Synthesis and Kinetic Studies on the Photochemical Behavior of Polymeric Mesoions from Novel Methacrylic Monomers and of Mesoionic Copolymers with Liquid Crystalline Properties

Alexander Theis and Helmut Ritter*

Institute of Organic Chemistry and Macromolecular Chemistry, Heinrich Heine University, Universitaetsstrasse 1, D-40225 Duesseldorf, Germany

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ABSTRACT: A new method for synthesis of mesoionic methacrylates with various spacer lengths was developed. Copolymers with methyl methacrylate and cholesteric monomers were prepared; the latter showed liquid crystalline properties. The rate constant of the photocyclization to the bis(β-lactame) structure of various spin-coated polymeric films was determined by irradiation with a HeCd laser (442 nm), whereby two different parameters controlling the rate constant could be found. It was shown that the length of the alkyl side chain on position 5 of the pyrimidinium-olate and the embedding of the mesoionic chromophore, which can be controlled by copolymerization with methyl methacrylate or liquid crystalline methacrylates, causes significant changes in the rate constant. In addition, heating of a polymer film caused a strong acceleration of the photoreaction above the glass transition temperature.

Introduction

During the past few years we have described the synthesis and polymerization behavior of various styrene-substituted mesoionic 6-oxo-1,6-dihydropyrimidin-3-ium-4-olates.[1−3] Recently, for the first time, the preparation of a polymerizable methacryl derivative that contained a short dimethylene spacer was carried out successfully as shown in Scheme 1.[4]

We also prepared polymers with mesoionic groups in the main chain[5,6] and mesoionic side chain polymers, which are based on phenols as polymerizable groups.[7] An interesting feature of the mesoionic moieties is their sensitivity to light. Upon irradiation with UV light between 320 and 490 nm, which depends on the substitution of the pyrimidinium-olate ring, the molecule **6** undergoes an intramolecular disrotatoric photocyclization, which results in formation of a bicyclic lactame structure **7**, as shown in Scheme 2.

The course of the photoreaction of mesoionic 6-oxo-1,6-dihydropyrimidin-3-ium-4-olates has been investigated on dissolved low molecular weight compounds[8] and polymers[1] as well as on polymeric films.[4] The change of the molecular structure has an effect on several properties of mesoionic polymer films such as color, specific volume, dipole moment, and refractive index. For this reason, mesoionic polymers are interesting candidates for manufacturing photosensitive materials for lithography or optical devices. It was shown by waveguide spectroscopy that irradiation of mesoionic polymer films causes strong effects on refractive index and film thickness.[6,7] Hence, these materials could also be used for optical data storage and relief printing.

Regarding technical applications, the kinetics of the photoreaction is an important factor. For many applications, a fast switching is required. However, also stability toward daylight, oxygen, and temperature of photosensitive compounds has to be considered.

In this study, films of novel mesoionic polymers were prepared. The kinetics of the photoresponse of the mesoionic systems was inspected to various parameters like temperature, spacer length, and chemical environment.

* Corresponding author: Tel +49 211 8114760; Fax +49 211 8115840; e-mail H.Ritter@uni-duesseldorf.de.

Experimental Section

Methods. Chemicals were used as received from Acros, Fluka, or Aldrich. Technical solvents were distilled before use. For chromatography silica gel with 30−60 μm particle size (Baker) or 32−63 μm particle size, 60 Å (ICN) was used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AM400 at room temperature. The deuterated solvent was used as lock and internal standard for the δ-scale relative to TMS. Infrared spectra were recorded using a Nicolet FT-IR spectrometer 5DXC (DTGS detector) or 5SXB (MCT detector). Mass spectra were performed on a Finnigan MAT 95 (FD). UV−vis spectra were carried out with a Shimadzu UV-2102 PC UV−vis spectrometer. Elementary analysis was done in the Microanalytical Lab of the Institute of Organic Chemistry, University of Mainz. SEC measurements were measured on a PSS installation with THF or chloroform (30 °C) as eluent. 150 μL was injected on column arrangement of PSS SDV 5 μ, 100, 1000, and 10000 Å porosity. A TSP UV 2000 UV−vis detector, a Shodex differential refractometer RI 71, and a WGE Dr. Bures η1001 differential viscosimeter were used as detectors. The data were evaluated with PSS-WinGPC 6.20; molecular weights were also calculated with universal calibration using the intrinsic viscosity. Therefore, the concentration was calculated by the RI signal. For determination of the rate constants, the 5−10 wt % solutions of the different polymers in chloroform were spin-coated with a thickness of about 1.5 μm on microscope object slides with a BLE Delta 10 spin-coater, using a spin rates of 600 U/min at highest acceleration for 1 min. For the liquid crystalline copolymers, dioxane was used as solvent, and exhaust air separation was used during the spin-coat process for 10 min. The kinetic measurements were performed using a layout as shown in Figure 1.

The light beam of a HeCd laser (442 nm wavelength) was adjusted by a lens to a definite cross section and aligned through a chopper to the sample. Behind the sample, the residual light intensity was detected by a laser power meter, and the data were recorded every second by a computer. At the beginning of the irradiation, the intensity of the transmitted radiation is reduced by the absorption of the sample. With progressing conversion to the bis(β-lactame), the absorption is reduced and the transmission increases, until the level of saturation is reached. Using constant laser intensity, the speed of the photoreaction should follow the laws of pseudo-first-order kinetics. For evaluation of the data, the intensity at the

