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Free Volume Determination of Azobenzene−PMMA Copolymer by a Pulsed Low-Energy Positron Lifetime Beam with in-Situ UV Illumination

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ABSTRACT: The free volume properties of a poly(methyl methacrylate)−azobenzene copolymer were for the first time directly probed by use of a low-energy positron lifetime beam with in-situ excitation capabilities, showing that the free volume cavity size was not appreciably influenced by photoisomerization and thermal isomerization in the temperature range 34−180 °C. Isomerization is therefore suggested to occur without any molecular rearrangement of the glassy polymer matrix, which would also account for the lack of any shift to shorter wavelengths for the photoisomerization occurring in a glassy polymer in comparison to a chloroform solution. A decrease in the thermal isomerization rate at room temperature caused by the glassy polymer is explained in terms of a model in which only a fraction of the azobenzene is free to isomerize. The *cis*-azobenzene was found to be an efficient inhibitor of positronium formation, which enabled measurements of thermal isomerization rates and changes in the steady-state concentration of *cis*-azobenzene for an illuminated sample as a function of temperature.

Introduction

Research on polymers into which azobenzene moieties are incorporated has been motivated by various intriguing potential applications.[1−3] The foremost of these include devices for optical data storage,[4] membranes with switch on/off permeability,[5] and polymers with controllable solubility,[6] miscibility, and wettability.[7] It is the possibility to induce stable and erasable birefringence in the polymer which has inspired hopes for optical data storage applications. The birefringence is induced by polarized light, which causes the azobenzene to align perpendicularly to the direction of the polarization. The birefringence can then be erased by a circularly polarized laser beam. In the latter examples of potential applications, it is the drastic changes in the physical properties of azobenzene, occurring when it is excited from the relaxed trans state to the excited cis state by UV illumination, that would be utilized in the various applications referred to. The relaxed trans state of the azobenzene moiety is in principle nonpolar and planar and has a c4−c4′ distance of roughly 9 Å. This contrasts with the highly polar cis state which is almost spherical and has a c4−c4′ distance of only about 5 Å. Figure 1 displays the photoisomerization (excitation) and thermal isomerization (relaxation) reactions of azobenzene.

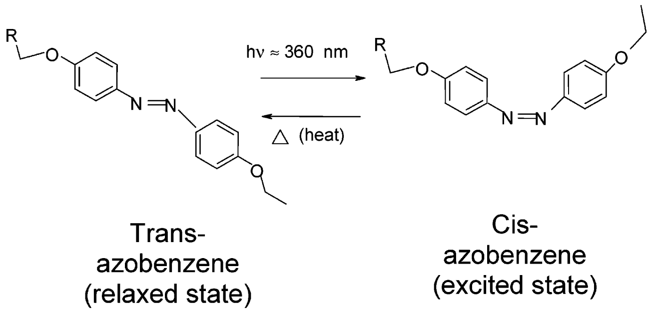

Figure 1. Two isomers of the ethoxy-substituated azobenzene moiety that was studied. The ground-state trans isomer has a flat geometry with a dipole moment of 0.5 D, whereas the excited cis isomer is roughly spherical, with a dipole moment of 3 D.

Since the isomerization processes need some "sweeping volume" to occur, it is reasonable to expect the isomerization kinetics to be coupled to the free volume available in the polymer matrix. One can calculate the free volume required for isomerization to 120 Å^3 or more, the exact volume depending upon the isomerization mechanism involved (rotation of the −N=N− bond or inversion of one or both of nitrogens) and the groups attached to the benzene ring.[8,9] This volume can be considered as quite large in relation to most estimates of the free volume cavity size in glassy polymers, which in polystyrene and PMMA at room temperature,[10−13] for example, is usually in the range 70−100 Å^3. On basis of these arguments, one should expect the isomerization kinetics to be considerably influenced by the glassy polymer matrix.

Investigations of the isomerization kinetics involved have mainly been carried out by use of UV-absorption spectroscopy. Photoisomerization and thermal isomerization kinetics have been studied on a wide range of polymer systems containing azobenzene. The azobenzene moiety has been introduced as a dopant in a polymer matrix[14] or covalently attached to the main polymer chain (directly on the polymer backbone, e.g., by means of a spacer[9,15,16] or as a part of the polymer backbone itself[9,17]). What is usually observed is that in

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a liquid solution of a polymer containing azobenzene the photoisomerization process occurs with a single rate constant that depends on the intensity of the UV light, whereas the thermal isomerization is a thermally activated process which also follows first-order kinetics.

If the solvent is removed, both the photoisomerization and thermal isomerization kinetics may be altered. The photoisomerization is often found to occur with one fast and one slow rate, which has been attributed to free volume restrictions for the isomerization.[9,17] Thermal isomerization is usually found to occur at only one rate at temperatures above the T_g. At temperatures below T_g, numerous studies have found that the thermal isomerization partly occur with an anomalously high rate.[17−23] This phenomenon has been attributed to a fraction of cis states being created in a stressed state. There are also investigations indicating the decay rate to be markedly reduced by the presence of a surrounding glassy polymer matrix.[17,24]

The interpretation of these behaviors in molecular terms has been a long-standing topic of scientific discussion.[15] Since a glassy polymer matrix is clearly able to influence the isomerization kinetics, extensive efforts have been made to determine the relationship between the isomerization kinetics of azobenzene and the free volume properties of the surrounding polymer matrix.[21] The photoisomerization and thermal isomerization rates have been measured as a function of temperature,[17,21] T_g,[20] the location of the azobenzene on the polymer backbone,[16,25] physical aging or annealing,[17,26] and a plethora of other variables, which presumably change the local free volume surrounding of the azobenzene.

