Polymeric Mesoions: Novel Synthetic Methods, Photochemistry, and Characterization in the Solid State by Dielectric and Waveguide-Mode Spectroscopy

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ABSTRACT: Photosensitive mesoionic polymers in which the polymerizable methacrylic group is attached to the malonic acid component of the mesoionic function were prepared and characterized. Dielectric measurements were performed, and the results were compared to those of liquid-crystalline mesoionic copolymers. The influence on the dielectric properties upon irradiation with UV light, which causes the photoconversion of the mesoionic groups to bis(β -lactame) structures, was determined. The glass-transition temperatures determined by dielectric spectroscopy were compared to those obtained by DSC. It could be observed by waveguide-mode spectroscopy that irradiating the mesoionic methacrylates results in remarkable effects on the film thickness and refractive index of spin-coated polymer films.

Introduction

In past decades, photosensitive materials have seen an increase in practical and scientific importance. They are useful for optical data storage and in photolithographic processes. Changes in different properties are desired, for example, changes in volume, solubility, color, or refractive index.

Our recent interest is focused on polymeric mesoions. They can be converted into $bis(\beta$ -lactames) by light irradiation in a wavelength regime between 320 and 490 nm depending on the substitution (Scheme 1).

To obtain stable, easy to handle, film-forming materials, the photoreactive mesoionic group must be covalently attached to a polymer. During the last several 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, different methods for the synthesis of polymerizable mesoionic methacryl derivatives have also been developed.^{4,5} We also prepared polymers that are based on phenols as the polymerizable group⁶ or polycondensates bearing mesoionic groups in the main chain.^{7,8} An alternative method is to modify technical polymers with dispersed crystals of photosensitive mesoions.⁹

For the estimation of changes in the physical properties by irradiation, different methods have been developed. For example, waveguide-mode spectroscopy can be used to determine changes in the refractive index and film thickness of spin-coated polymer films.^{6,8,9} Other methods involve changes in the solubility or spectroscopic characteristics.^{1,4}

In this study, a new synthetic route for the synthesis of methacryl-based mesoionic monomers, which has a strong impact on the photochemical properties, is presented. In addition, the effects of the overall chemical

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



structure on the photocyclization of the mesoionic compounds and the physical properties, which were analyzed by dielectric and waveguide spectroscopy, are described.

Experimental Section

Methods. Chemicals were used as received from Acros, Fluka, and Aldrich. Technical solvents were distilled before use. For chromatography, silica gel with particle sizes of 30-60 (Baker) or $32-63 \mu m$ (ICN), 60 Å was used. ¹H and ¹³C NMR spectra were recorded on a Bruker AC200 or AM400 at room temperature. The deuterated solvent was used as the lock and the internal standard for the δ scale relative to TMS. Infrared spectra were recorded using Nicolet FT-IR spectrometer 5DXC (DTGS detector) or 5SXB (MCT detector). The ATR measurements were performed with a Specac golden-gate diamond ATR unit on the 5SXB spectrometer. Mass spectra were obtained on a Finnigan MAT 95 (FD). UV-vis spectra were obtained with a Shimadzu UV-2102 PC UV-vis spectrometer. Elementary analysis was done in the micro analytical laboratory of the Institute of Organic Chemistry, University of Mainz. SEC measurements were made on a PSS installation with chloroform (30 °C) as the eluent. One hundred microliters was injected onto a column arrangement of PSS SDV 5μ 100-, 1000-, and 10 000-Å porosity. A TSP UV 2000 UV-vis detector and a Shodex RI 71 differential refractometer were used as detectors. The data were evaluated with PSS-WinGPC 6.20. The polymeric films were prepared from 5 to 10 wt % solutions of the polymer in chloroform by spin coating with a BLE Delta 10 spin coater using a spin rate of 600 rpm at the highest acceleration for 1 min. For the liquid-crystalline copolymers, dioxane was used as the solvent, and exhaust air separation was used during the spin-coating process for 10 min. Dielectric measurements have been performed using a temperaturecontrolled sample cell and a Novocontrol system composed of an Alpha frequency response analyzer and a Quattro temper-

