# Photo-Cross-Linking of Polymethacrylates with Stilbene Chromophores in the Side Chains

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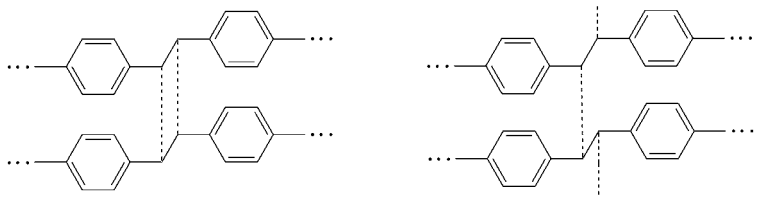
Methacrylates (=2-methylpropenoates) **5** with (*E*)-stilbene (=(*E*)-1,2-diphenylethene) building blocks on tethers of variable length were prepared (*Scheme 2*) and polymerized (*i.e.*, **5** → **6**; *Scheme 3*) in the presence of AIBN (=2,2′-azobis(2-methylpropanenitrile). 4-[(*E*)-2-Phenylethenyl]phenyl acetate (**7**) as model compound established the cyclodimerization as a single irreversible photoreaction. *i.e.*, (**7** → **8**–**11**; *Scheme 4*) in the absence of oxygen. The solution photolysis of the polymers **6** provided a similar result, whereby [2π + 2π] cycloadditions of stilbene units of neighboring tethers predominated. On the contrary, the desired photo-cross-linking of chaines occurred in the irradiation of polymer films.

**1. Introduction.** – Various stilbene (=1,2-diphenylethene) derivatives have been used as building blocks or dopants in materials for photochemical imaging and resist techniques [1–8]. On the other hand, irradiation of oligomers or polymers with stilbene units in the main chain leads often to undesired photoreactions, which make the material worse or even useless [8]. Similar observations have been made for stilbenoid dendrimers [9].

The major irreversible photoprocess of stilbene substructures in the absence of oxidants is due to the formation of C–C bonds between the initially olefinic C-atoms. Apart from the well-known concerted [$\pi^2$s + $\pi^2$s] cycloadditions to four-membered rings, radical reactions can occur, which lead to a cross-linking of several stilbene units [8][9]. The latter process is particularly important when energy-rich UV light is used. *Scheme 1* illustrates the two C–C bond-forming processes.

Scheme 1. *Formation of C–C Bonds by Irradiation of Stilbene Building Blocks in Oligomers, Dendrimers,* etc.



We tried now to apply these C–C bond formations for the development of imaging techniques and the generation of photoresists by photo-cross-linking of polymers that contain (*E*)-stilbene units in the side chains.

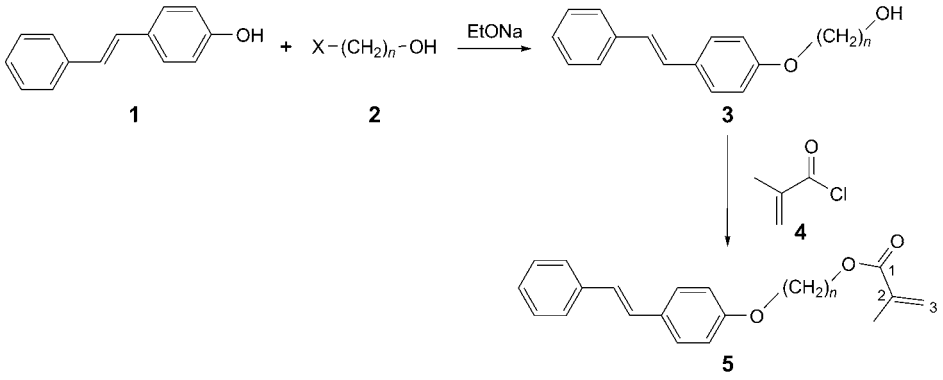
Such polymers can be prepared by applying two strategies: either by polymer-analog reactions, in which prepolymers with suitable functionalities are reacted with compounds, which contain stilbene units or form them in this process [1][10–13], or by polymerization of monomers, which already contain stilbene building blocks [1][14–18]. We decided to use the second concept and prepared various polymethacrylates (= poly(2-methylpropenoates)).

So far, polymethacrylates with stilbene building blocks in the side chains have been studied mainly in the context of liquid-crystalline phases and/or optoelectronic effects [15][19–39].

**2. Results and Discussion.** – Our target molecules were polymethacrylates with side chains which have (*E*)-stilbene chromophores on variable tethers. The length of the side chains could have a considerable influence on the film-forming properties and possibly on the photoreactions within one polymer chain, or between two or more stilbene units which belong to different main chains. For this purpose, a variety of methacrylates **5a**–**5f** were synthesized which contain terminal (*E*)-stilbene units on a tether of variable length.

4-(*E*)-Styrylphenol (=4-[(*E*)-2-phenylethenyl]phenol; **1**) was alkylated by ω-bromo- or chloro-alkanols **2a**–**2f** in the presence of EtONa (*Scheme 2*). The yields reach a maximum for **2f** ($n=11$) and a minimum for **2c** ($n=5$), because 5-chloropentan-1-ol cyclizes under these conditions to tetrahydropyran. The resulting ω-(4-styrylphenoxy)alkanols **3a**–**3f** were then subjected to *Einhorn* reactions with 2-methylacryloyl chloride (**4**). The obtained methacrylates **5a**–**5f**, as well as the alcohols **3a**–**3f**, showed decreasing melting points with increasing chain length (ester **5f** with eleven $CH_2$ groups is an exception).

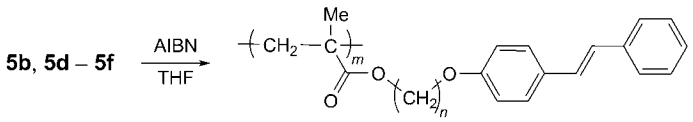
Scheme 2. *Preparation of ω-{4-[(*E*)-2-Phenylethenyl]phenoxy}alkyl 2-Methylprop-2-enoates* **5a**–**5f**




| | *n* | X | **3** | Yield of **3** [%] | M.p. of **3** [°] | **5** | Yield of **5** [%] | M.p. of **5** [°] |
|---|---|---|---|---|---|---|---|---|
| **2a** | 2 | Br | **3a** | 45 | 162 | **5a** | 45 | 100 |
| **2b** | 3 | Cl | **3b** | 37 | 163 | **5b** | 54 | 94 |
| **2c** | 5 | Cl | **3c** | 20 | 148 | **5c** | 51 | 89 |
| **2d** | 6 | Cl | **3d** | 41 | 144 | **5d** | 87 | 82 |
| **2e** | 8 | Cl | **3e** | 72 | 141 | **5e** | 77 | 75 |
| **2f** | 11 | Br | **3f** | 83 | 140 | **5f** | 80 | 85 |

Radical polymerization of the selected methacrylates **5b** and **5d**–**5f** afforded the polymers **6b** and **6d**–**6f**, respectively. Monomer concentrations of 0.2M in THF were used; 6 mol-% of AIBN (=2,2′-azobis(2-methylpropanenitrile)) led in 20–22 h to the yields compiled in *Scheme 3*. The polymers were moderately soluble in benzene, $CHCl_3$, THF, *etc*. Their molecular masses were estimated by gel permeation chromatography (GPC) in $CHCl_3$ by using polystyrene standards. The obtained $M_w$ values were in the range of $30 \times 10^3$ D, only **6d** was an exception with almost $M_w$ of $200 \times 10^3$ D. The polydispersity was broad – in particular for **6d**: $M_w/M_n = 17.96$. The melting of the polymers **6** was studied by differential scanning calorimetry (DSC; *Table*). None of the polymers exhibited liquid-crystalline properties.

