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POLY-DIELS-ALDER ADDITION WITH A BISOXAZOLE AS BISDIENE AND A BISMALEINIMIDE AS BISDIENOPHILE

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ABSTRACT

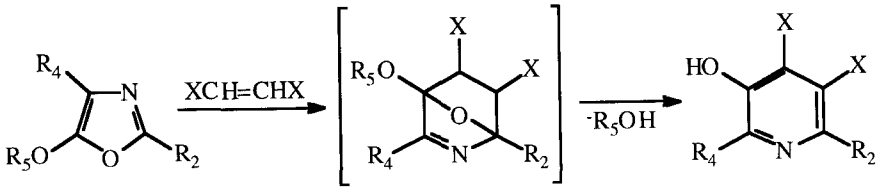
The poly-Diels-Alder addition between the new bisdiene 1,4-bis(5-methoxy-2-oxazolyl)benzene (**4**) and *N,N'*-hexamethylene-bis[2-(2,5-dihydro-2,5-dioxo-pyrrole-1-yl)acetamide] (**7**) is described. The structure of the resulting polyadduct **12** was proved by ^{1}H NMR spectroscopy with the aid of the low-molecular-weight model compounds1,4-bis(1,3-dihydro-7-hydroxy-1,3-dioxo-2-phenyl-pyrrolo[3,4-*c*]pyridine-4-yl)benzene (**9**) and *N,N'*-hexamethylene-bis[2-(1, 3-dihydro-7-hydroxy-6-methyl-1,3-dioxo-4-phenyl-pyrrolo[3,4-*c*]pyridine-2-yl)acetamide] (**11**). The reaction proceeds via the aromatization of the primarily formed cycloadducts. Polyadduct **12** shows a number average degree of polymerization $\overline{P}_n$ of about 11 - 12 ($\overline{M}_n$ = 8500 - 9200 g/mol), calculated from ^{1}H NMR end-group signals.

INTRODUCTION

In macromolecular chemistry, the classical Diels-Alder (DA) reaction has been successfully employed to synthesize oligomers and high-molecular-weight polymers via the polyaddition of bisdienes and bisdienophiles or monomers containing both a dienophile and diene group [1-15]. Many recent investigations describe the synthesis of ribbon-shaped (or ladder) polymers, which can be considered as precursors of polyacenes [16-22]. Other papers deal with repetitive

DA reactions of furfurylidene- and furfuryl-substituted maleamic acids [23], bistriazolinediones [24], bisfurfurylurethanes [25] and α-pyrones [26]. Recently, we reported on poly-DA additions with disorboylamides as bisdienes and a dimaleoylamide as bisdienophile [27]. We also performed kinetic studies on the DA reaction of furan-containing comb-like polymers with acetylenedicarboxylic acid dimethylester by means of ^1H NMR spectroscopy [28].

To our knowledge, derivatives of 5-alkoxyoxazoles have not yet been used as dienes for repetitive DA reactions, although they react in good yields with various dienophiles in low-molecular-weight cycloaddition reactions [29]. The primarily formed cycloadducts are usually extremely unstable and cannot be isolated. They undergo facile aromatization by elimination of one molecule of alcohol:



The final products are substituted 3-hydroxypyridines. Thus, DA reactions of 5-alkoxyoxazoles have widely been used to synthesize vitamin B_6 and various pyridoxine analogues [30]. In this context, we recently prepared pyridoxine by the DA reaction of 5-ethoxy-4-methyloxazole and the cyclic acetale of *cis*-2-butene-1,4-diol and poly(vinyl formal) as polymeric dienophile and support [31].

In this paper, we describe the synthesis of a new bisdiene, based on the 5-alkoxyoxazole system, and its poly-DA reaction with a bismaleinimide as bisdienophile. The structure of the cycloadduct was characterized by use of ^1H NMR spectroscopy and with help of low-molecular-weight model compounds.

EXPERIMENTAL

Synthesis of Bisdiene 4

N,N'-Bis(methoxycarbonylmethyl)terephthalic Acid Diamide (3) [35]

99,5g (0,49 mol) of terephthaloyl chloride (**1**) were added dropwise to a suspension of 126g (1,00 mol) of glycine methyl ester hydrochloride (**2**) in 1 L of CH_2Cl_2 and 253g (2,50 mol) of triethylamine at 0°C. The mixture was stirred at room temperature for 24 hours. Then the solvent was removed under reduced pressure. The residue was inserted into 300 mL of water. The colorless crystals were isolated and washed with 300 mL of dil. HCl (10%), sat. $NaHCO_3$, water and

tert-butyl methyl ether. Yield: 136g (90%) colorless needles, m. p. 153-154°C (Reference [35]: 148-150°C).

