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Influence of azobenzene concentration on the dielectric behavior of amorphous comb-like copolymers with photochromic side groups

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Abstract

Dielectric spectroscopy in the frequency range from 10^{-2} to 10^6 Hz and in the temperature range from 190 to 440 K is employed to study the effect of azobenzene concentration on the dielectric relaxation processes of an amorphous comb-like copolymethacrylate. Four concentrations ($x = 29$, 45.5, 54, and 74.5 mol%) of photochromic group 4-amino-azobenzene were investigated, where as comonomer a methacrylate unit having a derivative of benzanilide in the side group is used. Two prominent processes, the β-relaxation at low temperatures which is related to rotational fluctuations of the mesogenic unit around its long axes and the dynamic glass transition (α-relaxation, segmental dynamics) at higher temperatures are observed for all azobenzene concentrations. In addition in between the α- and the β-relaxation a β′-process is observed for the polymers with the two lowest azobenzene concentrations, which seems to be related to the azobenzene unit. The dependence of the dielectric strength and the relaxation rate of the relaxation processes on the azobenzene concentration is discussed and interpreted in a simple phenomenological model, where also data obtained by semi empirical quantum chemical calculations are used.

Keywords: Azobenzene; Comb-like copolymer; Dielectric relaxation

1. Introduction

Photochromic polymers are promising substances since they can be used as materials for optical data storage, information processing, holographic and electrooptic applications [1–9]. It is well known that below the glass transition temperature T_g of the polymer optical anisotropy in addition to photochromism [10–12] can be induced if the samples are irradiated by linearly polarized light. This was reported for main chain polymers (see Ref. [13]) but most often side chain polymers with the photochromic azobenzene group are studied in the literature. The modular construction of these systems allows some structural parameters to be individually modified. These comprise the length of flexible methylene spacer in the side chain, the substituent on the azobenzene moiety, the non-photochromic comonomer and the molecular weight of the investigated polymer. Moreover the photoreaction of the azobenzene group is reversible. The mechanism of the generation of the anisotropy is still poorly understood, because it takes place below T_g of the bulk polymer. But it seems to be clear that this process should be related to molecular mobility.

Dielectric spectroscopy (DS) is a powerful tool to study and to characterize the dynamic behavior of polymers. This method provides direct information about the molecular motions related to fluctuations of dipole moments. Fundamental investigations of the dielectric response yield a wealth of information about different molecular motions and relaxation processes. A unique characteristic of DS is the wide frequency range from 10^{-5} to 10^9 Hz which can be covered more or less routinely by DS. Detailed discussions of the basic aspects of dielectric behavior of polymeric materials can be found in several books and key reviews [14–20]. Moreover the molecular mobility of the system depends sensitively on its micromorphology. In that sense the change in structure can be investigated by dielectric spectroscopy indirectly taking the molecular mobility as a probe for it.

Comb-like macromolecules which having calamitic mesogens in the side group, have several polar groups which can take part in different relaxation processes. In the literature a variety of processes are discussed for such side

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group polymers [16,21] which can be amorphous or liquid-crystalline. A γ-relaxation is found at low temperatures followed by a β-, an α- and a δ-processes in order of increasing temperature. For polymethacrylates the γ-relaxation is assigned to fluctuations of the apolar methyl group [14]. The β-relaxation has been related to rotational fluctuations of the mesogenic unit around its long axis [21–23]. The temperature dependence of the γ- and β-relaxation rates or times follows an Arrhenius equation. For liquid crystalline side group polymers a pronounced dependence of the activation energy of the β-relaxation, $E_{A\beta}$, on the mesophase structure has been reported [24]. With increasing order of the mesophases $E_{A\beta}$ increases up to 80 kJ mol^{-1}, this is interpreted by a cooperative or at least coordinative character of the β-process which increases with the order of the mesophases.

The α-relaxation is connected with the segmental motion of the chain backbone but also fluctuations of the side groups might involved for amorphous polymers. The temperature dependence of its relaxation rate can be described for amorphous systems by a Vogel/Fulcher/Tammann law [25–27]. At low temperatures this temperature dependence correlates with the glass transition temperature [28]. The δ-relaxation is a characteristic feature of side group polymers. It can be observed for liquid crystalline [24] but also for amorphous systems [29]. Its molecular mechanism is still under controversial discussion but it seems to be clear that this process is related to rotational fluctuations of the calamatic moieties around their short axis.