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Figure 1. Setup for waveguide-mode spectroscopy with simultaneous irradiation of the mesoionic polymer sample.

ature controller. Two different sample geometries were used: The liquid-crystalline sample was sandwiched between two copper electrodes of 20 mm diameter and had a thickness of 50 μ m. Teflon spacers were used to control the geometry of the sample. The copolymer with methyl methacrylate was deposited by spin coating a concentrated solution onto a goldcovered copper electrode, and it had thickness of about 3 μ m. The upper electrode was placed in contact with the surface of the film and had a diameter of 20 mm. The dielectric measurements were carried out at different temperatures from 173 to 373 K (the LC-sample) and from 203 to 403 K (spin-coated samples) for frequencies from 10^{-2} to 10^{6} Hz. The dielectric properties are characterized by the complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$ (ϵ' is the real and ϵ'' is the imaginary part) as a function of frequency ω and temperature *T*. The frequencydependent permittivity spectra were analyzed using the empirical Havriliak-Negami function¹⁰ (eq 1):

$$\frac{\epsilon^*(T,\omega) - \epsilon_{\infty}(T)}{\Delta\epsilon(T)} = \frac{1}{\left[1 + (\mathrm{i}\omega\tau_{\mathrm{HN}}(T))^{\alpha}\right]^{\gamma}} \tag{1}$$

where $\tau_{\text{HN}}(T)$ is the relaxation time and $\Delta \epsilon(T) = \epsilon_0(T) - \epsilon_\infty(T)$ is the relaxation strength of the process under investigation. Exponents α and γ describe the symmetrical and asymmetrical broadening of the distribution of relaxation times, respectively. Only the imaginary parts of the spectra were used in the fitting procedure. The film was irradiated on the copper electrode using a doped mercury vapor mean pressure lamp, type TQ718 Z4 of a Heraeus Nobelight VG 700 irradiation reactor and an UB4 interference filter, manufactured by Prinz Optics (absorption <375 nm). The waveguide-mode spectroscopy experiments were carried out using a home-built spectrometer (Figure 1).

A grating with a periodicity Λ of 597 nm that was ion etched into the substrate¹¹ was used to couple a HeNe laser beam (λ = 632.8 nm) simultaneously in s- (TE) and p-polarized (TM) directions from the air into the waveguide by using a polarizer at an angle of 45°. The waveguide-mode spectrum was determined by scanning the angle of incidence of the incoming laser beam onto the grating while measuring the out-coupled power with a photodetector situated at the end of the waveguide.¹² From the coupling angles and the known parameter of the grating, the effective refractive indices of all modes N_{ij} can be calculated according to eq 2.

$$N_{i,j} = n_{\rm c} \cdot \sin \Theta + m \cdot \frac{\lambda}{\Lambda} \tag{2}$$

 $n_{\rm c}$ is the refractive index of the cladding (here, air with $n_{\rm c} = 1$), λ is the wavelength of the coupled light, Λ is the grating period, and m is the diffraction order. With a knowledge of the optical constants of the substrate, the thickness and refractive index for both polarization directions can be calculated iteratively as long as at least two modes for each direction can be detected. If more than two modes were detected, the errors in the thickness and refractive index were calculated

by a combination of all modes. The irradiation of the film was carried out with a HeCd laser at a wavelength λ of 442 nm with linear polarization at 0° angle of incidence and a power of 10 mW. Synthesis.

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6-Hydroxyhexyltosylate (5)



