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A New Spiroacetal Polymer[1]

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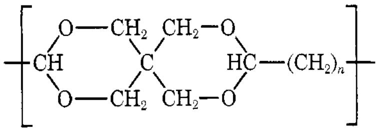
ABSTRACT: Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(methylenethiomethylene)] (IIa) was prepared by the condensation of 3,9-bischloromethyl-2,4,8,10-tetraoxaspiro[5.5]undecane (IVa) with sodium sulfide. Dimethyl sulfoxide (DMSO) is a uniquely effective solvent for this polymerization. Polymer end groups were capped with ethylene chlorohydrin prior to work-up to avoid thermal cross-linking. The polymer can be compression or injection molded at 200 to 260°. It can be cast into a clear, tough, flexible film from solution. This thermoplastic incorporates a balance of flexibility and strength as shown by its mechanical properties.

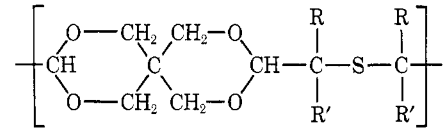
Only a few completely spiro polymers have been reported, and these materials are characteristically infusible, insoluble in common solvents, and expensive.[2] Of more practical interest has been the incorporation of a spiroacetal function into the backbone of a single-chain polymer. These semispiro polymers exhibit good oxidative and thermal stability.[3]



I

Linear polyspiroacetals with recurring structural unit I have been prepared by the acid-catalyzed reaction of tetraalkylacetals with pentaerythritol in organic solvents.[3b] These materials are good fiber formers. Similar polymers have been reported from the condensation of dialdehydes or diacetals with pentaerythritol in aqueous acid.[4] The high crystallinity of these polymers excludes their use in film applications. However, the crystallinity can be controlled by copolymerization with dipentaerythritol and subsequent cross-linking with pyromellitic dianhydride. Films prepared in this manner showed good flexibility and tensile strength.[5]

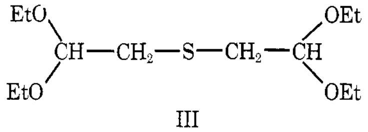
These results indicate that useful thermoplastic materials might be prepared if a suitable link could be incorporated between the spiroacetal functions. With this in mind, the synthesis and evaluation of polymers such as II were undertaken in the hope that an alkyl sulfide link might provide the desired flexibility to complement the rigid spiroacetal function.



IIa, $R = R' = H$
b, $R = H, R' = \text{-}CH_3$

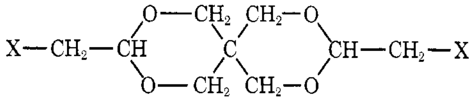
Results and Discussion

The tetraethyl acetal of 3-thiaglutaraldehyde (III) has been reported.[6] Condensation of III with pentaerythritol in DMSO or tetramethylene sulfone gave a low molecular weight polymer. Attempts to increase the molecular weight by raising the reaction temperature resulted in gelation. The majority of the polymeric product was insoluble in organic solvents.

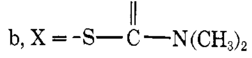


III

An alternate synthesis involved the condensation of sodium sulfide with the readily available 3,9-bischloromethyl-2,4,8,10-tetraoxaspiro[5.5]undecane (IVa).[7] It is reported that a halogen atom located on a carbon α to a carbon bearing two alkoxy groups is unreactive toward nucleophilic displacement.[8] The resistance of the bischloride IVa to nucleophilic displacement by cyanide, ammonia, and the anions of phenol and cyclohexanol has until now rendered it unattractive as a



IVa, $X = Cl$



b, $X = \text{-}S{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}N(CH_3)_2$

c, $X = \text{-}SH$

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[1] Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1971.

[2] A. A. Volpe and W. J. Bailey, *J. Polym. Sci., Part A-1*, **8**, 2109 (1970).

[3] (a) Symposium on Ladder and Spiro Polymers, *Prep., Amer. Chem. Soc., Div. Polym. Chem.*, **8** (1), 1967; (b) D. B. Capps, U. S. Patent 2,889,290 (1959).

[4] S. M. Cohen and E. Lavin, *J. Appl. Polym. Sci.*, **6**, 503 (1962).

[5] S. M. Cohen, C. F. Heint, R. E. Kass, and H. H. Markhart, *ibid.*, **6**, 508 (1962).

