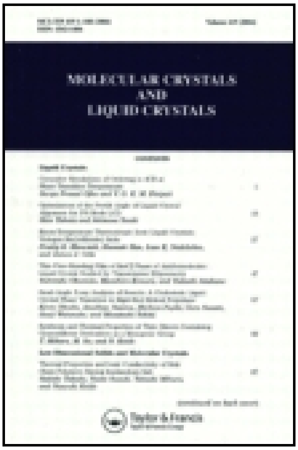

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Photoinduced Optical Anisotropy in thin Films of Amorphous Photochromic Side Chain Polymers

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PHOTOINDUCED OPTICAL ANISOTROPY IN THIN FILMS OF AMORPHOUS PHOTOCHROMIC SIDE CHAIN POLYMERS

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Abstract High values of optical anisotropy have been induced in glassy films of amorphous copolymers containing azobenzene moieties and rod–like side groups by angular-dependent photoselection. The photoinduced reorientation of the photochromic groups causes a reorientation of the non–photochromic groups due to a co–operative effect.

INTRODUCTION

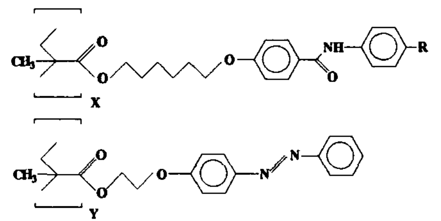
Angular–dependent photoselection is a well known phenomenon.[1] Aimed at the development of materials for optical data storage it has been used to modify the anisotropy in liquid crystalline polymers[2–4] (LCP´s) as well as to induce optical anisotropy in amorphous photochromic polymers[5]. However, the preparation of uniformly aligned films of LCP´s is a complicated procedure. On the other hand, the values of birefringence which have been induced in amorphous polymers are small.[6]
We have investigated the border between these two classes of polymers to find materials which combine the easy handling of amorphous films with the high values of optical anisotropy characteristic for LCP´s. Very recently we have reported on high values of light induced anisotropy in LCP´s which have been frozen–in to amorphous films.[7] In this paper we demonstrate that a strong anisotropy can be induced in films of amorphous polymers with photochromic and rod–like side groups.

RESULTS

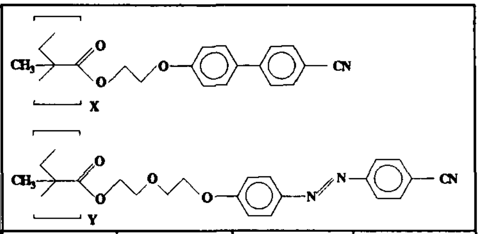
The investigated polymers are shown in Table 1. The synthesis was the same as described in [8] (polymer 1–3) and [9] (polymer 4–6). The polymers have been sandwiched between two glass plates (d=10µm) or spincoated from a THF solution (d=0,5µm).

Films of the amorphous polymers have been irradiated with linearly polarized light (λ=488 nm; P=40 mW/cm^2). The UV/Vis spectroscopic results for the irradiation of polymer **1** are shown in Figures 1 and 2.

TABLE 1 Investigated polymers and the corresponding glass temperatures T_g



Polymer	y/(x+y)	R	T_g(°C)
1	0,24	CN	97
2	0,40	OC_4H_9	73
3	0,50	OC_4H_9	81



Polymer	y/(x+y)	T_g(°C)
4	0,20	101
5	0,40	88
6	0,60	77

In the initial state the absorbance is completely isotropic. The polarized irradiation generates a dichroism at 365 nm (azobenzene) and at 285 nm (benzanilide), i.e. the long molecular axises of the photochromic as well as of the non-photochromic groups have been oriented preferably perpendicular to the electric vector of the actinic light.

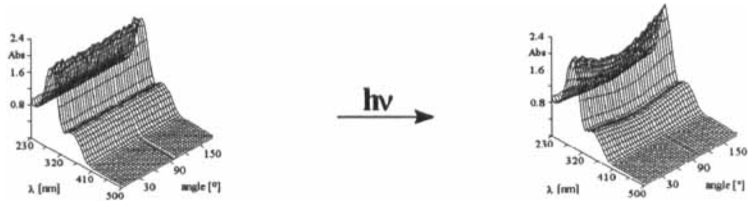


FIGURE 1 Polarized UV/Vis spectra of Polymer 1 (d=0,5μm) in the initial state and after polarized irradiation and relaxation; electric vector of actinic light in 90 degree direction

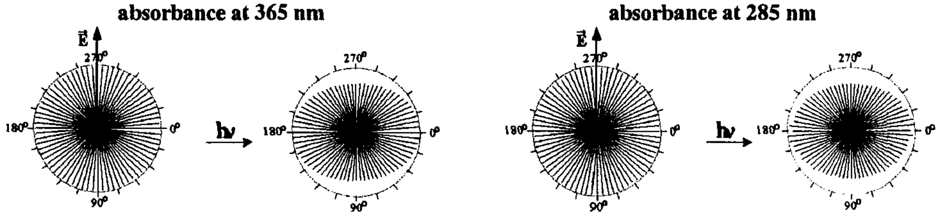


FIGURE 2 Angular dependence of the absorbance of Polymer 1 (d=0,5μm) in the initial state and after polarized irradiation; E is the direction of the electric vector of actinic light.