1,4-Bis(5-methoxy-2-oxazolyl)benzene (4)

20,0g (64,9 mmol) of **3** and 73,7g (0,52 mol) of phosphorus pentaoxide in 200 mL of dry chloroform were heated under reflux for 24 hours. After decanting the solvent, the flask was smashed and the residue crushed in a mortar. Then 600 mL of a 5,4 molar solution of sodium methylate in methanol were very cautiously (!) added dropwise to the reaction mixture to destroy surplus phosphorus pentaoxide. The resulting yellow solution was diluted with 500 mL of water. After the addition of 400 mL of *tert*-butyl methyl ether a slow crystallization set in between the organic and aqueous phase. The product was recrystallized from a mixture of ethyl acetate and *tert*-butyl methyl ether. Yield: 1,3g (7%) colorless shining needles, m. p. 187-188°C.

IR (KBr): 3125, 3090, 3020, 2985, 2935 2830 (CH), 1604, 1570 (N=C-O, C=C), 1281, 1089, 1068, 1039 (C-O) and 848 cm^{-1} (CH-out-of-plane).

^{1}H-NMR (d_6-DMSO, 250 MHz): δ= 7,93 (s, *p*-phenylene-H, 4 H), 6,52 (s, oxazole-H^4, 2 H) and 3,97 ppm (s, OCH_3, 6 H).

^{13}C-NMR ($CDCl_3$, 62,9 MHz): δ = 160,86 (oxazole-C^2, 2 C), 151,84 (oxazole-C^5, 2 C), 128,01 (*p*-phenylene-$C^{1/4}$, 2 C), 125,39 (*p*-phenylene-$C^{2/3/5/6}$, 4 C), 100,00 (oxazole-C^4, 2 C) and 58,52 ppm (OCH_3, 2 C).

MS: *m/z* (%) = 273 (7) (M^+ + H), 272 (39) (M^+), 257 (7) (M^+ - CH_3), 244 (5) (M^+ - CO), 229 (8) (M^+ - CO - CH_3), 202 (100) (M^+ - CH_3 - CO - HCN).

$C_{14}H_{12}N_2O_4$ (272,26)

Calcd.: C 61,76 H 4,44 N 10,29

Found: C 61,74 H 4,52 N 10,28

Synthesis of Bisdienophile 7

N,N'-Hexamethylene-bis[2-(2,5-dihydro-2,5-dioxo-pyrrole-1-yl)acetamide] (7)

A suspension of 5,34 g (34,4 mmol) of N-maleoylglycine (**5**) and 3,48g (34,4 mmol) of triethylamine in 250 mL of methylene chloride and 100 mL of tetrahydrofuran was cooled to about -10°C. Then 3,74g (34,4 mmol) of ethyl chloroformate were added dropwise. After 10 minutes stirring 2,00g (17,2 mmol) of hexamethylene diamine (**6**) in 100 mL of methylene chloride were added at about -15°C. After 24 hours stirring at room temperature, the solvents were removed under reduced pressure. The residue was put into 200 mL of sat. $NaHCO_3$. Then it

was isolated and washed with 200 mL of dil. HCl (10%) and 100 mL of water. The colorless crystals were recrystallized from ethanol. Yield: 4,3g (64%). M. p. 215 - 216°C.

IR (KBr): 3320 (NH), 3075, 2925, 2865 (CH), 1772, 1710 (C=O, imide), 1660 (C=O, amide I), 1548 (NH-bending, amide II), 834 and 696 cm^{-1} (CH-out-of-plane).

^{1}H-NMR (d_6-DMSO, 250 MHz): δ = 8,10 (t, NH, 2 H), 7,09 (s, HC=CH, 4 H), 3,99 (s, NCH_2, 4 H), 3,03 (m, $NHCH_2$, 4 H) 1,39 - 1,34 (m, $NHCH_2CH_2$, 4 H) and 1,23 ppm (m, $NH(CH_2)_2CH_2$, 4 H).

^{13}C-NMR (d_6-DMSO, 100,6 MHz): δ = 171,53 (C=O, imide, 4 C), 166,66 (C=O, amide, 2 C), 135,70 (C=C, 4 C), 40,58 (NCH_2, 2 C), 39,48 ($NHCH_2$, 2 C), 29,76 ($NHCH_2CH_2$, 2 C) and 26,81 ppm ($NH(CH_2)_2CH_2$, 2 C).

MS: *m/z* (%) = 390 (5) (M^+), 280 (35) ($M^+ - H_2CNC_4H_2O_2$), 110 (100) ($H_2CNC_4H_2O_2^+$).

