

Photo-Crosslinking of Copolymeric Methacrylates Bearing Stilbene Chromophores

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Radical polymerization of methyl methacrylate (**2**) as major component and the methacrylates **1a** or **1b**, which contain an (*E*)-stilbene unit fixed by a tether to the ester group, yield easily soluble copolymers **3a, b**. Whereas the dominant photoreactions in solution are (*E*) \rightleftharpoons (*Z*) isomerizations and intra-chain $[2\pi + 2\pi]$ cycloadditions, cast films of **3a, b** give an inter-chain photo-crosslinking on irradiation. Compared to homopolymers, the copolymers are not only better soluble and more easily processible, their films show less undesired light scattering. The cross-linked material is completely insoluble in organic solvents. Thus, it represents the basis for negative photoresists and the corresponding imaging techniques.

Key words: Radical Copolymerization, Stilbene Chromophore, Negative Photoresist

Introduction

(*E*)-Stilbene derivatives can be used as photoreactive building blocks or dopants in materials for imaging or resist techniques [1–8]. Recently we reported on polymethacrylates with (*E*)-stilbene chromophores in the side chains [9]. Similar results were obtained for stilbenoid dendrimers some years ago [10].

A certain drawback of compounds which contain many (*E*)-stilbene units is due to the normally low solubility in organic solvents, a fact which causes difficulties in the processing of such materials. The film-forming properties of homopolymethacrylates with stilbene building blocks in each side chain are very limited. We have tried now to improve the solubility by the use of copolymeric methacrylates which contain relatively few (*E*)-stilbene units.

Results and Discussion

A radical copolymerization of the methacrylates **1a** or **1b** and **2** in the presence of azoisobutyronitrile (AIBN) gave the desired polymers **3a, b** in good yields (Scheme 1). The portion of the (*E*)-stilbene-containing monomer **1a** was varied thereby from 3 to 30 mol-%. ¹H NMR spectra of the copolymers **3a-x** (*x* = 1–6)

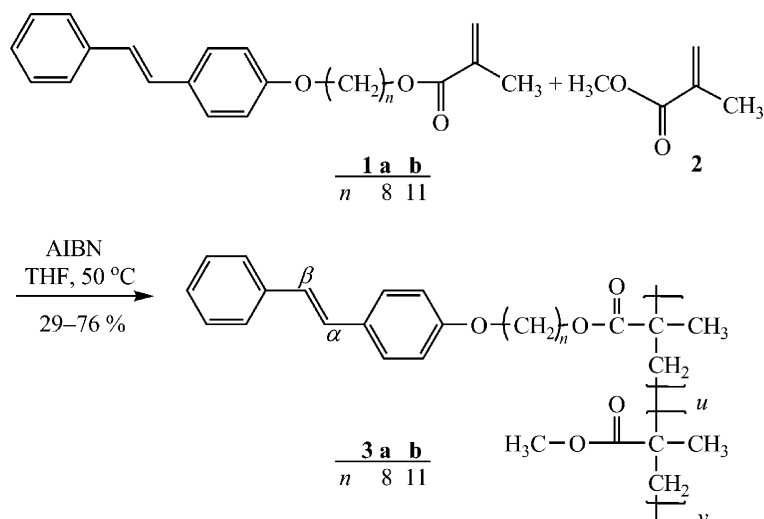
Table 1. GPC measurements.

	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	Polydispersity
Copolymer 3a-6	21.7	34.7	1.6
Homopolymer of 1a [9]	17.3	38.9	2.2
Copolymer 3b-2	11.8	22.1	1.9
Homopolymer of 1b [9]	6.2	25.8	4.2

showed within the limits of error that the ratio **1a** : **2** given at the start was maintained in the product of polymerization. That means a preference in the reactivity of **1a** or **2** could not be observed. The same effect was found for the copolymerization of **1b** and **2** to give **3b-x** (*x* = 1, 2). The yields of the copolymers increase with increasing concentration (see Experimental Section).

DSC measurements revealed glass transitions for all copolymers. The *T_g* values normally decrease with increasing portions of **1a** and **1b**. The solubility of the copolymers **3a, b** in CH₂Cl₂, CHCl₃ or C₆H₆ is much higher than the solubility of the homopolymers of **1a** or **1b**.

