Thermal Cis → Trans Isomerization of Covalently Attached Azobenzene Groups in Undrawn and Drawn Polyethylene Films. Characterization and Comparisons of Occupied Sites

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ABSTRACT: The thermal cis → trans isomerization of azobenzene groups covalently attached to chains of undrawn and drawn polyethylene films (Azo-PE) has been examined in a temperature range that is well above the glass transition and well below the melting transition. Isomerizations in undrawn films at all temperatures and in a drawn film at 70 °C, the highest temperature examined, follow single-component first-order kinetics. At 20−65 °C, two first-order components whose activation energies are both smaller than that of the undrawn film are needed to describe the isomerization kinetics in the drawn state. Doped (i.e., noncovalently attached) azobenzene groups in polyethylene films (Azo/PE) also exhibit a biexponential kinetics after drawing, but the fraction of the faster component is much smaller than that in the drawn Azo-PE films. Comparisons between the rate constants for isomerization of undrawn and drawn Azo-PE and Azo/PE films at the same temperature indicate that as a consequence of probe translocations the populations of sites occupied by the probe change significantly when the doped film is drawn. The faster and slower rate components in drawn Azo-PE are assigned to cis isomers residing in interfacial and amorphous sites, respectively, on the basis of differences in polymer chain ordering, rates of relaxation, and free volumes at occupied sites in interfacial and amorphous regions. These results are discussed in terms of how the micromorphological changes in PE when it is drawn affect the dynamics of the guest molecules and how the latter provides information about the local PE matrix.

Introduction

Films of low-density polyethylene (LDPE), a partially crystalline material, have been used extensively as media for photochemical reactions[1] and, in their drawn forms, for alignment of solute molecules for spectroscopic determinations of directions of transition dipoles.[2] Surprisingly, few investigations of the isomerization of azobenene in LDPE films have been reported, and there are none we can find of the kinetics of cis → trans thermal isomerization in drawn LDPE films. Recently, azo aromatic molecules were reported to isomerize much more slowly in poly(4-azophenyl *N*-phenylmethacryamide), an amorphous polymer, than in LDPE, and both rates were slower than that in isotactic polypropylene (iPP).[3] The structural compactness and lower effective free volumes of the semicrystalline polymers were proposed to be responsible for the slower rates. In this regard, the mean free volumes of some LDPE (ca. 140 Å^3)[4] and iPP (113 Å^3)[5] films have been measured by positron annihilation techniques.

The sites where guest molecules like azobenzenes can reside in LDPE and other partially crystalline polymer films are limited to amorphous regions and interfaces between amorphous and crystalline parts; they are excluded from the interiors of crystalline regions (Figure 1).[6] The mean free volumes available in these two site types probably differ, and it is reasonable to assume that the walls of amorphous sites are “softer” (i.e., undergo faster chain relaxations)[7,8] than those of interfacial ones due to the greater chain disorder in the amorphous part.[1,9] However, no definitive evidence for different free volumes in amorphous and interfacial sites of LDPE has been provided to date.[4]

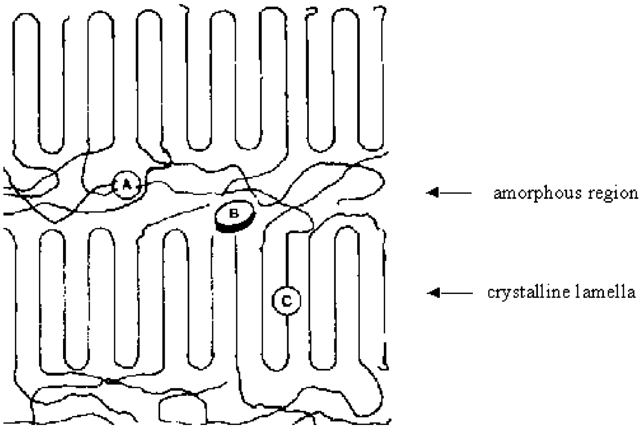

Figure 1. Schematic representation of polyethylene structure and morphology showing potential guest sites in (A) the amorphous region and along (B) folded-chain crystal surfaces and (C) lateral lamellae surfaces (modified from ref 6c).

Drawing (i.e., cold stretching) polyethylene films has several important morphological consequences: (1) in several steps, spherulitic crystalline aggregates are deformed and microfibrillar crystalline segments are generated;[10] (2) the overall chain orientation in the drawing direction and the degree of film crystallinity are increased;[6c] (3) the free volume is decreased, and the shapes and wall stiffness of sites where guest molecules reside are altered;[4,11] and (4) a fraction of guest molecules are translocated from amorphous to interfacial sites.[6c] These changes can alter the rates of reactions and product distributions from guest molecules,[1,9] including the photoisomerization rates of azobenzene molecules.[12]

The rates of photoinduced trans ⇄ cis[13] and thermal cis → trans[14,15] isomerizations of azoaromatics doped in

