

ORIGINAL ARTICLE

Terephthalaldehyde- and isophthalaldehyde-based polyspiroacetals

Hayal Bulbul Sonmez¹, Figen Gonul Kuloglu¹, Koksal Karadag¹ and Fred Wudl²

Condensations of polyhydroxyl monomers with terephthalaldehyde or isophthalaldehyde give the corresponding polyspiroacetals. The effects of various dialdehydes and multihydroxy monomers on the properties of the resulting polymer have been examined. Model compounds were synthesized by the condensation of multihydroxy monomers with benzaldehyde. The model compounds and polymers were characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance (NMR), thermogravimetric analysis and differential scanning calorimetry. The proposed polymer structure is supported by the solid-state CPMAS ¹³C NMR spectrum of the model compound. The synthesized polyspiroacetals are thermally stable, have a high degree of chemical stability and are soluble in hexafluoroisopropanol.

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INTRODUCTION

Ladder polymers have been pursued by many researchers because their rigidity results in a lack of rotational freedom and good thermal and chemical stability.¹ Spiro polymers are a subclass of ladder polymers where two adjacent rings share an atom.^{1,2} Ladder and spiro polymers are therefore of particular interest because they generally possess increased resistance to degradation compared with conventional polymers.^{2,3}

The first organic spiro polymer was synthesized by the reaction of 1,4 cyclohexanedione and pentaerythritol in the presence of an acid.⁴ This polymer was thermally stable and crystalline. A number of other polyspiroketals were also prepared by the condensations of various cyclic diketones and tetraols, resulting in polymers with good chemical and thermal stabilities.⁵ Several spiroacetals were prepared by the reaction of carbonyl compounds and multihydroxy monomers. Cohen and coworkers synthesized thermoplastic polyspiroacetal resins using dialdehydes with pentaerythritol or pentaerythritol–dipentaerythritol mixtures. Not surprisingly, these polymers had limited solubility in common solvents and exhibited high melting points.⁶ Later, the same group prepared spiro polymers and copolymers derived from pentaerythritol, dipentaerythritol and glutaraldehyde.⁷ Results show that spiroacetal unit-bearing polymers exhibited excellent mechanical properties, including high strength and hardness as well as heat and water resistance.⁸ In general, the high melting points and low solubilities of spiroacetals indicate strong inter-chain forces and a high degree of order. Recently, a series of new cyclic acetals of 2-hydroxybenzaldehyde has been investigated for a correlation between the acetal structure and its biological activity.⁹ Makhseed and McKeown¹⁰ prepared a spiro polymer that was soluble in organic

solvents from the reaction of pentaerythritol with an alkyl-bearing diketone.

Previously, we synthesized a spiro polymer by the reaction of 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane and terephthalaldehyde in toluene in the presence of a trace amount of acid.³ In this study, a series of spiro polymers based on terephthalaldehyde and isophthalaldehyde was synthesized to examine the effects of different dialdehyde and multihydroxy monomers on polymer properties.

EXPERIMENTAL PROCEDURE

Reagents and equipment

The highest purity grade of each chemical available from Aldrich (Taufkirchen bei München, Germany) was used without further purification.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer (Bio-Rad, Hercules, CA, USA) using KBr pellets. ¹³C solid-state nuclear magnetic resonance (NMR) spectra were recorded on a 500-MHz Varian Inova spectrometer (Varian, Palo Alto, CA, USA) in a magic angle spinning (MAS) probe at 75.476 MHz. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at 10 °C min⁻¹ with a Mettler Toledo model TGA/SDTA 851 (Mettler Toledo, Greifensee, Switzerland). Differential scanning calorimetry (DSC) was performed with a Mettler TA Instrument DSC 822 at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere.

Synthesis of the monomers

Synthesis of 2,2,6,6-Tetrakis(hydroxymethyl)cyclohexanone. This compound was synthesized according to Mannich and Brose.¹¹ m.p.: 142.6–143.5 °C. Mass *m/z* (M+Na): 241 g mol⁻¹. FT-IR: 3370, 2940, 2875, 1690, 1061 and 1000 cm⁻¹. ¹H-NMR (DMSO-d₆): δ (p.p.m.): 4.46 (-CH₂OH), 3.5–3.3 (C_{quaternary}-CH₂-OH) and 1.8–1.7 (-C(=O)-C_{quaternary}-CH₂- and -C(=O)-C_{quaternary}-CH₂-CH₂-).

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^{13}C NMR: (DMSO- d_6): δ (p.p.m.): 218 ($\underline{\text{C}}=\text{O}$), 64 ($\underline{\text{C}}\text{H}_2\text{-OH}$), 55 (C, quaternary), and 28 and 17 ($-\text{C}(=\text{O})\text{-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}$ and $-\text{C}(=\text{O})\text{-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-}$).

