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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Nuyken, Oskar , Spindler, Christian E. and Raether, R. Benedikt(1997) 'Synthesis and Thermal Properties of Crosslinked Poly(2,3-Tetrahydrofurandiyl)s', Journal of Macromolecular Science, Part A, 34: 12, 2389 – 2404

To link to this Article: DOI: 10.1080/10601329708010055

URL: <http://dx.doi.org/10.1080/10601329708010055>

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SYNTHESIS AND THERMAL PROPERTIES OF CROSSLINKED POLY(2,3-TETRAHYDROFURANDIYL)S

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ABSTRACT

Bi- and trifunctional monomers with 2,3-dihydrofuranyl moieties were synthesized. The polymerizable dihydrofuranyl groups were connected to each other with ester and ether linkages. Alkyl-, alkenyl- and arylspacers were used. The synthesized monomers were copolymerized with 2,3-dihydrofuran by photoinduced cationic polymerization. As photo acid (η^5 -cyclopentadienyl)-Fe(II)-(η^6 -isopropylbenzene) hexafluorophosphate was used. The thermal stability of the crosslinked poly(2,3-tetrahydrofurandiyl)s is dependent of the monomer structure. Higher stability was observed for poly(tetrahydrofurandiyl)s crosslinked with bis(2,3-dihydrofuranyl) compounds instead of tetraethyleneglycol bis-2-propenyl-ether.

INTRODUCTION

Poly(2,3-tetrahydrofurandiyl) was synthesized for the first time by D. A. Barr *et al.* [1] with boron trifluoride. The polymerization can also be carried out with aluminium chloride [2] and ethylaluminium dichloride [3], iodine [4], acetyl perchlorate [4], boron trifluoride etherate [5, 6] and 1-iodine-1-(2-methylpropyloxy) ethane/tetrabutylammonium perchlorate [7]. Moreover, the ring opening metathesis polymerization of 2,3-dihydrofuran is known [8].

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Recently, we have reported about the photoinduced cationic homopolymerization of 2,3-dihydrofurans with (η^5 -cyclopentadienyl)-Fe(II)-(η^6 -isopropylbenzene) hexafluoro-phosphate, demonstrating that 2,3-dihydrofuran is an extreme reactive enolether for photo-induced cationic polymerization, which is caused by its ring strain and cis-conformation at the double bond [9].

The crosslinking of poly(2,3-tetrahydrofurandiyl) by a free radical process is already described by R. A. Moore *et al.* [5]. In this paper, the synthesis of crosslinked poly(2,3-tetrahydrofurandiyl)s by photoinduced cationic polymerization with this photo acid is described.

As the photoinduced cationic polymerization of 2,3-dihydrofurans is very fast (100% conversion within two minutes), they seem to be suitable for applications like coating on automatical production routes, where a high reaction rate is required.

The reactivity of 2,3-dihydrofuran is large. It is, in fact, the most reactive enolether in cationic polymerization we know. It is obviously difficult to obtain regularly crosslinked polymers by using multifunctional monomers with less reactive polymerizable groups. Therefore, we synthesized different multi-functional 2,3-dihydrofurans to use them in the synthesis of crosslinked poly(2,3-tetrahydrofurandiyl)s.

EXPERIMENTAL

Materials

Allyl bromide, benzenetricarboxylic acid trichloride, 1,4-dibromobut-2-ene, imidazole, sodium, tetrabutylammonium bromide and toluenesulfonic acid chloride were available from Fluka. Succinyl chloride, α,α' -dibromo-p-xylene, 1,4-dibromobutane, 1,10-dibromodecane, 2,3-dihydrofuran and 3-furoic acid were received from Aldrich. Ammonia was received from Linde. (η^5 -cyclopentadienyl)-Fe(II)-(η^6 -isopropylbenzene) hexafluorophosphate (Irgacure®261) was kindly supplied by Novartis, while tetraethylenglycole-bis-2-propenylether was donated by BASF AG. Diethylether and tetrahydrofuran were dried over sodium/potassium-alloy, dichloromethane over calcium hydride and isopropanol over sodium. Butan-2-on and pyridine were dried over molecular sieve (4 Å).

α,α',α'' -tribromomesitylene [10], 1,3,5-benzenetricarboxylic acid triimidazolide and succinyl diimidazolide [11] were synthesized according to known literature procedures.

Characterization

The thermal behavior was investigated with thermogravimetry (Polymer Laboratories STA 1500 H) and differential scanning calorimetry (Perkin Elmer DSC 7). The decomposition temperatures (T_d) were obtained from thermogravimetical experiments, which were carried out under a nitrogen/oxygen atmosphere with a scanning rate of 10°C/min. The onset of the decomposition curve was taken as T_d . The glass transition temperature was determined with differential scanning calorimetry experiments, which were executed under a nitrogen atmosphere with a scanning rate of 20°C/min. The IR-spectra were obtained with a Bruker IFS 55 FT-IR apparatus, while the NMR spectra were performed with a Bruker ARX 300 (δ in ppm relative to TMS). Melting points were determined with a Büchi SMP 20 apparatus.

Synthesis

Sodium(2,3-Dihydrofuran-3-carboxylic Acid Allylester) (I)

To 500 mL liquid ammonia 50 mL (650 mmol) isopropanol was added. 7.0 g (62 mmol) 3-furoic acid was dissolved in the ammonia and 5.5 g (240 mmol) sodium was added. The solution was heated to reflux for 45 minutes at room temperature until the blue color of the solution disappeared. The ammonia was allowed to evaporate overnight. The residue was dissolved in 100 mL water. The pH was tuned to 7.5 by adding solid carbon dioxide to the solution. 2.5 g (62 mmol) sodium hydroxide and 20.00 g (62 mmol) tetrabutylammonium bromide was added. The water was removed under reduced pressure. The residue was suspended in 100 mL dimethylformamide. 21.60 g (180 mmol) allyl bromide were added. The reaction mixture was stirred for 20 hours at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in 150 mL water. The aqueous layer was extracted three times with 100 mL diethyl ether. The combined organic layers were washed two times with 50 mL of an aqueous solution of sodium chloride (2.8 mol/L) and dried over sodium sulphate. The solution was filtered. The solvent and remaining allyl bromide were evaporated. The product was purified by distillation (54°C, 0.5 mbar). Yield: 69 % (colorless liquid).