Scheme 3. *Polymerization* **5** → **6** *in the Presence of AIBN*




| | *n* | Yield [%] | $10^{-3}$ $M_n$ | $10^{-3}$ $M_w$ |
|---|---|---|---|---|
| **6b** | 3 | 80 | 18.3 | 33.4 |
| **6d** | 6 | 72 | 10.9 | 195.8 |
| **6e** | 8 | 85 | 17.3 | 38.9 |
| **6f** | 11 | 82 | 6.2 | 25.8 |

Table. *Phase Transitions of the Polymers* **6b** *and* **6d**–**6f**: *Maxima in the Differential Scanning Calorimetry*

| Compound | Second heating curve | | Second cooling curve |
|---|---|---|---|
| | *T* [°] | Δ*H* [J/g] | *T* [°] |
| **6b** | 162 | 24 | 147 |
| **6d** | 124 | 27 | 114 |
| **6e** | 120 | 21 | 111 |
| **6f**[a]) | 121 | 24 | 116 |

[a]) Compound **6f** has an additional glass transition, which appears at $T_g$ 68° in the second heating curve.

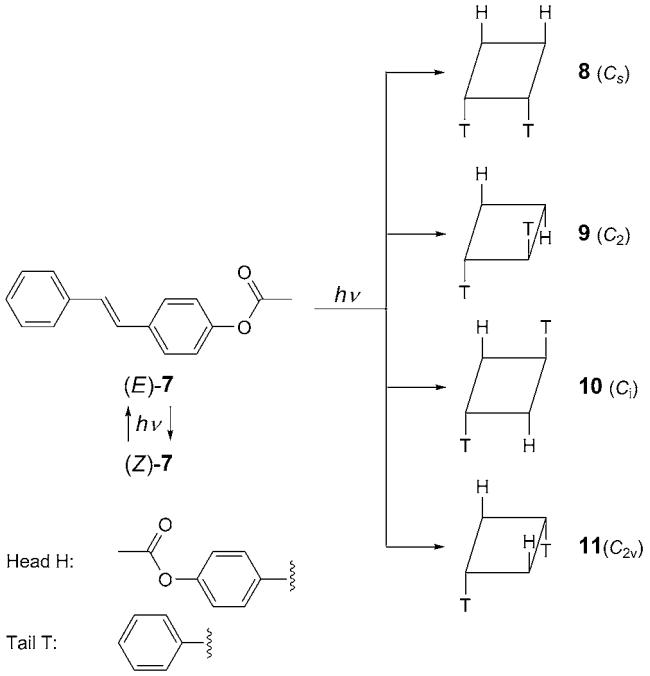
The UV absorption of the polymers **6** corresponds to the absorption of the monomers **5**; **5e** and **6e**, for example, have both in $CH_2Cl_2$ maxima at $\lambda_{max}$ 326 nm and $\varepsilon$ values of 15180 and 16120 $cm^{-1}$ $M^{-1}$, respectively. In the IR spectra in KBr, the band at 1630 $cm^{-1}$, which is typical for the unsaturated esters **5**, lacks in the polymers **6**. The $^1$H-NMR spectra of **6** in $CDCl_3$ contain broad signals. The region $5.5 \leq \delta \leq 6.1$ ppm, which contains the signals of the olefinic *AB* part of an $ABX_3$ spin system of **5**, is empty in the $^1$H-NMR spectra of **6**. $^{13}$C-NMR Solution spectra of **6** were not obtained because of the low solubility. The solid-state cross-polarization magic-angle spirring (CP-MAS) $^{13}$C-NMR spectrum of **6e** (*cf. Fig. 2*), contains, in the region $4 \leq \delta \leq 60$ ppm, the signals of $C_q$-atoms and $CH_2$ group of the main chain – originally $sp^2$-C atoms in the monomer **5e**, now $sp^3$-C-atoms.

The photodimerization of (*E*)-stilbene derivatives has been studied for a variety of compounds [8]. The regio- and stereoselectivity of the dimerization depends strongly on the special system and on the reaction conditions. Among the investigated examples, 4-methoxystilbene [40][41] represents the only 4-alkoxy compound – comparable to **5a**–**5f**. However, the irradiation of 4-methoxystilbene was performed for an inclusion complex in $\gamma$-cyclodextrin, a constrained medium [40]. The obtained mixture of *syn*-head-to-tail and *syn*-head-to-head dimers was characterized without separation by a $^1$H-NMR spectrum. *anti*-Head-to-head and *anti*-head-to-tail cycloadducts were not found. Moreover, it was shortly stated that the solution photolysis was very inefficient [40].

These results motivated us to study first a model compound. We selected 4-[(*E*)-2-phenylethenyl]phenol acetate ((*E*)-**7**) [42]. Irradiation ($\lambda > 290$ nm) of a 0.12M solution of (*E*)-**7** in oxygen-free benzene yielded (*Z*)-**7** and the dimers **8**–**11** (*Scheme 4*). *Fig. 1* depicts the amounts of (*E*)-**7**, (*Z*)-**7**, and **8**–**11** *vs.* the irradiation time. The long-wavelength absorption bands of (*E*)-**7** ($\lambda_{max}$ 312 nm; $CH_2Cl_2$) and (*Z*)-**7** ($\lambda_{max}$ 282 nm; $CH_2Cl_2$) overlapped in the irradiation range; both isomers absorbed light, but the photodimerization (*E*)-**7** → **8**–**11** prevented the formation of a photostationary state (*E*)-**7**/(*Z*)-**7**. A photo-oligomerization could not be observed under these conditions. However, when 254-nm light was used, a small amount of polymers was generated.

The dimers **8** and **10** were obtained in a pure state by column chromatography and fractionary crystallization; **9** and **11** were obtained as a mixture. The total yield of

Scheme 4. *Photoreactions of* (E)-**7**



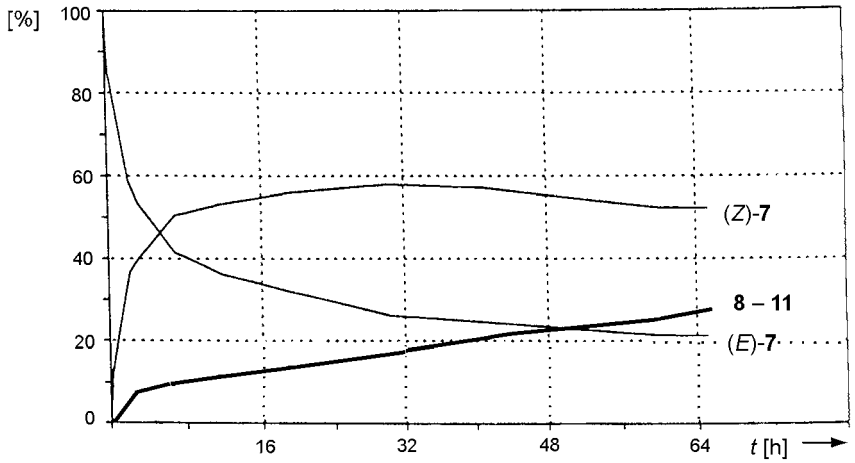



Fig. 1. *Product formation from the irradiation of* (E)-**7** (0.12M in oxygen-free benzene) *with a 450-W medium-pressure Hg lamp equipped with a* Pyrex *filter* ($\lambda \geq 290$ nm)

dimers (*Fig. 1*) amounted to 23% after a reaction time of 44 h, the corresponding distribution: **8**/**9**/**10**/**11** was *ca.* 40 : 18 : 40 : 2.