[6] M. Seefelder and H. Pasdach, German Patent 960,095 (1957).

[7] V. G. Mkhitaryan, *J. Gen. Chem. USSR*, **9**, 1923 (1939).

monomer.[8,9] We have found that the bischloride IVa condenses smoothly with sodium sulfide in DMSO at 80° to give high molecular weight polymer.

Dimethyl sulfoxide is a uniquely effective solvent for this polymerization. Numerous solvents were tried, including DMF, tetramethylene sulfone, alcohols, tetrahydrofuran, 1,4-dioxane, and toluene, but only DMSO gave high molecular weight polymer. The sodium sulfide used in the polymerization was technical fused flake which contained between 60 and 62% sodium sulfide, as determined by sulfur analysis. The sulfide content of the fused flake must be known within a few per cent, since the stoichiometry of condensation polymerizations requires that the monomers be present in equimolar amounts.

Elemental, infrared, and nmr analyses indicate that the product from this polymerization is poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(methylenethiomethylene)] (IIa). The nmr spectrum shows a doublet centered at δ 2.75 (4 H) which is assigned to the methylenes adjacent to sulfide. The infrared shows weak absorptions at 2650 and 2700 cm^{-1}, also assigned to these methylenes. These results indicate that the sulfide link in polymer IIa is resistant to the well-known sulfide oxidation by DMSO.[10]

The polymer is soluble in chloroform, methylene chloride, and cresylic acid at room temperature and in DMF and DMSO at higher temperatures. The inherent viscosity (0.5% in chloroform solution, 30°) ranged between 0.6 and 1.0. The solution viscosity steadily increased when dry polymer was heated at 100–150° in air or under vacuum. Prolonged heating gave partially insoluble polymer. The polymer maintained a constant viscosity upon heating when the end groups were capped with ethylene chlorohydrin prior to work-up.

Polymer IIa can be prepared by an alternate route. Condensation of bischloride IVa with sodium *N*,*N*-dimethyldithiocarbamate in DMSO gave the adduct IVb. Hydrolysis of IVb with sodium hydroxide in a DMSO–water mixture followed by neutralization gave 3,9-bis(mercaptomethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (IVc). The sodium salt of IVc reacted with bischloride IVa in either DMSO or DMF to give polymer IIa of high molecular weight.

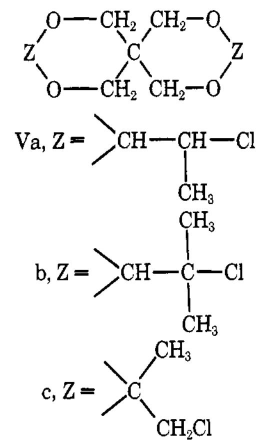
3,9-Bis(1-chloroethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Va) was prepared by the condensation of α-chloropropionaldehyde with pentaerythritol. Polymerization of Va with sodium sulfide in DMSO at 100–150° gives low molecular weight poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(ethylidenethioethylidene)] (IIb). The nmr spectrum of IIb shows a doublet centered at δ 1.25 (6 H) which is assigned to the methyl groups. Although the polymerization parameters of time, temperature, and solvent were varied, polymer IIb could not be obtained with an inherent viscosity greater than 0.1 (0.5% in chloroform solution).

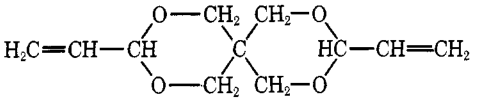
Polymer IIb has been reported to result from the Markovnikov addition of hydrogen sulfide to 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane (VI).[11] However, the nmr spectrum of this product shows a doublet centered at δ 1.25 (*ca.* 3 H) and two complex multiplets centered at δ 2.75 (*ca.* 2 H) and δ 1.9 (*ca.* 2 H). These results indicate that this product consists of about a 50/50 mixture of repeating units IIb and VII.