$^1\text{H NMR}$ (CDCl_3): (δ = 3.86 (m; 1H; CH), 4.42 (dd; $2J = 10$ Hz, $3J = 11$ Hz; 1H; $\text{OCHH}'\text{CH}$), 4.62 (dd; $3J = 6$ Hz, $4J = 2$ Hz; 2H; $\text{OCH}_2\text{CH}=\text{}$), 4.68 (dd; $3J = 7$ Hz; 1H; $\text{OCHH}'\text{CH}$), 5.05 (dd; $3J = 3$ Hz, $3J = 3$ Hz; 1H; $\text{OCH}=\text{CH}$), 5.25 (dd; $2J = 2$ Hz, $3J = 11$ Hz; 1H; $=\text{CHH}'$), 5.32 (dd; $3J = 17$ Hz; 1H; $=\text{CHH}'$), 5.92 (m; 1H; $\text{CH}=\text{CH}_2$), 6.41 (dd; $4J = 2$ Hz; 1H; $\text{OCH}=\text{}$).

^{13}C NMR (CDCl_3): (δ = 47.3 (-CH), 65.6 (OCH_2CH -), 71.2 (OCH_2CH =), 98.7 (OCHCH), 118.5 ($=\text{CH}_2$), 131.9 ($\text{CH}=\text{CH}_2$), 147.9 (OCHCH), 172.4 (COO).

IR(film): 2953 (- CH_2 -), 1735 (s, C=O), 1617 (m, C=C-O), 1330 (m, O-CO), 1183 (s, C-O), 1143 (m; C-O), 1079(m; C-O), 933 (m; C=C), 923 (s, $\text{CH}=\text{CH}_2$), 716 cm^{-1} (m, C=CH).

2,3-Dihydro-3-hydroxymethyl-furan (2)

2.36 g (62 mmol) lithium aluminium hydride was suspended in 75 mL diethyl ether. 14.7 g (96 mmol) **1**, dissolved in 25 mL diethylether, was added slowly at -30°C . The suspension was stirred for 20 hours at room temperature. The remaining lithium aluminium hydride was decomposed by slow addition of water at -30°C . The organic layer was decanted, the residue was dissolved in 150 mL water. The pH of the aqueous layer was adjusted to 7.5 by addition of solid carbon dioxide. The layer was extracted three times with 100 mL of diethylether. The combined organic layers were dried over sodium sulphate. The solution was filtered and the solvent was removed under reduced pressure. The product could be purified by distillation (93°C , 43 mbar). Yield: 71% (colorless liquid).

^1H NMR (CDCl_3): (δ = 1.49 (s; 1H; OH), 3.19 (m; 1H; -CH), 3.55 (d; ^3J = 5 Hz; 2H; CH_2OH), 4.25 (dd; ^2J = 9 Hz, ^3J = 6 Hz; 1H; ROCHH'), 4.37 (dd; ^3J = 9 Hz; 1H; ROCHH'), 4.88 (dd; ^3J = 3 Hz, ^3J = 3 Hz; 1H; OCHCH), 6.43 (dd; $^4\text{J}_{5,3}$ = 2 Hz; 1H; OCHCH).

^{13}C NMR (CDCl_3): (δ = 44.8 (-CH), 65.00 (ROCH_2), 72.5 (CH_2OH), 100.0 (OCHCH), 147.9 (OCHCH).

IR (film): 3373 (s; O-H), 2885 (s, $-\text{CH}_2$ -), 1614 (m, C=C-O), 1139(m, C-O), 1036(s; C-O), 725 cm^{-1} (m, C=C-H).

Multifunctional Monomers with Ether Bridges

1 eq of the dibromo compound and 2.4 eq **2** were added to an 50% aqueous solution of potassium hydroxide (4.8 eq KOH). 0.05 eq tetrabutyl-ammonium bromide was added. The reaction mixture was stirred for 24 hours at room temperature. 20 mL water was added. The aqueous layer was extracted three times with 30 mL of diethyl ether. The combined organic layers were washed two times with 30 mL of aqueous sodium chloride (5.6 mol/L), dried with sodium sulphate and filtered. The diethylether was removed under reduced pressure. The product was purified by column chromatography (eluent: hexane/ethyl acetate, 4/1, v/v).

1,8-Bis(2,3-dihydrofuran-3-yl)-2,7-dioxaoctane (3)

Yield: 73% (m.p. 35°C, colorless solid).

$^1\text{H NMR}$ (CDCl_3): ($\delta = 1.62$ (m; 4H; OCH_2CH_2), 3.20 (m; 2H; -CH), 3.27 (dd; $2J = 8$ Hz, $^3J = 8$ Hz; 2H; $\text{CHCHH}'\text{O}$), 3.38 (dd; $^3J = 5$ Hz; 2H; $\text{CHCHH}'\text{O}'$), 3.44 (m; 4H; OCH_2CH_2), 4.14 (dd; $2J = 9$ Hz, $^3J = 7$ Hz; 2H; $\text{OCHH}'\text{CH}$), 4.34 (dd; $^3J = 9$ Hz; 2H; $\text{OCHH}'\text{CH}'$), 4.89 (dd; $^3J = 3$ Hz, $^3J = 2$ Hz; 2H; $\text{OCH}=\text{CH}$), 6.36 (dd; $4J = 2$ Hz; 2H; $\text{OCH}=\text{CH}$).

$^{13}\text{C NMR}$ (CDCl_3): ($\delta = 26.7$ (OCH_2CH_2), 43.2 (-CH), 71.4 (OCH_2CH), 73.5 and 74.4 (CH_2OCH_2), 101.4 (OCHCH), 147.3 (OCHCH).

IR (KBr): 2858 (s, $-\text{CH}_2-$), 1613 (s, $\text{C}=\text{C}-\text{O}$), 1472 (m, $-\text{CH}_2\text{CH}_2$), 1362 (m, $-\text{CH}_2\text{CH}_2-$), 1137 (s, $\text{C}-\text{O}$), 1108 (s, $\text{C}-\text{O}$), 910 (m, $\text{C}=\text{C}-\text{H}$), 721 cm^{-1} (s, $\text{C}=\text{C}-\text{H}$).

