1,2,3-Thiadiazoles with Unsaturated Side Chains; Synthesis, Polymerization, and Photocrosslinking

Mousa Al-Smadi,*[a,b] Norbert Hanold,[b] Helga Kalbitz,[b] Herbert Meier*[b]

[a] Department of Applied Chemical Sciences, Jordan University of Science and Technology, Irbid, Jordan
E-mail: mariam10@just.edu.jo

[b] Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, 55099 Mainz, Germany
Fax +49(6131)3925396; E-mail: hmeier@mail.uni-mainz.de

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Abstract: 1,2,3-Thiadiazoles with polymerizable functionalities in the 4-position were synthesized as potential negative photoresists. The polymerization to soluble, film-forming materials must leave the heterocyclic rings intact, because they are needed for photocrosslinking reactions to give insoluble materials. 1,2,3-Thiadiazoles **1** cycloeliminate N_2 on irradiation. The resulting 1,3-diradicals **2** have various options for stabilization processes leading to alkynes **3** or to higher heterocycles **5**–**12**. The generation of atomic sulfur and its involvement in these subsequent reactions must be avoided. Therefore, systems like model compound **1a**, in which the 1,3-diradicals form 2-methylene-1,3-dithioles (dithiafulvenes) **9** were selected here. Optimization gave ultimately two materials for application as photoresists. Monomer **1c** could be polymerized in the presence of boron trifluoride to soluble **1c′**, which on irradiation formed **1c″** as a cross-linked insoluble polymer. Furthermore, thiadiazole **1f** was attached to polystyrene **26**. The resulting soluble polymer **1i′** yielded the insoluble material **1i″** on irradiation.

Key words: cyclodimerization, cycloelimination, heterocycles, photochemistry, photoresists

1,2,3-Thiadiazoles **1** represent a prominent class of heterocycles that have attracted attention for their interesting pharmacological and biological properties, but also because they can be used for the preparation of various sulfur-containing ring systems.[1] Thermal or photochemical extrusion of nitrogen generates 1,3-diradicals **2**, which can rearrange to thioketenes **5** or eliminate sulfur to yield alkynes **3** (Scheme 1). Thiirenes **4** are possible intermediates.[1] Apart from these monomolecular reactions, there are many dimerizations of **2**/**5** to heterocycles **6**–**12** with 1–4 sulfur atoms. Scheme 1 gives a survey of the formation of these heterocycles from four- to seven-membered rings.[2–12] (The examples given in refs. 2–12 are typically early established reaction examples.) Stereoisomers of **6**–**9** and regioisomers of **10**–**12** can be generated when the 1,2,3-thiadiazoles **1** have different substituents in the 4- or 5-positions. 1,2,3-Thiadiazoles with other substituents than alkyl or aryl groups have many additional routes for the stabilization of the initially formed 1,3-diradicals.[13]

The extremely high reactivity of the 1,3-diradicals **2** predestinates polymers with attached 1,2,3-thiadiazole rings for photocrosslinking reactions. Several compounds **1** with unsaturated side chains[14–24] and their polymers have been studied, but the non-uniform dimerization of **2**, in particular the generation of 'vagabonding' sulfur atoms in primary or secondary processes has proved to be a drawback for the fabrication of negative photoresists.[20,21] Therefore, we attempted now to find systems with fairly clean photoprocesses **1** to **9**. The dimers **9**, dithiafulvenes, have a much lower tendency for secondary sulfur extrusion than other dimers.

4-Phenyl-1,2,3-thiadiazole (**1a**) fulfills the above-mentioned preconditions as a model compound in a nearly perfect manner. After light-induced nitrogen extrusion, a 1,3-diradical **2a** is formed, in which the hydrogen atom has a high migration ability **2a**→**5a** (Scheme 2). The generated thioketene **5a** is involved in the cycloaddition of **2a** with **5a** to give (Z/*E*)-**9a**. The Z/*E* ratio is 10:1, when the irradiation of **1a** is performed in benzene with Vycor-filtered light (λ_{irr} 230 nm). Apart from **9a** some polymers are formed in the photocleavage of **1a**, but the other possible reaction routes leading to **3**, **6**, **7**, **8**, **10**, **11**, and **12** can be excluded.[5,25]

Our task was then to synthesize 1,2,3-thiadiazoles with 4-aryl substituents, which permit cationic polymerization.

In order to attach an olefinic chain to the 4-phenyl substituent in **1a**, we prepared first 4-(allyloxy)acetophenone (**15**) by the almost quantitative alkylation of 4-hydroxyacetophenone (**13**) with allyl bromide (**14**) (Scheme 3).[26] 4-Toluenesulfonyl hydrazide (**16**) yielded hydrazone **17**, which was subjected to Hurd–Mori reaction[27] with thionyl chloride to give 4-[4-(allyloxy)phenyl]-1,2,3-thiadiazole (**1b**). Finally a double bond shift to give (*Z*)- and (*E*)-4-[4-(prop-1-enyloxy)phenyl]-1,2,3-thiadiazole [(*E*/*Z*)-**1c**] could be induced by the Wilkinson catalyst chlorotris(triphenylphosphine)rhodium in the presence of 1,4-diazabicyclo[2.2.2]octane.

Thiadiazole **1d** (Scheme 4), which contains an oxirane ring, represents another polymerizable monomer. It could be obtained by oxidation of **1b** with 3-chloroperbenzoic acid (**18**). However, the yield of the oxidation was moderate, because the thiadiazole ring itself was sensitive to oxidation. Therefore, we elaborated a second route to **1d**, which started again with 4-hydroxyacetophenone (**13**). Its 4-toluenesulfonylhydrazone **19** was transformed to the 1,2,3-thiadiazole **1e**. Reaction of **1e** with epichlorohydrin (**20**) gave **1d**. The overall yield of **1d** from **13** via **15**, **17**,