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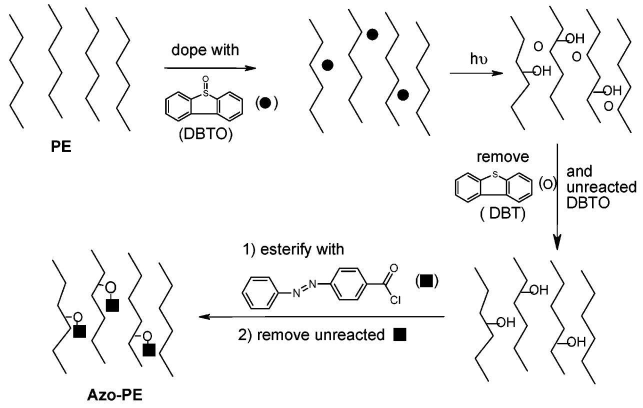
Scheme 1. Protocol for the Preparation of Azo-PE Films



or covalently attached to polymers are known to depend on polymer morphology. The observation that only one first-order rate constant is required to accommodate the kinetics in polymers above their glass transition but two are needed in the glassy state has been ascribed to differences in the free volume distribution and local structural relaxations in the two phases.[16−20] When the free volume in the vicinity of an azobenezene guest is above a critical limit, rapid trans → cis photoisomerization occurs; *trans*-azobenzene molecules in sites with a dearth of free volume isomerize to the cis more slowly[21] because they experience more restrictive steric interactions with polymer chains that constitute the site walls.[7] The cis isomers in such sites are "stressed" and have a greater propensity to return to the trans.[15a,21,22]

Here, 4-(phenylazo)benzoic acid groups have been *covalently attached* to polyethylene chains through ester linkages in the interiors of preformed LDPE films (Azo-PE; Scheme 1), and their rates of thermal cis → trans isomerization have been measured over a range of temperatures in the drawn and undrawn states to probe the influence of free volume and chain relaxation rates in different site types. For comparison purposes, a structural analogue of the attached azobenzene groups, hexyl 4-(phenylazo)benzoate, has been *doped* into the same LDPE, and its rate of thermal cis → trans isomerization has been measured in drawn and undrawn films at 30 °C. Because covalent attachment of the azobenzene groups prohibits their net translocation from amorphous to interfacial sites when films are drawn,[6c] the isomerization rates (1) permit a more critical examination of whether amorphous and interfacial site types can be differentiated and (2) probe whether additional constraints to isomerization are imposed by the inability of the azobenzene groups to translocate during film drawing. The isomerization rates of the noncovalently attached azobenezene molecules provide a benchmark for the kinetic behavior when diffusion between site types is possible.

Experimental Section

Instruments. UV spectra and kinetics of isomerization were monitored with a double-beam Perkin-Elmer Lambda-6 UV/vis spectrophotometer or a HP-8453 UV/vis spectrometer equipped with a single-beam diode array detector. FT-IR spectra were recorded on a MIDAC spectrophotometer using Spectra-Calc software or a Perkin-Elmer Spectrum One FTIR instrument. A Varian Mercury 300 MHz NMR spectrometer interfaced to a Sun Sparc station was used to record ^{1}H NMR spectra ($CDCl_3$/TMS). Melting points were measured using a Leitz 585 SM-LUX-POL microscope equipped with a Leitz 350 heating stage and an Omega HH21 microprocessor thermometer connected to a K/J thermocouple. HPLC analyses were conducted on an HP series 1100 chromatograph equipped with an autosampler, a silica gel column (IBM, 5 μm, 4.6 × 250 mm), and a diode array detector.

Materials. Low-density polyethylene was an additive-free, blown-type film from Poliolefinas of Brazil (140 μm thick, 0.917 g cm^{-3},[1] 24% crystallinity,[1] M_w = 510 000). Prior to use, it was immersed in three batches of chloroform for 1 day each to remove antioxidants and impurities. Interior sites were hydroxylated according to a method described previously (Scheme 1).[23] A native or interior-hydroxylated film (1 cm × 2 cm) was then esterified by immersing and stirring it gently in a solution of 0.16 g (0.6 mmol) of 4-(phenylazo)benzoyl chloride (Aldrich, 97%), 25 mg (0.2 mmol) of dimethylaminolpyridine (DMAP, Aldrich, 99%), a few drops of dry pyridine, and 5−10 mL of anhydrous chloroform (Aldrich, 99+%, stabilized with amylenes) at 40 °C under a dry atmosphere for 3 days. Additional amounts, as above, of acid chloride, DMAP, and pyridine were added, and heating and stirring were continued for 4 days more. Finally, the films were extracted exhaustively with chloroform to remove unattached species.[23]

Hexyl 4-(phenylazo)benzoate was synthesized from 4-(phenylazo)benzoyl chloride (0.7 mmol) and 1-hexanol (3.3 mmol, dried and distilled before use, Aldrich) in dry pyridine (6 mL) at room temperature. After separation by silica gel column chromatography (methylene chloride as eluent) and recrystallization from aqueous ethanol, an orange product (40%; 97% by HPLC) with mp 60.1−61.0 °C (lit.[24] 61−61.8 °C) was obtained. IR (KBr pellet): 1719 ($\nu_{C=O}$), 1270 (ν_{C-O-C}) cm^{-1}. ^{1}H NMR δ: 0.92 (t, *J* 6.9 Hz, 3H), 1.36 (m, 4H), 1.47 (m, 2H), 1.81 (m, 2H), 4.35 (t, *J* 6.8 Hz, 2H), 7.51−7.54 (m, 3H), 7.93−7.97 (d, *J* 8.7 Hz, 4H), 8.18−8.21 (d, *J* 8.7 Hz, 2H). Several pieces of 1 cm × 2 cm LDPE film were immersed overnight in a ca. 50 mM chloroform solution of the ester. The surfaces were dried, and surface-occluded dopant molecules were removed by dipping the films in methanol, a nonswelling solvent for LDPE.

The average concentration of covalently attached (Azo-PE) or doped (Azo/PE) azobenzene groups in each polyethylene film was calculated from Beer's law, the film thickness, and the UV absorbance at 326 nm (at least three spots on each film), assuming the molar extinction coefficient to be the same as that of ethyl 4-(phenylazo)benzoate at 324 nm in chloroform (ϵ_{324} = 23 300 M^{-1} cm^{-1} [25]). Some films were drawn manually to ca. 5 times their original lengths at room temperature after doping or derivatization.