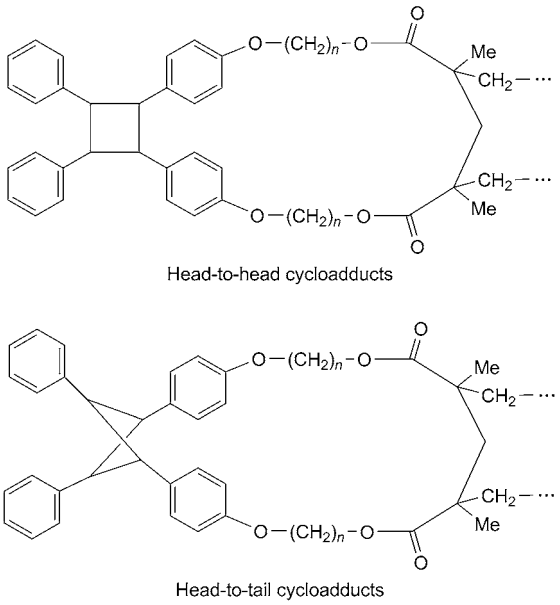
The structure determination of **8**–**11** is based on NMR and MS data. The differentiation between the head-to-head fraction **8**/**9** and the head-to-tail fraction **10**/**11** was achieved by the orthogonal decay of the molecular ions (EI, linked scan technique) [41].

The $^1$H-NMR signals of the cyclobutane H-atoms were very characteristic. The $AA'BB'$ spin pattern and the degenerate *singlet* signal at $\delta$ *ca.* 4.4 ppm belonged to **8** and **10**, respectively. Each four-membered ring H-atom has only one neighboring benzene ring in *cis*-position. The cycloadducts **9** and **11** contain four-membered ring H-atoms 'between' two *cis*-oriented benzene rings; therefore, their resonances appeared at higher field ($3.6 < \delta < 3.8$ ppm). The spin patterns allowed a further distinction [43]. Isomer **9** had four-membered ring H-atoms, which form an $AA'BB'$ spin system, whereas **11** exhibited an $A_2B_2$ spin system. Due to the very low portion of **11** (2%), its $^1$H-NMR signals were difficult to identify. Its $A_2B_2$ spin pattern was hidden at 3.7 ppm in the foot of the $AA'BB'$ pattern of **9**. Nevertheless, isomer **11** provided a complete set of $^{13}$C-NMR signals.

Whereas the regioselectivity of the cycloaddition was low: (**8** + **9**)/(**10** + **11**) 58 : 42, the stereoselectivity was high: **8**/**9** 40 : 18 and **10**/**11** 40 : 2. As usual in (*E*)-stilbene photochemistry [8], the *trans* arrangement of the benzene rings in (*E*)-**7** was completely preserved in the products **8**–**11**.

The irradiation ($\lambda \geq 290$ nm, $CH_2Cl_2$, 48 h) of the polymers **6b** and **6d**–**6f** yielded yellow-to-light brown powders. The insoluble portion was smaller than 5%. Integration of the $^1$H-NMR spectra (400 MHz, $CDCl_3$) of the soluble parts revealed that 60–80% of the olefinic CH groups were transformed to saturated CH groups. New signals appeared in the range of $3.3 \leq \delta \leq 4.5$ ppm. We assume for the soluble portion intramolecular $[2\pi + 2\pi]$ cycloadditions as major reaction route. According to the

Scheme 5. *Major Substructures Assumed for the Irradiated Polymers* **6b** *and* **6d**–**6f** (according to the model compound)




photodimerization of the model compound **7**, the formation of head-to-head and head-to-tail cycloadducts (*Scheme 5*) could be detected.

The photodimerization of stilbenes is characterized by the intermediate generation of excimers and pericyclic minima [8]. This effect can facilitate the formation of large rings, especially when the stilbene units of two neighboring pendants react (*Scheme 5*).

Moreover, (*Z*)-configured C=C bonds were detectable by UV spectroscopy ($\lambda_{max}$ 284 nm) and $^1$H-NMR spectroscopy in the region $6.4 \leq \delta \leq 6.8$ ppm. The photo-cross-linking between different chains led to the small insoluble portion of the photoproduct. The assumption of prevailing intrachain photocycloadditions is further sustained by GPC measurements. The GPC diagrams of irradiated and unirradiated **6e** are very similar. The $M_w$ value changed by irradiation from 38900 to 37600, and $M_n$ from 17300 to 17800.

*Fig.* 2 shows a comparison of the solid-state $^{13}$C-NMR spectra of the unirradiated and the irradiated polymer **6e**. In contrast to the $^1$H-NMR solution recordings, the insoluble portions of irradiated **6e** are included. Related to the signal at $15 \leq \delta \leq 35$ ppm ($CH_3$, pendant $CH_2$), the intensity of the aromatic/olefinic region $105 \leq \delta \leq 140$ ppm was decreased, and the intensity of the CH, $C_q$, $CH_2$ (main chain) region $40 \leq \delta \leq 60$ ppm was strongly increased in the irradiated probe. (arrows in *Fig. 2*, *b*).

When films of **6e** or **6f** were irradiated, a completely insoluble cross-linked material was generated fast. *Fig. 3* shows the UV film spectra for a monochromatic irradiation of **6e** at 366 nm – in the long-wavelength tail of the absorption. It is known that four-membered rings of the type as in **8**–**11** can be cleaved by energy-rich UV light [8]. This effect can be excluded for 366 nm irradiations.