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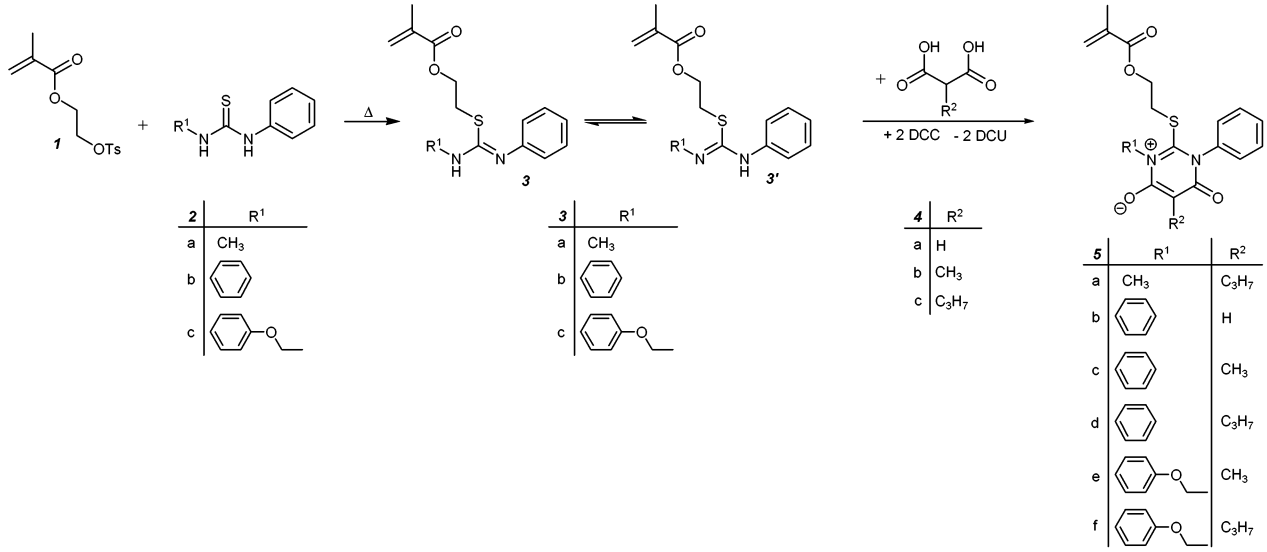
Scheme 1. Original Synthesis of Methacryl-Substituted Mesoions



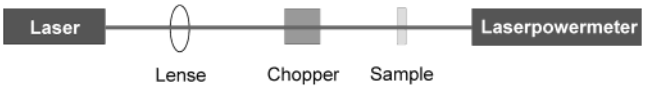
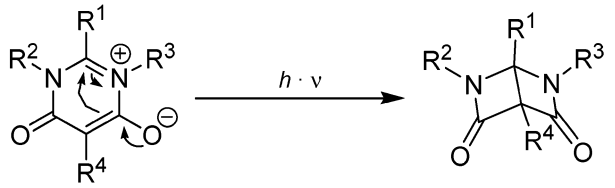


Figure 1. Schematic layout to determine the rate constant of photosensitive polymer films.

Scheme 2. Photochemical Reaction of Mesoionic 6-Oxo-1,6-dihydropyrimidin-3-ium-4-olates



saturated state I_s was obtained by signal averaging at the end of the measurement after the photoreaction was complete. The relative amount of unconverted mesoionic functions $[M]_t$ at the time t was calculated by eq 1 using the measured intensities at time t.

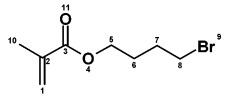
$$[M]_t \propto I_s - I_t \tag{1}$$

The first value of $[M]_t$ is per definition $[M]_0$. Using the law of first-order kinetics (eq 2), $\ln([M]_0/[M]_t)$ was spread against t.

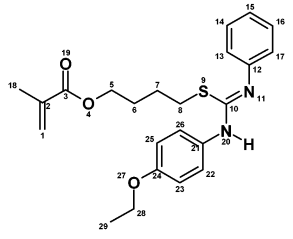
$$\ln\left(\frac{[M]_0}{[M]_t}\right) = kt \tag{2}$$

The slope calculated by linear regression is the rate constant k.

Synthesis. 4-Bromobutyl Methacrylate (10). 400 g (1.85 mol) of 1,4-dibromobutane, 46 g (0.37 mol) of sodium methacrylate, 1.85 g of tetrabutylammonium iodide as phase transfer catalyst, and 0.74 g of hydroquinone monopropyl ether were dissolved in 520 mL of ethyl acetate and heated to 80 °C for a period of 20 h. After cooling to room temperature, the precipitated NaBr was filtered off and the ethyl acetate was evaporated in a vacuum. The product was isolated by fractional distillation in high vacuum (bp 47−49 °C, 2×10^{-3} mbar); yield 59.5 g (73%). Colorless oil; 200 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 1.73−2.08 (m, 7H, 6,7,10-H), 3.42 (t, 2H, 8-H, J = 6.3 Hz), 4.15 (t, 2H, 5-H, J = 6.1 Hz), 5.54 (s, 1H, 1-H), 6.07 (s, 1 H, 1-H). 50 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 18.23 (C-10), 27.26 (C-7), 29.35 (C-6), 33.02 (C-8), 64.08 (C-5), 125.32 (C-1), 136.26 (C-2), 167.15 (C-3). IR (NaCl): λ^{-1} [cm^{-1}] = 2960, 2929, 2899, 2852 (aliph C−H), 1719 (C=O), 1638 (C=C); further signals at 1453, 1404, 1322, 1297, 1252, 1165, 1018, 942, 815, 750, 650, 563.

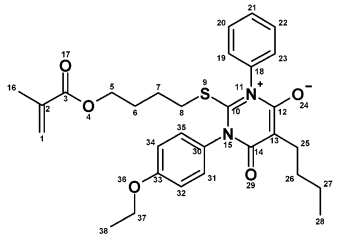


***S*-4-(Isopropenylcarbonyloxy)butyl-*N*-4-ethoxyphenyl-*N*′-phenylisothiourea (12).** 10.0 g (45.2 mmol) of 4-brombutyl methacrylate, 0.4 g of hydroquinone monopropyl ether, and 12.3 g (78 mmol) of *N*-4-ethoxyphenyl-*N*′-phenylthiourea[4] were added to 45 mL of ethanol p.a. and boiled for 4 h under reflux. Then the reaction mixture was cooled to room temperature, poured into a mixture of 170 mL of water and 17 mL of concentrated ammonia, and stirred for 1 min. After 10 min, the aqueous phase was decanted and extracted with chloroform. The chloroform phase and the oily phase were combined and dried with magnesium sulfate. The crude product, which was obtained by evaporating the chloroform, was purified by column chromatography over silica gel (ethyl acetate/petroleum ether 4/1 v/v); yield 9.2 g (49%). Colorless highly viscous oil; 200 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 1.38 (t, 3H, 29-H, J = 7.2 Hz), 1.55−1.75 (m, 4H, 6,7-H), 1.90 (s, 3H, 18-H), 2.78 ((br), 2H, 8-H), 3.98 (q, 2H, 28-H, J = 7.2 Hz), 4.10 (t, 2H, 5-H, J = 6.6 Hz), 5.51 (s, 1H, 1-H), 6.05 (s, 1 H, 1-H), 6.81 (d, 2H, 22,26-H, J = 8.8 Hz), 6.98−7.36 (m, 7H, 13,14,15,16,17,-23,25-H). 50 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 14.91 (C-29), 18.34 (C-18), 26.21/27.76/30.95 (C-6, C-7, C-8), 63.69 (C-28), 64.09 (C-5), 114.87 (C-23,25), 121.72 (C-13,17), 123.39 (C-15), 124.37 (br, C-22,26), 125.47 (C-1), 129.17 (C-14,16), 135.48 (br, C-21), 136.37 (C-2), 145.47 (br, C-12), 151.25 (br, C-10), 156.09 (C-24), 167.41 (C-3). IR (NaCl): λ^{-1} [cm^{-1}] = 3350 (N−H), 3055, 3032 (ar C−H), 2977, 2956, 2927, 2872 (aliph C−H), 1716 (C=O), 1622 (C=C, C=N), 1589 (ar C=C); further signals at 1510, 1497, 1437, 1408, 1393, 1298, 1240, 1221, 1167, 1130, 1117, 1090, 1048, 942, 915, 822, 757, 697. MS (FD): m/z (%) = 413 (100) [M$^+$].



