Attempted equilibration of an insoluble spiran polymer with monomers and oligomers through reversible chemical reactions: transketalization route to spiropolymers from 1,4-cyclohexanedione and pentaerythritol

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Transketalization reactions between the diketals of 1,4-cyclohexanedione and the diketonides of pentaerythritol yield a spiropolymer which is insoluble in all solvents tried, but which can be hydrolysed to 1,4-cyclohexanedione and pentaerythritol. At short reaction times, oligomers such as 3,3,21,21-tetramethyl-1,5,10,14,19,23,26,29-octaoxapentaspiro[5.2.2.2.2.5.2.2.2.2]untriacontane can be isolated. However, all attempts to achieve a genuine equilibrium between the monomers, oligomers and polymer were fruitless. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) n.m.r. spectrum of the polymer shows extra lines relative to those of soluble model compounds; this is probably due to a slow ring inversion of the 1,3-dioxane rings in the solid polymer.

(Keywords: spiropolymers; ketals; transketalization)

INTRODUCTION

We are interested in developing methods for the synthesis of two- and three-dimensional networks deriving their structural control from the conformational effects of quaternary centres[1,2], and which are based on the diamond lattice. As an example, the intermolecular ketalization of 5,5,13,13-tetrakis(2-hydroxyethyl)cyclohexadecane-1,9-dione might generate one of two interesting structures at equilibrium (*Figure 1*). These are a two-dimensional network of coplanar 16-membered rings in their preferred [4444] conformation[3–8], based on a local D_{2d} symmetry (A), or a three-dimensional zeolite-like network (B), based on local S_4 symmetry at the quaternary centres.

These structures are certain to be completely insoluble, and although we hope that reagent access might be possible by intercalation in A and through the channels in B, we anticipated the probable need to anneal these materials in order to obtain the preferred equilibrium structures. This might be possible if we chose to prepare a network containing bonds which are formed in readily reversible chemical reactions, such as the ketal formation implied by *Figure 1*. However, a fundamental question is whether chemical reversibility is enough, i.e. will the insolubility render equilibration impossible even if bond formation and bond breaking is rapid? Before embarking on the multistep synthesis of compounds such as 5,5,13,13-tetrakis(2-hydroxyethyl)cyclohexadecane-1,9-dione, we set out to test this idea on a simpler model, namely the formation of a rigid linear spiropolymer, and our results are described in this paper. We have chosen to re-examine the formation of the spiropolymer first prepared by Bailey and Volpe by direct reaction of 1,4-cyclohexanedione and pentaerythritol[9]. We have sought to prepare this polymer by transketalization from several diketals of 1,4-cyclohexanedione and several ketonides of pentaerythritol. We also briefly examined transketalization as a route to the related spiropolymer recently prepared from 1,3-dihydroxyacetone[10].

EXPERIMENTAL

Materials and general procedures

Pentaerythritol, *p*-toluenesulfonic acid monohydrate and 1,4-cyclohexanedione (Aldrich) were used as received. 2,2-Dimethoxypropane, 2,2-dimethylpropane-1,3-diol, ethylene glycol, 3-pentanone and 4-heptanone (Aldrich) were used after drying over molecular sieves. Toluene, stored over molecular sieves, was distilled from sodium metal before use.

All solution n.m.r. spectra were run on a JEOL-JNM-GX270 *FT*n.m.r. instrument. ^{13}C CP/MAS n.m.r. spectra were recorded at the EPSRC Solid State NMR Service at

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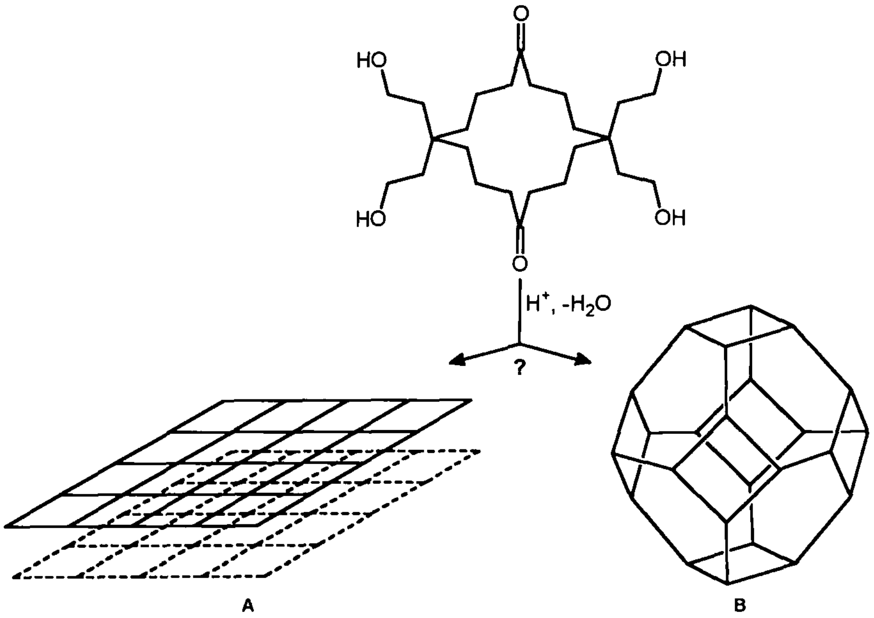


Figure 1 Possible two- and three-dimensional lattices from the ketalization of 5,5,13,13-tetrakis(2-hydroxyethyl)cyclohexadecane-1,9-dione. In the lower diagrams, each square represents a 16-membered ring in its preferred [4444] conformation

Durham University on a 75.43 MHz Varian *FT*n.m.r. spectrometer equipped with cross-polarization magic angle spinning accessories. The dry powdered samples were placed in a bullet-type rotor and rotated at a spinning rate of 4.5 kHz, using a contact time of 1 ms and a wait period of 3 s. Proton decoupling was used to obtain high resolution and sensitivity. The ^{13}C shifts were calibrated by substitution using external tetramethylsilane (TMS). Melting points were obtained on a Kofler Block apparatus and are corrected. Elemental analyses were performed by the microanalytical section in the School of Chemistry at Bristol University.