$C_{18}H_{22}N_4O_6$ (390,40)

Calcd: C 55,38 H 5,68 N 14,35

Found: C 55,35 H 5,71 N 14,33

Synthesis of Model Compounds 9 and 11

1,4-Bis(1,3-dihydro-7-hydroxy-1,3-dioxo-2-phenyl-pyrrolo[3,4-c]pyridine-4-yl)benzene (9)

0,34g (1,25 mmol) of bisoxazole **4** and 0,54g (3,12 mmol) of N-phenylmaleinimide (**8**) in 2,5 mL of dry DMSO were heated at 130°C. Soon a precipitate appeared, and after 3 days, the yellow suspension was poured into 50 mL of methanol. The yellow product was collected and purified by refluxing it in 50 mL of methanol for several hours. Yield: 0,63g (91%). M. p. > 360°C. Dec. starting at 370°C according to TG.

IR (KBr): 3500-3400 (OH), 3055 (CH), 1782, 1762, 1721 (C=O, imide), 1620 (C=N), 1591, 1495 (C=C), 1121 (C-O), 854, 763 and 694 cm^{-1} (CH-out-of-plane).

^{1}H NMR (d_6-DMSO, 400 MHz): δ = 11,7 (s, broad; OH), 8,76 (s, heteroaromatic H, 2 H), 7,94 (s, *p*-phenylene-H, 4 H), 7,52 (m, phenyl-$H^{2/6}$, 4 H) and 7,43 ppm (m, phenyl-$H^{3/4/5}$, 6 H).

MS: *m/z* (%) = 554 (11) (M^+).

$C_{32}H_{18}N_4O_6$ (554,52)

Calcd.: C 69,31 H 3,27 N 10,10

Found: C 69,12 H 3,24 N 9,92

*N,N'-Hexamethylene-bis[2-(1,3-dihydro-7-hydroxy-6-methyl-1,3-dioxo-4-phenyl-pyrrolo[3,4-c]pyridine-2-yl)acetamide] (**11**)*

0,30g (1,59 mmol) of oxazole **10** and 0,31g (0,79 mmol) of bismaleinimide **7** in 2 mL of dry DMSO were heated at 60-70°C for 28 hours. When the brown solution cooled down, a precipitate appeared. The suspension was given in 100 mL of ethanol. For purification the colorless solid was twice refluxed in 50 mL of ethanol and washed with 30 mL of *tert*-butyl methyl ether. Yield: 350 mg (63%). M. p. 234 - 237°C.

IR (KBr): 3380 (OH, NH), 3050, 2925, 2850 (CH), 1763 (C=O, imide), 1708 (C=O, imide) with shoulder at 1670 (C=O, amide I), 1538 (NH-bending, amide II), 1158, 1112, 1024 (C-O), 751 and 698 cm^{-1} (CH-out-of-plane).

^{1}H-NMR (d_6-DMSO, 400 MHz): δ = 8,11 (t, NH, 2 H), 7,83-7,80 (m, phenyl-$H^{2/6}$, 4 H), 7,48 - 7,44 (m, phenyl-$H^{3/4/5}$, 6 H), 4,12 (s, NCH_2CO, 4 H), 3,07 - 3,02 (m, $NHC\underline{H}_2$, 4 H), 2,59 (s, CH_3, 6 H), 1,38 (m, $NHCH_2C\underline{H}_2$, 4 H) and 1,24 ppm (m, $NHCH_2CH_2C\underline{H}_2$, 4 H).

^{13}C-NMR (d_6-DMSO, 100,6 MHz): δ = 167,39, 166,69, 166,51 (C=O, imide, 4 C; C=O, amide, 2 C), 157,76 (C^7, 2 C), 147,03 (C^6, 2 C), 145,90 (C^4, 2 C), 137,12 (phenyl-C^1, 2 C), 130,37, 128,48 (phenyl-$C^{2/6}$, 4 C; phenyl-$C^{3/5}$, 4 C), 129,80 (phenyl-C^4, 2 C), 122,49, 121,11 (C^{3a}, 2 C; C^{7a}, 2 C), 39,53 ($NHCH_2$, 2 C), 29,76 ($NHCH_2\underline{C}H_2$, 2 C), 26,82 ($NHCH_2CH_2\underline{C}H_2$, 2 C) and 21,02 ppm ($CH_3$, 2 C). $N\underline{C}H_2CO$ covered by d_6-DMSO signal.

MS: *m/z* (%) = 705 (18) (M^+ + H), 704 (38) (M^+), 437 (22) (M^+ - $C_{15}H_{11}N_2O_3$).

