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Photochromic Polymers

Effect of the Distance of the Photochromic Site on the Discolouration Process of Spiropyrans

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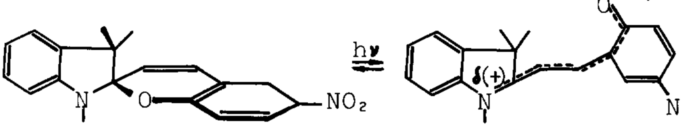
Summary

Two soluble photochromic polymers containing 1'-(ß-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] bound on a variously long side chain were prepared. It was found that the discolouration process depends on the length of the side chain to which the photochromic centre is bound.

Introduction

So far, little attention has been devoted to the investigation of relationships between reactions on soluble polymers and the distance of the reaction site from the main polymer chain. Different rates were determined for aminolytic (CHIN-PAO SU, MORAWETZ 1977; REJMANOVÁ et al. 1977; LABSKÝ, KÁLAL 1979) or enzymatic (DROBNÍK et al. 1976; TIEH-YIN FU, MORAWETZ 1976) reactions depending on the length of the side chain of the soluble polymer. It was found that the mobility of stable nitroxide radicals differed depending on the different length (LABSKÝ et al. 1977) and structure (LABSKÝ et al. 1979; PILAŘ et al. 1979) of the side chain.

The process observed after the irradiation of a molecule of 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] and of many analogous derivatives occurs via splitting of the bond between the spirane carbon atom and oxygen atom followed by rotation of parts of the molecule to occupy an energetically advantageous configuration.



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The process is a reversible one, and after removal of the source of radiation the original spiropyran molecule is recombined. It was found that already in slightly polar media (SMETS 1972; GUGLIELMETTI 1974) this reaction was satisfactory within the whole range of first-order kinetics, and its rate might be affected by temperature, viscosity of the medium, and some other factors.

Recombination of the spiropyran molecule, which may be examined spectroscopically, exhibits rather high steric requirements and has therefore been chosen for the investigation of the effect of the length of the side chain on the rate of the discolouration process of spiropyrans bound on variously long side chains of the soluble polymer.

Experimental

Monomers: 1'-(ß-methacryloyloxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (MA-SP) was prepared by a reaction between methacryloyl chloride and 1'-(ß-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (SMETS 1972). 1'[ß-(12"-methacryloylaminododecanoyloxy)ethyl]-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (MA-11-SP): 5 mmole of 12-methacryloylaminododecanoic acid (LABSKÝ, KÁLAL 1979) (1.5 g) and 5 mmole triethyl amine (0.5 g) were mixed in 20 ml of methylene chloride, and 5 mmole of ethyl chloroformiate (0.55 g) was added with cooling to -10°C. After 30 min., 5 mmole of 1'-(ß-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (1.76 g) was added at once. After 24 h, the reaction mixture was shaken with a 5% solution of $NaHCO_3$ and water. The raw products was crystallized from an ethyl acetate - hexane mixture. M.p.142-5°C. yield 1.5 g (48%).

Analysis	$C_{36}H_{47}N_3O_6$	(617.89)	
calculated	C 69.99	H 7.67	N 6.80
found	C 69.48	H 7.08	N 6.90

Copolymers: Prepared by solution radical polymerization in acetone (60°C, 8 h, 1.5 mass.% AIBN). The polymer solution was precipitated into methanol (150 ml) and reprecipitated twice

Molecular weights were measured by the light scattering method with a Photo-Gonio-Diffusometre Sofica 42 000 apparatus in dioxan (Table 1)

Measurement: The measurements was performed in a Cary 14 spectrophotometer using a 1 cm cell, with the solution thermostated to ± 0.2°C. The polymer solutions in acetone were irradiated with an HBO 200 UV lamp for 2 min. The suitable radiation was obtained by means of a VEB Zeiss Jena interference filter for 365 nm. The rate of the discolouration process was observed using

TABLE 1

Characterization of copolymers of methyl methacrylate with photochromic monomers

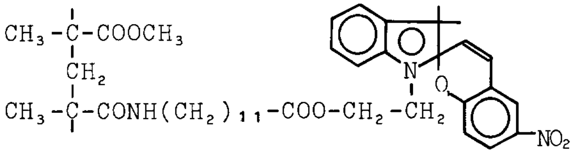
Monomer	SP content (mol.%)	mol.mass $\overline{M}_w$
MA-SP	2.5	48 000
MA-11-SP	2.1	65 000

The content of spiropyrans was determined spectroscopically, $\varepsilon = 3.4 \times 10^4 1\ \mathrm{cm}^{-1}\ \mathrm{mol}^{-1}$ at 360 nm

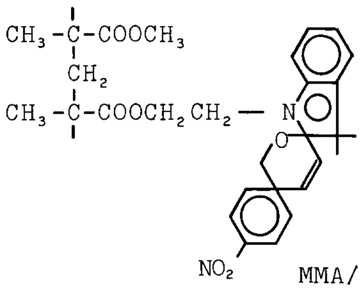
the decrease in absorption at a constant wavelength, λ = 570 nm. The SP concentration in solution was always 1.8×10^{-3}M.

