1,3-Dipolar Cycloaddition in Polymer Synthesis. 1. Polyadducts with Flexible Spacers Derived from Bis(*N*-methylnitrone)s and Bis(*N*-phenylmaleimide)s

Lyudmyla Vretik and Helmut Ritter*

Institute of Organic Chemistry and Makromolecular Chemistry II, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, 40225 Düsseldorf, Germany

Received October 7, 2002; Revised Manuscript Received May 14, 2003

ABSTRACT: The thermal 1,3-dipolar polycycloaddition of *N,N′*-dimethyl-*p*-phenylenedinitrone (**3**) and 4,4′-hexanediyldioxydi(*N*-methyl-*p*-phenylenenitrone) (**10**) with *N,N′*-(1,4-phenylene)dimaleimide and 1,6-hexanediylbis(carbamic acid) bis(*N*-methyl-*p*-phenylenenitrone) ester (**12**) with 1,6-hexanediylbis(carbamic acid) bis[*N*-(*p*-phenylene)maleimide] ester (**16**) in DMF solution and nitrogen atmosphere lead to the formation of corresponding polyadducts **5**, **13** and **17**. The comparison of ^{1}H NMR, ^{13}C NMR and IR spectra of a model compound 2-methyl-3-(4′-hydroxyphenyl)isoxazolidine-4,5-dicarboxyphenylimide (**8**) with model polymer **5** verified that the main chain is bearing an isoxazolidine ring. The molecular weight was found to be in the region of 28900−3600 (M_w) and 6600−1500 g/mol (M_n) according to SEC measurements. It was not possible to determine glass transition temperatures (T_g) for **17** by DSC measurements; for **5** and **13**, T_g values were found at 67 and 52 °C, respectively. Decomposition temperatures (T_d) for polymer samples **5**, **13** and **17** were 260, 247, and 192 °C, respectively. Polymer **17** exhibits good ability for coating formation on a glass surface.

1. Introduction

Nitrones are well-known as 1,3-dipoles in thermal cycloaddition reactions and the chemistry of nitrone's dipolar cycloaddition was surely reviewed by Hamer and Macaluso[1] in 1964 and Black et al.[2] in 1975. The general scheme of 1,3-dipolar cycloaddition is shown in Scheme 1.

The synthetic utility of nitrone cycloaddition reactions in the most cases deals with construction of low molecular weight five-membered heterocyclic ring systems and their further rearrangements and different decomposition pathways as well. According to our knowledge in the field of polymer chemistry, only minor pieces of information are available about the application of nitrone cycloaddition to prepare linear polymers.[3]

Regarding our interest in investigating the photochemical and chemical behavior of polymers bearing nitrone functions as side groups,[4,5] we now focused for the first time on the synthesis of various high molecular weight polymers bearing isoxazolidine ring and flexible spacer groups in a main chain. Good film formation ability as well as quite high thermal stability was also desired. We took into account that cycloaddition reactions only occur readily with nitrones derived from aldehydes (aldonitrones);[2] a utilization of *N*-methyl nitrones instead of *N*-phenyl nitrones could reduce the steric hindrance during cycloaddition; derivatives of maleic or fumaric acids, e.g., N-substituted maleimides, give almost 100% yield of cycloadduct without any side homopolymer formation.[6,7]

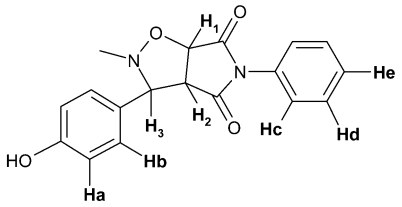
Thus, the presented paper deals with the synthesis and investigations of new polymers which were prepared via 1,3-dipolar polycycloaddition of *N,N′*-dimethyl-*p*-phenylenedinitrone (**3**) and 4,4′-hexanediyldioxydi(*N*-methyl-*p*-phenylenenitrone) (**10**) with *N,N′*-(1,4-phenylene)dimaleimide (**4**) and 1,6-hexanediylbis(carbamic acid) bis(*N*-methyl-*p*-phenylenenitrone) ester (**12**) with 1,6-hexanediylbis(carbamic acid) bis[*N*-(*p*-phenylene)-maleimide] ester (**16**).

* Corresponding author. Fax: +49 211 811 4788. E-mail: H.Ritter@uni-duesseldorf.de.

2. Experimental Section

2.1. Materials. All solvents of p.a. quality (Riedel de Haen, Fluka) were stored over molecular sieves of 3 or 4 Å. 4-Hydroxybenzaldehyde methylnitrone (**6**), 4,4′-hexanediyldioxydibenzaldehyde (**9**), 1,6-hexanediylbis(carbamic acid) bis(4′-formylphenyl) ester (**11**), and *N*-(4-hydroxyphenyl)maleimide (**14**) were prepared as described in the literature.[8−11] All other chemicals were purchased from Merck, Fluka, and Aldrich and used without further purification.

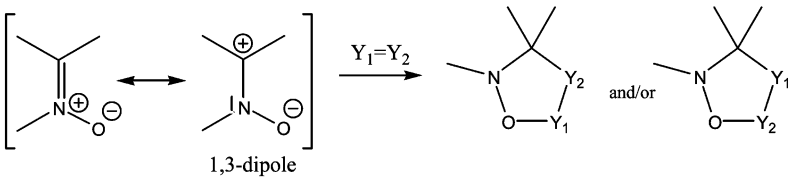
2.2. 2-Methyl-3-(4′-hydroxyphenyl)isoxazolidine-4,5-dicarboxyphenylimide (8). 4-Hydroxybenzaldehyde methylnitrone (**6**) (1.89 g, 0.0125 mol) was heated with *N*-phenylmaleimide (**7**) (2.16 g, 0.0125 mol) in 2 mL of DMF at 105 °C for 2.5 h. The reaction mixture was poured into water. Triturating of the resulted residue with hexane afforded the crude product, consisting of both possible isomers **8a** and **8b**; yield of a crude product: 2.25 g (56%). After three time recrystallization in methanol, 0.8 g of one pure diastereoisomer was obtained. Mp: 178 °C. R_f value (diethyl ether) = 0.47.