$C_{38}H_{36}N_6O_8$ (704,74)

Calcd.: C 64,76 H 5,15 N 11,92

Found: C 64,46 H 5,24 N 12,07

Poly-DA Addition

*Synthesis of Polycycloadduct (**12**)*

0,4000g (1,4692 mmol) of bisoxazole **4** and 0,5736g (1,4692 mmol) of bismaleinimide **7** in 2 mL of dry DMSO were heated at 100°C. After 5 hours, the high-viscous solution was added dropwise to 150 mL of acetone. For purification the yellow precipitate was washed with 50 mL of methanol and *tert*-butyl methyl ether and again dissolved in hot DMSO and precipitated in acetone. The product was dried at 80°C i. vac. for 3 days Yield: 580 mg (66%). Dec. starting at 250°C according to TG. $[\eta]$ = 21.6 ml/g.

IR (KBr): 3290 (OH, NH), 3085, 2930, 2855 (CH), 1772, 1711 (C=O, imide), 1655 (C=O, amide I) with shoulder at 1620 (C=N), 1548 (NH-bending, amide II), 1118, 1085 (C-O), 848 and 767 cm^{-1} (CH-out-of-plane).

^{1}H-NMR (d_6-DMSO, 400 MHz): δ = 11,74 (s, broad, OH), 8,73 (s, pyridine-H, 2 H), 8,10 (ps, NH, 2 H), 7,90 (s, *p*-phenylene-H, 4 H), 7,06 (s, HC=CH from maleinimide end-group), 6,50 (s, heteroaromatic H from oxazole end-group), 4,13 (s, NCH_2CO, 4 H), 3,98 (s, NCH_2CO from maleinimide end-group), 3,96 (s, OCH_3 from oxazole end-group), 3,05-3,04 (m, $NHCH_2$, 4 H), 1,38 (ps, $NHCH_2CH_2$, 4 H) and 1,24 ppm (ps, $NH(CH_2)_2CH_2$, 4 H).

$(C_{30}H_{26}N_6O_8)_n$ $(598,58)_n$

Calcd.: C 60,20 H 4,38 N 14,04

Found: C 60,87 H 4,66 N 13,47

Apparatus and Materials

IR spectra were recorded on a Perkin-Elmer 1420 ratio recording infra-red spectrophotometer, NMR spectra on a Bruker AC 250 (^{1}H: 250 MHz, ^{13}C: 62,9 MHz) and on a Bruker ARX 400 (^{1}H: 400 MHz, ^{13}C: 100,6 MHz), mass spectra on a Varian MAT 311 A (70 eV). Elemental analysis was performed with Perkin-Elmer 204 B. Melting points were determined with a Büchi melting point determinator 510 and are uncorrected, thermogravimetric measurements (TG) were recorded on a Mettler TA 3000 (heating rate 10°C/min. in air). Viscometric measurements were carried out with an Ostwald viscometer in DMSO at 25°C (c = 5 g/L).

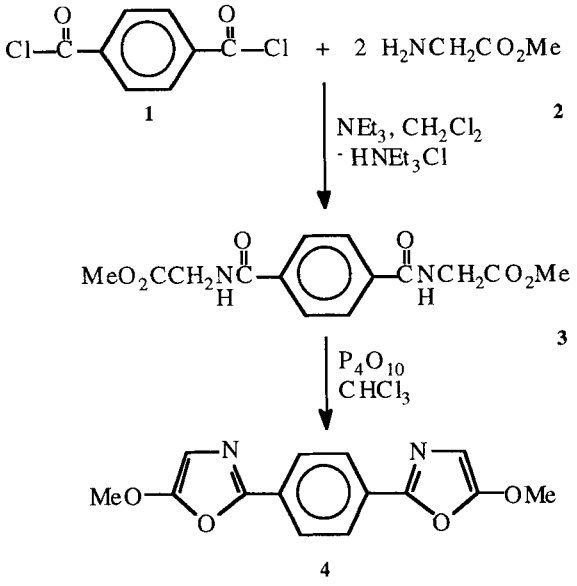
Maleinimide **5** was synthesized as described in Reference [33], 5-methoxy-oxazole **10** by cyclization of N-benzoylalanine methyl ester with phosphorus pentaoxide as described in Reference [32]. All other compounds were obtained from Fluka or Aldrich and were used without further purification.

