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Thermal Isomerization of Azobenzene-Based Acrylic Monomers and (Co)Polymers with Dimethylamino Substituents in Solution. Influence of Addition of (Poly)Acid, Copolymer Composition, Spacer Length, and Solvent Type[†]

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ABSTRACT: This study reports on a method for influencing the thermal isomerization of azobenzene-based acrylic monomers and (co)polymers by means of interaction between *basic* polymeric and monomeric azobenzenes (modified with a basic dimethylamino substituent, *(poly)azobases*) and (poly)*acids*. The results indicate that acid catalysis is the predominant effect, which is controlled by (inter)polymer cooperative hydrogen bonding, because on addition of the low molecular weight isobutyric acid (IBA) to the (poly)azobases no effect was observed, and on addition of poly(methacrylic acid) (PMA) to the monomeric azobases only a weak effect was found. On addition of PMA, the rate constant of the thermal *cis* to *trans* isomerization ($k(T_{\mathrm{isom}})$) of a polyazobase could be enhanced by a factor of 70. The influences of factors like copolymer composition, spacer length, solvent type, and stabilization time after mixing on the thermal isomerization were also investigated and explained in terms of polymer complexation. In the absence of PMA the rate of the thermal isomerization was found to decrease by introduction of a spacer, by lowering the azobase monomer content in copolymers and by improving the solvent quality. The results on the thermal *cis* to *trans* isomerization presented here were obtained from measurements in dilute solution with concentrations well below c^*, because in that case polymer matrix effects could be ruled out.

1. Introduction

It is known that polymeric and monomeric acids ((poly)acids) are able to catalyze the thermal *cis* to *trans* isomerization of polymeric and monomeric azobenzenes. This acid catalysis of the thermal *cis* to *trans* isomerization of azobenzenes is thought to be brought about by hydrogen bonding between the proton in the acid group and one of the nonbonding lone pairs on the nitrogen atoms of the azo linkage. The activation energy of the thermal isomerization is thereby lowered, leading to an increase of $k(T_{\mathrm{isom}})$.[1–3] Also copolymers of acid monomers with modified azobenzene-based (az.b) monomers without an acid or basic substituent showed an acceleration of the thermal isomerization. This probably was caused by autocatalysis, although no complex formation through hydrogen bonding was observed.[4–6] If complex formation between the (poly)azobase and the (poly)acid proceeds via hydrogen bonding to the azo linkage, no visible changes are expected in the UV spectra. If the interaction is stronger, leading to an ionic complex by transfer of the acid proton to the azo linkage in the azobase, then the az.b. side group would change from an azoid structure to a quinoid structure with disrupture of the azo linkage. As a consequence *cis* ↔ *trans* isomerization is not possible anymore [e.g. refs 7–9]. This significant change in structure would be visible as a large red shift in the UV spectrum, provided the complex does not precipitate.

The acid catalysis might be used for the acceleration of the reorientation of azobenzene groups in spin-coated thin films of liquid crystalline polymers caused by the "photoselection effect", as was described in a previous publication.[10] This class of liquid crystalline polymers with modified photoresponsive azobenzene side group exhibits reversible optical changes that can be used in a new type of optical data storage material. As these optical changes (storage of data) were initiated by the *cis* ↔ *trans* isomerization cycles of the azobenzene side groups, it might well be possible to accelerate the process of data storage if the number of *cis* ↔ *trans* isomerization cycles in time is increased. A convenient means for acceleration of the isomerization process might be acid catalysis of the thermal *cis* to *trans* isomerization.

In this paper the influence of interaction between a series of (poly)azobases (with a dimethylamino substituent, Figure 1) and PMA (Figure 2) on the thermal isomerization will be described. For comparison, parallel experiments were also performed on the corresponding az.b. monomers and the low molecular weight analogue of PMA, IBA (Figure 2), and also in the absence of PMA.

2. Experimental Section

2.1. Materials. The synthesis and the characterization of the azobenzene monomers and (co)polymers with methacrylate are described elsewhere.[11] The characterization of the molecular weight distribution was performed with a Waters Associates 150-C ALC/GPC in $CHCl_3$. Because of the lower molar percentage of az.b. side groups in the copolymers compared to the homopolymers, the concentrations of the (co)polymers are adjusted in such a way that the amount of az.b. chromophores in the solution were the same, viz. 5.0×10^{-5} M, i.e. twice that of the end concentration after mixing with solutions of the (poly)acids.

The (co)polymers of the azobase monomer **a4** (n, $m = 0$ in Figure 1; see also Table 1) with methyl acrylate were less soluble with the increasing content of az.b. side groups. Poly **a4** (homopolymer) had to be solubilized by sonification. In this way about 60% of the polymer could be dissolved (as determined by UV analysis), so the concentration was about 3.0×10^{-5} M. For the copolymers, sonification was not necessary. The thermal isomerization was measured in the experimental

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[†] Dedicated to Professor Dr. J. Klein on the occasion of his 60th birthday.