^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 9.45 (OH), 7.50 (t, J = 7.3; 7.9 Hz, 2H$_d$), 7.42 (t, J = 7.3, 1H$_e$), 7.20 (d, J = 7.3 Hz, 2H$_c$), 7.10 (d, J = 8.5 Hz, 2H$_a$), 6.74 (d, J = 8.5 Hz, 2H$_b$) [6.82 (d, J = 8.5 Hz, 0.8H′$_b$)], 5.13 (d, J = 6.6 Hz, 1H$_3$) [(d, J = 5.7 Hz, the number of protons H′$_3$ could not be calculated)], 3.89 (m, 1H$_1$, 1H$_2$), 2.53 (s, methyl). During this reaction two diastereoisomers in a ratio of about 55:45 were formed, which possibly differ in the positions of H$_3$ and H$_b$ protons. The

10.1021/ma0215565 CCC: $25.00
Published on Web 07/26/2003

Scheme 1. 1,3-Dipolar Cycloaddition Reaction of Nitrones



signals in ^{1}H NMR spectrum of the second diastereomer [H′] are set in brackets. C^{13} NMR and IR spectra were measured only for one pure isomer which was obtained in the higher yield.

^{13}C NMR (125 MHz, DMSO-d_6 [ppm]): δ = 175.4/173.0 (*C*=O); aromatic ring, 157.6 ((OH)*C*=CH), 132.4 (CH=*C*(CH=N)−CH), 128.8 ((CO−N)*C*=CH)), 115.7 ((OH)C=*C*H) and 129.4/129.3/127.0/124.7; 77.1 (O−*C*H−CO), 74.8 (N−*C*H), 54.4 (−*C*H$_3$), 42.7 (CH−*C*H−CO). IR: 3333 (OH), 3008, 2935, 2830 (aryl, alkyl), 1701 (C=O), 1615, 1595 (aryl), 1518, 1495 (aryl), 1205 (C−O), 1381, 1188 (C−N, N−O); further intensive signals, 1454, 1273, 1230, 1109, 819 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}N_2O_4$ (324.3): C, 66.66; H, 4.97; N, 8.64. Found: C, 66.84; H, 4.82; N, 8.63.

2.3. The synthetic root mentioned below was employed as a general procedure for dinitrone synthesis.

N,N′-Dimethyl-*p*-phenylenedinitrone (3). A solution of *N*-methylhydroxylamine hydrochloride (**2**) (8.35 g, 0.1 mol) in 5 mL of water was poured into a potassium hydroxide solution in 30 mL of ethanol. The matter formed in this solution (*N*-methylhydroxylamine) was slowly added to the suspension of terephthalaldehyde (**1**) (5.37 g, 0.04 mol) in 15 mL of ethanol. A new product partially precipitated. After overnight stirring the precipitated bis(nitrone) **3** was filtered off and washed with water. Yield of the crude product: 6.97 g (91%). The residue was purified by recrystallization in DMF, and 4.75 g (61%) of the colorless *N*,*N*′-dimethyl-*p*-phenylenedinitrone (**3**) was obtained.

Mp: 237−239 °C. R_f value (methanol) = 0.60.

^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 8.25 (s, 4H, Ar*H*), 7.88 (s, 2H, −C*H*=N), 3.08 (s, 6H, −C*H*$_3$). ^{13}C NMR (125 MHz, DMSO-d_6 [ppm]): δ = aromatic ring, 132.2 ((NO=CH)*C*=CH) and 127.9 ((NO=CH)C=*C*H); 133.8 (*C*H=N), 54.6 (−*C*H$_3$). IR: 3089, 3041, 2984 (aryl, alkyl), 1589 (C=N), 1165 (N−O), 936, 865 (1,4-disubstituted aryl); further intensive signals, 1416, 1310 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}N_2O_2$ (192.2): C, 62.49; H, 6.29; N, 14.57. Found: C, 62.53; H, 5.98; N, 14.55.

4,4′-hexanediyldioxydi(*N*-methyl-*p*-phenylenenitrone) (10).[16] Yield of the crude product: 93%. Yield after recrystallization in DMF: 77%. Mp: 173 °C. R_f value (methanol) = 0.52.

^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 8.97 (d, 4H, J = 8.8 Hz, Ar*H*), 8.20 (d, 4H, J = 8.8 Hz, Ar*H*), 7.73 (s, 2H, −C*H*=N), 4.02 (t, 4H, −OCH$_2$), 3.73 (s, 6H, −C*H*$_3$), 1.75 (m, 4H, −OCH$_2$C*H*$_2$), 1.49 (m, 4H, −OCH$_2$CH$_2$C*H*$_2$). ^{13}C NMR (125 MHz, DMSO-d_6 [ppm]): δ = aromatic ring, 159.9 ((−CH$_2$−O)-*C*=CH), 130.0 ((NO=CH)*C*=CH), 124.3 ((−CH$_2$−O)C=CH-*C*H), 114.5 ((NO=CH)C=CH−*C*H); 133.7 (−*C*H=N), 67.8 (−OCH$_2$), 53.9 (−*C*H$_3$), 28.9 (−OCH$_2$*C*H$_2$), 25.6 (−OCH$_2$-CH$_2$*C*H$_2$). IR: 2944, 2869 (aryl, alkyl), 1600 (C=N), 1504 (aryl), 1251 (C−O), 1157 (N−O), 944, 846 (1,4-disubstituted aryl); further intensive signals, 1472, 1393, 1017 cm^{-1}.

Anal. Calcd for $C_{22}H_{28}N_2O_4$ (384.5): C, 68.73; H, 7.34; N, 7.29. Found: C, 68.84; H, 7.48; N, 7.09.