However, few efforts have been made to combine measurements of the isomerization kinetics with direct detection of the free volume involved. Although various experimental techniques are available,[27,28] positron annihilation spectroscopy (PALS) has emerged as one of the most powerful tools for directly probing the free volume in amorphous polymers on a nanoscopic level. This technique involves positrons being implanted into a polymer and their lifetimes being recorded and collected in a spectrum. Positron lifetime spectra are sensitive to the size of the free volume cavities with a radius in the range of approximately 2.5 Å up to roughly a nanometer, i.e., free volume cavity sites in the size range of ca. 60 Å^3 to several hundred Å^3. This is a range which includes the volume required for the molecular reorientation of the azobenzene during isomerization. The relation between free volume cavity size and the positron lifetime is based on the annihilation of ortho-positronium (o-Ps), which is the bound state of a positron and an electron having parallel magnetic spins. In a vacuum, o-Ps has an intrinsic lifetime τ_3 of approximately 142 ns, whereas when located in a condensed material such as a polymer, the lifetime τ_3 is reduced to only a few nanoseconds. This reduction in τ_3 is a direct function of the local concentration of electrons with antiparallel spins and is therefore also directly correlated to the size of the free volume cavity in which the o-Ps resides during most of its lifetime. The semiempirical Tao−Eldrup equation relates the o-Ps lifetime to the radius of a spherical free volume cavity.[29,30]

Conventional PALS has been employed earlier in studying free volume in azobenzene−polymer systems and other photoresponsive polymers under dark conditions.[24,31−33] However, the classical PALS setup in which a positron source of Na^{22} is sandwiched between two relatively thick samples (≈1 mm) prevents the sample from being exposed to UV light. This is due to geometrical factors and to the high UV-absorbance of azobenzene, making thick samples unsuitable. There are no such limitations in a positron beam experiment, since in this case the sample surface can be exposed simultaneously to a positron beam and to UV illumination. Such an experimental setup is outlined in Figure 2. To the best of the authors' knowledge, this is the first experimental setup of its kind, enabling a variety of experiments relevant to the study of the free volume in photoresponsive polymers, for example, to be carried out.

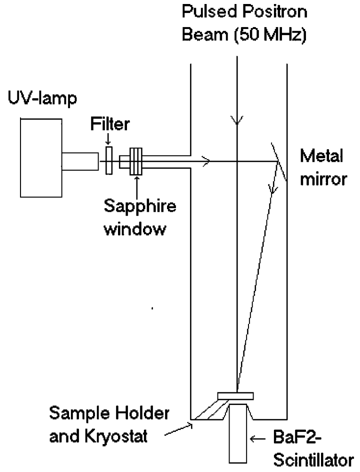

Figure 2. Basic features of a pulsed low-energy positron lifetime beam equipped with an optical system to photoisomerize the sample by means of UV light, enabling detection of the free volume characteristics during isomerization.

Pulsed low-energy positron beams have emerged during the past 15 years as versatile tools for depth probing of free volume characteristics,[34−36] and the depth profile for positrons in polymers has been established.[37] Low-energy positrons are obtained by slowing down of high-energy positrons obtained from the decay of Na^{22} in a moderator material. The positrons may then be accelerated and focused onto a sample, with implantation energies usually selected in the range 1−20 keV. By varying the positron implantation energy, the free volume can be probed, with median implantation depths ranging between a few nanometers to a few micrometers. Positron beams would thus appear to be a suitable tool for shedding light on the relationship between the free volume properties and the isomerization of azobenzene in polymers. Initial studies of the azobenzene copolymers[38] examined here showed PALS to be sensitive to the isomerization process, although considerable scatter in the data prevented a more detailed analysis of the effect of the excited state on the positron lifetime spectra from being carried out.

The aim of the present study was to use a pulsed low-energy positron beam, with a new in-situ excitation capability, for measuring the free volume and isomerization kinetics of an azobenzene−PMMA copolymer in the temperature range 34−180 °C. Complementary measurements were performed with a continuous positron beam which provided additional information on positron annihilation characteristics. A direct comparison between the positron annihilation characteristics and thermal isomerization kinetics was enabled by choosing a material which had been studied previously with UV-absorption spectroscopy.[24]

Materials and Methods

A copolymer of methyl methacrylate and 11-(4-ethoxyazobenzene-4′-oxy)undecyl methacrylate containing 4 mol % of the azobenzene monomer was used for the study. Details of the synthesis of the copolymer are provided elsewhere.[24,31] Thin films of the copolymer were prepared by spin-coating of a 10% copolymer−chloroform solution on top of glass substrates, yielding films about 1 μm thick. Solvent elimination and a controlled thermal history were obtained by annealing the samples in a vacuum at 150 °C for 1 h and then cooling them to room temperature at 0.5 °C/min.

