

Polymeric Nitrons. 2. Synthesis, Irradiation and Waveguide Mode Spectroscopy of Polymeric Nitrons Derived from Polymeric Benzaldehydes and *N*-Isopropylhydroxylamine

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ABSTRACT: Various vinylbenzaldehydes were prepared using the Heck reaction: 4-vinylbenzaldehyde (**14**), 3-vinylbenzaldehyde (**15**), 2-vinylbenzaldehyde (**18a**), 2-hydroxy-4-vinylbenzaldehyde (**16**) and 4-[(4-vinylbenzyl)oxy]benzaldehyde (**6**). The four monomers (**6**, **14**, **15**, **16**) were polymerized using AIBN as initiator at 70 °C for 24 h to yield the corresponding homopolymers (**7**, **19**, **23**, **25**) and a copolymer (**20**) with styrene. The molecular weights are about 10 000. The polymer analogous condensation of the aldehyde groups with an excess of *N*-isopropylhydroxylamine (**8**) at room temperature produces polymeric nitrons (**9**, **21**, **22**, **24**, **26**) in almost quantitative yields. All nitron functions were irradiated, and the intramolecular cyclization of the nitrons to the corresponding oxaziridines was examined. Waveguide mode spectroscopy of poly(4-vinylbenzaldehyde-*N*-isopropylnitron) (**21**) shows that the changes in film thickness are low but the changes in refractive indices are significant after irradiation. Oxaziridine **10** has high thermal stability with respect to ring opening. No structural change was detected after irradiation of the hydroxyphenyl-modified polynitron (**26**). A low molecular weight model compound (2-hydroxybenzaldehyde-*N*-methylnitron, **28**) was prepared in order to examine this abnormal photochemical behavior and also showed that it is highly resistant to UV irradiation.

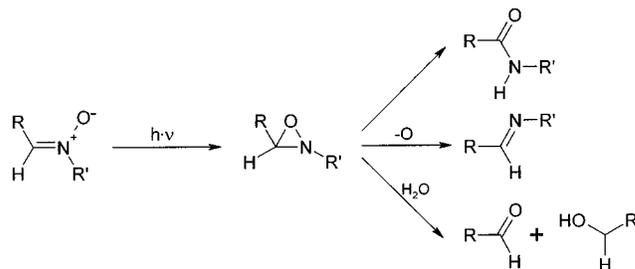
1. Introduction

The demand on storage capacity of data media increased exponentially during the past decades. To master this challenge in the future, new switchable polymeric materials are needed.¹ Dipolar nitrons may be used to develop photosensitive materials change polarity during irradiation.^{2–4} Typical photoinduced isomerization products of nitrons are summarized in Scheme 1. The photoinduced cyclization of the aryl-*N*-aryl-substituted nitrons ($R = R' = \text{aryl}$) leads to formation of substituted oxaziridines, which are unstable and rapidly decompose (Scheme 1).⁵ Irradiation gives a mixture of products, which are poorly applicable for photoactive materials. However, the *N*-alkyl-substituted nitrons formed stable oxaziridines.

The properties of polymers with a high concentration of reactive nitron groups near the backbone should be strongly influenced by irradiation. This paper presents the synthesis of vinylbenzaldehyde nitron precursors. Regarding former studies, nitrons inhibit the free radical polymerization.⁵ However, at 60 °C the 1,3-dipolar polycycloaddition of nitrons with (meth)acryl and vinyl groups is the preferred reaction. Enzymatic catalyzed polycondensations at room temperature were possible with phenol derivatives of nitrons.⁶

Optical data storage can be achieved by changes in the refractive index or thickness of the photosensitive material. This behavior of polynitrons and other photosensitive polymers like mesoions can be excellently examined by waveguide mode spectroscopy during UV irradiation.^{7,8} This method is based on the selective excitation of waveguide modes in thin films. From the

Scheme 1. Behavior of Nitrons during Irradiation



measured coupling angles of different waveguide modes the effective refractive indices N_{ij} of these modes can be calculated and converted into the thickness and the refractive index of the thin film using the dispersion relation. S- or p-polarized waveguide modes can also be used to determine the anisotropy of the thin polymer film.^{8,9} This paper reports the synthesis and photochemical behavior of new polymers bearing *N*-aliphatic substituted nitrons as photosensitive moieties.

2. Experimental Section

2.1. Materials. All solvents of p.a. quality (Riedel de Haen, Seelze, Germany) were stored over molecular sieves, 3 or 4 Å. Technical solvents and styrene were distilled before use. Benzaldehyde (98+%), 4-brombenzaldehyde (99%), 3-brombenzaldehyde (96+%), 2-brombenzaldehyde (97%), 4-hydroxybenzaldehyde (99%), 2-hydroxybenzaldehyde (99%), 2-hydroxy-4-brombenzaldehyde (98%), styrene (99%), triethylamine (99%), and tri(*o*-toloyl)phosphine (99%) were purchased from Acros Organics, Geel, Belgium, acetoneoxime (98+%), AIBN (98+%), NaCNBH₃ (95%) and 4-vinylbenzyl chloride (95+%) from Fluka GmbH, Deisenhofen, Germany, as well as *N*-methylhydroxylamine hydrochloride (98%) and palladium acetate (98%) from Aldrich, Taufkirchen, Germany. These chemicals were used without further purification. *N*-Isopropylhydroxylamine¹⁰ (**8**) and benzaldehyde-*N*-methylnitron¹¹ (**3**) were prepared as described in the literature.

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2.2. Synthesis of 4-[(4-Vinylbenzyl)oxy]benzaldehyde-N-isopropyl nitron (9). **2.2.1. Synthesis of 4-[(4-Vinylbenzyl)oxy]benzaldehyde (6).** *p*-Vinylbenzyl chloride (**4**, 15.2 g, 0.1 mol), *p*-hydroxybenzaldehyde (**5**, 12.2 g, 0.1 mol), and K_2CO_3 (25 g, 0.18 mol) were suspended in acetone (150 mL) and then refluxed for 7 h. After removing of the inorganic salts, the solvent was evaporated, yielding a brownish pulp. Column chromatography in chloroform/petrol ether (1/2, v/v) gave, after drying in a vacuum (oil pump), 13.3 g (56%) of a yellow colored oil (**6**). R_f value (technical chloroform) = 0.59. 1H NMR (200 MHz, $CDCl_3$ [ppm]): δ = 9.87 (s, 1H, $-CHO$), 7.83 (d, J = 8.8 Hz, 2H, *ArH*), 7.39 (m, 4H, *ArH*), 7.06 (d, J = 8.8 Hz, 2H, *ArH*), 6.75 (dd, J = 11.2 Hz, J = 17.6 Hz, 1H, $-CH=CH_2$), 5.77 (d, J = 17.6 Hz, 1H, $-CH=CH_2$), 5.27 (d, J = 11.2 Hz, 1H, $-CH=CH_2$), 5.12 (s, 2H, $O-CH_2-$).

2.2.2. Homopolymerization of 4-[(4-Vinylbenzyl)oxy]benzaldehyde (6). Monomer **6** (0.95 g, 4 mmol) in benzene (5 mL) was polymerized with AIBN (15 mg, 9×10^{-5} mol) for 24 h at 70 °C. Precipitating in methanol gave 0.4 g (42%) of poly{4-[(4-vinylbenzyl)oxy]benzaldehyde} (**7**).

SEC (RI): M_n = 11 800, PD = 2.29. DSC: T_g = 74 °C. 1H NMR (200 MHz, $CDCl_3$): δ = 9.78 (b, 1 H, $-CHO$), 7.71 (b, 2 H, *ArH*), 6.92 (b, 4 H, *ArH*), 6.53 (b, 2 H, *ArH*), 4.92 (b, 2H, $-CH_2-$), 2.50–1.00 (b, 3H, $-CH_2-CH-$). IR (KBr): 2924 (alkyl, aryl), 1691 (C=O) ester), 1602 (ring), 1509 (ring), 876, 832 (ring), further intensive signals at 1577, 1425, 1314, 1258, 1161, 1015 cm^{-1} .