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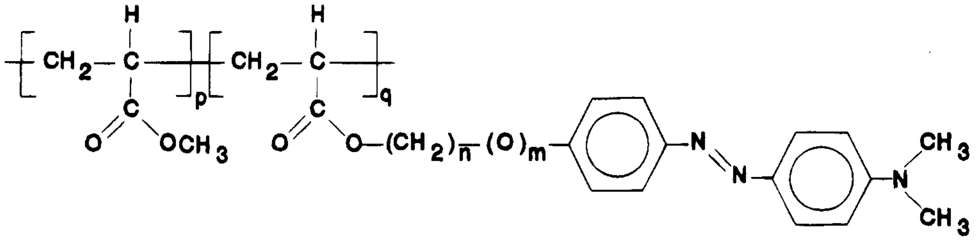
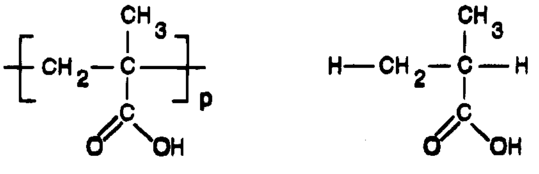


Figure 1. Structure of the used polyazobases: n = 0, 6, or 11, m = 0 or 1, p/q = 0/1.0, 0.5/0.5, 0.8/0.2, and 0.9/0.1.



PMA **IBA**

Figure 2. Structure of the used (poly)acids.

Table 1. Structure and Molecular Weights of the Used (Co)Polyazobases

(co)poly	n	m	p	q	$\bar{M}_w$
a4	0	0	0	1.0	5500
a4-50	0	0	0.5	0.5	7600
a4-20	0	0	0.8	0.2	11100
a4-10	0	0	0.9	0.1	20400
a5	6	1	0	1.0	6400
a6	11	1	0	1.0	7500

setup as described in section 2.3. [The glass equipment was extensively cleaned by sonification in EtOH and CH_2Cl_2, respectively, just before use. This cleaning was necessary because the glass equipment usually was contaminated with a very small amount of detergent, which was able to suppress completely the photoresponsive effects brought about by the (poly)acids.] In order to measure the effect of the concentration of (poly)acid on the $k(T_{isom})$ of the polyazobases, seven different concentrations of (poly)acid were prepared, while the final concentration of the polyazobase was kept constant. After mixing of the solutions, the ratios of the numbers of acid groups and azobase groups were 1, 2, 3, 5, 7, 10, 15, 20, 25, and 30. The absorbances at the absorption maximum of *trans* (λ_{max}(*trans*)) of the copolymers after mixing were of the same order as that for the homopolymers. The experiments were performed in *p*-dioxane/EtOH = 4/1 at 20 °C. EtOH was of p.a. quality (Merck Schuchardt, Germany) and was used without further purification. *p*-Dioxane was of approximately 95–98% purity (Janssen Chimica, Belgium), stored over 4 Å molecular sieves and used without further purification, since distilled *p*-dioxane showed no difference in the results. PMA (synthesized in this laboratory) was purified by means of reprecipitation from MeOH in dry diethyl ether; its $\bar{M}_v$ was 130 000 in EtOH of p.a. quality at 25 °C. IBA (Janssen Chimica, Belgium), was distilled under a nitrogen atmosphere under reduced pressure and subsequently stored under a nitrogen atmosphere. Polymer concentrations were well below c^*, the critical concentration for coil overlap, as determined by the empirical relation $c^* \sim 1/[\eta]$ introduced by Simha.[12]

The experiments in the absence of PMA were performed in CH_2Cl_2 (Merck Schuchardt, Germany; this solvent was used for comparison with literature data), *p*-dioxane/EtOH = 4/1, and DMF. The solutions in CH_2Cl_2 had to be stabilized with a very small amount of piperidine, in order to avoid adventitious catalytic effects.

2.2. Preparation of the Experimental Solutions. The solutions were prepared in the dark to prevent *cis* formation. The concentration of the az.b. chromophore was typically fixed at 2.5×10^{-5} M, because at that concentration the absorbance at λ_{max}(*trans*) in all cases was smaller than ~0.8. This was needed to ensure a linear relationship between absorbance and concentration, according to the law of Lambert and Beer.

2.3. Apparatus. The thermal isomerization was monitored over a period ranging from 500 to 1000 s. The excitation of the az.b. monomers from the *trans* to the *cis* configuration was brought about with a pulsed Questec 2240 (XeCl) excimer/dye laser 5200 B combination. The laser dye DPS (4,4′-diphenylstilbene, λ_{max}(emission) ~ 405.5 nm) was purchased from Radiant Dyes Chemie (Germany). *p*-Dioxane (Janssen Chimica, Belgium) stored over 4 Å molecular sieves was used as solvent for the dyes. The light intensity was 8 mJ/pulse (5 Hz) at 405.5 nm.

The photoresponsive experiments were carried out in the setup represented in Figure 3. The measuring instruments were placed in a black box to prevent stray light from interference with the photomultiplier signal, and contributing to the *cis* → *trans photo*isomerization.

In Figure 3 the excimer laser (1) emits light at λ = 308 nm with 80 mJ/pulse at 5 Hz, exciting the dissolved dye molecules in the dye laser (**2**). The dye solution was pumped around to prevent saturation of the dye solution during excitation. On decaying to their ground states, the excited dye molecules fluoresce at longer wavelengths, their spectrum being broad with one or more maxima. The desired wavelength could be selected by means of a built-in monochromator; i.e., the dye laser is *tunable*. In order to obtain the highest light intensity, the wavelength was chosen at the maximum of the dye emission spectrum. Under this condition the maximum amount of *cis* could be reached very fast, at a time scale in which the effect of the *thermal* isomerization on the *cis* content would be negligible. During the *trans* → *cis* excitation of the az.b. compound the entire solution could be illuminated, while it was stirred by a magnetic stirrer (11) on the bottom of the sample holder (9). The temperature of the sample holder was kept constant at 20 °C by a water thermostat (12), the temperature of the solution being measured by a thermocouple (13).