Tosyl chloride (76.26 g, 0.4 mol) and 47.27 g of 1,6-hexane-diol (0.4 mol) were dissolved in 160 mL of acetonitrile at room temperature. Afterward, the mixture was cooled in an ice bath, and 81 g (0.8 mol) of triethylamine was added under stirring in a nitrogen atmosphere for 2 h. Then the ice bath was removed, and the reaction mixture was stirred for another 2 h at room temperature. Later, the acetonitrile was distilled of in vacuum, and the residue was dissolved in 250 mL of chloroform. The solution was cooled again and stirred for 5 min together with a mixture of 280 g of ice and 100 mL of concentrated HCl. The aqueous phase was separated and extracted with chloroform. The combined chloroform phases were washed with water three times and dried with magnesium sulfate. The crude product, which was obtained after removing the chloroform in vacuum, was purified by column chromatography over silica gel (chloroform). Yield: 47.1 g (43%), colorless oil. ¹H NMR (200 MHz, CDCl₃, δ): 1.17–1.73 (m, 8 H, 3,4,5,6-H), 2.41 (s, 3 H, 18-H), 3.57 (t, 2 H, 2-H, J = 6.6 Hz), 3.98 (t, 2 H, 7-H, J = 6.6 Hz), 7.31 (d, 2 H, 12,14-H, J = 8.0Hz), 7.75 (d, 2 H, 11,15-H, J = 8.0 Hz). IR (NaCl): λ^{-1} (cm⁻¹) = 3550, 3376 (O-H), 3066 (ar. C-H), 2936, 2862 (aliph. C-H), 1357 (SO₂), 1177 (SO₂), additional signals at 1598, 1495, 1462, 1307, 1292, 1211, 1198, 1098, 1057, 1020, 967, 928, 817, 790, 755, 727, 665.

Di-(tert-butyl)-2-(6-hydroxyhexyl)malonate (7)



Absolute DMF (43 mL) was poured into an annealed flask, and 0.51 g of sodium hydride (95%; 20.2 mmol) was added with the exclusion of moisture. The suspension was cooled in an ice bath, and then 3.97 g (18.4 mmol) of di-(*tert*-butyl) malonate was injected with stirring through a septum with an injection needle for a period of 10 min. Afterward, the ice bath was removed, and the mixture was stirred for 2 h at room temperature. Then, the reaction mixture was cooled again with an ice bath, and 5 g (18.4 mmol) of 1,6-hexanediol monotosylate was added within 10 min through the septum. The ice bath was removed, and the mixture was stirred for 12 h. Then the DMF was distilled off in vacuum, and the crude product was diluted with diethyl ether and washed with a half-saturated solution of ammonium chloride. The aqueous phase was extracted with diethyl ether, and the combined ether fractions were dried with magnesium sulfate. After removing the ether, the crude product was purified by column chromatography over silica gel (petroleum ether/ethyl acetate 7:3 v/v). Yield: 2.8 g (48%), colorless oil. ¹H NMR (200 MHz, CDCl₃, δ): 1.21–1.62 (m, 26 H, 3,4,5,6,12,16,18,19,21,22-H), 1.75 (dt, 2 H, 7-H), 3.06 (t, 1 H, 8-H, *J* = 7.6 Hz), 3.59 (t, 2 H, 2-H, *J* = 6.3 Hz). IR (NaCl): λ^{-1} (cm⁻¹) 3432 (O–H), 2978, 2933, 2860 (C–H), 1744, 1728 (C=O); additional signals at 1478, 1458, 1393, 1369, 1345, 1292, 1257, 1142, 1057, 849, 757. MS (FD) *m*/*z* (%): [M + H⁺] 317 (100).

Di-(tert-butyl)-2-[6-(isopropenylcarbonyloxy)hexyl]malonate (9)