Mesoionic 5-Butyl-1-(4-ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate (14). 1.0 g (2.42 mmol) of *S*-4-(isopropenylcarbonyloxy)butyl-*N*-4-ethoxyphenyl-*N′*-phenylisothiourea and 1.0 g (4.84 mmol) of DCC were dissolved under stirring in 5 mL of dry dichloromethane. Then 0.39 g (2.42 mmol) of butylmalonic acid was added batchwise for a period of 10 min under exclusion of moisture. After 50 min of additional stirring, the precipitated urea was filtered off and washed with a small amount of dichloromethane. The combined dichloromethane fractions were concentrated in a vacuum, and 250 mL of petroleum ether was added under stirring. After 15 min, the petroleum ether was decanted, and the yellow residue was dried in a vacuum. For further purification, the crude product was chromatographed over silica gel (ethyl acetate/petroleum ether 7/3 v/v); yield 0.6 g (47%). Yellow highly viscous oil; 400 MHz ^{1}H NMR (DMSO-d_6): δ [ppm] = 0.85 (t, 3 H, 28-H, J = 6.8 Hz), 1.16−1.44 (m, 11 H, 6,7,26,-27,38-H), 1.83 (s, 3 H, 16-H), 2.17 (t, 2 H, 8-H, J = 6.8 Hz), 2.25 (t, 2 H, 25-H, J = 7.6 Hz), 3.89 (t, 2 H, 5-H, J = 6.1 Hz), 4.02 (q, 2 H, 37-H, J = 7.2 Hz), 5.65 (s, 1 H, 1-H), 5.94 (s, 1 H, 1-H), 7.00 (d, 2 H, 32,34-H, J = 8.8 Hz), 7.38 (d, 2 H, 31,35-H, J = 8.8 Hz), 7.42−7.53 (m, 5 H, 19,20,21,22,23-H). 50 MHz ^{13}C NMR (DMSO-d_6): δ [ppm] = 13.93 (C-28), 14.49 (C-38), 17.87 (C-16), 22.33/24.27/25.39/26.62/30.00/34.79 (C-6, C-7, C-8, C-25, C-26, C-27), 63.39 (C-5), 64.21 (C-37), 94.60 (C-13), 114.22 (C-32,34), 125.51 (C-1), 128.69 (C-19,20,22,23), 128.88 (C-21), 129.79 (C-31,35), 130.49 (C-30), 135.81 (C-2), 138.22 (C-18), 158.61/159.09/159.25/160.06 (C-10, C-12, C-14, C-33), 166.32 (C-3). IR (KBr): λ^{-1} [cm^{-1}] = 3061 (ar C−H), 2954, 2929, 2869 (aliph C−H), 1716 (C═O), 1641 (mesoion C═O), 1594 (ar C═C); further signals at 1510, 1478, 1455, 1394, 1366, 1319, 1299, 1249, 1171, 1116, 1068, 1045, 758, 699. UV (dichloromethane): λ_{max} [nm] (log ϵ) = 266 (4.03), 375 (3.26). MS (FD): m/z (%) = 537 (100) [M$^+$].

EA: $C_{30}H_{36}N_2O_5S$ (536.70). Calcd: C, 67.14; H, 6.76; N, 5.22; S, 5.97. Found: C, 66.35; H, 7.09; N, 5.33; S, 5.80.



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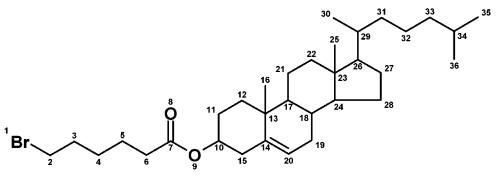
1-Bromhexanoic Acid Cholesteryl Ester (17). 15.46 g (40 mmol) of cholesterol, 8.25 g (40 mmol) of DCC, and 0.49 g (4 mmol) of 4-(dimethylamino)pyridine were dissolved in 70 mL of dichloromethane. Then 7.8 g (40 mmol) of 1-bromohexanoic acid was added under stirring over a period of 20 min, whereby the temperature was kept at room temperature by use of a water bath. The solution was stirred for additional 2 h, and then the precipitated urea was filtered off and washed with a small amount of dichloromethane. The combined dichloromethane fractions were evaporated in a vacuum. The dried crude product could be used without further purification; yield 22.5 g (100%). Colorless crystals; mp 110−113 °C; 400 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.64 (s, 3 H, 25-H), 0.77−2.02 (m, 46 H, 3,4,5,11,12,15,16,17,18,19,21,22,24,26,27,28,-29,30,31,32,33,34,35,36-H), 2.27 (t, 2 H, 6-H, J = 7.5 Hz), 3.38 (t, 2 H, 2-H, J = 6.8 Hz), 4.58 (m, 1 H, 10-H), 5.34 (m, 1 H, 20-H).

IR (KBr): λ^{-1} [cm^{-1}] = 2946, 2886, 2867 (C−H), 1733 (C═O); further signals at 1652, 1456, 1436, 1384, 1373, 1365, 1323, 1255, 1229, 1187, 1172, 999.