1,6-Hexanediylbis(carbamic acid) Bis(*N*-methyl-*p*-phenylenenitrone) Ester (12).[17] Yield of the crude product: 87%. Yield after recrystallization in DMF: 50%. Mp: 167 °C (with decomposition). R_f value (methanol) = 0.72.

^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 8.25 (d, 4H, J = 8.8 Hz, Ar*H*), 7.84 (t, 2H, NH), 7.82 (s, 2H, −C*H*=N), 7.16 (d, 4H, J = 8.8 Hz, Ar*H*), 3.78 (s, 6H, −C*H*$_3$), 3.07 (t, 4H, −CONHC*H*$_2$), 1.48 (m, 4H, −CONHCH$_2$C*H*$_2$), 1.33 (m, 4H, −CONHCH$_2$CH$_2$C*H*$_2$). ^{13}C NMR (125 MHz, DMSO-d_6 [ppm]): δ = 154.3 (C=O); aromatic ring, 152.1 ((−CO−O−)*C*=CH), 129.3 ((NO=CH)*C*=CH), 128.2 ((NO=CH)C=*C*H−), 121.9 ((−CO−O−)C=*C*H−); 133.4 (−*C*H=N), 54.3 (-*C*H$_3$), 40.8 (−NH*C*H$_2$), 29.5 (−NHCH$_2$*C*H$_2$), 26.3 (−NHCH$_2$CH$_2$*C*H$_2$). IR: 3201 (NH), 3008, 2935, 2866 (alkyl), 1717 (C=O), 1545 (C=N), 1500 (aryl), 1205 (C−O), 1158 (N−O), 941, 870 (1,4-disubstituted aryl); further intensive signals, 1665, 1417, 1264 cm^{-1}.

Anal. Calcd for $C_{24}H_{30}N_4O_6$ (470.5): C, 61.26; H, 6.43; N, 11.91. Found: C, 61.36; H, 6.49; N, 12.06.

2.4. 1,6-Hexanediylbis(carbamic acid) Bis[*N*-(*p*-phenylene)maleimide] Ester (16).[18] *N*-(4-Hydroxyphenyl)maleimide (**14**) (5.68 g, 0.03 mol) was dissolved in 50 mL of dry toluene at 90 °C, and a catalytic amount of triethylamine was added. Then 2.5 mL (0.016 mol) of hexamethylene diisocyanate (**15**) was added. After 13 h of refluxing, the precipitated bis(nitrone) **16** was filtered off from the hot reaction mixture and washed with hot toluene. Yield of the crude product: 6.5 g (80%). After recrystallization in dioxane, 5.82 g (67%) of the colorless **16** was obtained. Mp: 187 °C. R_f value (diethyl ether) = 0.56. ^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 7.83 (t, 2H, N*H*), 7.33 (d, 4H, J = 8.8 Hz, Ar*H*), 7.22 (d, 4H, J = 8.8 Hz, Ar*H*), 7.19 (s, 4H, CO−C*H*=C*H*-CO), 3.09 (t, 4H, −CONHC*H*$_2$), 1.50 (m, 4H, −CONHCH$_2$C*H*$_2$), 1.35 (m, 4H, −CONHCH$_2$-CH$_2$C*H*$_2$). ^{13}C NMR (125 MHz, DMSO-d_6 [ppm]): δ = 170.3 (=CH-*C*=O), 154.5 (−NH-*C*OO); aromatic ring, 150.7 ((−CO−O)*C*=CH), 128.5 ((NO=CH)*C*=CH−), 128.2 ((NO=CH)C=*C*H−), 122.6 ((−CO−O−)C=*C*H−); 135.1 (CO−*C*H=*C*H−CO), 40.8 (−NH*C*H$_2$), 29.5 (−NHCH$_2$*C*H$_2$), 26.3 (−NHCH$_2$CH$_2$*C*H$_2$). IR: 3374 (N−H), 2930, 2861 (aryl, alkyl), 1770 (C=O, urethane), 1710 (C=O, imide), 1504 (aryl), 1214 (C−O), 941, 845 (1,4-disubstituted aryl); further intensive signals, 1537, 1405, 1201, 687 cm^{-1}.

Anal Calcd for $C_{28}H_{26}N_4O_8$ (546.54): C, 61.53; H, 4.80; N, 10.25. Found: C, 61.75; H, 4.81; N, 9.99.

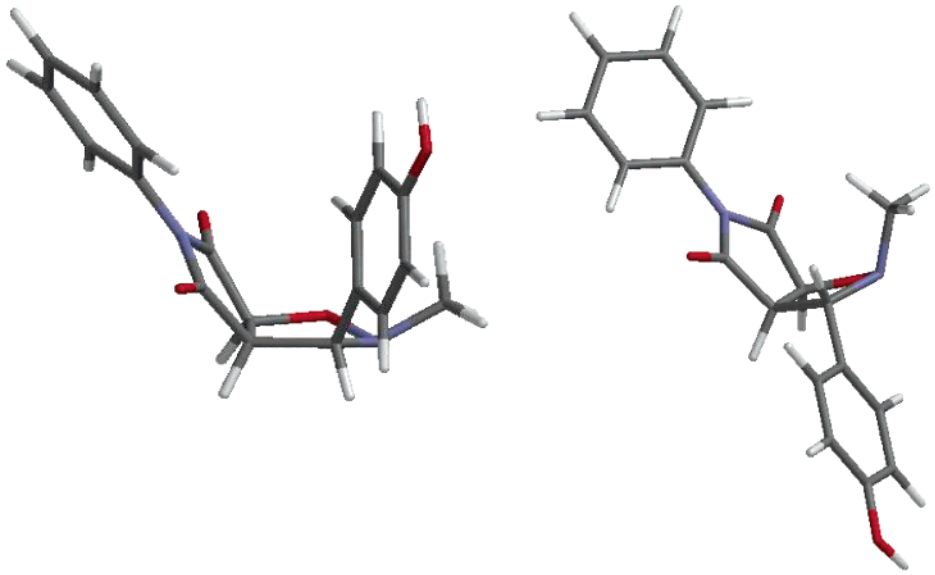
2.5. 1,3-Dipolar Polycycloaddition Procedure for Polymers 5, 13, and 17. All polycycloaddition experiments were carried out in DMF solutions under nitrogen atmosphere during 43 h with the same procedure given below:

Polymer Adduct 5 of 1,3-Dipolar Polycycloaddition of *N*,*N*′-Dimethyl-*p*-phenylenedinitrone (3) with *N*,*N*′-(1,4-Phenylene)dimaleimide (4). A suspension of 0.96 g (5 mmol) of *N*,*N*′-dimethyl-*p*-phenylenedinitrone (**3**) and 1.34 g (5 mmol) of *N*,*N*′-(1,4-phenylene)dimaleimide (**4**) in 6 mL of DMF was heated at 105−110 °C until a slightly yellow solution was formed. The obtained solution was flashed with N_2 during 40 min, cooled to 75 °C, and stirred for 43 h. Cooling to the ambient temperature interrupted the reaction, and the solution was dropped into 100 mL of water. The obtained polymer adduct **5** was filtered off, and after reprecipitation from DMF into ethanol, the polymer was dried in a vacuum at ambient temperature. Yield: 2.25 g (98%).

SEC (RI): M_n = 4300, M_w = 16 700, PD = 3.9. SEC (UV): M_n = 3300, M_w = 15 500, PD = 4.7. DSC: T_g = 67 °C. ^{1}H NMR (500 MHz, DMSO-d_6 [ppm]): δ = 7.34 (b, 8H, Ar*H*), 5.19 (b, 1H, C*H*−N), 4.04 (b, 2H, CO−C*H*−C*H*−CO). IR: 1715 (C=O imide), 1513 (aryl), 1367 (C−N), 1177 (N−O), 835 (aryl) cm^{-1}.

Polymer Adduct 13 of 1,3-Dipolar Polycycloaddition of 4,4′-Hexanediyldioxydi(*N*-methyl-*p*-phenylenenitrone) (10) with *N*,*N*′-(1,4-Phenylene)dimaleimide (4). Yield: 82%.

SEC (RI): M_n = 6600, M_w = 28 900, PD = 4.4. SEC (UV): M_n = 5600, M_w = 25 500, PD = 4.6. DSC: T_g = 52 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.34/7.20/6.92 (b, 12H, Ar*H*), 5.15 (b, 2H, C*H*-N), 3.94 (b, 4H, CO−C*H*-C*H*-CO and 2H −OC*H*$_2$)), 1.73 (b, 4H, −OCH$_2$C*H*$_2$), 1.48 (b, 4H, −OCH$_2$CH$_2$C*H*$_2$). IR:



8a **8b**

Figure 1. Stereoisomers of model compound **8** (calculated with semiempirical method AM1*).

2933, 2861 (aryl, alkyl), 1717 (C═O imide), 1511 (aryl), 1365 (C−N), 1244 (C−O−C), 1173 (N−O), 823 (aryl); further intensive signals, 1610,1105 cm^{-1}.

Polymer Adduct 17 of 1,3-Dipolar Polycycloaddition 1,6-Hexanediylbis(carbamic acid) Bis(*N*-methyl-*p*-phenylenenitrone) Ester (12) with 1,6-Hexanediylbis(carbamic acid) Bis[*N*-(*p*-phenylene)maleimide] Ester (16). Yield: 93%.

SEC (RI): $M_n = 1500$, $M_w = 3600$, PD = 2.5. SEC (UV): $M_n = 1200$, $M_w = 2700$, PD = 2.3. DSC: no transition between −10 and +110 °C observed. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.30/7.18 (b, 16H, Ar*H*), 5.13 (b, 2H, C*H*−N), 4.01 (b, 4H, CO−C*H*-C*H*-CO), 3.07 (b, 8H, −CONHCH_2)), 1.48 (b, 8H, −CONHCH$_2$CH_2), 1.33 (b, 8H, −CONHCH$_2$CH$_2$CH_2). IR: 3377 (NH), 2931, 2857 (aryl, alkyl), 1709 (C═O imide), 1499 (aryl), 1386 (C−N), 1202 (C−O−C), 1165 (N−O), 1100 cm^{-1}.

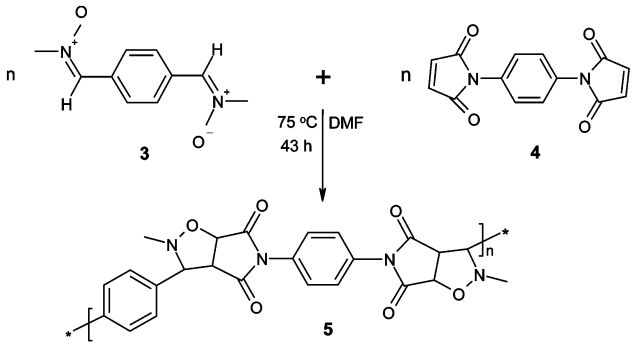
2.6. Measurements. Thin-layer chromatography was performed with Merck Kieselgel plates 60F254. NMR spectra were recorded with a Bruker AM500 FT-NMR-spectrometer (500 MHz) or on a Bruker AC200 FT-NMR-spectrometer (200 MHz) with DMSO-d_6 as internal standard. IR spectra were run on a Nicolet 5SXB FTIR-spectrophotometer. Elemental analyses were performed with a Perkin-Elmer 2400 elemental analyzer, and melting points were measured with a Büchi melting point determinator 510. SEC measurements were performed using a PSS apparatus with a Shodex refractive index (RI) detector and a TSP UV2000 UV−vis detector at 75 °C under the following conditions: PSS−SDV 5 μm, 8 × 50 mm column, 3 PSS−SDV 5 μm, 8 × 300 mm 10^2, 10^3, 10^4 Å columns, and DMF eluent containing LiBr at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using PSS polystyrene standards (374−10^6 D). Differential scanning calorimetry was carried out with a Perkin-Elmer DSC 7. The second heating data are presented. The molecular modeling calculations (Figure 1) were done by PC Spartan Pro 1.07, with the semiempirical method AM1 being used for geometry optimization.