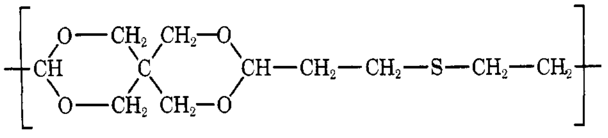
Table I

Mechanical Properties of Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(methylenethiomethylene)] (IIa)

Property	ASTM test no.	IIa
Tensile strength, psi	D638	10,000–12,000
Flexural strength, psi	D790	22,000
Flexural modulus	D790	5.5 × 10^5
IZOD impact	D256	0.7
Deflection temp, °F	D648	200
Volume resistivity, ohm cm	D257	5 × 10^{15}




VI


VII

Bischlorides Vb and Vc were prepared but are resistant to nucleophilic displacement by sulfide in DMSO up to 180°. This reactivity undoubtedly results from the severe steric hindrance to nucleophilic displacement at the tertiary chloride in Vb and at the neopentyl-like chloride in Vc.

Mechanical Properties

Polymer IIa can be compression or injection molded at 200–260° and can be cast into a clear, tough, flexible film from chloroform. Some mechanical and electrical properties of the compression molded polymer are shown in Table I. It is evident that this thermoplastic exhibits a desirable balance of flexibility and strength. The material possesses maximum mechanical strength in the 0.6–0.9 inherent viscosity range (of 0.5% solutions in chloroform, 30°).

Experimental Section

Dimethyl sulfoxide was used as purchased from Crown Zellerbach. Sodium sulfide was obtained as a fused technical flake from Mallinckrodt Chemical and contained 60.4% Na$_2$S. Chloroacetaldehyde dimethyl acetal was furnished by Elanco Products. The nmr spectra were taken in CDCl$_3$ with a Varian A-60 instrument.

3,9-Bischloromethyl-2,4,8,10-tetraoxaspiro[5.5]undecane (IVa). In a 12-l. resin pot were mixed 1912 g (15.2 mol) of chloroacetaldehyde dimethyl acetal, 1040 g (7.6 mol) of pentaerythritol, 4 l. of benzene, and 150 g of Dowex 50W-X4 cation-exchange resin which

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(9) W. E. Conrad, L. A. Levasseur, R. E. Murphy, N. L. Hare, and H. M. Conrad, *ibid.*, **27**, 2227 (1962).

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(11) H. A. Stansbury and H. R. Guest, U. S. Patent 2,998,427 (1961).

had been washed with methanol and dried. The stirred mixture was heated to about 75° while a benzene–methanol azeotrope was collected (bp 58°). The mixture was maintained at this temperature for 24 hr, then filtered and concentrated *in vacuo* to give a white crystalline product which was washed with ethanol and dried to give 1445 g (74%) of IVa. The bischloride was dissolved in hot ethanol and slowly precipitated into cold water to give IVa, mp 95–96°.

Anal. Calcd for $C_9H_{14}Cl_2O_4$: Cl, 27.58. Found: Cl, 27.30.

Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(methylenethiomethylene)] (IIa). In a 12-l. resin pot equipped with a mechanical stirrer, gas inlet tube, and thermocouple were mixed 1003 g (7.5 mol) of sodium sulfide flake, 1931 g (7.5 mol) of bischloride IVa, and 6 l. of DMSO. The mixture was stirred under nitrogen, then heated to 75–80°. When the exothermic reaction began, the external heat source was removed. The temperature reached 120–125° within 5 min and remained in this range for 20–25 min. During this time, the mixture became very viscous. It was cooled to room temperature and left overnight. The resultant solid mass was cut into pieces and washed with two 5-gal. portions of water in a Cowles dissolver to give a finely divided white polymer which was washed with 2 gal. of 95% ethanol and dried *in vacuo* to give 1500 g (92%) of polymer IIa, inherent viscosity 1.1 (0.5% chloroform solution at 30°).

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.53; H, 6.49; S, 14.69. Found: C, 49.26; H, 6.38; S. 14.63.

3,9-Bis(*N*,*N*-dimethyldithiocarbamyl)-2,4,8,10-tetraoxaspiro[5.5]-undecane (IVb). To 28.6 g (0.2 mol) of sodium *N*,*N*-dimethyldithiocarbamate in 100 ml of DMSO (distilled over calcium hydride) was added 25.7 g (9.1 mol) of bischloride IVa. The mixture was heated at 95–100° for 3 hr under nitrogen, then cooled and poured into 1 l. of water to give 37.1 g (87%) of IVb as a white powder, mp 198–205°. The adduct was recrystallized twice from benzene to give needles, mp 209–210°.

Anal. Calcd for $C_{15}H_{26}N_2O_4S$: C, 42.23; H, 6.14; N, 6.57. Found: C, 42.20; H, 6.30; N, 6.47.