Photoisomerizations. Irradiations to transform a fraction of the trans isomer to the cis within a film were conducted in air at room temperature using a UVP model UVGL-25 Mineralight lamp (18 W) with a band centered at 367 ± 2 nm. A UV absorption spectrum was recorded immediately after each irradiation. Net cis → trans photoconversions were achieved by irradiation of films for various periods with a 13 W incandescent light bulb.

Kinetic Measurements of Thermal Cis → Trans Isomerizations at Different Temperatures. After irradiation at 367 ± 2 nm for 20 min, a film containing azobenzene groups was placed in a rectangular quartz capillary cuvette (1 cm wide × 0.5 cm thick). The cuvette was filled with distilled water, closed with a Teflon cap, and placed in a 1 cm × 1 cm Pyrex cell that contained either distilled water (<40 °C) or hexadecane (>45 °C). The Pyrex cell was inserted into a sample holder that was thermostated by circulating water from a VWR 1130 or a Haake FK-2 constant temperature (±1 °C) water bath; the temperature in the Pyrex cell was read directly from a thermometer that was inserted into it at the end of each experiment. After several minutes, when the film and its holder had reached the equilibrium temperature, UV spectra were recorded periodically in the range 330−320 nm. When the dual-beam spectrophotometer was employed, spectra were recorded at 60 nm/min, and the wavelength of the incident radiation was kept at 600 nm between scans. When the single-beam spectrophotometer was employed, the shutter in front of the UV lamp was closed, and the sample was kept in the dark between scans in order to minimize the photochemical component of trans ⇄ cis isomerization during the kinetic runs.

Results

Preparation of LDPE Films with Azobenzene Groups Covalently Attached to Chains in Interior Positions. Our procedure for preparation of azobenzene-derivatized films involves two separate steps (Scheme 1). In the first, interior sites of a polyolefinic film are hydroxylated by irradiating films, either undoped (as a control) or doped with dibenzothiophene 5-oxide (DBTO).[23] The surfaces of the doped films were washed with methanol before irradiation to remove any surface-occluded DBTO. Irradiation converts DBTO to dibenzothiophene (DBT) and highly reactive oxygen atoms that lead primarily to hydroxylation and epoxidation of nearby hydrocarbon chains.[26] After removal of DBT and unreacted DBTO from the films, they and the undoped films were subjected to the second step, esterification. Treatment of the films with 4-(phenylazo)-benzoyl chloride dissolved in chloroform (a swelling solvent for polyethylene) and DMAP, and pyridine ensures that hydroxylated sites are accessible for esterification and that the HCl that forms as a byproduct is trapped. Finally, the films were extracted exhaustively with chloroform followed by hexanes to remove all unreacted acid chloride and dried. The concentration of covalently attached azobenzenyl groups depends on the concentration of DBTO doped into the film. When [DBTO] = 0,[27] 10 and 47 mmol $\mathrm{kg^{-1}}$, azobenzenyl concentrations were about 1.8, 5.3, and 7.5 mmol $\mathrm{kg^{-1}}$, respectively. The Azo-PE film containing 7.5 mmol $\mathrm{kg^{-1}}$ azobenzenyl groups showed the ester group at 1733 $\mathrm{cm^{-1}}$, but a 1.8 mmol $\mathrm{kg^{-1}}$ concentration is too low to allow IR detection of the ester band.

UV/vis absorption spectra of the Azo-PE films during irradiations to effect photoisomerization of the azobenzenyl groups are presented in Figure 2. As expected, irradiation at 367 nm results in a progressive decrease in the trans ($\pi \rightarrow \pi^*$) absorption maximum at 326 nm and an increase in the cis ($n \rightarrow \pi^*$) band maximum at 440 nm. The 326 nm band increased in intensity and the 440 nm band decreased when films irradiated initially at 326 nm were exposed to white light (causing a net cis → trans conversion). This cycle could be repeated several times without discernible decrease of absorption intensity. The isosbestic points at 238, 288, and 376 nm are an indication that the only process occurring is direct cis ⇄ trans isomerizations.