3. Results and Discussion

1,3-Dipolar polycycloaddition of *N*,*N*′-dimethyl-*p*-phenylenedinitrone (**3**) with *N*,*N*′-(1,4-phenylene)dimaleimide (**4**) was utilized as a model reaction to estimate the possibility of a real polymer chain formation by such polyaddition reaction. The condensation of bis(aldehydes) with methylhydroxylamine was selected as the simplest general method for bis(nitrone) preparation.

The bis(nitrone) **3** was synthesized via condensation of terephthalaldehyde (**1**) with *N*-methylhydroxylamine hydrochloride (**2**) in ethanol solution at ambient temperature.

The polycycloaddition of dinitrone **3** with *N*,*N*′-(1,4-phenylene)dimaleimide (**4**) was performed in DMF solution in an inert atmosphere at 75 °C. In accordance to the literature,[12−14] such a 1,3-dipolar cycloaddition reaction of maleic acid derivatives with common nitrones usually gives corresponding isoxazolidine adducts ($Y_1 = Y_2 =$ C in Scheme 1) with high yield (up to 100%), but in most cases, this reaction is not fast. It was the reason polyadduct **5** should be isolated no earlier than after 40 h.



To prove that main chain of polymer **5** is bearing an isoxazolidine ring, a low molecular model compound, 2-methyl-3-(4′-hydroxyphenyl)isoxazolidine-4,5-dicarboxyphenylimide (**8**), was prepared by 1,3-dipolar cycloaddition reaction of 4-hydroxybenzaldehyde methylnitrone (**6**) with *N*-phenylmaleimide (**7**).

Two stereoisomers **8a** and **8b** could be expected to be formed during the reaction.[8,12,13] Both isomers were found in a ratio of about 55:45 (the ratio was calculated from the ^{1}H NMR spectrum of the reaction mixture before purification).

By repeated recrystallization from methanol a colorless product with mp = 178 °C was isolated in a pure state. The ^{1}H NMR spectrum of this product is given in

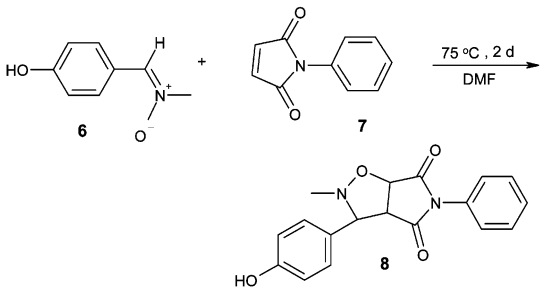


Figure 2. However, to which diastereoisomer (**8a** or **8b**) the spectrum corresponds could not be answered yet.

Although dihedral angles of **8a** and **8b** are appreciably different (about 0 and 120°), the real coupling constants $^3J_{H_2H_3}$ are too similar (5.7 and 6.6 Hz) and theoretical predictions were unsuccessful (ACD NMR simulations). Only X-ray investigation of single crystals for individually isolated compounds **8a** and **8b** would be the most correct method to distinguish these isomers. However, it should be pointed that during the synthesis of compound **8**, the reaction conditions (a solvent and a temperature) have simulated the synthetic conditions for polymer **5**, which means that polymer chain also contains both isomeric isoxazolidine rings in an almost equal ratio.

The comparison of this spectrum with ^{1}H NMR spectrum of polymer **5** (Figure 3) confirmed that the polymer main chain is bearing definitely repeating isoxazolidine structures. The single proton of the former nitrone group (H_3) appears after cycloaddition as doublet at 5.13 ppm in model compound (**8**) spectrum. Two former maleic protons (H_1 and H_2) can be assigned as multiplet at 3.89 ppm. If five-membered heterocycles have formed, the same signals must also be present in the spectra of the polymer **5**. In the ^{1}H NMR spectra of **5** the corresponding broad signals at 5.19 and 4.04 ppm show that polymer contains indeed five-membered isoxazolidine structure. However, the calculated integrals for these protons in polyadduct **5** did not give the exact ratio 1:2 as in the case of model compound **8** and additionally some side signals (e.g., 2.08, 9.99 ppm) appeared in the ^{1}H NMR spectrum of **5**. The pointed facts can be explained by side reactions during 1,3-dipolar polycycloaddition that might lead also to a reduction of molecular weight of the polymer.

Nitrones can be decomposed to aldehydes and hydroxylamines or rearranged to give O-alkylated oximes or acid amides in the presence of strong acids or bases.[15] In conditions of 1,3-dipolar cycloaddition (long time heating in DMF solution) the formation of an acid amide seems to be real and slight signals in ^{1}H NMR spectrum of **5** at 2.08 and 9.99 ppm might belong to acetamide function (CH_3− and NH−, respectively).

In accordance with the literature,[4−6,8] the ^{13}C NMR spectrum of **5** showed sharp peaks for the isoxazolidine function at 77.3 (carbon of the former nitrone function), 74.5 and 42.8 ppm (two former maleic carbons) which have almost the same position as in the model compound **8** (77.1, 74.8, and 42.7 ppm, respectively).

