

Photolysis, thermolysis, and protolytic decomposition of a triazene polymer in solution

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SUMMARY:

The depolymerization of a triazeno-group containing photopolymer, poly[oxy-1,4-phenylene-azo(methylimino)hexamethylene(methylimino)azo-1,4-phenylene], is investigated in a tetrahydrofuran (THF) solution. Irradiation of the material leads to a clean decomposition of the photolabile polymer, as monitored by UV spectroscopy and gel-permeation chromatography (GPC). As compared to the photolysis in THF solution, the light-induced decomposition rate of a polymer in a polymer film is shown to be much slower. The highly photosensitive triazeno group also decomposes thermally at temperatures above approx. 220 °C. The kinetics of thermal degradation of the polymer in substance was investigated at a temperature of 256 °C, and monitored by GPC measurements. During this decomposition, one first observes the development of higher molar-mass fractions, which result from grafting reactions of primary radicals. Upon further thermolysis the triazene polymer is completely degraded to low-molar-mass products. The volatile decomposition products were identified by gas chromatography/mass spectrometry (GC/MS) analysis. The protolytic decomposition, which represents the retrosynthesis of the triazene polymer, was studied in a 9:1 mixture of tetrahydrofuran and an aqueous citrate buffer solution. Although the decomposition rate in this solvent mixture is slow, as compared to the depolymerization in diluted hydrochloric acid, a clean decomposition of the triazene polymer is obtained.

Introduction

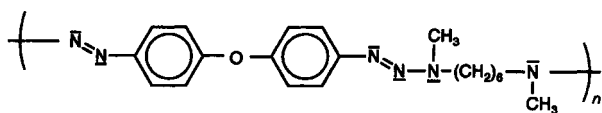
The chemical and biochemical properties of the triazeno group have been intensively investigated^{1,2)}. The discovery of cytostatic activity of several triazene compounds prompted research efforts directed towards the development of triazene-based drugs³⁾. More recently a novel application of triazenes in photo-microlithography has emerged. In the search for dry processing techniques in the laser structuring of polymer surfaces⁴⁾, triazene chromophores are investigated as sensitizers for polymer ablation at the emission wavelength of the XeCl*-excimer laser, i.e. 308 nm. Several 1-aryl-3,3-diethyltriazenes were successfully used as dopants for the ablation of

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poly(methyl methacrylate) (PMMA) at 308 nm⁵). In support of these investigations, the photolytic decomposition of various 1-aryl-3,3-diethyltriazene compounds was studied in dependence of the aromatic substitution pattern⁶.

As an alternative to exploit the photochemical behavior of low-molar-mass triazene promoters, novel triazeno-group containing photopolymers were designed for laser-microlithography applications^{7,8}. Recently we have reported on the synthesis⁹, characterization¹⁰, and laser-structuring of these triazene polymers^{7,8}. In the present study, the depolymerization of a triazene polymer by photolysis, as induced by irradiation with the light of a high-pressure xenon lamp, is investigated in solution and in a polymer film. The structural formula of the material studied, poly[oxy-1,4-phenyleneazo(methylimino)hexamethylene(methylimino)azo-1,4-phenylene], is shown in *Scheme 1*.



For the use in photoresist technology it is essential that the photopolymers are capable of withstanding temperatures up to 160 °C for several minutes, as used in prebaking and postbaking processes. This condition is met by the remarkably high thermostability of triazene polymers, as established by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements^{7,8,10}. Here the thermolytic decomposition of the triazene polymer at a temperature of 256 °C is quantified by gel-permeation chromatography (GPC); volatile products are identified by GC/MS analysis.

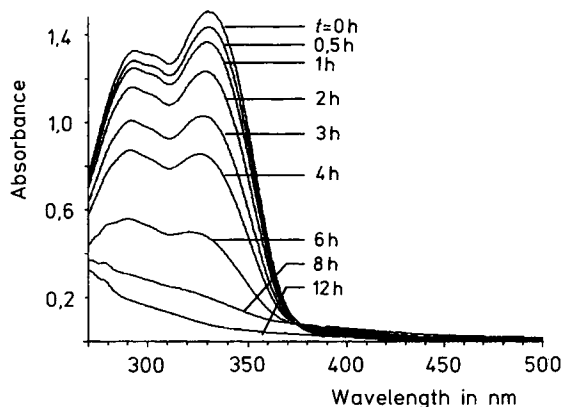
During microchip fabrication, the photoresist has to be stripped off from the substrate surface. Commonly, an oxygen plasma is used for this purpose; as an alternative, dilute mineral acids may be employed with the aim of completely decomposing the polymer into water soluble products. To establish the feasibility of the latter approach for our system, the depolymerization of the triazene polymer was studied in a mixture (vol ratio 9:1) of tetrahydrofuran (THF) and an aqueous citrate buffer solution. As the triazene polymer dissolves homogeneously in this mixture, the degradation of the polymer could be monitored by UV spectroscopy, and the progress of depolymerization was established by GPC measurements.