2.2.3. Polymer Analogous Reaction of Poly{4-[(4-vinylbenzyl)oxy]benzaldehyde} (7) with *N*-Isopropylhydroxylamine (8) To Produce Polynitron 9. A solution of poly{4-[(4-vinylbenzyl)oxy]benzaldehyde} (**7**, 0.31 g, 1.3 mmol) and *N*-isopropylhydroxylamine (**8**, 0.3 g, 4 mmol) in chloroform (1.5 mL) was stirred for 2 days at room temperature and then precipitated in diethyl ether, yielding 0.35 g (conversion 89%) of the polymeric nitron (**9**).

SEC (RI): M_n = 16 000, PD = 2.03. SEC (UV): M_n = 16 000, PD = 2.15. DSC: T_{dec} = 170 °C. 1H NMR (200 MHz, $CDCl_3$): δ = 9.78 (b, 0.11 H, $-CHO$), 8.16 (b, 1.75 H, ArH_{nit}), 7.66 (b, 0.89 H, $CH=N$), 0.22 H, ArH_{ald}), 6.94 (b, 4 H, *ArH*), 6.50 (b, 2 H, ArH_{ald} and ArH_{nit}), 4.82 (b, 2H, $-CH_2-$), 4.41 (b, 0.89 H, $N-CH(CH_3)_2$), 2.00–1.00 (m, 3 H, $-CH_2-CH-$), 5.5 H, $N-CH(CH_3)_2$). IR (KBr): 2979, 2930, 2870 (alkyl, aryl), 1602 (ring), 1506 (ring), 1147 ($N-O$ stretch), 844 (ring), further intensive signals at 1456, 1310, 1252, 1171, 1086, 1016 cm^{-1} . UV (methylene chloride): λ_{max}/nm = 306.

2.3. Heck Reaction of Different Bromobenzaldehydes with Ethene. In a typical procedure,¹² a pressure vessel was charged with 0.01 mol of bromobenzaldehyde (**11–13**, or **17**), palladium(II) acetate (22 mg, 10^{-4} mol), tris(*o*-toloyl)phosphine (60 mg, 2×10^{-4} mol) dissolved in DMF (30 mL), and triethylamine (9.1 g, 0.09 mol). The solution was bubbled with argon for more than 15 min, and a pressure of about 40 bar ethylene was applied. The autoclave was heated to 110 °C for 24 h. Then the mixture was added to 120 mL of water and extracted four times with ethyl acetate, and the organic phase was extracted two times with water and saturated NaCl solution, dried with $MgSO_4$, and evaporated. The brownish liquid was distilled and/or purified by chromatography with chloroform as eluant. Nevertheless about 5 mol % of the bromobenzaldehyde educt was present which did not disturb further polymerization.

2.3.1. Synthesis of 4-Vinylbenzaldehyde (14). Yield: 66%. 1H NMR (200 MHz, $CDCl_3$): δ = 9.98 (s, 1 H, $-CHO$), 7.83 (d, J = 8.3 Hz, 2 H, *ArH*), 7.54 (d, J = 8.3 Hz, 2 H, *ArH*), 6.76 (dd, J = 17.6 Hz, J = 10.7 Hz, 1 H, $-CH=CH_2$), 5.90 (d, J = 17.6 Hz, 2H, $-CH=CH_2$), 5.43 (d, J = 10.7 Hz, 3H, $-CH=CH_2$). IR (NaCl): 3089, 3010 (aryl), 2824, 2736 (alkyl), 1702 (C=O aldehyde), 1605 (ring), 842 (ring), further intensive signals at 1566, 1213, 1167, 991, 922 cm^{-1} .

2.3.2. Synthesis of 3-Vinylbenzaldehyde (15). Yield: 83%. 1H NMR (200 MHz, $CDCl_3$): δ = 9.97 (s, 1 H, $-CHO$), 8.07 (t, J = 1.7 Hz, 1 H, *ArH*), 7.91 (dd, J = 7.8, J = 1.5 Hz, 1 H, *ArH*), 7.56 (dt, J = 7.8 Hz, J = 2.4 Hz, 1 H, *ArH*), 6.77 (dd, J = 17.6 Hz, J = 10.7 Hz, 1 H, $-CH=CH_2$), 5.79 (d, J = 17.6 Hz, 1 H, $-CH=CH_2$), 5.79 (d, J = 10.7 Hz, 1 H, $-CH=$

CH_2). IR (KBr): 3061, 3011 (aryl), 2828, 2729 (alkyl), 1702 (C=O aldehyde), 1572 (ring), 787, 673 (1,3-disubstituted benzenes), further intensive signals at 1384, 1192, 991, 922 cm^{-1} .

2.3.3. Synthesis of 2-Hydroxy-4-vinylbenzaldehyde (16). Yield: 54%. 1H NMR (200 MHz, $DMSO-d_6$): δ = 10.90 (b, 1H, $-OH$), 10.20 (s, 1 H, $-CHO$), 7.65 (m, 2 H, *ArH*), 6.97 (d, J = 8.8 Hz, 1 H, *ArH*), 6.68 (dd, J = 17.6 Hz, J = 11.2 Hz, 1 H, $-CH=CH_2$), 5.90 (d, J = 17.6 Hz, 2H, $-CH=CH_2$), 5.43 (d, J = 11.2 Hz, 3H, $-CH=CH_2$). IR (NaCl): 3377 (b, OH) 3090, 3066, 3043 (aryl), 2959, 2927, 2872 (alkyl), 1663 (C=O aldehyde), further intensive signals at 1635, 1468, 1375, 1281, 1156, 893, 831, 768, 713 cm^{-1} .

2.3.4. Synthesis of 2-Vinylbenzaldehyde (18a). The Heck reaction leads to the formation of 2-ethylstyrene (**18b**) and 2-vinylbenzaldehyde (**18a**), which were quite difficult to separate. Data for 2-Ethylstyrene follow. 1H NMR (200 MHz, $DMSO-d_6$): δ = 7.50 (m, 1 H, *ArH*), 7.20 (m, 3 H, *ArH*), 7.01 (dd, J = 17.6 Hz, J = 11 Hz, 1 H, $-CH=CH_2$), 5.66 (d, J = 17.6 Hz, 2H, $-CH=CH_2$), 5.30 (d, J = 11 Hz, 3H, $-CH=CH_2$), 2.72 (q, J = 7.5 Hz, 2 H, $-CH_2-CH_3$), 1.21 (t, J = 7.5 Hz, 3 H, $-CH_2-CH_3$). IR (NaCl): 3086, 3063, 3015 (aryl), 2965, 2931, 2873, 2854 (alkyl), 1484, 1452 (alkyl), 773, 753 (1,2-disubstituted benzenes), further intensive signals at 1625, 1123, 990, 912 cm^{-1} .

2.4. Polymerization of the Different Vinylbenzaldehydes (14, 15, 16). **2.4.1. Polymerization of 4-Vinylbenzaldehyde (14). Homopolymerization.** *p*-Vinylbenzaldehyde (2.64 g, 20 mmol) was dissolved in benzene (10 mL) and bubbled with argon for 20 min. It was polymerized with AIBN (82 mg, 0.5 mmol) as initiator for 24 h at 70 °C. Precipitating in diethyl ether gave 2.0 g (75%) of the colorless polymer **19**.