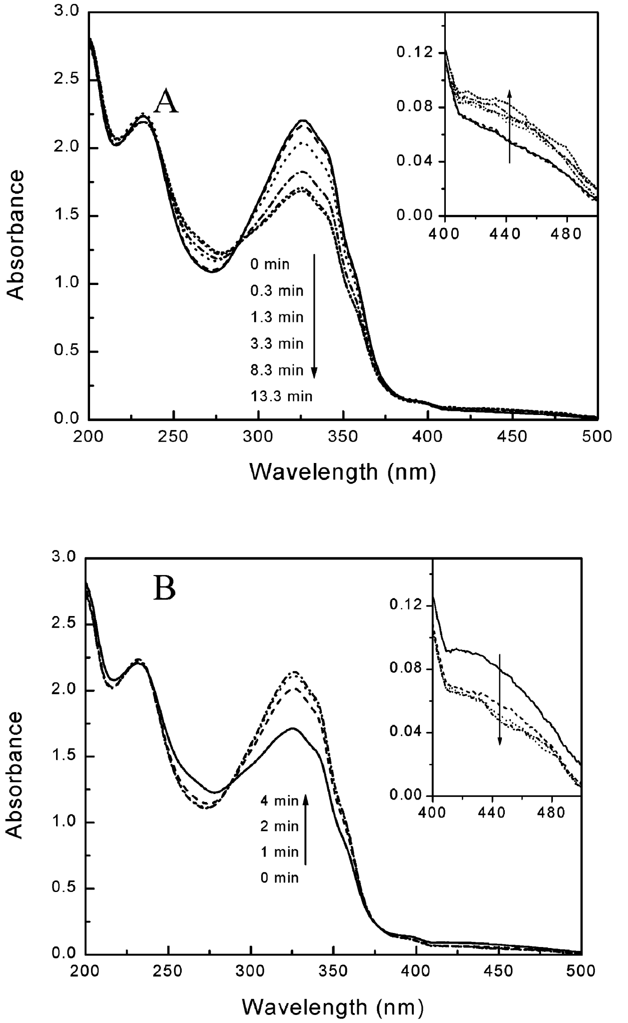


Figure 2. UV absorption spectra of an undrawn Azo-PE film with ca. 7.5 mmol $\mathrm{kg^{-1}}$ azobenzene groups covalently attached: (A) after irradiation at 367 nm (trans → cis) and (B) with white light (cis → trans) as a function of time.

Thermal Isomerizations of Azobenzene Groups in Undrawn LDPE Films at Different Temperatures. The kinetics of the thermally induced cis → trans isomerizations of the azobenzene groups in Azo-PE films was investigated at several temperatures above the glass transition temperature ($T_g \approx -40$ °C)[6c] and below the melting temperature of the crystalline portions ($T_m = 109$ °C).[8,28] One Azo-PE film ([azobenzenyl] ≈ 5.3 mol $\mathrm{kg^{-1}}$) was used for measurements at 20 and 30 °C, and another was used ([azobenzenyl] ≈ 7.5 mol $\mathrm{kg^{-1}}$) in the 45−70 °C range. The rate of isomerization of the Azo/PE film ([azobenzenyl] ≈ 3.5 mmol $\mathrm{kg^{-1}}$) was measured at one temperature, 30 °C. At each temperature, the optical density (OD) at 326 nm, where the trans isomer absorbs most strongly, was recorded as a function of time. The fraction of cis isomer at the initial reading (t = 0) was calculated to be around 30% according to eq 1.

$$\frac{[\mathrm{cis}]_t}{[\mathrm{trans}]_\infty} = \frac{1 - \mathrm{OD}_t/OD_\infty}{1 - \epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}} \qquad (1)$$

where $\epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}$, the ratio of molar extinction coefficients at 326 nm, is 0.059[29] and OD_∞, the optical density at 326 nm at time = ∞ (i.e., when the optical density ceased to increase perceptibly with time), is assumed to be exclusively from absorptions by the trans isomer. A *single*-component first-order reaction in which trans → cis isomerization is assumed to be negligible can be described by eq 2, and a plot of $\ln([\mathrm{cis}]_t/[\mathrm{cis}]_0)$ vs time should be fitted to a straight line whose slope is $-k$, the rate constant for cis → trans.

$$\ln([\mathrm{cis}]_t/[\mathrm{cis}]_0) = \ln[(\mathrm{OD}_\infty - \mathrm{OD}_t)/(\mathrm{OD}_\infty - \mathrm{OD}_0)] = -kt \qquad (2)$$

This equation accommodates the kinetic behavior for reaction in the DBTO/irradiated Azo-PE films at all temperatures examined (Figure 3) and the Azo/PE films at 30 °C. An activation energy (E_a) of 23.1 kcal $\mathrm{mol^{-1}}$ and a preexponential factor (A) of 7.2×10^{11} $\mathrm{s^{-1}}$ (with a large uncertainty) were calculated from an Arrhenius

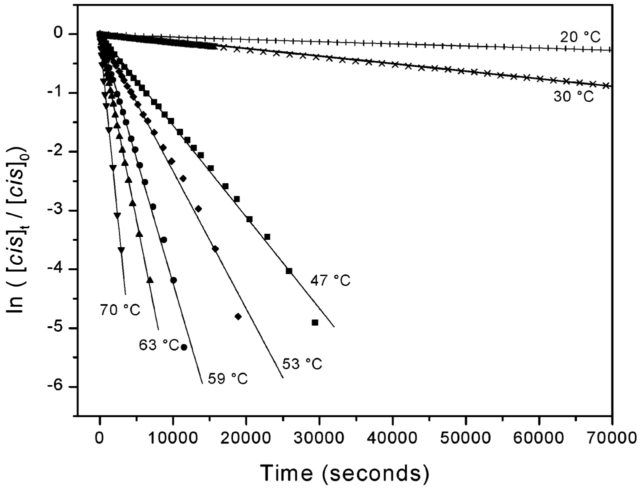


Figure 3. First-order kinetic plots of data for the cis → trans thermal isomerization of azobenzene groups in undrawn Azo-PE films at different temperatures. Solid lines are best linear fits of the data points to eq 2. See text for concentrations of azobenzene groups.

