Optical and broadband dielectric investigations of photochromic polymethacrylates

Małgorzata Serwadczak a, Michael Wübbenhorst b, Stanisław Kucharski a,*

a Wroclaw University of Technology, Faculty of Chemistry, Department of Polymer Engineering and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland
b Katholieke Universiteit Leuven, Afdeling Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, B-3001 Leuven, Belgium

Available online 17 October 2007

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.

© 2007 Elsevier B.V. All rights reserved.

PACS: 77.22.Gm; 82.30.Qt; 78.40.–q; 78.47.+p; 78.20.–e; 61.30.Vx

Keywords: Photochromics; Dielectric properties, relaxation, electric modulus; Photoinduced effects; Polymers and organics; Fragility

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.
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 11000 (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.
which was connected to a data acquisition system. The films were irradiated with 460 nm linearly polarized light from blue LED (type LB 5436 of OSRAM) providing a power density of 2.8 mW/cm². The pumping light was focused with a lens and then passed through a polarizer at 45° with respect to the polarization direction of the probe light, before hitting the film sample. UV–vis spectra were recorded using AvaSpec-102 Fiber Optic Spectrometer with photo diode array detector.

2.3. Dielectric measurements

For the dielectric studies thin films were spin-coated on metallized glass slides (aluminum, thickness [40 ± 10] nm), which resulted in polymer sample with a typical film thickness around 100 nm. After subsequent annealing of the samples at 80 °C for 4 h (or 110 °C for 1 h in case of the high-ITO materials), Al was evaporated at a high deposition rate of ~10 nm/s onto the polymer film to form a patterned top electrode.

Dielectric measurements were performed using a high resolution dielectric analyzer (ALPHA analyzer, Novocontrol Technologies) in combination with a Novocontrol Quatro temperature system providing excellent stability of the sample temperature (<0.05 K). Temperature dependent experiments were prepared by consecutive isothermal frequency sweeps (10 kHz–10⁶ Hz) in the temperature range from +170 °C to −40 °C in steps of 5 K, which resulted in an effective (mean) cooling rate of about 0.5 K/min. To separate the spectra into different relaxation processes and to classify these processes according to the type of thermal activation the isothermal loss spectra \( \varepsilon''(\omega) \) were fitted to the empirical function of Havriliak–Negami (Eq. (1)) [12]

\[
\varepsilon'' = \frac{\Delta\varepsilon}{(1 + i\omega\tau)^\beta} + \frac{\sigma}{\varepsilon_0\omega},
\]

where \( \Delta\varepsilon \) corresponds to the relaxation strength, \( \tau \) is the mean relaxation time, and \( a \) and \( b \) are the fractional shape parameters describing the symmetric and asymmetric broadening of the \( \log\varepsilon''(\log\omega) \) curve compared to a ‘single exponential’ (Debye) function. The parameters are related to the slopes of \( \log\varepsilon'' \) vs \( \log\omega \) for low and high frequencies with respect to \( 0 < a < 1 \) and \( 0 < ab < 1 \). The second term in Eq. (1) accounts for Ohmic conduction. A comprehensive description of analysis methods for dielectric data can be found in [13,14].

3. Results

3.1. Photoinduced alignment

The photoisomerization of azobenzene is an important and very convenient model reaction to study photoinduced reversible changes of physical properties of polymers. The photoisomerization changes the shape, the polarity and the direction of the transition moment of the azobenzene unit and the steady state is reached between the rod like, thermodynamically stable trans and bulky cis isomer. The trans–cis–trans isomerization can be used as a probe reaction to investigate the mobility of a photochromic moiety within the polymer. The trans–cis–trans isomerization is affected by molecular environment of the chromophores, namely by rigidity and molecular packing of the polymer network.