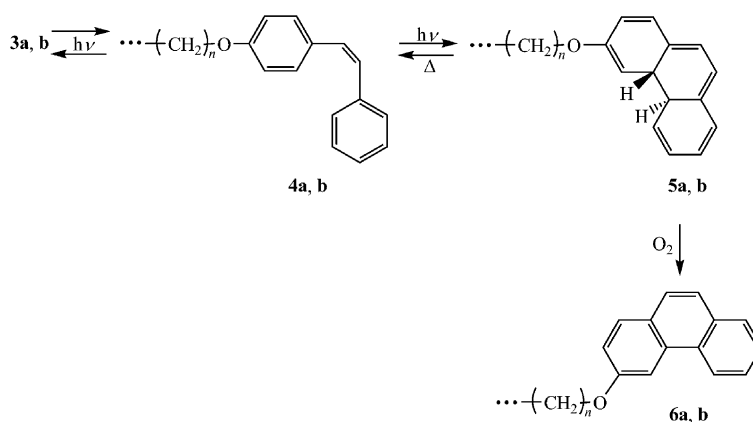
The molecular masses of **3a-6** and **3b-2** were determined by gel permeation chromatography (GPC) in CHCl₃ by applying polystyrene standards. Table 1 shows a comparison with the corresponding homopolymers.



	3a-1	3a-2	3a-3	3a-4	3a-5	3a-6
Portion of 1a , mol-%	3.75	8.33	7.45	8.59	17.83	28.87
T_g , °C	101	87	78	72	76	59

	3b-1	3b-2
Portion of 1b , mol-%	21.96	30.27
T_g , °C	51	48

Scheme 1. Preparation of copolymers of different methacrylates.

Scheme 2. Monomolecular reactions of the stilbene units in the copolymers **3a, b** in the presence of air.

Irradiation of the polymers **3a, b** in solution in benzene or dichloromethane led in all cases to an *E/Z* equilibration of the stilbene moiety (Scheme 2). The original absorption maximum of **3a, b** at $\lambda = 326$ nm in CH_2Cl_2 was shifted to the region of 283 ± 8 nm. In the

presence of air, an irreversible formation of phenanthrene units occurred. The process was not studied in detail, but the structured UV spectra in the region between 320 and 360 nm and the ^1H NMR singlet signals at low field ($\delta = 7.50 \pm 0.05$ ppm) [11] provide an

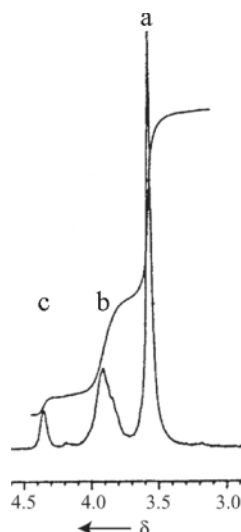
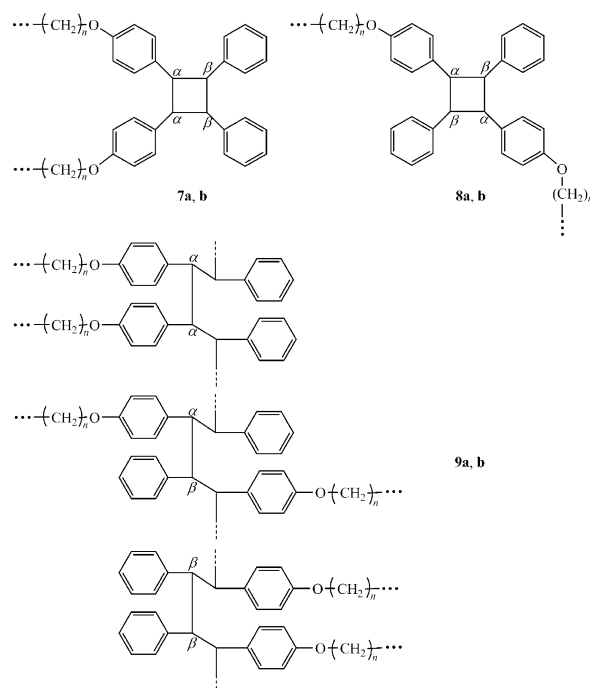


Fig. 1. Partial ^1H NMR spectrum (CDCl_3 , TMS as internal standard) of **3a-6** irradiated in CH_2Cl_2 ($\lambda > 300\text{ nm}$).

easy proof for the generation of phenanthrene. Therefore, degassed solutions of **3a, b** have to be used for the photo-crosslinking experiments.