$\text{C}_{14}\text{H}_{20}\text{O}_4$ (252.31):	Calcd.	C 66.12	H 8.72
	Found	C 65.97	H 8.75

1,8-Bis(2,3-dihydrofuran-3-yl)-2,7-dioxaoct-4-en (4)

Yield: 82% (colorless oil).

$^1\text{H NMR}$ (CDCl_3): ($\delta = 3.20$ (m; 2H; CH), 3.29 (dd; $2J = 8$ Hz, $^3J = 8$ Hz; 2H; $\text{CHCHH}'\text{O}$), 3.41 (dd; $^3J = 5$ Hz; 2H; $\text{CHCHH}'\text{O}$), 3.98 (dd; $^3J = 3$ Hz, $4J = 3$ Hz; 4H; $\text{OCH}_2\text{CH}=\text{}$), 4.16 (dd; $2J = 9$ Hz, $^3J = 6$ Hz; 2H; $\text{OCHH}'\text{CH}-$), 4.34 (dd; $^3J = 9$ Hz; 2H; $\text{OCHH}'\text{CH}'$), 4.89 (dd; $^3J = 2$ Hz, $^3J = 2$ Hz; 2H; OCHCH), 5.79 (m; 2H; OCH_2CH), 6.36 (dd; $4J_{5,3} = 2$ Hz; 2H; OCHCH).

$^{13}\text{C NMR}$ (CDCl_3): ($\delta = 42.9$ (CH) 71.1 (OCH_2CH) 73.1 and 73.5 (CH_2OCH_2), 100.9 (OCHCH), 129.4 ($\text{OCH}_2\text{CH}=\text{}$), 147.1 (OCHCH):

IR (film): 2852 (s, $\text{C}-\text{H}$), 1738(m,), 1613(m, $\text{C}=\text{C}-\text{O}$), 1242 (m,), 1139 (s, $\text{C}-\text{O}$), 1139 (s, $\text{C}-\text{O}$), 1106 (s, $\text{C}-\text{O}$), 1048 (s, $\text{C}-\text{O}$), 723 cm^{-1} (m, $\text{C}=\text{C}-\text{H}$).

$\text{C}_{14}\text{H}_{18}\text{O}_4$ (250.29):	Calcd.	C 67.18	H 7.25
	Found	C 67.13	H 7.26

1,4-Bis[3-(2,3-dihydrofuran-3-yl)-2-oxapropyl]benzene (5)

Yield 79% (m.p. 64°C, colorless solid).

$^1\text{H NMR}$ (CDCl_3): ($\delta = 3.28$ (m; 2H; -CH), 3.32 (dd; $2J = 8$ Hz, $^3J = 8$ Hz; 2H; CHOCHH'), 3.44 (dd; $^3J = 5$ Hz; 2H; $\text{CHCHH}'\text{O}$), 4.17 (dd; $2J = 9$ Hz, $^3J = 6$ Hz; 2H; $\text{OCHH}'\text{CH}$), 4.34 (dd; $^3J = 9$ Hz; 2H; $\text{OCHH}'\text{CH}$), 4.50 (s; 4H; OCH_2Ar), 4.89 (dd; $^3J = 2$ Hz, $^3J = 2$ Hz; 2H; OCHCH), 6.35 (dd; $4J = 2$ Hz; 2H; OCHCH), 7.30 (s; 4H; Ar).

^{13}C NMR (CDCl_3): ($\delta = 42.9$ (CH), 73.0 and 73.1 and 73.4 ($\text{OCH}_2\text{CHCH}_2\text{OCH}_2$), 100.9 (OCHCH), 128.1 (Ar), 137.7 (Ar), 147.1 (OCHCH).

IR (KBr): 2856 (m, C-H), 1615 (m, C=C-O), 1134 (s, C-O), 1101 (s, C-O), 1086 (s, C-O), 1017 (s, C-O), 904 (m), 806 (m), 724 cm^{-1} (m, C=C-H).

$\text{C}_{18}\text{H}_{22}\text{O}_4$ (302.37):	Calcd.	C 71.50	H 7.33
	Found	C 71.28	H 7.36

1,3,5-Tris[3-(2,3-dihydrofuran-3-yl)-2-oxa-propyl]benzene (6)

2.83 g (28.3 mmol) **2** was dissolved in 6.54 g aqueous potassium hydroxide (50 weight-%). 2.58 g $\alpha, \alpha', \alpha''$ -tribromomesitylene was added. Then 0.35 g (1.1 mmol) tetrabutylammonium bromide was suspended. The reaction mixture was stirred for 68 hours at room temperature. 50 mL water was added. The aqueous layer was extracted three times with 15 mL diethylether. The combined organic layers were dried over sodium sulphate and filtered. The solvent was removed under reduced pressure. The product was purified by column chromatography (eluent: hexane/ethyl acetate, 4/1, v/v). Yield: 54% (colorless oil).

^1H NMR (CDCl_3): ($\delta = 3.30$ (m; 3H; CH), 3.33 (dd; $^2\text{J} = 9$ Hz, $^3\text{J} = 9$ Hz; 3H; CHCHH'O), 3.45 (dd; $^3\text{J} = 5$ Hz; 3H; CHCHH'O), 4.17 (dd; $^2\text{J} = 9$ Hz, $^3\text{J} = 6$ Hz; 3H; OCHH'CH), 4.35 (dd; $^3\text{J} = 9$ Hz; 3H; CHH'CH), 4.51 (s; 6H; OCH_2Ar), 4.90 (dd; $^3\text{J} = 3$ Hz, $^2\text{J} = 3$ Hz; 3H; OCHCH), 6.36 (dd; $^4\text{J}_{5,3} = 2$ Hz; 3H; OCHCH), 7.25 (s; 3H; Ar).

^{13}C NMR (CDCl_3): ($\delta = 42.9$ (OCH_2CH), 73.0 and 73.1 and 73.6 ($\text{OCH}_2\text{CHCH}_2\text{OCH}_2\text{Ar}$), 100.9 (OCHCH), 126.1 (Ar), 138.7 (Ar), 147.1 (OCHCH).