Preparation of 2,2-dimethyl-5,5-di(hydroxymethyl)-1,3-dioxane 1

Into a 500 cm^3 round-bottomed flask, equipped with a long condenser and stirrer, concentrated HCl (5 cm^3) was added to a mixture of pentaerythritol (sparingly soluble, 13.62 g, 0.1 mol) in acetone (200 cm^3) and water (15 cm^3). The reaction mixture was stirred vigorously while refluxing at 70°C until the evolution of HCl gas had ceased (24 h). After cooling to room temperature, the unreacted material (5.2 g) was filtered off and washed with acetone:ether (1:1 vol/vol, 50 cm^3). The filtrate was stirred with anhydrous K_2CO_3 to neutralize the acid. Evaporation of the solvent in a rotary evaporator afforded 8.1 g (46%) of a white powder, which was recrystallized from acetone, filtered and dried *in vacuo* at 20°C. The purity was >99% (by g.l.c.), although the m.p. (108–109°C), was much lower than the values reported in the literature (135°C[11,12] and 128–9°C[13]); we presume that we isolated a different polymorph. Found: C, 54.29; H, 9.10%. $C_8H_{16}O_4$ requires: C, 54.53; H, 9.15%. ^1H n.m.r. (270 MHz in $(CD_3)_2CO$), δ (ppm): 1.33 (s, 6H, $C\underline{H}_3$), 2.85 (s, 2H, $CH_2O\underline{H}$), 3.59 (s, 4H, $OC\underline{H}_2$) and 3.70 (bs, 4H, $C\underline{H}_2OH$). ^{13}C n.m.r. (68 MHz in $(CD_3)_2CO$), δ (ppm): 24.16 ($\underline{C}H_3$), 62.90 and 63.10 ($\underline{C}H_2O$), 39.87 ($\underline{C}(CH_2O)$) and 98.32 ($\underline{C}(CH_3)_2(OCH_2)_2$).

Preparation of 2,2,8,8-tetramethyl-1,3,7,9-tetraoxaspiro[5.5]undecane 2

To a stirred solution of **1** (17.62 g, 0.1 mol) in dry acetone (25 cm^3) were added 2,2-dimethoxypropane (52.1 g, 0.5 mol) and *p*-toluenesulfonic acid monohydrate (0.01 g). This was refluxed for 2 h, and acetone and methanol were then slowly distilled off using a Dean–Stark type apparatus over a period of 5 h, during which time the reaction mixture became a homogeneous solution. The solvent and volatiles were removed on a rotary evaporator, the residue was dissolved in dichloromethane (40 cm^3), filtered through a glass sinter and anhydrous K_2CO_3 (5 g) was added. After stirring for 2 h, the solids were filtered off and the solvent evaporated in a rotary evaporator to give 20.15 g (93%) of white crystals, which were recrystallized from pentane. The purity (by g.l.c.) was >99%, but again the observed m.p. (93–95°C), was much lower than the values reported previously (115–115.5°C[13] and 116°C[11,12]). Found: C, 59.87; H, 9.61%. $C_{11}H_{20}O_4$ requires: C, 61.09; H, 9.32%; ^1H n.m.r. (270 MHz in $(CD_3)_2CO$), δ (ppm): 1.33 (s, 12H, $C\underline{H}_3$) and 3.73 (s, 8H, $C\underline{H}_2O$). ^{13}C n.m.r. (68 MHz in $(CD_3)_2CO$), δ (ppm): 24.03 ($\underline{C}H_3$), 64.25 ($\underline{C}H_2O$), 32.90 ($\underline{C}(CH_2O)$) and 98.86 ($\underline{C}(CH_3)_2(OCH_2)_2$).

Preparation of 2,2,8,8-tetraethyl-1,3,7,9-tetraoxaspiro[5.5]undecane 3

A ten-fold excess of 3-pentanone (8.16 g, 0.1 mol) was equilibrated with a solution of **2** (2.16 g, 0.01 mol) in toluene (20 cm^3) and *p*-toluenesulfonic acid monohydrate (0.0015 g), by stirring and refluxing for 1 h. Work-up was as described for **2** and gave 1.74 g (64%) of white crystals. Recrystallization from chloroform:pentane (1:4, vol/vol) gave material with a m.p. of 80–82°C. Found: C, 65.79; H, 10.28%. $C_{15}H_{28}O_4$ requires: C, 66.14; H, 10.36%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 0.80 (t, 12H, $C\underline{H}_3$), 1.63 (q, 8H, $C\underline{H}_2CH_3$) and 3.64 (s, 8H, $OC\underline{H}_2$). ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 7.33 ($\underline{C}H_3$), 25.55

($\underline{C}H_2CH_3$), 63.36 ($\underline{C}H_2O$), 31.82 ($\underline{C}(CH_2O)$) and 101.46 ($\underline{C}(CH_2CH_3)_2(OCH_2)_2$).

Preparation of 1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 4

A mixture of ethyleneglycol (12.41 g, 0.2 mol), 1,4-cyclohexanedione (11.21 g, 0.1 mol) and *p*-toluenesulfonic acid monohydrate (0.05 g) in toluene (120 cm^3) was refluxed for 1 h and water was removed azeotropically using a Dean–Stark-type apparatus over a period of 2.5 h. Toluene (100 cm^3) was then added and the mixture was refluxed overnight at 100°C; water was then distilled off azeotropically with toluene (2 h). After cooling to room temperature, the mixture was diluted with dichloromethane (50 cm^3) and stirred with anhydrous K_2CO_3 (10 g) for 1 h to neutralize the acid. Evaporation of the solvent gave 15.2 g (76%) of white crystals. Recrystallization from dichloromethane:pentane gave pure material (g.l.c. > 99%), m.p. 79–80°C (lit. 79–79.5°C[14]). Found: C, 59.56; H, 8.10%. $C_{10}H_{16}O_4$ requires: C, 59.98; H, 8.05%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 1.79 (s, 8H, $C\underline{H}_2$) and 3.95 (t, 8H, $C\underline{H}_2O$). ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 32.17 ($\underline{C}H_2$), 64.31 ($\underline{C}H_2O$) and 108.31 ($\underline{C}(OCH_2)_2$).