5-(Cholesterolcarbonyl)pentyl Methacrylate (19). 4.7 g (8.33 mmol) of 1-bromohexanoic acid cholesteryl ester, 1.03 g (8.33 mmol) of potassium methacrylate, 20 mg of hydroquinone monopropyl ether, and 0.044 g (0.12 mmol) of tetrabutylammonium iodide as phase transfer catalyst were



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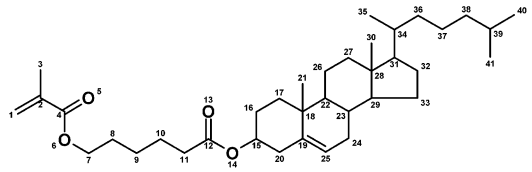
added to 55 mL of ethyl acetate and boiled under reflux for 24 h. The reaction mixture was cooled to room temperature, the precipitate was filtered off, and the ethyl acetate was removed by distillation in a vacuum. For purification, the crude product was dissolved in 6 mL of dichloromethane and precipitated in 70 mL of methanol. The product was filtered off, washed with additional methanol, and dried in a vacuum; yield 3.2 g (68%). Colorless crystals; 400 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.65 (s, 3 H, 30-H), 0.77−2.02 (m, 49 H, 3,8,9,10,16,17,20,21,22,-23,24,26,27,29,31,32,33,34,35,36,37,38,39,40,41-H), 2.27 (t, 2 H, 11-H, J = 7.3 Hz), 4.11 (t, 2 H, 7-H, J = 6.6 Hz), 4.59 (m, 1 H, 15-H), 5.34 (m, 1 H, 25-H), 5.52 (s, 1 H, 1-H), 6.06 (s, 1 H, 1-H). 100 MHz ^{13}C NMR ($CDCl_3$): δ [ppm] = 11.77 (C-30), 18.17 (C-3), 18.66 (C-35), 19.21 (C-21), 20.99 (C-26), 22.46/22.71 (C-40,41), 23.79 (C-37), 24.21 (C-33), 24.60 (C-9), 25.50 (C-10), 27.76 (C-16), 27.91 (C-39), 28.14 (C-32), 28.27 (C-8), 31.84 (C-23), 31.89 (C-24), 34.41 (C-11), 35.71 (C-34), 36.13 (C-36), 36.51 (C-18), 36.95 (C-17), 38.10 (C-20), 39.46 (C-27), 39.71 (C-38), 42.26 (C-28), 50.02 (C-22), 56.14 (C-31), 56.65 (C-29), 64.35 (C-7), 73.71 (C-15), 122.50 (C-25), 124.98 (C-1), 136.42 (C-2), 139.58 (C-19), 167.24 (C-4), 172.66 (C-12). IR (KBr): λ^{-1} [cm^{-1}] = 2945, 2867 (C−H), 1733, 1723 (C═O); further signals at 1638, 1467, 1377, 1366, 1321, 1297, 1255, 1236, 1169, 1029, 1012, 940. DSC: ΔC_p (negative) = 4 °C. Peak = 35 °C. Peak = 64 °C. MS (FD): m/z (%) = 569 (2) [M$^+$], 387 (10) [cholesterol$^+$], 369 (100) [cholesteryl$^+$].

EA: $C_{37}H_{60}O_4$ (568.89). Calcd: C, 78.12; H, 10.63. Found: C, 77.72; H, 10.34.



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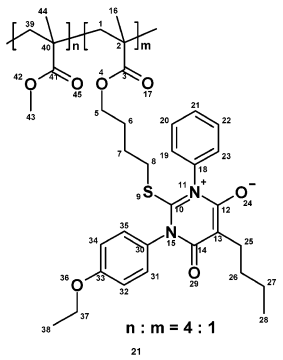
Copolymer of Methyl Methacrylate and Mesoionic 5-Butyl-1-(4-ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)-butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate (21). 0.50 g (0.93 mmol) of mesoionic 5-butyl-1-(4-ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate, 0.37 g (3.72 mmol) of methyl methacrylate, and 23.0 mg (0.14 mmol) of AIBN were dissolved in 2 mL of absolute DMF. The mixture was degassed by exposure to nitrogen bubbles for 30 min. Then the solution was polymerized for 20 h at 60 °C, and the polymer was precipitated in a mixture of 100 mL of methanol and 200 mL of water. After drying in a vacuum, the polymer was purified by dissolving in 5 mL of dichloromethane and reprecipitating in 150 mL of diethyl ether. The product was dried in a vacuum again; yield 0.6 g (69%). Yellow powder; 400 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.46−2.10 (m, 1,6,7,16,25,26,27,28,38,39,-44-H), 2.42 (m, 8-H), 3.55 (s, 43-H), 3.65−4.12 (m, 5,37-H), 6.32−7.59 (m, ar−H). IR (KBr): λ^{-1} [cm^{-1}] = 2987, 2950, 2871 (aliph C−H), 1730 (C═O), 1651 (mesoion. C═O); further signals at 1510, 1479, 1453, 1365, 1248, 1192, 1151, 1064, 995, 973, 924, 852, 757, 701. UV (dichloromethane): λ_{max} [nm] = 263, 380. DSC: T_g = 104 °C. SEC (chloroform, universal calibration by viscosity): M_n = 27 000, M_w = 280 000, PD = 11.

EA for n:m = 4:1. Calcd: C, 64.08; H, 7.31; N, 2.99; S, 3.42. Found: C, 63.35; H, 7.29; N, 3.07; S, 3.89.



