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# Effect of Spacer on the Isomerization of Bound Azobenzene in Soluble Polymers

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## Summary

Two polymerizable derivatives of 4-aminoazobenzene, viz., 4-methacryloylaminoazobenzene (MA-AAB) and 4-(12-methacryloylaminododecanoyl)aminoazobenzene (MA-12-AAB) were prepared and copolymerized with methacrylic acid (MA) and N-(2-hydroxypropyl)methacrylamide (HPMA). The cis-trans thermal isomerization of these copolymers was investigated as a function of temperature, side chain length and character of the polymer carrier.

## Introduction

The effect of the side chain length of soluble polymers on the behaviour of the substrate bound at the end of the side chain has been investigated by several authors. Different rates of aminolytic reactions depending on the side chain length have been described; (SU and MORAWETZ 1977, REJMANOVÁ et al. 1977, LABSKÝ and KÁLAL 1979) enzymatically catalyzed hydrolyses, which proceeded at different rates according to the spacer used, were influenced similarly. (FU and MORAWETZ 1976, DROBNÍK et al. 1976, LABSKÝ et al. 1979) The rotational correlation time, which is a measure of the mobility of nitroxide radicals, depends linearly on the side chain length on which the radical is bound. In this case also the dependence on the side chain structure was demonstrated. (LABSKÝ et al. 1977, LABSKÝ et al. 1979a, PILAŘ et al. 1979)

Azobenzene as a photochromic molecule was bound in the side chain of soluble polymers, and the cis-trans isomerization was found to depend on the viscosity and pH of the medium. (KAMAGAWA et al. 1968, PAIK and MORAWETZ 1972, LOVRIEN and WADINGTON 1964)

The mechanism of isomerization of azobenzene has been discussed by several authors. (CURTIN et al. 1966, HABERFIELD et al. 1975, LJUNGGREN and WETTERMARK 1971) It is assumed that the transition of the cis form, which arises after azobenzene has been irradiated with light of a suitable wavelength, to the stable trans form proceeds as a first - order reaction.

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## Experimental

Monomers:

4-Methacryloylaminoazobenzene was prepared by reacting methacryloylchloride with 4-aminoazobenzene in pyridine. (PAIK and MORAWETZ, 1972) N-(2-hydroxypropyl methacrylamide was prepared as described earlier. (REJMANOVÁ et al. 1977)

4-(12-Methacryloylaminododecanoyl)aminoazobenzene (MA-12-AAB): 2.8 g of 12-methacryloylaminododecanoic acid (0.01 mole) (LABSKÝ and KÁLAL, 1979) was dissolved with 1 g of triethyl amine (0.01 mole) in 150 ml methylenechloride, cooled to 0°C, and 1.1 g of ethyl chloroformiate (0.01 mole) was added. After 40 min. still with cooling, 2 g of 4-aminoazobenzene (0.01 mole) was added. After 24 h the reaction mixture was shaken three times with diluted HCl (1:1). The product was crystallized from a methylenechloride-hexane mixture. M.p. 155-6°C. Yield 1.7 g (38%). Analysis (in%) for $C_{28}H_{38}N_2O_4$ (462.63):

| | | | |
|---|---|---|---|
| Calculated: | C 72.69, | H 8.27, | N 12.11; |
| Found: | C 72.58, | H 8.42, | N 11.95. |

Copolymers:

The copolymers were obtained by radical precipitation copolymerization in acetone (15 wt.% of monomers, 1.2% of AIBN, 60°C, 6 h) and reprecipitated from methanolic solution into acetone. The molecular weights were precipitated with a Photo Gonio Diffusometer Sofica 42 000 by light scattering (measured in water). The characteristics of the copolymers are summarized in Table 1.

TABLE 1
Characteristics of copolymers[a]

| Monomer | Copolymer with HPMA (content AAB/mol %) | $\bar{M}_w$ | Copolymer with MA (content AAB/mol %) | $\bar{M}_w$ |
|---|---|---|---|---|
| MA-AAB | 3.6 | 45 000 | 3.0 | 112 000 |
| MA-12-AAB | 2.8 | 37 000 | 2.7 | 75 000 |

[a] Content of azo compound determined spectrometrically ($\varepsilon = 3.2 . 10^4 cm^{-1} mol^{-1}$ at 348 nm).

Photochemical method

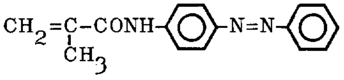
Aqueous solutions of the polymers were irradiated with a UV discharge tube HBO 200 at a distance of 5 cm for 2 min. Suitable radiation was selected by means of a VEB Carl Zeiss Jena interference filter for 365 nm. The measurement was performed with a Cary 14 spectrophotometer, the temperature of the sample was maintained by thermostating the cell surroundings to ± 0.2°C. The isomerization was observed using the increase in absorbancy at 348 nm (the absorption maxima of the trans isomer). The shift of the absorption maxima of the cis and trans isomers was not considered in the measurement.

Sample preparation: Aqueous polymer solutions were kept in the dark for 72 h. After that, the concentration of the chromophores was adjusted to $3.125 \times 10^{-5}$ mol $l^{-1}$ ($\varepsilon = 3.2 \times 10^{4}$ cm$^{-1}$mol$^{-1}$ at 348 nm). The evaluation was carried out using kinetic relation of first-order reaction:

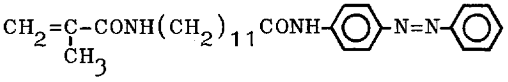
$\ln (E_e - E_o)/(E_e - E_t) = kt$ in which $E_t$ is absorbancy at a time t, $E_e$ is absorbancy of the sample after 72 h in dark, $E_o$ is absorbancy immediately after irradiation.