No residual N−O stretch vibration at 1165 cm^{-1} as well as C═N vibration of nitrone function at 1589 cm^{-1} could be detected in IR spectrum of resulting polymer product **5**. Instead, a strong broad signal of N−O vibration at 1178 cm^{-1} of isoxazolidine function appeared. Unexpected slight signal at 1656 cm^{-1} can be assigned with side amide structures. It must be noted, that due to broad signals in IR and ^{1}H NMR spectra of polymer **5** it is not possible to make a definitive conclusion about the absence of residual nitrone and maleimide functions in the polymer sample.

To reduce steric hindrance in the main chain, some bis(nitrone)s with flexible aliphatic spacer between two *N*-methylnitrone functions were utilized for next polycycloaddition. For this purpose, two bis(nitrone)s, 4,4′-hexanediyldioxydi(*N*-methyl-*p*-phenylenenitrone) (**10**) and 1,6-hexanediylbis(carbamic acid) bis(*N*-methyl-*p*-phenylenenitrone) ester (**12**), were prepared via con-

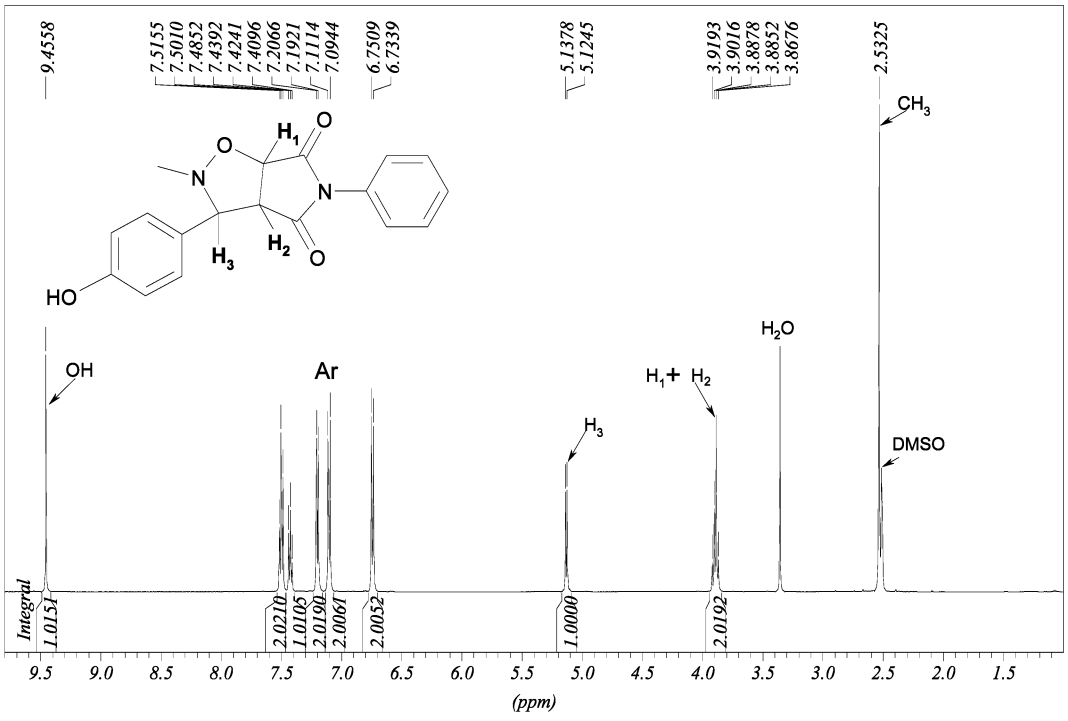


Figure 2. ^{1}H NMR spectrum of the model compound **8**.

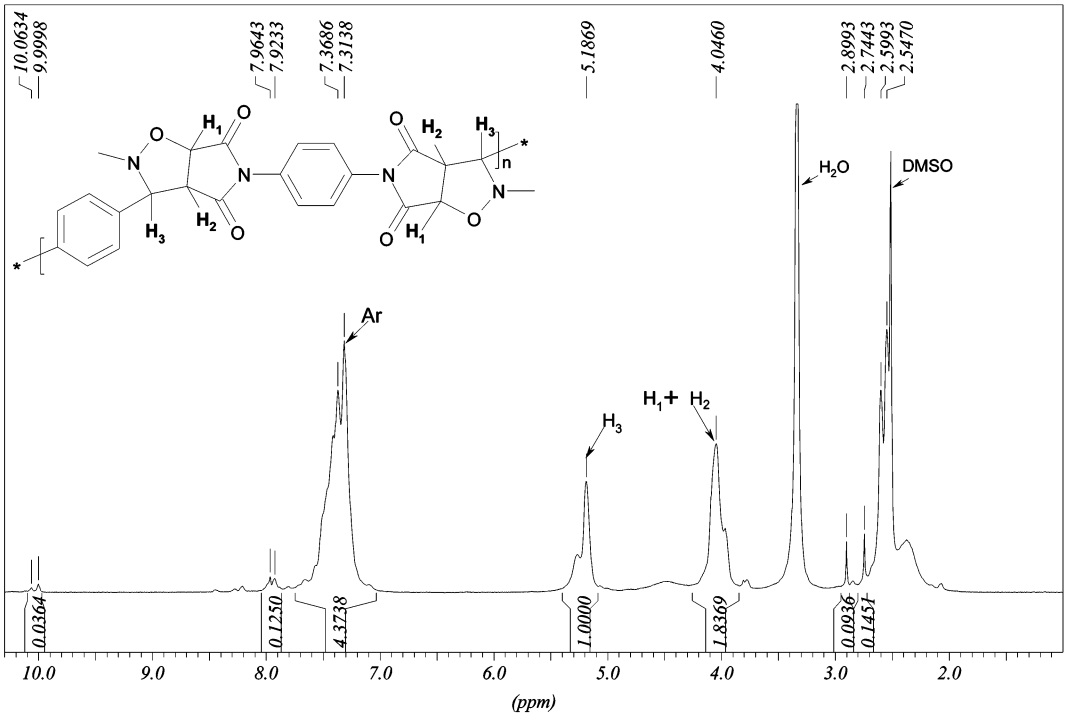
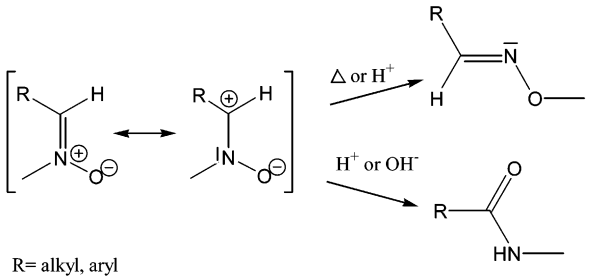
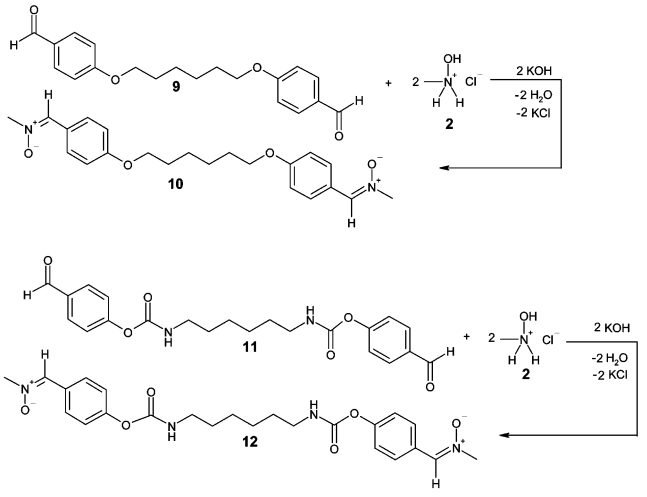