CyanoaZobenzenes, according to the Rau classification [4,5], are characterized spectroscopically by overlapped high intensity \( \pi-\pi^* \) band and low intensity \( n-\pi^* \) band in visible region. The absorption maximum in the UV–vis spectrum of the polymers from pCNO series is located at around 450 nm due to \( \pi-\pi^* \) transition of azobenzene groups attributable to its trans form. The \( \lambda_{\max} \) of the copolymer is affected by composition as listed in Table 2.

For investigation of the photoinduced alignment, the pumping beam, selected at 460 nm corresponding to the \( \pi-\pi^* \) transition, was linearly polarized to induce uniaxial alignment of the photoisomerizable units. Fig. 2 shows the effect of illumination with linearly polarized light at \( \lambda = 460 \text{ nm} \) on the absorption spectrum of pCNO30.

![Fig. 2. UV–vis spectra of the pCNO30 film before illumination, after 27 s illumination with linearly polarized blue light, and after thermal relaxation.](image-url)
Starting from an unoriented polydomain sample, the absorbance rapidly decreases during the first seconds of irradiation and reaches a substantially lower saturation value. After switching off the light source, the original absorbance recovers on a time scale of 1000 s, indicating the photoalignment process is completely reversible.

An analysis of the magnitude of changes in the absorbance peak and the characteristic retardation (switching ‘on’) and relaxation (switching ‘off’) times revealed a couple of interesting observations that are summarized in Figs. 3 and 4 and in Table 2:

1. The highest alignment effect indicated by the highest relative change in the absorbance under illumination was found for the copolymers with the lowest azobenzene content. Though this trend holds for both copolymer series (cf. Table 2), it is particularly well seen for the pCN series.

2. The switching times, both the retardation and relaxation times, show a similar inverse proportionality to the chromophore content as seen from Fig. 3.

3. The existence of two similar trends implied the existence of a correlation between the alignment efficiency $\Delta A$ and the switching times, particularly the thermally driven relaxation time of the axial order. Fig. 4 indeed proves the existence of such correlation, which will be discussed later in more detail.

### 3.2. Dielectric relaxations

To understand the molecular mechanism underlying the optical switching kinetics, particularly the relation between the polymer structure and the molecular dynamics of both the polymer matrix and the chromophore mobility, we have performed extensive measurements by dielectric relaxation spectroscopy on all compounds in a wide frequency range ($10^{-1}–10^6$ Hz) and at temperatures typically varying from $-40$ °C to 170 °C. A typical result, showing the three-dimensional representation of the ‘conduction-free’ dielectric loss $\varepsilon''_{\text{der}}(f, T)$ for pCNOhomo.
dimensional representation of the ‘conduction-free’ dielectric loss $\varepsilon'_{\text{deriv}}(f, T)$ [14] for pCNOhomo is given in Fig. 5.

Like in previous work, we have used the quantity $\varepsilon'_{\text{deriv}}(f, T)$, which is computed from the real part of the dielectric spectrum $\varepsilon'(f)$ by an optimized numerical algorithm [14], to eliminate excessive contributions from Ohmic conduction to the loss spectra and thus to enable the analysis of possible ‘hidden’, slow relaxation processes. From Fig. 5 we can identify three relaxation processes: A strong $\alpha$-process being the dielectric manifestation of the dynamic glass transition, an even stronger relaxation ($\beta$) showing up at higher temperatures, and a third, weak and broadened process below the glass transition temperature ($T_{g,\text{DSC}} = 72^\circ\text{C}$).

The peak relaxation times, obtained by fits of $\varepsilon'(f)$ to one or two Havriliak–Negami functions (cf. Experimental section), are plotted in the Arrhenius diagrams Fig. 6(a) and (b). As expected, we can distinguish various relaxation processes according to their characteristic temperature dependence.