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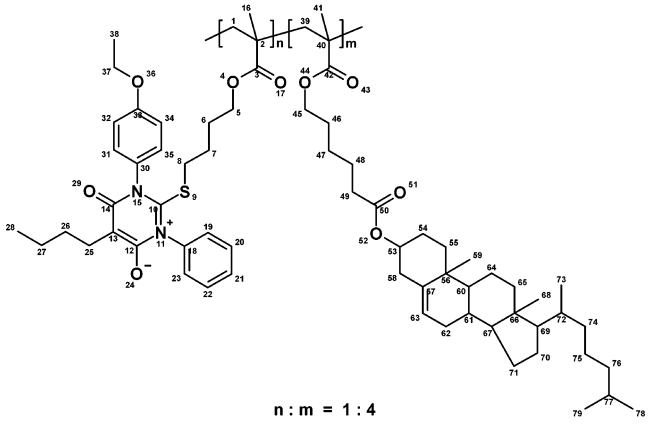
Copolymer of Mesoionic 5-Butyl-1-(4-ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate and 5-(Cholesterolcarbonyl)pentyl methacrylate (23). 0.25 g (0.466 mmol) of mesoionic 5-butyl-1-(4-ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate, 0.75 g of (1.32 mmol) 5-(cholesterolcarbonyl)pentyl methacrylate, and 10.0 mg (0.0609 mmol) of AIBN were dissolved in 5 mL of absolute THF. The mixture was degassed by exposure to nitrogen bubbles for 10 min. Then the solution was polymerized for 15 h at 60 °C, and the polymer was precipitated in 100 mL of methanol. The product was dried in a vacuum; yield 0.96 g (96%). Pale yellow powder; 400 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.65 (s, 68-H), 0.71−2.05 (m, 1,6,7,16,26,27,28,38,39,41,46,47,48,54,55,58,59,60,61,62,64,65,-67,69,70,71,72,73,74,75,76,77,78,79-H), 2.06−2.40 (m, 25,49-H), 2.54 (m, 8-H), 3.79 (t, 5-H), 3.90 (m, 45-H), 4.02 (q, 37-H), 4.57 (m, 53-H), 5.34 (m, 63-H), 6.94 (d, 32,34-H), 7.10 (d, 31,-35-H), 7.21 (t, 21-H), 7.40−7.54 (m, 19,20,22,23-H). IR (KBr): λ^{-1} [cm^{-1}] = 2947, 2867 (aliph C−H), 1731 (C═O), 1654 (mesoion C═O); further signals at 1510, 1467, 1375, 1248, 1169, 1064, 1012, 960, 842, 754, 699. UV (dichloromethane): λ_{max} [nm] = 264, 380. DSC: ΔC_p = 54 °C. Peak = 128 °C. SEC (THF, PS standard): M_n = 32 000, M_w = 110 000, PD = 3.5.

EA for *n*:*m* = 1:4. Calcd: C, 76.02; H, 9.89; N, 1.00; S, 1.14. Found: C, 75.16; H, 10.23; N, 1.09; S, 2.03.



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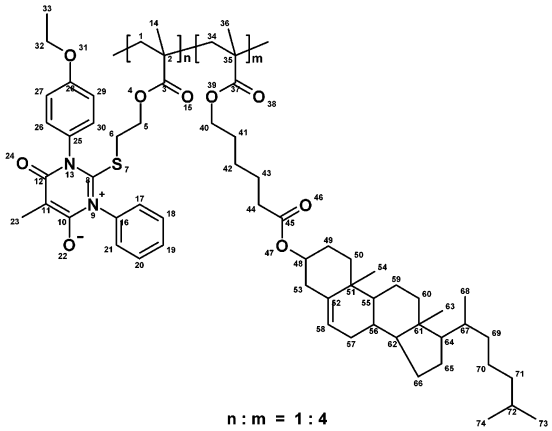
Copolymer of Mesoionic 1-(4-Ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)ethylthio]-5-methyl-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate and 5-(Cholesterolcarbonyl)pentyl Methacrylate (29). 0.25 g (0.536 mmol) of mesoionic 1-(4-ethoxyphenyl)-2-[2-(isopropenylcarbonyloxy)-ethylthio]-5-methyl-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4-olate,[4] 0.75 g (1.32 mmol) of 5-(cholesterolcarbonyl)-pentyl methacrylate, and 10.0 mg (0.0609 mmol) of AIBN were dissolved in 5 mL of absolute THF. The mixture was degassed by exposure to nitrogen bubbles for 10 min. Then the solution was polymerized for 15 h at 60 °C, and the polymer was precipitated in 100 mL of methanol. The product was dried in a vacuum; yield 0.91 g (91%). Pale yellow powder; 400 MHz ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.65 (s, 63-H), 0.72−2.15 (m, 1,-14,23,33,34,36,41,42,43,49,50,53,54,55,56,57,59,60,62,64,65,-66,67,68,69,70,71,72,73,74-H), 2.19−2.33 (m, 44-H), 2.40 (m, 6-H), 3.60 (m, 5-H), 3.90 (m, 40-H), 4.03 (m, 32-H), 4.57 (m, 48-H), 5.34 (m, 58-H), 6.94 (m, 27,29-H), 7.10 (m, 26,30-H), 7.24 (m, 19-H), 7.30−7.54 (m, 17,18,20,21-H). IR (KBr): λ^{-1} [cm^{-1}] = 2945, 2867 (aliph C−H), 1732 (C═O), 1653 (mesoion C═O); further signals at 1510, 1467, 1376, 1251, 1170, 1058, 1012, 960, 843, 746, 702. UV (dichloromethane): λ_{max} [nm] = 264, 370. DSC: ΔC_p = 59 °C. Peak = 129 °C. SEC (THF, PS standard): M_n = 21 000, M_w = 36 000, PD = 1.8.

EA for *n*:*m* = 1:4. Calcd: C, 75.78; H, 9.78; N, 1.02; S, 1.17. Found: C, 74.90; H, 10.07; N, 1.40; S, 1.92.



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Results and Discussion

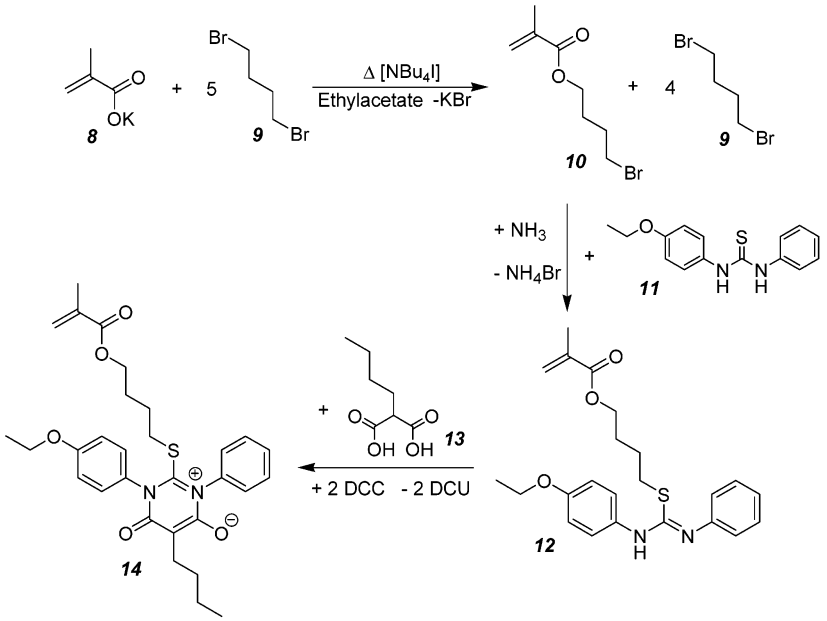
1,ω-Dibromoalkanes **(9)** were used for the synthesis of mesoionic monomers with various spacer lengths. The methacryl based ω-bromoalkane **(10)** was prepared under phase-transfer conditions using potassium methacrylate **(8)** and a 5-fold excess of 1,4-dibromobutane **(9)**. The distilled product **(10)** was boiled in alcoholic solution with *N*-(4-ethoxyphenyl)-*N*′-phenylthiourea **(11)** and worked up under basic conditions to form the isothiourea structure **(12)**. The mesoionic monomer **(14)** was prepared using butylmalonic acids **(13)** and DCC as condensation reagent (Scheme 3).