For the polymers with an azobenzene moiety in the side group an additional relaxation process, called β′-process, was detected [29,30] between the β- and the α-peak. The temperature dependence of this relaxation process follows an Arrhenius equation with an activation energy of about 70 kJ mol^{-1}. It is supposed that this process is related to the Z/E-isomerization [31,32] of the azobenzene group because a similar activation energy and frequency temperature position is found for the latter by optical measurements. From a more general point of view a relaxation process in between the β- and α-relaxation was found for several polymers like polycarbonate [33], poly(amide imides) [34], poly(ethylene 2,6-naphthalene dicarboxylate) [35,36] or poly(ester imides) [13] with a higher activation energy compared to the β-relaxation. So it can be speculated that this relaxation process in between the β- and α-relaxation might be a general feature of the relaxation behavior of polymers containing aromatic groups. In some cases this intermediated region was assigned to molecular aggregates [35].

Although there are some initial studies on the dielectric properties of polymers having azobenzene in the side group [30,37,38], only a little is known about the influence of the concentration of azobenzene on the different relaxation processes. It is the aim of this study to investigate the effect the azobenzene concentration on the observed relaxation of processes which are quantitatively analyzed. In a second step the extracted parameters are correlated with molecular data obtained by semi empirical quantum chemical calculations like the dipole moment of the azobenzene group.

2. Experimental

2.1. Materials

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. Intra and intermolecular hydrogen bonding, OH bonds, can be formed between the oxygen atom and the hydrogen atoms of the phenyl rings.

The polymers were synthesized by radicalic copolymerization of the two monomers at a temperature of 343 K in *N*,*N*-dimethylformamide (DMF) using AIBN as initiator. For details see Ref. [39]. The polymerization reaction results in statistical copolymethacrylates, where the azobenzene content is varied by the formulation and determined for the obtained polymers from the nitrogen value measured by elemental analysis.

Differential scanning calorimetry was carried out with a cooling and heating rate of 10 K/min. These investigations show that the system under investigation is amorphous and has only one glass transition temperature T_g as given in Table 1. In addition Table 1 gives also the molecular weight and the used nomenclature of the samples.

2.2. Dielectric measurements

The dielectric experiments were carried out in parallel plate geometry. The samples were pressed at a temperature of 438 K between two gold-plated stainless steel electrodes of 20 mm diameter. Fused silica fibers with a diameter of 50 μm were used as spacer material. The complex dielectric function

$$\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f) \tag{1}$$

(f is frequency, ε' is the real part, ε'' is the imaginary part, $i = \sqrt{-1}$) was measured in a frequency range from 10^{-2} to

Table 1
Characterization of the investigated samples

Sample	Azobenzene x (mol%)	M_n (g/mol)	T_g (K)
S1	29.0	26,300	402
S2	45.5	27,600	403
S3	54.0	23,600	398
S4	74.5	16,800	389

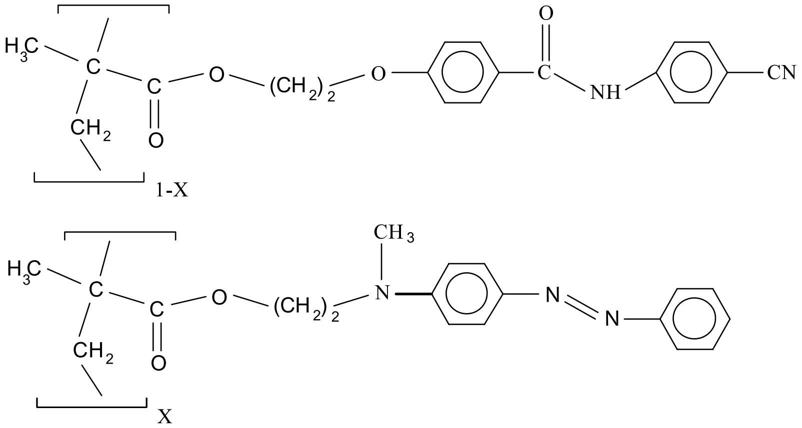

Fig. 1. Chemical structure of the investigated copolymer system.

10^6 Hz using a Schlumberger frequency response analyser FRA 1260, supplemented by a Chelsea Dielectric Interface with a buffer amplifier of variable gain [40–42]. The temperature of the sample was varied from 193 to 443 K by a custom-made nitrogen gas jet heating system. The stability of the temperature was about ±0.05 K.