Below $T_g$, two well separated relaxations, $\beta_1$ and $\beta_2$, were found. Both of them obey Arrhenius equation (Eq. (2))

$$\tau = \tau_\infty \exp \left( \frac{E_a}{RT} \right),$$

as being typical for secondary, sub-$T_g$, relaxation processes in polymers. Interestingly, the fast ($\beta_2$) process could only be detected in azobenzene-rich samples, a fact that points to its molecular origin in the presence of the aromatic side group [15]. Such relaxation, typically exhibiting activation energies in the range from 50 – 80 kJ/mol and pre-exponential factors from $10^{-18}$ – $10^{-13}$ s [8,16] has been discussed before and were assigned to a fast rotational diffusion of the chromophore around its long axis. Due to the small lateral dipole moment of the azobenzene group, the $\beta_2$-process is correspondingly weak in intensity and could only be detected unambiguously in the samples with the highest chromophore concentration.

Opposed to the $\beta_2$-process, the slower $\beta_1$-relaxation was found in the materials with the lowest concentration of azo-groups, which implied its assignment to as local relaxation process involving the (butyl methacrylate) co-monomer. To prove this idea we compared the $\beta_1$-relaxation time data with data from the literature obtained for poly(butyl methacrylate) [15] and found a good agreement within the experimental error limits.

Inspection of the relaxation time data above the glass transition temperature in Fig. 6(a) and (b) further shows that for all samples an $\alpha$ and $\delta$ relaxation were found. For one particular material, pCNO50, an additional relaxation mode ($\alpha^*$) was observed being located on an intermediate position between the $\alpha$ and $\delta$ relaxation (cf. Fig. 7).
Table 3
VFT parameters, $T_g$ ($\tau = 100$ s) values, and steepness index $m$ for the $\alpha$ and $\delta$ relaxations in pCNO and pCN series

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_V$ [kJ/mol]</th>
<th>$T_V$ [K]</th>
<th>log($\tau_\infty$) (s)</th>
<th>$T_g$ ($\tau = 100$ s) [°C]</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pCN30</td>
<td>23.4</td>
<td>194.3</td>
<td>-12.9</td>
<td>50.5</td>
<td>53.6</td>
</tr>
<tr>
<td>pCN50</td>
<td>26.4</td>
<td>235.7</td>
<td>-13.3</td>
<td>55.2</td>
<td>45.5</td>
</tr>
<tr>
<td>pCN80</td>
<td>20.4</td>
<td>263.8</td>
<td>-12.3</td>
<td>64.4</td>
<td>28.0</td>
</tr>
<tr>
<td>pCNhomo</td>
<td>24.5</td>
<td>286.5</td>
<td>-13.1</td>
<td>65.8</td>
<td>48.5</td>
</tr>
<tr>
<td>pCNO30</td>
<td>32.7</td>
<td>194.3</td>
<td>-14.5</td>
<td>47.3</td>
<td>29.0</td>
</tr>
<tr>
<td>pCNO50</td>
<td>22.0</td>
<td>226.8</td>
<td>-12.8</td>
<td>58.2</td>
<td>22.4</td>
</tr>
<tr>
<td>pCNO80</td>
<td>22.6</td>
<td>234.5</td>
<td>-12.7</td>
<td>57.7</td>
<td>26.7</td>
</tr>
<tr>
<td>pCNOhomo</td>
<td>15.2</td>
<td>268.9</td>
<td>-11.0</td>
<td>70.5</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Fig. 8. Concentration dependence of the dielectric glass transition temperatures $T_g$ ($\tau = 100$ s) for the $\alpha$ and $\delta$ process. For comparison, calorimetric $T_g$-data are given as well. Figure below: Correspondent values of the dynamic fragility obtained from the $\alpha$-process (left) and $\delta$-process (right).
As expected, all high temperature processes possess a more or less pronounced curvature in the Arrhenius presentation indicating that their temperature dependence can be described by the Vogel–Fulcher–Tammann (VFT) \[17–19\] equation rather than by the Arrhenius law

\[
\tau = \tau_\infty \exp \left( \frac{E_V}{R(T - T_V)} \right),
\]

were \(\tau_\infty\) is the so-called pre-exponential factor, \(E_V\) and \(T_V\) are the ‘Vogel-activation energy’ and Vogel temperature, respectively.