Synthesis of 2,2,6,6-Tetrakis(hydroxymethyl)cyclohexanol. This compound was synthesized according to Witcoff.¹² m.p.: 127–132 °C. Mass m/z (M+Na): 243 g mol^{-1} . FT-IR: 3497, 3267, 2954, 1400, 1016 and 776 cm^{-1} . ^1H NMR (DMSO- d_6): δ (p.p.m.): 4.66 ($\underline{\text{C}}\text{H-OH}$), 4.48 ($\underline{\text{C}}\text{H}_2\text{-OH}$), 3.71 ($\underline{\text{C}}\text{H-OH}$), 3.55 and 3.45 ($\underline{\text{C}}\text{H}_2\text{-OH}$), and 1.5 and 1 ($-\underline{\text{C}}\text{H}_2\text{-}$). ^{13}C NMR (DMSO- d_6): δ (p.p.m.): 76 ($-\underline{\text{C}}\text{H-OH}$), 67 and 62 ($-\underline{\text{C}}\text{H}_2\text{-OH}$), 43 (C, quaternary), 27 and 16 ($-\text{HO}\underline{\text{C}}_{\text{tertiary}}\text{H-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}$ and $-\text{HO}\underline{\text{C}}_{\text{tertiary}}\text{H-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-}$).

Synthesis of 2,2,5,5-Tetrakis(hydroxymethyl)cyclopentanone. This compound was synthesized according to Ray.¹³ m.p.: 145.9–147.5 °C. Mass m/z (M+Na): 227 g mol^{-1} . FT-IR: 3200, 2960, 2888, 1725 and 1045 cm^{-1} . ^1H NMR (DMSO- d_6): δ (p.p.m.): 4.59 ($\underline{\text{C}}\text{H}_2\text{-OH}$), 3.43–3.24 ($\underline{\text{C}}\text{H}_2\text{-OH}$) and 1.97 ($-\underline{\text{C}}\text{H}_2\text{-}$). ^{13}C NMR (DMSO- d_6): δ (p.p.m.): 222 ($\underline{\text{C}}=\text{O}$), 62 ($\text{C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-OH}$), 59 (C, quaternary) and 24 ($-\text{C}(=\text{O})\text{-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}$ or $-\text{C}(=\text{O})\text{-C}_q\text{-}\underline{\text{C}}\text{H}_2\text{-}\underline{\text{C}}\text{H}_2\text{-}$).

Synthesis of 1,4 dicarbaldehydecyclohexane. This compound was synthesized according to Feuerbacher *et al.*¹⁴ FT-IR: 2938, 2857, 1715, 1445, 1136 and 915 cm^{-1} . ^1H -NMR (CHCl_3): δ (p.p.m.): 1.31–1.37 ($\underline{\text{C}}\text{H}_2$), 1.74–1.80 ($\underline{\text{C}}\text{H}_2$), 2.10–2.2- ($\underline{\text{C}}\text{H}_2$) and 9.60–9.63 ($\underline{\text{C}}\text{HO}$).

Synthesis of 1,1,4,4-Tetrakis(hydroxymethyl)cyclohexane. This compound was synthesized according to Herwig *et al.*¹⁵ using cis,trans-cyclohexane-1,4-dicarbaldehyde and formaldehyde. The resulting product was recrystallized from ethyl acetate. m.p. 222 °C (reported 219–225 °C). Mass m/z (M+Na): 227 g mol^{-1} . FT-IR: 3370, 2904, 2842, 1070, 1017 and 672 cm^{-1} . ^1H -NMR (DMSO- d_6): δ (p.p.m.): 4.26 ($\underline{\text{OH}}$), 3.38 ($-\underline{\text{C}}\text{H}_2\text{-OH}$) and 1.2 ($\underline{\text{C}}\text{H}_2$). ^{13}C NMR: (DMSO- d_6): δ (p.p.m.): 65.2 ($\underline{\text{C}}\text{H}_2\text{-OH}$), 39.8 (C, quaternary) and 24.2 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring).

Synthesis of model compounds

Synthesis of Model 1: 3,11-diphenyl-2,4,10,12-tetraoxadispiro[5.1.5.3]hexadecan-7-one. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.5 g (2.29 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone in 2 ml *N*-methyl-2-pyrrolidone (NMP), 0.49 g (4.63 mmol) benzaldehyde, 20 mg methane sulfonic acid and 50 ml benzene. The mixture was heated under reflux until no more water was collected in the Dean–Stark trap, followed by cooling to room temperature. The resulting precipitate was collected by filtration and washing with a 5% sodium bicarbonate solution and ether. The residue was crystallized from ethanol to give 0.6 g (66%) of 3,11-diphenyl-2,4,10,12-tetraoxadispiro[5.1.5.3]hexadecan-7-one. m.p.: 241.1 °C. Mass m/z (M+Na): 417 g mol^{-1} . FT-IR: 3040, 2961, 2884, 1666, 1448, 1119, 760 and 690 cm^{-1} . ^1H NMR (CDCl_3), δ (p.p.m.): 1.9 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 2.2 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 4.0 ($\underline{\text{C}}\text{H}_2\text{-O}$), 5.3 ($\underline{\text{C}}\text{H-O}$) and 7.4 (benzene ring). ^{13}C NMR (CDCl_3), δ (p.p.m.): 17 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 31 ($\underline{\text{C}}\text{H}_2\text{C}$, cyclohexane ring), 49 (C, quaternary, cyclohexane ring), 72 ($\underline{\text{C}}\text{H}_2\text{O}$), 102 ($\underline{\text{C}}\text{HO}_2$, acetal), and 126, 130 and 138 (benzene ring).