Methacrylic acid (0.544 g, 6.3 mmol), 1 mg of hydroquinone monopropyl ether, 2 g (6.3 mmol) of di-(tert-butyl)-2-(6-hydroxyhexyl) malonate, and 76 mg (0.63 mmol) of 4-(dimethylamino)pyridine were dissolved in 2.5 mL of dry dichloromethane. Then a solution of 1.31 g (6.3 mmol) of dicyclohexylcarbodiimide in 1 mL of dry dichloromethane was added with stirring for a period of 15 min. The temperature of the reaction mixture was kept at room temperature by a water bath, and the mixture was stirred for an additional 2 h. Afterward, the precipitated urea was filtered off and washed with a small amount of dichloromethane. The combined fractions were evaporated and dried in vacuum. For purification, the product was chromatographed with a silica gel column with chloroform. Yield: 1.46 g (60%), colorless oil. ¹H NMR (200 MHz, CDCl₃, δ): 1.24-1.38 (m, 6 H, 7,8,9-H), 1.42 (s, 18 H, 15,21,23,24,-26,27-H), 1.53-1.84 (m, 4 H, 6,10-H), 1.90 (s, 3 H, 16-H), 3.07 (t, 1 H, 11-H, J = 7.6 Hz), 4.09 (t, 2 H, 5-H, J = 6.6 Hz), 5.51 (s, 1 H, 1-H), 6.06 (s, 1 H, 1-H). ¹³C NMR (50 MHz, CDCl₃, δ): 18.28 (C-16), 25.71/27.05/28.44/28.49/28.89 (C-6, C-7, C-8, C-9, C-10), 27.89 (C-15,21,23,24,26,27), 53.91 (C-11), 64.65 (C-5), 81.17 (C-14,20), 125.10 (C-1), 136.50 (C-2), 167.46 (C-3), 168.93 (C-12,18). IR (NaCl): λ^{-1} [cm⁻¹]: 2978, 2933, 2860 (C-H), 1745, 1725 (C=O), 1639 (C=C); additional signals at 1456, 1393, 1369, 1322, 1297, 1254, 1167, 1057, 1012, 940, 850, 816, 757.

2-[6-(Isopropenylcarbonyloxy)hexyl]malonic acid (10)



Di-(tert-butyl)-2-[6-(isopropenylcarbonyloxy)hexyl] malonate (6.77 g, 17.6 mmol) and 5 mg of hydroquinone monopropyl ether were added to 18 mL of trifluoroacetic acid (90%) and stirred for 2 h with the exclusion of moisture at room temperature. Then the reaction mixture was dilluted with 10 mL of toluene, and the azeotropic boiling solvents were distilled off in vacuum. This procedure was repeated two times to remove residual trifluoroacetic acid. The product was dried in vacuum and purified by column chromatography over silica gel with a solvent gradient from chloroform to chloroform/ methanol (4/1 v/v). Yield: 4.1 g (86%), colorless crystals, mp: 60 °C. ¹H NMR (200 MHz, CDCl₃, δ): 1.25-1.45 (m, 6 H, 7,8,9-H), 1.65 (tt, 2 H, 6-H), 1.81-2.03 (m, 5 H, 10,14-H), 3.43 (t, 1 H, 11-H, J = 7.3 Hz), 4.13 (t, 2 H, 5-H, J = 6.6 Hz), 5.56 (s, 1 H, 1-H), 6.09 (s, 1 H, 1-H), 9.64 (br, 2 H, COO-H). ¹³C NMR (50 MHz, CDCl₃, δ): 18.26 (C-14), 25.62/27.85/28.41/28.57/ 28.76 (C-6, C-7, C-8, C-9, C-10), 51.52 (C-11), 64.88 (C-5), 125.60 (C-1), 136.35 (C-2), 167.94 (C-3), 174.74 (C-12,16). IR (KBr): λ^{-1} [cm⁻¹] 3450, 3183, 3104 (O–H), 2936, 2861 (C–H), 1717 (C=O), 1636 (C=C); additional signals at 1455, 1407, 1325, 1301, 1180, 1046, 1014, 944, 817.

Mesoionic 2-cyano-1,3-diphenyl-5-[6-(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin- 3-ium-4-olate (12)