RESULTS AND DISCUSSION

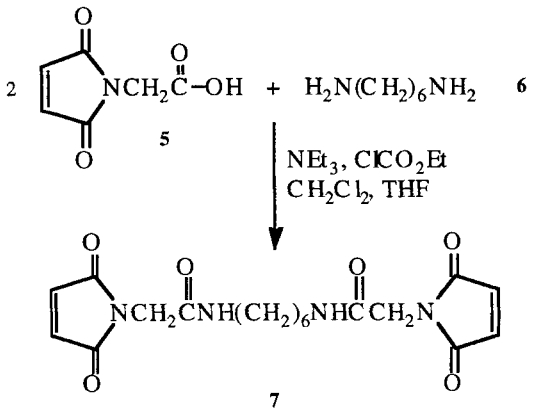
Synthesis of Monomers

The classical method to synthesize 5-alkoxyoxazoles is the cyclization of acylated α-amino acid esters by dehydrating agents such as phosphorus pentachloride or phosphorus pentaoxide [32]. Thus, for the synthesis of bisdiene 1,4-bis(5-methoxy-2-oxazolyl)benzene (**4**) terephthaloyl chloride (**1**) was condensed

with two equivalents of glycine methyl ester (**2**). The resulting *N,N'*-bis(methoxycarbonylmethyl)terephthalic acid diamide (**3**) was then cyclized with phosphorus pentaoxide in chloroform, resulting in bisdiene **4**:



The bisdienophile *N,N'*-hexamethylene-bis[2-(2,5-dihydro-2,5-dioxo-pyrrole-1-yl)acetamide] (**7**) was prepared by condensing two equivalents of *N*-maleoylglycine (**5**) [33] with hexamethylene diamine (**6**) via a mixed anhydride as activating intermediate:



Synthesis of Model Compounds

The low-molecular-weight model compounds 1,4-bis(1,3-dihydro-7-hydroxy-1,3-dioxo-2-phenyl-pyrrolo[3,4-*c*]pyridine-4-yl)benzene (**9**) and *N,N'*-

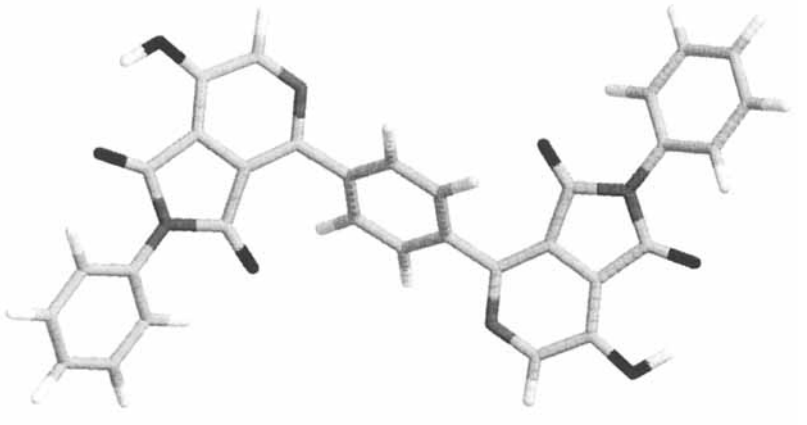
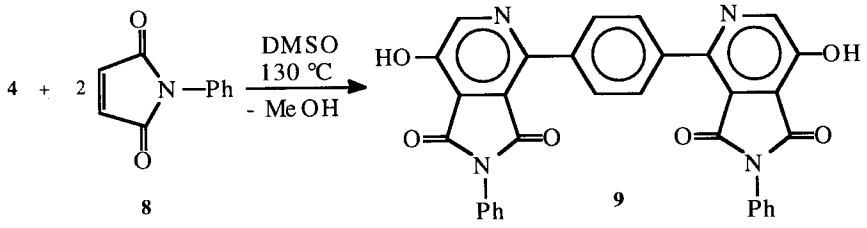


Figure 1. Model of an energy-minimized conformation of compound **9.**

hexa-methy-lene-bis[2-(1, 3-dihydro-7-hydroxy-6-methyl-1,3-dioxo-4-phenyl- pyrrolo[3,4-*c*]pyridine-2-yl)acetamide] (**11**) were prepared to explore the reaction conditions for the poly-DA addition and to assign the ^{1}H NMR signals of polyadduct **12**.