Preparation of 3,3,12,12-tetramethyl-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane 5[15,16]

The procedure was identical to that employed for **4**. The quantities used were the same, except that 2,2-dimethyl-1,3-propanediol (20.83 g, 0.2 mol) and *p*-toluenesulfonic acid monohydrate (0.08 g) were used in this case. The yield was 10.70 g (69%); recrystallized from pentane, purity by g.l.c. >99%, m.p. 152–154°C. Found: C, 66.99; H, 9.90%. $C_{16}H_{28}O_4$ requires: C, 67.57; H, 9.92%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 0.94 (s, 12H, $C\underline{H}_3$), 1.83 (s, 8H, $C\underline{H}_2$) and 3.47 (s, 8H, $OC\underline{H}_2$). ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 22.68 ($\underline{C}H_3$), 28.15 ($\underline{C}H_2$), 70.12 ($\underline{C}H_2O$), 30.13 ($\underline{C}(CH_3)_2$) and 97.36 ($\underline{C}(OCH_2)_2$).

Preparation of 1,4,9,13,18,21,24,27-octaoxapentaspiro[4.2.2.2.2.4.2.2.2.2]nonaeicosane 6

Solutions of **4** (2.00 g, 0.01 mol) in toluene (5 cm^3) and **2** (1.08 g, 0.005 mol) in toluene (5 cm^3) were added to a stirred solution of *p*-toluenesulfonic acid monohydrate (0.001 g) in toluene (25 cm^3). This solution was placed in an oil bath maintained at 140–145°C and then refluxed by using a Dean–Stark-type apparatus for 30 min, during which time a white precipitate formed. After cooling to room temperature, the insoluble precipitate was filtered off and dried *in vacuo* at 20°C to give 0.061 g of **9**. The filtrate was diluted with dichloromethane (20 cm^3) and stirred with anhydrous K_2CO_3 (2 g) for 30 min to neutralize the acid; the solution was then filtered and evaporated. Pentane (20 cm^3) was added to the precipitate in order to remove any unreacted starting materials (**4** and **5**) which were soluble in pentane, stirred, and the precipitate was then filtered off. The precipitate was washed with pentane (2 × 5 cm^3) and dried *in vacuo* at 20°C to give 0.743 g of **6** as a white powder. Found: C, 60.84; H, 7.80%. $C_{21}H_{32}O_8$ requires: C, 61.15; H, 7.82%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 1.69 (d, 8H, $C\underline{H}_2$), 1.92 (d, 8H, $C\underline{H}_2$), 3.75 (s, 8H, $C\underline{H}_2O$) and 3.94 (t, 8H, $OC\underline{H}_2C\underline{H}_2O$). ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 29.42 and 30.91 ($\underline{C}H_2$), 64.33 ($O\underline{C}H_2\underline{C}H_2O$), 63.66 ($\underline{C}H_2O$), 32.83 ($\underline{C}(CH_2O)$), 97.91 (six-membered ring $\underline{C}(OCH_2)_2$) and 108.48 (five-membered ring $\underline{C}(OCH_2)_2$).

Preparation of 3,3,21,21-tetramethyl-1,5,10,14,19,23,26,29-octaoxapentaspiro[5.2.2.2.2.5.2.2.2.2]untriacontane 7

The procedure and work-up were identical to that used for **6**, with the following quantities employed: **5** (2.844 g, 0.01 mol) in toluene (5 cm^3), and **2** (1.080 g, 0.005 mol) in toluene (5 cm^3). The material which was insoluble in toluene yielded **9** (0.033 g) (see below); **7** (0.472 g) was isolated from the filtrate as a white powdery material. Found: C, 65.18; H, 8.90%. $C_{27}H_{44}O_8$ requires: C, 65.30; H, 8.93%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 0.96 (s, 12H, $C\underline{H}_3$), 3.5 (s, 8H, $OC\underline{H}_2$), 1.83 and 1.85 (d, 16H, $C\underline{H}_2$) and 3.73 (s, 8H, $C\underline{H}_2O$). ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 22.68 ($\underline{C}H_3$), 28.17 ($\underline{C}H_2$, cyclohexane ring), 70.14 ($O\underline{C}H_2$), 63.57 ($\underline{C}H_2O$, pentaerythritol unit), 30.15 ($\underline{C}(CH_3)_2$), 32.79 (central carbon of pentaethritol unit), and 97.25 and 98.29 (ketal carbons).

Preparation of 3,3,12,12-tetrakis(hydroxymethyl)-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane 8

The experimental procedure was the same as that used for the previous experiment but the following quantities were used in this case: **2** (2.16 g, 0.01 mol) in toluene (5 cm^3) and **5** (1.42 g, 0.005 mol) in toluene (5 cm^3). The insoluble precipitate was filtered from the toluene solution. Work-up of the filtrate was carried out as described for **6** in order to recover any of the unreacted materials **2** and **5**. Dry acetone (25 cm^3) was added to the precipitate and stirred well for 30 min. The remaining precipitate was filtered and washed with acetone (2 × 25 cm^3); this insoluble material was confirmed as **9** (0.064 g). The filtrate, on evaporation, gave **8** (0.218 g) as a slightly off-white precipitate, which was recrystallized from acetone:water (1:2, vol/vol). Found: C, 54.81; H, 7.97%. $C_{16}H_{28}O_8$ requires: C, 55.16; H, 8.10%. ^1H n.m.r. (270 MHz in D_2O), δ (ppm): 1.69 (s, 8H, cyclohexane ring), 3.36 (s, 8H, $C\underline{H}_2O$), 3.60 (s, 8H, $C\underline{H}_2OH$) and 4.52 (s, 4H, $CH_2O\underline{H}$). ^{13}C n.m.r. (68 MHz in D_2O), δ (ppm): 28.25 ($\underline{C}H_2$, cyclohexane ring), 60.38 ($\underline{C}H_2O$), 61.12 ($\underline{C}H_2OH$), 39.07 (central carbon of pentaethritol unit) and 96.67 ($\underline{C}(OCH_2)_2$). **8** was also obtained when the reaction was conducted as above by taking **4** and **2** in a 1:2 molar ratio.