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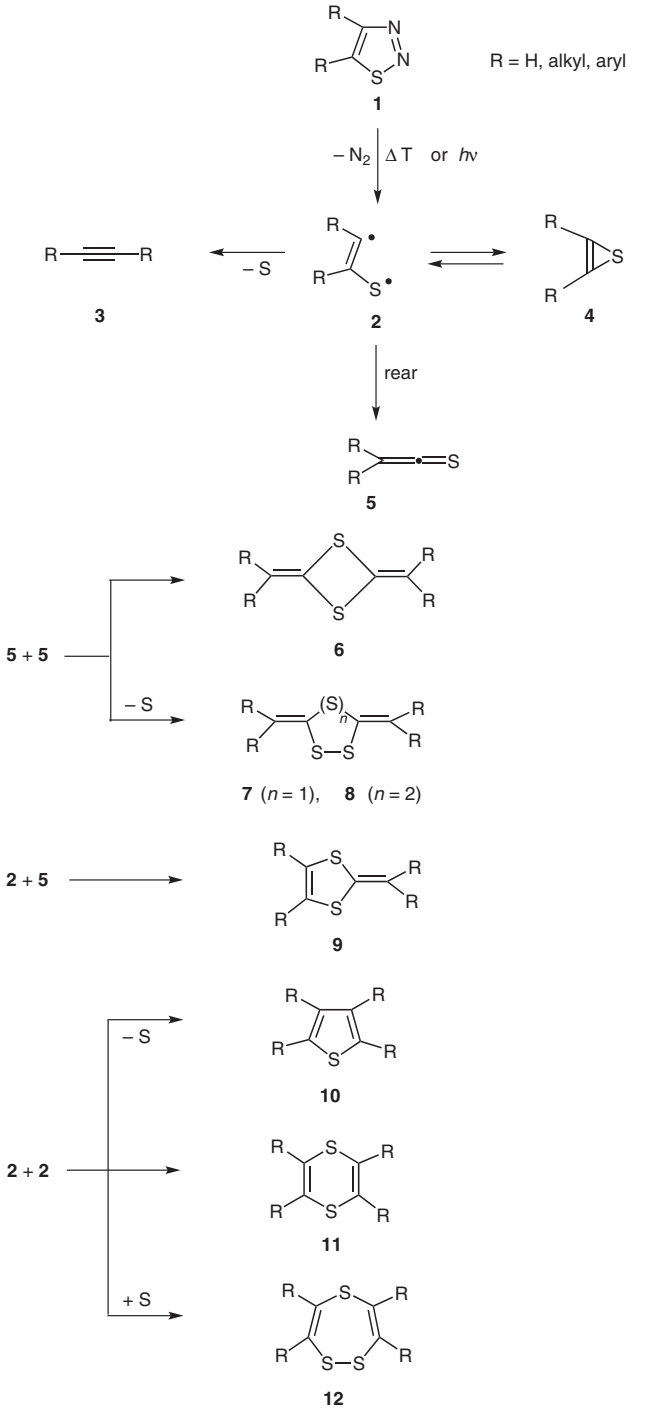
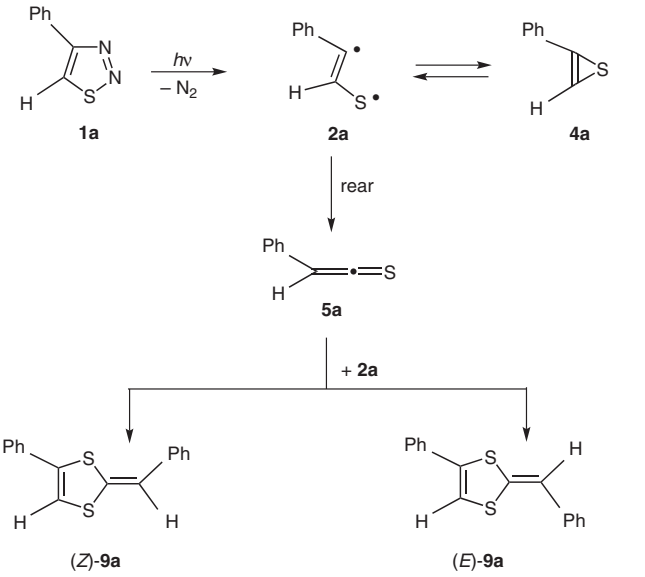


Scheme 1 Formation of S-heterocycles by ring cleavage of 1,2,3-thiadiazoles **1**: 2,4-dialkylidene-1,3-dithietanes **6**,[2] 3,5-dialkylidene-1,2,4-trithiolanes **7**,[3,4] 3,6-dialkylidene-1,2,4,5-tetrathianes **8**,[3] 2-alkylidene-1,3-dithioles **9**,[5–10] thiophenes **10**,[3,6,7,9,11,12] 1,4-dithiines **11**,[5,6,7,9] and 1,2,5-trithiepines **12**[8]



Scheme 2 Photolysis of 4-phenyl-1,2,3-thiadiazole (**1a**) to 2-benzylidene-4-phenyl-1,3-dithiole [(*Z*/*E*)-**9a**]

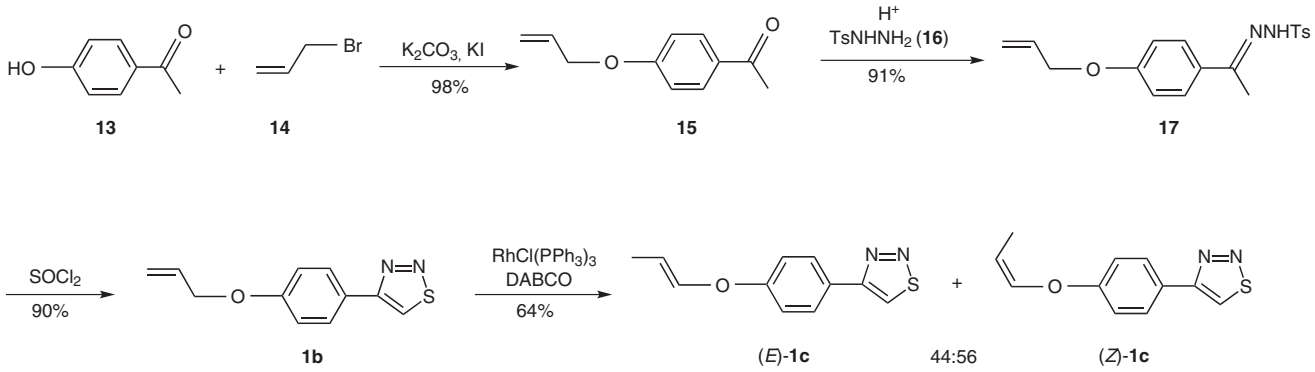
and **1b** was 29% whereas the total yield for the alternate process via **19** and **1e** amounted to 47%.

The vinyl ether **1c** and the oxirane **1d** were polymerized in the presence of the Lewis acid boron trifluoride–diethyl ether complex. The cationic process was almost quantitative (90–97%) and left the great majority of the 1,2,3-thiadiazole rings intact, which is important for a good solubility. Figure 1 demonstrates the ^{1}H and ^{13}C chemical shifts of **1c** and its polymer **1c′**. The signals of the olefinic part of **1c** disappear and new signals of **1c′** appear in the saturated region. The NMR data of the 4-phenyl-1,2,3-thiadiazole moiety are almost the same for monomer **1c** and polymer **1c′**.