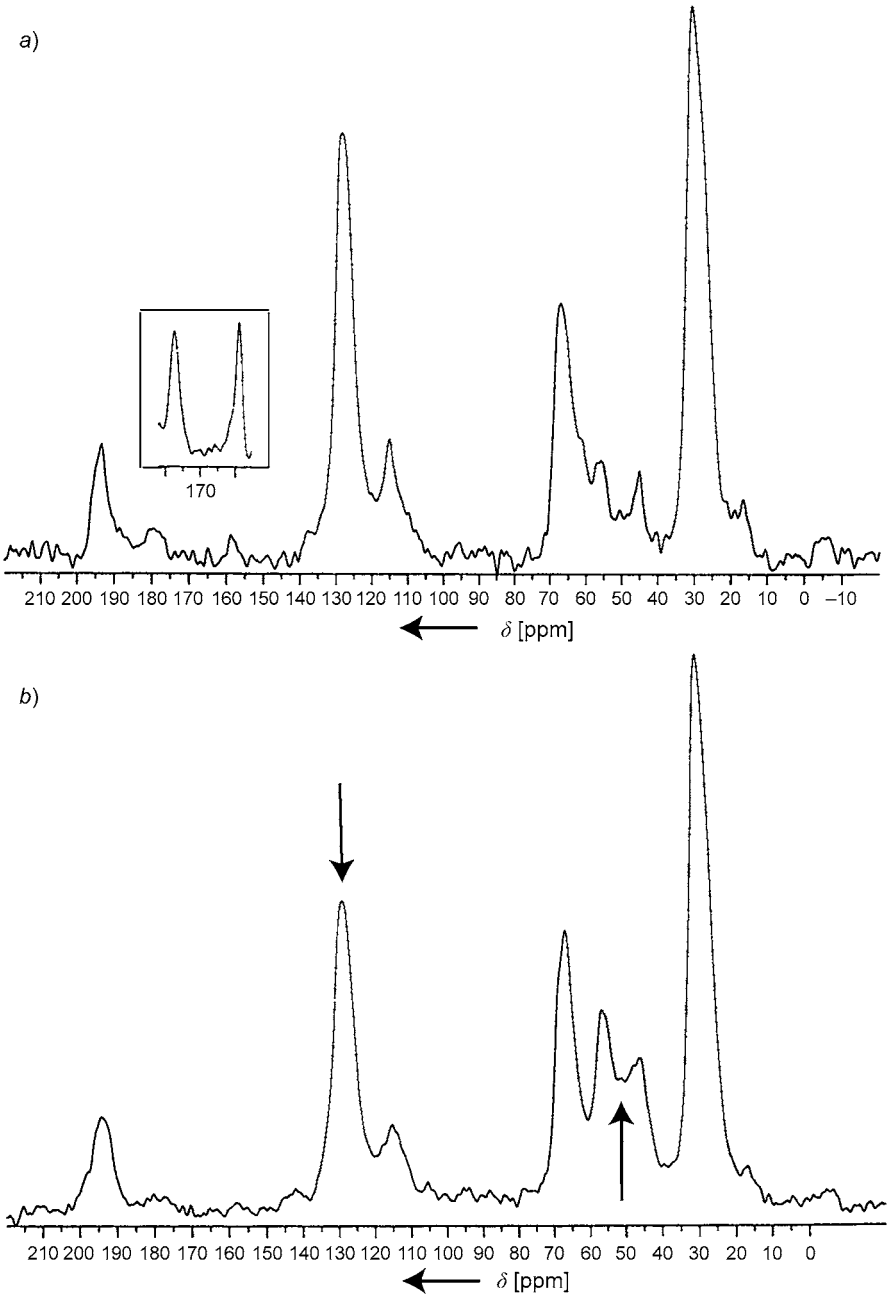



Fig. 2. *Solid-state CP-MAS* $^{13}$*C-NMR spectra of a*) *unirradiated* **6e** (cross polarization, 50 μs) *and b*) *irradiated* **6e** (cross-polarization, 10 μs). The recordings were performed at 100 MHz and a rotation frequency of 5000 Hz. *Inset:* The quaternary C-atoms are more visible and distinguishable from sidebands (for example $\delta$ 195) for the cross polarization of 2000 μs. For the detailed assignment of the signals, see *Exper. Part.*

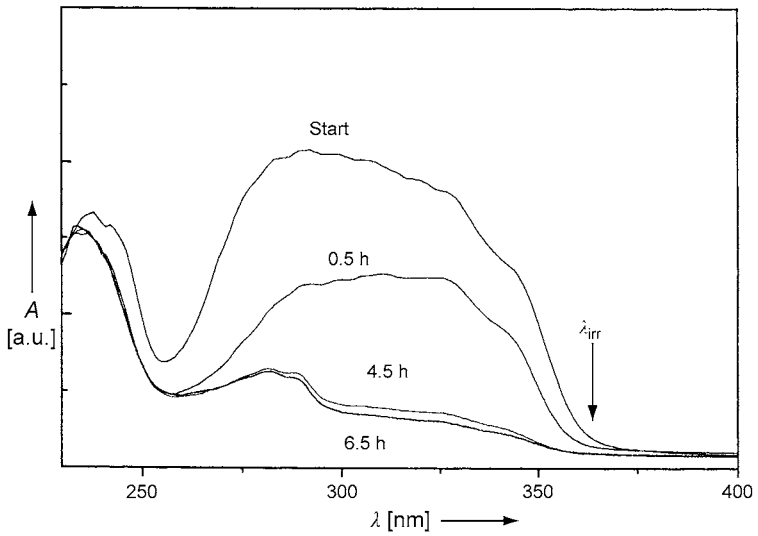



Fig. 3. *Reaction spectra of the irradiation* ($\lambda_{irr.}$ 366 nm) *of films of* **6e** (casted of a solution in benzene)

The film spectrum of **6e** exhibited a maximum ($\lambda_{max}$ 292 nm) which is hypsochromically shifted in comparison to the solvent spectrum ($\lambda_{max}$ 326 nm). This indicates the generation of H aggregates, which are favorable for both types of C–C bond formations in the cross-linking (*Scheme 1*).

The photo-cross-linking was very fast in the beginning and slowed down after *ca.* 30 min. The final state of the films was reached after *ca.* 6 h. Then, an absorption maximum at 282 nm was deteceted for **6e** as well as for the film irradiation of **6b**, **6d**, and **6f**. The tailing of the curves in *Fig. 3* from 375 to 400 nm is due to some light scattering.

The film-forming properties of **6b** and **6d** were less favorable. Films of **6b** and **6d** become soon turbid.

**3. Conclusions.** – Polymethacrylates, which contain (*E*)-stilbene building blocks fixed on tethers of variable length, were prepared from the corresponding monomers by radical polymerization.

Irradiation of 4-[(*E*)-2-phenylethenyl]phenyl acetate (**7**) as model compound revealed the formation of head-to-head and head-to-tail cycloadducts as only irreversible photoreaction in the absence of oxidants.

The polymethacrylates, dissolved in $CH_2Cl_2$, behaved on irradiation in a similar way whereby intrachain $[2\pi + 2\pi]$ cycloadditions are favored. Irradiated and unirradiated probes gave nearly identical GPC diagrams ($M_w$ and $M_n$ values). On the contrary, the irradiation ($\lambda_{irr.}$ 366 nm) in neat films afforded very fast completely insoluble materials by an interchain photo-cross-linking. Increasing length of the tethers improved the film-forming properties. The photochemistry of the films represents the basis for imaging techniques and negative photoresists.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

## Experimental Part

*General*. M.p.: *Büchi* melting point apparatus. The phase transitions of **5** and **6** were determined with a differential scanning calorimeter *DSC-7* from *Perkin-Elmer*. UV/VIS Spectra: *MCS-224*/*MCS-234* diode array spectrometer from *Zeiss*. IR Specra: *Beckman Acculab 4*. $^1$H- and $^{13}$C-NMR soln. spectra: *AM-400* spectrometer from *Bruker*; $CDCl_3$ as solvent and $Me_4Si$ as internal standard; $\delta$ in ppm and $J$ in Hz. Solid-state $^{13}$C-NMR spectra: *DPX-400* from *Bruker*. FD-MS: *Finnigan-MAT-95* spectrometer, 5 kV ionization energy. EI-MS: *Finnigan-MAT-95* ionization energy 70 eV. GPC: *Program Millenium-2010*, polystyrene standard from PSS, $CHCl_3$ as eluent.

*Preparation of the Alkanols* **3a**–**3f**. 4-[(*E*)-2-Phenylethenyl]phenol (**1**; 1.0 g, 5.1 mmol) was added to a soln. of Na (160 mg, 6.9 mmol) in 70 ml of dry EtOH. The soln. turned yellow; 6.2–7.0 mmol of $\omega$-bromoalkanol, **2a** and **2f**, or $\omega$-chloroalkanol, **2b**–**2e**, were added portionwise under Ar. The mixture was stirred and refluxed, until TLC ($SiO_2$; $Et_2O$) indicated the complete consumption of **1**. The products **3a**–**3f** started to precipitate after 12 h. The total reaction time amounted to 1–4 d. The precipitate was washed with cold EtOH and recrystallized from EtOH.