SEC (RI): M_n = 5500, M_w = 5900, PD = 1.07. SEC (UV): M_n = 5000, PD = 1.15. DSC: no transition. 1H NMR (200 MHz, $CDCl_3$): δ = 9.84 (b, 1 H, $-CHO$), 7.50 (b, 2 H, *ArH*), 6.55 (b, 2 H, *ArH*), 2.5–1.0 (m, 3H, $-CH-CH_2-$). IR (KBr): 2926, 2849, 2829, 2736 (alkyl), 1704 (C=O aldehyde), 1605 (ring), further intensive signals at 1575, 1307, 1214, 1170, 1015, 842, 829 cm^{-1} .

Copolymerization. *p*-Vinylbenzaldehyde (2.0 g, 15 mmol) and styrene (1.6 g, 15 mmol) were dissolved in benzene (20 mL) and bubbled with argon for 20 min. The mixture was polymerized with AIBN (123 mg, 0.75 mmol) as described before, yielding 2.8 g (~78%) of the colorless polymer **20** (styrene:4-vinylbenzaldehyde = 0.85:1).

SEC (RI): M_n = 15 600, PD = 1.30. SEC (UV): M_n = 14 900, PD = 1.68. DSC: T_g = 110 °C. 1H NMR (200 MHz, $CDCl_3$): δ = 9.87 (b, 1 H, $-CHO$), 7.49 (b, 2 H, ArH_{ald}), 7.01 (b, 2.55 H, $ArH_{styrene}$), 6.51 (b, 2 H, ArH_{ald}), 1.7 H, $ArH_{styrene}$), 2.5–1.0 (m, 5.6 H, $-CH-CH_2-$). IR (KBr): 3058, 3025 (aryl), 2924, 2849, 2827, 2733 (alkyl), 1704 (C=O aldehyde), 1605 (ring), further intensive signals at 1575, 1452, 1306, 1213, 1169, 1015, 842, 829, 763, 703 cm^{-1} .

2.4.2 Polymerization of 3-Vinylbenzaldehyde (15). The polymerization of 3-vinylbenzaldehyde (**15**, 0.6 g, 4.5 mmol) in benzene (2.5 mL) with AIBN (17 mg, 0.1 mmol) was carried out as described in section 2.4.1 (homopolymerization), yielding 0.42 g (70%) of **23**.

SEC (RI): M_n = 12 600, PD = 3.42. SEC (UV): M_n = 11 800, PD = 3.45. DSC: no transition. 1H NMR (200 MHz, $CDCl_3$): δ = 9.76 (b, 1 H, $-CHO$), 7.47 (b, 1 H, *ArH*), 7.02 (b, 2 H, *ArH*), 6.60 (b, 1 H, *ArH*), 2.5–1.0 (m, 3H, $-CH-CH_2$). IR (KBr): 3060, 3030, 3010 (aryl), 2925, 2848, 2814, 2728 (alkyl), 1699 (C=O aldehyde), 1601 (ring), 798, 698 (1,3-disubstituted benzenes), further intensive signals at 1585, 1450, 1391, 1232, 1153 cm^{-1} .

2.4.3. Polymerization of 2-Hydroxy-4-vinylbenzaldehyde (16). The polymerization of 2-hydroxy-4-vinylbenzaldehyde (**16**, 0.81 g, 5.5 mmol) in dioxane (4.5 mL) with AIBN (21 mg, 0.13 mmol) was carried out as described in section 2.4.1, yielding 0.49 g (60%) of polymer **23**.

SEC (RI): M_n = 8000, M_w = 34 700, PD = 4.32. SEC (UV): M_n = 8400, M_w = 33 500, PD = 4.00. DSC: no transition points found. 1H NMR (200 MHz, $DMSO-d_6$): δ = 10.41 (b, 1 H, $-OH$), 9.97 (b, 1 H, $-CHO$), 6.63 (b, 3 H, *ArH*), 2.5–1.0 (m,

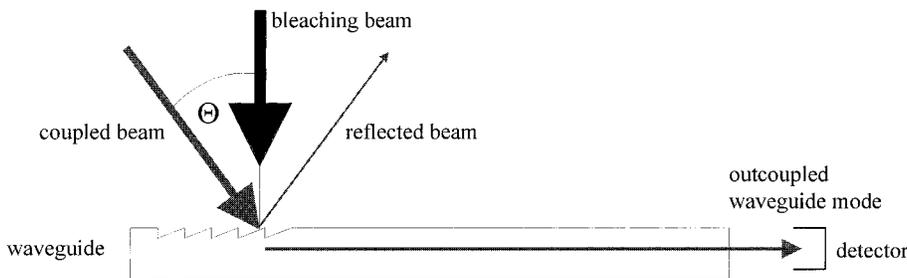


Figure 1. Setup for waveguide mode spectroscopy with simultaneous irradiation of the sample.

3H, $-CH-CH_2$). IR (KBr): 3442 (OH), 2925, 2852 (alkyl), 1658 (C=O aldehyde), 1590 (ring), 1485 (alkyl), 835, 772 (substituted benzenes), further intensive signals at 1281, 1210 cm^{-1} .

2.5. Polymer analogous Reaction of the Polyaldehydes to the Polynitrons. 2.5.1. Polymer analogous Reaction of 19 to Poly(4-vinylbenzaldehyde-*N*-isopropylnitron). Homopolymer 21. A solution of polymer 19 (0.34 g, 2.6 mmol) and *N*-isopropylhydroxylamine (8, 0.6 g, 8 mmol) in chloroform (3 mL) was stirred for 24 h at room temperature under exclusion of light. Precipitating in diethyl ether gave polymer 21, showing a conversion to the nitron of 100%.

SEC (RI): $M_n = 16\ 300$, PD = 9.24. DSC: $T_{dec} = 190\ ^\circ C$. 1H NMR (200 MHz, DMSO- d_6): $\delta = 7.97$ (b, 1 H, ArH), 7.72 (b, 1H, $-CH=N-$), 6.55 (b, 2 H, ArH), 4.27 (b, 1 H, $=N-CH(CH_3)_2$), 2.5–1.0 (m, 6 H, $=N-CH(CH_3)_2$, 3H, $-CH-CH_2$). IR (KBr): 2978, 2932 (alkyl), 1605 (ring), 1452 ($-CH_2-$), 1148 (N–O-stretch), 852 (substituted benzenes), further intensive signals at 1641, 1585, 1312, 1175, 1086, 929 cm^{-1} .

Copolymer 22. The condensation of polymer 20 (2.0 g = 9.0 mmol aldehyde groups) and *N*-isopropylhydroxylamine (8, 1.2 g, 16 mmol) in chloroform (13 mL) was carried out as described before, yielding the polymeric nitron 22 (conversion: 100%, styrene: 4-vinylbenzaldehyde = 0.85:1).

SEC (RI): $M_n = 18\ 800$, PD = 1.40. SEC (UV): $M_n = 16\ 300$, PD = 1.54. DSC: $T_{dec} = 195\ ^\circ C$. 1H NMR (200 MHz, DMSO- d_6): $\delta = 7.90$ (b, 2 H, ArH_{nitron}), 7.36 (b, 1 H, $-CH=N$), 6.99 (b, 2.55 H, ArH_{styrene}), 6.49 (b, 1.7 H, ArH_{styrene}), 2 H, ArH_{nitron}), 4.19 (b, 1H, $=N-CH(CH_3)_2$), 2.5–1.0 (m, 6H, $=N-CH(CH_3)_2$, 5.6 H, $-CH-CH_2$). IR (KBr): 3024 (aryl), 2977, 2928 (alkyl), 1604 (ring), 1452 ($-CH_2-$), 1149 (N–O stretch), 849, 703 (substituted benzenes), further intensive signals at 1635, 1582, 1310, 1175, 1088 cm^{-1} . UV (methylene chloride): $\lambda_{max}/nm = 302$.

