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Optical and broadband dielectric investigations of photochromic polymethacrylates

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Abstract

The molecular dynamics and optical switching behavior (photo alignment) of novel azobenzene containing side-group (co)polymers were studied by time-resolved optical spectroscopy and broadband dielectric spectroscopy (BDS). To elucidate the effect of the molecular structure on the photochromic properties, two series of poly(methacrylates) with different aliphatic spacer units and four different concentrations of the chromophoric monomer were investigated. For both series, an inverse relation between the switching (retardation and relaxation) times and the chromophore content was found as well as a strong correlation between switching times and alignment efficiency. Dielectric spectroscopy on all materials revealed up to three relaxation processes (α, α*, δ) above the glass transition temperature that were assigned to the dynamic glass transition of the polymer backbone and the fast and slow fluctuation of the chromophores around their long and short molecular axes. In the glassy state, occasionally two Arrhenius-type relaxations were observed that were identified as local motions of the butyl side group and the chromophore in its anisotropic environment. Both materials series showed a monotonic increase in T_g and the dynamic fragility with increasing chromophore concentration, which was explained by an increasing effect of physical crosslinking provided by the increasingly dense packed side groups.

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1. Introduction

Photochromic polymethacrylates with a cyanoazobenzene moiety in the side group are perspective materials for holographic applications due to high optical quality of the polymer matrices in combination with excellent photochromic properties of the dye. Among organic dyes, the azobenzene derivatives are of particular interest because of their ability to reversible *trans–cis–trans* isomerization, which is accompanied with strong changes in dielectric properties such as: molecular dipole moment, refractive index and the low-frequency permittivity, all being relevant for practical optoelectronic applications. The photochromic polymeric materials can find potential applications in information storage devices such as conventional optical data media and holographic recording materials [1–3].

In this work, we deal with two series of methacrylate push–pull side-chain azobenzene homo- and co-polymers that contain a cyanoazobenzene side group linked to the polymer backbone via two kinds of flexible spacers (Fig. 1). The cyanoazobenzene chromophores are push-pull derivatives of the pseudostilbene type, according to Rau classification [4,5], which are characterized by strong overlapping in the absorption spectra of the *cis* and *trans* isomers. This increases the rate of the *cis–trans* thermal isomerization. Pseudostilbenes are also a good choice in view of an efficient photoinduced orientation, because both isomerization reactions (*trans–cis* and *cis–trans*) are photo-addressable and thus allow a fast photo switching in both directions.

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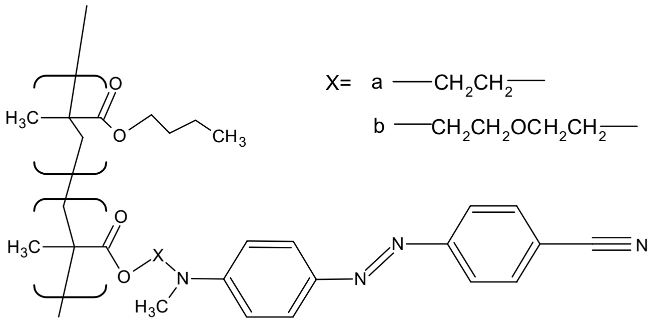

Fig. 1. Structural formulae of the photochromic pCN (X = a) and pCNO (X = b) polymer series.

The photoinduced alignment process of azobenzene mesogenic groups is a complex process that comprises several angular selective *trans–cis* and *cis–trans* photoisomerization cycles in conjunction with rotational diffusion of the chromophores and thermally driven *cis–trans* isomerization. By repetition of these *trans–cis–trans* isomerization cycles and corresponding changes in the chromophore transition moment, the optical axis of azobenzene groups becomes aligned perpendicular to the electric vector of the polarized light [2,6].

To study the molecular dynamics of the photochromic polymethacrylates, we have employed dielectric relaxation spectroscopy (DRS) [7]. The aim of DRS experiment in this work is twofold: On the one hand, we want to elucidate the rotational diffusion of the chromophores in the *glassy state*, i.e. the temperature where photoalignment is effective, by studying the β-relaxation associated with the azobenzene group. Previous work has suggested a correlation between the alignment kinetics and thermal activation parameters of the β-process being related to the degree of local anisotropy in the chromophoric packing density [8]. On the other hand, the analysis of the dynamic processes related to the dynamic glass transition will likely provide information about the inter-chromophore interactions, molecular packing and other parameters that affect the rotational degrees of freedoms of the chromophores on a large-scale.

The present work is focused on the interplay between photoinduced alignment and molecular relaxation behavior of thin polymeric films deposited on glass substrates. The effect of the azobenzene concentration and spacer length in both series of polymethacrylates was investigated with broadband dielectric and optical spectroscopy. The longer spacer was used with the aim to improve the flexibility of the dye moiety. The flexibility of the molecule may also have an effect on response rate of the material on illumination.

2. Experimental

2.1. Materials

All polymers were synthesized, according to procedure described in Ref. [9], by free radical homo and copolymerization of the photochromic methyl methacrylate monomers in THF and γ-butyrolakton as a solvent using 2,2′-azoisobutyronitrile (AIBN) (8% by wt) as an initiator. Butyl methacrylate was used as a non-photochromic co-monomer. The polymerization reaction yielded homopolymers and statistical copolymethacrylates, where the azobenzene co-monomer content was varied between 30 and 100 (wt%). The average molecular mass of the polymers determined by GPC was between 8000 and 11 000 (cf. Table 1). Thermogravimetric analysis (TGA) indicated a very good thermal stability with initial decomposition temperatures above 230 °C for all polymers. Differential Scanning Calorimetry (DSC) measurements was used to measure the glass transition temperature (T_g) that generally showed an increasing trend with the increase of the azobenzene fraction (cf. Table 1). While all materials from the series with the shorter ethylene spacer between mesogen and main polymethacrylate chain, pCN (Fig. 1, X=a), were found to be amorphous, most of the polymers with longer ethoxyethylene spacer, pCNO (Fig. 1, X=b), showed liquid crystalline behaviour (smectic C) above T_g.

2.2. Optical experiments

Optical experiments were performed with a setup similar to that described in the literature [10,11]. The low-intensity probing beam (tungsten halogene lamp type HL-2000-LL of AVANTES), passed through a pair of two polarizers, was used to probe the induced photo alignment. The intensity of the probe light was detected with a photodiode,

Table 1
Results of the GPC and DSC analysis for the pCN and pCNO polymer series

Sample	Weight % of azo block	M_n (g/mol)	M_w (g/mol)	D	Phase	Transition temperature (°C)
pCN30	30	3085	7914	2.57	am.	g 32 I
pCN50	50	3670	7905	2.15	am.	g 60 I
pCN80	80	3051	7612	2.49	am.	g 82 I
pCNhomo	100	3078	7489	2.43	am.	g 102 I
pCNO30	30	5881	11 356	1.93	am.	g 29 I
pCNO50	50	2932	8075	2.75	LC	g 32 S 166 I
pCNO80	80	3218	10 081	3.13	LC	g 37 S 150 I
pCNOhomo	100	3190	7996	2.51	LC	g 72 S 148 I

g = glass transition, S = smectic phase, I = isotropic phase (isotropic melt).