*2-{4-[(*E*)-2-Phenylethenyl]phenoxy}ethanol* (**3a**). Yield 552 mg (45%). Colorless crystals. M.p. 162° ([44]: 148–149°). $^1$H-NMR ($CDCl_3$): 2.04 (*t*, *J* = 6.2, OH); 3.96 (*q*, *J* = 6.2, $CH_2$(1)); 4.11 (*t*, *J* = 6.2, $CH_2$(2)); 6.91/7.45 (*AA′BB′*[1]), 4 arom. H); 6.97/7.07 (*AB*, *J* = 15.8, 2 olef. H); 7.18–7.52 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 61.5 (C(1)); 69.4 (C(2)); 114.9, 126.4, 127.1, 127.4, 127.9, 128.3, 128.7 (arom. and olef. CH); 130.8, 137.7, 158.5 (arom. $C_q$). EI-MS: 240 (100, $M^+$), 196 (71), 195 (25). Anal. calc. for $C_{16}H_{16}O_2$ (240.1): C 79.97, H 6.71; found: C 79.91, H 6.67.

*3-{4-[(*E*)-2-Phenylethenyl]phenoxy}propan-1-ol* (**3b**). Yield 480 mg (37%). Colorless crystals. M.p. 163°. $^1$H-NMR ($CDCl_3$): 1.73 (*t*, *J* = 6.2, OH); 2.00–2.15 (*m*, $CH_2$(2)); 3.86 (*q*, *J* = 5.7, $CH_2$(1)); 4.14 (*t*, *J* = 5.9, $CH_2$(3)); 6.89, 7.46 (*AA′BB′*, 4 arom. H); 6.94/7.06 (*AB*, *J* = 15.8, 2 olef. H); 7.18–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 32.1 (C(2)); 60.5 (C(1)); 65.8 (C(3)); 114.9, 126.3, 126.8, 127.2, 127.7, 128.2, 128.6 (arom. and olef. CH); 130.5, 137.7, 158.5 (arom. $C_q$). EI-MS: 254 (99, $M^+$), 196 (100), 195 (67), 165 (67), 152 (41). Anal. calc. for $C_{17}H_{18}O_2$ (254.3): C 80.28, H 7.13; found: C 80.41, H 7.13.

*5-{4-[(*E*)-2-Phenylethenyl]phenoxy}pentan-1-ol* (**3c**). Yield 290 mg (20%). Colorless crystals. M.p. 148°. $^1$H-NMR ($CDCl_3$): 1.28 (*s*, OH); 1.51–1.67 (*m*, $CH_2$(2), $CH_2$(3)); 1.79–1.90 (*m*, $CH_2$(4)); 3.63–3.72 (*m*, $CH_2$(1)); 3.97 (*t*, *J* = 6.4, $CH_2$(5)); 6.86, 7.42 (*AA′BB′*, 4 arom. H); 6.94, 7.05 (*AB*, *J* = 15.8, 2 olef. H); 7.21–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 22.4, 29.0, 32.4 (C(2), C(3), C(4)); 62.8 (C(1)); 67.9 (C(5)); 114.8, 126.2, 126.6, 127.1, 127.7, 128.3, 128.6 (arom. and olef. CH); 130.5, 137.7, 158.5 (arom. $C_q$). EI-MS: 282 (56, $M^+$), 196 (100). Anal. calc. for $C_{19}H_{22}O_2$ (282.4): C 80.82, H 7.85; found: C 80.75, H 7.83.

*6-{4-[(*E*)-2-Phenylethenyl]phenoxy}hexan-1-ol* (**3d**). Yield 620 mg (41%). Colorless crystals. M.p. 144°. $^1$H-NMR ($CDCl_3$): 1.26 (*s*, OH); 1.41–1.66 (*m*, $CH_2$(2), $CH_2$(3), $CH_2$(4)); 1.72–1.87 (*m*, $CH_2$(5)); 3.61–3.71 (*m*, $CH_2$(1)); 3.96 (*t*, *J* = 6.4, $CH_2$(6)); 6.86, 7.42 (*AA′BB′*, 4 arom. H); 6.94, 7.05 (*AB*, *J* = 15.9, 2 olef. H); 7.17–7.49 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 25.6, 25.9, 29.3, 32.7 (C(2), C(3), C(4), C(5)); 62.9 (C(1)); 67.9 (C(6)); 114.7, 126.2, 126.5, 127.2, 127.7, 128.3, 128.6 (arom. and olef. CH); 130.0, 137.7, 158.8 (arom. $C_q$). EI-MS: 296 (48, $M^+$), 196 (100). Anal. calc. for $C_{20}H_{24}O_2$ (296.4): C 81.04, H 8.16; found: C 80.74, H 7.76.

*8-{4-[(*E*)-2-Phenylethenyl]phenoxy}octan-1-ol* (**3e**). Yield 1190 mg (72%). Colorless crystals. M.p. 141°. $^1$H-NMR ($CDCl_3$): 1.24 (*t*, OH); 1.36–1.58 (*m*, $CH_2$(2), $CH_2$(3), $CH_2$(4), $CH_2$(5), $CH_2$(6)); 1.72–1.86 (*m*, $CH_2$(7)); 3.59–3.70 (*m*, $CH_2$(1)); 3.96 (*t*, *J* = 6.4, $CH_2$(5)); 6.87, 7.44 (*AA′BB′*, 4 arom. H); 6.94, 7.05 (*AB*, *J* = 15.8, 2 olef. H); 7.21–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 25.7, 25.9, 29.2, 29.3, 29.3, 32.8 (C(2), C(3), C(4), C(5), C(6), C(7)); 63.0 (C(1)); 68.1 (C(8)); 114.8, 126.3, 126.6, 127.2, 127.7, 128.4,

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[1]) Coupling constants of *AA′BB′* spin patterns were not determined by simulation.

128.6 (arom. and olef. CH); 130.1, 137.8, 159.0 (arom. $C_q$). EI-MS: 324 (91, $M^+$), 196 (100). Anal. calc. for $C_{22}H_{28}O_2$ (324.5): C 81.44, H 8.70; found: C 81.30, H 8.62.

*11-{4-[(*E*)-2-Phenylethenyl]phenoxy}undecan-1-ol* (**3f**). Yield 1550 mg (83%). Colorless crystals. M.p. 140°. $^1$H-NMR ($CDCl_3$): 1.17–1.60 (*m*, $CH_2$(2), $CH_2$(3), $CH_2$(4), $CH_2$(5), $CH_2$(6), $CH_2$(7), $CH_2$(8), $CH_2$(9), OH); 1.70–1.84 (*m*, $CH_2$(10)); 3.56–3.68 (*m*, $CH_2$(1)); 3.95 (*t*, $J$ = 6.5, $CH_2$(11)); 6.86, 7.41 (*AA′BB′*, 4 arom. H); 6.94, 7.05 (*AB*, $J$ = 15.9, 2 olef. H); 7.17–7.49 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 25.7, 26.0, 29.2, 29.3, 29.3, 29.4, 29.4, 29.5, 32.8 (C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10)); 63.0 (C(1)); 68.1 (C(11)); 114.7, 126.2, 126.5, 127.1, 127.6, 128.3, 128.5 (arom. and olef. CH); 130.0, 137.7, 158.9 (arom. $C_q$). EI-MS: 367 (59, $M^+$), 196 (100). Anal. calc. for $C_{25}H_{34}O_2$ (366.6): C 81.92, H 9.35; found: C 81.98, H 9.28.