Synthesis of Model 2: 3,11-diphenyl-2,4,10,12-tetraoxa-dispiro[5.1.5.3]hexadecan-7-ol. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 1 g (4.54 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol in 2 ml NMP, 0.92 ml (9.08 mmol) benzaldehyde, 20 mg methane sulfonic acid and 50 ml benzene. The mixture was heated under reflux until no more water was collected in the Dean–Stark trap, followed by cooling to room temperature. The resulting precipitate was collected by filtration and washing with a 5% sodium bicarbonate solution and ether. The residue was crystallized from ethanol:benzene (95:5) to give 0.37 g (20%) of 3,11-diphenyl-2,4,10,12-tetraoxadispiro[5.1.5.3]hexadecan-7-ol. m.p.: 187.5–189 °C. Mass m/z : 419 g mol^{-1} (M+Na). FT-IR: 3400, 3095, 2998, 2820, 1115, 1011, 788, 604 and 530 cm^{-1} . ^1H NMR (CDCl_3), δ (p.p.m.): 1.19 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 2.4 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 3.5 ($\underline{\text{C}}\text{H}_2\text{-O}$), 4.26 ($\underline{\text{C}}\text{H-OH}$), 4.40 ($\underline{\text{OH}}$, cyclohexanol), 5.4 ($\underline{\text{C}}\text{H-O}$) and 7.52–7.4 (benzene ring). ^{13}C NMR (CDCl_3), δ (p.p.m.): 17 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 26 ($\underline{\text{C}}\text{H}_2\text{C}$, cyclohexane ring), 37.9 (C, quaternary, cyclohexane ring), 76 ($\underline{\text{C}}\text{H}_2\text{O}$), 79 ($\underline{\text{C}}\text{H-OH}$), 101 ($\underline{\text{C}}\text{HO}_2$, acetal), and 126, 128 and 138 (benzene ring).

Synthesis of Model 3: 3,11-diphenyl-2,4,10,12-tetraoxa-dispiro[5.1.5.2]pentadecan-7-one. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 1 g (4.9 mmol) 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone in 2 ml NMP, 1 ml (9.8 mmol) benzaldehyde, 20 mg methane sulfonic acid and 50 ml benzene. The mixture was heated under reflux until no more water was collected in the Dean–Stark trap, followed by cooling to room temperature. The resulting precipitate was collected by filtration and washing with a 5% sodium bicarbonate solution and ether. The residue was crystallized from ethanol:benzene (95:5) to give 0.56 g (30%) of 3,11-diphenyl-2,4,10,12-tetraoxa-dispiro[5.1.5.2]pentadecan-7-one. m.p.: 203 °C. Mass m/z : 403 g mol^{-1} (M). FT-IR: 3300, 2975, 2860, 1715, 1465, 1105, 760 and 690 cm^{-1} . ^1H NMR (CDCl_3), δ (p.p.m.): 2.4 ($\underline{\text{C}}\text{H}_2$, cyclopentane ring), 3.9 ($\underline{\text{C}}\text{H}_2\text{-O}$), 5.5 ($\underline{\text{C}}\text{H-O}$) and 7.3–7.6 (benzene ring). ^{13}C NMR (CDCl_3), δ (p.p.m.): 29 ($\underline{\text{C}}\text{H}_2$, cyclopentane ring), 53 (C, quaternary, cyclopentane ring), 71.5 ($\underline{\text{C}}\text{H}_2\text{O}$), 101 ($\underline{\text{C}}\text{HO}_2$, acetal), and 125, 130 and 138 (benzene ring).