For embedding the mesoionic functions into a liquid crystalline environment, copolymers containing liquid crystalline components were prepared. For this purpose, the cholesteric methacrylate **19** was synthesized. This monomer could be copolymerized statistically with the mesoionic methacrylates and does not show any self-absorption in the interesting wavelength region, which could be used for irradiation. The cholesteric monomer was obtained by a new synthetic route in high yield (Scheme 4).

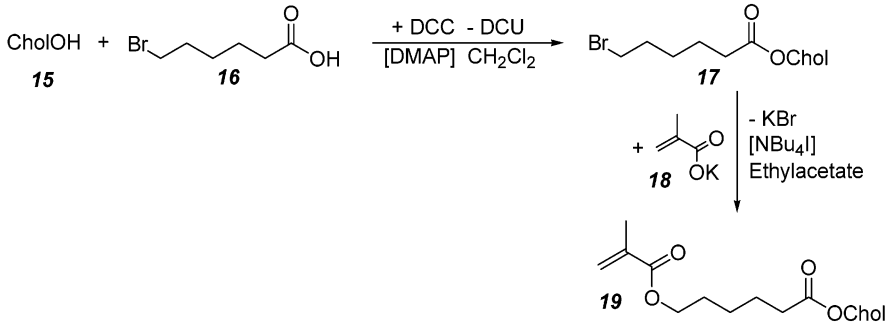
The copolymerization of the mesoionic monomer **14** with methyl methacrylate **(20)** was carried out in *N*,*N*-dimethylformamide (DMF) as solvent using 2,2′-azobis-(isobutyronitrile) (AIBN) as initiator. Probably due to the long time of polymerization (24 h), the polydispersity of polymer **21** was relatively high. Surprisingly, the copolymerization of monomer **14** with the cholesteric monomer **19** in DMF resulted in a mixture of the homopolymers. Obviously, the cholesteric monomer has a tendency to form aggregates in the polar DMF. In contrast, by using tetrahydrofuran (THF) as solvent, a nearly homogeneous statistical copolymer was obtained (Scheme 5).

For comparison, the homopolymer **25**[4] of the mesoionic monomer 1-(4-ethoxyphenyl)-2-(2-methacryleth-

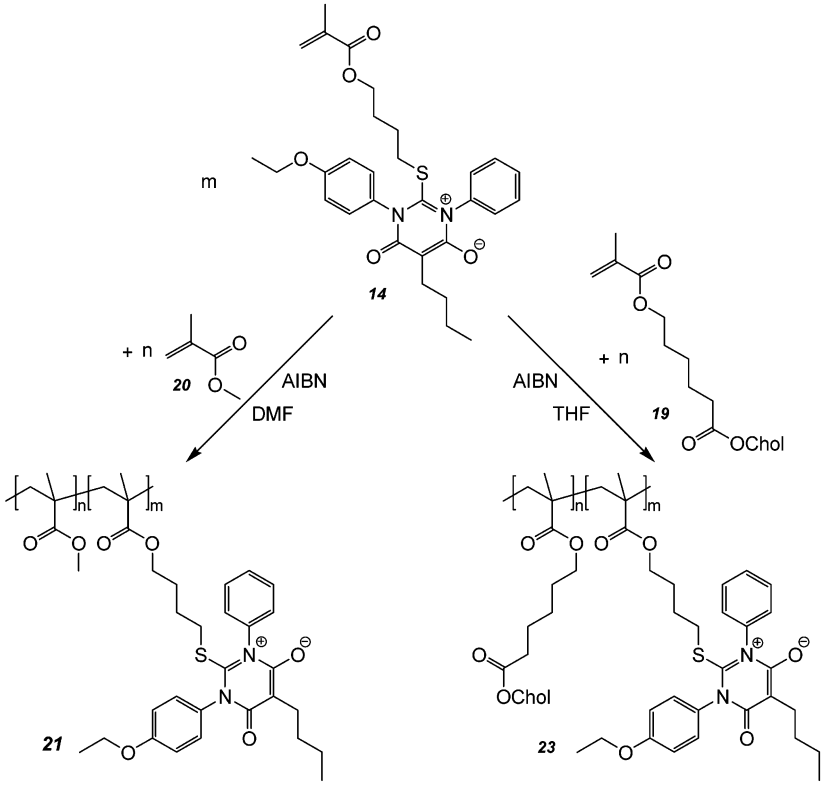
Scheme 3. Pathway for Preparation of the Mesoionic Methacrylate



Scheme 4. Synthesis of the Liquid Crystalline Monomers



Scheme 5. Preparation of Mesoionic Copolymers



Scheme 6. Additional (Co)polymers

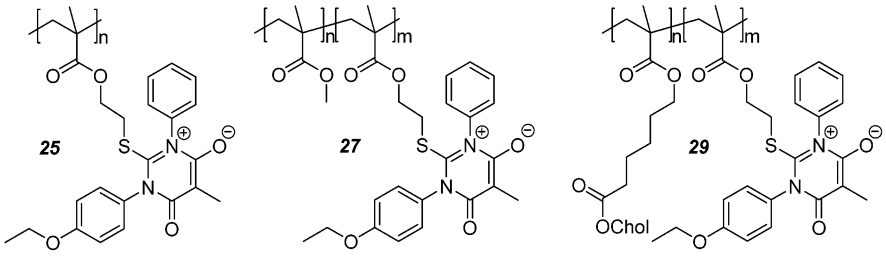


Table 1. Properties of the Prepared Copolymers

polymer	**21**	**23**	**29**
yield [%]	69	96	91
n:*m* (polymer)	4:1	4:1	4:1
M_n [g/mol]	27000	32000	21000
M_w [g/mol]	400000	110000	36000
PD	11	3.5	1.8
ΔC_p (T_g) [°C]	104	54	59
peak (T_{cl}) [°C]		128	129

ylthio)-5-methyl-6-oxo-3-phenyl-1,6-dihydropyrimidinium-4-olate[4] and the copolymer **27**[4] with methyl methacrylate were used. Additionally, the copolymer **29** of 1-(4-ethoxyphenyl)-2-(2-methacrylethylthio)-5-methyl-6-oxo-3-phenyl-1,6-dihydropyrimidinium-4-olate[4] and the cholesteric monomer **19** was prepared (Scheme 6).