*Preparation of the Methacrylates* **5a**–**5f**. The alkanol **3a**–**5f** (3.0 mmol) and 2-methylprop-2-enoyl chloride (3.5 mmol) were reacted under Ar in 100 ml of $CCl_4$ in the presence of 800 mg molecular sieves (3 Å). TLC Control ($SiO_2$; $Et_2O$) provided a reaction time of 2–5 d. The mixture was filtered, and the solvent was evaporated. CC ($SiO_2$; 4 × 40 cm, $CH_2Cl_2$) to yield anal. pure products **5a**–**5f** the melting points of which were determined by DSC (10°/min).

*2-{4-[(*E*)-2-Phenylethenyl]phenoxy}ethyl 2-Methylprop-2-enoate* (**5a**). Yield 407 mg (44%). Colorless solid. M.p. 100°. $^1$H-NMR ($CDCl_3$): 1.95–1.96 (*m*, Me); 4.23 (*t*, $J$ = 6.5, $CH_2O$); 4.50 (*t*, $J$ = 6.6, $CO_2CH_2$); 5.58–5.61 (*m*, $H_E$–C(3)); 6.14–6.15 (*m*, $H_Z$–C(3)); 6.91, 7.45 (*AA′BB′*, 4 arom. H); 6.98, 7.07 (*AB*, $J$ = 16.4, 2 olef. H); 7.19–7.51 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.2 (Me); 63.0 ($CO_2CH_2$); 66.1 ($CH_2O$); 114.9, 126.3, 126.9, 127.3, 127.7, 128.1, 128.6 (arom. and olef. CH); 125.9 (C(3)); 130.7, 137.6, 158.3 (arom. $C_q$); 136.0 (C(2)); 167.3 (C(1)). EI-MS: 308 (5, $M^+$), 113 (100), 69 (63). Anal. calc. for $C_{20}H_{20}O_3$ (308.4): C 77.90, H 6.54; found: 77.51, H 6.69.

*3-{4-[(*E*)-2-Phenylethenyl]phenoxy}propyl 2-Methylprop-2-enoate* (**5b**). Yield 520 mg (54%). Colorless solid. M.p. 94°. $^1$H-NMR ($CDCl_3$): 1.94–1.95 (*m*, Me); 2.11–2.24 (*m*, $CH_2$); 4.06 (*t*, $J$ = 6.5, $CH_2O$); 4.33 (*t*, $J$ = 6.6, $CO_2CH_2$); 5.55–5.58 (*m*, $H_E$–C(3)); 6.10–6.11 (*m*, $H_Z$–C(3)); 6.89, 7.44 (*AA′BB′*, 4 arom. H); 6.94, 7.07 (*AB*, $J$ = 16.3, 2 olef. H); 7.15–7.51 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.2 (Me); 28.7 ($CH_2$); 61.5 ($CO_2CH_2$); 64.6 ($CH_2O$); 114.8, 126.3, 126.8, 127.2, 127.7, 128.3, 128.6 (arom. and olef. CH); 125.4 (C(3)); 130.4, 137.7, 158.6 (arom. $C_q$); 136.4 (C(2)); 167.4 (C(1)). EI-MS: 322 (9, $M^+$), 254 (43), 196 (61), 195 (49), 165 (43), 127 (100). Anal. calc. for $C_{21}H_{22}O_3$ (322.4): C 78.23, H 6.88; found: C 77.99, H 6.93.

*5-{4-[(*E*)-2-Phenylethenyl]phenoxy}pentyl 2-Methylprop-2-enoate* (**5c**). Yield 535 mg (51%). Colorless solid. M.p. 89°. $^1$H-NMR ($CDCl_3$): 1.93–1.94 (*m*, Me); 1.50–1.86 (*m*, 3 $CH_2$); 3.98 (*t*, $J$ = 6.5, $CH_2O$); 4.17 (*t*, $J$ = 6.6, $CO_2CH_2$); 5.54–5.57 (*m*, $H_E$–C(3)); 6.08–6.09 (*m*, $H_Z$–C(3)); 6.86, 7.43 (*AA′BB′*, 4 arom. H); 6.94, 7.07 (*AB*, $J$ = 16.2, 2 olef. H); 7.18–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.2 (Me); 22.6, 28.4, 28.9 ($CH_2$); 64.5 ($CO_2CH_2$); 67.7 ($CH_2O$); 114.8, 126.2, 126.6, 127.2, 127.7, 128.3, 128.6 (arom. and olef. CH); 125.2 (C(3)); 130.1, 137.3, 158.8 (arom. $C_q$); 136.5 (C(2)); 167.5 (C(1)). EI-MS: 350 (93, $M^+$), 196 (100), 69 (99), 41 (81). Anal. calc. for $C_{23}H_{26}O_3$ (350.5): C 78.83, H 7.48; found: C 78.45, H 7.39.

*6-{4-[(*E*)-2-Phenylethenyl]phenoxy}hexyl 2-Methylprop-2-enoate* (**5d**). Yield 950 mg (87%). Colorless powder. M.p. 82°. $^1$H-NMR ($CDCl_3$): 1.92–1.93 (*m*, Me); 1.41–1.86 (*m*, 4 $CH_2$); 3.96 (*t*, $J$ = 6.5, $CH_2O$); 4.14 (*t*, $J$ = 6.6, $CO_2CH_2$); 5.52–5.55 (*m*, $H_E$–C(3)); 6.08–6.09 (*m*, $H_Z$–C(3)); 6.85, 7.43 (*AA′BB′*, 4 arom. H); 6.94, 7.06 (*AB*, $J$ = 16.3, 2 olef. H); 7.17–7.49 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.3 (Me); 25.7, 25.8, 28.6, 29.1 ($CH_2$); 64.6 ($CO_2CH_2$); 68.0 ($CH_2O$); 114.7, 126.2, 126.6, 127.1, 127.7, 128.3, 128.6 (arom. and olef. CH); 125.0 (C(3)); 130.1, 137.7, 158.9 (arom. $C_q$); 136.6 (C(2)); 167.5 (C(1)). EI-MS: 364 (78, $M^+$), 196 (100). Anal. calc. for $C_{24}H_{28}O_3$ (364.5): C 79.09, H 7.74; found: C 79.12, H 7.40.

*8-{4-[(*E*)-2-Phenylethenyl]phenoxy}octyl 2-Methylprop-2-enoate* (**5e**). Colorless powder. Yield 905 mg (77%). M.p. 75°. $^1$H-NMR ($CDCl_3$): 1.93–1.94 (*m*, Me); 1.37–1.82 (*m*, 6 $CH_2$); 3.96 (*t*, $J$ = 6.5, $CH_2O$); 4.14 (*t*, $J$ = 6.6, $CO_2CH_2$); 5.52–5.55 (*m*, $H_E$–C(3)); 6.08–6.09 (*m*, $H_Z$–C(3)); 6.88, 7.44 (*AA′BB′*, 4 arom. H); 6.94, 7.07 (*AB*, $J$ = 16.3, 2 olef. H); 7.18–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.4 (Me); 25.9, 26.0, 28.6, 29.2, 29.3, 29.3 ($CH_2$); 64.8 ($CO_2CH_2$); 68.0 ($CH_2O$); 114.7, 126.2, 126.5, 127.2, 127.7, 128.3, 128.7 (arom. and olef. CH); 125.2 (C(3)); 130.0, 137.7, 158.9 (arom. $C_q$); 136.6 (C(2)); 167.5 (C(1)). EI-MS: 392 (21, $M^+$), 196 (100). Anal. calc. for $C_{26}H_{32}O_3$ (392.5): C 79.56, H 8.22; found: C 79.50, H 8.27.