From the VFT fit-parameters, which are listed in Table 3, operationally defined ‘dielectric glass transition temperatures’ \(T_g = T(\tau = 100 \text{ s})\) were derived (cf. Table 3 and Fig. 8(a)) that are in well agreement with the values obtained by DSC (Table 1).

Apart from the glass transition temperature, the so-called steepness index \(m\) or dynamic fragility \[20\] that can be derived according to Eq.:

\[
m = \frac{d \log(\tau)}{d(T_g/T)} \bigg|_{T = T_g},
\]

which is linked to the VFT parameters by

\[
m = \frac{E_V}{2.303R} \frac{T_g}{(T_g - T_V)^2}.
\]

From the formal point of view, the parameter \(m\) represents a measure for the degree of curvature in the \(\tau(T)\) curve that allows the classification of glass forming materials into fragile (high \(m\)) and strong (low \(m\)-values) materials. In this picture, a fragile glass formers is characterised by a high apparent activation energy of the structural relaxation time in the vicinity of \(T_g\), being an expression of the cooperative nature of the dynamic glass transition as will be discussed below.

Fig. 8 shows that both sample series show a clear trend towards both a higher glass transition temperature and an increased dynamic fragility increasing concentration of the cyanoazobenzene side group.

4. Discussion

4.1. Effect of chromophore concentration on switching behaviour

Upon irradiation with linearly polarized light, the rate of photoisomerization becomes angular depended since the chromophores transition dipole moment axis has its main component in parallel to the light polarization. The irradiation causes trans–cis isomerization of the diazo group which can proceed via rotation around dihedral \(\angle C=N=N=C_2\) angle or (and) inversion of the \(\angle C=N=N_\perp\) bond angle. Quantum chemical calculations of molecular potential energy by the \textit{ab initio} B3LYP/6-31 g option yielded an energy difference between \textit{trans} and \textit{cis} forms in the order of 68 kJ/mol \[21\] and the energy barrier from \textit{trans} to \textit{cis} was equal to about 132 kJ/mol. This barrier could be assumed to be an activation energy. The energy barrier for molecule to relax from \textit{cis} to \textit{trans} was equal to 64 kJ/mol, and this explained why the cis–trans process proceeded by thermal relaxation. It is to mention that the latter value was of the same dimension as Arrhenius activation energy of the \(\beta\) relaxation.

On irradiation of the photochromic diazo material the molecules that have been transformed to the \textit{cis} form are no longer prone to light absorption because their dipole moment directions are no longer in parallel to the light polarization plane. So, the mesogenic fragment can relax back to the \textit{trans} form with a change of dipole moment direction in such a way to not to be affected by parallel light polarization. The most probable dipole orientation can be perpendicular to the light polarization plane or in the direction of the film depth.

Our optical experiments show that the photoinduced alignment of the side-group polymers strongly depends on the concentration of photoswitchable azo-units. While there was no clear trend found for the characteristic (retardation) time to attain the aligned state, the thermally driven relaxation time revealed a clear decrease with increasing chromophore content. This relaxation time appeared also to be highly correlated with the achievable degree of orientational order (alignment efficiency). Such correlation can be rationalized by two assumptions:

1. An increasing chromophore content induces anisotropic packing of the chromophores that ultimately manifests itself in the occurrence of liquid crystalline order (PCNO series 30, 50 and 100%). This local anisotropy imposes a strong angular potential (e.g. of Maier-Saupe-type) to an increasing fraction of individual chromophore moieties, which get impaired with respect to the photoalignment process.

2. Though the local anisotropy likely inhibits individual \textit{trans–cis} photoisomerisation and/or (multi-step) photoalignment events, the remaining switchable fraction of chromophores benefits from the anisotropic (mean) field by speeding up the recovery of the initial (random) orientational order.