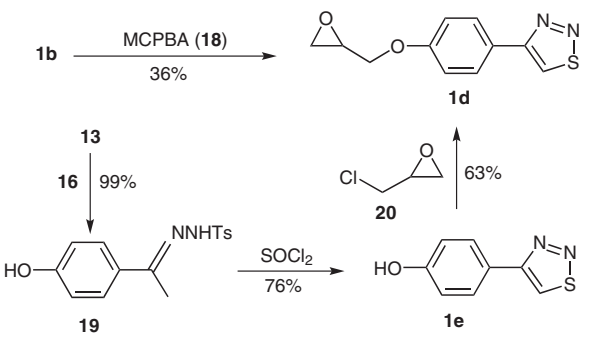
The cationic ring-opening polymerization of oxirane **1d**, performed with boron trifluoride under the same conditions as for **1c**, was less uniform.[28–30] Additionally, a partial fragmentation of the 1,2,3-thiadiazole rings could not be avoided. The polymer **1d′** was still soluble in organic solvents like chloroform or acetone, but the lack of uniformity prompted us to exclude **1d′** from further studies.

Finally we tried another approach to polymers containing 1,2,3-thiadiazole rings (Scheme 5). The phenolic OH group of **13** was alkylated with 1,3-dibromopropane (**21**) to give ketone **22**, whose 4-toluenesulfonylhydrazone **23** was subjected to the Hurd–Mori reaction.[27] The reactivity of the carbonyl group in **22** toward 4-toluenesulfonyl hydrazide (**16**) is much higher than the reactivity of the bromo substituent. Thus, excellent yields of hydrazone **23** and 1,2,3-thiadiazole **1f** could be obtained. The terminal bromo group in **1f** could then be used for the formation of arylalkyl ethers. Whereas unsubstituted phenol (**24**) generated monomer thiadiazole **1g**, the analogous reaction of **1f** and 4-isopropenylphenol (**25**) led directly to polymer **1h′**. The obtained ochre powder turned out to be insoluble in all common organic solvents. Its sulfur content was correct, its nitrogen content was too low.

When commercial poly(4-hydroxystyrene) (**26**) was reacted with **1f**, an ochre powder **1i′** was obtained, which was soluble in acetone. Its nitrogen and sulfur content corresponded largely to intact 1,2,3-thiadiazole rings and a complete alkylation of all phenolic OH groups. The photocrosslinking of the polymers **1c′** and **1i′** could be per-



Scheme 3 Preparation of 4-[4-(prop-1-enyloxy)phenyl]-1,2,3-thiadiazole [(*Z*/*E*)-**1c**]



Scheme 4 Preparation of 4-[4-(oxiran-2-ylmethoxy)phenyl]-1,2,3-thiadiazole (**1d**)

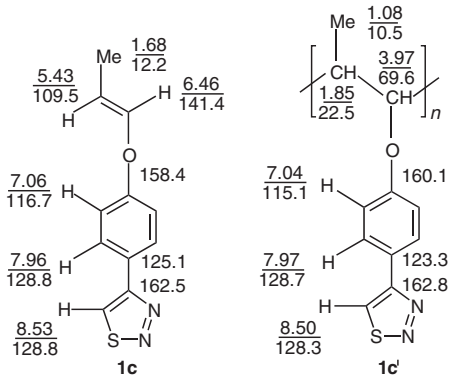


Figure 1 ^1H and ^{13}C NMR data of the monomer (*E*)-**1c** and the polymer **1c′** ($CDCl_3$, TMS, δ).

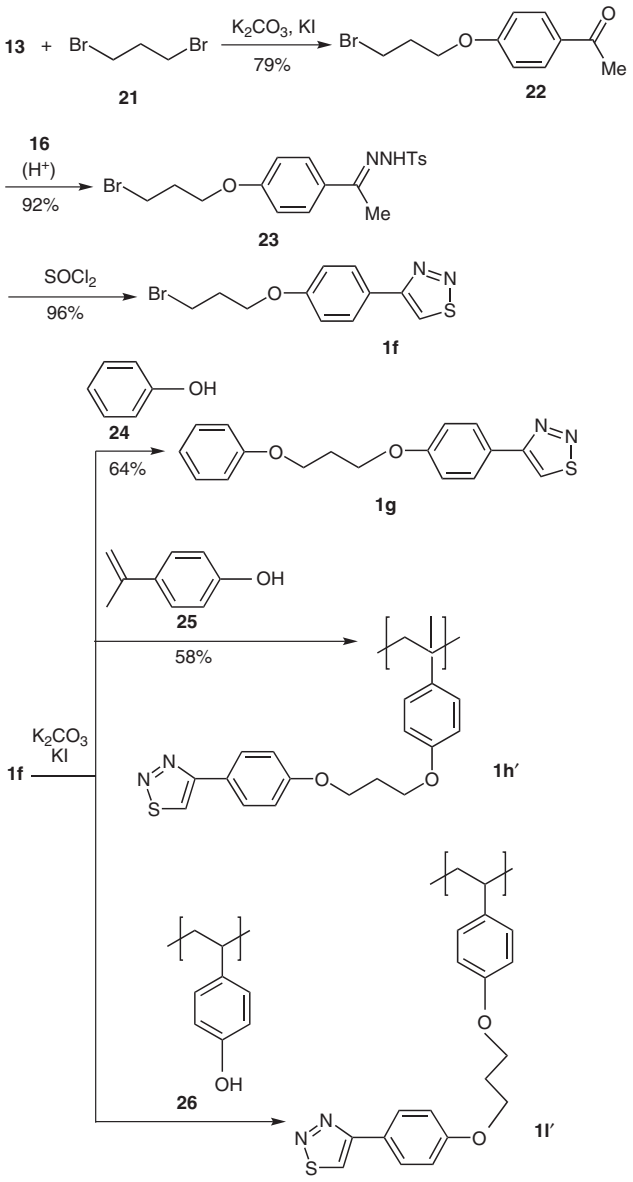
formed in solution (benzene or dichloromethane) or in thin neat films, which were spin-coated or produced by evaporation of saturated solutions. The absorption maxima of **1c′** and **1i′** occur at 260 nm; additionally to this π→π* transitions, n→π* transitions appear in the form of an extended shoulder at about 310 nm (CH_2Cl_2).