The pulsed low-energy positron system used in the present investigation[34] has a time resolution of roughly 280 ps. About 1 million counts or more were recorded per spectrum. The spectra were recorded at 1, 3, and 5 keV implantation energy, corresponding to median implantation depths of approximately 25, 150, and 365 nm into the polymer.[37] The measurements were performed during a cooling cycle, starting with the sample being exposed to UV light in the temperature range 180−34 °C in steps of 10 °C. UV illumination of the sample in situ was obtained by use of a xenon short arc light bulb (XBO 450W/1) in the optical system shown in Figure 2. At 34 °C the measurements were continued isothermally under dark conditions in order to follow the thermal isomerization from the excited cis state to the relaxed trans state. The temperature program was then repeated with the UV light shut off, again starting at 180 °C and going down to 34 °C in steps of 10 °C. Thermal isomerization experiments at two additional temperatures (−190 and 90 °C) were performed after illumination at the same temperature for 1 h. The intensity of the UV light falling on the sample was estimated to 290 mW/cm^2 by measuring the intensity at an equivalent distance from the lamp in ambient atmosphere outside the positron beam and assuming a loss of 4% at every surface crossed by the light before reaching the sample inside the beam.

The positron lifetime spectra were evaluated using a modified version of PATFIT.[39] Three lifetimes (τ_1, τ_2, and τ_3) with corresponding intensities (I_1, I_2, and I_3) were fitted to the data. Each lifetime is attributed to annihilation from one of three possible states of positrons in polymer: τ_1 is the lifetime of the parapositronium (p-Ps, a bound state consisting of an electron and a positron with antiparallel spins), τ_2 is the free positron lifetime, and τ_3 is the orthopositronium lifetime (o-Ps, a bound state of an electron and positron with parallel spins). The free positron lifetime τ_2 was found to be independent of temperature, implantation energy, and time and was fixed to 475 ps in the final evaluation of the data. This was done in order to reduce the scatter in the other fitted parameters.

Additional measurements were performed with a continuous positron beam.[40] The annihilation radiation was detected by a HPGe detector with a 25% efficiency and a resolution of 1.17 keV at 514 keV. The Doppler broadened annihilation line was characterized using the *S* parameter. The *S* parameter represents the ratio of the content in a central part of the annihilation line to the total content. By its definition the *S* parameter is a linear combination of the *S* parameters of the different annihilation processes and can thus be written as $S = f_{\text{p-Ps}}S_{\text{p-Ps}} + f_{\text{o-PS}}S_{\text{o-Ps}} + f_{\text{free}}S_{\text{free}}$, where f stands for the corresponding fractions. While the p-Ps annihilation is characterized by a high *S* parameter compared to the annihilation of free positrons, the *S* parameter of o-Ps is approximately equal to that of free positron annihilation.

For the continuous beam experiments, reference spectra were recorded, after which the sample was exposed to UV light outside the beam at room temperature for 30 min, and then transferred into the beam again. Spectra were then repeatedly measured at room temperature at 1 and 3 keV under dark conditions.

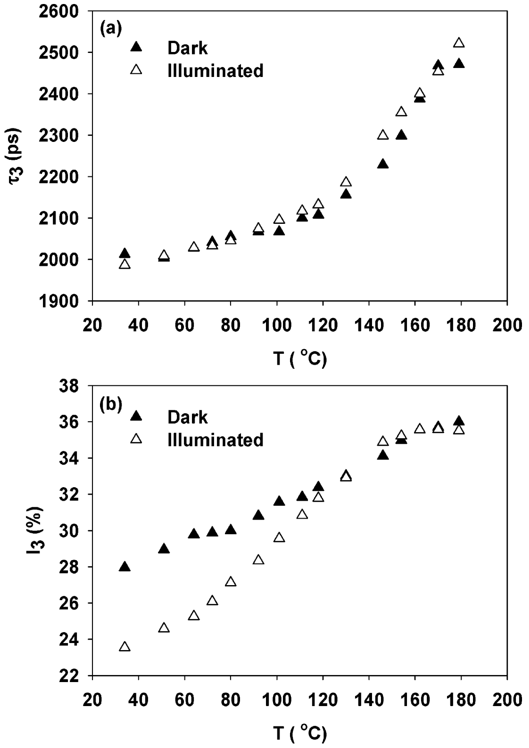

Figure 3. τ_3 and I_3 measured at 3 keV implantation energy (median implantation depth 150 nm) in the temperature range 180−34 °C. The measurements were performed in a cooling program with the sample exposed to UV illumination (△). The same temperature program was then repeated in dark conditions (▲). The sample was held at each temperature for more than 5 h, permitting measurements at 1 and 5 keV (only data of 3 keV are shown in the graph).

Results

Results from the pulsed low-energy positron lifetime beam are displayed in Figure 3a,b. The o-Ps lifetime τ_3 and its intensity I_3 are displayed as a function of temperature in the range 34−180 °C. Only the data for 3 keV are shown in the figure because the results of the other two energies (1 and 5 keV) were essentially the same and did not provide any further information concerning the polymer, other than the saturation of the illumination throughout the film. The measurements were performed starting at high temperature, the polymer being cooled then in 10 °C steps while being continuously exposed to the UV illumination. The same temperature program was repeated under dark conditions. An important feature to be noted in Figure 3a is the change in the temperature derivative $d\tau_3/dT$ at the glass transition temperature T_g, which can be observed in the vicinity of 125 °C. This is apparently a slightly higher temperature than measured for identical material previously.[24] The discrepancy in the estimates can be partly due to the typically poor resolution of T_g on the basis of $\tau_3(T)$ data and as well on differences in the thermal histories involved and in details of the experimental conditions. However, the location of T_g, as well as the slopes of τ_3 vs T, appear to not have been affected by the UV illumination. These observations are invariant with the implantation energy of the positrons (1, 3, and 5 keV, with the corresponding median implantation depths of 25, 150, and 365 nm). In the narrow temperature range of 130−150 °C, somewhat higher values of τ_3 are evident in the illuminated sample than in the dark sample, although these differences are too small