IR(KBr): 2854 (s, C-H), 1612 (s, C=C-O), 1457 (m, Ar), 1354 (m), 1239 (m), 1139 (s, C-O), 1101 (s, C-O), 1049 (m, C-O), 1002 (m), 908 (m), 861 (m), 723 cm^{-1} (s, C=C-H).

$\text{C}_{24}\text{H}_{30}\text{O}_4$ (414.50):	Calcd.	C 69.55	H 7.30
	Found	C 68.90	H 7.20

α, ω -Bis(2,3-dihydrofuran-3-carboxylato)-compounds

To 250 mL liquid ammonia 25 mL (325 mmol) isopropanol was added. 3.25 g (29 mmol) 3-furoic acid was dissolved in the ammonia. Then 2.55 g (111 mmol) sodium was added. The solution was heated to reflux 45 minutes until the blue color of the solution disappeared. The ammonia was removed overnight. The residue was dissolved in 50 mL water. The pH was tuned to 7.5 by adding solid carbon dioxide to the solution. 1.16 g (29 mmol) sodium hydroxide and 9.4 g (28

mmol) tetrabutylammonium bromide were added. The solvent was removed under reduced pressure. The residue was suspended in 50 mL dimethylformamide. 14 mmol of the dibromo compound were added. The reaction mixture was stirred for 24 hours. The solvent was removed under reduced pressure. The products were purified as follows.

1,10-Bis(2,3-dihydrofuran-3-carboxylato)decane (7)

7 was purified by flash chromatography (eluent hexane/ethyl acetate, 2:1, v/v). Yield: 53% (m.p. 37°C, colorless solid).

¹H NMR (CDCl₃): (δ = 1.30 (m; 12H; (CH₂)₂(CH₂)₃), 1.66 (m; 4H; OCH₂CH₂), 3.81 (m; 2H; CH), 4.12 (t; ³J = 7 Hz; 4H; OCH₂), 4.40 (dd; ²J = 9 Hz, ³J = 9 Hz; 2H; OCHH'CH), 4.66 (dd; ³J = 7 Hz; 2H, OCHH'CH), 5.03 (dd; ³J = 5 Hz, ³J = 3 Hz; 2H; OCHCH), 6.40 (dd; ⁵J = 2 Hz; 2H; OCHCH).

¹³C NMR (CDCl₃): (δ = 25.8, 28.6 and 29.2 and 29.4 (OCH₂(CH₂)₄), 47.4 (CH), 65.3 (OCH₂CH), 71.3 (CO₂CH₂), 98.86 (OCHCH), 147.8 (OCHCH), 172.8 (CO₂).

IR (film): 2924 (m, C-H), 2854 (m, C-H), 1734 (s, C=O), 1616 (m, C=C-O), 1465 (m, C-C), 1346 (m, O-CO), 1194 (m, C-O), 1142 (m, C-O), 1080 (m), 922 (m), 715 cm⁻¹ (m, C=C-H).

C ₂₀ H ₃₀ O ₆ (280.27):	Calcd.	C 65.55	H 8.25
	Found	C 65.28	H 8.18

1,4-Bis(2,3-dihydrofuran-3-carboxylato)but-2-en (8)

The product was purified by flash chromatography (eluent: hexane/ethyl acetate, 2:1, v/v). Yield: 62% (m.p. 37°C, colorless solid).

¹H NMR (CDCl₃): (δ = 3.83 (m; 2H; CHCO₂), 4.42 (dd; ²J = 9 Hz, ³J = 11 Hz; 2H; OCHH'CH), 4.63 (dd; ³J = 3 Hz, ⁴J = 2 Hz; 4H; OCH₂CH), 4.67 (dd; ³J = 7 Hz; 2H; OCHCH), 5.04 (dd; ³J = 3 Hz, ³J = 3 Hz; 2H; OCHCH), 5.86 (dd, ³J_{9,9'} = 2 Hz; 2H; OCH₂CH=), 6.42 (dd; ⁴J_{5,3} = 2 Hz; 2H; OCHCH).

¹³C NMR (CDCl₃): (δ = 47.3 (CHCO₂), 64.4 (OCH₂CH-), 71.2 (OCH₂CH), 96.6 (OCHCH), 128.0 (OCH₂CH=), 148.0 (OCHCH), 172.4 (CO₂).

IR (film): 2954 (m, C-H), 1735 (s, C=O), 1671 (m, C=C), 1616 (m, C=C-O), 1334 (m, O-CO), 1183 (s, C-O), 1142 (m, C-O), 1082 (m, C-O), 924 (m), 718 cm⁻¹ (m, C=C-H).

C ₁₄ H ₁₆ O ₆ (280.27):	Calcd.	C 60.00	H 5.75
	Found	C 60.32	H 5.79

1,4-Bis[(2,3-dihydrofuran-3-carboxylato)methyl]benzene (9)

The product was purified by recrystallization from hexane. Yield: 85% (m.p. 62°C, colorless solid).

¹H NMR (CDCl₃): (δ = 3.84 (m; 2H; CHCO₂), 4.41 (dd; ²J = 9 Hz, ³J = 11 Hz; 2H; OCH₂CH), 4.69 (dd; ³J = 7 Hz; 2H; OCH₂CH'), 5.05 (dd; ³J = 3 Hz; ³J = 5 Hz; 2H; OCHCH), 5.15 (s; 4H; OCH₂Ar), 6.41 (dd; ⁴J = 2 Hz; 2H; OCHCH), 7.35 (s; 4H; Ar).

¹³C NMR (CDCl₃): (δ = 47.3 (CHCO₂), 66.4 (OCH₂CH), 71.2 (OCH₂Ar), 98.6 (OCHCH), 128.5 (Ar), 135.9 (Ar), 148.0 (OCHCH), 172.5 (CO₂).

IR (KBr): 3088 (m, Ar-H), 2955 (m, C-H), 1727 (s, C=O), 1612 (m, C=C-O), 1438 (m, Ar-H), 1302 (s, O-CO), 1221 (s, C-O), 1086 (m, C-O), 984 (m), 914 (w), 748 cm⁻¹ (m, C=C-H).