3. Results

As a representative example, Fig. 2 gives the log ε'' versus temperature at some selected frequencies for the sample S1 ($x = 29$ mol%). Several relaxation processes can be detected indicated by peaks and shoulders in the dielectric loss curve. At low temperatures the β-relaxation is observed. As expected this peak shifts towards higher temperatures with increasing frequency. In addition the peak broadens with increasing frequency. At higher temperatures an α-relaxation process is observed as a shoulder overlaid by a strong conductivity contribution. In the temperature range in between those two processes a further relaxation process can be observed named β′. In more detail Fig. 3 shows the α-relaxation peak which is observed at higher temperatures overlaid by a conductivity at lower frequencies for the investigated azobenzene concentrations. No relaxation-peak which can be directly assigned to the δ-process is obtained. The inset of this figure illustrates ε'' as a function of frequency (log–log scale) at low temperatures (β-relaxation), also for the investigated concentrations.

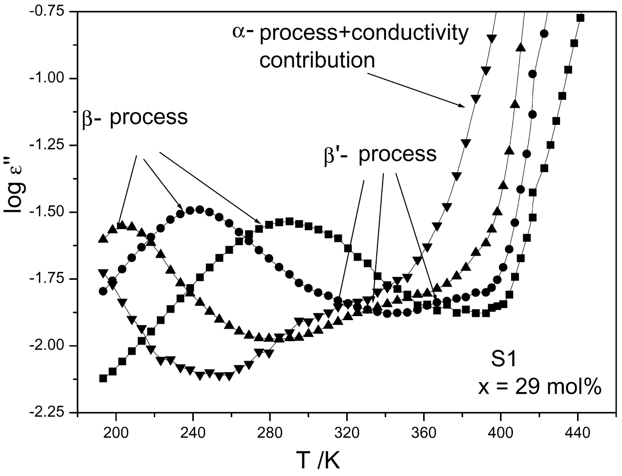

Fig. 2. log ε'' versus temperature at some selected frequencies for the sample S1 (log(f/Hz) = −1 (▼), 1 (▲), 3 (●), 5 (■)). Lines are guides for the eyes.

The β- and α-relaxation peaks could be observed for all concentrations of azobenzene. The γ- at low temperatures and the β′-relaxation peaks in between the β- and α-relaxation processes are observed only for lower azobenzene concentrations. A possible interpretation reason for this is discussed below.

The model function of Havriliak–Negami (HN-function) [43] is fitted to the isothermal data [44] to separate the spectra into different relaxation processes and to extract the relaxation rate at maximal loss f_p and the dielectric strength $\Delta\varepsilon$. The HN-function reads

$$\varepsilon^*_{\mathrm{HN}}(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1 + \left(\mathrm{i}\dfrac{f}{f_0}\right)^{\beta_{\mathrm{HN}}}\right)^{\gamma_{\mathrm{HN}}}} \tag{2}$$

with the parameters: $\Delta\varepsilon$-dielectric strength or intensity, f_0 characteristic frequency which is related to the peak frequency f_p but depends on the asymmetry parameter γ_{HN} [20] and $\varepsilon_\infty = \varepsilon'(f)$ for $f \gg f_p$. The fractional shape parameters β_{HN} and γ_{HN} describe the symmetric and asymmetric broadening of the complex dielectric function compared to the Debye function. Because they are related to the slopes of $\log \varepsilon''$ versus $\log f$ for low and high frequencies with respect to f_p $0 < \beta_{\mathrm{HN}} \le 1$ and $0 < \beta_{\mathrm{HN}}\gamma_{\mathrm{HN}} \le 1$ holds [20]. Conductive effects are treated in the usual way by adding a conductivity contribution $\sigma_0/\varepsilon_0(2\pi f)^s$ to the dielectric loss, where σ_0 is related to the DC-conductivity of the sample and ε_0 is the dielectric permittivity of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}$ As V^{-1} m^{-1}).