This picture will be tested in the following by discussion the molecular dynamics as measured by dielectric spectroscopy.

4.2. Dielectric relaxations

4.2.1. Rotational diffusion of the chromophores in the glassy state

In a previous section, the \(\beta_2\)-relaxation was assigned to local fluctuations of the chromophoric side group, which is essentially visible below the glass transition temperature of the polymer backbone. Since the glassy environment inhibits large scale (flip-over) fluctuations of the azobenzene groups, rotational diffusion of the chromophores is
basically restricted to small angle rotations around their long axis. Table 4 displays the activation parameters of the $\beta_2$-relaxation for four compounds, which reveal a clear trend towards increasing activation energies with increasing concentration of the azobenzene units. An analogue trend is observed for the pre-exponential factors that varies from roughly $10^{-12}$ s (pCNO50) to $10^{-18}$ s for the pCNO homopolymer.

A correlated variation of the activation parameters has been discussed earlier for liquid crystalline side group polymers by Schönhals et al. who have reported a pronounced effect of chromophore concentration on the glass transition dynamics [23]). Given the fact that the activation energy of the $\beta_2$-process provides a measure for the degree of side-group interactions in various polymers, both the generally higher molecular anisotropy in the PCNO series as well as the effect of chromophore concentration on the $\beta_2$-relaxation are reflected in the activation data (Table 4) in a consistent way.

### Table 4

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_a$ [kJ/mol]</th>
<th>$\log(\tau_{a\alpha})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pCN30</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>pCN50</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>pCN80</td>
<td>39.0</td>
<td>−12.5</td>
</tr>
<tr>
<td>pCNhomo</td>
<td>54.7</td>
<td>−15.0</td>
</tr>
<tr>
<td>pCNO30</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>pCNO50</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>pCNO80</td>
<td>66.0</td>
<td>−16.9</td>
</tr>
<tr>
<td>pCNOhomo</td>
<td>73.4</td>
<td>−18.1</td>
</tr>
</tbody>
</table>

*Process not detected or not analyzed.

### 4.2.2. Effect of side group interactions on the glass transition dynamics

While the $\beta_2$-relaxation was proven to yield direct information about the strength of inter-chromophoric interactions, additional support for our physical picture can be deduced from an analysis of the glass transition dynamics ($\alpha$-process) and related ($\alpha^*$ and $\delta$) relaxation processes. The highly correlated increase of both the glass transition temperature and the dynamic fragility $m$ (cf. Fig. 8 and Table 3) with increasing content of azobenzene units is a typical feature of covalently bonded [24–28] and physical networks [29], where $T_g$ and $m$ increase with increasing crosslink density. While a solely increase in $T_g$ upon cross-linking could also be rationalized by local stiffening of the polymer structure by introducing rigid (azobenzene) side-groups, the simultaneous increase in $T_g$ and $m$ favors an interpretation in terms of an increased degree of intermolecular cooperativity of the dynamic glass transition [30]. According to this idea, enhanced intermolecular cooperativity, provoked by the presence of strong intermolecular interactions (covalent bonds, H-bonds) or side-group anchoring in (occasionally liquid crystalline) azobenzene-rich clusters, facilitates the progressive slow-down of the glass transition dynamics and thus drives the polymer system into the glassy state at a higher temperature.

Additional information about the degree of anisotropic packing of the chromophores can also be deduced from the ratio of the relaxation times $\tau_\delta$ relative to the $\alpha$-process, $\tau_\alpha$, which is displayed as function of the temperature and the degree of chromophoric content in Fig. 9. Since this ratio reflects the actual decoupling of the large chromophore fluctuations ($\delta$-process) from the segmental dynamics of the polymer backbone, $\tau_\delta/\tau_\alpha$ is expected to depend on two major factors, the length of the aliphatic spacer and the degree of local anisotropy (e.g. expressed by a nematic order parameter) within the nano-phase separated azobenzene fraction.