Isolation of polymer 9

The white jelly-like precipitate was filtered off from the toluene, washed with water:methanol (1:10 vol/vol, 2 × 10 cm^3), pentane (2 × 10 cm^3), and dried overnight in an evacuated drying apparatus at 40°C. The i.r. spectrum was almost identical to that reported by Bailey and Volpe[9] in the fingerprint region but showed no carbonyl absorption and only a very weak absorption in the OH region.

Attempted equilibrations of polymer 9 with monomers 4 and 5

Polymer **9** (0.212 g, 1 mmol), suspended in toluene, xylene, or dimethyl sulfoxide (DMSO) (25 cm^3), with **4** (0.20 g, 1 mmol) or **5** (0.284 g, 1 mmol) and varied amounts of *p*-toluenesulfonic acid monohydrate (0.001 to 0.015 g) in a 100 cm^3 round-bottomed flask, were refluxed for 30 h and the volatile products were then removed in a

Dean–Stark trap over a period of 5 h. After cooling, the insoluble material was filtered, washed with pentane ($2 \times 25\,cm^3$) and dried *in vacuo* at 40°C. The filtrate was stirred with anhydrous K_2CO_3 (1 g), and filtered. After evaporation of the solvent, the residue was analysed by n.m.r. spectroscopy, but only monomer **4** (or **5**) was recovered; no sign of **6** (or **7**) was seen.

Kinetic studies of equilibration reactions between 2 and 5

A series of experiments under identical reaction conditions were carried out at different intervals of time (15 min to 29 h), with a view to understanding the mechanism of formation of the oligomers and polymers, by taking a 1:1 mole ratio of **2** (0.2163 g, 0.001 mol) and **5** (0.2844 g, 0.001 mol) with *p*-toluenesulfonic acid monohydrate (0.001 g), and toluene ($30\,cm^3$). The results are given in *Table 1*. The polymer (**9**), oligomer (**7**), and unreacted materials (**2** and **5**) were quantitatively determined by separating the insolubles from the toluene solution (**9**), and then separating the toluene-soluble material into pentane-insoluble (**7**) and soluble fractions (**2** and **5**), respectively. The ratio of **2** to **5** in the pentane-soluble fraction was determined from an average of the values from the integration ratio of the $C\underline{H}_2O$ peaks (at 3.47 and 3.73 ppm, for **5** and **2**, respectively) and that for the $C\underline{H}_3$ peaks (at 0.94 and 1.33 ppm, for **5** and **2**, respectively). Spectra were run in $CDCl_3$.

Hydrolysis of polymer 9

A mixture of the finely powdered spiropolymer **9** (0.21 g) and aqueous HCl ($20\,cm^3$, 0.05 M) was refluxed for 35 h. The insoluble precipitate was filtered (0.054 g). Dichloromethane ($2 \times 25\,cm^3$) was added to the filtrate, and after separation of the layers, the dichloromethane extract was evaporated to give 1,4-cyclohexanedione (0.062 g). The aqueous layer yielded pentaerythritol (0.079 g).

Preparation of 2,2,10,10-tetramethyl-1,3,7,9,11,14-hexaoxadispiro[4.2.4.2]tetradecane 10

1,3-Dihydroxyacetone dimer (Aldrich) (1.80 g, 0.01 mol) was heated with 2,2-dimethoxypropane (10 g, 0.096 mmol) containing *p*-toluenesulfonic acid monohydrate (0.001 g) while slowly distilling off MeOH over a period of 2.5 h. On cooling to room temperature, the reaction mixture solidified, and was dissolved in $CHCl_3$ ($20\,cm^3$) and then stirred with anhydrous K_2CO_3 to remove the catalyst. After filtration and evaporation, the white solid (diacetonide **10**) was recrystallized from $CHCl_3$:ether (5:1 vol/vol), m.p. 162–163°C. Found: C, 54.92; H, 7.61%. $C_{12}H_{20}O_6$ requires: C, 55.37; H, 7.74%. ^1H n.m.r. (270 MHz in $CDCl_3$), δ (ppm): 1.45 and 1.51 (6H each, $C\underline{H}_3$ groups), 3.62 and 4.18 (4H, AB quartet, J 11.4 Hz), 3.75 and 4.04 (4H, AB quartets, J 9.3 Hz), two types of $C\underline{H}_2$ groups. ^{13}C n.m.r. (68 MHz in $CDCl_3$), δ (ppm): 26.34, 26.70 ($\underline{C}H_3$), 65.46 ($\underline{C}H_2O$), 71.85 ($\underline{C}H_2O$), 100.42 (spiroketal carbon) and 112.13 ($\underline{C}(CH_3)_2$).