Synthesis of Model 4: 3,12-diphenyl-2,4,11,13-tetraoxadispiro[5.2.5.2]hexadecane. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.5 g (1.9 mmol) 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane in 1 ml dimethyl sulfoxide (DMSO), 0.39 ml (3.8 mmol) benzaldehyde, 20 mg methane sulfonic acid and 50 ml benzene. The mixture was heated under reflux until no more water was collected in the Dean–Stark trap, followed by cooling to room temperature. The resulting precipitate was collected by filtration and washing with a 5% sodium bicarbonate solution and ether. The residue was crystallized from ethanol to give 0.34 g (54%) of 3,12-diphenyl-2,4,11,13-tetraoxadispiro[5.2.5.2]hexadecane. m.p.: 208–210 °C. Mass m/z : 381 g mol^{-1} (M). FT-IR: 3300, 2978, 2808, 1123, 1034, 1010, 755 and 690 cm^{-1} . ^1H NMR (CDCl_3), δ (p.p.m.): 1.23 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 1.8 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 3.9 ($\underline{\text{C}}\text{H}_2\text{-O}$), 5.32 ($\underline{\text{C}}\text{H-O}$) and 7.0–7.8 (benzene ring). ^{13}C NMR (CDCl_3), δ (p.p.m.): 25 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 26.9 ($\underline{\text{C}}\text{H}_2$, cyclohexane ring), 33 (C, quaternary, cyclohexane ring), 74.3 ($\underline{\text{C}}\text{H}_2\text{O}$), 102.8 ($\underline{\text{C}}\text{HO}_2$, acetal), and 126, 129 and 139 (benzene ring).

Synthesis of polymers

Synthesis of Poly 1: synthesis of spiro polymer from 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone and terephthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.5 g (2.29 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone in 3 ml DMSO, 0.32 g (2.27 mmol) terephthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 60 ml of benzene. After the mixture had been heated with rapid stirring, another 30 ml of benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.33 g of white powdered polymer was obtained. FT-IR: 3500, 3040, 2980, 2835, 1693, 1368, 1305 and 1119 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): $-\text{C}=\text{O}$ at 200, aromatic rings at 120–140, 101 acetal C, $-\text{C}_q\text{-O}$ 60–80, quaternary C 50, $-\text{C}_q\text{-}$ at 20–32.

Synthesis of Poly 2: synthesis of spiro polymer from 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol and terephthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 1 g (4.55 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol in 1 ml NMP, 0.61 g (4.55 mmol) terephthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 1.36 g white powdered polymer was obtained. FT-IR: 3500, 2950, 1707, 1380, 1300, 1633, 1126, 1693 and 1119 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): $-\text{C}=\text{O}$ at 200, aromatic rings at 127–140, 103 acetal C, $\text{C}_q\text{-OH}$ at 88, $-\text{C}_q\text{-O}$ at 75 p.p.m. and $-\text{C}_q\text{-}$ (cyclohexane) at 15–38.

Synthesis of Poly 3: synthesis of spiro polymer from 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and terephthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 1 g (4.90 mmol) 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone in 1 ml NMP, 0.66 g (4.9 mmol) terephthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.82 g of white powdered polymer was obtained. FT-IR: 3400, 2990, 2828, 1693, 1465, 1296, 1212 and 1105 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): $-\text{C}=\text{O}$ at 200, aromatic rings at 110–140, 100 acetal C, $-\text{CH}_2-\text{O}$ at 60–80 and $-\text{CH}_2-$ (cyclopentane) at 10–50.

Synthesis of Poly 4: synthesis of spiro polymer from 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane and terephthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.4 g (1.9 mmol) 1,1,4,4-tetrakis(hydroxymethyl)cyclohexanol in 1 ml NMP, 0.254 g (1.9 mmol) terephthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.51 g white powdered polymer was obtained. FT-IR: 3300, 2987, 2808, 1700, 1376, 1235, 1137 and 1073 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): quaternary C of phenyl ring at 180, aromatic rings at 140–125, 101 acetal C, CH_2-O at 80, quaternary C of cyclohexane ring at 41.3 and $-\text{CH}_2-$ (cyclohexane) at 21–35.

Synthesis of Poly 5: synthesis of spiro polymer from 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone and isophthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.5 g (2.38 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone in 1 ml NMP, 0.32 g (2.38 mmol) isophthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.3 g white powdered polymer was obtained. FT-IR: 3350, 2985, 1700, 1377, 1300 and 1118 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): $\text{C}=\text{O}$ at 193, quaternary C of phenyl ring at 180, aromatic rings at 141–125, 100 acetal C, CH_2-O at 65–76 p.p.m., quaternary C of cyclohexane ring at 48 and $-\text{CH}_2-$ (cyclohexane) at 12–35.

Synthesis of Poly 6: synthesis of spiro polymer from 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol and isophthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.5 g (2.3 mmol) 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol in 1 ml NMP, 0.30 g (2.3 mmol) isophthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.52 g white powdered polymer was obtained. FT-IR: 3630, 3171, 2988, 2804, 1720, 1678, 1395, 1176, 1120 and 1071 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): quaternary C of phenyl ring at 180, aromatic rings at 130–123, 96–100 acetal C, CH_2-O at 88–71 p.p.m., quaternary C of cyclohexane ring at 49 and $-\text{CH}_2-$ (cyclohexane) at 35–40.