C ₁₈ H ₁₈ O ₆ (330.34):	Calcd.	C 65.45	H 5.49
	Found	C 65.41	H 5.42

Bis[2,3-dihydrofuran-3-(methyloxycarbonyl)] Compounds*1,2-Bis[2,3-dihydrofuran-3-(methyloxycarbonyl)]ethane (10)*

1.79 (18 mmol) of **2** was dissolved in 25 mL of tetrahydrofuran. 0.1 g sodium (4.3 mmol) was added. The solution was heated to reflux for 1 hour and then was allowed to cool to room temperature. 1.30 g (6 mmol) of succinyl diimidazolide were added. The reaction mixture was stirred for 10 hours. The solvent was removed under reduced pressure. The residue was dissolved in 30 mL water and was extracted three times with 20 mL of diethyl ether. The solvent was removed under reduced pressure. The product was purified by flash chromatography (eluent: hexane/ethyl acetate; 1:1; v/v). Yield: 57% (m.p.: 42°C, colorless solid).

¹H NMR (CDCl₃): (δ = 2.63 (s; 4H; CH₂CO₂), 3.26 (m; 2H; CH), 3.94 - 4.17 (m; 6H; CH₂CHCH₂O₂C), 4.33 (dd; ²J = 9 Hz, ³J = 7 Hz; 2H; CH₂O₂C), 4.88 (dd; ³J = 3 Hz, ³J = 5 Hz; 2H; OCHCH), 6.39 (dd; ⁴J_{5,3} = 3 Hz; 2H; OCHCH).

¹³C NMR (CDCl₃): (δ = 29.0 (CH₂CO₂), 41.9 (CH), 66.8 (ROCH₂CH), 72.5 (CH₂O₂C), 100.1 (OCHCH), 147.8 (OCHCH), 172.1 (CO₂).

IR (film): 2955 (m, C-H), 2892 (m, CH), 1735 (s, C=O), 1613 (m, C=C-O), 1354 (m, O-CO), 1158 (s, C-O), 1044 (m, C-O), 1009 (m, C-O), 912 (m), 725 cm⁻¹ (s, C=C-H).

C ₁₄ H ₁₈ O ₆ (282.29):	Calcd.	C 59.57	H 6.43
	Found	C 58.91	H 6.41

1,3,5-Tris[2,3-dihydrofuran-3-(methyloxycarbonyl)]benzene (II)

2.5 g (25.0 mmol) **2** and 0.1 g (4.3 mmol) sodium were dissolved in 25 mL tetrahydrofuran. The solution was heated to reflux until all sodium had reacted. 1.5 g (4.2 mmol) 1,3,5-benzenetricarboxylic acid triimidazolide was dissolved in 20 mL tetrahydrofuran and added to the solution. The reaction mixture was stirred for 16 hours. The solvent was removed under reduced pressure. The residue was dissolved in 100 mL water and extracted four times with 50 mL diethyl ether. The combined organic layers were dried over sodium sulphate and filtered. The solvent was removed under reduced pressure. The product was purified by column chromatography (eluent: hexane/ethyl acetate, 1:1, v/v). Yield: 15% (m.p. 72°C, colorless solid).

¹H NMR (CDCl₃): (δ = 3.46 (m; 3H; -CH), 4.20 - 4.62 (3m; 9H; CHH'CHCH₂), 4.43 (dd; ²J = 10 Hz, ³J = 10 Hz; 3H; CHH'CHCH₂), 4.99 (dd; ³J = 3 Hz, ³J = 3 Hz; 3H; OCHCH), 6.45 (dd; ⁴J = 2 Hz; 3H; OCHCH), 8.76 (s; 3H; Ar).

¹³C NMR (CDCl₃): (δ = 42.0 (CH), 67.6 (ROCH₂), 72.5 (CH₂O₂C), 100.0 (OCHCH), 131.3 (Ar), 134.7 (Ar), 148.1 (OCHCH), 164.8 (CO₂).

IR (KBr): 2955 (m, C-H), 2892 (m, C-H), 1730 (s, C=O), 1613 (s, C=C-O), 1446 (m, C-C), 1384 (m, C-C), 1335 (m, O-CO), 1235 (s, C-O), 1141 (m, C-O), 1104 (m), 1042 (m), 1006 (m), 914 (m), 739 cm⁻¹ (s, C=C-H).

C ₂₄ H ₂₄ O ₉ (456.45):	Calcd.	C 63.15	H 5.30
	Found	C 63.01	H 5.32

Polymerizations

315 mg (4.50 mmol) 2,3-dihydrofuran and 7.70 mg (0.02 mmol) Irgacure[®]261 were mixed with **3-6** (0.10 mmol equivalents of 2,3-dihydrofuranyl moieties). **7-11** (0.10 mmol equivalents of 2,3-dihydrofuranyl groups) was mixed with 315 mg (4.50 mmol) 2,3-dihydrofuran and 19.32 mg (0.05 mmol) of Irgacure[®]261. The solutions were diluted with dichloromethane to 2 mL. 1 mL of the solution was irradiated with an Ushio UXM 200H Hg-Xe high pressure lamp at 200 mW cm⁻². The resulting polymer was washed with methanol and dried for 30 hours at 60°C and 5 mbar and finally analyzed by IR-spectroscopy.

Poly{[2,3-dihydrofuran]-co-[1,8-bis(2,3-dihydrofuran-3-yl)-2,7-dioxaoctane]} (**3a**)

IR (KBr): 2940 (s, C-H), 2870 (s, C-H), 1451 (m, C-C), 1365 (m, C-C), 1219(s, C-O), 1061(s, C-O), 851(m), 695 cm⁻¹ (m, C-H).

Poly{[2,3-dihydrofuran]-co-[1,8-bis(2,3-dihydrofuran-3-yl)-2,7-dioxaoct-2-en]}
(4a)

IR (KBr): 2934 (s, C-H), 2867 (s, C-H), 1458 (m, C-C), 1364 (m, C-C), 1219(s, C-O), 1063(s, C-O), 851(m), 697 cm⁻¹ (m, C-H).