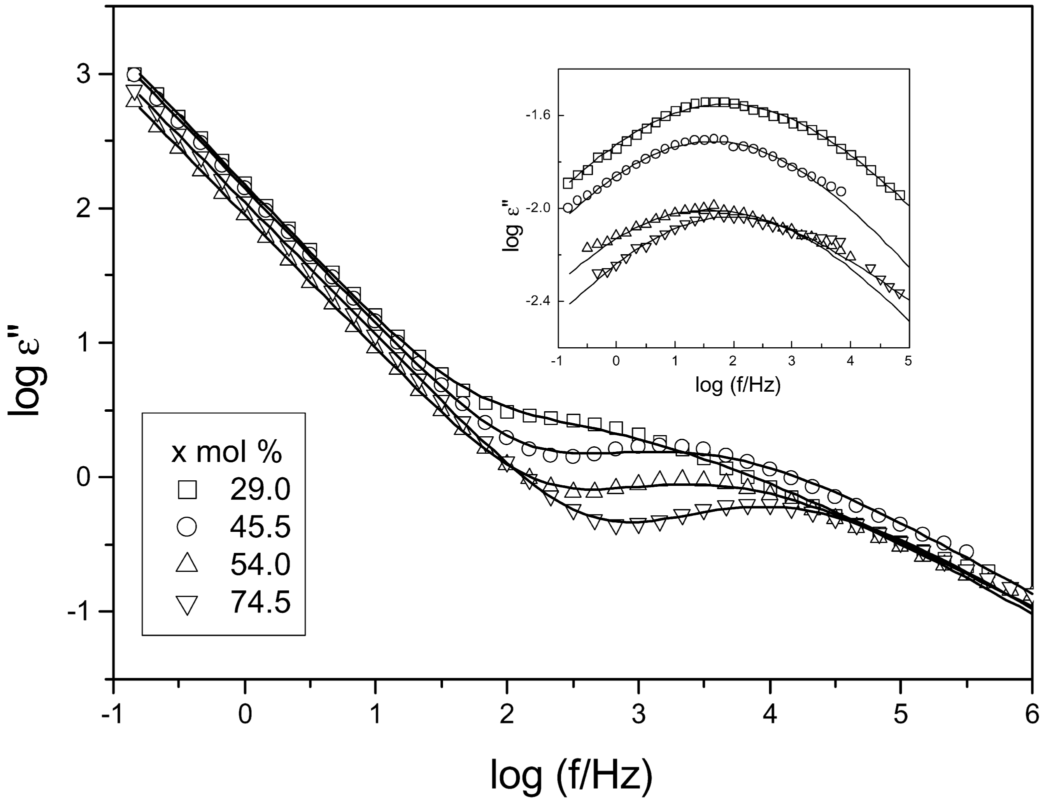

Fig. 3. The α-relaxation peak at a temperature of $T = 448$ K overlaid by a conductivity contribution at lower frequencies for the investigated samples. Lines are fits of the HN-function including a conductivity contribution to the data. The inset shows the β-relaxation peak at a temperature of $T = 213$ K. The lines are fits of the HN-function to data. The symbols are the same as that in the main figure.

The parameter S ($0 < S \leq 1$) describes for $S < 1$ non-Ohmic effects in the conductivity. For details see Ref. [20].

4. Discussion

Fig. 4 shows the temperature dependence of the relaxation rate $\log f_p$ for each process of the sample S1.

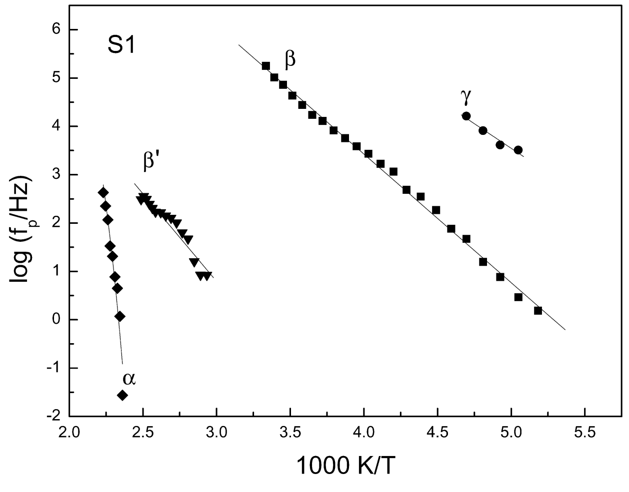

Fig. 4. $\log f_p$ versus $1/T$ for the different relaxation processes of the sample S1. Lines are fits of the Arrhenius relation (γ, β, β′-relaxation) and of the VFT equation (α-relaxation) to the data.

The temperature dependence of $\log f_p$ for the γ and the β-relaxation can be described by an Arrhenius relation

$$\log(f_p) = \log(f_\infty) - \frac{\ln 10 E_A}{k_B T}, \tag{3}$$

where f_∞ is the so-called pre-exponential factor, k_B is the Boltzmann constant and T is the temperature. E_A is the corresponding activation energy of the process. The estimated activation parameters, using Eq. (3), are given in Table 2 for the investigated polymers.