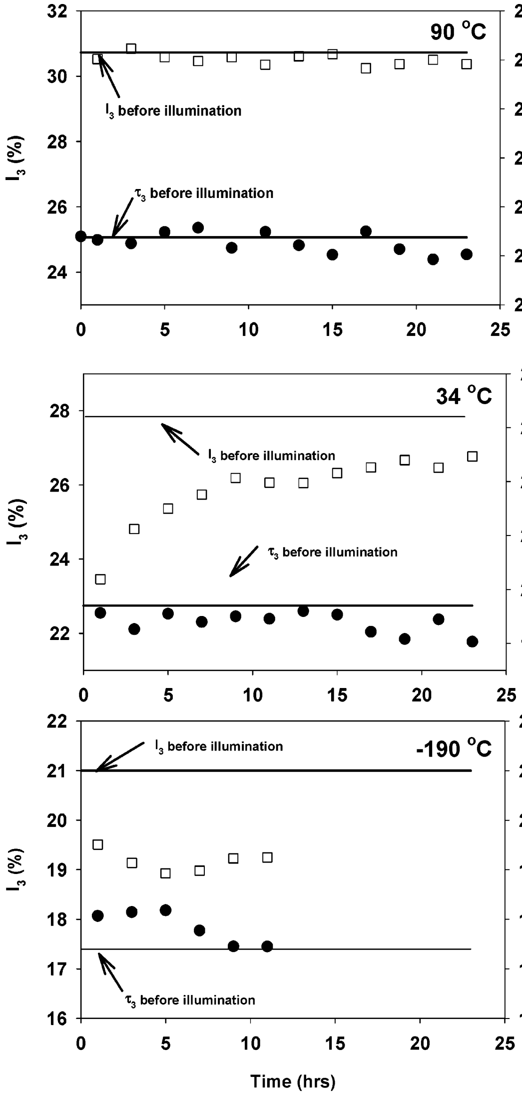

Figure 4. Thermal isomerization experiments at 90, 34, and −190 °C under dark conditions (τ_3 = ●, I_3 = □). The measurements at 34 °C were performed immediately after the end of the illuminated temperature program sequence dealt with in Figure 3, whereas the measurements at −190 and 90 °C were made after 1 h of illumination of a fully relaxed sample at the same temperature.

for any definite conclusions to be drawn regarding the effects of the isomerization upon the free volume.

In contrast to τ_3 being largely independent of the isomerization of azobenzene, I_3 showed an appreciable reduction when the sample was exposed to UV light. In Figure 3b, which displays I_3 in the temperature range 34−180 °C, a clear decrease in I_3 can be observed in the illuminated sample at temperatures below approximately 125 °C. This temperature is in agreement with the T_g, as the data for τ_3 vs temperature displayed in Figure 3a indicate.

The effects which thermal isomerization of the excited azobenzene has on the positron lifetime parameters were studied at three different temperatures: −190, 34, and 90 °C (Figure 4). Measurements at 34 °C were started immediately after the cooling program under illumination came to an end. Since the sample had been exposed to illumination during a period of time longer than the time needed for thermal isomerization,[24] saturation was ensured. The results are displayed in Figure 4, together with the measurements at −190 and 90 °C, which were made after 1 h of UV illumination of a fully relaxed sample at the same temperature. The levels of τ_3 and I_3 for the nonirradiated sample, indicated by a line for each temperature in the graph, were determined from reference spectra prior to illumination.

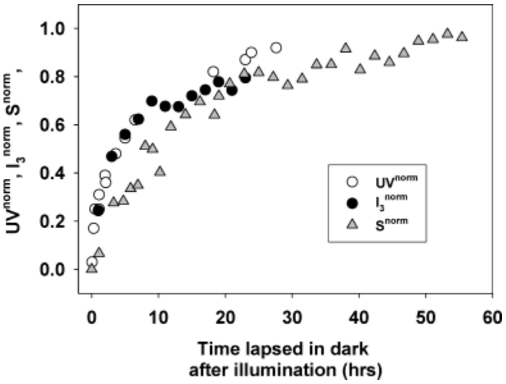

Figure 5. Thermal isomerization in dark conditions of excited azobenzene at room temperature, reflected in parameters from three different techniques: UV-absorption spectroscopy (UV^{norm}), pulsed low-energy positron lifetime spectroscopy (I_3^{norm}), and continuous positron beam (S^{norm}).

The o-Ps lifetime τ_3 does not appear to change appreciably during the time scale of the thermal isomerization experiments, with the possible exception of the lowest temperature, −190 °C. At this temperature, the initial increase in τ_3 during the first 5 h is only 25 ps, which is only slightly larger than the scatter found in the data. Much clearer differences between the various temperatures can be observed in the transient behavior of I_3. At room temperature, the reduction in I_3 is approximately 6% at time zero and decays as a function of time.