Irradiations of the films with a mercury medium pressure lamp, equipped with a Vycor filter (λ_{irr} 230 nm) generated cross-linked polymers **1c″**, and **1i″**, which were totally insoluble in organic solvents. Exactly this behavior is a fundamental precondition for the application of **1c′**/**1c″** and **1i′**/**1i″** as negative photoresists. According to the reaction of the model compound **1a**→**9a**, we assumed a photocrosslinking by formation of 1,3-dithioles. Scheme 6 illustrates the processes **1c′**→**1c″** and **1i′**→**1i″**. Due to the rigid cross-linking segment in **1c″**, such a process is unlikely within a chain (intramolecular reaction). The cross-linking segment of **1i″** is more flexible. Therefore, intra- and intermolecular photoreactions are possible.

How can the presumed type of photocrosslinking shown in Scheme 6 be verified? For this purpose we reinvestigated the ^{13}C NMR and IR characterization of model compound **9a**,[31,32] which we obtained by irradiation of **1a** in benzene. The *Z*/*E* ratio amounted to 10:1. The *E*-isomer has low solubility in toluene, so we could obtain the pure (*Z*)-isomer by fractional crystallization. Its ^{13}C NMR signals in $CDCl_3$ range from δ = 111.7–113.2 for the methine CH of the 2-methylene-1,3-dithiole moiety, to δ = 132.6–134.3 for the C_q of the S-heterocycles and to δ = 135.2–136.7 for the C_q of the benzene rings. The remaining aromatic CH signals are between δ = 125.6–128.8. The solid state ^{13}C NMR of the cross-linked polymers **2c″** and **2i″** exhibit strongly superimposed signals in this area 110 ≤ δ ≤ 140, but the resolution of the magic angle spinning measurement was much too low in order to verify the 1,3-dithiole substructure. Therefore, we had to rely on the IR measurement in potassium bromide.

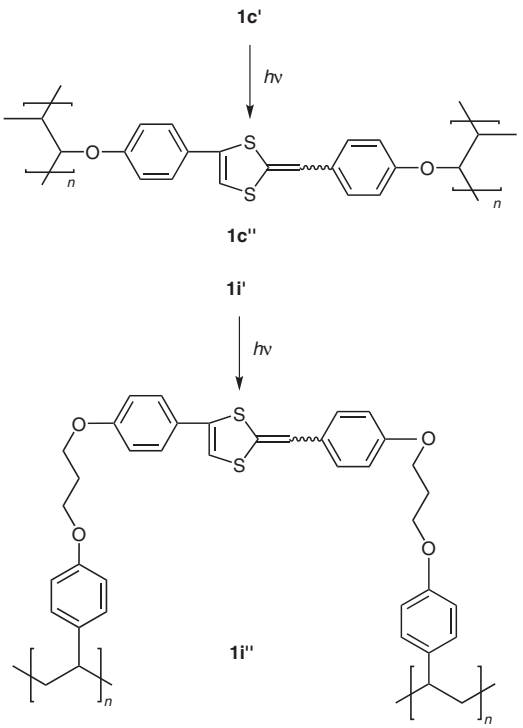
Model compound **9a** exhibits intense bands at 1578, 1556, and 1484 cm^{-1},[33] which appear also in IR spectra of polydithiafulvenes.[34,35] The IR spectra of the cross-linked polymers **1c″** and **1i″** contain indeed strong, overlapping bands in the region 1480–1500 and 1550–1600 cm^{-1}. 2-Benzylidene-4-phenyl-1,3-dithiole (**9a**) generates a red 1,3-dithiolium salt, soluble in trifluoroacetic acid.[5] When **1c″** and **1i″** were treated with trifluoroacetic acid, the ochre color changed to red-brown, but the cross-linked polymers remained insoluble. We take the IR measurements and the behavior toward trifluoroacetic acid as good hints for the cross-linking type shown in Scheme 6.

Summarizing the results, we can make the following statement: Soluble polymers **1c′** and **1d′** could be prepared by cationic polymerization of the 4-phenyl-1,2,3-thiadiazoles **1c** and **1d**, which contain polymerizable functionalities in 4-position of the phenyl groups. In a sec-



Scheme 5 Preparation of the polymers **1h′** and **1i′**

ond approach polymer **1i′** was obtained by attaching 1,2,3-thiadiazole containing side chains to the main chain of poly(4-hydroxystyrene). The uniform polymers **1c′** and **1i′** have intact 1,2,3-thiadiazole rings, which show nitrogen extrusion on irradiation. The resulting 1,3-diradicals rearrange partly to thioketenes, which then enter a cycloaddition with the remaining 1,3-diradicals to form 1,3-dithioles as cross-linking segments between the main chains. These materials **1c″** and **1i″** are completely insoluble, so that the systems **1c′/1c″** and **1i′/1i″** fulfill the conditions for negative photoresists. Since 1,2,3-thiadiazole rings can also be cleaved by synchroton radiation and electron beams, further resist techniques seem to be applicable. A major advantage of the polymers **1c′** and **1i′** is due to the fact that 'vagabonding' atomic sulfur is not formed during the photocrosslinking. Therefore, high resolution of imaging techniques with these negative photoresists can be expected.



Scheme 6 Photoreactions of the soluble polymers **1c′** and **1i′** to the insoluble cross-linked polymers **1c″** and **1i″**, respectively

Melting points were determined on a Büchi melting point apparatus and are uncorrected. The Bruker spectrometers AM 400 and ARX 400 served for the measurement of the ^{1}H and ^{13}C NMR spectra. $CDCl_3$ was used as solvent and TMS as internal standard, if not otherwise stated. FT-IR spectra were recorded on a GX Perkin-Elmer and IR spectra on a Beckman Acculab spectrophotometer. A Zeiss MCS 224/234 diode array spectrophotometer was used for the UV spectroscopy. Mass spectra were obtained on a Finnigan MAT 95 and a Micromass TOF spec E spectrometer. Column chromatography was carried out on silica gel (60 M, 230–400 mesh, Macherey-Nagel). Elemental analyses were performed in the Microanalytical Laboratory of the Institute of Organic Chemistry of the University of Mainz.