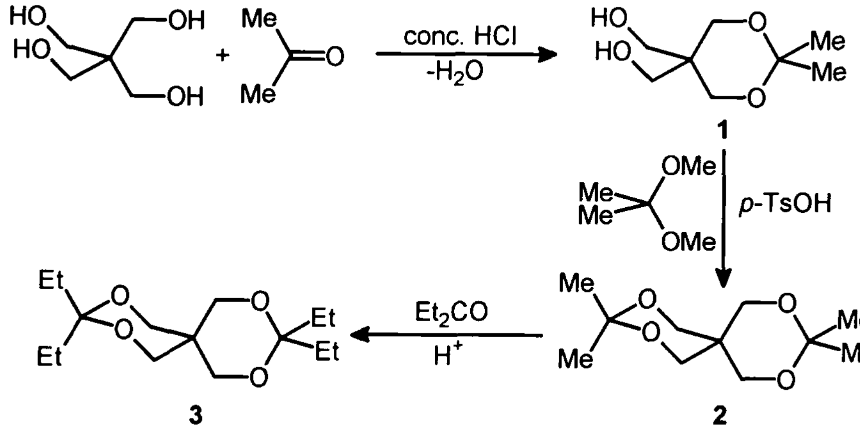
Polymerization of 2,2,10,10-tetramethyl-1,3,7,9,11,14-hexaoxadispiro[4.2.4.2]tetradecane 10

Diacetonide **10** was heated in toluene containing *p*-toluenesulfonic acid monohydrate, with a slow distillation of acetone, and polymer **11** was isolated by the same method as used for **9**. This polymer was soluble in DMSO. ^1H n.m.r. (270 MHz in DMSO-d_6/D_2O), δ (ppm): 4.2 (s, $C\underline{H}_2O$). ^{13}C n.m.r. (68 MHz in DMSO-d_6/D_2O), δ (ppm): 65.46 ($C\underline{H}_2O$); the quaternary carbon was not seen. Signals for methyl groups (end-groups) were not observed.

RESULTS AND DISCUSSION

Preparation of monomers

Surprisingly, it is not entirely simple to convert pentaerythritol to bisketonides, and this is only partly because of the insolubility of pentaerythritol in organic solvents. We found it convenient to prepare the hemi-acetonide **1** from acetone and pentaerythritol, using aqueous HCl[17], and then to prepare the bisacetonide **2** from this, using 2,2-dimethoxypropane and *p*-toluenesulfonic acid (*Scheme 1*). The bisketonide **3**, from 3-pentanone, was prepared by a similar two-step process, or from **2**, but we were quite unable to obtain the bisketonide from 4-heptanone. An equilibration reaction between **2** and 4-heptanone in toluene, using *p*-toluenesulfonic acid as a catalyst, failed to yield 2,2,8,8-tetrapropyl-1,3,7,9-tetraoxaspiro[5.5]undecane under varied conditions. We also failed in attempts to



Scheme 1 Preparation of 2,2,8,8-tetramethyl-1,3,7,9-tetraoxaspiro[5.5]undecane, **2**, and 2,2,8,8-tetraethyl-1,3,7,9-tetraoxaspiro[5.5]undecane, **3**

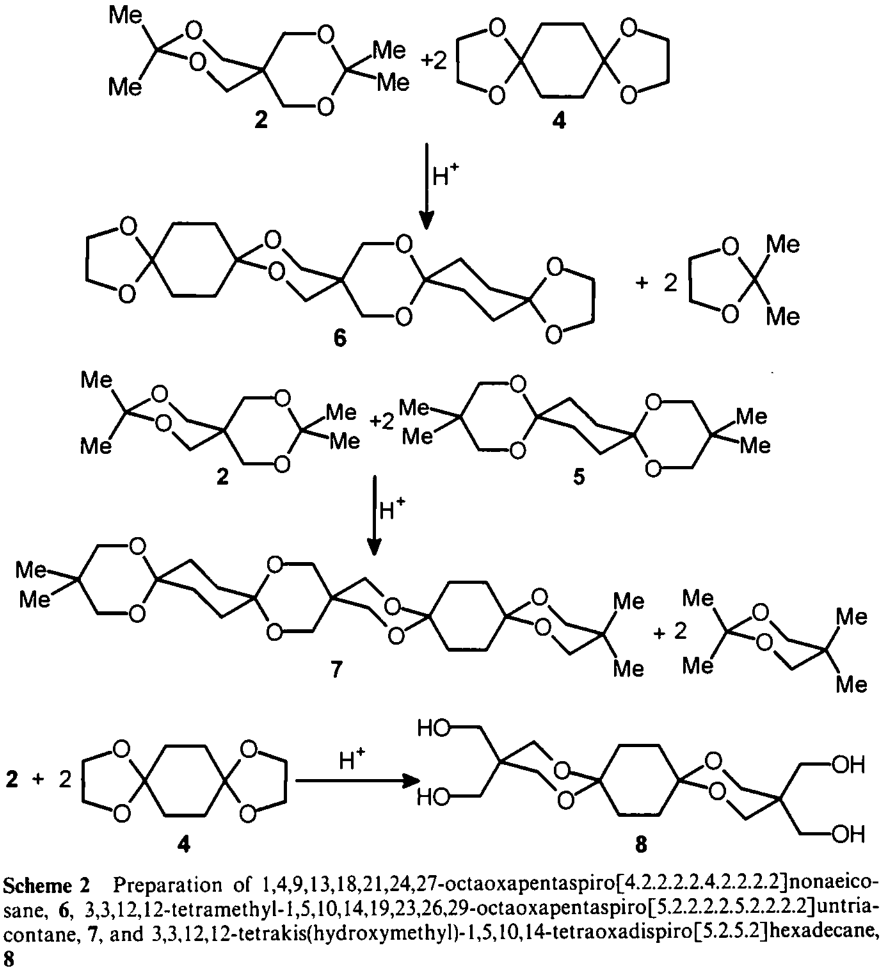
equilibrate one mole of **2** and two moles of 2,2-dipropyl-1,3-dioxolane under similar conditions in toluene, and simply isolated 4-heptanone and the half-acetal of pentaerythritol, **1**. We can offer no convincing explanation for this curious behaviour. On the other hand, 1,4-cyclohexanedione is readily converted to the bisketals, 1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane (**4**), and 3,3,12,12-tetramethyl-1,5,10,14-tetraoxadispiro[5.2.5.2]tetradecane (**5**), under standard ketalization conditions.