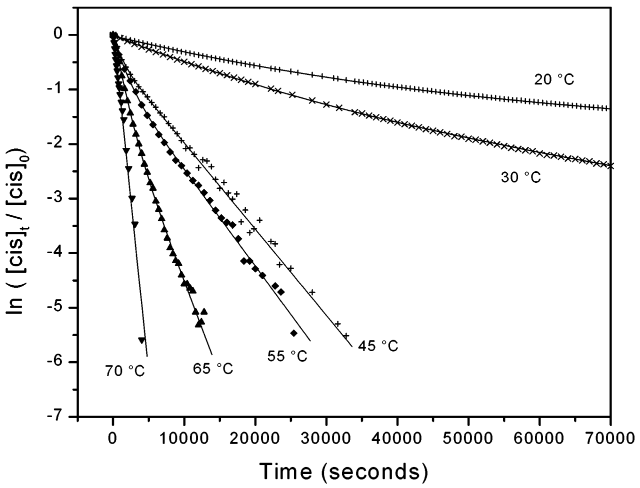


Figure 4. First-order kinetic plots of data for the cis → trans thermal isomerization of azobenzene groups in ca. 5× drawn Azo-PE films at different temperatures. Solid lines are best linear fits of the data points to eq 2 for the 70 °C data and to eq 3 for the lower temperature data. See text for concentrations of azobenzene groups.

plot (Figure 5) of rate data from the Azo-PE films (Table 1). Both are similar to the values found for cis → trans isomerizations of azobenzenes in liquid solutions.[30] The rate constant for isomerization of the doped groups in the Azo/PE film at 30 °C, 1.15×10^{-5} s^{-1}, is surprisingly close to the value found for Azo-PE (Table 1).

Thermal Isomerizations of Azobenzene Groups in Drawn LDPE Films at Different Temperatures. Except for kinetic runs at 20 and 30 °C, where one Azo-PE film was used for both, a different piece of 5× drawn Azo-PE film was used for each. The concentrations of azobenzene groups in Azo-PE films before drawing were ca. 7.5 mmol kg^{-1} for the film employed at 70 °C and ca. 5.3 mmol kg^{-1} for all others.

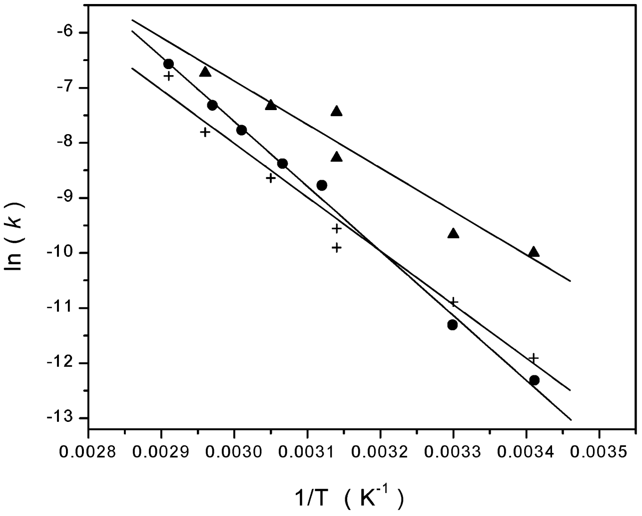


Figure 5. Arrhenius plots for the cis → trans thermal isomerization of azobenzene groups of Azo-PE films using the data in Figures 2 (●) and 3 (▲, faster component; +, slower component). See Table 1.

Table 1. Kinetic Parameters for the Thermal Cis → Trans Isomerization of 4-(Phenylazo)benzoate Groups Covalently Attached to (Azo-PE) or Doped within (Azo/PE) the Interiors of PE Films

undrawn		drawn			
temp (°C)	k (s^{-1})	temp (°C)	k_1 (s^{-1})	k_2 (s^{-1})	α
		Azo-PE			
20	4.51×10^{-6}	20	4.54×10^{-5}	6.74×10^{-6}	0.62
30	1.23×10^{-5}	30	6.35×10^{-5}	1.87×10^{-5}	0.68
47	1.55×10^{-4}	45	5.85×10^{-4}	7.09×10^{-5}	0.40
53	2.30×10^{-4}	45	2.55×10^{-4}	5.01×10^{-5}	0.37
59	4.22×10^{-4}	55	6.54×10^{-4}	1.77×10^{-4}	0.49
63	6.60×10^{-4}	65	1.19×10^{-3}	4.08×10^{-4}	0.46
70	1.40×10^{-3}	70		1.13×10^{-3}	
E_a (kcal/mol^{-1})	23.1 ± 0.7		15.7 ± 2.2	19.4 ± 1.1	
log A (s^{-1})	11.8 ± 0.5		7.3 ± 1.2	9.2 ± 0.7	
		Azo/PE			
30	1.20×10^{-5}	30	2.60×10^{-4}	1.56×10^{-5}	0.05
30	1.10×10^{-5}	30	1.40×10^{-4}	1.50×10^{-5}	0.04

The kinetics of the cis → trans thermal isomerizations in drawn Azo-PE films could be fitted satisfactorily to eq 2 at 70 °C. Reasonable fits of the kinetic data from Azo-PE below 70 °C and from drawn Azo/PE ([azobenzenyl] ≈ 7.0 mmol kg^{-1} before drawing) at 30 °C were not possible with eq 2, but good fits were achieved with eq 3, containing two first-order terms (Figure 4). In eq 3, k_1 and k_2 are the rate constants for the faster and slower components of isomerization, respectively, and α is the fraction of the faster component. The kinetic parameters are presented in Table 1.

$$[\mathrm{cis}]_t/[\mathrm{cis}]_0 = \alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t) \quad (3)$$

The activation energies from Arrhenius plots (Figure 5), $E_{a1} = 15.7$ kcal mol^{-1} and $E_{a2} = 19.4$ kcal mol^{-1}, are lower than that found in the undrawn Azo-PE film (tending to facilitate isomerization), but the corresponding estimated preexponential factors, $A_1 = 2.0 \times 10^7$ s^{-1} (faster component) and $A_2 = 1.6 \times 10^9$ s^{-1} (slower component), are also smaller (tending to attenuate isomerization)! Although the activation energy and preexponential factor for the slower component are near those in solutions, the values for the faster component are much smaller.[30]

Two first-order components are also needed to fit the kinetic data from drawn Azo/PE films, but the fraction of the faster component is considerably smaller than in the drawn Azo-PE film (vide infra). However, the k_2 values at 30 °C from the drawn Azo/PE and Azo-PE films are the same within experimental error, and the k_1 values are very close.