The change in the *trans* content of the az.b. chromophore was followed by means of an Oriel 450W Xe UV lamp (6) as a probing light source, with the light beam perpendicular to the laser excitation beam. The probe wavelength was selected with a monochromator (7) at λ_{max}(*trans*), the intensity was attenuated to a few μW/cm^2 by 150 μm vertical slits in the monochromator and a 1 mm^2 pinhole (8) in front of the sample holder. The very low illumination intensity (spectrophotometer level) did not cause an additional *trans* → *cis photo*isomerization, so the effect on the isomerization was negligable.

The change in the absorption of the probe light at λ_{max}(*trans*) was detected by an EMI 9780B CsSb semiconductor photomultiplier (10) which was connected via a PCL 711-s ADDA converter (4) to a microcomputer (3). The digitized analog signal is proportional to the light intensity transmitted through the UV fluorescence cuvette (measuring cell). These data were gathered by the microcomputer.

2.4. Performance of the Experiments. The experiments were performed for a fixed routine. First I_i (incident light) and I_{trans} (transmitted light intensity at t = 0, 100% *trans*) were recorded, before the measurement of the thermal isomerization took place. When the laser was switched on (while stirring the solution), the absorbance decreased quickly from A_{trans} (absorbance of *trans*) to A_{cis} and then stabilized. *Cis* absorbs only weakly at λ_{max}(*trans*), ϵ(*trans*) ≈ 20ϵ(*cis*). At this point the equilibrium mixture of *cis* and *trans* was attained with a *cis* content of about 90%, as estimated from the residual absorbance at λ_{max}(*trans*). After the laser had been switched off, the relaxation to the *trans* of the unstirred solution was followed (with values A_t).

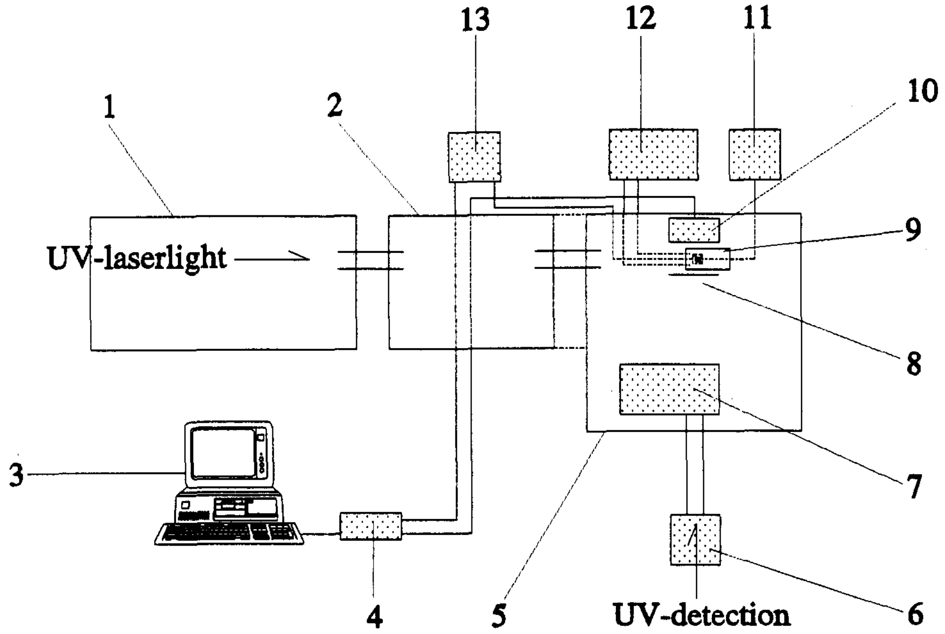


Figure 3. Experimental setup for the photoresponsive measurements: (1) XeCl excimer pulsed gas laser; (2) dye laser; (3) computer; (4) ADDA converter; (5) black box; (6) UV lamp (probe light); (7) monochromator; (8) pinhole (diaphragm); (9) thermostated sample holder for a (fluorescence) cuvette (light path 1 cm); (10) photomultiplier; (11) magnetic cuvette stirrer; (12) water thermostat; (13) thermocouple.

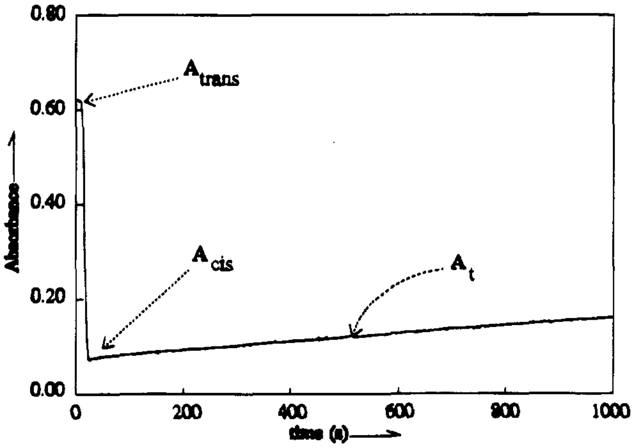


Figure 4. Example of the change of A_i at $\lambda_{max}(trans)$ for the monomer **a4** at a concentration of 2.5×10^{-5} M in CH_2Cl_2 (stabilized with a very small amount of piperidine), during the experiment.

