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Relationship of Photochemical and Dynamic Behavior of an Amorphous Photochromic Polymer containing Azobenzene Moieties in the Side Group

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SUMMARY: An amorphous copolymer with photochromic azobenzene moieties in the side chain is investigated by UV/Vis and real time dielectric spectroscopy. The aim of this study is to monitor both the reversible E/Z isomerization of the dyes and the influence of the photoreaction onto the matrix. The change of the absorbance and of the dielectric function is measured for the E/Z and the Z/E isomerization. To compare the results model functions are fitted to the measured data and the obtained parameters compared for both experiments. So a correlation between the two spectroscopic methods is established. This analysis leads to a model of the molecular mechanism which is based on excess free volume generated by the photoreaction.

Introduction

Photochromic polymers are very interesting materials for different optical applications such as data storage, display techniques or information processing[1-4]. It is well known that optical anisotropy can be induced for this purpose in addition to photochromism if the samples are irradiated by linearly polarized light[5-7]. The mechanism of the generating of the anisotropy which should be related to molecular mobility is still poorly understood, because such a photoorientation process is effective below the glass transition temperature T_g of the polymer.

The photoorientation process takes place via angular dependent exitation, a number of photoisomerization cycles and rotational diffusion within the steady state of the photoisomerization below the glass transition temperature T_g of the polymer. The relationship

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of the elementary photochemical process, its matrix dependence and the molecular dynamics seems to be the key for the understanding of the mechanism. The angular dependent E/Z and Z/E isomerization events which are totally reversible are the „molecular engines". During the isomerization process the geometrical shape and the polarity of the azobenzene group became changed. For a dense polymeric system like a layer or a film the microstructure and also the molecular dynamics should be influenced by the photoreaction. A combination of optical spectroscopy with real time dielectric spectroscopy is used to investigate the structural changes generated by the E/Z isomerization. The optical spectroscopy monitors selectively the photoreaction whereas the real time dielectric spectroscopy is sensitive to the change of dipoles in the supramolecular structure in general. So the E/Z and the Z/E isomerization of the azobenzene moieties (optical spectroscopy) and of the optical induced change of the structure of the whole polymer matrix (dielectric spectroscopy) can be separately investigated and compared.

Experimental

Materials

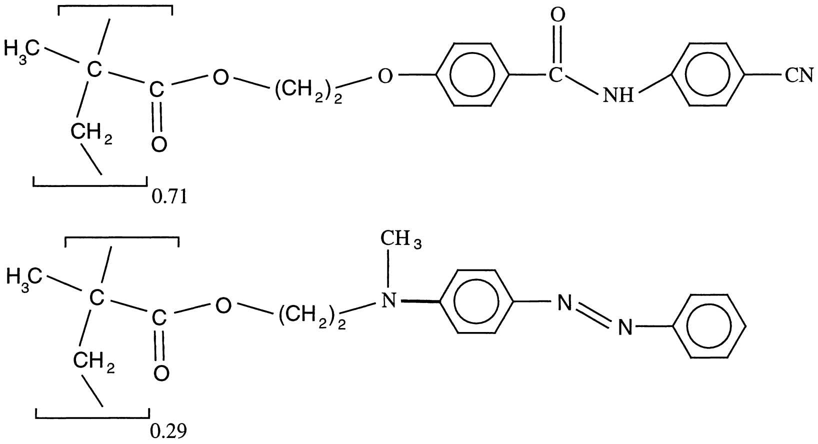

Fig. 1: Chemical structure of the studied copolymer system.

The chemical structure of the investigated side chain copolymethacrylate is given in Fig. 1. The photochromic group 4-amino-azobenzene is linked by a $(CH_2)_2$ spacer to the methacrylate main chain. As comonomer a methacrylate unit having a derivative of benzanilide in the side group is used which form H bonds. The average number of the molecular weight is 26300 g mol^{-1}. The thermal analysis shows that the system is amorphous with a glass transition temperature $T_g = 400$ K.

For both the dielectric and the UV/Vis experiments the wavelength of the irradiation light was 413 nm which corresponds to the $\pi\pi^*$ transition of the donor substituted azobenzene moieties in the solid state.