Synthesis of the Monomeric 1,2,3-Thiadiazoles

4-(Allyloxy)acetophenone (15)

4-Hydroxyacetophenone (**13**, 5.2 g, 38.1 mmol), 3-bromoprop-1-ene (**14**, 4.6 g, 38.3 mmol), K_2CO_3 (5.2 g, 37.5 mmol), and KI (4.6 g, 27.7 mmol) were heated in anhyd acetone (85 mL) to reflux for 40 h. The mixture was then stirred with H_2O (60 mL) at r.t. for 10 min and extracted with CH_2Cl_2 (3 × 50 mL). The soln was dried ($MgSO_4$), concentrated, and purified by column filtration (silica gel, 8 × 15 cm, CH_2Cl_2) to give a viscous oil that solidified below 20 °C; yield: 6.6 g (98%). The product was identified by comparison with an authentic sample.[26]

^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 4.32–4.37 (m, 2 H, CH_2), 5.02–5.07 (m, $^3J_{cis}$ = 10.0 Hz, 1 H, =CH_2), 5.22–5.28 (m, $^3J_{trans}$ = 17.0 Hz, 1 H, =CH_2), 5.78–5.83 (m, 1 H, =CH), 6.70/7.68 (AA′BB′, 4 H, H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 25.7 (CH_3), 68.2 (OCH_2), 113.8, 129.9 (CH_{arom}), 117.3 (=CH_2), 129.7, 161.9 (arom-C_q), 132.0 (=CH), 195.8 (CO).

4-(Allyloxy)acetophenone 4-Toluenesulfonylhydrazone (17)
Ketone **15** (3.0 g, 17.0 mmol) was added to a boiling solution of $TsNHNH_2$ (**16**, 3.17 g, 17.02 mmol) in EtOH (15 mL). The mixture was refluxed for 1 h and then concentrated till the product started to precipitate. Recrystallization (EtOH) gave **17** (5.3 g, 91%) as a colorless powder; mp 138 °C.

^{1}H NMR ($CDCl_3$): δ = 2.11 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 4.50–4.55 (m, 2 H, CH_2), 5.25–5.29 (m, $^3J_{cis}$ = 10.0 Hz, 1 H, =CH_2), 5.38–5.43 (m, $^3J_{trans}$ = 17.0 Hz, 1 H, =CH_2), 5.98–6.03 (m, 1 H, =CH), 6.82/7.90 (AA′BB′, 4 H, H_{arom}), 7.28/7.55 (AA′BB′, 4 H, H_{arom}), 7.94 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 13.2, 21.5 (CH_3), 68.8 (OCH_2), 114.4, 127.7, 128.1, 129.5 (CH_{arom}), 117.8 (=CH_2), 132.9 (=CH), 130.1, 135.6, 144.0, 159.8 (arom C_q), 152.6 (CN).

MS (FD): *m*/*z* (%) = 344 (100) [M^+].

Anal. Calcd for $C_{18}H_{20}N_2O_3S$ (344.4): C, 62.77; H, 5.85; N, 8.13. Found: C, 62.47; H, 5.82; N, 8.12.

4-[4-(Allyloxy)phenyl]-1,2,3-thiadiazole (1b); Typical Procedure
Hydrazone **17** (2.0 g, 5.81 mmol) was added portionwise at r.t. to freshly distilled $SOCl_2$ (8.0 mL, 13.1 g, 110 mmol). The vigorously stirred mixture started immediately to react. The temperature was kept at 10–15 °C by cooling in an ice bath and stirred for 1 h and this was continued at r.t. for 6 h. The excess $SOCl_2$ was removed (1 kPa) and the residue purified by column chromatography (silica gel, 5 × 100 cm, toluene). After the first fraction of TsCl, **1b** (1.1 g, 90%) was obtained as a colorless powder; mp 74 °C.

^{1}H NMR ($CDCl_3$): δ = 4.58–4.63 (m, 2 H, CH_2), 5.25–5.30 (m, $^3J_{cis}$ = 10.0 Hz, 1 H, =CH_2), 5.45–5.49 (m, $^3J_{trans}$ = 16.0 Hz, 1 H, =CH_2), 6.03–6.08 (m, 1 H, =CH), 7.00/7.93 (AA′BB′, 4 H, H_{arom}), 8.50 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ = 68.8 (OCH_2), 115.3, 128.7 (CH_{arom}), 117.9 (=CH_2), 132.9 (=CH), 128.4 (C5), 123.6, 159.5 (arom C_q), 162.6 (C4).

MS (FD): *m*/*z* (%) = 218 (100) [M^+].

HRMS: *m*/*z* [M^+] calcd for $C_{11}H_{10}N_2OS$: 218.0514; found: 218.0518.

(*Z*/*E*)-4-[4-(Prop-2-enyloxy)phenyl]-1,2,3-thiadiazole [(*E*/*Z*)-1c]
DABCO (0.69 g, 6.37 mmol), $RhCl(PPh_3)_3$ (0.5 g, 0.54 mmol), and **1b** (1.14 g, 5.20 mmol) were added to a mixture of EtOH (220 mL), toluene (80 mL), and H_2O (30 mL). The reaction was performed at 85 °C under an N_2 atmosphere [monitored by TLC (silica gel, toluene)]. After 30 h the volatile parts were evaporated (1.0 kPa) and the residue purified by column chromatography (silica gel, 3 × 100 cm, CH_2Cl_2–EtOH, 25:1); **1c** (0.70 g, 64%) was the first fraction; colorless crystals; mp 81–82 °C; ratio *Z*/*E* 56:44 (^{1}H NMR). Later fractions consist of starting compound **1b** and some 4-(1,2,3-thiadiazol-4-yl)phenol (**1e**), which was formed by ether cleavage.

^{1}H NMR ($CDCl_3$): δ [(*E*)-**1c**] = 1.65–1.69 (m, 3 H, CH_3), 5.41–5.46 (m, ^3J = 15.0 Hz, 1 H, =CH), 6.43–6.48 (m, ^3J = 15.0 Hz, 1 H, =CH), 7.06/7.96 (AA′BB′, 4 H, H_{arom}), 8.53 (s, 1 H, H5); δ [(*Z*)-**1c**] = 1.70–1.74 (m, 3 H, CH_3), 4.92–4.97 (m, ^3J = 8.0 Hz, 1 H, =CH), 6.40–6.45 (m, ^3J = 8.0 Hz, 1 H, =CH), 7.09/7.98 (AA′BB′, 4 H, H_{arom}), 8.53 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ [(*E*)-**1c**] = 12.2 (CH_3), 109.5, 141.1 (=CH), 116.7, 128.8 (CH_{arom}), 125.1, 158.4 (arom C_q), 128.8 (C5), 162.5 (C4).