Poly{[2,3-dihydrofuran]-co-[1,4-bis[3-(2,3-dihydrofuran-3-yl)-2-oxapropyl]-benzene]} (5a)

IR (KBr): 2941 (s, ArH), 2868 (s, C-H), 1637 (w, ArC), 1452 (m, ArC), 1362 (m, C-C), 1215(s, C-O), 1061(s, C-O), 924 (m), 809(m, ArH), 733 (m), 697 cm⁻¹ (m, C-H).

Poly{[2,3-dihydrofuran]-co-[1,3,5-tris[3-(2,3-dihydrofuran-3-yl)-2-oxapropyl]-benzene]} (6a)

IR (KBr): 2926 (s, ArH), 2868 (s, C-H), 1734 (w), 1609 (w, ArC), 1458 (m, ArC), 1364 (m, C-C), 1081(s, C-O), 730 (m), 697 cm⁻¹ (m, C-H).

Poly{[2,3-dihydrofuran]-co-[1,10-bis(2,3-dihydrofuran-3-carboxylato)decane]}
(7a)

IR (KBr): 2936 (s, C-H), 2857 (s, C-H), 1735 (s, C=O), 1457 (m, C-C), 1391 (m, C-C), 1353 (m, O-CO), 1185 (m, C-O), 1061 (s, C-O), 922 (m), 698 cm⁻¹ (m, C-H).

Poly{[2,3-dihydrofuran]-co-[1,4-bis(2,3-dihydrofuran-3-carboxylato)but-2-en]}
(8a)

IR (KBr): 2944 (s, C-H), 2871 (s, C-H), 1736 (s, C=O), 1451 (m, C-C), 1389 (m, O-CO), 1180 (m, C-O), 1061 (s, C-O), 975 (m), 921 (m), 732 (w), 698 cm⁻¹ (w, C-H).

Poly{[2,3-dihydrofuran]-co-[1,4-bis[(2,3-dihydrofuran-3-carboxylato)-methyl]benzene]} (9a)

IR (KBr): 2945 (s, ArH), 2871 (s, C-H), 1736 (s, C=O), 1451 (m, C-C), 1384 (m, O-CO), 1168 (m, C-O), 1056 (s, C-O), 923 (m), 732 (w), 697 cm⁻¹ (w, C-H).

Poly{[2,3-dihydrofuran]-co-[1,2-bis(2,3-dihydrofuran-3-(methyloxycarbonyl))-ethane]} (10a)

IR (KBr): 2970 (s, C-H), 2873 (s, C-H), 1737 (s, C=O), 1452 (m, C-C), 1357 (m, O-CO), 1266 (m, C-O), 1159 (m, C-O), 1062 (s, C-O), 922 (m), 732 (w), 695 cm⁻¹ (w, C-H).

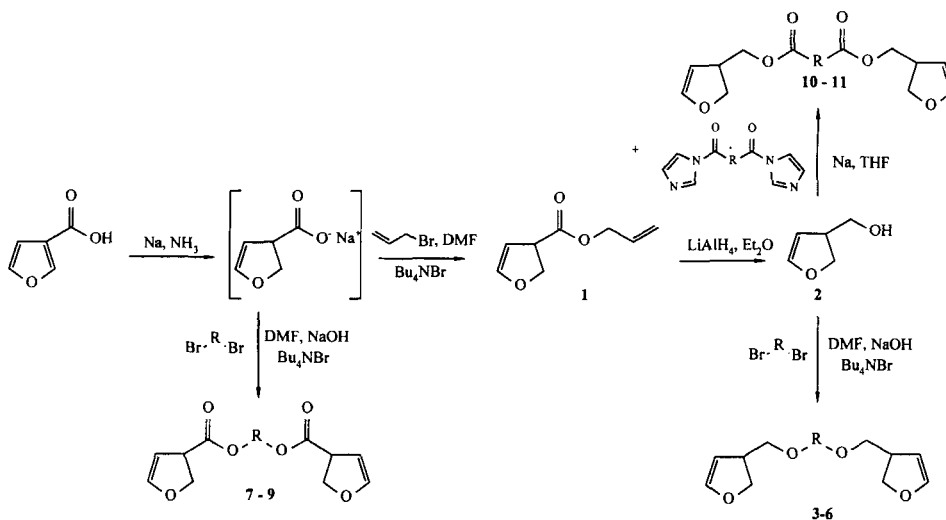


Figure 1. Synthesis of multifunctional 2,3-dihydrofuran derivatives.

Poly}{[2,3-dihydrofuran]-co-[1,3,5-tris(2,3-dihydrofuran-3-(methyloxycarbonyl)-benzene)]} (11a)

IR (KBr): 2944 (s, ArH), 2871 (s, C-H), 1734 (s, C=O), 1451 (m, C-C), 1331 (m, O-CO), 1241 (m, C-O), 1055 (s, C-O), 974 (m), 922(m), 740 cm^{-1} (m, C-H).

RESULTS AND DISCUSSION

Synthesis

Different multifunctional 2,3-dihydrofuran compounds with ether- and ester linkages and alkyl, alkenyl- and arylspacers were synthesized according to the procedures shown in Figure 1. 3-Furoic acid was reduced with a *Birch*-reduction to 2,3-dihydrofuran carboxylic acid sodium salt. The salt was converted to the esters **1** and **7-9** by $\text{S}_{\text{N}}2$ - reactions under phase transfer conditions.

1 could be easily isolated and reduced to 2,3-dihydro-3-hydroxymethylfuran **2**. From **2** the ethers **3-6** could be synthesized with *Williamson* ether synthesis with tetrabutylammonium bromide as a phase transfer catalyst. **2** could be converted to the corresponding oxycarbonylic compounds **10-11** by reaction with carboxylic acids imidazolides. The synthesized multifunctional monomers are shown in Figure 2.