Results and discussion

Photolysis

The changes in the UV spectrum of the triazene polymer upon continuous irradiation with a xenon lamp are shown in Fig. 1. The photodecomposition proceeds according to a one-step mechanism, as confirmed by an analysis according to the method of Mauser¹¹. Owing to the total absorption of the incident light, the kinetics is zero order except for the latest part of the reaction; the rate of the monomolecular photolysis is controlled by the intensity of the UV source.

Fig. 1. UV spectroscopic study of *photolytic* depolymerization. A solution of the triazene polymer in tetrahydrofuran was irradiated with the light of a 150 W xenon high pressure lamp. Aliquots for spectroscopic analysis were taken after the times indicated in the figure, and diluted for spectroscopic analysis as described in the Exptl. part

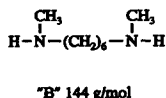
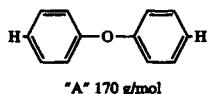


As a consequence of the comparatively high concentration of the triazene polymer solution and the high layer thickness of the quartz Schlenk tube used, the apparent rate of photolysis is very slow, i. e. it proceeds on a time scale of hours (Fig. 1). In reference experiments performed at concentrations of approx. 10^{-6} moles of chromophore per litre, which are typical for photolysis in quartz cuvettes, the triazene absorption disappeared in about one minute upon exposure to the specified intensity of the UV irradiation.

Laser photolysis experiments were carried out by irradiating dilute solutions of the polymer in THF with XeCl* excimer laser pulses at 308 nm. Again, the decomposition proceeded in a single step without observable intermediates on the time scale of our measurements. From the observed absorption decrease, quantum yields of photolysis were determined as the number of chromophores destroyed per number of quanta absorbed. Thereby, a value of 0,26% for the quantum yield was obtained.

GPC analysis of the irradiated samples of the polymer solution provides evidence for depolymerization upon exposure to light. This is clearly seen in the GPC traces of Fig. 2 recorded on THF solutions of the polymer that had been exposed to different times of irradiation.

The structures of the two molecular products expected from a simple photoextrusion of nitrogen from the polymer, followed by hydrogen abstraction from the solvent, are displayed in *Scheme 2*. Diphenyl ether (A) is clearly seen in the appropriate low-molar-mass range (approx. 170 g/mol) of the GPC traces with UV detection at 254 nm (Fig. 3). The bifunctional secondary amine (B in *Scheme 2*) gives rise to a strong signal with the RI detection at a molar mass of ca. 140 g/mol; as a consequence of the low absorption at 254 nm, only a small signal is registered in UV detection.



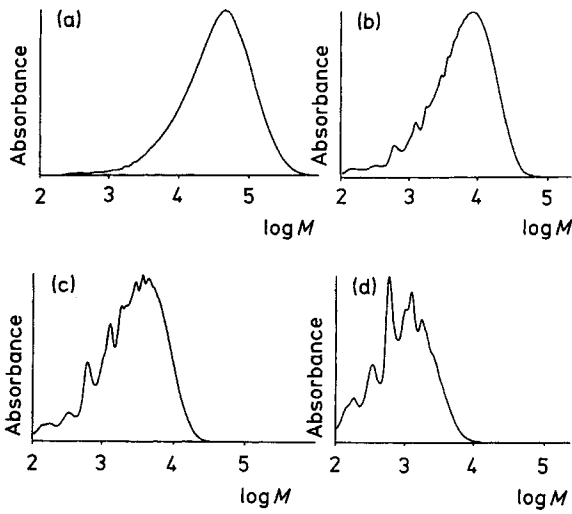


Fig. 2. GPC traces from samples of the triazene polymer solution in THF (a) without irradiation; (b) after 60 min of exposure to UV light; (c) after 120 min of exposure to UV light; (d) final state irradiated for 4 h