The oligomers **6** (1,4,9,13,18,21,24,27-octaoxapentaspiro-[4.2.2.2.2.4.2.2.2.2]nonaeicosane) and **7** (3,3,21,21-tetramethyl-1,5,10,14,19,23,26,29-octaoxapentaspiro[5.2.2.2.-2.5.2.2.2.2]untriacontane), for comparison with polymer structure **9**, were prepared by the reaction of one mole of **2** with two moles of **4** or **5** using *p*-toluenesulfonic acid, as shown in *Scheme 2*. These '1:2-mers' are probably among the longest well characterized polyspirans, e.g. **7** has a calculated length (using Allinger's MM2 parameters) between the end carbons of the six-membered rings of just over 17 Å. Another model compound, i.e. 3,3,12,12-tetrakis(hydroxymethyl)-1,5,10,14-tetraoxadispiro[5.2.5.2]-hexadecane, **8**, was prepared in a satisfactory yield by the reaction of two moles of **2** with one mole of **4** or **5**.

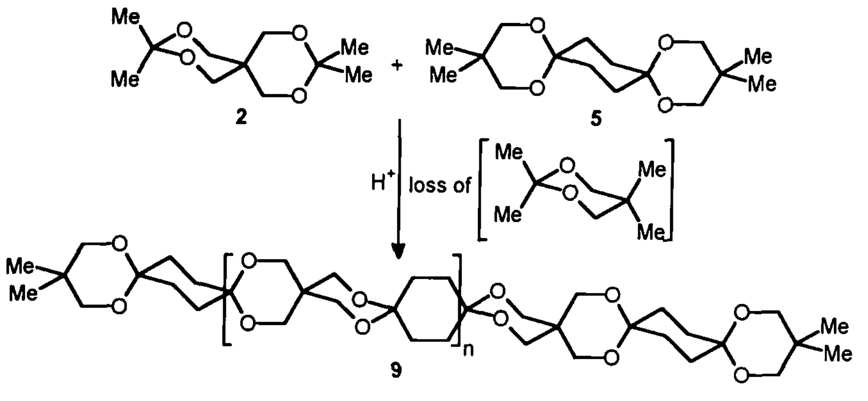
Transketalization reactions

All our attempts to study the reaction of **2** and **5** in a homogeneous solution were complicated by the precipitation of **9** from toluene (and from all of the other solvents that were tried), even at the lowest concentrations. Polymer formation (*Scheme 3*) was conducted as follows. Toluene, containing 0.5 mol% of *p*-toluenesulfonic acid monohydrate, was slowly distilled through a Vigreax column to remove water, and then **2** and an equimolar quantity of either **4** or **5** were added, and the slow distillation continued. The insoluble polymer began to separate after a few minutes and continued to form for at least 30 h. Formation of the expected volatile ketal (2,2-dimethyl-1,3-dioxolane, when **4** was used, and 2,2,5,5-tetramethyl-1,3-dioxane, in reactions involving **5**) was confirmed. The polymer obtained by this method was insoluble in all common organic solvents, including DMSO and *N*,*N*-dimethylformamide (DMF), and also did not appear to swell in any of these solvents. It also failed to dissolve in hexafluoroisopropanol, which Bailey and Volpe had previously reported to dissolve their polymer[9]. This difference could be due in part to the differing end groups. Our polymer shows no significant i.r. absorption for OH or carbonyl groups and probably has ketal (or ketonide) end-groups, whereas the polymer prepared according to Bailey and Volpe's direct method presumably had either hydroxy and/or ketone end groups. It is also likely that our polymer has a higher molecular weight (see below).

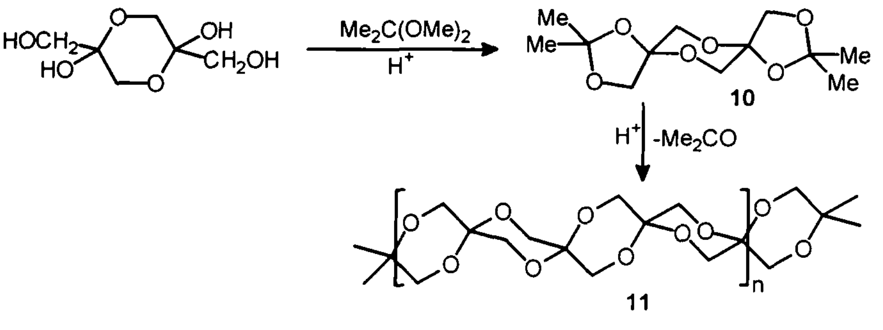
When the polymer-forming transketalization reactions were stopped after a short time, another product could be isolated, which was soluble in toluene, but not in pentane. (**3**, **4**, and **5** are soluble in pentane.) Characterization by n.m.r. spectroscopy showed this product to be the oligomer **6** when **3** was used, or **7** when **4** was taken as the starting material. The isolation



Scheme 2 Preparation of 1,4,9,13,18,21,24,27-octaoxapentaspiro[4.2.2.2.2.4.2.2.2.2]nonaeicosane, **6**, 3,3,12,12-tetramethyl-1,5,10,14,19,23,26,29-octaoxapentaspiro[5.2.2.2.2.5.2.2.2.2]untriacontane, **7**, and 3,3,12,12-tetrakis(hydroxymethyl)-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane, **8**



Scheme 3 Preparation of spiropolymer **9** from **2** and **5**; a similar scheme operates for formation of **9** from **2** and **4**



Scheme 4 Preparation of diacetonide **10** and its conversion to polymer **11**

Table 1 Results obtained from equilibration reactions between **2** and **5**

Run No.	Time (h)	Yields (mg) Recovered **2**	Recovered **5**	Oligomer **7**	Polymer **9**
1	0.25	218	131	19	42
2	0.50	137	75	85	57
3	1	73	28	129	74
4	2	10	3	130	94
5	4	9	3	61	106
6	7	8	3	56	127
7	17	9	5	54	163
8	24	9	6	21	182
9	29	5	6	18	194

of these oligomers provides some support for the formulation of the insoluble material as a linear spiropolymer, rather than a two- or three-dimensional material (see below).

The time-course of a reaction between **3** and **5** was followed for 29 h, with the products being divided into (a) pentane-soluble, (b) pentane-insoluble but toluene-soluble, and (c) insoluble, giving the results shown in *Table 1*. Clearly, **7** (or **8**) builds up during the early stages of the reaction, but is eventually converted to polymer.