The data obtained from all new polymers are summarized in Table 1.

The liquid crystalline phase of the cholesteric copolymers was confirmed by polarizing microscopy. The kinetic constant of the photoreaction of the different polymers was determined in the solid state using spin-coated films of a thickness of about 1.5 μm and a HeCd laser (442 nm). The calculated first-order rate constants *k* are summarized in Table 2.

By comparison of the rate constants, two different main factors can be attributed to the speed of cyclization. Similar to the photoreaction of mesoionic pyrimidinium-olates in solution,[1] the reduction of the alkyl chain length in position 5 of the mesoionic function led to an increase of the cyclization rate. This can be explained by the improved mobility, if fewer atoms have to be moved. Thus, the methyl substituent in the 5-position allowed the highest conversion rate during UV irradiation. Depending on the copolymer, the rate constant could be enlarged by a factor of 2−3.

As expected, also a strong influence of the liquid crystalline state was observed. The liquid crystalline copolymers **23** and **29** permit a switching rate to the bis(β-lactame) structure about a factor of 3.5−4.5 higher than the analogous homopolymer **25** or copolymers **21** and **27** with methyl methacrylate, which do not show any remarkable deviation to the homopolymer with respect to the glass transition temperature and rate constant. In this connection, less hindrance for the photochemical rearrangement in the liquid crystalline polymers is caused by the low glass transition temperature next to the temperature, where the measurements were achieved. Therefore, the quantum yield and reaction rate are enlarged.

However, the lowest photosensitivity was detected in the case of the mesoionic polymer **31** obtained by 2-phenylpolyamidine.[6] In this type of main chain polymer, the photoreaction requires a certain rearrangement of the backbone, which is strongly restricted at temperatures much below the glass transition at 160 °C.

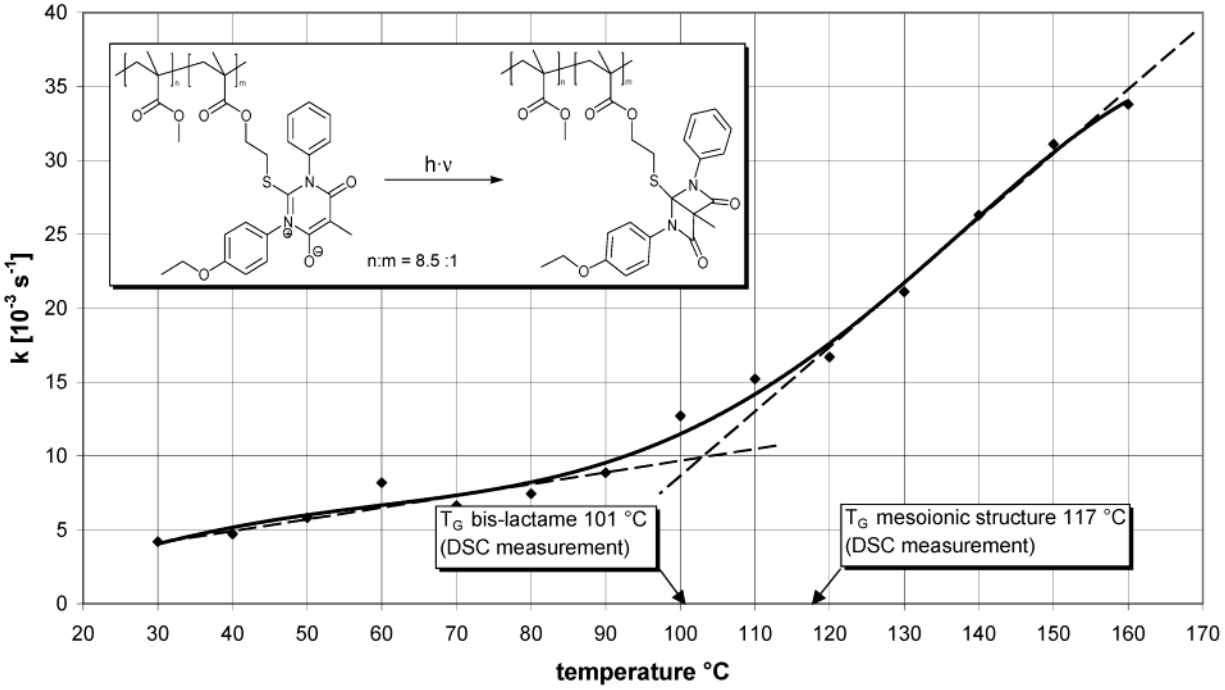
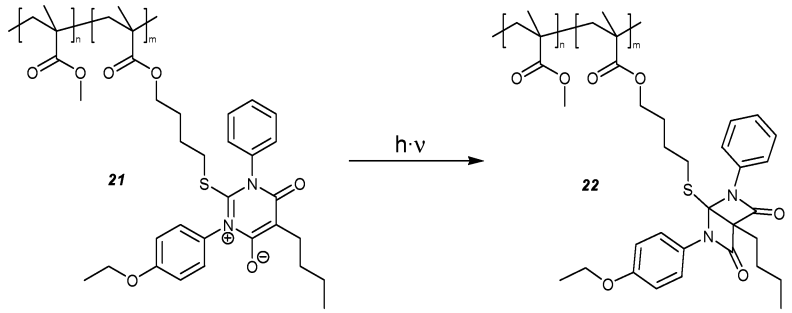
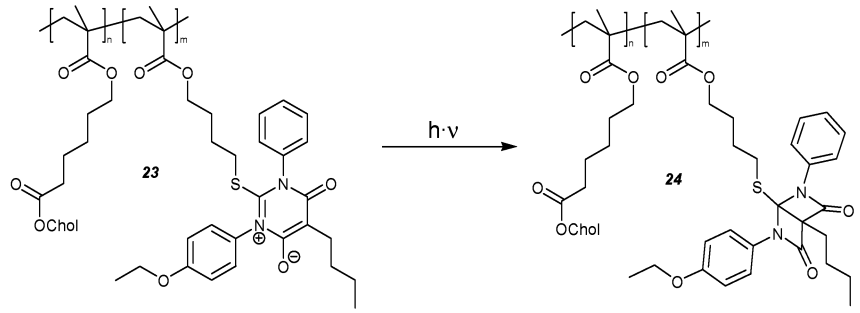
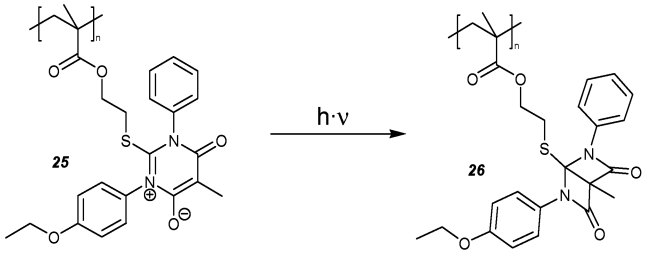
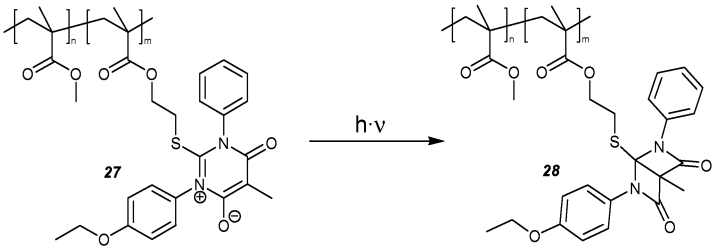
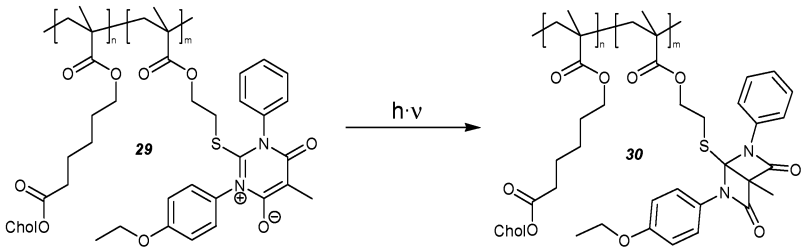
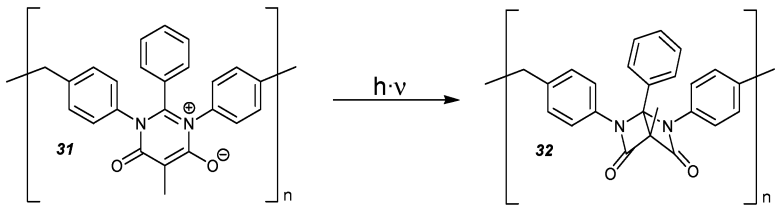