Synthesis of Poly 7: synthesis of spiro polymer from 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and isophthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 1 g (2.3 mmol) 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone in 1 ml NMP, 0.32 g (2.3 mmol) isophthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.5 g white powdered polymer was obtained. FT-IR: 3350, 2985, 1720, 1377, 1286 and 1180 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): $\text{C}=\text{O}$ 215, quaternary C of phenyl ring at 188, aromatic rings at 125–180, 100 acetal C, CH_2-O at 69–74 p.p.m., quaternary C of cyclopentane ring at 50 and $-\text{CH}_2-$ (cyclohexane) at 25–29.

Synthesis of Poly 8: synthesis of spiro polymer from 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane and isophthalaldehyde. A 100-ml round-bottomed flask equipped with a magnetic stirrer, a Dean–Stark trap and a reflux condenser was charged with 0.4 g (1.9 mmol) 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane in 1 ml NMP, 0.254 g (1.9 mmol) terephthalaldehyde and 20 mg methane sulfonic acid. The mixture was refluxed in 50 ml benzene. After the mixture had been heated with rapid stirring, another 30 ml benzene was added, and the mixture was refluxed until no further water was collected in the trap. After filtration, the solid was washed with a sodium bicarbonate solution, water and finally with ether. The solid was dried under vacuum and 0.45 g white powdered polymer was obtained. FT-IR: 3370, 2994, 2810, 1714, 1690, 1380, 1238, 1114 and 1059 cm^{-1} . ^{13}C CPMAS NMR: δ (p.p.m.): quaternary C of phenyl ring at 180, aromatic rings at 140–117, 100 acetal C, CH_2-O at 85–66 p.p.m., quaternary C of cyclohexane ring at 43–37 and $-\text{CH}_2-$ (cyclohexane) at 25–29.

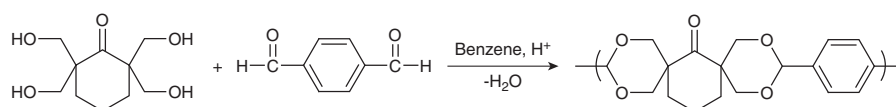
RESULTS AND DISCUSSION

To prepare the desired polyspiroacetals, the synthesis of certain tetraol monomers was required. To this end, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol, 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane were synthesized and characterized.

The synthesized tetrakis hydroxyl monomers were condensed with terephthalaldehyde and isophthalaldehyde in the presence of an acid catalyst and continuous water removal to afford new polyspiroacetals as white polymer precipitates. The polymerization reaction of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone and terephthalaldehyde is given in Scheme 1 as an example.

For polymerization by acetalization, equimolar quantities of the multihydroxy monomer and the dialdehyde monomer were dissolved in benzene. **Poly 1** through **Poly 4** used terephthalaldehyde as the dialdehyde monomer, and **Poly 5** to **Poly 8** used isophthalaldehyde (Table 1). In our previous work, we reported the synthesis of **Poly 4**, which was synthesized from the condensation of 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane and terephthalaldehyde.³ In the present study, we repeated this polymerization to allow a direct comparison between this polymer and the other polymers synthesized here. The structures of the resulting polymers were determined by FT-IR, solid-state CPMAS ^{13}C NMR and thermal analysis.

To better understand the polymer structures, model compounds were synthesized by the reactions of the multihydroxy monomers with benzaldehyde (Scheme 2). The tetraols 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone, 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol



Scheme 1 Polymerization of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanone with terephthalaldehyde.

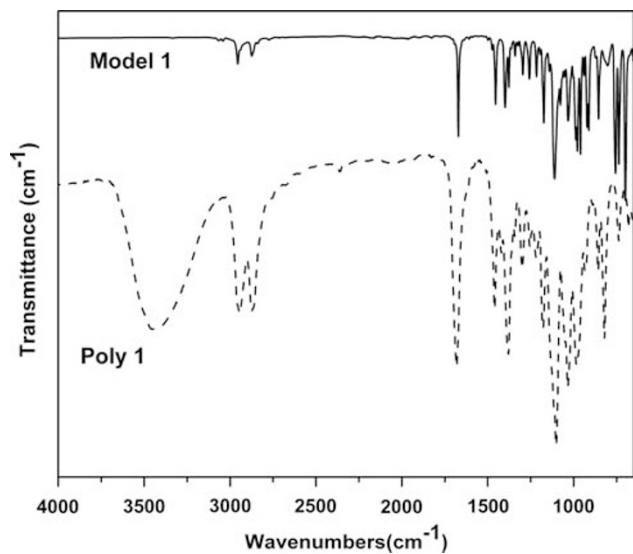


Figure 1 FT-IR spectra of **Model 1** and **Poly 1**.