2.5.2. Polymer Analogous Reaction of 23 to Poly(3-vinylbenzaldehyde-*N*-isopropylnitron) (24). The condensation of polymer 23 (0.26 g, 2.0 mmol) and *N*-isopropylhydroxylamine (8, 0.5 g, 6.7 mmol) in chloroform (2 mL) was carried out as described in section 2.5.1, yielding the polymeric nitron 24 (conversion: 100%).

SEC (RI): $M_n = 13\ 400$, PD = 3.53. DSC: no transition. 1H NMR (200 MHz, DMSO- d_6): $\delta = 8.22$ (b, 1 H, $-CH=N$), 7.05 (b, 3H, ArH), 6.54 (b, 1 H, ArH), 4.20 (b, 1 H, $=N-CH(CH_3)_2$), 2.5–1.0 (m, 3H, $-CH-CH_2$, 6 H, $=N-CH(CH_3)_2$). IR (KBr): 3424 (OH), 3072 (aryl), 2979, 2933, 2872 (alkyl), 1582 (ring), 1452 (alkyl), 808, 701 (1,3-disubstituted benzenes), further intensive signals at 1635, 1365, 1309, 895 cm^{-1} . UV (methylene chloride): $\lambda_{max}/nm = 298$.

2.5.3. Polymer Analogous Reaction of 25 to Poly(2-hydroxy-4-vinylbenzaldehyde-*N*-isopropylnitron) (26). The condensation of polymer 25 (0.35 g, 2.35 mmol) and *N*-isopropylhydroxylamine (8, 0.6 g, 8 mmol) in THF (2.5 mL) was carried out as described in section 2.5.1, yielding the polymeric nitron 26 (conversion: 100%).

SEC (RI): $M_n = 12\ 800$, $M_w = 29\ 600$, PD = 2.30. DSC: $T_{dec} = 190\ ^\circ C$. 1H NMR (200 MHz, DMSO- d_6): $\delta = 12.58$ (b, 1 H, $-OH$), 6.63 (b, 1 H, $-CH=N$), 6.61 (b, 3H, ArH), 4.36 (b, 1 H, $=N-CH(CH_3)_2$), 2.5–1.0 (m, 3H, $-CH-CH_2$, 6 H, $-CH(CH_3)_2$). IR (KBr): 3439 (OH), 2981, 2925 (alkyl), 1589 (ring), 1495 (alkyl), 830, 781 (substituted benzenes), further intensive signals at 1611, 1454, 1404, 1281, 1152, 1065 cm^{-1} . UV (methylene chloride): $\lambda_{max}/nm = 286, 343$.

2.6. Synthesis of 2-Hydroxybenzaldehyde-*N*-isopropylnitron (28). 2-Hydroxybenzaldehyde (27, 3.05 g, 25 mmol) and *N*-isopropylhydroxylamine (8, 1.88 g, 25 mmol) were dissolved in ethanol (10 mL) and stirred at room temperature over night. The solvent was evaporated and purified by column chromatography with chloroform, yielding 1.9 g (43 %) pure yellowish crystals of 2-hydroxybenzaldehyde-*N*-isopropylnitron (28) with a melting point of 46 $^\circ C$.

1H NMR (200 MHz, DMSO- d_6): $\delta = 12.61$ (s, 1 H, $-OH$), 8.20 (s, 1 H, $-CH=N$), 7.37 (m, 2 H, ArH), 6.82 (m, 2 H, ArH), 4.36 (heptett, $J = 6.3$ Hz, 1 H, $=N-CH(CH_3)_2$), 1.36 (d, $J = 6.3$ Hz, 6 H, $-CH(CH_3)_2$). ^{13}C NMR (200 MHz, DMSO- d_6): $\delta = 158.6$ (1 C, C–OH), 138.3 (1 C, $-CH=N$), 133.2, 132.2, 118.7, 118.5, 117.2 (5 C, arom. ring), 64.8 (1 C, $=N-CH(CH_3)_2$), 20.4 (2 C, $-CH(CH_3)_2$). IR (KBr): 3453 (OH), 3061 (aryl), 2987, 2936 (alkyl), 1596, 1580 (ring), 757 (1,2-disubstituted benzenes), further intensive signals at 1479, 1430, 1286, 1152, 1056, 994, 920, 848, 771 cm^{-1} . UV (methylene chloride): $\lambda_{max}/nm = 283, 333$. Anal. Calcd for $C_{10}H_{13}NO_2$ (179): C, 67.02; H, 7.31; N, 7.82; O, 17.85. Found: C, 66.60; H, 8.05; N, 7.73; O, 17.62.

2.7. Measurements. NMR spectra were recorded on a Bruker AM400 FT-NMR spectrometer (400 MHz) or on a Bruker AC200 FT-NMR spectrometer (200 MHz) with $CDCl_3$ or DMSO- d_6 as internal standard. IR spectra were run on a Nicolet 5SBX- or a 5DXC-FTIR spectrophotometer and the UV spectra on a Nicolet UV540 UV-vis spectrometer. The irradiations were carried out in a 700 mL reactor with a 700 W mercury medium pressure lamp TQ718Z4 from Heraeus (using an edge filter with a transmission of $\lambda < 300$ nm) in 2×10^{-4} molar solution in CH_2Cl_2 . Elemental analyses were carried out with a Foss Heraeus vario EL and the uncorrected melting points with a Büchi melting point determinator. SEC measurements were performed using a PSS apparatus with a Shodex refractive index (RI) detector and a TSP UV2000 UV-vis detector at 75 $^\circ C$ under the following conditions: HEMA 10 μm , 8×50 mm precolumn with a porosity of 40 Å, three HEMA 10 μm , 8×300 mm columns with porosities of 40, 10², 3000 Å, and DMF eluent containing 0.1 wt % LiBr at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using PSS polystyrene standards (374–10⁶ D).

The polymeric films were prepared using an ~16 wt % solution of the polymer in DMF on a BLE Delta 10 spin-coater (600 rpm, highest acceleration). The waveguide mode spectroscopy experiments were carried out using a home-built setup shown in Figure 1. The irradiation was carried out with an unfocused HBO 100 W mercury short arc lamp from Osram. A grating with a periodicity Λ of 1091.5 nm ion etched into the substrate¹³ before spincoating the polymeric waveguide was used to couple a HeNe laser beam ($\lambda = 632.8$ nm) in the s- (TE) and/or p-polarized (TM) direction from the air into the waveguide.

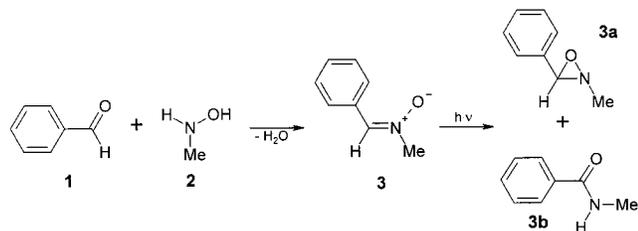
The waveguide mode spectrum was determined by scanning the angle of incidence of the incoming laser beam onto the grating while measuring the outcoupled power with a photo detector situated at the end of the waveguide.¹⁴ From the coupling angles and the known parameter of the grating and the substrate, the effective refractive indices of all modes N_{ij} were calculated according to eq 1¹⁵

$$N_{ij} = n_c \sin \alpha + m\lambda/\Lambda \quad (1)$$

where n_c is the refractive index of the cladding (here air with $n_c = 1$), λ is the wavelength of the coupled light, Λ is the grating period, and m is the diffraction order. If the optical constants of the substrate are known, the thickness and the refractive indices for both polarization directions can be calculated iteratively as long as at least two modes can be detected for each polarization direction. If there is a redundancy of modes, you can make an error calculation.