*11-{4-[(*E*)-2-Phenylethenyl]phenoxy}undecyl 2-Methylprop-2-enoate* (**5f**). Yield 1040 mg (80%). Colorless powder. M.p. 85°. IR (KBr): 2920, 2850, 1705, 1630, 1600, 1510, 1470, 1325, 1290, 1270, 1250, 1175, 1040, 1020, 970, 960, 830, 815, 755, 695. $^1$H-NMR ($CDCl_3$): 1.93–1.94 (*m*, Me); 1.29–1.81 (*m*, 9 $CH_2$); 3.95 (*t*, $J = 6.5$, $CH_2O$); 4.12 (*t*, $J = 6.6$, $CO_2CH_2$); 5.52–5.54 (*m*, $H_E$–C(3)); 6.08–6.09 (*m*, $H_Z$–C(3)); 6.87, 7.44 (*AA′BB′*, 4 arom. H); 6.94, 7.06 (*AB*, $J = 16.2$, 2 olef. H); 7.17–7.50 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 18.2 (Me); 25.9, 26.0, 28.6, 29.2, 29.3, 29.3, 29.4, 29.4, 29.5 ($CH_2$); 64.8 ($CO_2CH_2$); 68.1 ($CH_2O$); 114.8, 126.2, 126.5, 127.1, 127.7, 128.3, 128.6 (arom. and olef. CH); 125.1 (C(3)); 130.0, 137.7, 158.9 (arom. $C_q$); 136.6 (C(2)); 167.5 (C(1)). EI-MS: 434 (84, $M^+$), 196 (100). Anal. calc. for $C_{29}H_{38}O_3$ (434.6): C 80.14, H 8.81; found: C 79.92, H 8.93.

*Polymerization of* **5b** *and* **5d**–**5f**. Ar was purged through dry THF (10–20 ml) for 20 min in order to get an oxygen-free solvent. The selected monomer **5** (2.0 mmol) and AIBN (20 mg, 0.12 mmol) were added, and the mixture was heated to 60° for 20–24 h under Ar. The mixture was poured into 150 ml of $H_2O$. The obtained precipitate was twice dissolved in hot THF and precipitated with cold MeOH to remove unreacted monomer. The colorless polymer was dried at $1.3 \times 10^2$ Pa and 20° for 8 h.

*Polymer* **6b**. Yield 518 mg (80%). M.p. 162°. IR (KBr): 1705, 1590, 1500, 1240, 1170, 960. $^1$H-NMR ($CDCl_3$): 0.5–2.3 (*m*, Me, $CH_2$, main chain and side chains[2])); 3.6–4.2 (*m*, $CH_2O$); 6.6–7.5 (*m*, arom. and olef. H).

*Polymer* **6d**. Yield 525 mg (72%). M.p. 124°. IR (KBr): 1705, 1590, 1500, 1240, 1170, 960. $^1$H-NMR ($CDCl_3$): 0.5–2.2 (*m*, Me, $CH_2$, main chain and side chains); 3.4–4.2 (*m*, $CH_2O$); 6.6–7.5 (*m*, arom. and olef. H).

*Polymer* **6e**. Yield 670 mg (85%). M.p. 120°. IR (KBr): 1710, 1600, 1505, 1250, 1175, 960. $^1$H-NMR ($CDCl_3$): 0.5–2.2 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.2 (*m*, $CH_2O$); 6.7–7.5 (*m*, arom. and olef. H). $^{13}$C-NMR (solid state, CPMAS): 10–40 (Me, $CH_2$ side chains); 40–50 ($C_q$, main chain); 50–60 ($CH_2$, main chain); 60–70 ($CH_2O$); 110–120 (arom. *C*H–$C_q$O); 120–135 (arom. CH and $C_q$ *para* to $C_q$O); 135–140 (arom. $C_q$, Ph); 155–165 (arom. $C_q$O); 175–180 (C=O).

*Polymer* **6f**. Yield 715 mg (82%). M.p. 121°. $T_g$ 66°. IR (KBr): 1710, 1600, 1510, 1250, 1175, 960. $^1$H-NMR ($CDCl_3$): 0.7–2.0 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.1 (*m*, $CH_2O$); 6.6–7.5 (*m*, arom. and olef. H).

Due to incomplete combustion, no elemental analyses of **6b** and **6d**–**6f** could be obtained.

*Irradiation of 4-[(*E*)-2-Phenylethenyl]phenyl Acetate* ((*E*)-**7**) *as Model Compound.* Ester (*E*)-**7** [42] (5.67 g, 23.8 mmol) was dissolved in 200 ml of oxygen- and thiophene-free benzene. Irradiation under Ar with a *Hanovia-450-W* medium pressure Hg lamp equipped with a *Pyrex* filter ($\lambda \geq 290$ nm[3]) led to a yellow soln. After stirring at r.t. for 44 h, the mixture was separated by CC ($SiO_2$; $5 \times 60$ cm, $CH_2Cl_2$). The first fractions consisted of pure (*Z*)-**7** (550 mg, 10%) and (*E*)/(*Z*)-**7** mixtures. $SiO_2$ provokes a slow catalytic isomerization (*Z*)-**7** → (*E*)-**7**. The following fractions consisted of the dimers **8**/**10**, followed by the dimers **9**/**11**. The total yield of dimers was 1.30 g (23%), and the ratio **8**/**9**/**10**/**11** obtained by $^1$H-NMR spectroscopy was *ca.* 40 : 18 : 40 : 2. The mixture of dimers **9**–**11** was a waxy solid. Anal. calc. for $C_{32}H_{28}O_4$ (476.6): C 80.65, H 5.92; found: C 80.77, H. 5.69.

The fraction **8**/**10** was then separated by fractionary crystallization from EtOH or EtOH/$Et_2O$ 1 : 1. A separation of the stereoisomers **9** and **11** was not achieved.

The course of the photoreaction (*E*)-**7** → (*Z*)-**7** + **8**–**11**, shown in *Fig. 1*, was determined under the same conditions. Probes of the soln. were evaporated, and the residue was dissolved in $CDCl_3$ to obtain the amount of the components by $^1$H-NMR spectroscopy.

*4-[(*Z*)-2-Phenylethenyl]phenyl Acetate* ((*Z*)-**7**). Oil. UV ($CH_2Cl_2$): 283 (19970). $^1$H-NMR ($CDCl_3$): 2.26 (*s*, Me); 6.53, 6.59 (*AB*, $J = 12.3$, 2 olef. H); 6.93, 7.23 (*AA′BB′*, 4 arom. H); 7.18–7.25 (*m*, 5 arom. H). $^{13}$C-NMR ($CDCl_3$): 21.1 (Me); 121.3, 127.2, 128.3, 128.8, 129.2, 129.9, 130.5 (arom. and olef. CH); 134.8, 137.1 (arom. $C_q$); 149.6 (arom. $C_q$O); 169.3 (C=O). EI-MS: 238 (21, $M^+$), 196 (100). The compound was indentical with an authentic sample [45].

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[2]) The H-atom chemical shifts ($\delta$ values) of the irradiated and unirradiated polymers are given here with a single digit, because the second digit is not reproducible.