Procedures

For the dielectric and photochemical studies thin film of about 500 nm were prepared by spin-coating on glass substrates. Electrodes strips of ITO (Indium-Tin-oxide, bottom electrode) and aluminum (top electrode) are used for the dielectric measurements. The transparent ITO-electrode allows to estimate the dielectric properties during the on-line irradiation as a function of irradiation time, temperature and frequency f. The dielectric function $\varepsilon^*(f) = \varepsilon'(f) - i\,\varepsilon''(f)$ (ε'-real part, ε''-imaginary part and $i = \sqrt{-1}$) is measured from $f = 10^{-1}$ to $f = 10^5$ Hz using a dielectric interface (BDC, Novocontrol) and a lock-in amplifier (Stanford Research 830). The temperature of the sample is controlled by a liquid nitrogen buffered cryostat which has an optical window. For the irradiation an optical bench with a XBO-lamp (150 W) and a monochromator is employed to select the wavelength. At this wavelength the power density on the sample is estimated to 50 μ W cm^{-2}.

The change of absorption was measured by UV/Vis spectroscopy using a diode-array-spectrometer (XDAP 2.03). The samples were irradiated at room temperature using a xenon lamp in combination with a monochromator a well. The power density was 2 m W cm^{-2} in that case.

Results and Discussion

Optical spectroscopy

Irradiation: Fig. 2 (inset) gives the change of the absorption at 413 nm due to the E/Z photoisomerization versus the irradiation time at room temperature. A steady state is reached after approximately 100 s. 67 % of the azobenzene moieties are converted from the E form to the Z form. The time dependence of the absorption can be well described by an exponential function

$$A(t) = A_{0_{ir}} - \Delta A_{ir}\left(1 - e^{-\frac{t}{t_{0_{ir}}}}\right) \qquad (1)$$

where $A_{0_{ir}}$ is the initial absorbance, ΔA_{ir} is the difference between the initial and the final state and $t_{0_{ir}}$ is the time constant. It should be noted that the optical data can be well described by a first order kinetics.

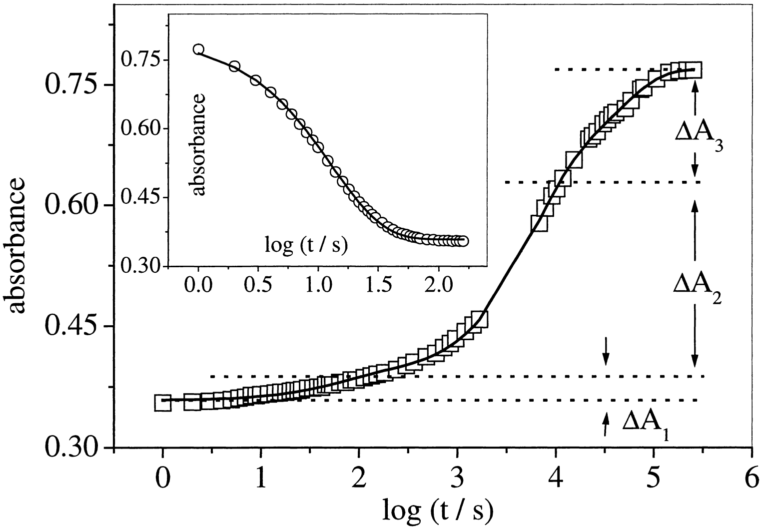

Fig. 2: Time dependence of the absorption at 413 nm for the thermal Z/E isomerization (back reaction) at room temperature. The solid line represents the fit of equation 2 to the data. The inset shows the E/Z isomerization at the same absorption wavelength. The solid line is the fit of equation 1 to the data.

Back reaction in the dark: The thermal Z/E reaction shows compared to the irradiation a more complicated time dependence (Fig. 2) which have to be described by a sum of three exponential functions

$$A(t) = A_0 + \sum_{i=1}^{3} \Delta A_i \left(1 - e^{-\frac{t}{t_{0_i}}} \right) \qquad (2)$$

where A_0 is the initial absorbance of the steady state, ΔA_i are the differences between the initial and the final states and t_{0_i} are the corresponding time constants for each process. If the separation of the long time behavior into two processes is true or only accidentally requires additional investigations.

Also Eisenbach has found a complicated time dependence of the thermal Z/E reaction of azobenzenes and spiropyranes in different polymeric matrices[8] which was discussed in the frame of a free volume approach. But a direct comparison of these results with the studied copolymer in this paper is not possible because the investigated polymers had an azobenzene content less than 1%. Therefore the disturbance of the polymer matrix by the photoreaction is much smaller and can be neglected. The photoreaction is used as a probe to study molecular mobility of the matrix. In the present case the concentration of the azobenzene groups is 29% and a great disturbance of the matrix by the photoreaction is expected.