Figure 3. ^{1}H NMR spectrum of polymer **5**.

Scheme 2. Possible Rearrangements of Nitrones

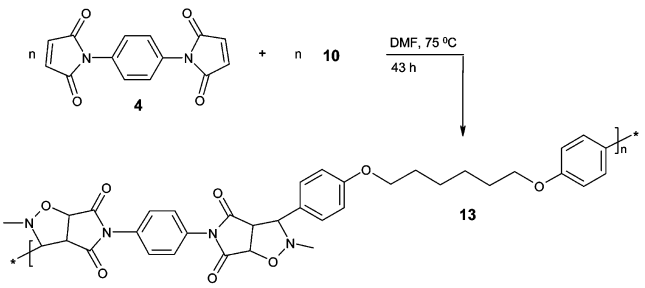


densation of corresponding 4,4′-hexanediyldioxydibenzaldehyde (**9**) and 1,6-hexanediylbis(carbamic acid) bis(4′-formylphenyl) ester (**11**) with *N*-methylhydroxylamine hydrochloride (**2**).



1,3-Dipolar polycycloaddition of dinitrone **10** with dimaleimide **4** was performed using the same method as for dinitrone **3**.

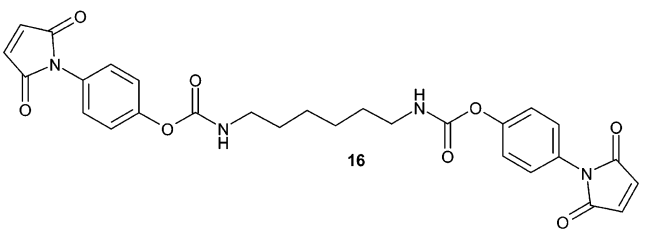
The structure of the new polymer product **13** was determined by H^1 NMR and IR spectroscopy. Broad



signals in the ^{1}H NMR spectrum at 5.15 and 3.94 ppm (compare with spectrum of the model compound **8**, Figure 2) and strong N−O vibration at 1173 cm^{-1} in IR spectrum proved that the obtained polymer contains isoxazolidine structure.

Although the molecular weight (M_w = 28 900, M_n = 6600, SEC measurements using DMF/LiBr as eluent) of polymer product **13** was relatively high for film preparation, up to now our attempts to produce film or coating on a glass surface also were unsuccessful as well as in the case of polymer **5**.

Finally, an additional aliphatic spacer was incorporated between two *N*-phenylmaleimide functions. 1,6-Hexanediylbis(carbamic acid) bis[*N*-(*p*-phenylene)maleimide] ester (**16**) was used for the polycycloaddition reaction with bis(nitrone) **12**.



Compound **16** was synthesized via condensation of *N*-(4-hydroxyphenyl)maleimide (**14**) with hexamethylene diisocyanate (**15**).

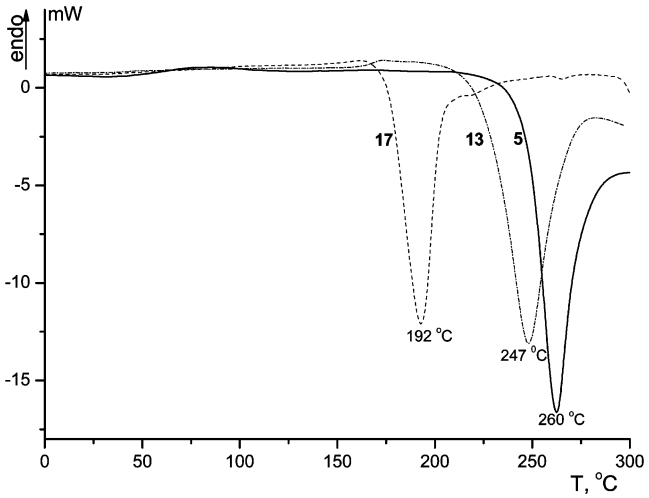
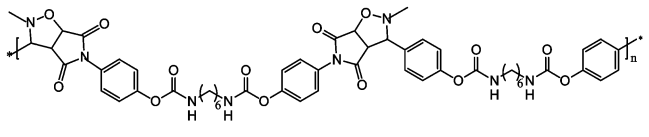


Figure 4. DSC thermograms for polymer samples **5**, **13**, and **17**. Heating rate: 5 °C/min.