It was noticed that the γ-peak—which has a weak dielectric strength—appears only for the sample with the lowest azobenzene concentration (S1). For pure poly(methyl methacrylate) (PMMA) in the same temperature range also

Table 2
Activation parameters of the β- and α-relaxation for the different azobenzene concentrations

x (mol%)	β-relaxation		α-relaxation		
	Log (f_∞/Hz)	$E_{A\beta}$ (kJ mol^{-1})	Log (f_∞/Hz)	A_{VFT} (K)	T_0 (K)
29.0	14.1	50.9	11.2	903	324
45.5	14.6	52.6	11.0	825	334
54.0	14.5	53.0	11.9	1061	328
74.5	15.9	57.0	10.8	825	356

a relaxation process is found by mechanical measurements [9] which was assigned to fluctuations of the CH_3-groups. Therefore and because the low polarity of the methyl-group also for the investigated system the γ-relaxation is assigned to rotational librational motions of the CH_3-groups. As it is discussed in more detail below, the increase of azobenzene concentration increases the packing density and so, the CH_3-groups have a limited space to rotate. This leads to the disappearance of this process for the samples with higher azobenzene concentrations.

The β-relaxation peak is observed for all investigated polymers. For liquid crystalline side group polymers this relaxation process has been assigned to rotational fluctuation of the mesogenic unit around its long axes [16,28]. Such a motional process seems to be also possible for the investigated system. But in another line of argumentation the β-relaxation can be also related to fluctuation of the ester group modified by its local environment. In Fig. 5 the activation energy $E_{A\beta}$ of the β-relaxation is plotted versus the azobenzene concentration. In the range of the investigated composition $E_{A\beta}$ seems to increase linearly with increasing azobenzene concentration. This supports the picture that the mechanism of β-relaxation is a rotational fluctuation of the mesogenic group around its long axis. The dependence of $E_{A\beta}$ on the azobenzene concentration can be discussed according to a simple model. In general the side groups have the tendency to order parallel or anti-parallel to minimize the energy of the whole system in the dense state. This leads to liquid crystalline structures if the mesogenic groups are decoupled from the main chain by long spacers. Of course for amorphous systems that preferential ordering can take place only on a local scale. Semi-empirical quantum chemical calculations show that compared to the benzanilide side groups, the azobenzene moieties are more flat [45]. Therefore with increasing azobenzene concentration a better local preordering of the side groups can take place. This leads to a hindrance of the β-relaxation (rotational fluctuation around the long axes of the molecule) with increasing azobenzene concentration reflected by an increase of the corresponding activation energy. In the inset of Fig. 5 it is shown that $\log f_\infty$ increases with the activation energy $E_{A\beta}$. This is an expression of the well-known compensation law [46–48]. For details see also Ref. [24]. Therefore the systematic increase of the pre-exponential factor $\log f_\infty$ with azobenzene concentration can be explained with the same line of argumentation than the increase of the activation energy.

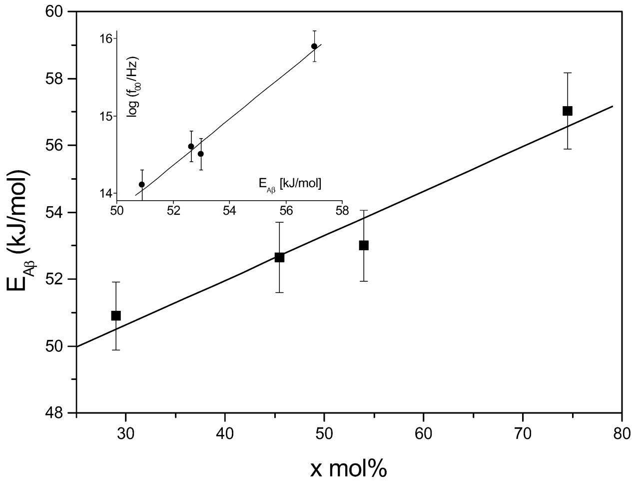

Fig. 5. Dependence of the activation energy of the β-relaxation $E_{A\beta}$ on the azobenzene concentration. The line is a linear regression to the data. The inset shows $\log f_\infty$ versus $E_{A\beta}$. The line is a linear regression to the data.

For the investigated system in the high temperature region only one relaxation process overlaid by a strong conductivity contribution is observed. There is no indication of a separate δ-relaxation. Therefore this relaxation region is assigned to an α-process. Generally the α-relaxation is associated with the dynamic glass transition and corresponds to segmental dynamics induced by conformational rearrangements of the main chain but also fluctuations of the side groups might be involved for the presented system. Fig. 6 gives the temperature dependence of the relaxation rate $f_{p\alpha}$ of the α-process for the four azobenzene concentrations under consideration. The temperature dependence of all data can be well described by the Vogel/Fulcher/Tammann (VFT) equation [25–27],

$$\log(f_{p\alpha}) = \log(f_\infty) - \frac{A_{VFT}}{T - T_o}, \tag{4}$$

where $\log(f_\infty)$ is the prefactor, A_{VFT} is a constant and T_o is the ideal glass transition or the so-called Vogel temperature usually found about 50–70 K below T_g. The estimated parameters $\log(f_\infty)$, T_o and A_{VFT} are collected in Table 2. In agreement with the decrease of the thermal glass transition temperature estimated by DSC with increasing azobenzene concentrations the temperature dependence of the relaxation rate of the α-relaxation shifts also to lower temperatures. Using the estimated VFT-parameters a dielectric glass transition temperature $T_g^{Diel} = T(f_{p\alpha} = 10^{-2}\,\text{Hz})$ can be estimated. In Fig. 7 the difference of this dielectric glass