It is interesting that while alternative '2:1-mers' are obviously possible, and longer oligomers (e.g. a '3:2-mer') might be formed, there did not appear to be any significant quantities of other compounds in the material which was insoluble in pentane, but which could be extracted from the polymer with a number of more powerful solvents. Of course, it is possible that other oligomers are simply too insoluble to be extracted from the polymer. For this reason, the synthesis of the bisketal of 4-heptanone with pentaerythritol was attempted, with a view to making the corresponding longer oligomers more soluble, but this was unsuccessful, as discussed above. Nevertheless, we could not isolate any trace of oligomers other than **6** and **7** in spite of exploring the reactions between (i) **3** and **4**, or **3** and **5**, (ii) **2** and **6**, or **2** and **7**, and (iii) **3** and **6**, or **3** and **7**, in various molar ratios, and using solvents like DMSO. This may indicate that oligomers other than **6** and **7** are highly reactive to condensation and rapidly lead to polymeric material. In general the formation of this particular type of oligomer suggests a more rapid turnover of the pentaerythritol bisketals, and is perhaps in line with the relative difficulty of obtaining these bisketals in the first place.

Reactions conducted as described above are, of course, driven by the removal of the low-molecular-weight volatile ketals. When the reactions were repeated under total reflux, (i.e. without any slow distillation of the toluene), polymer formation still occurred, although it was slower and, even after 30 h, less complete, than in the reactions described above. It is clear that the formation of polymer is partly driven forward by its insolubility. Is there any degree of equilibration between the polymer and the low-molecular-weight materials in these reactions? The reactions described so far suggest that there is indeed no equilibration. To test this further, we attempted transketalization reactions between the preformed polymer and both monomers, hoping to observe the formation of oligomers, but these were completely unsuccessful, with only polymer and the monomers being recovered.

We have made a brief study (*Scheme 4*) of transketalization as a route to the 1,3-dihydroxyacetone spiropolymer reported by Akar and Talinli[10]. The spirodiacetonide of 1,3-dihydroxyacetone, **10**, which is soluble in many organic solvents (unlike 1,3-dihydroxyacetone itself) was prepared and reacted with *p*-toluenesulfonic acid in toluene, under partial reflux with the slow distillation of volatiles (acetone). The polymer **11** was soluble in DMSO and gave the expected spectroscopic data. Signals for methyl groups (end-groups) were not observed, so the degree of polymerization (*DP*) is probably >10, but specific oligomers were not detected. The structure of polymer **11** is interesting because the rings can adopt conformations in which each $C(OCH_2)$ group can benefit from the maximum anomeric effect[18]. In polymer **9**, this is not possible.

Polymer structure

It has been assumed up to this point that the material reported by Bailey and Volpe[9], and also that prepared by us by transketalization, are both linear spiropolymers containing six-membered rings. However, these earlier authors produced little evidence which would rule out a crosslinked network structure; the material was only characterized by i.r. spectroscopy and no molecular weights were reported. Our product has a similar i.r. spectrum to the Bailey and Volpe polymer in the fingerprint region, but shows no carbonyl absorption, and only a very small amount of absorption in the OH region. Whereas Bailey and Volpe[9] reported that their polymer was soluble in hexafluoroisopropanol, our polymer **9** did not dissolve at all in this or any other solvent that we tried. This could be due to higher average molecular weights for our material, or to the different end-groups (ketals in our case), or even to both of these factors.

Specimens of polymer **9**, prepared from **2** and **4**, **2** and **5**, and **3** and **5**, were essentially identical in their i.r. spectra, thus suggesting no major contributions from the end-groups to the absorption in these spectra. In the ^{13}C CP/MAS n.m.r. spectrum of our polymer (*Figure 2a*), as derived from **2** and **4**, there is only a small absorption at 109 ppm which could be due to the ketal carbon in a dioxolane ring. (The quaternary ketal carbons of 1,3-dioxolane rings absorb at ~105–110 ppm, whereas quaternary ketal carbons of 1,3-dioxane rings absorb at 95–100 ppm.) Based on the isolation of oligomer **6** from the reaction of **2** with **4**, one would expect the majority of end-groups to be dioxolane rings in this case, so that on this basis, the average *DP* must be $\geqslant 10$. In agreement with this proposal, there are no absorptions due to methyl groups of acetonides in the ^{13}C CP/MAS n.m.r. spectrum of this polymer.

We have sought an answer to the question of a linear spiropolymer *versus* a crosslinked structure for polymer **9** by comparing the ^{13}C CP/MAS n.m.r. spectrum of **9** (*Figure 2a*) with the corresponding spectra of oligomers such as **6** and **7** (*Figures 2b* and *2c*, respectively). Chemical shifts in the spectra of **6** and **7** were assigned by comparison with the corresponding solution spectra (see the Experimental section). The agreement between the absorptions due to carbons