3. Results and Discussion

3.1. Synthesis and Irradiation. To study the influence of irradiation on the structure of *N*-aryl-substituted nitrons,⁵ a low molecular weight benzaldehyde-*N*-methylnitron (**3**) was prepared by condensation of benzaldehyde (**1**) and *N*-methylhydroxylamine (**2**).

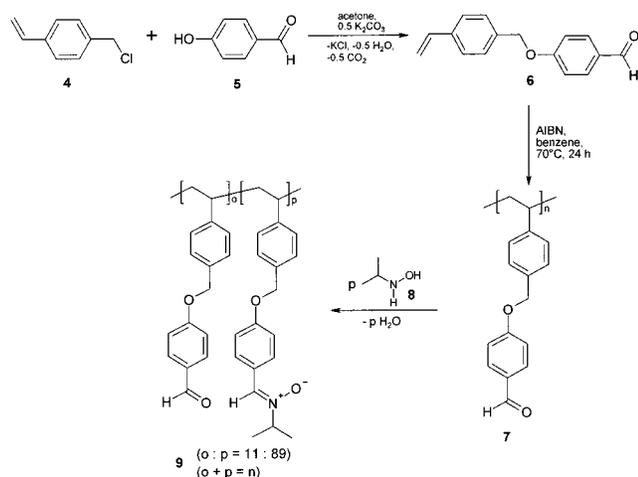


The photochemical cyclization of the nitron (**3**) was very fast. After 1 min of irradiation with a 700 W mercury medium-pressure lamp in a 5×10^{-4} M solution in ethanol, the nitron cyclized preferentially to the phenylmethyloxaziridine (**3a**) and only small amounts of the *N*-methylbenzamide (**3b**) were formed. However, further irradiation leads to decomposition of **3a** to **3b** (Table 1).

Table 1. Yield of Products **3a** and **3b** after Irradiation of the Benzaldehyde-*N*-methylnitron (**3**)

| irradiation time | 1 min | 2 min | 3 min |
|-------------------------------|-------|-------|-------|
| oxaziridine (3a) [%] | 85 | 55 | 40 |
| benzamide (3b) [%] | 15 | 45 | 60 |

The polyaldehydes should condense with *N*-alkylhydroxylamines to produce the desired polynitrons in good yields. For this purpose, 4-[(4-vinylbenzyl)oxy]benzaldehyde (**6**) was prepared from 4-vinylbenzyl chloride (**4**) and 4-hydroxybenzaldehyde (**5**), and then polymerized in benzene to produce poly{4-[(4-vinylbenzyl)oxy]benzaldehyde} (**7**).



The polyaldehyde (**7**) was then condensed with *N*-isopropylhydroxylamine (**8**) in solution to the corre-

sponding polymeric nitron (**9**) in > 90% yields. The resulting polymeric nitron still contained some residual benzaldehyde groups.

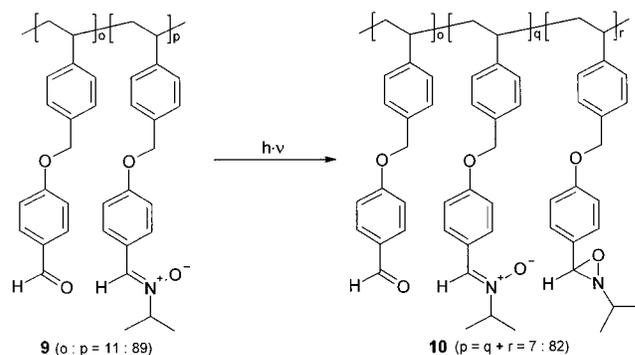
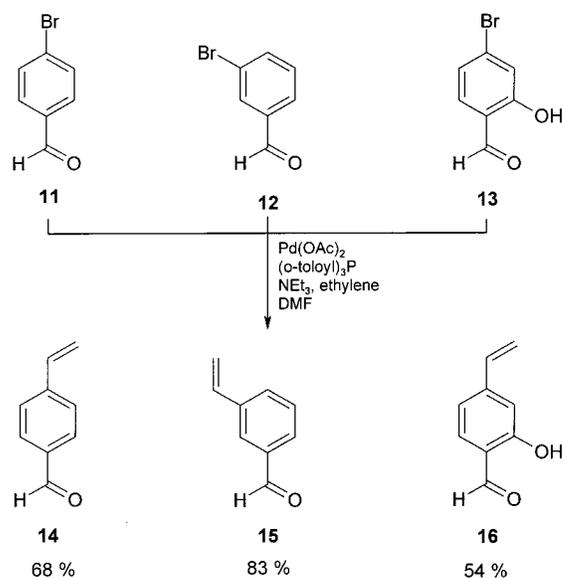
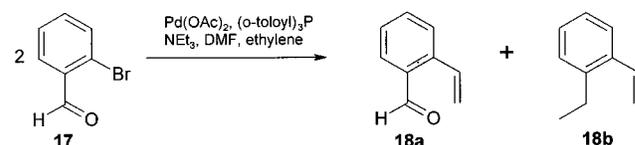


Figure 2 demonstrates that the cyclization reaction of the polymeric nitron **9** to the corresponding oxaziridine (**10**) (2×10^{-4} molar solution in CH_2Cl_2) is fast. After only about 30 s of irradiation, the ring formation was nearly complete. The ^1H NMR spectra indicate that only traces of the nitron were still present. Further irradiation leads to decomposition of the three-membered ring (see Scheme 1 and compound **3b**).



4-Vinylbenzaldehyde (**14**), 3-vinylbenzaldehyde (**15**), and 2-hydroxy-4-vinylbenzaldehyde (**16**) were synthesized via Heck reactions of 4-bromobenzaldehyde (**11**), 3-bromobenzaldehyde (**12**), and 2-hydroxy-4-bromobenzaldehyde (**13**). Small amounts of educt impurities (bromobenzaldehydes **11**, **12**, and **13**) did not disturb the polymerization and were easily separated from the polymeric aldehydes.



The Heck reaction of ethylene with 2-bromobenzaldehyde (**17**) was not successful. The main product was *o*-ethylstyrene rather than the desired vinylbenzalde-

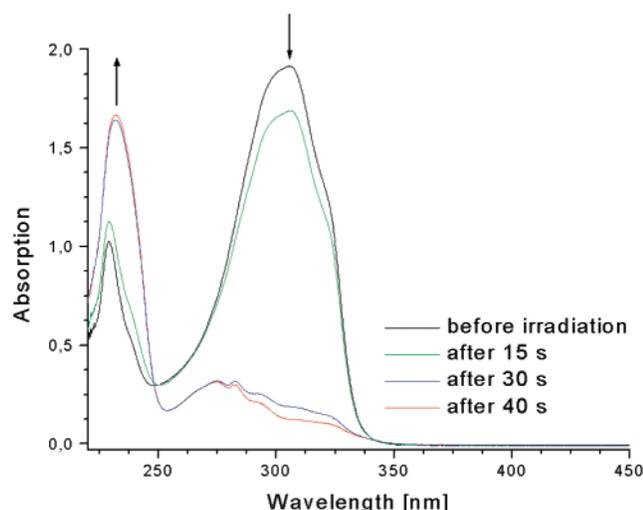
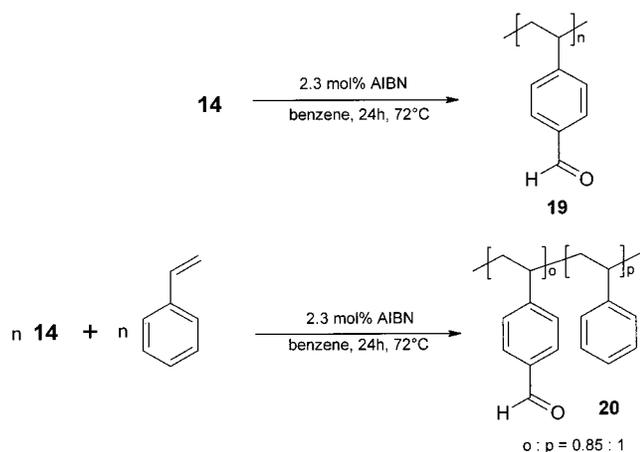


Figure 2. Change of UV absorption of polynitron **9** during irradiation.