2-Nitrilo-N,N-diphenylacetamidine (2.56 g, 11.5 mmol),¹³ 4.77 g (23.1 mmol) of DCC, and 5 mg of hydroquinone were dissolved with stirring in 23 mL of dry dichloromethane. Afterward, 3.15 g (11.5 mmol) of 2-[6-(isopropenylcarbonyloxy)hexyl]malonic acid was added batchwise for a period of 15 min with the exclusion of moisture. After 30 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 vacuum, and then 250 mL of petroleum ether was added under stirring. After 15 min, the petroleum ether was decanted, and the red residue was dried in vacuum. For further purification, the crude product was chromatographed over silica gel (ethyl acetate/petroleum ether 7/3 v/v). Yield: 1.10 g (21%); red, highly viscous oil. ¹H NMR (200 MHz, DMSO-d₆, δ): 1.25–1.79 (m, 8 H, 6,7,8,9-H), 1.86 (s, 3 H, 17-H), 2.35 (t, 2 H, 10-H, J = 6.8 Hz), 4.07 (t, 2 H, 5-H, J = 6.1 Hz), 5.64 (s, 1 H, 1-H), 6,00 (s, 1 H, 1-H), 7.57-7.70 (m, 10 H, ar.-H). ¹³C NMR (50 MHz, DMSO-d₆, δ) 17.92 (C-17), 24.40/25.23/27.18/27.99/28.65 (C-6, C-7, C-8, C-9, C-10), 64.25 (C-5), 101.37 (C-11), 106.91 (C-26), 125.42 (C-1), 128.26/ 129.25 (C-21,25,29,33, C-22,24,30,32), 130.53 (C-23,31), 135.94 (C-2), 136.02 (C-20,28), 157.64 (C-14), 166.53 (C-3). The C-12 and C-16 signals could not be detected. IR (ATR): λ^{-1} [cm⁻¹] 3060 (ar. C-H), 2927, 2856 (aliph. C-H), 1694 (C=O), 1651 (mesoion C=O), 1593 (ar. C=C); additional signals at 1551, 1489, 1455, 1399, 1358, 1322, 1296, 1263, 1167, 1061, 1002, 943. UV (dichloromethane): $\lambda_{\rm max}$ [nm] (log $\epsilon)$ 262 (3.67), 303 (3.43), 491 (2.97). MS (FD) m/z (%): [M⁺] 458 (100). EA: Calcd for C₂₇H₂₇N₃O₄ (457.53): C, 70.88; H, 5.95; N, 9.18. Found: C, 70.50; H, 6.29; N, 9.51.

Poly[mesoionic 2-cyano-1,3-diphenyl-5-[6-(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin-3-ium-4-olate] (13)



Mesoionic 2-cyano-1,3-diphenyl-5-[6-(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin-3-ium-4-olate (0.994 g, 2.17 mmol) and 7.18 mg (0.040 mmol) of AIBN were dissolved in 11 mL of absolute DMF. The solution was twice frozen in liquid nitrogen and degassed two times. Afterward, the solution was polymerized for 24 h at 60 °C, and the accrued polymer was precipitated in a mixture of 75 mL of methanol Scheme 2. Synthesis of Novel Mesoionic Monomers



and 150 mL of water. After drying in 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 vacuum again. Yield: 0.44 g (44%), red powder. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 0.45–2.20 (m, 1,6,7,8,9,17-H), 2.34 (m, 10-H), 3.82 (m, 5-H), 7.10–7.73 (m, ar.-H). IR (ATR): λ^{-1} [cm⁻¹] 3067 (ar. C–H), 2930, 2858 (aliph. C–H), 1695 (C= O), 1657 (mesoion C=O), 1595 (ar. C=C); additional signals at 1489, 1456, 1389, 1359, 1259, 1153, 1073, 1002, 969, 753, 692. UV (dichloromethane): λ_{max} [nm] (log ϵ) 261 (3.67), 313 (3.04), 485 (3.09). DSC: T_g = 78 °C. SEC (chloroform, PS standard): M_n = 11 000, M_w = 24 000, PD = 2.1.

Copolymer of methyl methacrylate and mesoionic 2-cyano-1,3-diphenyl-5-[6-

(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin-3-ium-4-olate (15)