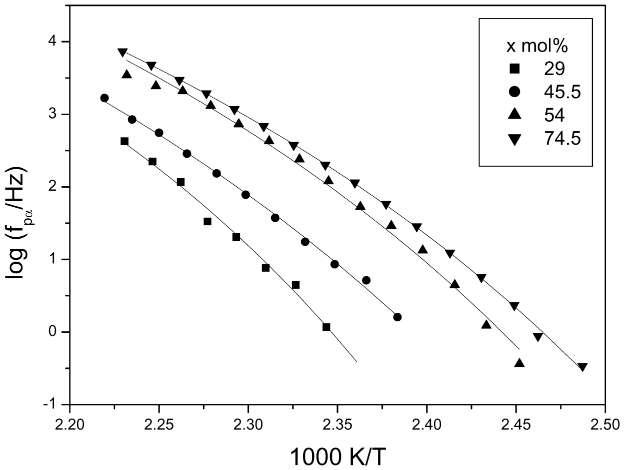

Fig. 6. $\log f_{p\alpha}$ versus $1/T$ for the labeled azobenzene concentrations. The lines are fits of the VFT equation to the data.

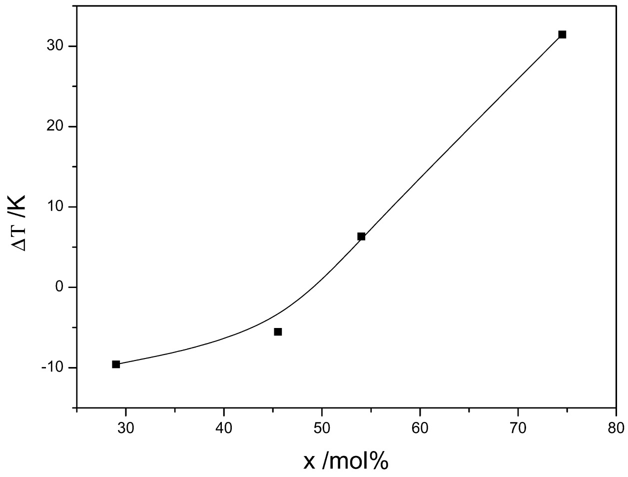

Fig. 7. $\Delta T = T_g^{\text{Diel}} - T_g^{\text{DSC}}$ versus azobenzene concentration. The line is a guide for the eyes.

transition temperature and the thermal glass transition temperature $\Delta T = T_g^{\text{Diel}} - T_g^{\text{DSC}}$ is plotted versus azobenzene concentration. Difference between both temperatures are known but for a given system this difference should be approximately constant. Surprisingly Fig. 7 shows that this difference is not constant as expected but increases strongly with increasing azobenzene concentration. So the α-peak measured by dielectric spectroscopy is systematically shifted to higher temperatures, with increasing azobenzene concentrations, compared to the step-like change in the DSC trance indicating the thermal glass transition. Clearly both methods due not measure exactly the same processes but one explanation can be that in the α-process contributions of δ-like processes are involved although only one peak is observed which cannot be separated in two components. This contributions should increase with the azobenzene concentration. To clear up this temperature modulated DSC measurements are in preparation (see Ref. [49]).

The relation between the relaxation strength and the dipole moment μ involved in the motional process has been derived by Debye, later modified by Kirkwood, Onsager and Fröhlich [50] as

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = FgN\frac{\mu^2}{k_B T}, \tag{5}$$

where ε_s and ε_∞ are the unrelaxed and relaxed permittivity. $F = \varepsilon_s(\varepsilon_\infty + 2)^2/3(2\varepsilon_s + \varepsilon_\infty)$ is the Onsager internal field factor which describes shielding effects and N is the dipole density which is constant for the investigated systems. The Kirkwood correlation factor g describes static interactions—like parallel or antiparallel ordering—between the dipoles (see Ref. [15]). $\Delta\varepsilon_\alpha$ decreases with increasing temperatures for all azobenzene concentrations (Fig. 8), which means that $g\mu^2$ is constant in the investigated temperature range. But the slope of $\Delta\varepsilon_\alpha$ versus $1/T$ decreases with increasing azobenzene concentration indicating that the comonomer has a higher dipole moment because the structure of the main chain and therefore its contribution to the dipole moment is not changed. It is known that the Onsager factor F is an unspecific quantity [15] and therefore it is assumed that it is independent of the azobenzene concentration. This means the slope of $\Delta\varepsilon_\alpha$ versus $1/T$ is a measure for the product $g\mu^2$ and moreover for its change with composition.