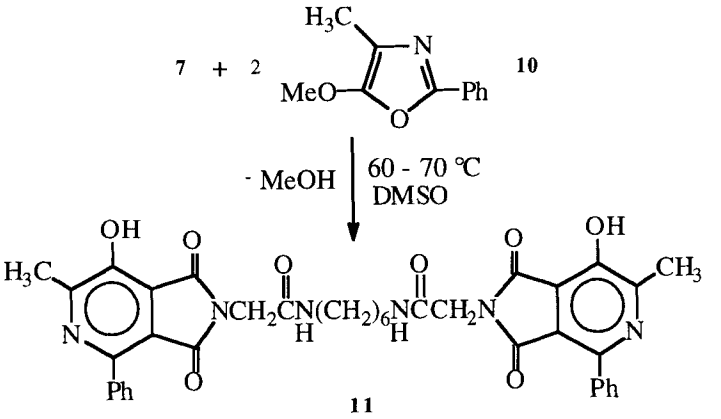
Bispyridine **9** was obtained from N-phenylmaleinimide (**8**) and bisoxazole **4** in 91% yield:



8 **9**

Figure 1 shows an energy-minimized molecular model of compound **9** that was obtained on a semiempirical AM1-level [34]. According to this calculation, the pyrrolo[3,4-*c*]pyridine units and the central phenylene ring prefer a *trans* oide conformation.

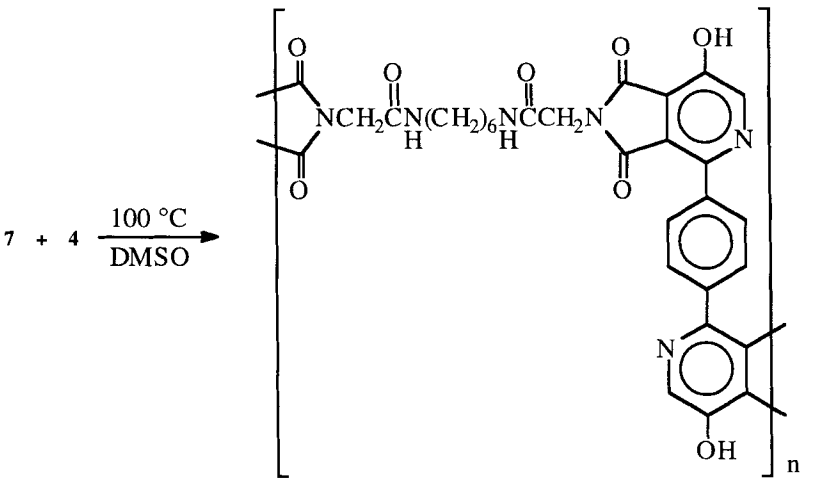
Model compound **11** was prepared from bismaleinimide **7** and 5-methoxy-oxazole (**10**):



Both model compounds are insoluble in common solvents such as ethyl acetate, chloroform, methylene chloride, alcohols, ethers or *N,N*-dimethylformaide. They only dissolve in hot DMSO.

Poly-DA Addition

The poly-cycloaddition reaction between bisoxazole **4** and bismaleinimide **7** was performed in DMSO at 100°C:



During the reaction the viscosity of the solution strongly increased. Polyadduct **12** was isolated by precipitating it in acetone.