Mesoionic 2-cyano-1,3-diphenyl-5-[6-(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin-3-ium-4-olate (0.45 g, 0.988 mmol), 0.395 g (3.95 mmol) of methyl methacrylate, and 7.18 mg (0.040 mmol) of AIBN were dissolved in 11 mL of absolute DMF. The solution was twice frozen in liquid nitrogen and degassed two times. Afterward, the solution was polymerized for 24 h at 60 °C, and the accrued polymer was precipitated in a mixture of 100 mL of methanol and 200 mL of water. After drying in vacuum, the polymer was purified by dissolving in 5 mL of dichloromethane and reprecipitating in 200 mL of diethyl ether. The product was dried in vacuum again. Yield: 0.56 g (66%), red powder. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 0.72 (s, syndiot. 17,40-H), 0.90 (s, heterot. 17,-40-H), 1.12 (s, isot. 17,40-H), 1.22–2.20 (m, 1,6,7,8,9,35-H), 2.35 (m, 10-H), 3.51 (s, 39-H), 3.86 (m, 5-H), 7.24–7.68 (m, ar.-H). IR (ATR): λ^{-1} [cm⁻¹] 2989, 2929, 2866 (aliph. C–H), 1726 (C=O), 1663 (mesoion C=O), 1596 (ar. C=C); additional signals at 1489, 1448, 1385, 1243, 1190, 1149, 1060, 985, 840, 753, 694. UV (dichloromethane): λ_{max} [nm] 258, 312, 484. DSC: $T_{\rm g} = 104$ °C. SEC (chloroform, PS standard): $M_{\rm n} = 12\ 000$, $M_{\rm w} = 25\ 000$, PD = 2.1.

Results and Discussion

Novel polymers in which the polymerizable methacrylic group is attached to the malonic acid component of the mesoionic function were prepared. This procedure allows the use of various low-molecular-weight amidines as condensating compounds. In contrast to former methacrylic monomers, which were synthesized via the use of isothioureas,^{4,5} this method does not require any sulfur atoms in the molecule.

The monomers were obtained via monotosylated 1,6hexanediol (5), which was used as the electrophilic compound in the alkylation of di-(*tert*-butyl)-malonate (6). The malonate (6) itself was deprotonated by NaH in *N*,*N*-dimethylformamide (DMF) as the solvent. The hydroxyl group of the resulting alkylated malonate (7) was esterified with methacrylic acid (8) in the presence of dicyclohexylcarbodiimide (DCC) as the condensation agent and 4-(dimethylamino)pyridine as the catalyst. Then, the *tert*-butyl protecting groups of di-(*tert*-butyl)-2-[6-(isopropenylcarbonyloxy)hexyl]malonate (9) were removed with trifluoroacetic acid, resulting in a malonic acid with a polymerizable methacrylic group attached to the end of an alkane spacer (10). This product was cyclocondensed with 2-nitrilo-*N*,*N*-diphenylacetamiScheme 3. Preparation of Mesoionic Copolymers



Table 1. Polymer Properties

polymer	homopolymer <i>13</i>	copolymer 15
yield [%]	44	66
<i>n/m</i> (polymer)		4:1
M _n [g/mol]	11 000	12 000
$M_{\rm w}$ [g/mol]	24 000	25 000
PD	2.1	2.1
$\Delta C_p (T_g) [^{\circ}C]$	78	104

dine,¹⁰ resulting in mesoionic 2-cyano-1,3-diphenyl-5-[6-(isopropenylcarbonyloxy)hexyl]-6-oxo-1,6-dihydropyrimidin-3-ium-4-olate (Scheme 2).

In comparison to similar mesoions with aromatic groups instead of the cyano function, which show an absorption corresponding to the HOMO–LUMO transition at 365 nm, the strong electron-withdrawing effect of the cyano function causes a strong bathochromic shift to 491 nm, which results in an intensely red-colored product.

The polymerization of monomer **12** was carried out in DMF with 2,2'-azobisisobutyronitrile (AIBN) as the initiator at 60 °C. Homopolymer **13** as well as copolymer **15** with methyl methacrylate **(14)** was prepared (Scheme 3). The polymer properties are listed in Table 1.

Because of their zwitterionic structure, a high dipole moment for the mesoionic pyrimidiniumolates can be expected. Thus, they should be orientable in an electric field. For a detailed analysis, dielectric spectroscopic measurements were carried out with copolymer **15** and compared with the results obtained from poly[mesoionic 5-butyl-1-(4-ethoxyphenyl)-2-[4-(vinylcarbonyloxy)butylthio]-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4olate-*co*-5-(cholesterolcarbonyl)-pentylacrylate **(16)**.⁵ The molecular structure of **16** is shown in Scheme 4.