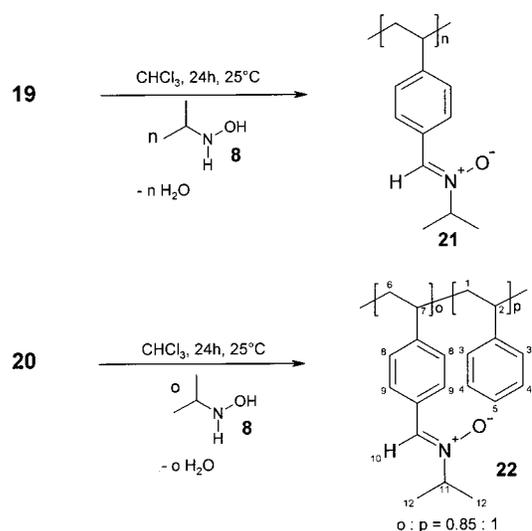
hyde **18a**. The vicinal aldehyde seems to interact with the Pd complex, which results in a decarbonylation and insertion of ethylene (**18b**). Because of the presence of the hydroxy group in **13**, only a low yield was achieved indicating a strong interaction with the Pd. Therefore, polymerizations with **18b** were not yet carried out.



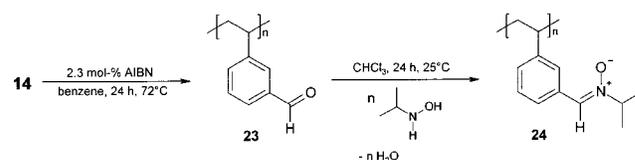
4-Vinylbenzaldehyde (**14**) was homo- and copolymerized with styrene in benzene at 70 °C for 24 h. The molecular weight (M_n) of **19** was only about 5500. This indicates that aldehydes transfer their carbonyl hydrogen. Only copolymerization of **20** with styrene produced polymers with molecular weights up to 15 000, which shows a lower transfer rate because of lower aldehyde concentration. For the preparation of polymer films the low M_n values are favorable, because the polymer is better processable.

As described above, the polymer analogous reaction of **19** and **20** with *N*-isopropylhydroxylamine (**8**) quantitatively produces to the corresponding polymeric nitrons **21** and **22**.

No residual aldehyde at 9.85 ppm could be detected by ^1H NMR or at 1704 cm^{-1} by IR spectroscopy of **20**. The aromatic signals ortho to the aldehyde function shifted from 7.53 to 7.97 ppm, and the former aldehyde proton appears at 7.72 ppm. The composition of copolymer **20** was calculated by ^1H NMR spectroscopy. The integrated signal of the aldehyde proton at 9.85 ppm



was compared with the total integral of the aromatic region minus four protons of the aldehyde component.



Analogously, 3-vinylbenzaldehyde (**14**) was polymerized to yield the polymeric aldehyde **23** and then condensed with *N*-isopropylhydroxylamine (**8**) to the polynitron (**24**). The conversion to the nitron was approximately 100%. No aldehyde functions of **24** could be detected by ^1H NMR and IR spectroscopy.

Figure 3 shows the degradation of the nitron band at 298 nm due to UV irradiation. After 45 s, the intramolecular cyclization to the oxaziridine ring was nearly complete. This corresponds to a cyclization rate of about 1 mmol in 5 min.

2-Hydroxy-4-vinylbenzaldehyde (**16**) was polymerized radically yielding polymer **25** with relatively low molecular weight ($M_n = 8400$), which is similar to that of poly(4-vinylbenzaldehyde) (**19**) and poly(3-vinylbenzaldehyde) (**23**). The conversion of **25** with the *N*-isopro-

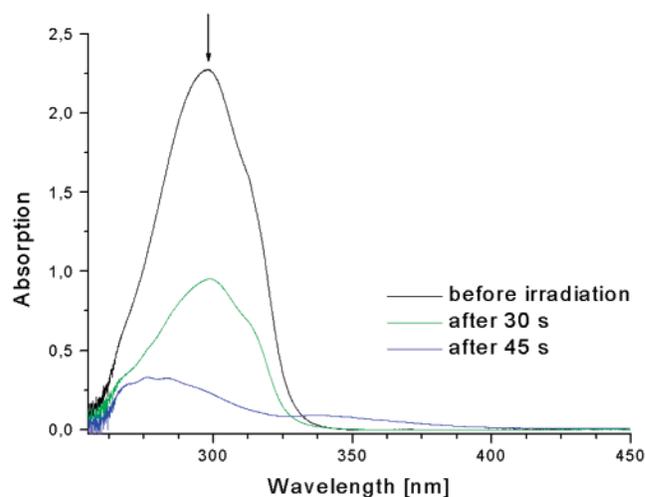
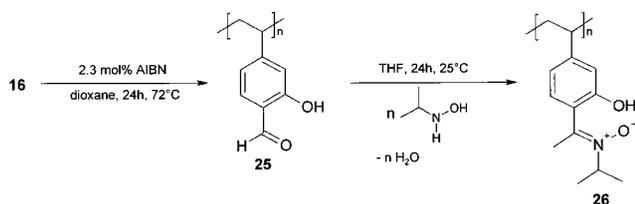
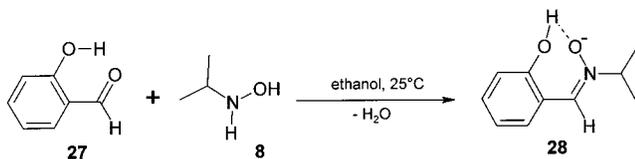


Figure 3. Change of UV absorption of polynitron **24** during irradiation.



pylhydroxylamine (**8**) was also nearly 100% as determined by IR and ^1H NMR spectroscopy.

Surprisingly, nitron **26** seems to be stable against UV light (Figure 4). Only the intensity of the UV absorption bands at 290 and 345 cm^{-1} are lowered in the same ratio. This indicates that the hydroxyphenyl-substituted polymeric nitron does not cyclize to the polyoxaziridine. The nitron is partially degraded. The ^1H NMR spectrum shows that the signal of nitron **26** is overlaid with several new sharp small signals not yet assigned.



To study the behavior of polymer **26** in detail, a low molecular model compound 2-hydroxybenzaldehyde-*N*-isopropylnitron (**28**) was prepared from 2-hydroxybenzaldehyde (**27**) and *N*-isopropylhydroxylamine (**8**). However, UV irradiation of a solution of **28** showed that only the two UV absorption bands decrease slightly which is consistent with the behavior of the corresponding polynitron **26** (Figure 4). In contrast, the nitron group of *p*-hydroxybenzaldehyde-*N*-methylnitron undergoes a nonretarded cyclization during UV irradiation.⁸ Therefore, the hydroxy function ortho to the nitron must be responsible for this photostability. The structure of **28** indicates that the *o*-OH group will form a H-bond with the N–O group. This ortho effect may also be responsible for the stability against UV irradiation in solution.

Hydrogen bridges between the hydroxy group and nitron oxygen were verified with semiempirical methods (PC Spartan Pro, Version 1.07, calculated on the PM3-level). Thus, the typical 1,3-dipolar structure of the nitron group is clearly disturbed, which evidently prohibits a photoinduced cyclization of **28**.