[3]) Without filter, the energy-rich radiation ($\lambda = 254$ nm) caused a polymer cover on the irradiation vessel.

r-*1*,c-*2*-*Bis(4-acetoxyphenyl)*-t-*3*,t-*4*-*diphenylcyclobutane (= *[(1*R**,2*S**,3*R**,4*S**)-3,4-Diphenylcyclobutane-1,2-diyl]dibenzene-4,1-diyl Diacetate*; **8**). Colorless crystals. M.p. 200°. $^1$H-NMR ($CDCl_3$): 2.22 (*s*, 2 Me); 4.40, 4.43 (*AA′BB′*, 4 cyclobutane H), 6.86, 7.09 (*AA′BB′*, 8 arom. H); 7.02–7.14 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3$): 21.1 (Me); 46.9, 47.8 (CH, cyclobutane), 121.1, 126.0, 127.9, 128.1, 129.0 (arom. CH); 138.2, 140.3 (arom. $C_q$); 148.3 (arom. $C_qO$); 169.3 (CO). FD-MS: 476 (10, $M^+$), 238 (100). EI-MS: 296 (5), 254 (10), 238 (55), 212 (10), 196 (100), 180 (5). The linked scan technique established, that the ion peak at *m*/*z* 212 had the 'parents' 254 and 296.

r-*1*-t-*3*-*Bis(4-acetoxyphenyl)*-c-*2*,t-*4*-*diphenylcyclobutane (= *(*trans-*2,4-Diphenylcyclobutane-1,3-diyl)dibenzene-4,1-diyl Diacetate*; **10**). Colorless crystals. M.p. 200°. $^1$H-NMR ($CDCl_3$): 2.22 (*s*, 2 Me); 4.43 ('*s*', 4 cyclobutane H), 6.85, 7.08 (*AA′BB′*, 8 arom. H); 7.06–7.16 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3$): 21.0 (Me); 46.9, 47.7 (CH, cyclobutane); 120.9, 126.1, 128.0, 128.1, 128.9 (arom. CH); 138.2, 140.3 (arom. $C_q$); 148.8 (arom. $C_qO$); 169.3 (CO). FD-MS: 476 (10, $M^+$), 238 (100). EI-MS: 238 (100), 196 (80). The linked scan technique established, that the ion peak at *m*/*z* 196 had the 'parent' 238.

r-*1*-t-*2*-*Bis(4-acetoxyphenyl)*-c-*3*,t-*4*-*diphenylcyclobutane (= *[(1*R**,2*R**,3*S**,4*S**)-3,4-Diphenylcyclobutane-1,2-diyl]dibenzene-4,1-diyl Diacetate*; **9**) *and* r-*1*,c-*3*-*Bis(4-acetoxyphenyl*-t-*2*,t-*4*-*diphenylcyclobutane (= *(cis-*2,4-Diphenylcyclobutane-1,3-diyl)dibenzene-4,1-diyl Diacetate*; **11**). Oil. $^1$H-NMR ($CDCl_3$) of **9**: 2.28 (*s*, 2 Me); 3.65, 3.68 (*AA′BB′*, 4 cyclobutane H); 7.02, 7.28 (*AA′BB′*, 8 arom. H); 7.25–7.38 (*m*, 10 arom. H). $^1$H-NMR ($CDCl_3$) of **11**: 2.31 (*s*, 2 Me); 3.60–3.67, 3.67–3.73 (2*m*, 2 H each of cyclobutane); 7.00–7.03 (*m*, 4 arom. H); 7.25–7.38 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3$) of **9**: 21.1 (Me); 51.1, 51.7 (CH, cyclobutane); 121.5, 126.7, 127.0, 127.8, 128.5 (arom. CH); 139.9, 142.0 (arom. $C_q$); 149.3 (arom. $C_qO$); 169.4 (CO). $^{13}$C-NMR ($CDCl_3$) of **11**: 21.0 (Me); 51.0, 51.8, (CH, cyclobutane); 121.7, 126.4, 126.6, 127.5, 128.0 (arom. CH); 139.8, 142.1 (arom. $C_q$); 150.0 (arom. $C_qO$); 169.3 (CO). FD-MS: 476 (10, $M^+$), 196 (100).

When an oxygen-containing soln. of **7** was irradiated, the formation of 4-[(2*R**,3*R**)-3-phenyloxiran-2-yl]phenyl acetate and traces of phenanthren-3-yl acetate could be observed.

*Irradiation of the Polymers* **6b** *and* **6d**–**6f** *in Soln.* The selected polymer **6** (1.2 mmol related to the monomer) was dissolved in oxygen-free $CH_2Cl_2$ (30 ml) and irradiated under Ar with a *Hanovia-450-W* medium-pressure Hg lamp equipped with a *Pyrex* filter ($\lambda \geq 290$ nm). After 48 h, the solvent was evaporated, and the residue was dried at r.t. and $1.3 \times 10^2$ Pa for 2–3 d. The yellow-to-light brown solid is moderately soluble in $CDCl_3$. Small amounts of insoluble products ($\leq 5\%$) were obtained as coating on the irradiation vessel.

*Irradiated Polymer* **6b**. IR (KBr): 1715, 1605, 1510, 1250, 1180, 1050. $^1$H-NMR ($CDCl_3$): 0.7–2.1 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.2 (*m*, $CH_2O$, CH); 4.2–4.4 (*m*, CH); 6.4–6.5 (*m*, olef. H *Z*); 6.5–7.5 (*m*, arom. and olef. H). According to the integration, 80% of the olefinic C=C bonds reacted.

*Irradiated Polymer* **6d**. IR (KBr): 1710, 1600, 1500, 1235, 1175. $^1$H-NMR ($CDCl_3$): 0.6–2.2 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.2 (*m*, $CH_2O$, CH); 4.2–4.4 (*m*, CH); 6.4–6.5 (*m*, olef. H (*Z*)); 6.5–7.5 (*m*, arom. and olef. H). According to the integration, 60% of the olefinic C=C bonds reacted.

*Irradiated Polymer* **6e**. IR (KBr): 1705, 1600, 1500, 1245, 1170. $^1$H-NMR: 0.6–2.2 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.2 (*m*, $CH_2O$, CH); 4.2–4.4 (*m*, CH); 6.4–6.5 (*m*, olef. H (*Z*)); 6.5–7.5 (*m*, arom. and olef. H). According to the integration, 65% of the olefinic C=C bonds reacted. Solid-state CP-MAS $^{13}$C-NMR: 10–40 (Me, $CH_2$, side chains); 40–60 (CH, $C_q$, main chain, $CH_2$, main chain); 60–70 ($CH_2O$); 110–120 (arom. *C*H–$C_qO$); 120–135 (arom. and olef. CH and $C_q$); 135–140 (arom. $C_q$); 155–165 (arom. $C_qO$); 175–180 (CO).

*Irradiated Polymer* **6f**. IR (KBr): 1710, 1600, 1500, 1245, 1175. $^1$H-NMR: 0.5–2.2 (*m*, Me, $CH_2$, main chain and side chains); 3.6–4.2 (*m*, $CH_2O$, CH); 4.2–4.4 (*m*, CH); 6.4–6.5 (*m*, olef. H (*Z*)); 6.5–7.5 (*m*, arom. and olef. H). According to the integration, 65% of the olefinic C=C bonds reacted.

*Irradiation of Casted Films of* **6e** *and* **6f**. Sat. solns. of **6e** and **6f** (4–5 mg/ml) in $CHCl_3$ or thiophene-free benzene were poured on to quartz plates. After complete evaporation of the solvent at 40°/80 Torr, transparent films were obtained, which were monochromatically irradiated (366 nm filter) for 6 h. Transparent, completely insoluble films were obtained, which showed a panchromatic absorption between 250 and 360 nm with a maximum at $\lambda$ 282 nm in both cases.

In contrast to all unirradiated polymers **6**, the irradiated materials do not melt.

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*Received June 15, 2011*