The measurements of the thermal isomerization at room temperature in Figure 4 may be directly compared with the corresponding measurements with the continuous positron beam and some reference UV-absorption measurements. Since it is only the relative change in the quantity yielded from each technique which is of interest, one may normalize each quantity so that the normalized value increases from 0 to 1 during the course of the thermal isomerization. The initial cis-rich state at early times ($t = 0$) is defined as 0, and the trans-rich state after infinite time is defined as 1, corresponding to the state before irradiation. The normalized I_3 was defined as $I_3^{norm} = (I_3(t) - I_3(0))/(I_3(\infty) - I_3(0))$ and $I_3(0) = 22\%$ and $I_3(\infty) = 28\%$. The normalized S parameter was defined as $S^{norm} = (S(t) - S(0))/(S(\infty) - S(0))$ with $S(0) = 0.4929$ and $S(\infty) = 0.5000$. The normalized UV light absorption values are taken directly from Blomquist et al.[24] in which $UV^{norm} = 1 - [cis]_t/[cis]_0$.

In Figure 5, I_3^{norm}, S^{norm}, and UV^{norm} are plotted vs time, and there is clearly a good agreement in the transient behavior of the three parameters, in particular between I_3^{norm} and UV^{norm}. Since the S parameter correlates with p-Ps annihilation and I_3 with o-Ps annihilation, it thus appears that the effect of the excited state is to reduce both p-Ps and o-Ps annihilation.

It is of interest here to consider the efficiency of the positronium quenching effect by the excited cis isomer, i.e., to relate the mass fraction that the excited cis state constitutes in the copolymer for a particular loss in I_3. The weight fraction of the azobenzene moiety (not including the ethylene spacer) is roughly 0.08. The *cis*-

azobenzene can thus constitute a weight fraction with a maximum of 0.08 at time zero, which causes a reduction in I_3 by a factor of 0.2 (I_3 decreases from 28% to 22%). One can thus conclude that the quenching effect is quite efficient, since the relative loss in I_3 is at least 2.5 times as large as the maximum weight fraction of the cis states. With these considerations in mind, one can relate the reduction in I_3 to the concentration of the cis states by use of the time-independent relationship expressed in eq 1.

$$I_3 = I_3^0(1 - a[\text{cis}]) \qquad (1)$$

In eq 1, I_3^0 is a reference state containing no cis states, corresponding to $I_3(\infty)$ in the thermal isomerization experiments above, [cis] = the weight fraction of the cis states, and a is a constant. The constant a can be estimated to have a value larger than 2.5, following the arguments above concerning the maximum weight fraction of the excited state.

To be able to interpret the reduction in I_3 as being a unique function of the concentration of the excited states, one needs to determine that the UV light is unable to influence the forming and annihilation of o-Ps in the PMMA matrix. To examine this possibility, control experiments on pure PMMA illuminated under the same conditions were performed. Treatment of the pure PMMA in this way did not reveal any effect on I_3 within an estimated error level less than 0.5%, this suggesting the UV illumination is indeed unable to directly influence I_3 in the PMMA matrix.

Isothermal measurements at −190 °C show a 2% decrease in I_3 immediately following the illumination, indicating photoisomerization to be possible even at 300 K below the T_g. The smaller decrease in I_3 of only 2% as compared with the 6% obtainable at 34 °C could reflect an increase in the difficulty in exciting azobenzene far below the T_g.[9] However, the decrease in I_3 is still appreciable, strongly suggesting that photoisomerization of the azobenzene is possible. Previous studies of isomerization of azobenzene in PMMA at −269 °C (4 K) showed that photoisomerization was relatively efficient in relation to various other amorphous polymers.[41] This was attributed to the presence of rotating ester groups at 4 K, which could also explain the presence of photoisomerization at −190 °C in the present study. One can also observe that during the first 11 h of measurement no systematic increase in I_3 occurred, which indicates the relaxation time of the thermal isomerization to be very long. Similar observations have been made in previous investigations[20] and are the expected result of a thermally activated reaction.

In contrast to the observation of relatively long relaxation times in the glassy state, at 90 °C, the relaxation time appears to be shorter than the time needed to record the first spectrum (1 h), since no difference could be detected between the nonirradiated sample and the average state of the sample during the first hour after the light was shut off. The relaxation time at 90 °C can thus be estimated to be shorter than 1 h.

Discussion

The photoisomerization and thermal isomerization processes of azobenzene occurring in the illuminated sample did not lead to any large or systematic observable changes in the o-Ps lifetime. This suggests that isomerization reactions of azobenzene does not change the free volume cavity size to an appreciable extent. One should nevertheless consider the possibility that isomerization creates free volume of a “nonequilibrium” type which disappears with a decay rate faster than the thermal isomerization of the azobenzene moieties. Since under such conditions the concentration of this additional free volume is dependent upon both its decay rate and the concentration of the isomerizing azobenzene, it may be below the detection level of the experiment. If the absence of any effect on τ_3 results from such rapid relaxation of the surrounding matrix, this elimination of free volume effects would be expected to disappear at very low temperatures, since the relaxation process must be based on a molecular rearrangement with some activation energy. As shown in Figure 4, the excitation of azobenzene at −190 °C (i.e., roughly 300 °C below the T_g in PMMA) only resulted in very small changes in τ_3. Although the creation of additional free volume cannot be excluded on the basis of the data, other results presented below strongly suggest that the isomerization is in fact not able to change the free volume in the surrounding matrix at room temperature and should therefore also be unable to do so at −190 °C.