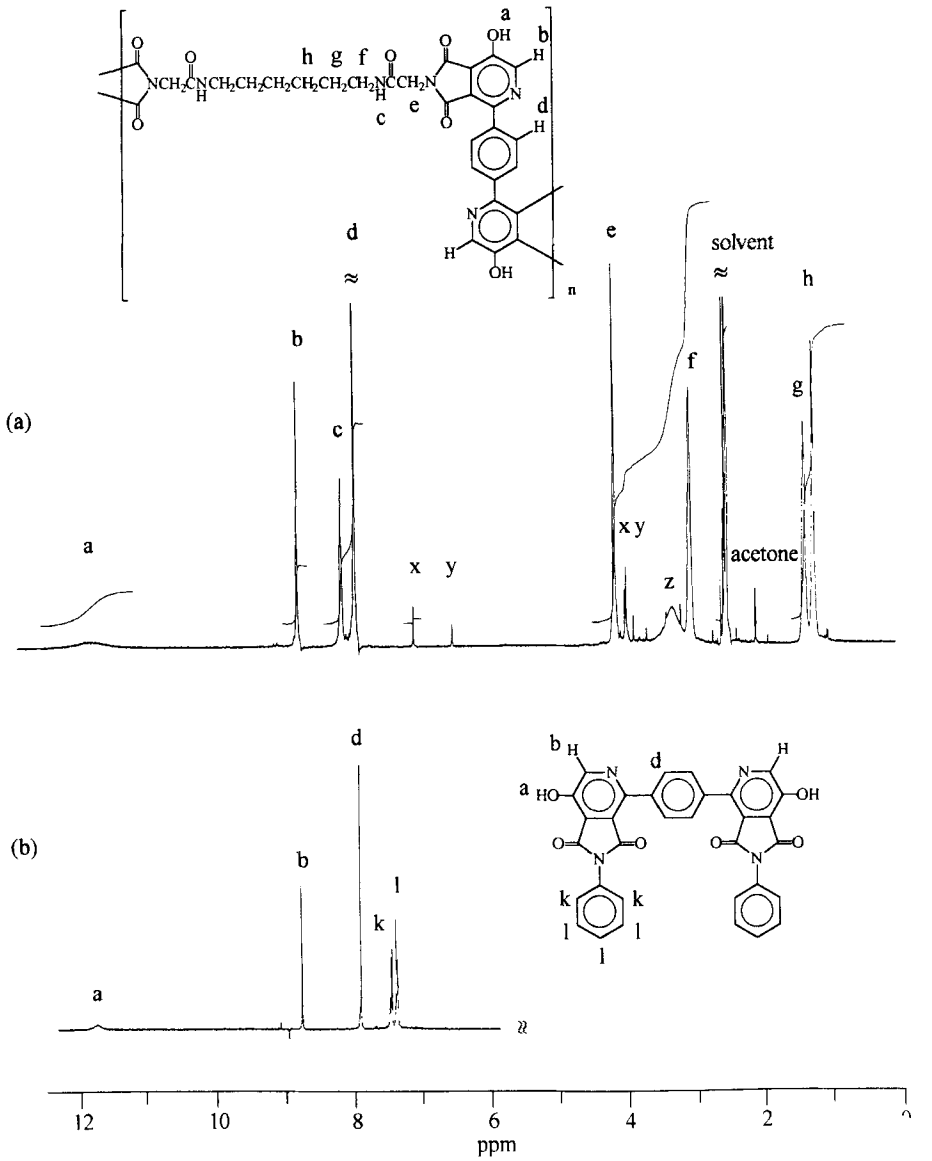


Figure 2. ^{1}H NMR spectra (d_6-DMSO, 400 MHz) of poly-DA adduct **12** (a) and model compound **9** (b). In spectrum (a) signals of dienophile end-groups are marked with x, those of diene end-groups with y. z corresponds to water in d_6-DMSO.

The structure of **12** was proved by means of ^1H NMR spectroscopy (Figure 2).

The most characteristic shifts appear at 11,7 (pyridine-OH), 8,73 (hetero-aromatic pyridine-H) and 4,13 ppm (NCH_2-imide). They show that the poly-DA reaction proceeds via the aromatization of the primarily formed cycloadducts. These shifts coincide with those of model compounds **9** and **11** and establish the proposed structure of polyadduct **12**. Besides, weak signals of diene and dienophile end-groups appear at 7,06 (HC=CH from maleinimide, *see* x in Figure 2), 6,50 (heteroaromatic oxazole-H, *see* y in Figure 2), 3,98 and 3,96 ppm (imide-NCH_2 from maleinimide and OCH_3 from oxazole ring, *see* x and y in Figure 2), indicating that oligomers were obtained. With the help of these end-groups, the number average degree of polymerization $\overline{P}_n$ of **12** was calculated. The evaluation of the signal intensity ratios results in a $\overline{P}_n$ of about 11 - 12 ($\overline{M}_n$ = 8500 - 9200 g/mol).

The yellow-orange product is insoluble in methylen chloride, tetrahydro-furan, ethyl acetate, alcohols, but slightly soluble in *N,N*-dimethylformamide and readily dissolves in warm dimethylsulfoxide. From viscosity measurements (25°C, DMSO) a reduced viscosity (η_{sp}/c of 21.6 mL/g was obtained. When cast from DMSO solutions, only brittle films could be obtained, which is a further hint that oligomers were formed during the cycloaddition reaction. DSC measurements of **12** showed no glass transition up to 250°C. Decomposition starts at about 250°C.

CONCLUSION

The poly-DA reaction between bis-(5-alkoxyoxazole) **4** and bismaleinimide **7** provides oligomers with 3-hydroxypyridine units in the main chain. The hydroxy groups could be employed for further functionalization, e.g. for the synthesis of comb-like oligomers. Besides, the maleinimide end-groups of oligomers **12** may be used to prepare new networks by radical polymerization.

REFERENCES

[1] *Reviews*: W. J. Bailey, "*Diels-Alder Polymerization*", in: *Step-Growth Polymerization*, D. H. Soloman, Ed., Dekker, New York 1972, Chapt. 6; J. K. Stille, F. W. Harris, H. Mukamal, R. O. Rakutis, C. L. Schilling, G. K. Noren, and J. A. Reed, *Adv. Chem. Ser., 91*, 628 (1969).

[2] G. C. Tesoro and V. R. Sastri, *Ind. Eng. Chem. Prod. Res. Dev., 25*, 444 (1986).