The ^1H NMR spectra (Figure 5) of the polynitron before (**22**) and after irradiation (**22a**) shows that about 80% of the nitron has cyclized to the corresponding oxaziridine. The intensity of the nitron signals is drastically reduced: The methine proton of the isopropyl group shifted from 4.2 to 2.3 ppm and the "azomethine" proton from 7.4 to 4.4 ppm. The degree of cyclization was calculated with these two signals. The aromatic protons (H-16) suffer a small shift to a higher field. The

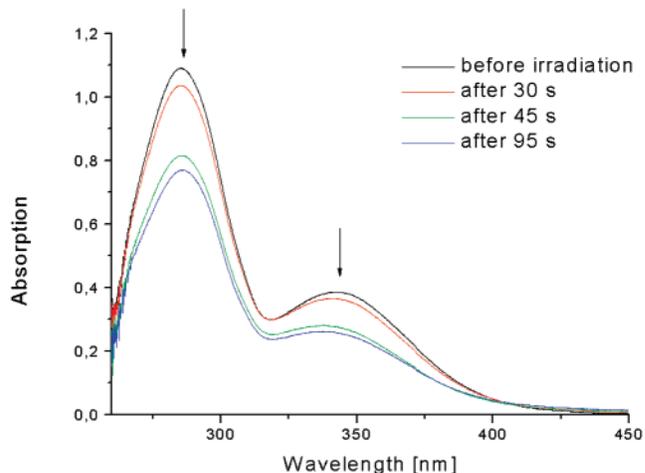


Figure 4. Change of UV absorption of polynitron **26** during irradiation.

spectra show that cyclization takes place without any side reaction. To avoid undesired decomposition, the irradiation time was limited; however, small amounts of the nitron are still present in polymer **22a**.

3.2. Ring Opening of Nitrons. According to the literature,¹⁶ the cyclization of nitrons to oxaziridines may be thermally reversible. To evaluate this predicted thermal ring opening of polymer bound oxaziridine functions, a KBr pellet of polymer **10** was heated to 100 °C for 2 h, 120 °C for 4 h, and 150 °C for 2 h. The IR spectra were recorded to show the possible ring opening after thermal treatment (Figure 6).

The N–O stretch vibration of nitrons appears in the region of about 1147 cm^{-1} . This band is degraded after irradiation because of oxaziridine formation. The IR spectrum of the oxaziridine **10** shows no bands in this region. After heating **10** for 8 h, a small signal appears at 1148 cm^{-1} , which strongly indicates that a few ring molecules were opened thermally. Additionally, two signals disappeared due to heating; the OH vibration at 3432 cm^{-1} belongs to the crystal water of the nitrons, which disappears above 100 °C. The aldehyde signal at 1691 cm^{-1} due to the presence of untransformed polyaldehyde components in the polymer disappeared, probably due to oxidation. There are no significant changes in the fingerprint region. Therefore, a significant thermal ring opening of the oxaziridine to the nitron does not seem to take place.

3.3. Waveguide Mode Spectroscopy. Due to the photoinduced intramolecular cyclization of the polar nitron groups to the less polar oxaziridine ring, the refractive index should change. Spin-coated films of **21** with a thickness of about 1.2 μm were prepared for waveguide mode spectroscopy using DMF as solvent. Figure 7 shows the coupling angles of three different

Table 2. Refractive Indices and Thicknesses of the Polymer Film of 21 before and after UV Irradiation

| | before irradiation polarized light | | after irradiation polarized light | |
|------------------|------------------------------------|-----------------|-----------------------------------|----------------|
| | TE | TM | TE | TM |
| refractive index | 1.6023 ± 0.0004 | 1.6067 ± 0.0008 | 1.5451 ± 0.002 | 1.5500 ± 0.002 |
| thickness (nm) | 1426 ± 7 | 1447 ± 14 | 1405 ± 28 | 1417 ± 47 |

Table 3. Refractive Indices and Thicknesses of the Polymer Film of 24 before and after UV Irradiation

| | before irradiation polarized light | | after irradiation polarized light | |
|------------------|------------------------------------|-----------------|-----------------------------------|-----------------|
| | TE | TM | TE | TM |
| refractive index | 1.6014 ± 0.0006 | 1.6064 ± 0.0006 | 1.5466 ± 0.0010 | 1.5507 ± 0.0011 |
| thickness (nm) | 1474 ± 11 | 1470 ± 10 | 1488 ± 17 | 1482 ± 19 |

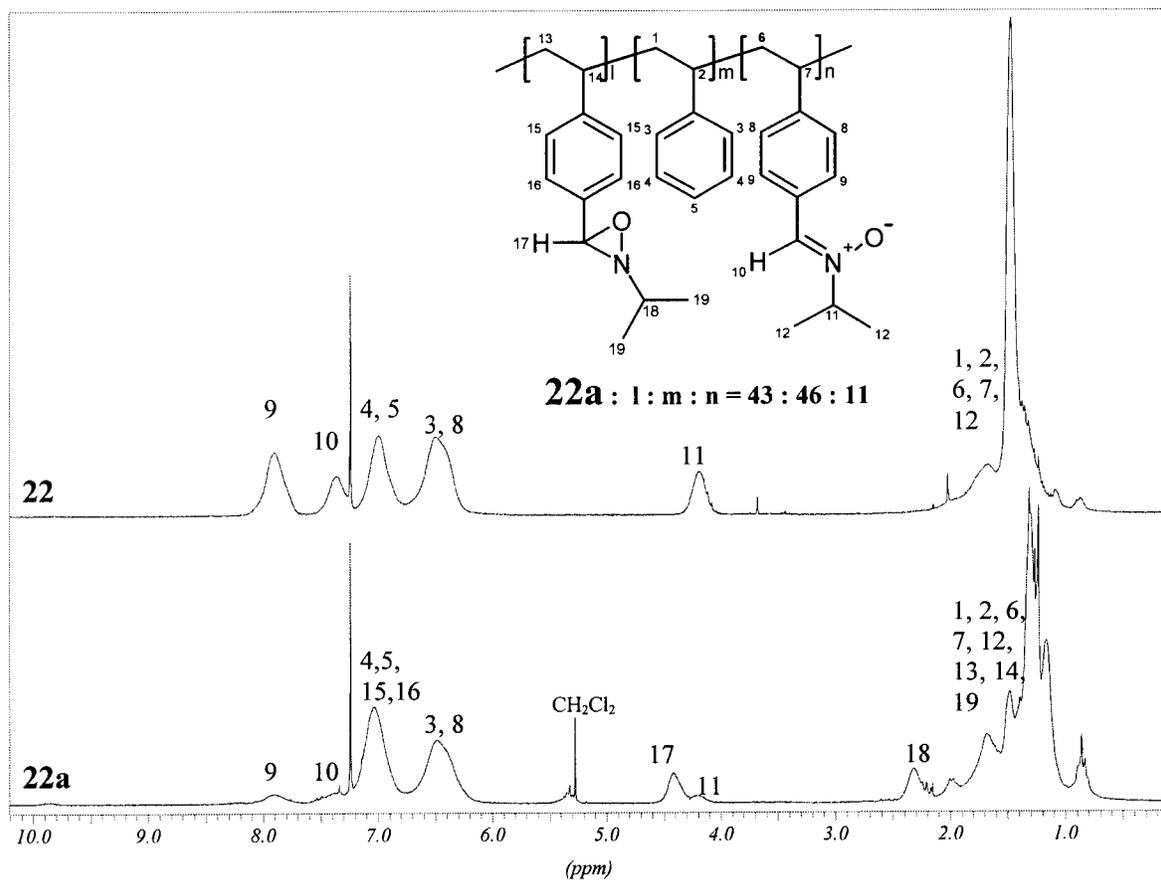


Figure 5. Comparison of the ^1H NMR spectra of polynitron **22** and the corresponding polyoxaziridine (**22a**).