2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane were allowed to react with benzaldehyde to give **model compounds 1–4**. The FT-IR spectra of the model compounds and polymers were essentially superimposable (Figure 1). The presence of a carbonyl peak at 1700 cm^{-1} and a hydroxyl function at $\sim 3400\text{ cm}^{-1}$ in the FT-IR spectrum of the polymers is an indication of the desired structure containing carbonyl and hydroxyl functionalities as end groups. From the FT-IR spectra of representative polyspiroacetals, strong absorption bands resulting from spiroacetal groups appeared at $1000\text{--}1300\text{ cm}^{-1}$. **Model compounds 2 and 4** gave no spectral evidence of a carbonyl functionality, as expected from their structures.

Comparison of the CPMAS solid-state ^{13}C NMR spectra of **model compound 1** and **Poly 1** (Figure 2) confirm the proposed structure of the polymer. In the solid-state ^{13}C NMR spectrum of the polymer, the resonances at 200 p.p.m. are attributed to the carbonyl group and aromatic ring carbons appearing at 120–140 p.p.m. The resonances at 101 and 60–80 p.p.m. confirm the presence of the acetal carbon and the $\text{CH}_2\text{-O}$ moiety, respectively. The signals at 20–32 p.p.m. are attributed to the cyclohexane carbons, and those at

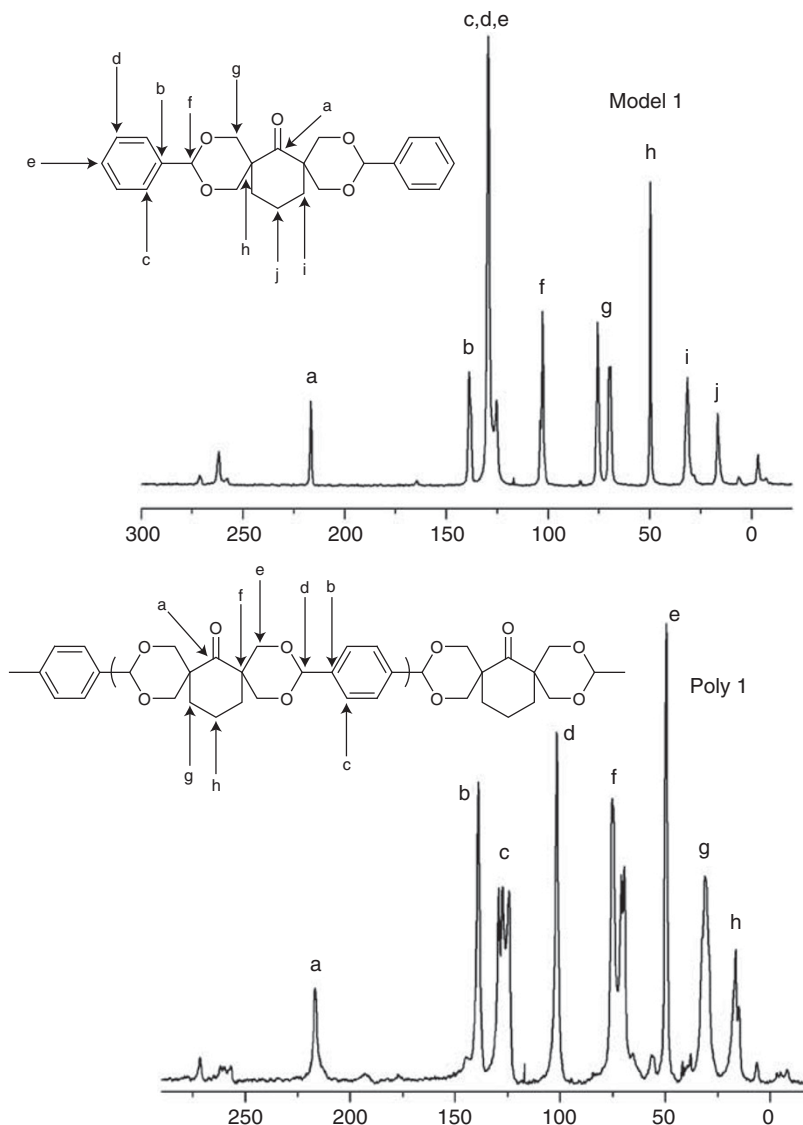


Figure 2 CPMAS solid-state NMR spectra of **Model 1** and **Poly 1**.