3,9-Bismercaptomethyl-2,4,8,10-tetraoxaspiro[5.5]undecane (IVc). To 25 g (0.059 mol) of IVb in a 500-ml round-bottomed flask was added 170 ml of DMSO, 50 ml of water, and 25 g (0.63 mol) of sodium hydroxide pellets. The mixture was magnetically stirred, flushed with nitrogen, and heated between 90 and 115° for 18 hr. It was cooled and poured into 500 ml of water, then carefully neutralized with concentrated HCl to pH 4–5. A white precipitate which formed was separated on a filter and then dissolved in methylene chloride. This solution was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated *in vacuo* to give 12 g (83%) of the bismercaptan IVc. Two recrystallizations from cyclohexane gave white needles, mp 84–87°. Distillation *in vacuo* gave a white solid, mp 87–89° (bp 148–152° (0.1 mm)). The molecular weight was found by vapor pressure osmometry to be 250.

Anal. Calcd for $C_9H_{16}O_4S_2$: C, 42.83; H, 6.39; S, 25.41. Found: C, 43.0; H, 6.35; S, 25.70.

3,9-Bis(1-chloroethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Va). To 55 g (0.6 mol) of α-chloropropionaldehyde (bp 86°) were added 40.8 g (0.3 mol) of pentaerythritol, 2 g of *p*-toluenesulfonic acid monohydrate, and 350 ml of benzene. The stirred mixture was heated to 75° for 2 hr as a water–benzene azeotrope was collected (10 ml). After the cooled solution was filtered, it was concentrated *in vacuo* to give 60 g of a white solid. This material was dissolved in methylene chloride. The solution was washed with dilute sodium carbonate solution and water then dried over anhydrous magnesium sulfate. It was filtered and concentrated to give 56 g (66%) of bischloride. Recrystallization from 95% ethanol gave white crystals, mp 85–89°.

Anal. Calcd for $C_{11}H_{18}Cl_2O_4$: C, 46.33; H, 6.36. Found: C, 46.0; H, 6.17.

Poly[2,4,8,10-tetraoxaspiro[5.5]undecan-3,9-ylene-9-(ethylidenethioethylidene)] (IIIb). To 10 g (0.035 mol) of bischloride Va were added 4.6 g (0.035 mol) of sodium sulfide flake and 40 ml of DMSO. The mixture was stirred and heated under nitrogen to 150° for about 2 hr. After cooling, the solution was poured into 1 l. of water and the resultant off-white powder was collected on a filter, washed with additional water and 95% ethanol, and dried *in vacuo* to give 6 g (70%) of low molecular weight polymer, mp 90–100°. The molecular weight by vapor phase osmometry was 1300–1400.

Anal. Calcd for $C_{11}H_{18}O_4S$: S, 13.0. Found: S, 12.4.

Acknowledgment. The molding characteristics and mechanical properties of the spiroacetal polymer were determined by Mr. M. Hudak and Mr. L. Cech.

Poly(*p*-phenylene). The Reaction of 5,5′-*p*-Phenylenebis-2-pyrone with *p*-Diethynylbenzene[1]

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ABSTRACT: The reaction of 5,5′-*p*-phenylenebis-2-pyrone with *p*-diethynylbenzene in solution at 200–300° produces poly(*p*-phenylene) *via* a Diels–Alder reaction followed by the elimination of carbon dioxide. In the formation of the new phenylene ring as a result of the cycloaddition reaction, predominant para catenation is predicted on the basis that the reaction of 2-phenylpyrone with phenylacetylene affords ~90% *p*-terphenyl (~10% meta isomer). The poly(*p*-phenylene) is yellow (λ_{max} 340 nm), insoluble in all solvents, highly crystalline, and thermally stable. Its sulfonation affords a soluble polymer which has an intrinsic viscosity of 0.14–0.23.

High molecular weight phenylated polyphenylenes obtained from the 1,4-cycloaddition reaction of biscyclopentadienones or bispyrones with bisacetylenes[2–6] have properties which are quite different from those of unsubstituted polyphenylenes prepared by other methods. The phenylated

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(1) For a preliminary account of this research, see J. K. Stille and Y. Gilliams, *Macromolecules*, **4**, 515 (1971).

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