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Photoresponsive polymers

V. Preparation and polymerization of methacrylic acid-[1-((4-phenylazo)-phenylazo)]-2-naphthyl-ester

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Summary

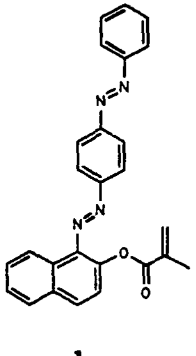
The preparation and polymerization behavior of methacrylic acid-[1-((4-phenylazo)-phenylazo)]-2-naphthyl-ester 1 is described. 1 shows a retarding effect on radical polymerization. Unipolymers could not be obtained and the copolymer of 1 and methacrylic acid sets free Sudan Red III by ester cleavage. Investigations of the photoisomerization of the azo monomer shows only a poor effect.

Introduction

In the recent years there has been an increasing interest in photoresponsive polymers. Such polymers are macromolecules which have chromophores in their backbone or as pendant groups. The chromophores should reversibly change their properties upon irradiation. The response time should be in the range of seconds or minutes to find technical applications. Appropriate chromophores are

- azogroups: using the trans/cis stereoisomeric effect of the azo group
- spiropyranes: using the spiro/merocyanine-photoisomerization
- triphenylmethane dyes: using the dissociation of carbinoles, cyanides or sulfites into the stable triphenylmethyl cation and the correspondent counterion.[1,2]

In this paper we describe the preparation of the new azomonomer methacrylic acid-[1-((4-phenylazo)-phenylazo)]-2-naphthyl-ester 1 and the results of uni- and copolymerization experiments. In addition the photoisomerization of the monomer was investigated.



1

Experimental

All solvents were purified and dried by usual procedures.

Preparation of the monomer 1: To an ice-cooled solution of Sudan Red III 2 (Fluka) and triethylamine in benzene or toluene a solution of a threefold excess of methacryloylchloride in the same solvent was added drop-

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*Author to whom all correspondence should be addressed wise. The reaction mixture was stirred 5–10 days at room temperature until the conversion of **2** was complete (confirmed by thin-layer-chromatography). After filtering off the triethylamine hydrochloride the reaction mixture was poured into an excess of ice-cooled diluted hydrochloric acid. The organic layer was separated, diluted with ether and washed with 0.5 N hydrochloric acid, sat. sodiumhydrogencarbonate solution and water. The solvents were removed under reduced pressure and the crude product was purified by repeated recrystallization from ethanol.

- yield: 70%
- m.p.: 116°C (389 K)
- ^{1}H NMR ($CDCl_3$): δ = 2.08 (t; 3 H α-methylgroup), 5.79 and 6.36 (dq; 2 H, geminale protons of methacrylic acid), 7.2 – 8.2 (m; 14 H, aromatic protons), 8.74 ppm (m; 1 H, proton of C8 of naphthalene)
- IR (KBr): 3050 (w, C=H), 2920 (w, C–H) 1725 (s, C=O), 1130 (s, C–O), 850 and 940 cm^{-1} (w, C=C)
- UV (cyclohexane): λ_{max} = 341, 387 and 480 nm
- analysis: $C_{26}H_{20}N_4O_2$ (420.47) Calc. C 74.27 H 4.79 N 13.33
  Found C 74.13 H 4.79 N 12.74

Copolymerization of **1** *with methacrylic acid* **3**[3)]*:* The copolymerizations were carried out in tetrahydrofuran (conc. of the monomers 0.9 mol/l) initiated with AIBN. The conditions are given in table 1. The copolymers were precipitated into petroleum ether and filtered off. The polymer was reprecipitated five times from THF/petroleum ether, filtered off and dried i.vac.

Table 1: Radicalic copolymerizations of **1** with **3**

No.	[**3**] mol%	[**1**] mol%	[AIBN] mol% (1)	T °C	time h
1	97.6	2.4	1.9	55	70
2	94.9	5.1	3.1	55	71
3	90.0	10.0	4.8	55	65

(1) concerning the total amount of the comonomers

Photoisomerizations: Irradiations were carried out with a Philips HPK 125 W high pressure mercury lamp and the wavelength of illumination was selected with the aid of Dema filters (UVW-55, 300 nm < λ < 400 nm and FW-161, λ > 470 nm). The UV/VIS-spectra were recorded with a Perkin Elmer Lambda 5 Spectrometer. To ensure the same defined conditions in all experiments, the solutions were irradiated for 40 min at λ > 470 nm before irradiating at 300 nm < λ < 400 nm for UV/VIS-measurements of trans-cis-isomerization.

Dilatometer: The experiments were carried out in a capillary tube with 0.7 mm in diameter thermostated at 60±0.1°C. The polymerization was initiated by AIBN. Concentrations are given in table 2.