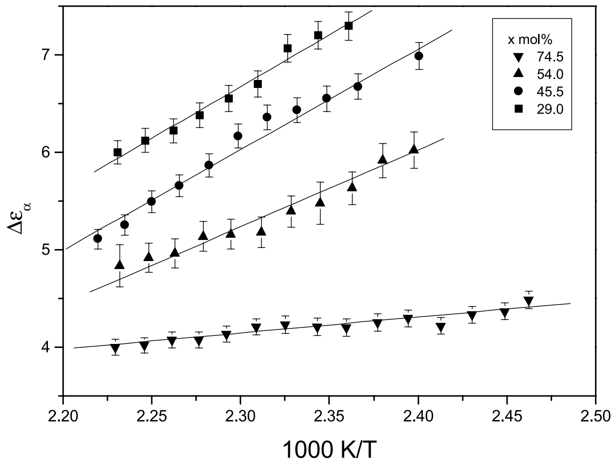

Fig. 8. Dielectric strength of the α-process, $\Delta\varepsilon_\alpha$, versus $1/T$ at the labeled azobenzene concentrations. The line is a linear regression to the data.

In the following the macroscopic estimated parameter $\Delta\varepsilon_\alpha$ will be correlated with the change in the microscopic dipole moment due to the change in the azobenzene concentration. In general the dipole moment of a repeating unit is the sum of the dipole moment of the metharcylate part and that of the side group. Because both comonomers have the same metharylate part its contribution to dipole moment and also to the dielectric relaxation strength $\Delta\varepsilon$ of the sample is not changed by the copolymerization process. Therefore the change in dipole moment and in the dielectric strength with azobenzene concentration is due to the changes in the side groups. If it is assumed that the side groups due not interact with each other or its interaction do not change with azobenzene concentration the change in the dipole moment $\Delta\mu$ with x can be estimated using a linear relation:

$$\Delta\mu = \mu_{\text{azo}}x + (1 - x)\mu_{\text{com}}, \tag{6}$$

where μ_{azo} and μ_{com} are the dipole moments of the azobenzene side group and that of the side group of the comonomer, respectively. Using the semi empirical quantum chemical method PM3 [51,52] the dipole moments of the side chains can be estimated theoretically [45] to $\mu_{\text{azo}} = 1.0$ and $\mu_{\text{com}} = 7.1$ Debye.

Fig. 9 shows the relation between the slope of $\Delta\varepsilon_\alpha$ versus $1/T$—which is in fact directly related to the $g\mu^2$ value and the change in dipole moment $\Delta\mu^2$ calculated from Eq. (6). If the interaction of the side groups (this means g) is not changed this slope should vary linearly with $\Delta\mu^2$. Therefore the strong non-linearity dependence of $g\mu^2$ versus the theoretical calculated change dipole moment with composition shown in Fig. 9 points to a strong dependence of the Kirkwood correlation factor g on the azobenzene

