is of course trans ("E") and $s^{\pm}$ (or $s^{\mp}$) designates approximate skew conformations:



s^+



s^-

In the exact skew conformation, the C═C and C—H bonds are eclipsed and the dihedral angle is 120°. The chain packing is a hexagonal array. Above approximately 75 °C the stable form, called form II, is of lower density but with the chains still parallel to each other and still in a hexagonal array.[3–6] They are believed to be in a disordered state, as judged by the blurring of all nonequatorial reflections in the X-ray diffraction pattern, and the marked decrease of the second moment of the wide-line proton NMR spectrum[7] indicates the onset of molecular motion. However, the details of the form II chain conformation and the nature of the motion are not well established. Suehiro and Takayanagi[3] proposed that the chain has a single definite structure, similar to that of form I except that the skew angle is decreased from ±109° to ±80°. They further proposed that the motion consists of large torsional oscillations about the carbon–carbon single bonds. Evans and Woodward[5] employed this conformation to calculate the heat capacity of form II and reported good agreement with experiment below and above the form I → form II transition; they did not consider chain motion nor attempt to calculate the heat capacity during the transition. Iwayanagi and Miura[7] proposed that instead of undergoing large torsional oscillations the chains are rotating about their long axes. Wunderlich et al.[8,9] made thermodynamic calculations similar to those of Evans and Woodward[5] but assumed a conformationally disordered state for form II. De Rosa et al.[6] also proposed a disordered conformation—based on packing energy calculations—consisting of a 50:50 equilibrating mixture of (a) and (b):

(a) E $s^{\pm}_{(90°)}$ t $s^{\mp}_{(90°)}$ E

(b) E $s^{\pm}_{(90°)}$ t cis E

This corresponds to a 25% probability of cis for CH–CH$_2$ bonds.

We have previously reported[10] the solid-state ^{13}C NMR spectra of TPBD at room temperature. The results demonstrate that it is possible to independently observe carbon nuclei in the crystalline and the mobile fold surface regions of TPBD single crystals. The olefinic and methylene carbons in the folds appear from their chemical shifts to have essentially the same average conformation as the 1,4-trans sequences in amorphous bulk polybutadiene. In addition, the ^{13}C spin–lattice relaxation times (T_1) of the folds are observed to be the same as for amorphous polymer,[11] indicating that chain motions in the two phases are similar.

In this work we examine the conformational and motional properties of the chains in the crystalline region of TPBD as a function of temperature. The 50.31-MHz cross-polarized (CP), magic-angle spinning (MAS), dipolar-decoupled (DD) spectra were recorded at 23–80 °C on a Varian XL-200 spectrometer by using a Doty Scientific probe with Al$_2$O$_3$ rotors and the standard Varian temperature controller. Sample spinning rates of 2.5–5.0 kHz and a high-power, dipolar decoupling level of ca. 10 G were employed. The TPBD sample was a fraction ($\bar{M}_v = 2.5 \times 10^4$) of a polymer synthesized by the rhodium chloride catalyst method.[12] Following solution fractionation the material was dissolved in toluene and precipitated from methanol. The sample morphology is probably multilamellar in nature.[13]

In Figure 1 are shown CPMAS/DD spectra as a function of temperature. The spectrum at 23 °C was obtained by using a 1.0-ms contact time and shows single olefinic and methylene resonances for the crystalline stems of form I. As the temperature is increased new resonances appear at higher field positions for both carbons, reflecting the onset of the solid–solid phase transition. At temperatures where both form I and form II are present a contact time of 2.0 ms was chosen to permit observation of both forms. However, we must emphasize that because of substantial differences in chain mobility (vide infra) the intensities of these resonances do not quantitatively reflect the ratio of these phases. Despite this, we can estimate the midpoint of the transition to be ca. 60 °C; it is essentially complete at 65 °C. It should be noted that the midpoint observed in the initial heating of solution-crystallized TPBD is ca. 50 °C. The higher transition point observed following cooling and subsequent heating is probably the result of crystalline annealing during the first heating.

At 23 °C the chemical shifts of the olefinic and methylene carbons of form I are 130.7 and 35.2 ppm, respectively.[14] Those of form II are more shielded by 1.2 and 1.8 ppm, differences very close to those reported for fold surface (i.e., amorphous) carbons versus crystal stem carbons for form I.[11] Despite the close similarity in chemical shift between the crystal stem carbons of form II and amorphous carbons, individual resonances can be observed in non-cross-polarized spectra. These phases can be clearly differentiated in the course of an inversion–recovery[16] T_1 measurement. In Figure 2 are shown the T_1 spectra for the methylene carbons observed at 70 °C and

0024-9297/87/2220-2954$01.50/0