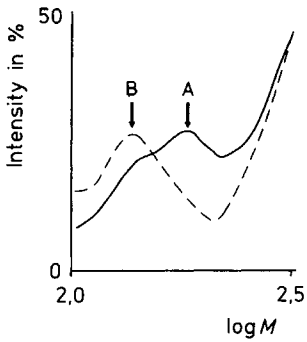


Fig. 3. Expanded section of the 100–320 g/mol region of the GPC analysis shown in Fig. 2(d) (sample irradiated for 4 h); comparison of traces recorded with (—) UV (product A) and (---) RI (product B) detection

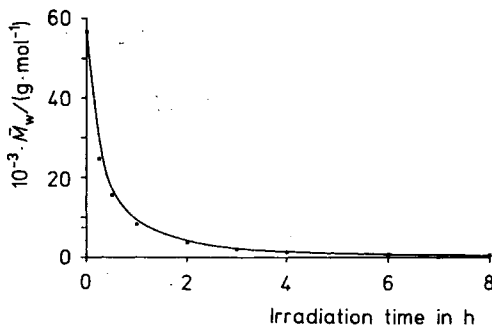


Fig. 4. Decrease of the molar mass during the irradiation of a $0,15 \text{ mol} \cdot \text{L}^{-1}$ solution with the Xe lamp at room temperature

The dependence of the average molar mass on irradiation time is displayed in Fig. 4. Only oligomeric fractions are remaining after two hours of irradiation. These oligomers are observed to undergo further photochemical decomposition on a more extended time scale (six hours). The comparatively long time required for decomposing the polymer in solution (at the given irradiation conditions) is again due to the high solution concentration ($0,15 \text{ g} \cdot \text{L}^{-1}$).

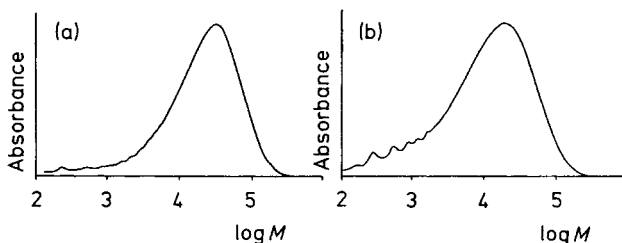


Fig. 5. GPC traces of the triazene polymer (a) without irradiation, and (b) after 4 h of irradiation of a film of the polymer of $200 \mu\text{m}$ thickness

In a solid polymer film of $200 \mu\text{m}$ thickness, the molar-mass decrease is very slow, as shown in Fig. 5. After an irradiation time of four hours, the molar mass has only been reduced from $34000 \text{ g} \cdot \text{mol}^{-1}$ to about $22000 \text{ g} \cdot \text{mol}^{-1}$. Previous evidence⁸⁾ indicates that the photolysis in polymer films proceeds by a mechanism similar to the one observed in organic solvents, i. e. nitrogen is eliminated *via* a radical pathway.

Thermolysis

The thermolysis kinetics, as characterized by DSC measurements, followed a two-step mechanism (of type $A \rightarrow B \rightarrow C$), as revealed by data reduction with the "Netzsch Thermokinetic analysis[®]" program. The following values for the thermochemical parameters and activation energies of the two steps were obtained from the quantitative analysis:

T_{dec} (DSC)	T_{dec} (TGA)	ΔH_{dec}	E_{A^1}	E_{A^2}
282°C	227°C	$-255 \text{ kJ} \cdot \text{mol}^{-1}$	$211 \text{ kJ} \cdot \text{mol}^{-1}$	$203 \text{ kJ} \cdot \text{mol}^{-1}$

In view of the obtained decomposition temperatures, the polymer was heat-treated at 256°C for various lengths of time. The resulting THF-soluble residues were analyzed by GPC, as shown in Fig. 6. In addition to the soluble fractions of decreasing molar mass, some insoluble products were found; a possible source of the latter is the development of a polymer network due to grafting reactions of radical fragments onto neighbouring polymer chains. The behaviour is illustrated in Fig. 7 (top) with a GPC curve recorded after a short thermolysis time of 1 min; both an increase in the number of oligomers and the development of high-molar-mass polymers can be seen. The number-average molar mass (\bar{M}_n) of the polymer decreases from $4900 \text{ g} \cdot \text{mol}^{-1}$ to