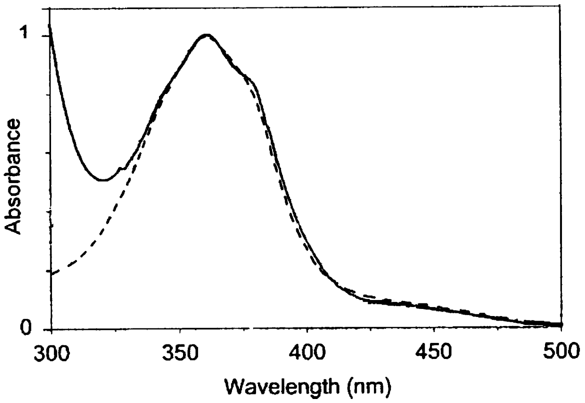

Figure 6. UV-absorption spectra of the copolymer in a chloroform solution (broken line) and in the glassy state (solid line). Both spectra are recorded at room temperature, i.e., at approximately 80 °C below the T_g of the pure polymer.

Some interesting observations regarding the relation between isomerization and the state of the surrounding matrix of azobenzene can be made from the UV light absorption spectra found in different media. Figure 6 displays the UV light absorption spectra[24] of the azobenzene copolymer in chloroform solution and in the glassy polymer state. The spectra reflect the energy required to photoisomerize individual azobenzene moieties in the glassy polymer matrix and the polymer in the chloroform solution. Since the two UV-absorption curves overlap almost completely, it appears that the photoisomerization of azobenzene in a glassy polymer and in a solution requires essentially the same energy. The overlap between the UV-absorption curves has been observed previously[16,42] and is hence not specific to the present study. It is of interest here to compare the energy which is provided with the UV light, with the energy required to induce segmental movement in the glassy polymer matrix. Such a comparison would indicate how much the UV-absorption curves would shift to shorter wavelengths in order to provide the additional energy needed rearrange the glassy polymer matrix which is surrounding the azobenzene. For example, a very small displacement similar to the β-relaxation process of PMMA[43] (i.e., rotation of a methacrylate group) would require an activation energy of about 20 kcal/mol. If this energy were supplied by the UV light, the absorbed wavelength would be reduced from approximately 360 nm to about 300 nm. Since the UV spectra obtained show no indication of a shift in the absorbed wavelengths, even such a slight displacement of the surrounding polymer matrix can be excluded, and any displacement larger than this as well. This interpretation is also consistent with the idea of *cis*-azobenzene occurring in a stressed state being responsible for the anomalously fast thermal decay, which is often found in glassy polymers.[9,15,19,20] Such a stressed state of the *cis*-azobenzene would be likely to be produced only if no molecular rearrangement of the surrounding matrix occurred during the time scale of the thermal isomerization.

The absence of any increase in absorption of shorter wavelengths for the photoisomerization inside the glassy polymer matrix may be interpreted in two ways. One is that most of the *trans*-azobenzene moieties inside the glassy polymer matrix occur in a state in which photoisomerization is possible without any rearrangement of the polymer matrix. However, if this would be the case, one would also predict that the excitation rate in a photoisomerization experiment to be the same in a glassy polymer and in a liquid. This interpretation stands in conflict with most investigations on photoisomerization rates in different media, which show appreciably reduced photoisomerization rates of azobenzene inside glassy polymers.[9,17]

The other interpretation is that only the azobenzene which can photoisomerize without rearrangement of the polymer matrix is photoisomerized, thus resulting in overlapping UV-absorption spectra. The fraction of azobenzene which would require any rearrangement of the glassy polymer matrix is unable to isomerize and does thus not contribute to the UV-absorption spectrum. The fraction of *trans*-azobenzene unable to isomerize would thus result in a decreased rate of photoisomerization, as observed experimentally.

Since the photoisomerization appears to be possible only if the azobenzene is unrestricted by the polymer, one would expect the thermal isomerization also to be prevented by any requirement to rearrange the surrounding polymer matrix. Thus, it is reasonable to assume that the photoisomerization and thermal isomerization process of a single azobenzene moiety in the glassy PMMA matrix occur between two unrestricted states, as if unaffected by the surroundings. The observation of reduced photoisomerization and thermal isomerization rates may then be attributed to a reduction in the fraction of azobenzene in the trans state and cis state which is free to isomerize. According to these observations, one could describe the photoisomerization and thermal isomerization of azobenzene in a glassy polymer with a four-state model (eq 2). In this model, the trans−cis isomerization occurs only between two unrestricted states ([trans]^u and [cis]^u) with the photoisomerization rate constant k_3 and thermal isomerization rate constant k_4 being the same in a glassy polymer and in a liquid. The decrease in the photoisomerization and thermal isomerization rates caused by the glassy polymer matrix is then attributed to a fraction of the azobenzene moieties being unable to isomerize, i.e., [cis]^r and [trans]^r, due to free volume restrictions. The rate constants k_1, k_2 and k_5, k_6 describe the rate of free volume redistribution in the vicinity of the azobenzene moieties.

$$[\text{trans}]^{\text{r}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{trans}]^{\text{u}} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [\text{cis}]^{\text{u}} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [\text{cis}]^{\text{r}} \qquad (2)$$