Discussion

The free volume available to an azobenzene guest in a polymer matrix depends on several structural factors, including chain flexibility, size and shape of the guest, and whether (and how) it is attached to polymer chains.[7,17] Whenever relaxation of polymer chains, constituting the walls of sites occupied by molecules of the cis that have been formed in situ photochemically from the trans, is more rapid than the rate of thermal cis → trans isomerization, the influence of stress induced by the different shapes of the cis and trans isomers will not be detectable. That is generally *not* the case when polymer matrices are in their glassy states, and it has been shown in the glassy state of polystyrene, polycarbonate, copolymers of methacrylates and styrene, or copolymers of acrylates and methacrylates that a fraction of the cis azo groups isomerizes very rapidly while the remainder revert to the trans at rates near those observed in liquid solutions![14,15] Thus, the faster thermal (as well as the more efficient photo) component of cis → trans isomerization of azo aromatics in several systems has been ascribed to molecules in more stressed states (i.e., sites with stiffer walls and a dearth of free volume[7]) than those in sites with more flexible walls and larger amounts of free volume.[15a,22] For example, two components were needed to describe the kinetics of thermal cis → trans isomerization of azobenzene in a glassy polycarbonate film for which the cis isomer was made photochemically from the trans in situ, while the faster component was nearly absent when the cis isomer was incorporated directly by casting it into the film.[14b] Also, the photoisomerization of cis azo compounds to their trans isomers became slower when the poly(methyl methacrylate) host films were either stored in the dark at a low temperature for a protracted period or heated for a short period prior to being irradiated.[22b] Both pretreatments alleviate stress at sites where cis isomers reside. While the thermal isomerization of azobenzene in rubbery polymers can usually be fitted to a single first-order rate process, it can also be more complex and depend on annealing protocols.[16]

Our kinetic results for the thermal cis → trans isomerization of covalently attached and doped azobenzene groups in *undrawn* films in the temperature range 20−70 °C (i.e., significantly above the glass transition temperature (T_g) and well below the melting temperature of the crystalline portions (T_m)) can be accommodated by a simple first-order kinetic expression. Furthermore, the activation energy and preexponential factor from Azo-PE are similar to those found in liquid solutions.[30] This indicates that at least the sites in which the fraction of trans azobenzene groups that undergo photoisomerization to the cis are located either contain large amounts of free volume or have very rapid rates of chain relaxation along the site walls, or both. Furthermore, if (as we suspect) the isomerizing azobenzene groups are in both amorphous and interfacial sites, they cannot be distinguished kinetically by our probe.

These results differ from those found when azobenzene groups were covalently attached to undrawn low-density polyethylene films at both *surface and interior sites* through amide linkages.[3] There, the kinetics of thermal cis → trans isomerization were not cleanly first order. We suspect that the deviations from first-order derive from differences between sites at or near the film surfaces and in the interior rather than the nature of the amide linking group. As mentioned, our Azo-PE films contain azobenzene groups almost exclusively at interior sites,[23] and their rates of isomerization at a common temperature, 30 °C, are within experimental error of the rates for doped azobenzene molecules of similar structure within the same PE film type. Regardless, the different linking groups and, to a smaller extent, different film crystallinities and morphologies[31] in the two cases lead to different isomerization rates: the half-lives of the cis isomers are ca. 940 min at 30 °C in our Azo-PE or Azo/PE films (i.e., an ester linkage in conjugation with the azobenzene group) and 510 min at 25 °C in the polyethylenes with amide linkages to azobenzene groups (i.e., an amide linkage in conjugation with the azobenzene group).[3]

In *drawn* Azo-PE films, the thermal cis → trans isomerization at 65 °C and below consists of a faster component (k_1) in addition to a slower component (k_2) that is comparable to the rate in the *undrawn* films at all temperatures (Table 1). Two parallel first-order cis → trans rate processes have been observed for azobenzene groups incorporated within the main chains of an annealed polymer as well, and the rate of the slower one is similar to the unique rate measured in newly prepared (unannealed) films.[16] The appearance of the faster component when films are either annealed or drawn suggests that it is associated with "stressed" cis isomers in sites in the regions where polymer chains are more ordered, the free volume is smaller, and chain relaxation is slower.

In LDPE, these sites are in the interfacial regions. They are expected to suffer larger decreases in free volume and more decreased rates of chain relaxations than sites in the amorphous region as films are drawn.[32] As mentioned, drawing destroys crystalline spherulites within polyethylene films but leads to arrays of microfibrillar crystallite segments and, in many cases, an increased degree of crystallinity and crystal surface area.[6c] For instance, by differential scanning chromatography, the LDPE film used in this work is 24% crystalline before drawing and 33% afterward.[1] The increased ordering and compactness of polymer chains surrounding guest molecules, especially in interfacial sites, "stiffens" their walls and slows relaxation.[7] As a result, cis isomers in interfacial sites of drawn films (that are converted from the trans upon irradiation) should experience more steric strain than cis groups in the amorphous sites and revert to the trans more rapidly. Additionally, van der Waals interactions with polymer chains along the lateral lamellar surfaces of crystallites will be larger for planar rodlike molecules (like *trans*-azobenzene) that can be aligned rather specifically within interfacial sites than for the less planar and more globular cis isomer.[6c] Thus, an increase of van der Waals forces is another driving force for cis→ trans isomerization in interfacial sites.