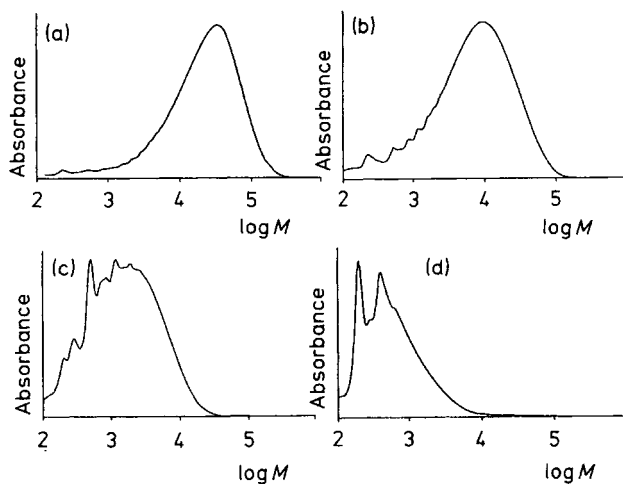


Fig. 6. GPC analysis of THF soluble residues from the thermolysis experiments: (a) polymer before thermolysis; (b) after 2 min, (c) after 5 min, and (d) after 20 min of thermolysis

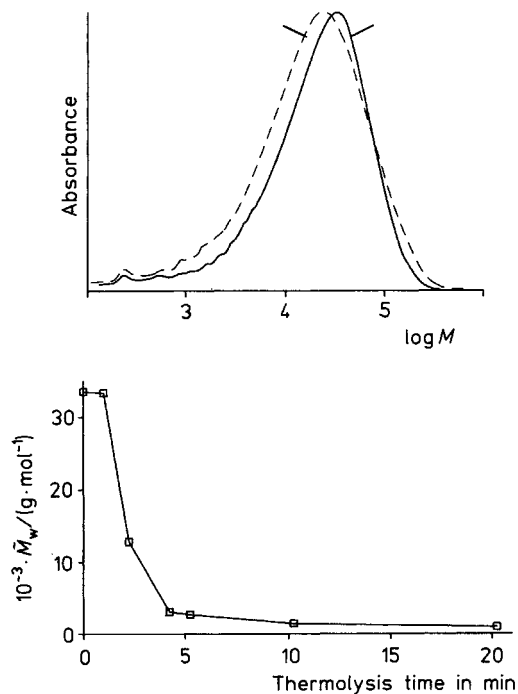
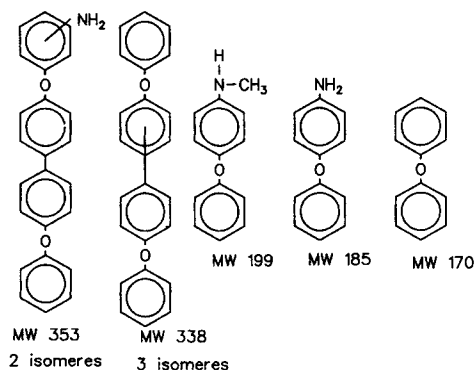


Fig. 7. GPC studies of thermolytic triazene polymer decomposition in solution. Top: the short time behaviour is analyzed by comparing GPC traces recorded before thermolysis (full line) and after a thermolysis time of 1 min (broken line). Bottom: the decrease of \bar{M}_w is monitored over a more extended period of time



Fragments of the aliphatic part of the molecule:

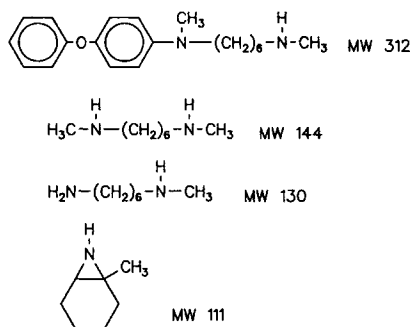


Fig. 8. Products of the thermolysis at 300 °C identified by GC/MS

3800 g · mol⁻¹ after the thermolysis; in contrast, the mass-average molar mass (\bar{M}_w) remains constant in the initial phase, as a consequence of the mentioned development of a polymer network. The thermolytic degradation over longer periods of time is illustrated by the results of Fig. 7 (bottom): An initial period of constant \bar{M}_w is followed by the expected drastic reduction of the molar mass. After a thermolysis time of 20 min, the polymer is completely decomposed.