## Results and Discussion

Two polymerizable derivatives of azobenzene with the following structure were prepared:

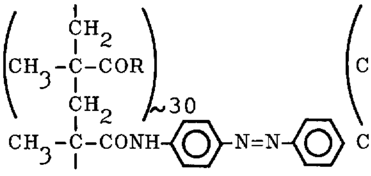


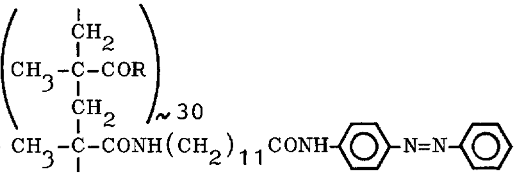
MA-AAB



MA-12-AAB

After copolymerization with HPMA or methacrylic acid they yielded polymers in which the low content of the photochromic monomer guarantees the isolated character of the photochrome in the polymer. (LABSKÝ and KÁLAL, 1979) Polymers of the following composition were obtained:





The copolymers are denoted as follows: For R = -OH copolymers MA/AAB and MA/MA-12-AAB, for R = $-NH-CH_2-CH(OH)-CH_3$; Copolymers HPMA/MA-AAB and HPMA/MA-12-AAB).

The rate of the cis-trans thermal isomerization of the azobenzene molecule was investigated in two types of soluble polymers in which the photochromic site was bound on variously long side chains.

The copolymers HPMA/MA-AAB and HPMA/MA-12-AAB are nonionizable polymer molecules. The activation energy of the isomerization process and the frequency factor were calculated from the dependence of the rate constant on temperature (Table 2).

TABLE 2
Rate constants ($k_1$) and frequency factor (A) of the thermal cis-trans isomerization of the azobenzene structural unit of photochromic polymers in water

| Photochromic system | Rate constant $k_1 \times 10^3$, $s^{-1}$, T, °C | | | A, $s^{-1}$ |
|---|---|---|---|---|
| | 40 | 50 | 60 | |
| MA/MA-AAB | 16.6 | 40.8 | 108.1 | $3.26 \times 10^{13}$ |
| MA/MA-12-AAB | 26.0 | 59.3 | 161.2 | $4.87 \times 10^{13}$ |
| HPMA/MA-AAB | 2.6 | 6.7 | 18.8 | $5.76 \times 10^{12}$ |
| HPMA/MA-12-AAB | 3.7 | 10.3 | 21.3 | $6.42 \times 10^{12}$ |

The activation energy $E_A$ = 92.4 kJ/mol (22.1 kcal/mol) is the same for all polymers. It was found that the azobenzene molecule bound in the close vicinity of the main polymer chain of the soluble polymer and transformed into the cis form by irradiation isomerized more slowly to the corresponding trans form of azobenzene compared with the same photochrome bound on a long side chain (monomer MA-12-AAB). This phenomenon is probably due to the effect of the polymer chain which sterically hinders the isomerization process of azobenzene. The long side chain of the copolymer HPMA/MA-12-AAB increases the distance between the photochromic site and the main polymer chain, thus eliminating steric hindrances caused by the polymer chain and facilitating a faster process of isomerization.

Copolymers of methacrylic acid and monomers MA-AAB and MA-12-AAB exhibit a dependence of the rate of isomerization of bound azobenzene on temperature analogous to that of nonionized polymers (Table 2). An essential rise in the rate of the isomerization reaction of copolymers of methacrylic acid is due to the increased concentration of hydrogen ions in the surroundings of the -N=N- bond of the photochrome which reduces the order of binding between the nitrogen atoms, thus facilitating a freer rotation of parts of the photochromic molecule in the isomerization.

The investigation of the effect of the spacer on the behaviour of similar photochromic systems will continue.

## References

CURTIN, D.Y., GRUBBS, E.J. and McCARTY, C.G.: J.Am.Chem. Soc. 88, 2775 (1966)
DROBNÍK, J., KOPEČEK, J., LABSKÝ, J., REJMANOVÁ, P., EXNER, J., SAUDEK, V. and KÁLAL, J.: Makromol.Chem. 177, 2833 (1976)
FU, TIEH-YIN and MORAWETZ, H.: J.Biol.Chem. 251, 2083 (1976)
HABERFIELD, P., BLOCK, P.M. and LUX, M.S.: J.Am.Chem. Soc. 97, 5804 (1975)
KAMOGAWA, H., KATO, M. and SUGYIAMA, H.: J.Polym.Sci. A/1, 6, 2967 (1968)
LABSKÝ, J. and KÁLAL, J.: Eur.Polym. J. 15, 167 (1979)
LABSKÝ, J., PILAŘ, J. and KÁLAL, J.: Macromolecules 10, 1153 (1977)
LABSKÝ, J., PILAŘ, J. and KÁLAL, J.: Polym.Bull. 1, 585 (1979)
LABSKÝ, J., PILAŘ, J. and KÁLAL,J.: J.Polym.Sci., Polym. Symposia 66, 33 (1979 a)
LJUNGGREN, S. and WETTERMARK, G.: Acta Chem.Scand. 25 (5), 1599 (1971)
LOVRIEN, R. and WADINGTON, J.C.B.: J.Am.Chem.Soc. 86, 2315 (1964)
PAIK, S. and MORAWETZ, H.: Macromolecules 5, 171 (1972)
PILAŘ, J., LABSKÝ, J., KÁLAL, J. and FREED, J.H.: J.Phys.Chem. 83, 1907 (1979)
REJMANOVÁ, P., LABSKÝ, J. and KOPEČEK, J.: Makromol. Chem. 178, 2159 (1977)
SU, CHIN-PAO, and MORAWETZ, H.: J.Polym.Sci., Polym. Chem. Ed. 15, 185 (1977)

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