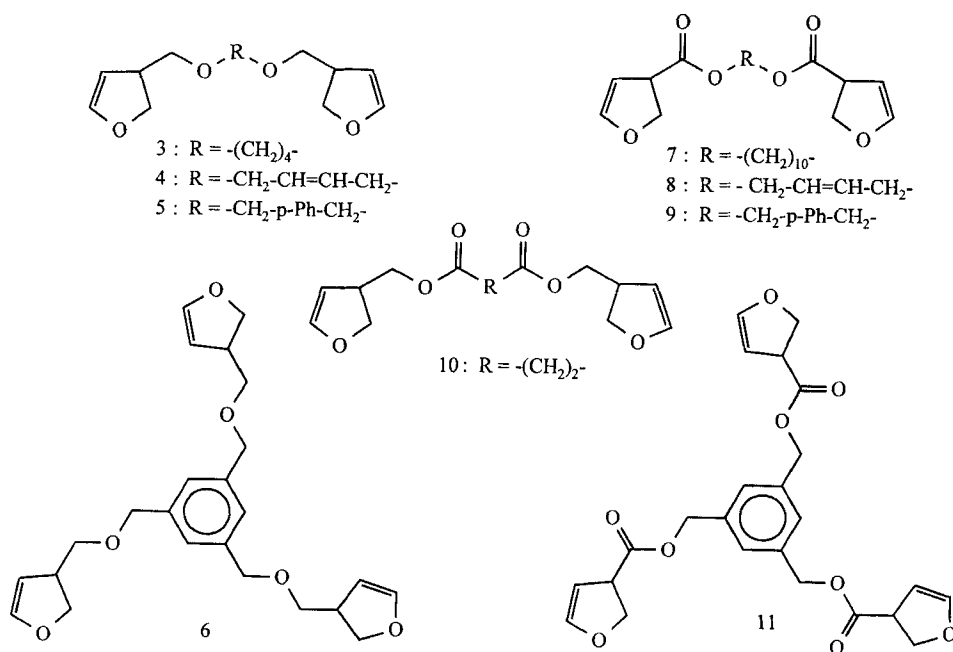


Figure 2. Synthesized multifunctional monomers.

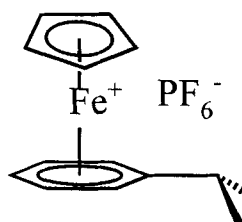


Figure 3. Irgacure[®]261.

The behavior of these multifunctional monomers in the photoinduced cationic polymerization was investigated. As initiator (η^5 -cyclopentadienyl)-Fe(II)-(η^6 -isopropylbenzene) hexafluorophosphate (Irgacure[®]261) was used (Figure 3).

Reactivities

Reactivity and thermal behavior depend on the structure of the multifunctional compound. 2,3-Dihydrofuran copolymerizes faster with ether compounds like **3-6** than with esters like **7-11**. The relative reactivities were

estimated by observation of the gelation point during copolymerization. It was found that the gelation point for **3-6** was reached between 1 and 3 minutes (t_{GP}). The copolymers with **7-11** showed a gelation point after 4 to 5 minutes, although the initiator concentration in copolymerization with **7-11** was more than twice as high as in copolymerization with **3-6**. We propose that the lower reactivity of esters is due to their carbonyl groups. It is known that carbonyl oxygen atoms tend to complex protons more strongly than ether oxygen atoms. These complexations can retard cationic polymerization [12, 13].

Thermal Behavior

The copolymers **3a-11a** decompose between 350°C (**8a**) and 384°C (**11a**). These decomposition temperatures (T_d) are slightly higher as the of linear poly(2,3-tetrahydrofurandiyl) (350°C) [9]. Therefore, the limiting factor should not be a decomposition of the ester- or ether linkages. To compare the thermal properties of different crosslinked poly(2,3-tetrahydrofurandiyl)s, the length of the spacers was varied.

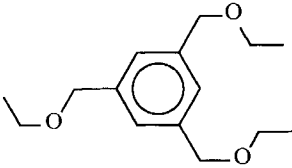
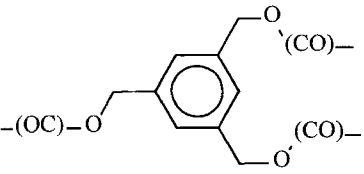
While the thermal stability of the ethers **3a** and **6a** are similar to that of the oxycarbonylic compounds **10a** and **11a**, the carboxylato compound **8a** is less stable as its ether analogous **4a**. Moreover, the compounds **3a** and **7a** containing alkyl spacers are more stable than their alkenyl analogous **4a** and **8a** and as the corresponding aryl compounds **5a** and **9a**. These results are summarized in Table 1.

The glass transition temperature (T_g) depends also on the chosen spacer. The glass transition temperatures of the copolymers synthesized with the trifunctional compounds as **6a** or **11a** are higher compared to their bifunctional analogous as **5a**. The T_g of the ether compound **4a** is shifted to higher temperatures compared with its analogous carboxylic compound **8a**. The T_g of **3a** is lower than that of the comparable oxycarbonylic compound **10a**.

Within the substance class of the ether-linked comonomers, the T_g of the copolymer synthesized alkenyl compound **4a** is higher than that of the similar alkyl compound **3a**. When the chain length of the alkyl compound is much larger than that of the alkenyl compound the opposite tendency is observed. Therefore the T_g of the carboxylato compound **7a** is higher than that of the carboxylato compound **8a**.

From these results, the following conclusions can be drawn: crosslinked poly(2,3-tetrahydrofurandiyl)s, synthesized with etherlinked multifunctional monomers or with oxycarbonylic compounds are thermally more stable than comparable copolymers containing carboxylic functions. Copolymers, which contain cross-linking units with alkyl spacers, are more stable than those with alkenyl- or aryl-

TABLE 1: T_d , T_g and t_{GP} of **3a** - **11a**.