Such an expression would be consistent with both the observation that the glassy PMMA matrix is unable to change the excitation energy (by overlapping of the UV-absorption spectra) whereas still able to reduce the thermal isomerization rate. The observed decrease in the total thermal isomerization rate is caused not from a change in k_4 due to the presence of the glassy polymer surrounding the azobenzene, but rather by the fraction [cis]^u available for thermal isomerization being reduced by the exchange of the restricted and the unrestricted state, i.e., k_5 and k_6, in the glassy polymer matrix. The extent to which the total reaction rate decreases reflects then the fraction of azobenzene in which thermal isomerization is unable to occur. The relationship between the apparent thermal isomerization rate, k_4', in the glassy polymer matrix and the "real" thermal isomerization rate, k_4, observed in a liquid solution thus follows the relationship given in eq 3

$$k_4'([\text{cis}]^{\text{u}} + [\text{cis}]^{\text{r}}) = k_4[\text{cis}]^{\text{u}} \qquad (3\text{a})$$

$$\frac{k_4'}{k_4} = \frac{[\text{cis}]^{\text{u}}}{[\text{cis}]^{\text{u}} + [\text{cis}]^{\text{r}}} \qquad (3\text{b})$$

One can estimate the fraction of azobenzene available for thermal isomerization directly then from the ratio of the two reaction constants k_4' and k_4. The reaction rates in the present system, both in the pure glassy state of the polymer and in a chloroform solution, have been quantified earlier by means of UV-absorption spectrometry,[24] the values $k_4 = 2 \times 10^{-2}$ min^{-1} (chloroform solution) and $k_4' = 1.2 \times 10^{-3}$ min^{-1}(glassy polymer) having been obtained. One can then estimate the fraction [cis]^u of the total concentration of the cis isomers present during thermal decay to about 6%. This number can, however, not be expected to describe the situation very early in the thermal decay, since the value of k_4' is based on data recorded 2 h of after dark conditions, i.e., data insensitive to any fraction of very rapidly decaying cis isomers.

The two relaxation rates of the thermal isomerizations commonly observed in systems of this sort can be interpreted in terms of this model by k_5 and k_6 being the rate-determining steps during thermal isomerization. At shorter times, the population of [cis]^u is rapidly drained by the "fast" thermal isomerization rate k_4, leading to an observed decay rate similar to that found in the liquid state. After some time, the remaining [cis]^u becomes dominated by the rate of exchange (k_5 and k_6).

This model predicts the thermal isomerization rate to increase with temperature more than that predicted with a constant activation energy. This is due to that the fraction of *cis*-azobenzene available for thermal isomerization, i.e., [cis]^u/([cis]^r + [cis]^u), is expected to increase as a function of temperature due to the thermal expansion of the free volume sites according to Figure 3a. However, the thermal isomerization experiments presented here do not permit a resolving of the free volume effects from thermal effects on the rate of thermal isomerization.

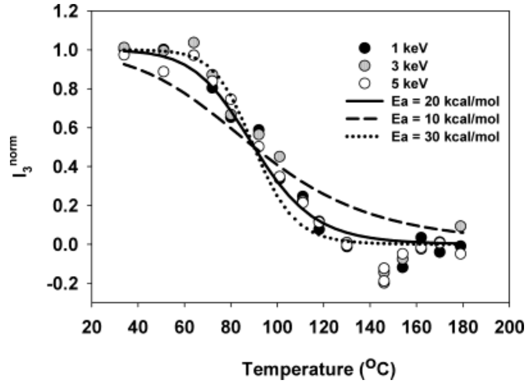

Figure 7. Relative decrease of I_3 caused by the UV illumination in the temperature range 34−180 °C. Plotted are the results from all energies together with the expected values from a thermally activated isomerization with no consideration to the free volume change (eqs 4 and 5 in the text).

The idea of isomerization being restricted by a glassy matrix is not new. Already in 1972, Paik and Morawetz[9] interpreted their isomerization kinetics results in a glassy polymer in terms of a fraction of the free volume preventing both photoisomerization and thermal isomerization of the azobenzene moieties from occurring. Later, Lamarre et al.[17] and Yu et al.[16] interpreted the occurrence of two different excitation rates as indicating only a fraction α of the azobenzene moieties to be located in a free volume surrounding that permitted excitation to occur, and α being a function of the free volume and the rate of free volume redistribution in the polymer matrix. In 1978, Eisenbach reported that a WLF-type graph could explain the temperature dependency of the thermal isomerization rate, which was interpreted in terms of free volume dependency of the isomerization.[15] Very recently, in 2003, Wang et al.[18] suggested a model in terms of which the thermal isomerization kinetics of azobenzene was assumed to occur in two different free volume surroundings in a polymer matrix.

Temperature Dependence of Cis Concentration during Continuous Illumination. According to eq 1, there is a direct relationship between a decrease in I_3 and the concentration in *cis*-azobenzene. I_3 was thus used to study the relative change in the steady-state concentration of *cis*-azobenzene as a function of temperature. In Figure 7, the relative decrease in I_3 caused by the illumination is plotted as a function of temperature. The results for 1, 3, and 5 keV possess essentially the same features. Their temperature range can be divided into three regions: $T < 60$ °C, 60 °C $< T < 125$ °C, and $T > 125$ °C. In the low-temperature region, the concentration of cis isomers appears to be largely independent of the temperature. This can be interpreted as reflecting a slow thermal isomerization rate ($k_4 \ll k_3$), leading to a high concentration of cis states. Between 60 and 125 °C the cis fraction decreases with temperature, indicating the thermal isomerization rate to increase to a sufficient extent to influence the steady-state concentration of the cis states. At temperatures above 125 °C, the reduction in I_3 is below the detection level, indicating the concentration of excited states to be very low ($k_4 \gg k_3$).