Further 1,3-dipolar polycycloaddition of **16** with bis(nitrone) **12** was performed by the similar method as for bis(nitrone)s **3** and **10** but in a DMF solution containing 5 wt % of $CaCl_2$ with a view to reduce intermolecular hydrogen-bond interactions in order to increase solubility of carbamic acid esters **12** and **16**.



17

Regardless of the fact that molecular weight of the obtained polymer **17** was relatively low ($M_w = 3600$, $M_n = 1500$, SEC measurements using DMF/LiBr as eluent), this polymer showed good capability for coating formation on a glass surface. Completely mechanically stable transparent coatings were obtained even directly from the reaction mixture.

The molecular weight distributions for polymers **5**, **13**, and **17** are broad and molecular weights are low. It could be explained by many side reactions which take place during long time heating (43 h) at the relatively high temperature. The additional experiments focused on the magnification of the molecular weight and minimization of molecular weight distribution are still required.

Thermal properties of polymers **5**, **13**, and **17** were investigated by DSC measurements. It was not possible to determine correct glass transition temperature (T_g) for polymer **17**; for polymer samples **5** and **13** T_g values were found at 67 and 52 °C, respectively. DSC thermograms shown in Figure 4 indicate that all samples exhibit sharp exothermic peaks in the region 190−260 °C. Drastic changes of sample color from white to dark red or black at 192, 247, and 260 °C, respectively, for polymer samples **17**, **13**, and **5** and additional IR measurements convinced us that such exothermic peaks could be attributed to oxidative decomposition process. In the IR spectrum of polymer sample **5**, due to decomposition processes in a main chain the signal of carbonyl group was shifted from 1717 to 1704 cm^{-1}, and new very broad overlapping signals at 1649 and 1603 cm^{-1} were observed. The thermal stability of these polymers does not seem to be strongly dependent on the isoxazolidine ring presence in main chain but is under determinative control of the spacer. Decomposition temperature (T_d) for polymer samples **13** and **17** with hexamethylene spacer was shifted to lower temperatures; the most unstable sample was polymer **17** with urethane bonds in the main chain.

4. Conclusions

1,3-Dipolaric polycycloaddition reactions of bis(nitrone)s **3**, **10**, and **12** with bis(maleimide)s **4** and **16** yield polymer products with M_w values in the region 29000-4000 g/mol and M_n values in the region 6600−1500 g/mol. The presence of isoxazolidine ring in the main chain was proved by IR, ^1H NMR, and ^{13}C NMR spectroscopy. The successful preparation of polymers by such polycycloaddition demands long reaction time and inert atmosphere. However, pure 1,3-dipolar polycycloaddition reaction does not occur, which leads to relatively low molecular weights and high polydispersity of polymer products (PD = 2.5−4.4). DSC experiments conducted confirm that the thermal stability of these polymers is high enough (192−260 °C).

Acknowledgment. We gratefully acknowledge the Deutsche Forschungsgemeinschaft for support of this work.

References and Notes

(1) Hamer, J.; Macaluso, A. *Chem. Rev.* **1964**, *64*, 473−495.

(2) Black D. St. C.; Croizier R. F.; Davis, V. C. *Synthesis* **1975**, 205−221 and references therein.

(3) Iwakura, Y.; Akiyama, M.; Shiraishi, Sh. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 513−514.

(4) Heinenberg, M.; Ritter, H. *Macromol. Chem. Phys.* **1999**, *200*, 1792−1805.

(5) Heinenberg, M.; Menges, B.; Mittler, S.; Ritter, H. *Macromolecules* **2002**, *35*, 3448−3455.

(6) Huisgen, R.; Hauck, H.; Gashey, R.; Seidel, H. *Chem. Ber.* **1969**, *102*, 736−745.

(7) Iwakura, Y.; Uno K.; Hong, S.; Hongu, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 192−195.

(8) Heinenberg, M.; Reihmann, M. H.; Ritter, H. *Des. Monomers Polym.* **2000**, *3*, 501−9.

(9) Guilani, B.; Rasco, M. L.; Hermann, C. F. K.; Gibson, H. W. *J. Heterocycl. Chem.* **1990**, *27*, 1007−1009.

(10) Sallet, R.; Sillon, B.; Gaudemaris, G. *Bull. Soc. Chim. Fr.* **1968**, **8**, 3378−3386.

(11) Hoon, C. D.; Sangyup, S.; Sang, J. W.; Nakjoong, K. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1996**, *280*, 17−26.

(12) Joucla, M.; Gree, D.; Hamelin, J. *Tetrahedron* **1973**, *29*, 2315−2322.

(13) Iwakura, Y.; Uno, K.; Hongu, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2882−2885.

(14) Gree, R.; Carrie, R. *Bull. Soc. Chim. Fr.* **1975**, *2*, 1319−1324.

(15) Rundel, W. In *Houben-Weyl, Methoden der organische Chemie*, 4th ed.; Georg Thieme Verlag: Stuttgart, Germany, 1974; Vol. 10/4, p 314 ff.

(16) IUPAC name (provided by author): amino{[4-(6-{4-[(hydroxymethylylidene)methyl]phenoxy}hexyloxy)phenyl)methylene}-methyl-1-ol.

(17) IUPAC name (provided by author): {4-[(hydroxymethylylidene)methyl]phenoxy}-*N*-[6-({4-[(hydroxymethylylidene)-methyl] phenoxy}carbonylamino)hexyl]carboxamide.

(18) IUPAC name (provided by author): [4-(2,5-dioxo(3-pyrrolinyl))phenoxy]-*N*-(6-{[4-(2,5-dioxo(3-pyrrolinyl))phenoxy]-carbonylamino}hexyl)carboxamide.

MA0215565