Dielectric spectroscopy

Measuring the dielectric function under on-line irradiation of the sample shows a reversible optical-dielectric effect (Fig. 3). The real part of the dielectric function ε' is directly related to the molecular dipole moment of the system. For the investigated azobenzene group semiempiral quantum mechanical calculations (PM3) have shown that the dipole moment of the Z state (3.6 D) is greater then that of the E state (1.0 D). Therefore ε' increases with the irradiation time. It must be noted that the dielectric spectroscopy is sensitive for all dipoles in the copolymer so the changes of the azobenzene moieties and all changes of the whole polymer matrix are measured.

Irradiation: The time dielectric ε' at a frequency of 1 kHz for the E/Z isomerization (inset) increases with increasing irradiation time. A steady state is reached after about 1000 s in difference to the optical experiments (100 s). This difference in the times to reach the steady state is related to the different irradiation densities for the dielectric and the optical experiments.

The time dependence of ε' can be described in contradiction to the optical measurements by a stretched exponential function

$$\varepsilon'(t) = \varepsilon_{0_{ir}} + \Delta\varepsilon_{ir}\left(1 - e^{-\left(\frac{t}{t_{D_{ir}}}\right)^{\beta_{ir}}}\right) \qquad (3)$$

where $\varepsilon_{0_{ir}}$ is the initial state, $\Delta\varepsilon_{ir}$ is the difference between the initial and the final state, β_{ir} is the form parameter and $t_{D_{ir}}$ is the time constant for the process.

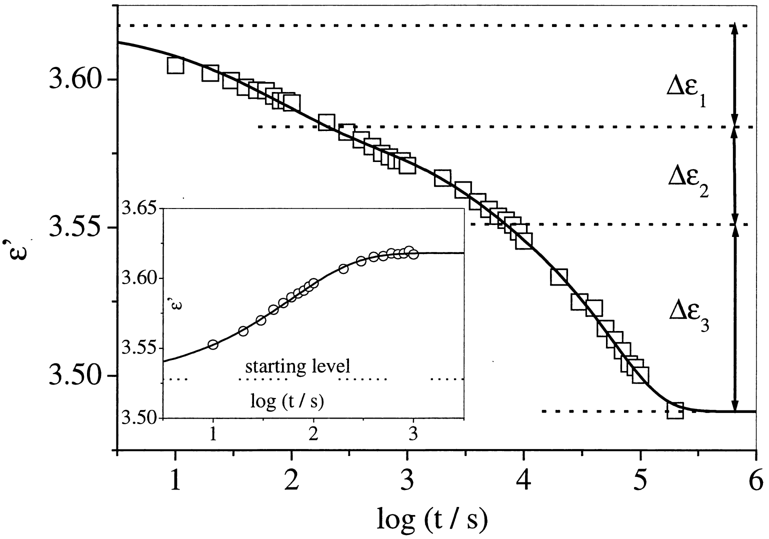

Fig. 3: Time dependence of ε' at 1 kHz for the back reaction at 303 K. The solid lines represent the fit of equation 4 to the data. The inset shows the time dependence of ε' at 1 kHz during the irradiation also at 303 K. The solid line is the fit of equation 3 to the data.

Back reaction in the dark: Also for the thermal Z/E isomerization monitored by the dielectric experiments the time dependence of ε' is very complicate like in the case of the optical measurements. But in contradiction to the optical experiments the time dependence of ε' at 1 kHz for the thermal back reaction cannot be described by a combination of exponential functions. Only a combination of three stretched exponential functions

$$\varepsilon'(t) = \varepsilon_0 - \sum_{i=1}^{3} \Delta\varepsilon_i \left(1 - e^{-\left(\frac{t}{t_{D_i}}\right)^{\beta_i}} \right) \qquad (4)$$

where ε_0 is the initial state, $\Delta\varepsilon_i$ are the differences between the initial and the final states, β_i are the form parameter and t_{D_i} are the corresponding time constants for each process describe the data satisfactorily. For all temperatures the parameter β_1 was fixed to 0.6, β_2 to 0.7 and β_3 to 1 to reduce the number of parameters and to obtain stable results. The first relaxation time t_{D_1} seems to be independent of temperature and was kept constant to the mean value of about 60 s in a second fitting step.

Correlation of the optical and dielectric experiments

E/Z isomerization: Fig. 4 displays the temperature dependence of the dielectric intensity $\Delta\varepsilon_{ir}$ for the irradiation process which shows a maximum value at 323 K and beyond this maximum it decreases with increasing temperature. An extrapolation to $\Delta\varepsilon_{ir} = 0$ leads to a value of 483 K which is higher than the glass transition temperature T_g of the system. An explanation for this temperature dependence is: The E/Z isomerization results in an equilibrium. So, on the one hand the equilibrium is shifted to the E form with increasing temperature. Therefore $\Delta\varepsilon_{ir}$ decreases with increasing temperature. At 483 K there is no effect of the photoreaction on the matrix. But on the other hand with decreasing temperature more and more azobenzene moieties are trapped by the polymer matrix and can not converted to the Z isomer. At 323 K the competition of this two trends results in a maximum of $\Delta\varepsilon_{ir}$.