MS (FD): *m*/*z* (%) = 218 (24) [M^+], 190 (87), 158 (32), 148 (100), 77 (41).

Anal. Calcd for $C_{11}H_{10}N_2OS$ (218.3): C, 60.53; H, 4.62; N, 12.83. Found: C, 60.62; H, 4.65; N, 12.81.

4-[4-(Oxiran-2-ylmethoxy)phenyl]-1,2,3-thiadiazole (1d) by Epoxidation of 1b
MCPBA (**18**, 0.78 g, 4.52 mmol) dissolved in anhyd CH_2Cl_2 (9 mL) was added dropwise to a soln of **1b** (0.70 g, 3.21 mmol) in anhyd CH_2Cl_2 (10 mL) at 0 °C. The mixture was stirred vigorously at r.t. for 6 h and at reflux for 3 h. The mixture was filtered and the soln was washed with 10% NaOH (3 × 10 mL) and H_2O (2 × 20 mL). The dried ($MgSO_4$) and concentrated solution was chromatographed (silica gel, 3 × 80 cm, EtOH–CH_2Cl_2, 1:40). The first fraction consisted of unreacted **1b** and the second fraction of the product **1d** (0.30 g, 36%); colorless crystals; mp 77–78 °C.

^{1}H NMR ($CDCl_3$): δ = 2.75–2.79/2.90–2.95/3.35–3.39 (3 m, 3 H, oxirane ring), 3.95–3.99/4.26–4.30 (2 m, 2 H, OCH_2), 7.04/7.93 (AA′BB′, 4 H, benzene ring), 8.52 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ = 44.5 (CH_2, oxirane ring), 50.0 (CH, oxirane ring), 68.9 (OCH_2), 115.3, 128.8 (CH_{Ph}), 124.1, 159.4 (C_q-Ph), 128.5 (C5), 162.5 (C4).

MS (FD): *m*/*z* (%) = 234 (100) [M^+].

Anal. Calcd for $C_{11}H_{10}N_2O_2S$: C, 56.40; H, 4.30; N, 11.96; S, 13.69. Found: C, 56.63; H, 4.23; N, 11.93; S, 13.71.

4-Hydroxyacetophenone 4-Toluenesulfonylhydrazone (19)
4-Hydroxyacetophenone (**13**, 2.19 g, 16.0 mmol) was added to a hot soln of $TsNHNH_2$ (**16**, 3.0 g, 16.0 mmol) in EtOH (16 mL). The mixture was refluxed for 1 h then concentrated till the product started to precipitate. The obtained yellowish powder was washed (cold EtOH) and recrystallized (EtOH); yield: 4.8 g (99%); mp 93–94 °C.

^{1}H NMR (DMSO-d_6): δ = 2.12 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 6.77/7.83 (AA′BB′, 4 H, H_{arom}), 7.42/7.51 (AA′BB′, 4 H, H_{arom}), 9.79 (s, 1 H, NH), 10.29 (s, 1 H, OH).

^{13}C NMR (DMSO-d_6): δ = 14.0, 20.9 (CH_3), 115.0, 127.4, 127.5, 129.3 (CH_{arom}), 128.3, 136.3, 143.1 (arom C_q), 153.4 (CN), 158.7 (arom C_qO).

MS (EI): *m*/*z* (%) = 304 (13) [M^+], 149 (100), 119 (55), 92 (53).

Anal. Calcd for $C_{15}H_{16}N_2O_3S$ (304.4): C, 59.19; H, 5.30; N, 9.20. Found: C, 59.22; H, 5.31; N, 9.18.

4-(1,2,3-Thiadiazol-4-yl)phenol (1e)
Following the typical procedure for **1b** using **19** (3.0 g, 9.87 mmol) yielded **1e** (1.3 g, 76%) as an ochre powder; mp 166 °C. The product was identified by comparison with an authentic sample.[36,37]

^{1}H NMR (DMSO-d_6): δ = 6.95/7.97 (AA′BB′, 4 H, H_{arom}), 8.97 (s, 1 H, OH), 9.39 (s, 1 H, 5-H).

^{13}C NMR (DMSO-d_6): δ = 116.0, 128.7 (CH_{arom}), 121.8, 158.6 (arom C_q), 130.7 (C5).

4-[4-(Oxiran-2-ylmethoxy)phenyl]-1,2,3-thiadiazole (1d) by Reaction of 1e with (±)-Epichlorohydrin (20)
A mixture of thiadiazole **1e** (0.23 g, 1.29 mmol), (±)-2-(chloromethyl)oxirane (**20**, 0.23 g, 2.49 mmol), K_2CO_3 (O.30 g, 2.16 mmol), and KI (0.30 g, 1.81 mmol) in anhyd acetone (30 mL) was refluxed for 30 h. The mixture was treated with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The dried ($MgSO_4$) organic phase was evaporated and the residue purified by column chromatography (silica gel, 4 × 70 cm, CH_2Cl_2–EtOH, 20:1) to give **1d** as colorless crystals; yield: 0.20 g (63%); mp 77–78 °C.

4-(3-Bromopropoxy)acetophenone (22)
1,3-Dibromopropane (**21**, 30.0 g, 148.6 mmol), ketone **13** (2.0 g, 14.9 mmol), and K_2CO_3 (20.0 g, 145.0 mmol) in anhyd acetone (80 mL) were refluxed for 40 h. The filtered mixture was evaporated (1 kPa); the solvent and excess **21** distilled off. The residue was purified by column chromatography [silica gel, 5 × 100 cm, petroleum

ether (bp 40–70 °C) to remove residual **21** and then EtOAc–CH_2Cl_2, 35:65]. Product **22** was obtained as an almost colorless, viscous oil; yield: 3.0 g (79%). The product was identified by comparison with an authentic sample.[38]

^{1}H NMR ($CDCl_3$): δ = 2.26–2.30 (m, 2 H, CH_2), 2.50 (s, 3 H, CH_3), 3.55 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 4.11 (t, ^3J = 5.9 Hz, 2 H, OCH_2), 6.88/7.86 (AA′BB′, 4 H, H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 26.2 (CH_3), 29.6 (CH_2), 32.1 (CH_2Br), 65.6 (CH_2O), 114.2, 130.5 (CH_{arom}), 130.5, 162.6 (arom C_q), 196.5 (CO).