Supplementing the GPC measurements, the volatile products of a thermolysis run at 300 °C were analyzed with GC/MS; products identified are shown in Fig. 8. The formation of these molecules can be explained in terms of combination reactions of photolytically generated radicals, which reside after release of gaseous nitrogen. In addition to the obvious combination products, the development of amine functionalities is observed. In summary, the results of the GC/MS analysis provide clear evidence for a radical pathway of decomposition, thereby confirming the conclusions derived from the GPC measurements.

Protolysis

As a third alternative, the depolymerization of the triazene polymer in an aqueous buffer solution was investigated. In view of the fact that the polymer is insoluble in water, a mixture of tetrahydrofuran (90 vol.-%) and of an aqueous citrate/hydrochloric acid buffer solution (10 vol.-%) was used for the protolysis studies. Obviously the measured time constant of protolytic depolymerization, as well as the time development of molar masses from GPC analysis, exhibit a strong dependence on the ratio of organic solvent and aqueous buffer, and the pH value of the solution.

UV spectra recorded during protolysis are shown in Fig. 9. The behaviour is notably different from the photolysis results: a hypochromic shift of the absorption maximum from 332 to 300 nm is detected. On the basis of pH-dependent studies, the long-wavelength band was assigned to a diazonium species; the shorter wavelength absorption at 300 nm is due to a bis-diazonium salt resulting from chain cleavage at two adjacent positions.

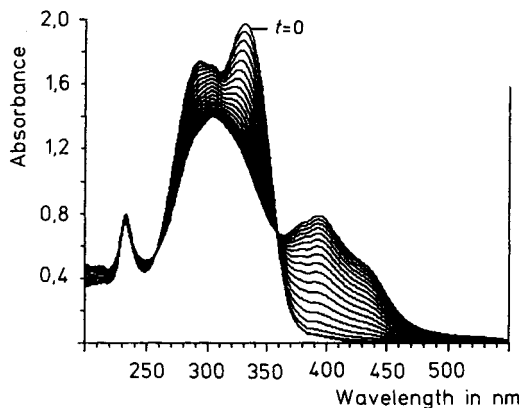


Fig. 9. UV spectra recorded during protolytic decomposition (THF/citrate buffer 9:1, room temperature). The time increment between successive measurements was 1 h

In view of the strong dependence of the protolysis rate and products (diazonium salts) on the pH value, the investigations have only a qualitative character. Yet, the ongoing decomposition of the polymer during the protolysis is clearly seen in the GPC curves (Fig. 10). The main product seen in Fig. 10d, with a molar mass of $580 \text{ g} \cdot \text{mol}^{-1}$, was identified as being due to phenolic compounds, into which the diazonium salts are converted during the preparation of the samples for the GPC runs (cf. Experimental part). Thus, it appears that the protolytic decomposition proceeds via the diazonium- or bis-diazonium salt, in a one- or two-step mechanism depending on the pH value, followed by thermolysis of the diazonium compounds to the corresponding phenols.

The decrease of the molar mass as a function of protolysis time for the given reaction conditions is shown in Fig. 11. Exhaustive protolysis is reached after the relatively long period of 25 h. We reemphasize that this value is strongly dependent on the protolysis pH.

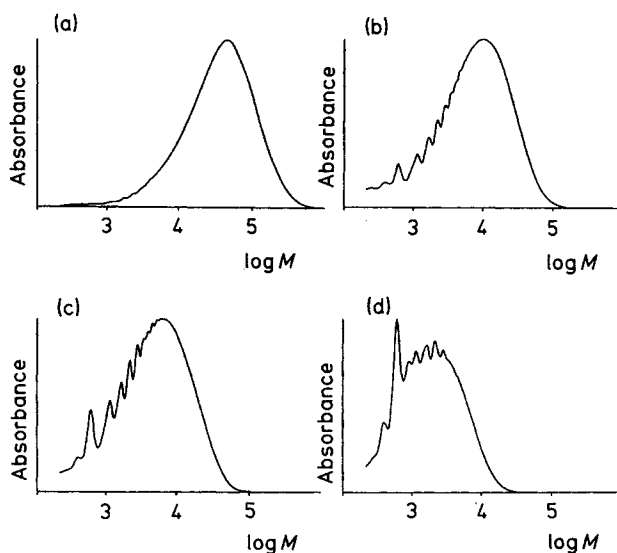


Fig. 10. Time dependence of protolytic decomposition in THF/citrate buffer solution (9 : 1, pH = 2,3) at room temperature. GPC traces were obtained with aliquots of the solution (a) before protolysis; (b) after 4 h, (c) after 6 h, and (d) after 25 h of reaction in the indicated solvent mixture