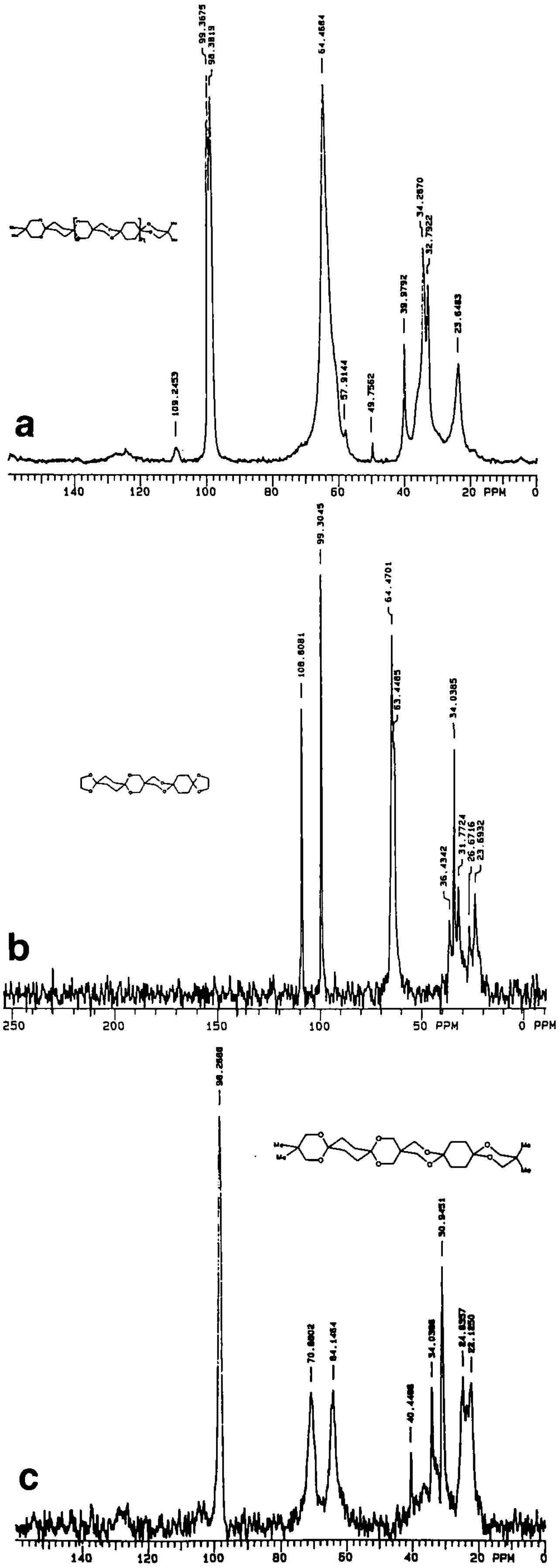


Figure 2 ^{13}C CP/MAS n.m.r. spectra of: (a) polymer **9** prepared from **2** and **4**, where the lines at 23.6 and 34.9 ppm (broad line under the 34.26 ppm line) and at 64.46 ppm were identified, by a polarization transfer experiment, as being due to CH_2 groups; (b) oligomer **6**; (c) oligomer **7**

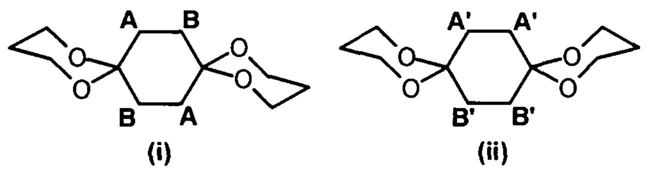


Figure 3 Alternative conformations around a cyclohexanedione-derived ring in **6**, **7** and **9**. Ring inversion in the dioxolane rings interconverts carbons A and B in case (i) and A' and B' in case (ii)

adjacent to oxygen in the corresponding spectra is good. when the lower resolution of the CP/MAS n.m.r. spectra is taken into account, but extra lines are observed for the CH_2 groups in the cyclohexanedione-derived rings. Thus for **6**, the two absorptions in solution at 29.42, and 30.91 ppm are replaced by four absorptions in the solid state at 23.69, 26.67, 34.04, and 36.43 ppm. (The line at 31.77 is probably the quaternary carbon of the pentaerythritol moiety, seen at 32.83 in the solution spectrum.) We suggest that the 1,3-dioxane rings are not undergoing chair–chair ring inversion in the solid state. Slow ring inversion would be expected to result in at least a doubling of the number of lines due to the methylene groups in the cyclohexanedione-derived rings, as shown in *Figure 3*. There are actually two possible local environments, i.e. cases (i) and (ii), but the actual chemical shifts for the type-A carbons in case (i) are likely to be very similar to those for A' in case (ii); similarly, the B and B' chemical shifts may well not be resolved in the CP/MAS n.m.r. spectrum. We also note that the actual magnitudes of the chemical shifts between the carbons which become equivalent in the solution spectra are quite consistent with axial/equatorial chemical shift differences which largely derive from γ-effects. This process of ring inversion requires quite large changes to the overall shape of **6**, and so would be expected to be severely inhibited in the solid state. In accord with this proposal, the average of the two absorptions in solution is 30.16, and the average of the four lines from the solid-state spectrum is 30.21 ppm. Of course, a similar restriction on the inversion of the cyclohexanedione-derived rings might be expected to produce a doubling of the lines for the CH_2 groups in the dioxane rings of **6**. The appropriate peak is merely rather broad; it may be that the chemical shift differences are smaller in this case.

Very similar effects are to be seen when comparing the solution and solid-state spectra for **7** and, most importantly, in the CP/MAS n.m.r. spectrum of polymer **9**. The CH_2 groups in the cyclohexanedione-derived rings of the latter absorb at 23.6 and 34.9 ppm (these absorptions were detected in a polarization-transfer spectrum) and are thus very similar to those seen for the oligomers **6** or **7** in the solid state. We suggest, therefore, that this is rather strong evidence for polymer **9** having a structure which is closely related to **6** and **7**.

Differential scanning calorimetry

D.s.c. measurements, using a Perkin-Elmer DSC2, were conducted up to a temperature of 600°C using a heating rate of 20°C min^{-1}. When the heating is limited to 600°C, the main features of the d.s.c. curves are reproducible, whereas higher temperatures affect the results due to thermal degradation. A glass transition temperature was not detectable in the d.s.c. curves, and decomposition started from 550°C onwards. These polymers have better thermal stability than the previously reported[9] spiropolymers, perhaps due to their higher molecular weights. The absence of any glass transition temperatures also suggests a higher degree of crystallinity in these materials[19].

CONCLUSIONS

Transketalization is a good route to ketal spiropolymers, but despite the reversibility of all of the chemical reactions involved, true equilibration between the monomers, oligomers, and polymer could not be attained, due to the extreme insolubility of the polymer. The ^{13}C CP/MAS n.m.r. spectrum of the polymer supports a spiroketal rather than a crosslinked network structure.

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