Figure 2. Temperature-dependent cyclization kinetics of the copolymer (**27**) prepared from mesoionic 1-(4-ethoxyphenyl)-2-[2-(isopropenylcarbonyloxy)ethylthio]-6-oxo-3-phenyl-5-propyl-1,6-dihydropyrimidin-3-ium-4-olate and methyl methacrylate at different temperatures.

Table 2. Rate Constant *k* for the Photoreaction of Different Polymers

polymer	k [10^{-3} s^{-1}]
	0.63
	2.1
	1.4
	1.5
	6.8
	0.40

According to the above-described results, the reaction rate of mesoionic polymers should generally be increasable simply by heating the polymer films. This feature was checked for example by measuring the reaction rate of copolymer **27** at different temperatures between 30 and 160 °C (Figure 2).

Up to a temperature of about 100 °C, only a slight increase of the rate constant could be observed. Above

this temperature, the increase is accelerated up to about 120 °C, where acceleration stops and the increase remains nearly constant at a high level. The region, in which the course increases, is lying within the interval of the glass transition temperatures of the mesoionic polymer **27** (117 °C) and the corresponding photoconverted bis(*β*-lactame) polymer **28** (101 °C).

This temperature-dependent behavior could be explained by the fact that the mobility of mesoionic functions is restricted by the rigid environment below the glass transition temperature. Reaching the glass transition temperature by heating, the free volume of the polymer is typically increased, so the photoreaction rate is significantly enlarged. Above 160 °C, the polymer decomposes. It was therefore not possible to measure the rate constants at higher temperatures. Generally, the reaction rate could be enlarged by factor 8 simply by heating the polymer.

Conclusions

Novel mesoionic methacrylates with various spacer lengths were synthesized by a new route and characterized. Copolymers with methyl methacrylate and cholesteric monomers were prepared by radical polymerization in organic solvents; the cholesteric copolymer showed liquid crystalline properties above the T_g of 54 °C. The polymers reached molecular weights up to M_n = 21 000−32 000 and a polydispersity range of 1.8−11. By determination of the rate constant of the photocyclization to the bis(*β*-lactame) structure, it was shown that a decrease of the length of the alkyl side chain on position 5 of the pyrimidinium-olate and the embedding of the mesoionic chromophore into liquid crystalline polymers caused a strong increase of the rate constant. In addition, heating of a polymer film with a T_g of 104 °C caused an acceleration of the photoreaction above the glass transition temperature up to a factor of 8. These results have clearly shown that the photochemical induced photocyclization of mesoionic polymers is strongly controlled by the mobility of the polymer segments, especially the polymers with liquid crystalline behavior showing relatively high rate constants.

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References and Notes

(1) Ritter, H.; Sperber, R.; Weisshuhn, C. M. *Macromol. Chem. Phys.* **1994**, *195*, 3823.
(2) Ritter, H.; Sperber, R. *Macromol. Rapid Commun.* **1995**, *16*, 407.
(3) Deutschmann, T.; Ritter, H. *Macromol. Chem. Phys.* **2000**, *201*, 1200.
(4) Theis, A.; Ritter, H. *Des. Monomers Polym.* **2001**, *4*, 177.
(5) Deutschmann, T.; Ritter, H. *Macromol. Rapid Commun.* **1996**, *17*, 723.
(6) Theis, A.; Ritter, H.; Böhme, F.; Klinger, C.; Menges, B.; Mittler, S. *Chem. Mater.* **2002**, *14*, 2109.
(7) Tonami, H.; Uyama, H.; Kobayashi, S.; Menges, B.; Mittler, S.; Theis, A.; Ritter, H. *Macromol. Chem. Phys.* **2003**, *204*, 1079.
(8) Gotthardt, H.; Schenk, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 687.

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