The digitized analog signal from the photomultiplier during the photoresponsive experiment was named I_t. The absorbance during the measurement A_t was calculated by dividing I_i (with pure solvent) through I_t (both corrected for the background signal I_b in the absence of probe or laser light) and taking the log of the quotient, according to the law of Lambert and Beer; see eq 1. A_t was calculated at constant time

$$A_t = \log\left(\frac{I_i - I_b}{I_t - I_b}\right) \qquad (1)$$

intervals (taken at a fixed time of 1 s). An example of the variation of A_t during the routine of the photoresponsive experiment is presented in Figure 4 for the monomer **a4**, at a concentration of 2.5×10^{-5} M in CH_2Cl_2 (stabilized with a very small amount of piperidine). The A_t data were transformed to kinetic data by means of the first-order rate equation in eq 2. A_{trans} is the absorbance of 100% *trans* before excitation

$$kt = \ln\left(\frac{A_{trans} - A_{cis}}{A_{trans} - A_t}\right) \qquad (2)$$

(or after $t = \infty$), A_{cis} is the absorbance after the laser was switched off, and A_t is the absorbance at time t (s). With the kinetic parameter (kt) a plot was constructed, presented in Figure 5. From the slope of the curve k could be calculated, the velocity constant of the thermal isomerization $k(T_{isom})$. Data acquisition and processing were performed with the programs SHG, MANIPUL (F. de Haan, Department of Physical Chemistry, University of Groningen), KINETIEK, and UV-MULT (E. J. Vorenkamp, Department of Polymer Chemistry, University of Groningen).

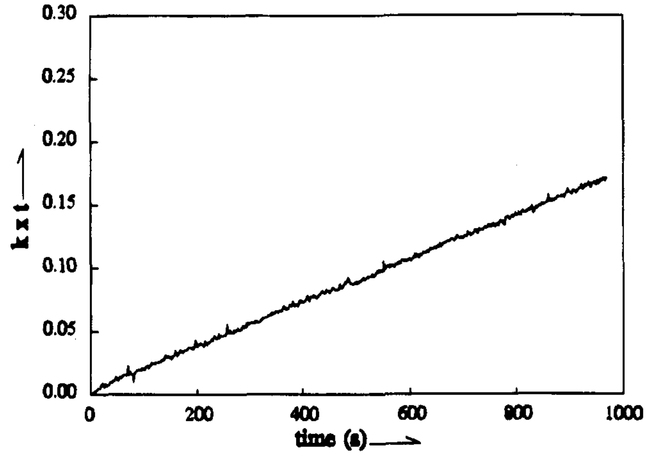


Figure 5. Plot of kt versus time t (s) based on the processing of the data in Figure 4 by eq 2.

3. Results and Discussion

3.1. Experiments in the Absence of Acid: Effects of Copolymer Composition, Spacer Length, and Solvent Type. In the literature, many authors have reported on the synthesis of (co)polymers with different amounts of az.b. side groups, tethered on several types of polymer backbone. Investigations of their photoresponsive behavior in solution were mainly focused on its effect on the properties of the polymers, only a few were concerned with the thermal isomerization of the az.b. side groups.[13-21] Two trends have been reported about the properties of the az.b. polymers compared to

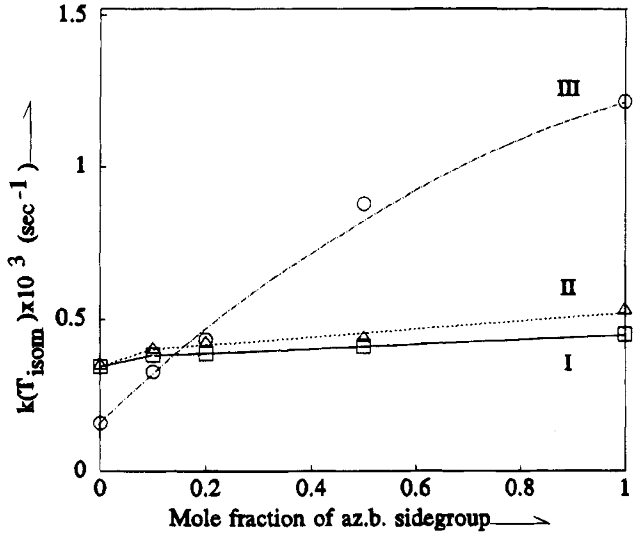


Figure 6. Influence of the copolymer composition and spacer length on the thermal isomerization of polyacrylates with az.b side groups modified with a $N(CH_3)_2$ substituent (polyazobases) in CH_2Cl_2 at 20 °C; (co)poly **a5** ($n = 6$, $m = 1$; I); (co)poly **a6** ($n = 11$, $m = 1$; II); (co)poly **a4** (n, $m = 0$; III). The corresponding monomers (no polymer backbone) are placed at 0.

that of the corresponding monomers. First, there is the dependency of λ_{max}(*trans*) on the composition of the copolymer, viz. a decreasing λ_{max}(*trans*) with increasing content of az.b. side group in the (co)polymer because of increasing interactions between the π-systems of adjacent az.b. side groups.[22-24] Secondly, there are indications that the rate of the thermal isomerization of the (co)polymers is about the same as that of the corresponding az.b. monomers. In some cases $k(T_{isom})$ of the polymers was slightly increased or decreased, but no trends were observed.[13,21,25]

In Figure 6 the results are presented for our experiments performed in CH_2Cl_2 at 20 °C. The value of $k(T_{isom})$ at a mole fraction of 0 is that of the corresponding azobenzene monomer. The lower value of $k(T_{isom})$ for mono **a4** might be explained by the decreased electron density on the azobenzene group due to the electron-accepting oxycarbonyl substituent instead of the electron-donating oxyalkyl substituent in monomers **a5** and **a6**. Surprisingly $k(T_{isom})$ of the (co)polymers with az.b. side groups is generally larger than that of the corresponding az.b. monomers. The highest value of $k(T_{isom})$ is about 1.2×10^{-3} s^{-1} (corresponding to a half-life time $t_{1/2}$ for *cis* of about 10 min) for the polyazobase poly **a4** without a spacer. The value of $k(T_{isom})$ increases with the mole fraction of az.b. side groups, especially in case of the (co)polymers of **a4** without a spacer (Figure 6; n, $m = 0$, curve III), where the maximum increase amounts to a factor 6 in the case of the homopolymer. It also was observed that the solubility of these polymers decreases with the increasing content of az.b. side groups.