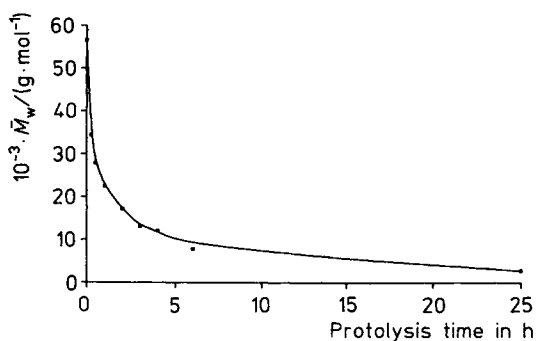


Fig. 11. Decrease in molar mass of the polymer during protolysis, as specified in the text

When a *film* of the polymer is immersed into a 0,1 molar aqueous HCl solution, an instantaneous foaming up and decomposition of the sample is observed. This behaviour demonstrates the property that the triazene polymer film can be easily stripped of from a substrate with an aqueous acid, which is desired for applications in microlithography.

Conclusions

In the present paper we have reported on the depolymerization of a novel triazeno-group containing photopolymer. Exposure of a THF solution of the polymer to UV light shows a fast degradation, which was quantified by UV spectroscopy and by GPC

analysis. The high photosensitivity of the triazene polymer, combined with adequate stability at temperatures of 160 °C, qualifies this material for the use in laser-micro-lithography applications.

Thermolysis at higher temperatures (220–300 °C) leads to a decomposition in substance. The identified products show that the thermolysis takes place via a radical pathway. Radical combination reaction and grafting reactions give rise to a simultaneous building-up of a polymer network, which is eventually broken up into fragments upon extensive thermolysis.

As a third possibility, the triazeno-group containing polymer may be decomposed by protolysis in aqueous solutions. GPC measurements demonstrate that a clean depolymerization of the triazene polymer is effected by the attack of protons on the triazene functional group.

Experimental part

Apparatus

Gel-permeation chromatography (GPC): Waters, model 590 (UV₂₅₄, RI detector); eluent tetrahydrofuran (THF); calibration with PMMA standards; columns: 500, 10³, 10⁴, 10⁵ Å.

Differential scanning calorimetry (DSC): Perkin-Elmer, model DSC 7 (*T_g* measurements); Netzsch, model DSC 200 (thermolysis and kinetics).

UV/Vis spectroscopy: Hitachi, model U-3000 UV spectrometer.

UV lamp: LTI, model A 1020, 150 W xenon high pressure lamp.

Thermogravimetric analysis (TGA) measurements: Netzsch, 'Simultan-Thermoanalyse', model STA 409C.

Synthesis

The synthesis of the triazene polymer has been reported in detail elsewhere⁹. All solvents were freshly distilled and carefully degassed (THF, Aldrich p. a.). The citrate/HCl buffer was obtained from Fluka.

Photolysis

The polymer was irradiated in a tetrahydrofuran solution at a concentration of 0,02 mol of chromophore per litre. All experiments and measurements were carried out at room temperature. The solution was contained in a 30 mL quartz Schlenk tube, of 1,5 cm diameter, and was agitated with a magnetic stirrer during irradiation, to prevent any inhomogeneities in polymer concentration. Photolysis was driven by the light of a 150 W xenon high pressure lamp placed at a distance of 40 cm. In order to prevent heating of the solution due to irradiation, an infrared-filter was used. After given intervals of time, aliquots of 1 mL solution were taken from the reaction mixture, transferred to calibrated flasks, and diluted to 100 mL for UV measurements. Samples of 2 mL were taken from the solution for GPC analysis.

Thermolysis

For the thermolysis, 10 mg of the polymer were heated in DSC pans at 256 °C in a Heraeus oven for different times. The residue was dissolved in 5 mL of THF, and analyzed by GPC.

Protolysis

In the protolysis studies, a solution of 20 mg of polymer in 10 mL of THF was added into a mixture of 20 mL citrate/HCl buffer (pH = 2) and 170 mL of THF. After different reaction times the solution was neutralized by addition of aqueous NaOH solution, as controlled with a pH-electrode. The solvent was removed, the residue dissolved in 4 mL of THF, and analyzed by GPC.

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