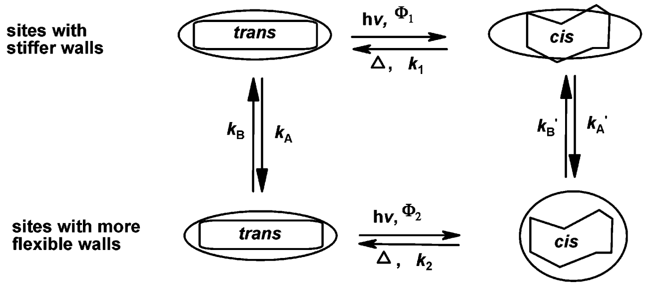
As a corollary, the slower isomerizing component (k_2) is associated with cis groups in the amorphous region. These attributions are consistent with E_{a1} being smaller than E_{a2}. They are consistent also with A_1 being *smaller* than A_2 if more specific polyethylene chain motions are required to attain the transition state for cis→ trans isomerization of azobenzene groups in the interfacial sites. In addition, changes in the activation energy and preexponential factor brought by drawing indicate that sites in the amorphous region are also affected somewhat by film drawing, albeit to a much smaller extent than sites in the interfacial region. Other studies have demonstrated that guest molecules in amorphous regions are not oriented when films are drawn.[6c] Our observations suggest that drawing Azo-PE films does result in changes in amorphous sites that can be detected kinetically. E_{a2} is somewhat smaller than E_a (from the undrawn film) and so is $A_2 < A$. A part of this effect may be attributed to the overall decrease in free volume that accompanies film drawing.[11] From positron annihilation measurements, the mean free volume per site in the LDPE film used in this work decreases from 142 to 122 Å^3 upon ca. 5× drawing.[4]

In *drawn* Azo-PE films, the kinetic data for the thermal cis → trans isomerization at 70 °C, the highest temperature examined, can be fitted satisfactorily to a single-component first-order equation; much of the isomerization via the faster mode is completed within a short period of time, making difficult its detection by our data-fitting routines. In addition, the rate constants for the fast and slow components approach a common value near 70 °C due to the "compensation effects" between the E_a and A values; the temperature at which k_1 and k_2 are predicted to be equal (0.16 s^{-1}) based upon the activation parameters in Table 1 is 152 °C. The tendency of the two processes to exhibit indistinguishable rates is exacerbated by the onset of α-relaxation processes (near 60−80 °C[33]) that involve chain motions associated with the crystalline parts of the polymer. If present at 70 °C, these relaxation modes would allow cis isomers in "stressed" *interfacial* sites to relax through local mode motions along the lamellar surfaces of crystallites (i.e., the sites should behave more like those in the amorphous region). These relaxations and those caused by melting of the crystalline regions near 109 °C[28] will reduce the predicted coalescence temperature for the two kinetic processes to well below the extrapolated value of 152 °C.

In that regard, we note that the values of α in Table 1 are lower limits of the fraction of the faster isomerization component due to the unavoidable time delay between the end of irradiations (to create large populations of the cis isomer) and the beginning of thermal kinetic measurements. Regardless, the α values from drawn Azo-PE films indicate that comparable amounts of *cis*-azobenzene groups isomerize in each of the two distinguishable site types. However, only a very small fraction of the hexyl *cis*-4-(phenylazo)benzoate molecules isomerize by the rapid mode in drawn Azo/PE films. The vast majority of the doped molecules reside in unstressed sites *at the moment that they undergo isomerization to the trans isomer*. This must be due to the enhanced mobility of the doped molecules that allows them to translocate rapidly between sites and find those that accommodate better their shapes;[34] the covalently attached *cis*-azobenzenyl groups are forced to remain in the same sites where they were created photochemically from the differently shaped trans isomer.

The salient features of a reaction model that is consistent with the results in drawn PE films is encapsulated in Scheme 2. It assumes that the isomerization processes for hexyl 4-(phenylazo)benzoate occur in distinguishable site types when films are drawn. The sites with stiffer walls (i.e., that do not allow large shape changes on the time scale associated with the trans → cis isomerization of the guest molecules) are considered to be in the interfacial regions of the polymer, and those with more flexible walls are placed in the amorphous regions.[35] In addition to their stiffer walls, the interfacial sites are also considered to have smaller amounts of free volume on average than sites in the amorphous regions. Although the stiffer walls and smaller free volumes of the interfacial sites should make the initial trans → cis photoisomerization of hexyl *trans*-4-(phenylazo)benzoate molecules more difficult (so that $\Phi_1 < \Phi_2$), they should facilitate the thermal isomerization of the more globular-shaped hexyl *cis*-4-(phenylazo)benzoate molecules formed in this region of the polymer by retaining for longer periods the templated shape of the more linear trans isomer. By contrast, the more flexible walls and larger free volumes of sites within the amorphous regions are able to adapt more rapidly to the size and shape of the cis isomer upon its formation from the trans.[7,36] As a result, a larger fraction of the excited hexyl *trans*-4-(phenylazo)benzoate molecules should undergo isomerization, and thermal reconversion to the trans isomer will be slower due to the greater stabilization of cis molecules in the (rapidly relaxing) amorphous sites.