The decrease in the cis concentration with increasing temperature can be interpreted in terms of eq 2. During constant illumination, the azobenzene copolymer reaches a quasi-equilibrium state in which $k_3[\text{trans}]^u = k_4[\text{cis}]^u$. This equilibrium can be expected to be temperature-dependent since k_3 (the reaction rate constant for the photoisomerization) should be only a very weak function of the temperature and to mainly be governed by the intensity of the UV illumination, whereas k_4, describing a thermally activated reaction, is expected to display an Arrhenius behavior. An increase in the free volume per se is not expected to change the concentration of the excited states under continuous illumination very much. This is because the expansion of the free volume should change the fraction of both *cis*-azobenzene and *trans*-azobenzene which is free to isomerize by roughly the same factor. Assuming that the total fraction of cis and trans follows linearly from the concentration of cis and trans in the unrestricted state, one can express the total fraction of cis states as a function of the ratio k_4/k_3:

$$\frac{[\text{cis}]^u + [\text{cis}]^r}{[\text{trans}]^u + [\text{trans}]^r + [\text{cis}]^u + [\text{cis}]^r} = \frac{1}{1 + \dfrac{k_4}{k_3}} \quad (4)$$

If one assumes $k_4/k_3 = 1$ at 90 °C (=363 K) and that k_3 is constant in the temperature range that is studied, one can fit the activation energy to the I_3^{norm} curve. The ratio k_4/k_3 then becomes temperature-dependent according to eq 5

$$\frac{k_4}{k_3} = \frac{A \exp(-E_a/RT)}{k_3} \quad (5)$$

In eq 5, E_a is the activation energy for the thermal isomerization in kcal/mol, $R = 1.987$ cal K^{-1} mol^{-1}, and T is the temperature in kelvin. The preexponential constant A may be determined from the condition that at 90 °C, $k_4 = k_3$.

Curves of 10, 20, and 30 kcal/mol are plotted in Figure 7. Both 20 and 30 kcal/mol produce reasonable agreement with the experimental data. One can conclude that the decrease in the concentration of cis states during steady-state illumination as the temperature increases can be explained simply in terms of a thermally activation decay reaction (k_4) and an excitation reaction which is independent of temperature (k_3). There seems to be no reason to take into account the expansion of the free volume, which could indicate that the increase in the free volume leads to an increase in the fractions of $[\text{cis}]^r/([\text{cis}]^u + [\text{cis}]^r)$ and $[\text{trans}]^r/([\text{trans}]^u + [\text{trans}]^r)$ by roughly the same factor. Previous measurements indicate that the activation energy E_a of azobenzene is relatively independent of the exact structure of the azobenzene moiety, often yielding values around 20 kcal,[15,18,42,44] which is completely in agreement with our experimental data.

Quenching of I_3 by the Cis State. In conventional PALS studies of polymers, I_3 has been found to correlate with some other physical properties, particularly polarity and conductivity, which both reduce I_3. The exact reason for this quenching effect by increased polarity and conductivity is not known, since the details of the o-Ps formation mechanism in polymers has not yet been thoroughly elucidated. In terms of the spur model,[45] there are several steps in the positronium formation which might be influenced by an increase of the polarity of the material. One could point to the polar *cis*-azobenzene state as possibly reducing diffusion of thermalized positrons and electrons or reducing the screening length between a positron–electron pair or direct trapping of positrons and spur electrons, being responsible for the reduced Ps formation. Since the Ps formation occurs on a picosecond time scale without emitting or absorbing any detectable amount of energy, the different factors involved in its formation have been difficult to analyze experimentally. Most efforts on this topic have for this reason been limited largely to theoretical calculations.[46]

Conclusions

The isomerization of the azobenzene–PMMA copolymer was found not to influence the free volume cavity size of the copolymer, since no large or systematic changes in o-Ps lifetimes could be observed as a function of UV light exposure in the temperature range 34–180 °C. This was consistent with the strong overlap of the UV-absorption spectra of the copolymer recorded in its glassy state and in a chloroform solution, suggesting that no additional energy is provided during excitation, which would have been required in order for a molecular rearrangement of the surrounding polymer matrix to occur.

The change in the intensity I_3 of the o-Ps annihilation was found to be directly correlated with a change in the cis state concentration. I_3 was used to probe the thermal isomerization processes at different temperatures. The excited cis state was also found to reduce the S parameter derived from the Doppler broadening measurements. This was interpreted as the excited cis state reducing both o-Ps and p-Ps annihilation, thus being an inhibitor for the formation of positronium. The decrease in positronium annihilation in the presence of the excited state is suggested to be caused by an increase in the polarity of the polymer.

The lower thermal isomerization rate observed in the glassy state than in a chloroform solution was interpreted in terms of a four-state model, in which the trans isomer and the cis isomer occur in an unrestricted and restricted state, respectively. In this model, photoisomerization and thermal isomerization are possible for the unrestricted states with the same rate constants as found in a liquid, whereas the restricted states are unable to isomerize.

The concentration of excited states was studied as a function of temperature during continuous illumination in the temperature range 34–180 °C. It was found that the concentration of cis states decreased as a function of temperature. This finding was consistent with the thermal isomerization having an activation energy of roughly 20 kcal/mol, the photoisomerization rate being independent of temperature, and that the increase of the fraction of azobenzene free to isomerize increased with the same factor for both the trans and cis isomer.

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