[3] X. He, V. R. Sastri, and G. C. Tesoro, *Makromol. Chem., Rapid Commun., 9*, 191 (1988).

[4] M. A. B. Meador, M. A. Meador, M.-K. Ahn, and M. A. Olshavsky, *Macromolecules, 22,* 4385 (1989).

[5] L.-S. Tan, F. E. Arnold, and E. J. Soloski, *J. Polym. Sci., Part A: Polym. Chem., 26,* 3103 (1988).

[6] L.-S. Tan and F. E. Arnold, *J. Polym. Sci., Part: Polym. Chem., 25*, 3159 (1987).

[7] L.-S. Tan, E. J. Soloski, and F. E. Arnold, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem., 27,* 240 (1986).

[8] L.-S. Tan, E. J. Soloski, and F. E. Arnold, *Ibid, 27*, 453 (1986).

[9] R. A. Ryntz and R. T. Kohl, *Ibid, 24*, 322 (1983).

[10] J. M. Dineen, E. E. Howell, and A. A. Volpe, *Ibid, 23,* 282 (1982).

[11] J. M. Dineen and A. A. Volpe, *Ibid, 19*, 34 (1978).

[12] R. M. Ottenbrite and J. G. Smith, *Ibid*, *30,* 199 (1989).

[13] C. I. Simionescu and M. Grigoras, *J. Polym. Sci., Part C: Polym. Lett., 28,* 39 (1990).

[14] M. P. Stevens, *J. Polym. Sci., Polym. Lett. Ed., 22,* 467 (1984).

[15] S. Dumitrescu, M. Grigoras, and A. Natansohn, *J. Polym. Sci., Polym. Lett. Ed., 17,* 553 (1979).

[16] M. Löffler, A.-D. Schlüter, K. Geßler, W. Saenger, J.-M. Toussaint, and J.-L. Brédas, *Angew. Chem., 106,* 2281 (1994).

[17] A.-D. Schlüter, M. Löffler, and V. Enkelmann, *Nature, 368,* 831 (1994).

[18] M. Rack and M. Hanack, *Angew. Chem., 106,* 1712 (1994).

[19] B. L. Schürmann, V. Enkelmann, M. Löffler, and A.-D. Schlüter, *Angew. Chem., 105,* 107 (1993).

[20] U. Scherf and K. Müllen, *Synthesis, 1-2,* 23 (1992).

[21] K. Blatter, A. Godt, T. Vogel, and A.-D. Schlüter, *Makromol. Chem., Macromol. Symp., 44*, 265 (1991).

[22] A.-D. Schlüter, *Nachr. Chem. Tech. Lab., 38,* 8 (1990), and references cited
therein.

[23] J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem., 30*, 125 (1992).

[24] M. Kuhrau and R. Stadler, *Makromol. Chem., Rapid Commun., 11,* 635 (1990).

[25] H. S. Patel and H. S. Vyas, *Eur. Polym. J., 27,* 93 (1991).

[26] G. Alhakimi, H. Görls, and E. Klemm, *Macromol. Chem. Phys., 195,* 1569 (1994).

[27] M. Reinecke and H. Ritter, *Ibid., 195,* 2445 (1994).

[28] H. Ritter, R. Sperber, and C. M. Weisshuhn, *Makromol. Chem., 194,* 1721 (1993).

[29] *Reviews:* I. J. Turchi and M. J. S. Dewar, *Chem. Rev., 75,* 389 (1975); R. Lakhan and B. Ternai, *Adv. Heterocycl. Chem., 17,* 99 (1974); M. Y. Karpeiskii and V. L. Florent'ev, *Russ. Chem. Rev., 38,* 540 (1969).

[30] *see e.g.*: H. König and W. Böll, *Chem.-Ztg., 100,* 105 (1976).

[31] R. Sperber and H. Ritter, *Macromolecules, 27,* 5919 (1994).

[32] *see e.g.*: P. Karrer, E. Miyamichi, H. C. Storm, and R. Widmer, *Helv. Chim. Acta., 8,* 205 (1925); P. Karrer, and C. Gränacher, *Ibid, 7,* 763 (1924).

[33] D. H. Rich, P. D. Gesellchen, A. Tong, A. Cheung, and C. K. Buckner, *J. Med. Chem.,* 18, 1005 (1975).

[34] AM1 calculation by HyperChem Release **4**, HyperCube Inc. 1994.

[35] T. M. Frunze, V. V. Korshak, and L. V. Kozlov, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk,*, 535 (1959); *Chem. Abstr., 53*, 21885 b (1959).

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