polymer	bridge	T_d / °C	T_g / °C	t_{GP} / min
3a	$-\text{CH}_2\text{-O-(CH}_2)_4\text{-O-CH}_2\text{-}$	383	120	3.0
4a	$-\text{CH}_2\text{-O-CH}_2\text{-CH=CH-CH}_2\text{-O-CH}_2\text{-}$	377	130	2.5
5a	$-\text{CH}_2\text{-O-CH}_2\text{-p-Ph-CH}_2\text{-O-CH}_2\text{-}$	373	110	1.5
6a		379	161	3.0
7a	$-(\text{CO})\text{-O-(CH}_2)_{10}\text{-O-(CO)-}$	381	127	4.0
8a	$-(\text{CO})\text{-O-CH}_2\text{-CH=CH-CH}_2\text{-O-(CO)-}$	348	109	5.0
9a	$-(\text{CO})\text{-O-CH}_2\text{-p-Ph-CH}_2\text{-O-(CO)-}$	358	106	5.0
10a	$-\text{CH}_2\text{-O-(CO)-(CH}_2)_2\text{-(CO)-O-CH}_2\text{-}$	382	130	3.5
11a		384	133	5.0
poly(2,3-tetrahydrofuran-2-yl)	---	350	130	---

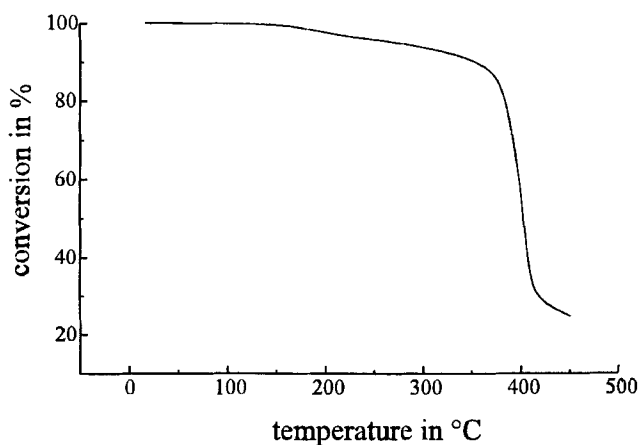


Figure 4. Decomposition curve of **5a**.

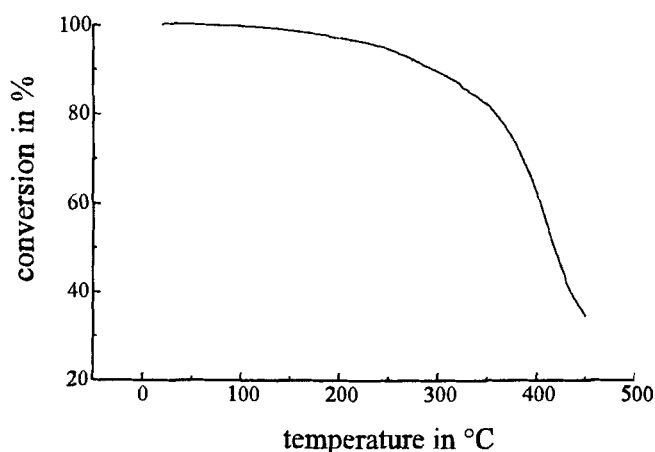


Figure 5. Decomposition curve of **9a**.

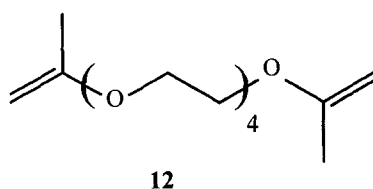


Figure 6. Tetraethyleneglycol-bis-2-propenylether.

spacers, if the connecting functional group is constant. The T_g can be increased using comonomers with more than two polymerizable groups. The T_g can be also maximized by the choice of the substance class of the comonomer. The T_g of oxycarbonylic compounds is higher than that of ether or carboxylato compounds. Moreover, within one substance class, the use of alkenyl compounds leads to a higher T_g than the of alkyl- or aryl compounds.

The decomposition behaviors of ether- and ester functionalized copolymers are different. The decomposition behaviors of **5a** and **9a** are shown in Figures 4 and 5, respectively. While **7a** to **11a** show a longer region within, they decompose, **3a** to **6a** have a definite decomposition point.

In order to compare the differences between multifunctional monomers with 2,3-dihydrofuranyl moieties and other polymerizable groups, 2,3-dihydrofuran was copolymerized with tetraethyleneglycol-bis-2-propenylether (**12**).

12 seemed to be a useful multifunctional comonomer for crosslinking, since its reactivity towards 2,3-dihydrofuran should be high enough to guarantee the

synthesis of homogenous networks [9]. While the polymers synthesized with **3a** to **11a** are at least thermally as stable as poly(2,3-tetrahydrofuran diyl), the copolymer of 2,3-dihydrofuran with **12** (**12a**) decomposed at 180°C. This low T_d might be due to its quaternary (-C-atom next to ether oxygen. Such ethers can be cleaved thermally by a S_N1 -reaction under acid catalysis. The protons, necessary for the cleavage, might be supplied from photo acid, which could not be removed quantitatively.

ACKNOWLEDGEMENT

The authors wish to thank the BASF AG for financial support.

REFERENCES

- [1] D. A. Barr and J. B. Rose, *J. Chem. Soc.*, 3766 (1954).
- [2] J. B. Kim and I. Cho, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3733 (1989).
- [3] F. Sanda and M. Matsumoto, *Macromolecules*, **28**, 6911 (1995).
- [4] Y. Ogawa, M. Sawamoto, and T. Higashimura, *Polym. J.*, **16**, 415 (1984).
- [5] J. A. Moore and R. Wille, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **24**(2), 317 (1983).
- [6] G. J. Schmitt and C. Schuerch, *J. Polym. Sci.*, **49**, 287 (1961).
- [7] O. Nuyken and S. Aechtner, *Polym. Bull.*, **28**, 117 (1992).
- [8] C. T. Thu, T. Bastelberger, and H. Höcker, *Makromol. Chem., Rapid. Commun.*, **2**, 383 (1981).
- [9] O. Nuyken, R. B. Raether, and C. E. Spindler, manuscript submitted.
- [10] W. Reppe and W. J. Schwekendiek, *Liebigs Ann. Chem.*, **560**, 104 (1948).
- [11] H. A. Staab and A. Mannschreck, *Chem. Ber.*, **95**, 1284 (1962).
- [12] S. Aoshima and T. Higashimura, *Macromolecules*, **22**, 1009 (1989).
- [13] T. Higashimura, Y. Kishimoto, and S. Aoshima, *Polym. Bull.*, **18**, 111 (1987).

Received June 16, 1997

No Revisions