The temperature dependence of the time constants $t_{D_{ir}}$ (Fig. 4, inset) has at low temperatures a nearly constant value. But unexpectedly $t_{D_{ir}}$ increases with increasing temperature. This can be explained taking into consideration the efficiency of the E/Z isomerization equilibrium which shifts to the E isomer with increasing temperature. To reach a steady state requires a higher number of isomerization cycles and although the time constant of E/Z isomerization shifts to shorter values a longer time scale is needed to build up the steady state. Also the β-value decreases with increasing temperature supporting this explanation.

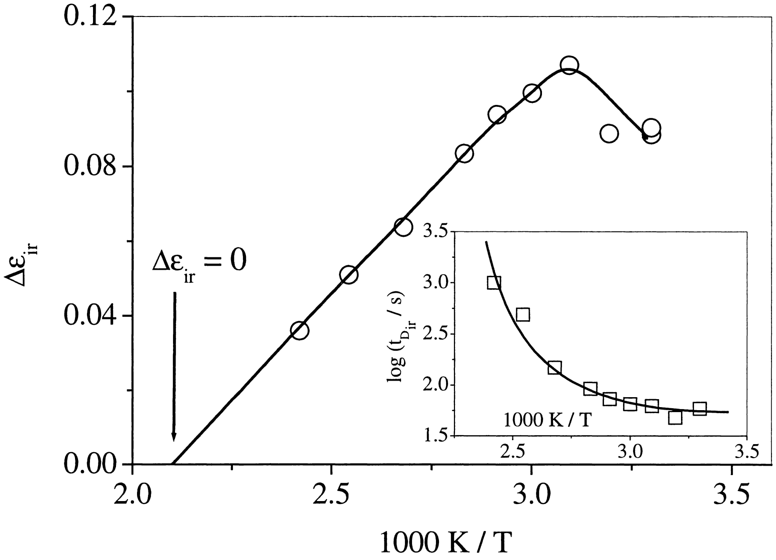

Fig. 4: Temperature dependence of the intensities $\Delta\varepsilon_{ir}$ taken from the dielectric on-line experiments of the irradiation process. The inset shows the temperature dependence of the time constants $t_{D_{ir}}$. The lines are guides for the eyes.

Z/E isomerization: Fig. 5 displays the temperature dependence of the time constants t_{D_i} taken from the dielectric experiments and t_{0_i} taken from the UV/Vis measurements. The first time constant t_{D_1} (dielectric) which was kept to a constant value corresponds with the first time constant t_{0_1} (UV/Vis). The second and the third time constant (t_{D_2} and t_{D_3}) for the back reaction taken from the dielectric on-line experiments exhibits an activated temperature dependence (activation energies: $E_A(t_{D_2}) = 21$ kJmol^{-1}, $E_A(t_{D_3}) = 18$ kJmol^{-1}). Extrapolating this dependence to room temperature a value is obtained which corresponds to that of t_{0_2} and t_{0_3} taken from the optical data. This means that the same processes are monitored by both the optical and the dielectric method as well. It has be concluded that both methods are monitor the same molecular processes.

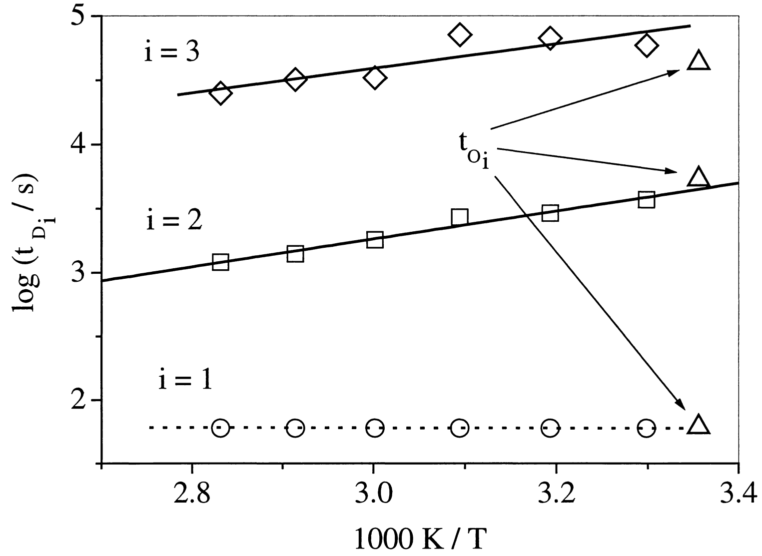

Fig. 5: Temperature dependence of the dielectric time constants: ™ : t_{D_1}, £ : t_{D_2}, ˉ : t_{D_3}. The solid lines are fits of the Arrhenius equation to the data. The dotted lines are guides for the eyes. The triangles represent the time constants t_{0_i} taken from the optical experiments.