Table 2 Weight-loss percentages at various temperatures

Polymer	Percentage of weight loss (%) at various temperatures (°C)				
	100	200	300	400	500
Poly 1	0	2.39	7.4	30.77	35.66
Poly 2	0.86	2.49	9.89	69.08	83.30
Poly 3	0	1.08	7.72	58.62	69.15
Poly 4	0.65	2.23	4.77	41.59	90.29
Poly 5	1.36	3.83	8.53	62.42	90
Poly 6	1.63	4.19	29.20	61.44	83.92
Poly 7	0.47	2.93	9.86	56.97	76.16
Poly 8	0.43	1.65	4.98	32.48	93.19

Table 3 Solubility of the polyspiroacetals

Solvents	Poly 1	Poly 2	Poly 3	Poly 4	Poly 5	Poly 6	Poly 7	Poly 8
Water	–	–	–	–	–	–	–	–
Acetone	–	–	–	–	–	–	–	–
Ethanol	–	–	–	–	–	–	–	–
Ether	–	–	–	–	–	–	–	–
Methanol	–	–	–	–	–	–	–	–
Hexane	–	–	–	–	–	–	–	–
Benzene	–	–	–	–	–	–	–	–
Toluene	–	–	–	–	–	–	–	–
DMSO	–	–	–	–	δ	+	–	δ
THF	–	δ	–	–	δ	+	δ	–
DMF	–	δ	–	–	δ	δ	δ	–
DCM	–	–	–	–	–	–	–	–
Chloroform	–	–	–	–	–	–	–	–
NMP	–	+	–	–	–	+	δ	δ
HFIP	+	+	+	+	+	+	+	+

Abbreviations: DMC; dichloromethane; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; HFIP; hexafluoroisopropanol; NMP, *N*-methyl-2-pyrrolidone; THF, tetrahydrofuran; δ, slightly soluble; +, soluble; –, insoluble.

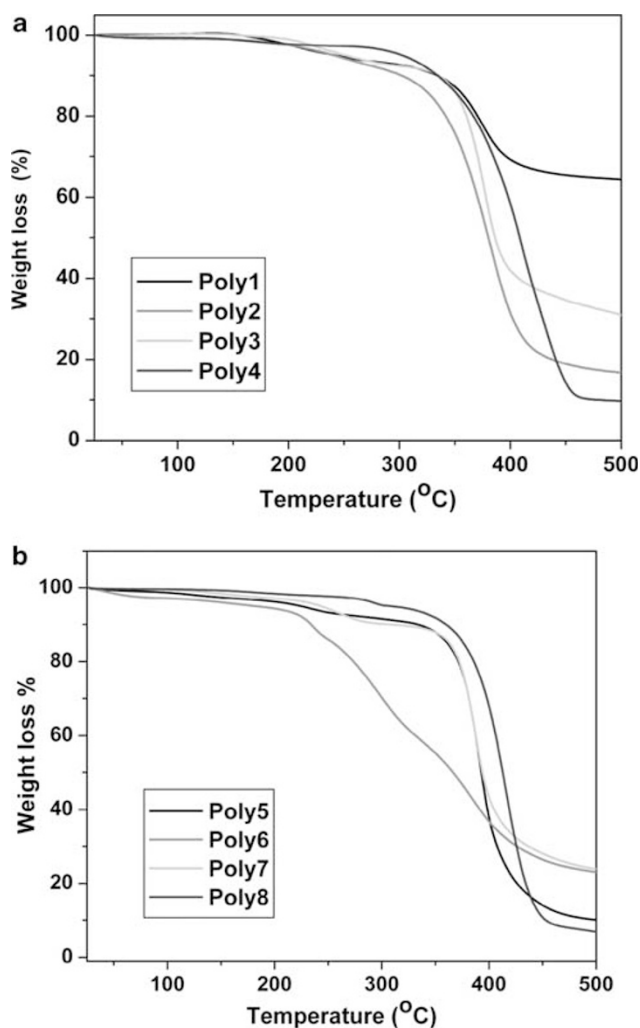


Figure 3 TGA thermograms of terephthalaldehyde-based polymers (a) and isophthalaldehyde-based polymers (b). A full color version of this figure is available at *Polymer Journal* online.

50 p.p.m. are attributed to the quaternary carbon atoms of the cyclohexane ring.

The thermal properties of the polymers were evaluated by DSC and TGA. These data are summarized in Table 2 and Figure 3, which show

the weight-loss percentages of the polymers at different temperatures. In the thermal analysis, neither a glass transition temperature nor a melting point was observed. As Figure 3 illustrates, the majority of these polymers exhibited relatively good thermal stability. The thermal stability of the polymers decreased in the following order: **Poly 4** > **Poly 1** ≈ **Poly 3** > **Poly 2** for the terephthalaldehyde-based polymers and **Poly 8** > **Poly 5** > **Poly 7** > **Poly 6** for the isophthalaldehyde polymers. The polymers with carbonyl functionalities had better thermal stability than the hydroxyl-bearing monomers. Similar behaviors were observed for the isophthalaldehyde-based polymers. As expected from the high degree of order in their structures, the terephthalaldehyde-based polymers were much more stable than the isophthalaldehyde-based polymers. Though the majority of the polymers synthesized in this study exhibited good thermal stability, **Poly 4** was the most thermally stable because of its more linear structure. The TG curves revealed a weight loss of ~2% at 200 °C for all polymers, except **Poly 5** and **Poly 6**. These two were slightly less stable compared with the others, exhibiting weight losses of 3.8% and 4.2% at 200 °C.