Although the number of (*E*)-stilbene units in the copolymer chains was much lower than in the homopolymers [9], the irradiation in solution (CH_2Cl_2 or C_6H_6 , $\lambda \geq 300\text{ nm}$) led predominantly to intra-chain reactions to give **7a, b** (Scheme 3). The corresponding $[2\pi + 2\pi]$ photocycloaddition worked very well for **3a-6** and **3b-1, 2**. The copolymers **3a-1-3a-5**, which have a portion of monomer **1a, b** of less than 20 mol-%, dimerized very slowly or not at all. Fig. 1 shows the important part of the ^1H NMR spectra between $\delta = 3.5$ and 4.5 ppm . The sharp singlet signal **a** at 3.56 ppm belongs to the OCH_3 groups and the broad signal **b** between 3.75 and 4.05 ppm to the different OCH_2 groups. As mentioned before, the ratio of these signals corresponds to the molar ratio at the start of the copolymerization. The signal **c** at 4.35 ppm grows during the irradiation. It results from head-to-head and head-to-tail stilbene dimers as in the case of the homopolymers [9]. Both regioisomers have predominantly a stereochemical arrangement in which each proton of the four-membered ring has only one *cis*-standing phenyl neighbor. 1,2,3,4-Tetraphenylcyclobutane derivatives with cyclobutane protons which have two *cis*-standing benzene ring neighbors give signals for the ring protons at $\delta =$



Scheme 3. Bi- and polymolecular photoproducts of the stilbene units in the copolymers **3a, b**.

$3.6-3.7\text{ ppm}$ [12]. The photodimerization came to an end after 48 h. The ratio of the signals **b**:**c** revealed that 35% of the stilbene units had reacted. The formation of crosslinked material, that means the generation of CC single bonds between different chains appears to be very rare. The amount of insoluble material is below 5%.

The situation was completely different when cast films were irradiated ($\lambda = 366\text{ nm}$). Fig. 2 shows that the absorption of the stilbene building block disappeared. More and more insoluble material was formed, when films of **3a-x** ($x = 1-6$) or **3b-x** ($x = 1, 2$) were irradiated. This behavior is fairly independent of the portion of **1a** and **1b** present in the copolymers **3a, b**. Therefore, the very well soluble copolymers **3a-x** ($x = 1-3$), which have a low portion of stilbene units, are best suited. Another advantage of the copolymer films is due to the fact that no light scattering can be observed ($\lambda > 360\text{ nm}$). The tendency to form microcrystals is higher in the homopolymer films. The proof for the structures **7, 8** and **9** (Scheme 3) have already been proven for the homopolymers [9]. Solid-state ^{13}C NMR is thereby a very valuable tool.

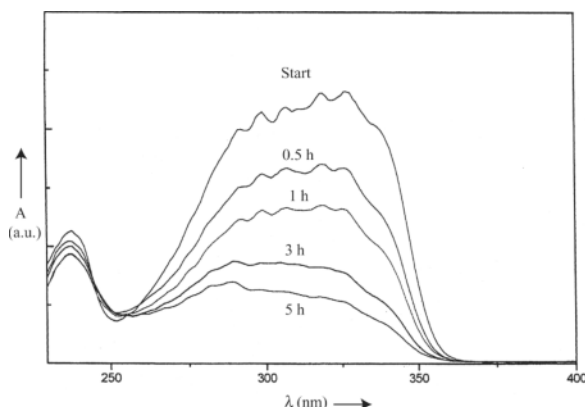


Fig. 2. Reaction spectra of the irradiation ($\lambda = 366$ nm) of a film of **3a-3** cast from a concentrated solution in benzene.

Conclusion

Copolymers of two methacrylates, of which the minor component contains an (*E*)-stilbene unit fixed by a tether on the COO group, show different photoreactions. Apart from the $E \rightleftharpoons Z$ isomerization, intra-chain $[2\pi + 2\pi]$ cycloadditions of the (*E*)-stilbene units occur when the average density of this unit in the chain is high enough.

In cast films, however, an inter-chain photocrosslinking is triggered by irradiation. An insoluble material is formed. This process represents the basis for imaging techniques and photoresists. The advantage of copolymers with a relatively low percentage of stilbene units, compared to homopolymers, is given by the much better solubility and processability of the copolymers. Moreover, the undesired light scattering of the copolymer films is lower than that of the homopolymer films.