4-(3-Bromopropoxy)acetophenone 4-Toluenesulfonylhydrazone (23)

Ketone **22** (1.5 g, 5.83 mmol) and $TsNHNH_2$ (**16**, 1.1 g, 5.91 mmol) were heated in EtOH (8 mL) to reflux. After 1 h the soln was concentrated till the product began to precipitate. The colorless powder was washed (cold EtOH) and recrystallized (EtOH); yield: 2.3 g (92%); mp 126 °C.

^{1}H NMR ($CDCl_3$): δ = 2.11 (s, 3 H, CH_3), 2.26–2.30 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 3.58 (t, ^3J = 6.3 Hz, 2 H, CH_2Br), 4.08 (t, ^3J = 5.9 Hz, 2 H, OCH_2), 6.82/7.90 (AA′BB′, 4 H, H_{arom}), 7.29/7.57 (AA′BB′, 4 H, H_{arom}), 7.91 (s, 1 H, NH).

^{13}C NMR ($CDCl_3$): δ = 13.2, 21.5 (CH_3), 29.7, 32.2, 65.4 (CH_2), 114.2, 127.8, 128.1, 129.5 (CH_{arom}), 130.2, 135.6, 144.0, 152.5 (arom C_q), 152.5 (CN).

MS (FD): *m*/*z* (%) = 424/426 (100) [M^+, Br isotope pattern].

Anal. Calcd for $C_{18}H_{21}BrN_2O_3S$ (425.35): C, 50.83; H, 4.98; Br, 18.79; N, 6.59; S, 7.54. Found: C, 50.88; H, 5.19; Br, 18.45; N, 6.60; S, 7.44.

4-[4-(3-Bromopropoxy)phenyl]-1,2,3-thiadiazole (1f)

Hydrazone **23** (0.5 g, 1.18 mmol) was slowly added to freshly distilled $SOCl_2$ (24.0 mL, 39.3 g, 330 mmol). The vigorously stirred mixture started immediately to react at r.t.; an ice-water bath was used for cooling. Further hydrazone **23** (1.95 g, 458 mmol) was added in small portions over 20 min. The mixture was stirred at r.t. for 6 h and then excess $SOCl_2$ was removed and the residue purified by column chromatography (silica gel, 5 × 100 cm, toluene). The 1st fraction consisted of TsCl and the 2nd fraction contained the product **1f** (0.30 g, 96%) as colorless crystals; mp 95–97 °C.

^{1}H NMR ($CDCl_3$): δ = 2.30–2.36 (m, 2 H, CH_2), 3.61 (t, ^3J = 6.4 Hz, 2 H, CH_2Br), 4.15 (t, ^3J = 5.9 Hz, 2 H, OCH_2), 6.99/7.96 (AA′BB′, 4 H, H_{arom}), 8.50 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ = 29.7, 32.3, 65.6 (CH_2), 115.2, 128.8 (CH_{arom}), 123.9, 159.7 (arom C_q), 128.4 (C5), 162.6 (C4).

MS (EI): *m*/*z* (%) 300/298 (5) [M^+, Br isotope pattern], 149 (100).

Anal. Calcd for $C_{11}H_{11}BrN_2OS$: C, 44.16; H, 3.71; N, 9.36. Found: C, 43.79; H, 3.99; N, 9.06.

4-[4-(3-Phenoxypropoxy)phenyl]-1,2,3-thiadiazole (1g)

Phenol (**24**, 0.1 g, 1.06 mmol), **1f** (0.30 g, 1.00 mmol), K_2CO_3 (0.15 g, 1.09 mmol), and KI (0.35 g, 2.11 mmol) were heated to reflux in anhyd acetone (30 mL). After 30 h, the mixture was treated with H_2O (40 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The dried ($MgSO_4$) organic phase was evaporated and the residue recrystallized (CH_2Cl_2) to give an ochre powder; yield: 0.2 g (64%) ; mp 67–68 °C.

^{1}H NMR ($CDCl_3$): δ = 2.80–2.85 (m, 2 H, CH_2), 4.14–4.19 (m, 2 H, CH_2), 4.20–4.26 (m, 2 H, OCH_2), 6.90–6.95 (m, 3 H, H_{arom}), 7.03/7.96 (AA′BB′, 4 H, H_{arom}), 7.25–7.29 (m, 2 H, H_{arom}), 8.49 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ = 29.4, 64.3, 64.8 (CH_2), 114.6, 115.2, 120.8, 128.8, 129.5 (CH_{arom}), 123.7, 158.9, 159.9 (arom C_q), 128.3 (C5), 162.7 (C4).

MS (EI): *m*/*z* (%) = 312 (55) [M^+], 284 (86), 207 (57), 151 (100).

Anal. Calcd for $C_{17}H_{16}N_2O_2S$ (312.4): C, 65.36; H, 5.16; N, 8.97. Found: C, 65.38; H, 5.21; N, 8.93.

Synthesis of Polymers

Polymer 1c′; Typical Procedure

(*E*/*Z*)-**1c** (0.2 g, 0.92 mmol), dissolved in anhyd CH_2Cl_2 (4 mL), was treated under N_2 at 0 °C with BF_3·OEt_2 (2 drops). The mixture was stirred at 0 °C for 30 min and at r.t. for 90 min and the reaction was quenched by addition of MeOH (5 mL). The volatile parts were evaporated, the filtered residue washed (cold MeOH) and dried in vacuo (0.1 kPa) for 48 h to give **1c′** (195 mg, 97%) as an ochre product that started to melt at 62 °C and decomposed at 167 °C. It was soluble in many organic solvents. In order to remove small oligomers, which can be seen in the MS (FD), we precipitated it several times from THF.

^{1}H NMR ($CDCl_3$): δ = 1.08 (d, ^3J = 6.4 Hz, 3 H, CH_3), 1.82–1.86 (m, 1 H, CH), 3.97 (t, ^3J = 5.7 Hz, 1 H, OCH), 7.04/7.97 (AA′BB′, 4 H, H_{arom}), 8.50 (s, 1 H, H5).

^{13}C NMR ($CDCl_3$): δ = 10.5 (CH_3), 22.5 (CH), 69.6 (OCH), 115.1, 128.7 (CH_{arom}), 123.3, 160.1 (arom C_q), 128.3 (C5), 162.8 (C4).

The NMR data are related to the repeat unit; end groups could not be identified. Comparison of the elemental analysis (Table 1) with the data of the monomer reveals that the 1,2,3-thiadiazole rings were intact.