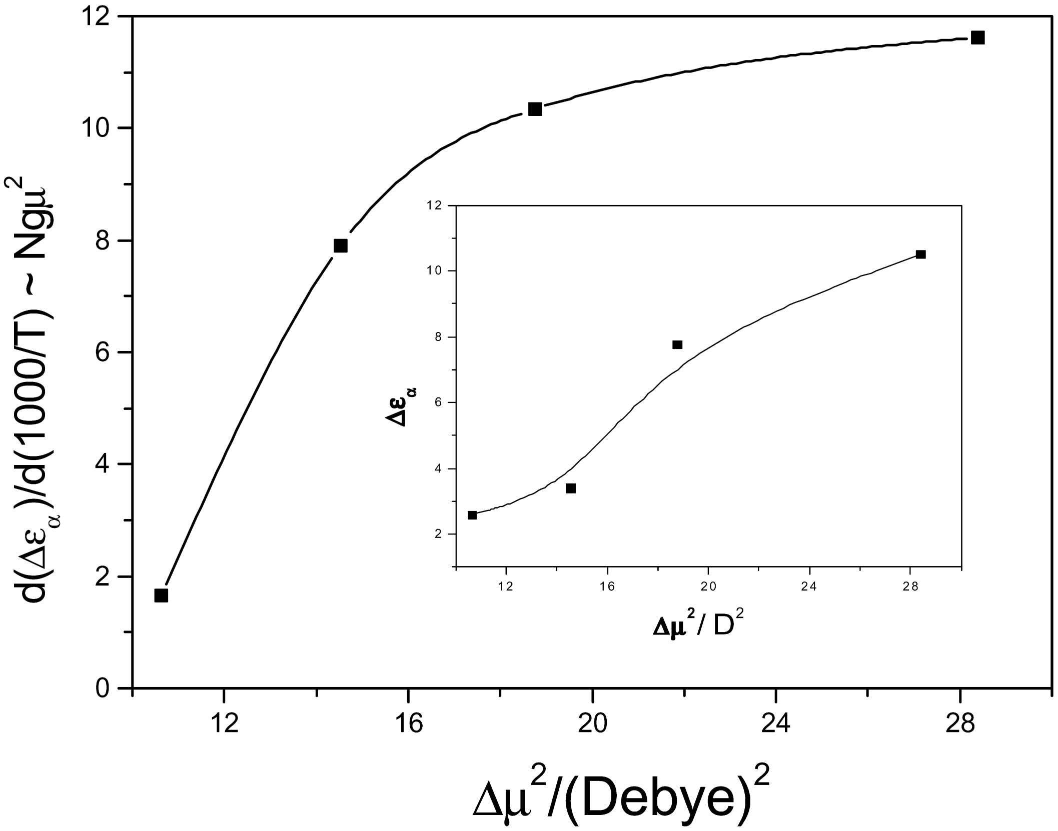

Fig. 9. $d(\Delta\varepsilon_\alpha)/d(1000/T)$ versus the calculated change in dipole moment $\Delta\mu^2$. The inset shows the dielectric strength $\Delta\varepsilon_\alpha$ for α-relaxation versus $\Delta\mu^2$. Lines are guides for eyes.

concentration. Because g is introduced in Eq. (5) to describe correlation between dipoles this reflects the expected dipole–dipole interactions which increase with decreasing the azobenzene concentration and supports the picture of local preferential ordering. In the inset of Fig. 9 $\Delta\varepsilon_\alpha$, for α-relaxation, is plotted versus calculated dipole moments. The non-linearity of the relation $\Delta\varepsilon_\alpha - \Delta\mu^2$ reflects once again the cooperative nature of the side groups motion.

A β′-relaxation process is observed in between β- and α-processes as shown in Figs. 3 and 5. It is not present in the conventional polymethacrylate and in the homopolymer without the azobenzene side chain. For that reason this process must be related to the azobenzene moieties. The temperature dependence of the relaxation rate of this process can also be described by an Arrhenius relation. The activation energy of this process is rather high (75 kJ/mol) in comparison with that for the β- and the local γ-process. So it can be speculated if nature of the process is cooperative or at least coordinative. But up to now the underlying molecular assignment remains unclear. Therefore addition investigations are necessary. This includes also dielectric investigation under irradiations to change the ratio between the trans and the cis conformation of the azobenzene unit because the latter is more polar than the trans one (see Ref. [38]). The further increase of azobenzene concentration (S3, S4) leads to disappearance of this process due to the increase of hindrance. A more detailed molecular assignment of this relaxation process needs further experimental studies.

5. Conclusions

By means of dielectric spectroscopy we have reported the effect of azobenzene side group concentration on the different relaxation processes investigated in the comb-like copolymer. The results emphasize a linear increase of the activation energy of the β-relaxation as a function of the azobenzene concentration. This is attributed to the flatness nature of the side group in comparison with the benzanilide side groups.

Although the peak of the α-process observed for all investigated concentrations could not be separated into two components, the strong dependence of ΔT (where $\Delta T = T_g^{\mathrm{Diel}} - T_g^{\mathrm{DSC}}$) on the azobenzene concentration indicates that contributions of δ-like processes should be considered.

An additional relaxation process β′, of high activation energy, was observed which is not found in the usual poly methacrylate or homopolymer without azobenzene side groups. It may be due to coordinative fluctuations of the azobenzene around its long axes.

The non-linear relation between calculated and determined dipole moment of the investigated polymers reflects the cooperative nature of the mechanism of the side group.

Further measurements should be done on the effect of azobenzene concentration dependence of Z/E and of the thermal Z/E photoisomerisation.

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