The influence of the spacer length on the separation $\tau_\delta/\tau_\alpha$ is indeed seen from Fig. 9, which shows in average higher
The effect of the azobenzene concentration on \( \tau_0 \tau_a \) is less evident: Both sample series show a clear decrease of \( \tau_0 \tau_a \) with higher chromophore content, a trend being in apparent contradiction with the previous assumption that the \( \tau_0 \tau_a \) separation is governed by the local (mesophase) order parameter. We think that this unexpected trend can be explained as follows:

(i) Though the separation between the \( \delta \)-process and the backbone dynamics (\( \alpha \)-relaxation) is certainly sensitive to the degree of ‘mesomorphic’ order, a true measure for the degree of side-group anisotropy is rather given by the ratio \( \tau_0 \tau_a^* \) as displayed for the sample PCNO50 in Fig. 7. The existence of such two relaxation modes in side-group LCP being well separated from a distinct dynamics of the polymer backbone has been reported for LC polycarbonates [31] and LC polyurethanes [14,32], and their link to a local order parameter was discussed in detail [33]. Since both ‘mesogenic’ relaxation modes (\( \alpha^* \) and \( \delta \), also labeled as \( \lambda_1 \) and \( \lambda_2 \) in previous work [31]) could only be resolved for PCNO50, a possible trend in \( \tau_0 \tau_a^* \) as function of the chromophore concentration can not be discussed in this work. Nevertheless, the results from PCNO50 confirm earlier finding from LC polycarbonates \[ \log(\tau_0 \tau_a^*) \sim 2.2 \] and suggest that likely variations in the smectic order parameters are far too small to rationalize the effect of azobenzene concentration on \( \tau_0 \tau_a \).

A more plausible interpretation for the increasing ratio in \( \tau_0 \tau_a \) upon ‘dilution’ of the azobenzene content considers the fact that in a random copolymer, parts of the backbone get topologically and dynamically much more separated than in the case of the corresponding homopolymer. Hence, lowering in the azobenzene content allow both the side groups and the backbone for an efficient phase separation as expressed by an increasing ratio \( \tau_0 \tau_a \). In other words, though the trend shown in Fig. 9 does not proof the degree of ‘mesogenic’ order, it strongly supports our initial picture of nano-phase separated azobenzene ‘clusters’, which impair an efficient photo-alignment behavior at high chromophore-rich materials. This interrelation between cooperative high-temperature dynamics, quantified by the steepness index \( m \), and the optical switching behavior is finally emphasized by Fig. 10, showing a more or less pronounced correlation between the optical switching times with \( m \). Detailed features of this and other possible correlations remain subject of further discussions.

5. Conclusions

In this paper, we have studied the molecular dynamics and optical switching behavior (photo alignment) of novel azobenzene containing side-group (co)polymers by time-resolved optical spectroscopy and broadband dielectric spectroscopy (BDS). To focus on the effect of the molecular structure on the photochromic properties, two series of poly(methacrylates) with different aliphatic spacers 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 yielded up to three relaxation processes (\( \alpha, \alpha^*, \delta \)) 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. Here, the latter
process revealed an increasing activation energy with increasing azobenzene content, which was interpreted in terms of increasing anisotropy in the chromophore packing. Furthermore, both series showed a monotonic increase in \( T_g \) and the dynamic fragility \( m \) with increasing chromophore concentration, which was explained by an increasing effect of physical crosslinking provided by the increasingly dense packed side groups.

From the optical and dielectric results a physical picture of a nano-phase separated chromophore/polymer system emerges, which shows a concentration dependent trade-off between high switching efficiency (low azobenzene content) and fast optical relaxation times (chromophore-rich systems).

Acknowledgment

This work was supported by Grant No. 3 T08E 088 29 of Polish Ministry of Science and Informatics.

References