Table 2: Solutions for measurements in the dilatometer

No.	[AIBN] mol/l (1)	[azodye] mol/l	[azodye] mol% (2)
1	0.043	-	-
2 (3)	0.043	0.0430	0.50
3	0.043	0.0043	0.05
4	0.043	0.0220	0.25
5	0.043	0.0430	0.50

(1) 0.5 mole% concerning styrene
(2) concerning styrene
(3) azobenzene

Results and discussion

The polymerizable azo dye 1 was obtained by esterification of Sudan Red III 2 with methacryloylchloride. To obtain the methacrylic acid-[1-((4-phenylazo)-phenylazo)]-2-naphthyl-ester 1 in good yields it is necessary to use the strong basic triethylamine (pk_a = 10.65[4]) and to apply an excess of methacryloylchloride.

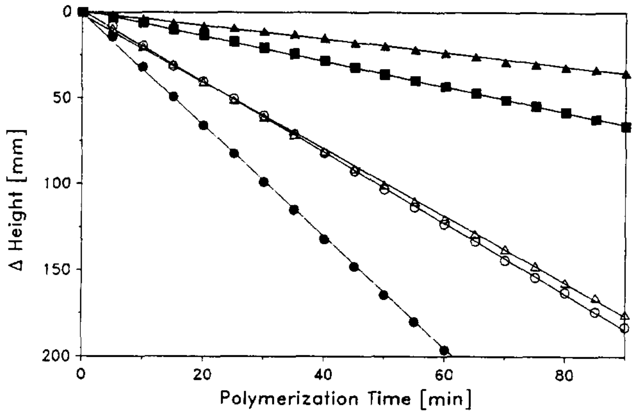

Fig. 1.
Dilatometer measurement of the rate of polymerisation of styrene in the presence of different contents of azo dyes.
(▲) styrene + 0.5% 1
(■) styrene + 0.25% 1
(△) styrene + 0.5% azobenzene
(o) styrene + 0.05% 1
(●) styrene

It is well known that azobenzene derivates have retarding or inhibiting effects on radical polymerizations. These effects are due to the formation of a stable hydrazyl radical.[5] To investigate the retarding effect of 1 dilatometer experiments were carried out with the following solutions: styrene, styrene with different amounts of 1 and and styrene with azobenzene. As a result of the measurements 1 as well as azobenzene shows a retarding effect. Increasing the concentration of 1 increases the retarding effect. Comparing the same concentrations of azogroupequivalents of 1 and azobenzene, the effect of azobenzene is much lower than of 1.

Unipolymers of the monomer 1 could not be obtained.

Copolymerizations of **1** with methacrylic acid **3** were carried out in THF, a solvent which dissolves both the water soluble **3** and the organic soluble **1**, with AIBN as initiator. The polymerization time had to be extended to 70 h because of the retarding effect of the azo dye as seen in the dilatometer experiments. In spite of long polymerization times the conversion of the monomer is not complete, **1** and **3** were still detectable in the reaction mixture after the polymerization. It is remarkable that during the reaction Sudan Red III **2** was set free. This is due to an ester cleavage of **1** into **2** and methacrylic acid probably caused by the acidic protons of the methacrylic acid.

Isomerization of the azo group causes a change of the UV/VIS absorption.[6] The UV/VIS-spectra of **1** show that under the chosen conditions almost no isomerization occures. It is possible that the cis-isomer is so unstable that it cannot be obtained. Surprisingly, in spite of the absence of acidic protons Sudan Red III **2** was set free upon irradiation.

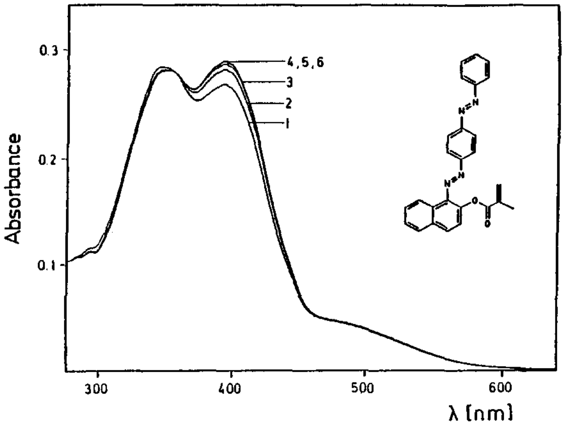

Fig. 2.
Absorption spectra of **1** ($c = 1.119 \cdot 10^{-5}$ mol/l) in cyclohexane after different periods of irradiation at 360±50 nm.
1: before irradiation
2: 1 min
3: 3 min
4: 7 min
5: 15 min
6: 31 min

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