Scheme 2. Cartoon Representation of the Kinetics for Isomerization and Site Interchange of Doped Hexyl 4-(Phenylazo)benzoate Molecules in Polyethylene Films



As mentioned, only one isomerization rate process is present in the undrawn films, and the corresponding rate constants are intermediate between the slow and fast components of the drawn Azo-PE films and similar to the slower rate constant of the drawn Azo/PE films. These observations can be accommodated within the model in Scheme 2 if (1) the walls of interfacial sites within undrawn films are sufficiently flexible that they relax around the cis isomer (after its photochemical formation from the trans) more rapidly than it isomerizes thermally back to the trans (i.e., the interfacial and amorphous sites interact with their guest molecules in a kinetically indistinguishable way), (2) all of the cis isomers reside in the amorphous regions of undrawn films (i.e., $\Phi_1 \ll \Phi_2$), or (3) diffusion of cis molecules from interfacial to amorphous sites is much faster than the rate of cis → trans isomerization (i.e., $k_A' \gg k_1$ and k_B'), so that the fraction of the faster isomerization component (k_1) is too small to be detected. The second and third possibilities seem unlikely because the covalently attached azobenzene groups of undrawn Azo-PE also give only one isomerization component.

Drawing is known to promote the translocation of doped molecules from amorphous to interfacial regions,[1,6c] so that $(k_B/k_A)_{undrawn} < (k_B/k_A)_{drawn}$ for the trans population, where k_A and k_B are the rate constants for diffusion of hexyl 4-(phenylazo)benzoate from amorphous (A) to interfacial (B) and from B to A regions, respectively. However, after UV irradiation, the noncovalently attached cis isomers in slowly relaxing ("stressed") interfacial sites will tend to move to amorphous sites. Thus, diffusion of the cis population should follow the relation, $(k_B'/k_A')_{undrawn} > (k_B'/ k_A')_{drawn}$.

The much larger values of α from the drawn Azo-PE films than from the drawn Azo/PE films support the hypothesis that relaxation of site walls in the interfacial regions of drawn LDPE is slower than the rates of thermal cis → trans isomerization. Were this not the case, we would have expected α from Azo-PE to be very small as well. Furthermore, since diffusion of only 10–30 Å is sufficient to move molecules from the interfacial to amorphous region,[37] it is quite reasonable that the rate of diffusion is higher than the rate of thermal isomerization (e.g., $k_A' > k_1$)[34] when the probe molecules are not linked to the polymer chains.

Conclusions

In undrawn PE films, the thermal cis → trans isomerization of covalently attached 4-(phenylazo)benzoate groups at different temperatures ($T_g < T < T_m$) follows simple first-order kinetics; molecules isomerizing in amorphous and interfacial sites cannot be differentiated kinetically. Film drawing changes somewhat the morphology of the PE matrix and profoundly affects the kinetics of cis → trans isomerization. Most notable is the introduction of a second (faster) isomerization pathway whose associated activation energy and preexponential factor are much smaller than those in the undrawn films. It is assigned to 4-(phenylazo)benzoate groups attached to sites within the interfacial region of the polymer. It is believed that the available free volume is smaller and chain relaxation rates are slower in these sites (making them more constraining) than in sites within the amorphous region. Since the chains constituting these sites are disposed initially to accommodate the size and shape of the trans isomer, the cis finds itself in a highly stressed environment that favors its rapid return to the trans. The slower isomerization component is believed to derive from *cis*-4-(phenylazo)benzoate groups affixed to sites with “softer” walls (i.e., composed of polymer chains that relax more rapidly than within the interfacial region) that adapt more rapidly to the more globular shape of the cis than it isomerizes back to the trans. The rate constants for cis → trans isomerization from azobenzene groups residing in these sites are like those in undrawn films, but the activation energy and preexponential factor are somewhat smaller, suggesting that the stiffness of walls of amorphous sites in undrawn and drawn films are only slightly different.

Hexyl 4-(phenylazo)benzoate molecules, doped in PE films, are able to diffuse and translocate between amorphous and interfacial regions. For this reason, the fraction of the faster rate component (due to hexyl *cis*-4-(phenylazo)benzoate molecules suffering greater conformational constraints at the time of their isomerization to the trans) in drawn Azo/PE films is very small and much smaller than found in the Azo-PE films (where translocation of *cis*-4-(phenylazo)benzoate groups is prohibited by their covalent attachment to polyethylene chains).

Thermal isomerizations of azobenzene guest molecules in unannealed, undrawn rubbery polymers have been described satisfactorily by a single-component first-order rate process, but two first-order processes were necessary to describe the kinetics in the glassy state[14,15] or when the polymers were annealed at temperatures above the glass transition.[16] Consistent with these observations, the distribution of free volume at sites is narrowed upon annealing (physical aging) of poly(methyl methacrylate) below its glass transition temperature; the number of sites with larger free volumes is decreased more than the ones with smaller free volumes.[38] Here, we have demonstrated that the thermal cis → trans isomerizations of azobenzenyl groups also follows two distinct kinetic pathways in drawn, partially crystalline polyethylene above the glass transition temperature. Because the duality of the isomerization process is most apparent in films with covalently attached azobenzenyl groups, differences in the free volume and wall flexibility of sites in the interfacial and amorphous regions appear to be responsible. Those differences are apparent only in drawn films, where wall stiffness of sites increases and free volume decreases. In our case here and those reported previously, the faster isomerization component can be attributed to the presence of *cis*-azobenzenyl groups in sites that are “stressed” (i.e., with smaller free volumes and stiffer walls than before the perturbation to the matrix was applied).

These results demonstrate the utility of attaching reporter groups to the polymer matrix to explore micromorphological changes that are introduced by physical perturbations at the macroscale. Furthermore, we have shown that comparison between the dynamic behavior of attached and diffusing probes can provide additional useful information about the nature of the matrix. This strategy may be useful as well in the design of polymers with azoaromatic groups for reversible optical memory and photonic applications.[39]

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References and Notes

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