This is proved by the angular dependence of the integrated areas of the CN stretching vibration at 2229 cm^{-1} measured by polarized IR spectroscopy (Figure 3). In case of polymer 1 (CN group only at the non-photochromic moiety) the light induced UV and IR dichroism are qualitatively the same. In case of polymer 6 (CN group at all side chains) the irradiation results also in a symmetric distribution of the IR absorbance with the maximum perpendicular to the electric vector of actinic light. The spectroscopic degree of order calculated from the IR dichroism is 0.12 in case of polymer 1 (25% azobenzene moieties) and 0.14 for polymer 6 (60% azobenzene moities).

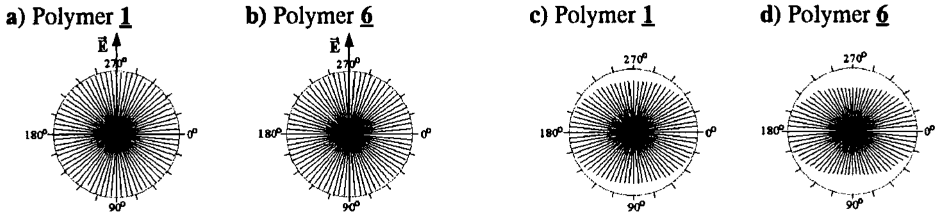

a) Polymer 1 b) Polymer 6 c) Polymer 1 d) Polymer 6

FIGURE 3 Angular dependence of the integrated areas of the CN bands in the initial state [a) and b)] and after polarized irradiation and relaxation [c) and d)]

These findings demonstrate that the non-photochromic but rod-like moieties have been reoriented in the same direction and to the same amount as the photochromic moieties. This can be explained by a multistep co-operative nearest neighbour process between photochromic and rod-like moieties within the steady state of the photoisomerization. The uniformly directed reorientation of all side groups of the polymers results in an orientational order and in this way in the emergence of an optical axis. The increase of birefringence due to this process has been measured during irradiation (see Figure 4).

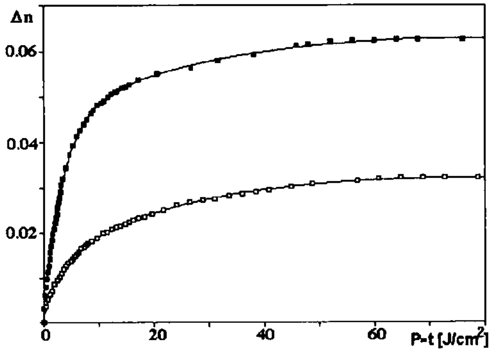


FIGURE 4 Increase of birefringence in films of polymer 1 (open squares) and polymer 6 (filled squares) due to light induced reorientation (d=10μm, λ=488 nm; P=40 mW/cm^2)

The values of induced birefringence shown in Table 2 are up to one order of magnitude higher as that obtained in polymers in which the rod-like moieties had been replaced by methyl groups.

TABLE 2 Light induced birefringence (λ=488 nm; Polymers 1-3 P=40 mW/cm^2; Polymers 4-6 P=200 mW/cm^2)

Polymer	1	2	3	4	5	6
Δn	0.0312	0.035	0.025	0.040	0.052	0.080

This demonstrates, that the presence of side groups with a high anisotropy of the geometrical shape and the molecular polarizibilty supports high values of inducable birefringence. Furthermore the incorporation of non–photochromic but rod–like side groups leads to a higher stability of the induced birefringence. Thus, in case of polymer **1** the loss of induced birefringence due to relaxation processes was less then two percents.

CONCLUSION

A detailed discussion of the mechanism has been given in a previous paper.[7] In initially amorphous films the angular–dependent photoselection process generates an orientational order of all form anisotropic side groups by a co–operative physical reorientation process. The reorientation takes place mainly within the photostationary equilibrium of the molecular photoreaction and a large number of single E–Z and Z–E photoisomerization steps of the azobenzene moieties is involved in this process.

Amorphous photochromic polymers with incorporated rod–like side groups combine the advantages of liquid crystalline polymers and conventional amorphous polymers: On the one hand transparent, non–scattering films can easily be prepared. On the other hand high values of birefringence with a high long–term stability can be induced, modified by irradiation with light of another polarization and erased thermally or by unpolarized irradiation. Thus, these polymers are very promising materials for the use in optical data storage.

The dependence of the amount of inducable anisotropy on the structure of the photochromic copolymers, the content of the photochromic groups and on the operating temperature will be discussed in a forthcoming paper.

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