The spectra of the dielectric loss ϵ'' of mesoionic liquidcrystalline copolymer **16** measured at different temperatures are sketched in Figure 2. Three dielectrically active relaxation processes can be distinguished and are

Scheme 4. Liquid-Crystalline Mesoionic Copolymer



denoted on the graph as α , β , and γ . The linear rise of ϵ'' at low frequencies for the highest temperatures is due to the DC conductivity in the sample.

Measurements on copolymer **15** were performed on spin-coated films. The transparent material allows an excellent photochemical conversion of the mesoionic film, which was remeasured after conversion. Examples of the spectra measured at various temperatures both before and after conversion are shown in Figure 3.

It was also found that the dielectric storage function ϵ' decreases by irradiation. This phenomenon is independent of the frequency and can therefore be a result of the decreased molecular polarizability, which can be explained by the conversion of π bonds to σ bonds, whereby the system of conjugated double bonds in the molecules is lost. The parameters of the Havriliak–Negami fit of the observed processes are given in the Table 2.



Figure 2. Dielectric loss spectra of liquid-crystalline mesoionic copolymer 16 at different temperatures.



Figure 3. Dielectric loss spectra for mesoionic copolymer **15** at various temperatures. Filled and open symbols correspond to spectra measured before and after irradiation, respectively.

 Table 2. Parameters of the Havriliak–Negami Fit of the Dielectric Processes

sample	process	$T\Delta\epsilon~(\mathbf{K})^a$	α_{HN}	$\gamma_{ m HN}$
15	β	2.5 - 3.5	0.34 ± 0.05	0.86 ± 0.03
15 irradiated	β	1.6 - 4.9	0.25 ± 0.05	1
16	α	450 - 780	0.28 ± 0.5	1
	β	2.3 - 4.4	0.40 ± 0.4	1
	γ	11-20	0.25 ± 0.2	1

 a This parameter is temperature-dependent; therefore, the low- and high-temperature limits are given.

The α process of sample **16** was strong; the remaining processes were very weak. All processes are broad but symmetric, which is indicated by relatively low values of α_{HN} and γ_{HN} , which are close to or equal to 1, respectively. The variation in the parameters with temperature is within the error limits (given in Table 2).

To characterize the temperature dependence of the observed relaxation processes in the studied samples, an activation plot (log τ vs T^{-1}) is presented in Figure 4.

The low-temperature processes show linear dependencies in this plot and can therefore be described as

$$\log(\tau_{\max}) = \log(\tau_0) + \frac{E_A}{2.303 \cdot kT}$$
(3)

where τ_0 is the relaxation time at infinite temperature and E_A is the activation energy. For the γ process visible



Figure 4. Activation plot (relaxation times of the dielectric processes vs temperature) for all detected relaxation processes in polymers *15* and *16*. The vertical arrows indicate reciprocal values of the calorimetric glass-transition temperatures of the two polymers.

 Table 3. Comparison of the Glass-Transition

 Temperatures from DSC Measurements and Dielectric

 Spectroscopy

	1 10	
polymer	$T_{\rm g}$ (DSC) [°C]	Tg (dielectric) [°C]
15	104	107
16	45	37

only in liquid-crystalline polymer **16**, the activation energy $E_{\rm A} = 12.2 \pm 0.2$ kJ/mol K has been determined. The β process in this polymer has a higher activation energy of $E_{\rm A} = 21.70 \pm 0.08$ kJ/mol K. For the process assigned as β in copolymer **15**, the activation energies $E_{\rm A} = 34.9 \pm 0.4$ and 32.7 ± 0.2 kJ/mol K have been obtained for states before and after irradiation, respectively.