Poly 1, **Poly 3** and **Poly 4** were completely insoluble in common organic solvents and also did not appear to swell in any of these solvents (Table 3). The other polymers, **Poly 2**, **Poly 5**, **Poly 6**, **Poly 7** and **Poly 8**, were soluble in certain solvents. Except for the case of **Poly 2**, this solubility is indicative of the influence of the isophthalaldehyde groups on the polymer properties and can be explained by a decrease in crystallinity. In comparing the solubility of the terephthalaldehyde- and isophthalaldehyde-based polymers, terephthalaldehyde resulted in more solvent-resistant polymers because of the high degree of order imposed on the structure. In another words, the use of isophthalaldehyde instead of terephthalaldehyde resulted in structural irregularities that reduced the linearity of the polymers. **Poly 2**, which was synthesized from the reaction of 2,2,6,6-tetrakis(hydroxymethyl)cyclohexanol and terephthalaldehyde, was slightly soluble in tetrahydrofuran (THF) and dimethylformamide (DMF). **Poly 5** was slightly soluble in DMSO, DMF and THF, whereas the hydroxyl-bearing **Poly 6** exhibited complete solubility in THF, DMSO and NMP as well as partial solubility in DMF. The replacement of the carbonyl group with a hydroxyl group increased the solubility of the polymer. This enhanced solubility may be ascribed to a decrease in the crystallinity by *cis*- and *trans*-isomerism of the cyclohexanol ring. **Poly 7**, which

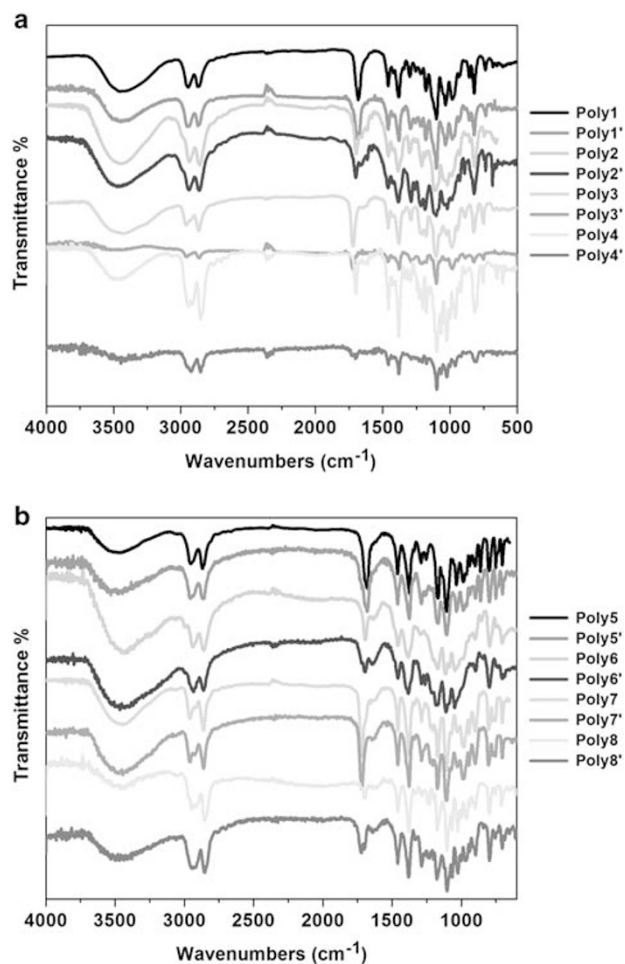


Figure 4 FT-IR spectra before (**Poly**) and after (**Poly'**) dissolution in hexafluoroisopropanol for terephthalaldehyde-based polymers (**a**) and isophthalaldehyde-based polymers (**b**). A full color version of this figure is available at *Polymer Journal* online.

was synthesized by the condensation of 2,2,5,5-tetrakis(hydroxymethyl)cyclopentanone and isophthalaldehyde, was partially soluble in THF, DMF and NMP. Clearly, inserting the isophthalaldehyde in place of terephthalaldehyde resulted in increased polymer solubility. The direct condensation of 1,1,4,4-tetrakis(hydroxymethyl)cyclohexane and isophthalaldehyde gave **Poly 8**, a polymer that was also

slightly soluble in DMSO and NMP. All polyspiroacetals exhibited complete solubility in hexafluoroisopropanol. Despite the acidic nature of the solvent before and after dissolution, all polymers could be recovered from this solvent with no changes in the FT-IR spectra (Figure 4).

In conclusion, a series of terephthalaldehyde- and isophthalaldehyde-based polyspiroacetals have been synthesized. The effects of different dialdehyde and multihydroxy monomers on the polymer properties have been examined. These polymers are thermally stable and insoluble in many common solvents, but they are completely soluble in hexafluoroisopropanol.

ACKNOWLEDGEMENTS

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