Results and Discussion

Copolymerization of spiropyran monomers 1'-(ß-methacryloyloxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (MA-SP) and 1'-(12''-methacryloylaminododecanoyloxy)ethyl -3',3'-dimethyl-6-nitrospiro [2H-1-benzopyran-2,2'-indoline](MA-11-SP) with methyl methacrylate yielded soluble polymers MMA/MA-SP and MMA/MA-11-SP with a low content of spiropyran molecules, so that it may be assumed that spiropyran structural units do not affect each other (LABSKÝ, KÁLAL 1979)



MMA/MA-11-SP



MMA/MA-SP

It was found that for both polymers the rate of recombination of the spiropyran molecule in acetone followed the first-order kinetics within the whole range (Table 2)

TABLE 2

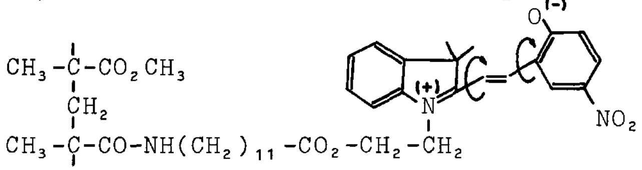
Rate constants (k_1) of recombination of the spiropyran skeleton and of the frequency factor (A) of photochromic polymers in acetone

Photochromic system	Rate constant $k_1 \times 10^4$, s^{-1}					A, s^{-1}
T, °C	14	19	23	27	31	
MMA/MA-SP	5.1	9.7	14.9	24.7	50.0	1.04×10^{14}
MMA/MA-11-SP	12.8	22.5	39.4	63.8	103.4	2.64×10^{14}

The activation energy of this photochromic process is the same for both polymers: 87 J/mole (22.8 kcal/mole).

Recombination of the spiropyran skeleton which takes place after removal of the source of radiation is accompanied by rotation of split parts of the molecule from the sterically advantageous structure of the merocyanine molecule to the sterically different molecule of spiropyran (GUGLIELMETTI 1974, FLANNERY 1968). The shift of parts of the molecule necessary for recombination of the original molecule of spiropyran has considerable steric requirements and may be strongly hindered by the presence of the polymer chain.

For the sake of illustration, one of the probable configuration of merocyanine after irradiation of the polymer solution MMA/MA-11-SP is given below.



The indicated rotations needed for the formation of the spiropyran molecule may be slowed down by interaction of parts of the rotating molecule with the polymer chain.

The different rates of the discolouration reaction of spiropyrans obtained for the recombination reaction on variously long side chains of soluble methyl methacrylate copolymers may be explained by the fact that the larger distance of the photochromic site in the copolymer MMA/MA-11-SP facilitates the recombination of the spiropyran molecule compared with the copolymer MMA/MA-SP. The higher rate of recombination of the photochromic molecule in the polymer MMA/MA-11-SP is due to the higher frequency factor compared with MMA/MA-SP. The frequency factor generally involves the activation energy of recombination, which represents the steric factor in the reaction and is a measure of statistically possible configurations of the molecule in the formation of an activated complex, in agreement with our qualitative interpretation.

An investigation of analogous photochromic systems is forthcoming.

References

DROBNÍK, J., KOPEČEK, J., REJMANOVÁ, P., EXNER, J., SAUDEK, V., KÁLAL, J.: Makromol.Chem. 177, 2833 (1976)
FU, T.-Y., MORAWETZ, H.: J.Biol.Chem. 251, 2083 (1976)
FLANNERY, J.B., Jr.: J.Am.Chem.Soc. 90, 5660 (1968)
GUGLIELMETTI, R.: J.Photographic Sci. 22, 77 (1974)
LABSKÝ, J., KÁLAL, J.: Eur.Polym.J. 15, 167 (1979)
LABSKÝ, J., PILAŘ, J., KÁLAL, J.: Macromolecules 10, 1153 (1977)
LABSKÝ, J., PILAŘ, J., KÁLAL, J.: J.Polym.Sci., Polym. Symposia, 66, 33 (1979)
REJMANOVÁ, P., LABSKÝ, J., KOPEČEK, J.: Makromol.Chem. 178, 2159 (1977)
SMETS, G.: Pure Appl.Chem. 30, 1 (1972)
SU, Ch.-P., MORAWETZ, H.: J.Polym.Sci., Polym.Chem.Ed. 15, 185 (1977)

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