Polymer 1d′

The cationic polymerization of **1d** to **1d′** was performed according to typical procedure to give **1c′**. A yellow solid (90%) was obtained, which started to melt at 58 °C and decomposed above 190 °C. The ^{1}H and ^{13}C NMR characterization of the well-soluble product showed a large number of broad signals, which hint to a non-uniform ring-opening polymerization. The elemental analysis revealed a too low content of N (10.93%) and S (11.87%) compared to the monomer: N (11.89%), S (13.64%). These values permit the conclusion that 8–13% of the 1,2,3-thiadiazole rings did not survive the polymerization. Therefore we did not continue our studies with polymer **1d′**.

Polymer 1h′

4-Isopropenylphenol (**25**, 0.33 g, 2.44 mmol), 1,2,3-thiadiazole **1f** (0.73 g, 2.44 mmol), K_2CO_3 (0.35 g, 2.52 mmol), and KI (0.78 g, 4.70 mmol) were heated in anhyd acetone (60 mL) to reflux. After 40 h the mixture was stirred with H_2O (30 mL). A pale brown precipitate was filtered off, washed with CH_2Cl_2 and dried in vacuo (0.1 kPa). The product could not be dissolved in NMR solvents such as $CDCl_3$, acetone-d_6, DMSO-d_6, etc.

Anal. Calcd for the repeat unit $C_{20}H_{20}O_2N_2S$: C, 68.16; H, 5.72; N, 7.95; S, 9.10. Found for the polymer **1h′**: C, 69.44; H, 6.64; N, 7.21; S, 8.91. These values reveal that almost all OH groups reacted with the bromide and that the majority of 1,2,3-thiadiazole rings were kept intact. Due to the insolubility, the material cannot be used as negative photoresist.

Polymer 1i′

1,2,3-Thiadiazole **1f** (0.33 g, 1.10 mmol), which bears a bromo substituent, was reacted with poly(4-hydroxystyrene) (**26**, 0.12 g, 1.00 mmol related to monomer, M_w = 5800), K_2CO_3 (0.15 g, 1.08 mmol), and KI (0.36 g, 2.17 mmol) in anhyd acetone (40 mL). The mixture was heated to reflux for 30 h and then H_2O (30 mL) was added to the vigorously stirred mixture. Extraction with CH_2Cl_2 (3 × 50 mL) gave an organic phase, which was dried ($MgSO_4$) and evaporated. The obtained ochre powder **1i′** (0.33 g, 98%) was washed (cold Et_2O) and purified by dissolving and precipitating

Table 1 Change of the Elemental Composition by Photocrosslinking of the Polymers **1c′** and **1i′** to **1c″** and **1i″**, Respectively

	Analysis (%)			
	C	H	N	S
Calcd for repeat unit $C_{11}H_{10}N_2OS$	60.53	4.62	12.83	14.69
1c′ found	60.90	5.01	12.60	14.58
1c″ (film)	67.99	5.34	0.21	16.55
1c″ (soln)	64.46	5.76	0.53	16.42
Calcd for repeat unit $C_{19}H_{18}N_2O_2S$	67.43	5.36	8.28	9.47
1i′ found	67.81	5.66	8.09	9.37
1i″ (film)	73.12	6.20	0.31	10.48
1i″ (soln)	78.41	7.25	0.74	10.63

from acetone. The carefully dried yellow-ochre product (0.31 g, 92%) started to melt at 70 °C and decomposed above 110 °C.

^{1}H NMR (acetone-d_6): δ = 1.23–1.29 (m, 2 H, CH_2), 2.25–2.31 (m, 2 H, CH_2), 3.01–3.07 (m, 1 H, CH), 3.43–3.49 (m, 2 H, OCH_2), 4.12–4.19 (m, 2 H, OCH_2), 6.63–6.69 (m, 4 H, H_{arom}), 7.09/8.08 (AA′BB′, 4 H, H_{arom}), 9.24 (s, 1 H, H5). The data are related to the repeat units, in which the OH groups have completely reacted.

^{13}C NMR (acetone-d_6): δ = 22.9, 23.1 (CH_2), 33.8 (CH), 68.7, 68.7 (CH_2), 115.9, 115.9, 120.1, 124.9, 129.5, 130.7, 155.8, 160.8, 163.7 (arom and heteroarom CH and C_q).

Elemental analysis in Table 1.

Photoreactions

(*Z*)-2-Benzylidene-4-phenyl-1,3-dithiole (*Z*-9a); Photochemistry of the Model Compound 1a

4-Phenyl-1,2,3-thiadiazole[27,39] (**1a**, 1.62 g, 10.0 mmol), dissolved in O_2-free, anhyd benzene (600 mL) was irradiated in an N_2 atmosphere with a 450-W Hanovia medium pressure lamp, equipped with a Vycor filter (λ 230 nm). When the TLC control (silica gel, toluene) indicated the complete consumption of **1a**, the solvent was evaporated and the residue (1.34 g, 100%) purified by column filtration (silica gel, 10 × 15 cm, HCO_2H) to give (*Z*/*E*)-2-benzylidene-4-phenyl-1,3-dithiole [(*E*/*Z*)-**9a**] (0.94 g, 70%) as colorless crystals. The identification was achieved by comparison with an authentic sample.[25] Crystallization (MeOH) afforded the pure (*Z*)-2-benzylidene-4-phenyl-1,3-dithiole [(*Z*)-**9a**]; mp 207 °C.

^{1}H NMR (DMSO-d_6): δ = 6.73 (s, 1 H, =C*H*Ph), 7.19 (s, 1 H, H5), 7.31–7.54 (m, 10 H, H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 111.7 (HC5), 113.2 (*exo*-CH), 125.6, 126.2, 126.6, 128.3, 128.5, 128.8 (CH_{arom}), 132.6 (C_q-2), 134.3 (C_q-4), 135.2, 136.7 (arom C_q).

Photocrosslinking of the Polymers; General Procedure

Sat. solns of **1c′** or **1i′** in CH_2Cl_2, $CHCl_3$, acetone were used for the formation of films by spin-coating (DELTA T) or by evaporation on quartz plates (1 × 3.5 cm). Analogous experiments were made with concentrated solutions of **1c′** or **1i′** [polymer (100 mg) in CH_2Cl_2 (200 mL)]. A 450-W Hanovia medium pressure lamp, equipped with a Vycor filter (λ 230 nm) served for the irradiation of the films or solns. In both cases N_2 was evolved and after an irradiation period of 20 min (film) or 60–100 min (soln) an ochre material was obtained, which was insoluble in organic solvents (including solvents like NMP or 1,2-dichlorobenzene).

The elemental analyses (Table 1) revealed a negligible N content and a preserved S content in **1c″** and **1i″**.

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