If the UV spectra of the monomers and their (co)polymers are compared to each other, λ_{max}(*trans*) for the (co)polymers is always shifted to shorter wavelengths, especially for the homopolymers without a spacer like poly **a4** (Figure 7). Generally, the shift of λ_{max}(*trans*) is correlated to a higher $k(T_{isom})$. It seems that some cooperative mechanism is involved in the thermal isomerization of these compounds. The general trend that can be deduced from the results in Figures 6 and 7 is that a *stronger* interaction between the az.b. side groups yields a higher $k(T_{isom})$. So, steric crowding along the polymer backbone enhances $k(T_{isom})$. Hence the influence of the polymer backbone is largest when the az.b. side groups are located close to it, and so it seems quite logical that the cooperative effect is largest in (co)polymers of **a4** containing az.b. side groups without a spacer.

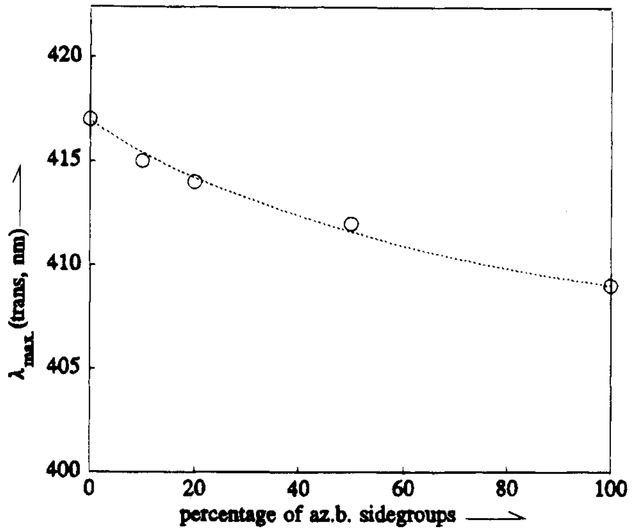


Figure 7. λ_{max}(*trans*) vs percentage of az.b side groups in (co)poly **a4** in CH_2Cl_2. The monomer (no polymer backbone) is placed at 0.

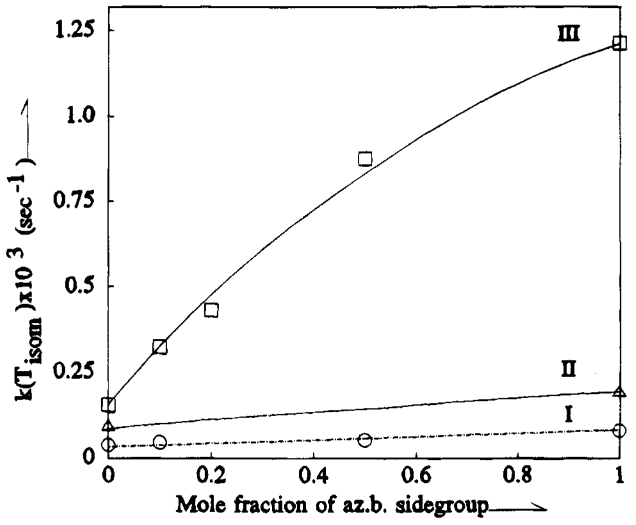


Figure 8. Influence of solvent type on the thermal isomerization of the (co)polymers of **a4**, in CH_2Cl_2 (III), DMF (II), and p-dioxane/EtOH = 4/1 (I) at 20 °C.

The shift of λ_{max}(*trans*) is less evident for more flexible systems, i.e. the (co)polymers of **a5** (Figure 6; $n = 6$, $m = 1$; curve I) and **a6** (Figure 6; $n = 11$, $m = 1$; curve II) with a flexible spacer, or copolymers with a lower content of az.b. side groups. The reason for this is probably the much greater mobility of the az.b. side groups in the more flexible systems. The shift of λ_{max}(*trans*) is caused by the interaction (exciton coupling) of the π-systems of adjacent az.b. side groups, which is intensified with the increasing content of az.b. side groups and decreasing spacer length.