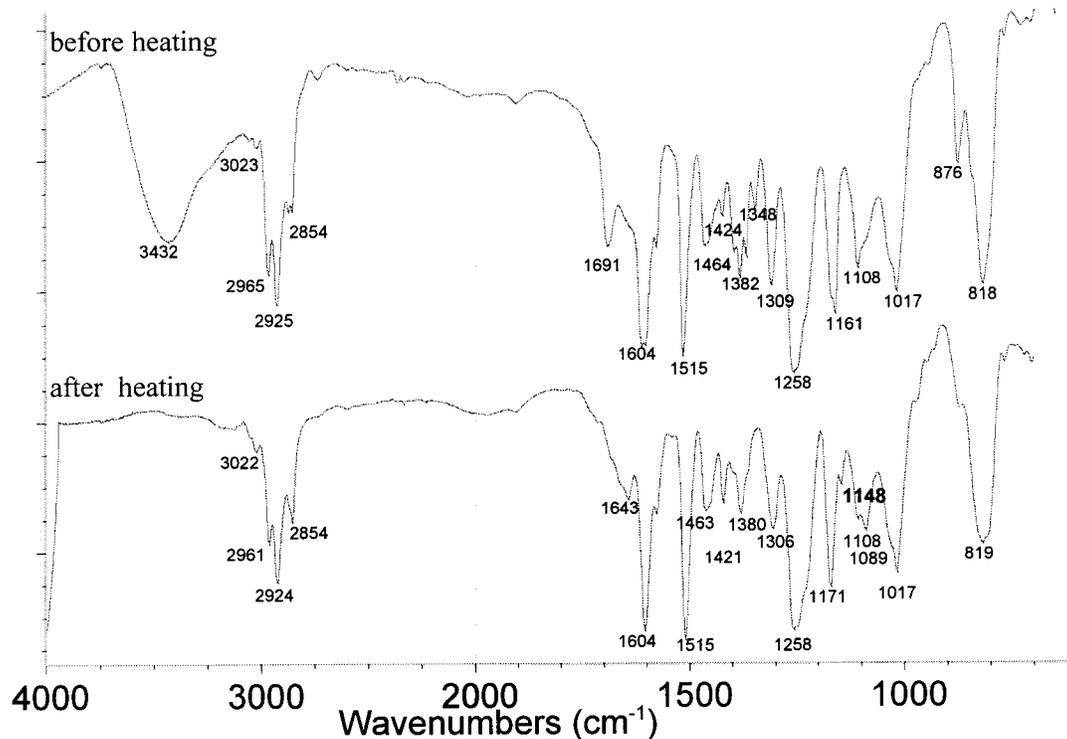


Figure 6. Changes in the IR spectra of polyoxaziridine **10** before and after heating for about 8 h.

TM (p-polarized) waveguide modes before and after irradiation.

The intensive mode at 25.15° results from the glass substrate, which does not shift during irradiation of the polymer film. The shift of the different coupling angles

up to 2.5° indicates that the refractive index of the polymer waveguide decreases after irradiation. An online observation of the TE_1 mode during irradiation shows the kinetic behavior of the bleaching effect (Figure 8).

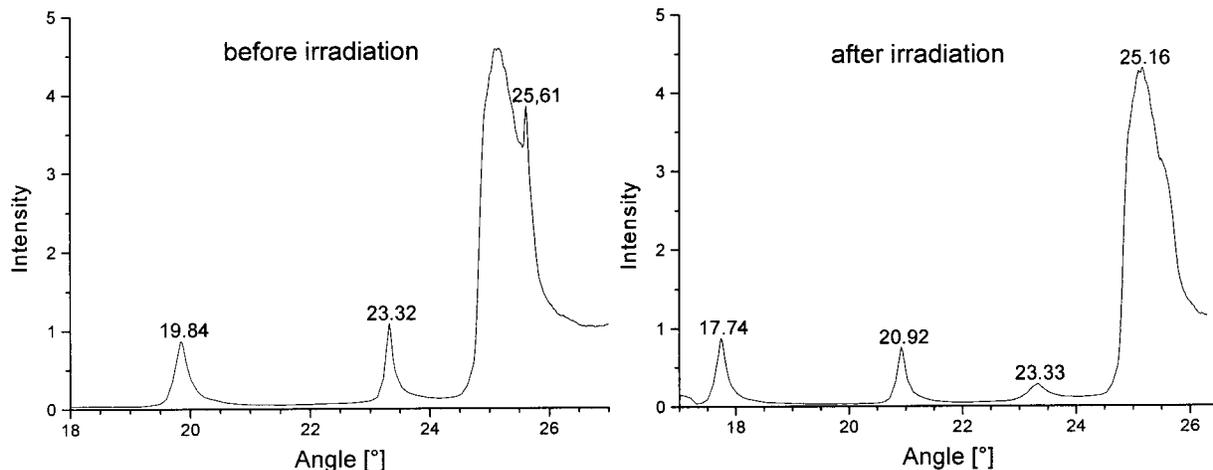


Figure 7. Waveguide mode spectra in p-polarization before and after irradiation of polymer **21**.

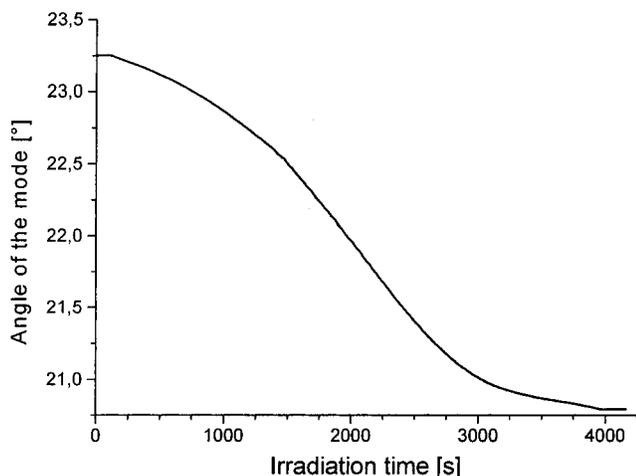


Figure 8. Changes of the coupling angle of the TM_1 waveguide mode during irradiation.

For further kinetic measurements, the irradiation should be carried out using a suitable laser instead of filtered light of an unfocused 100 W mercury arc lamp. However, the irradiation curve shows that after about 1 h the coupling angle has stabilized. This is much faster than in mesoionic systems.^{7,17} The exact values of the changes in the refractive index and of film thickness are shown in Table 2.

The refractive index decreases significantly due to irradiation. In contrast, the film thickness remains almost constant during isomerization, indicating that the resulting three-membered ring occupies nearly the same space as the nitron group. Between p- and s-polarized light, a significant difference of about 0.005 was observed. This may be attributed to the anisotropic structure of the waveguide resulting from the spin-coating process. Waveguide mode spectroscopy of the polymeric nitron **24** shows the same results and nearly the same values for the refractive indices and the thickness (Table 3) as the polymeric nitron **21** (Table 2).

4. Conclusion

In contrast to previous studies,⁷ the photochemically generated oxaziridines obtained from aryl-*N*-alkyl nitrons are relatively stable. Since the nitron acts as a radical inhibitor, polymeric nitrons were obtained from polyvinylaldehydes, which were condensed with *N*-isopropylhydroxylamine in almost quantitative yield.

If the nitron bears a hydroxy group in the ortho position, photochemical cyclization was not possible, because the typical 1,3-dipole is disturbed. The refractive index measured by waveguide mode spectroscopy decreases greatly, whereas the thickness remains almost constant. Waveguide mode spectroscopy is an excellent method for examining the photochemical behavior of the polymers bearing photosensitive nitron functions. These kinds of nitrons do not seem to be switchable, because a thermal ring opening of the oxaziridines to the nitrons could not be detected. This is a disadvantage for information storage, but the rapidness of the cyclization to the oxaziridine is an advantage.

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