In both of the polymers that were studied, slower processes were also detected; these are assigned here as α processes because they show features typical of the vitrification of polymer segments in glass-forming systems. They do not show linear dependencies in the activation plot, and they slow with decreasing temperature to relaxation-time values reaching nearly 100 s at the corresponding calorimetric glass-transition temperatures (indicated in the Figure by vertical arrows).¹⁴ Taking this into account, one can consider these slower relaxations to be responsible for a cooperative segmental motion in the studied polymers. Any precise molecular assignment of the other relaxation processes is not possible on the basis of our recent information. Considering, however, their rates and activation energies, we can say that they have to correspond to structural units smaller than the monomeric segments in the polymers. The glass-transition temperatures of the studied system determined by means of differential scanning calorimetry are compared in Table 3 with temperatures at which the α relaxations reach relaxation times of 100 s. In the case of polymer 15, the values concern the unirradiated sample. After irradiation, the α process was slower (indicating a higher glass-transition temperature) and was masked by the DC conductivity, making a detailed distinction impossible.

A detailed analysis of the molecular polarizability was performed by waveguide-mode spectroscopy. In liquidcrystalline copolymer **1**% prepared from mesoionic 1-(4-



Figure 5. Time-dependent changes in the refractive index and the film thickness of copolymer 17 during irradiation. Errors: $\Delta n = \pm 0.0009$ and $\Delta d = \pm 29$ nm.



Figure 6. Time-dependent change of the coupling angle of the TE_0 mode of polymer **13**.

ethoxyphenyl)-2-[4-(isopropenylcarbonyloxy)ethylthio]-5-methyl-6-oxo-3-phenyl-1,6-dihydropyrimidin-3-ium-4olate and 5-(cholesterolcarbonyl)pentyl methacrylate, three waveguide modes of both polarization directions could be detected, from which a film thickness of 1733 nm and an isotropic refractive index of 1.539 could be calculated. The changes in the film thickness and isotropic refractive index during irradiation are shown in Figure 5.

Similar to formerly described observations on the homopolymer of the mesoionic methacrylate,⁸ the irradiation of the copolymer results in an increase in the film thickness and a decrease in the refractive index. In comparison to the homopolymer, the effects are smaller because of the reduced amount of the mesoionic chromophore. In conclusion, the film thickness increased up to 20 nm (1.2%), and the refractive index significantly decreases about 0.005. For a determination of the percentage change, the optical susceptibility χ can be calculated from eq 4.

$$\chi = n^2 - 1 \tag{4}$$

Therefore, a decrease in the optical susceptibility χ of 1.1% was found.

In another experiment with polymer 13, the refractive index of the unirradiated sample was determined to be 1.573. The film thickness was 795 nm. During irradiation, the coupling angle of the TE₀ mode was automatically followed as illustrated in Figure 6.

After irradiation, the waveguide-mode spectrum was scanned again. In this case, a film thickness of 829 nm

was detected, that is, 34 nm (4.3%) larger than before irradiation. The refractive index decreased by about 0.014 down to 1.559, which correlates to a decrease in the optical susceptibility χ of 3.0%. For both polymers, the increase in film thickness could be explained by the change from the planar mesoionic structure to the angled bis(β -lactam) structure, which has a higher steric demand. The reduction in the refractive index common to all experiments is caused by the decreased molecular polarizability and is amplified by the decreased density of the polarizability carrying units.

Conclusions

Novel mesoionic monomers in which the polymerizable methacrylic group is attached to the malonic acid component of the mesoionic function were prepared and characterized. The (co)polymers obtained by radical polymerization with AIBN in an organic solvent had molecular weights of $M_n = 11\,000$ to 12 000 and a polydispersity of 2.1. Dielectric measurements on the copolymer with methyl methacrylate revealed two dielectrically active processes: an Arrhenius β process below the glass-transition temperature and a non-Arrhenius α process above it. In liquid-crystalline copolymer 16, an additional fast γ process reflecting localized motions of the liquid-crystalline side chain appears. The relaxation times of the α processes determined by dielectric spectroscopy reached 100 s at temperatures close to the $T_{\rm g}$ obtained by DSC. Irradiated sample 15 shows a higher glass-transition temperature (slower α process), and the values of dielectric function ϵ' were reduced as a result of the reduced polarizability of the molecule. It could be observed by waveguide-mode spectroscopy that the irradiation of mesoionic methacrylates results in an increase in film thickness caused by the change in the molecular structure and an isotropic decrease in the refractive index. In liquid-crystalline copolymer 17, both effects could be detected with decreased strength.

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