The cooperative effect is also influenced by the solvent quality, as demonstrated by the thermal isomerization of the (co)polymers of **a4**, performed in p-dixoane/EtOH = 4/1 and in DMF at 20 °C (Figure 8). Indeed, in these better solvents the effect is much smaller (curves I and II) than in CH_2Cl_2 (curve III). Moreover, the decrease of $\lambda_{max}(trans)$ in the UV spectra with the increasing content of az.b. side groups in the (co)polymers has disappeared in the better solvents. Probably the az.b. side groups are shielded from each other by the more polar solvent molecules. Nevertheless, the cooperative effect is still weakly present in DMF and *p*-dioxane/EtOH = 4/1. The difference between $k(T_{isom})$ in the two solvents may be caused by the difference in solvent polarity: the higher polar DMF induces a higher $k(T_{isom})$ in the weakly dipolar az.b. side groups.[26]

3.2. Influence of Acid Addition. Poly(methacrylic acid) (PMA) was chosen as the polyacid because it was readily available in our laboratory, well characterized, and pure. Because PMA was not soluble in CH_2Cl_2 and its acid groups were more or less "neutralized" in the slightly basic solvent DMF, the experiments were now only performed in *p*-dioxane/EtOH = 4/1. In this mixture both PMA and the (co)polyazobases were soluble, *p*-dioxane being a good solvent for the (co)polyazobases and EtOH for PMA. The mixtures of the monomeric azobases (mono **a4** (n, $m = 0$) and mono **a5** ($n = 6$, $m = 1$)) and of the (co)polymeric azobases (poly **a4** ($p = 0$, $q = 1$), copoly **a4−50** ($p = q = 0.5$), copoly **a4−10** ($p = 0.9$, $q = 0.1$), and poly **a5** ($p = 0$, $q = 1$), all with methylacrylate as comonomer; see also Table 1) with the acids PMA or IBA at the experimental concentrations yielded no visible or spectroscopic evidence for strong complex formation, as described in the Introduction. No red shift was observed in the UV spectra, not even on an increase in the concentration and subsequent stabilization for a few days, which means that no protonation of the azo linkage in the azobases had occurred. Also no protonation of the electron-donating $N(CH_3)_2$ terminal group had occurred, which would also be visible in the UV spectra. Moreover, the protonated $N(CH_3)_2H^+$ group would be weak electron-accepting, leading to a decrease of $k(T_{isom})$ instead of the increase found by us. This is not surprising since both the (poly)azobases and the (poly)acids are rather weak, so that the stability constant of the interpolymer complex is rather small.[27,28] In fact this rather weak interpolymer complex formation is a desirable feature, since more tight polycomplexes would probably precipitate and could not be investigated anymore.

i. Polymer Effects. For poly **a4** a large difference can be observed in Figure 9 between, $k(T_{isom})$ values of poly **a4** upon addition of the polymeric acid PMA (I) or the low molecular weight acid IBA (III). On addition of PMA, after passing an acid/azobase group ratio of 8, $k(T_{isom})$ gradually increases to 70 times the original value without PMA. Since on addition of IBA no effect was found, the result is clearly due to the polymeric nature of PMA. Curve I levels off at an acid/azobase group ratio of about 50. Its sigmoidal shape suggests the existence of a cooperative process, probably caused by some complex formation between the two polymers. The stability constant of this interpolymer complex is rather small, which is demonstrated by the fact that an 8-fold excess of PMA is needed before any effect becomes noticeable.

For mono **a4**, it is first noticed that $k(T_{isom})$ is about a factor 10 lower than for poly **a4** (Figure 9, II and I), due to the cooperative effect along the polyazobase (see section 3.1). It is surprising that PMA addition also enhances $k(T_{isom})$ for mono **a4**, although the maximum increase by a factor 10 is smaller than that for poly **a4**. Upon addition of low molecular weight IBA again no effect was found (III). Curve II also has a sigmoidal shape. If we stick to the suggested cooperative effect, then a monomer/polymer complex has to be assumed between mono **a4** and PMA. This means that the monomeric azobase molecules should be located near the polyacid. However, as no blue shift of $\lambda_{max}(trans)$ was observed (caused by interaction between π-systems of az.b. side groups), the azobases are probably not located very close to each other. A similar effect was found by Lovrien et al.,[29] but the most specific reason that was given for the macromolecular catalysis was that "interaction" with the acid groups lowered the activation energy of the thermal isomerization, while complex formation was not mentioned.

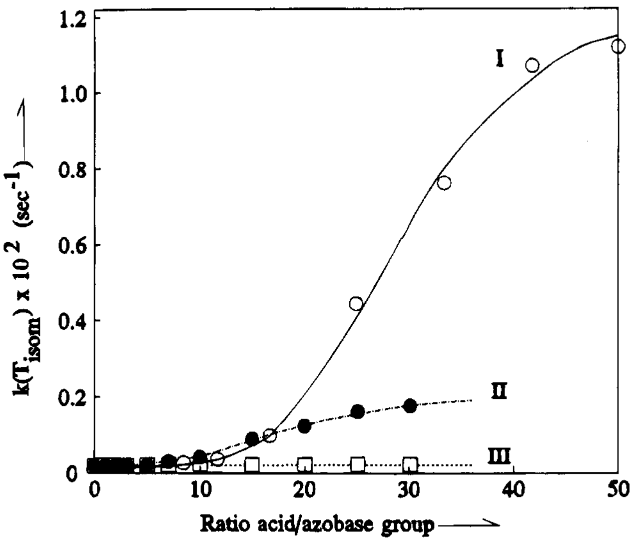


Figure 9. Effect of PMA addition on the rate of the thermal isomerization of poly **a4** (n, $m = 0$, I) and mono **a4** (n, $m = 0$, II). Effect of IBA addition to poly **a4** and mono **a4** (combined in III). Measured in *p*-dioxane/EtOH = 4/1 at 20 °C.

ii. Influence of Copolymer Composition. In order to investigate the effect of "dilution" of the azobase side groups along the polymer backbone on the enhancement of $k(T_{isom})$ and thus on the supposed complex formation, the effect of PMA addition on two copolymers of **a4** was investigated. The data on copoly **a4-10** (I) and copoly **a4−50** (II) are collected in Figure 10, together with those on poly **a4** (III) for comparison. In order to investigate whether polymer complexes were actually formed, viscosity measurements were performed on mixtures of PMA with copoly **a4−50** in *p*-dioxane/EtOH = 4/1 at 20 °C and a total concentration of 0.06 g/dL. The flow times showed a small deviation from the additive values with a minimum at an acid group/azobase ratio of about 2:1. So, some evidence was found for polymer interaction, and possibly complex formation.