Experimental Section

Glass transitions were determined with a differential scanning calorimeter DSC-7 from Perkin-Elmer. UV/Vis spec-

tra were measured with a diode array spectrometer MCS-224/MCS-234 from Zeiss, and IR spectra with a Beckman Acculab 4 instrument. GPC was performed with a Program Millenium-2010 device and polystyrene standards from PSS (CHCl_3 as eluent). ^1H NMR spectra were recorded with an AM-400 spectrometer from Bruker. CDCl_3 served as solvent and TMS as internal standard.

Copolymerization of the methacrylates **1a**, **b** and **2**

Argon was purged through dry THF (30–50 mL) for 15–20 min in order to get an oxygen-free solvent. Monomer **1a** or **1b**, freshly distilled methyl methacrylate (**2**), and AIBN were added in a ratio shown in Table 2. The mixture was stirred at 60 °C in an argon atmosphere, and after the reaction time registered in Table 2 about 500 mL of water were poured in. A precipitate was formed which was twice dissolved in THF and precipitated with cold methanol in order to remove unreacted monomers. The obtained solid was carefully dried at 0.1 kPa.

The copolymers are colorless solids which have similar IR spectra, showing (in KBr) strong bands at 2940, 1720, 1245, and 1150 cm^{-1} .

An increasing content of (*E*)-stilbene building blocks is documented by increasing band intensities at 1510 and 960 cm^{-1} . The T_g values are listed in Scheme 1. The ^1H NMR spectra of **3a** and **3b** are very similar: δ (CDCl_3) = 0.7–2.1 (CH_3 , CH_2), 3.5–3.6 (OCH_3), 3.8–4.0 (OCH_2), 6.8–7.5 ppm (aromat. and olefin. H).

Irradiation in solution

About 300 mg of **3a-x** ($x = 1-6$) or **3b-x** ($x = 1, 2$) was dissolved in degassed, dry and thiophene-free benzene or CH_2Cl_2 (20 mL) and irradiated under argon with a Hanovia-450 W medium-pressure Hg lamp equipped with a Pyrex filter ($\lambda \geq 300$ nm). After 48 h the solvent was removed and the beige residue carefully dried at 0.1 kPa. The UV, IR and ^1H NMR spectra of all probes are very similar. – UV (CH_2Cl_2): broad absorption band with a maximum at $\lambda_{\text{max}} = 282$ nm. – IR (KBr): strong bands at $\nu = 1710, 1500, 1235$ and 1170 cm^{-1} . – ^1H NMR (CDCl_3): $\delta = 0.7-2.1$ (CH_3 , CH_2), 3.5–3.6 (OCH_3), 3.8–4.1 (OCH_2), 4.3–4.4 (4-ring protons), 6.5–7.6 ppm (aromat. and remaining olefin. H).

Copolymer	1a mg (mmol)	2 mg (mmol)	AIBN mg (mmol)	THF (mL)	Reaction Time (h)	Yield mg (%)
3a-1	177 (0.45)	1157 (11.56)	94 (0.57)	30	22	391 (29)
3a-2	392 (1.0)	1100 (11.0)	92 (0.56)	50	15	527 (35)
3a-3	357 (0.91)	1132 (11.31)	103 (0.62)	30	22	758 (51)
3a-4	392 (1.0)	1065 (10.64)	100 (0.61)	50	24	876 (60)
3a-5	1040 (2.65)	1223 (12.21)	40 (0.24)	30	24	1294 (57)
3a-6	1872 (4.77)	1176 (11.75)	35 (0.21)	30	24	2313 (76)
3b-1	1431 (3.29)	1171 (11.69)	41 (0.25)	40	24	1550 (60)
3b-2	2362 (5.44)	1255 (12.53)	55 (0.33)	50	24	2354 (65)

Table 2. Reaction conditions of the copolymerizations **1a** + **2** \rightarrow **3a-x** ($x = 1-6$), **1b** + **2** \rightarrow **3b-x** ($x = 1, 2$).

Irradiation of cast films

Saturated solutions (ca. 3 mL) of **3a-x** ($x = 1-6$) or **3b-x** ($x = 1, 2$) in CHCl_3 or thiophene-free benzene were poured onto quartz plates. After complete evaporation of the solvent at $40^\circ\text{C}/10\text{ kPa}$, transparent films remained which were monochromatically irradiated (366 nm filter) for 6 h. Transparent, completely insoluble films were obtained which gave

a panchromatic absorption between 230 and 360 nm with a maximum at $\lambda = 236 \pm 5\text{ nm}$. The crosslinked polymers do not show a glass transition nor a melting point.

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