However, the intensity ratios of the relaxation steps $\Delta\varepsilon_i$ and of the UV/Vis steps ΔA_i for the thermal back reaction are not the same for the two spectroscopy methods (table 1.). To interpret these results it must be reminded that the optical spectroscopy is only sensitive for the ration of azobenzene isomers and the dielectric spectroscopy is sensitive for the photochromic moieties and the whole polymer matrix.

In general the E/Z isomerization is an equilibrium reaction therefore the process is repeated many times during the irradiation and in the steady state a definite amount of Z isomers is generated. Because the Z isomer is much more bulky than its E form an additional (excess) amount of free volume is generated during the irradiation of the sample which depends on the concentration of the azobenzene moieties.

Switching off the light both the UV/Vis and the dielectric spectroscopy indicate that the thermal Z/E isomerization takes place in three steps. It is assumed that the photochemical moieties and the polymer matrix relaxes back to the corresponding equilibrium. In the first step a part of the excess free volume relaxes back. This relaxation process is found independent on the temperature. The intensity of this process amount only 7% measured by UV/Vis spectroscopy and for the dielectric spectroscopy 26% of the whole responses. So it is concluded that the first relaxation process is mainly a reaction of the polymer matrix. In a second step the main part of Z isomers relaxes back to the E form with a time constant which should be comparable to the time constant of the azobenzene molecules in solution[9]. This is indicated by the great intensity of this process in the UV/Vis spectroscopy (58%) and a moderate intensity of the dielectric intensity (25%). The third step represents the back relaxation of trapped azobenzene moieties which takes place with a reorientation of the polymer matrix or a redistribution of free volume. The intensities of this process are 34% indicated by the UV/Vis spectroscopy and 49% for the dielectric spectroscopy.

Table 1. Intensity ratios for the UV/Vis and for the dielectric spectroscopy

i		$\Delta A_i / \sum \Delta A_i$	$\Delta \varepsilon_i / \sum \Delta \varepsilon_i$
	T	(298 K)	(303 K)
1		0.07	0.26
2		0.58	0.25
3		0.34	0.49

Conclusions

An amorphous photochromic copolymer with azobenzene moieties in the side group was investigated by dielectric spectroscopy at different temperatures and by optical spectroscopy at 298 K. Thereby the change of the optical absorbance and the dielectric function was studied upon irradiation establishing a steady state with a high ration of Z isomers and the subsequent thermal relaxation in the dark. For the UV/Vis investigations the time dependence of the E/Z isomerization could be described by an exponential function but the Z/E isomerization has to be described by a sum of three exponential functions. Dielectric measurements under on-line irradiation showed a reversible optical-dielectric effect and the time dependence of the E/Z isomerization could be described by a stretched exponential function but the Z/E isomerization only by a combination of three stretched exponential functions.

On irradiation the dielectric intensity shows a maximum value at 323 K and an extrapolation to $\Delta\varepsilon_{ir} = 0$ leads to a value of 483 K which is higher than the glass transition temperature T_g of the polymer. The time constants of the E/Z isomerization shows in the dielectric experiments a increasing with increasing temperatures. In the dielectric experiments the thermal back reaction exhibits one time constants with constant value and an activated temperature dependence for two time constants. For all dielectric time constants an extrapolation to room temperature obtain a value which corresponds quite well with the optical time constants.

The intensity ratios of the relaxation and the steps are not the same for the two spectroscopy methods. So, the following simple model was discussed: In the first step the excess free volume relaxes back which is a main reaction of the polymer matrix. In the second step the main part of Z isomers relaxes back to the E form. The third step represents the back reaction of trapped azobenzene moieties which takes place with a reorientation of the polymer matrix or a redistribution of free volume.

In general it seems that a reaction from the Z to the E isomer in a polymer matrix is only possible if molecular motional processes provide the necessary amount of free volume for the reaction. An approximate mechanism for such a redistribution of free volume could be the dielectric β-relaxation[10].

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