The copolymers are more soluble than poly **a4**, so that for these copolymers the actual acid/azobase group ratio did not exceed 30. The sigmoidal shape of the curve is also present for both (co)polymers. For copoly **a4−10** the maximum of $k(T_{isom})$ is about a factor 10 higher than that in the absence of PMA. For copoly **a4−50** the maximum is about a factor 40 higher. So, these data show that with a decreasing content of az.b. side groups in the (co)polymer the maximum of $k(T_{isom})$ decreases. Apparently, the accelerating effect of complex formation diminishes with a lower content of az.b. side groups in the (co)polymer, because less compact polymer complexes can be formed. Although the same total amount of azobase groups is present, this might indicate that a

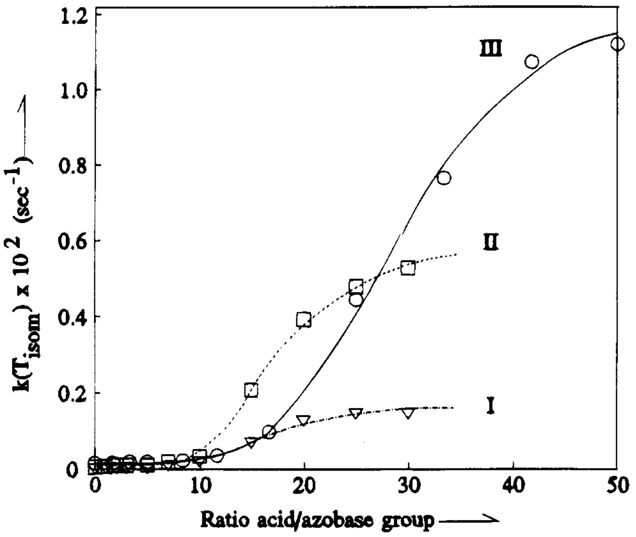


Figure 10. Eight of the copolymer composition on the enhancement of the rate of the thermal isomerization by PMA: copoly **a4–10** (I), copoly **a4–50** (II), and poly **a4** (III), for all n, m = 0. Measured in p-dioxane/EtOH = 4/1 at 20 °C.

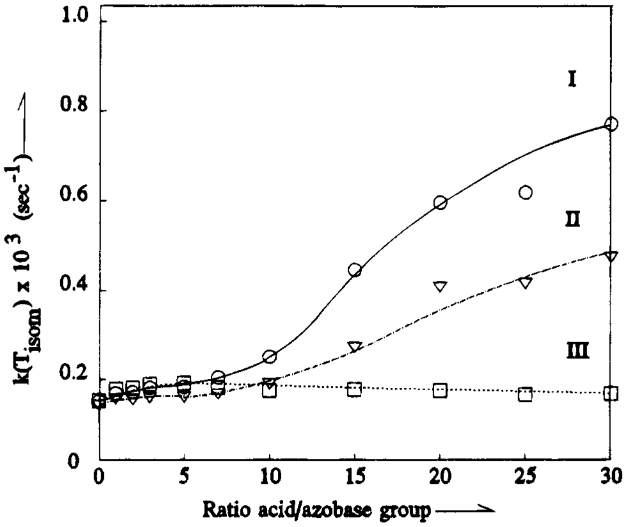


Figure 11. Effect of the spacer on the enhancement of the rate of the thermal isomerization by addition of PMA to mono **a5** (n = 6, m = 1; II) and to poly **a5** (I). Also the effect of IBA on poly **a5** (III) is incorporated. Measured in p-dioxane/EtOH = 4/1 at 20 °C.

certain number of contacts have to be made to induce a cooperative interaction after which complex formation takes place.

Solubility is another factor that possibly contributes to the dependency of the enhancement of $k(T_{isom})$ on the content of az.b. side groups in the (co)polymers. It was already mentioned that the solubility of the (co)polymers decreased with the increasing content of az.b. side groups in the (co)polymer. The modest solubility of PMA in the solvent mixture may also contribute to the formation of complexes, the strongest tendency being in the direction of increasing PMA concentration and increasing az.b. side group content.

iii. Influence of Spacer. The effect of the incorporation of a spacer between the az.b. side group and the polymer backbone on $k(T_{isom})$ is presented in Figure 11. It can be seen that the enhancement of $k(T_{isom})$ of poly **a5** (n = 6, m = 1) upon addition of polyacid (I) is much smaller than for poly **a4** (n, m = 0; Figure 9, I), and the same holds for monomer **a5** (II) with respect to mono **a4** (Figure 9, II). In general, the shapes of the curves are similar, but the axis is expanded 10 times with respect to Figure 9. Again, sigmoidal curves, a lower acceleration for the monomer than for the polymer, and no effect of low molecular weight acid are found (Figure 9, III). Here the onset of the acceleration is located at an acid/azobase group ratio of about 5. As discussed in section 3.1 the difference in $k(T_{isom})$ between poly **a5** and poly **a6** is small compared to the difference with poly **a4**. Therefore, poly **a6** was omitted here.

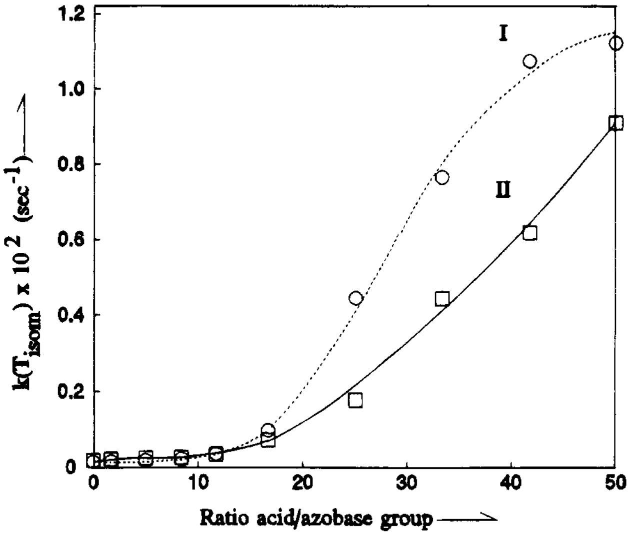


Figure 12. Influence of the solvent polarity on the enhancement of the rate of the thermal isomerization by PMA: poly **a4** (n, m = 0), measured in p-dioxane/EtOH = 4/1 (I) and 3/1 (II) at 20 °C.

A possible reason for the smaller increase upon addition of polyacid may be the fact that poly **a5** (having a spacer) is more soluble than poly **a4**, so the driving force for complex formation is decreased, and hence the enhancement of $k(T_{isom})$. Also the higher mobility of the azobase groups with a spacer may suppress complex formation and/or exciton coupling between az.b. side groups.

iv. Influence of Solvent Quality. In order to investigate the effect of solvent quality, the influence of PMA on poly **a4** was also measured in p-dioxane/EtOH = 3/1. This more polar medium increases the solubility of PMA and diminishes its tendency to form interpolymer complexes, and hence should yield a smaller increase of $k(T_{isom})$ and a shift to higher concentrations of PMA. In Figure 12 it can be seen that this is the case. So, complex formation seems plausible as an explanation for enhancements of $k(T_{isom})$.

Both curves in Figure 12 show a sigmoidal shape, indicating a cooperative effect. This means that a certain initial amount of polyacid had to be present before sufficient contacts could be made for complex formation. As this process might also depend on the time lapse after mixing the polymer solutions (stabilization time), $k(T_{isom})$ was measured as a function of time at an acid/azobase group ratio of 25. It appeared that no influence on the acceleration effect was found over a period of 3 h after mixing. This means that complex formation was already complete within a few minutes after mixing.

v. Effect of Polyacid on Polyazobase in Thin Solid Films. This subject is not yet fully investigated. However, preliminary results of measurements performed with thin solid polymer films (spin coated from *p*-dioxane/EtOH = 4/1) containing the polyazobase poly **a4−50** and PMA with a ratio of acid to azobase groups of only 1, showed already an enhancement of $k(T_{\mathrm{isom}})$ by a factor of 4.[10] So, the tendency to form complexes seems to be stronger in the undiluted state, as could be expected.

4. Conclusions

The rate constant of thermal isomerization $k(T_{\mathrm{isom}})$ of the (co)polymers with az.b. side groups is generally larger than that of the corresponding az.b. monomers. When the UV spectra of the monomers and their (co)polymers are compared to each other, $\lambda_{\max}(trans)$ of the polymers is always shifted to lower wavelengths, especially for the homopolymers without a spacer. This shift is less evident for more flexible systems, i.e. (co)polymers with a flexible spacer or a lower content of az.b. side groups. The shift of $\lambda_{\max}(trans)$ is caused by the cooperative interaction (exciton coupling) of the π-systems of adjacent az.b. side groups. The interaction between the az.b. side groups is shielded when a better solvent is used, by which also the shift of $\lambda_{\max}(trans)$ disappears. Generally, the shift of $\lambda_{\max}(trans)$ is correlated to a higher $k(T_{\mathrm{isom}})$.

Upon addition of the polyacid PMA $k(T_{\mathrm{isom}})$ was enhanced by a maximum factor of 10 and 70 for the *monomeric* and *polymeric* azobases, respectively. For the polymeric azobases this means that $t_{1/2}$ of the thermal isomerization had decreased to only 1 min. The curves of $k(T_{\mathrm{isom}})$ vs the acid/azobase group ratio were sigmoidally shaped, which is typical for cooperative interactions with PMA. Accordingly, the enhancement of $k(T_{\mathrm{isom}})$ was absent when the low molecular weight acid IBA was added. The (hydrogen bond) interactions with the azo group nitrogens are weak, and dynamic complexes are formed, which was confirmed by the observation that a large excess of PMA was needed, and none of the investigated polyacid/(poly)azobase combinations showed a red shift in the UV spectra typical for the formation of strong ionic acid−azobase complexes. The thermal isomerization is accelerated by enhanced mutual interaction of az.b. side groups as well as a higher local acid group concentration in the polymer complexes.

In accordance with the above explanation a smaller increase of the rate of the thermal isomerization was found be introducing a spacer or lowering the azobase group content in the copolymers. In all of these cases the solubility of the (co)polymers increased and less compact complexes were formed. This was also the case when the solvent polarity was increased, because this improved the solubility of PMA.

Finally, preliminary experiments on the same type of polyazobases in spin-coated thin solid polymer films showed very promising results concerning acceleration of the thermal isomerization by addition of PMA.

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