

Preparation and properties of poly(2,2-dialkyltrimethylene sulphones)

Robert Cook*, Eric Schweitzer**, Alan Shuldiner†, Cynthia Market and William Felmy

Department of Chemistry, Lafayette College, Easton, PA 18042, USA
(Received 9 March 1981; revised 20 April 1981)

INTRODUCTION

Several sulphone polymers of structure $(\text{CH}_2-\text{CR}_1\text{R}_2-\text{CH}_2-\text{SO}_2)_n$ have been synthesized¹⁻⁴. All have had small R groups and are characterized by high crystalline melting points (e.g. $\text{R}_1/\text{R}_2 = \text{H}/\text{H}$, 290°C; CH_3/CH_3 , 290°C; $\text{CH}_3/\text{C}_2\text{H}_5$, 280°C) and correspondingly negligible solubilities in common organic solvents. In a previous note⁴ we suggested that, based on X-ray data for poly(2-n-butyl-2-ethyl-trimethylene sulphone), one might envision a sheet-like structure of parallel polymer chains in extended trans conformations, with strong head-to-tail dipole interactions between SO_2 groups on adjacent chains. If the substituent R groups are small, they can be thrust out above and below the plane and not interfere with planar regularity. Recent work in our laboratory has focused on structural modification of these hanging groups in an effort to alter this proposed sheet-like structure. We have now synthesized a series of polymers with $\text{R}_1 = \text{CH}_3$ and $\text{R}_2 = n\text{-C}_6\text{H}_{13}$, $n\text{-C}_8\text{H}_{17}$, $n\text{-C}_{10}\text{H}_{21}$, and $n\text{-C}_{12}\text{H}_{25}$, as well as the polymer where the substituted carbon is part of a cyclohexyl ring. It was our hope that by modifying the chain substituents we could effect a reduction of crystallinity and a partial modification of certain polymer properties.

EXPERIMENTAL

The trimethylene sulphone polymers studied were prepared by multistep syntheses beginning with diethyl methyl-malonate and the appropriate alkyl bromide which through base addition and subsequent reduction gave the 2-alkyl-2-methyl-1,3-propane-diol^{5,6}. In the case of the 2,2-pentamethylene-trimethylene sulphone polymer, the 2,2-pentamethylene-1,3-propane-diol was prepared by a crossed Cannizaro reaction with cyclohexane carboxaldehyde⁷. The diols, which were found to be significantly hygroscopic, were dried under vacuum at 110°C and then converted to cyclic carbonates by reaction

with diethyl carbonate⁸. The cyclic carbonate intermediates, isolated by distillation, were significantly contaminated with diol. These impurities were difficult to separate but did not interfere with the subsequent reactions to form the monomer thietanes. The cyclic carbonates were reacted with KSCN to yield the desired 2,2-disubstituted thietanes⁹. The reaction conditions to produce the thietanes were modified from those in the literature by the addition of catalytic quantities of 18-crown-6 to the reaction mixture. The reaction mixture was then heated under 1.0 atm of N_2 for 1.5 h at 210°C during which time CO_2 was produced by the reactants, forming a thiocyanate intermediate. After cooling, the thietane was distilled from the reaction vessel at reduced pressure as it was formed. Since several of the monomer intermediates have not previously been reported, a summary of their properties is given in Table 1.

The polysulphides were obtained by BF_3 -etherate initiated ring-opening polymerizations of the substituted thietanes after distillation from CaH_2 . The crude polymers were taken up in chloroform and reprecipitated in methanol¹¹. Inherent viscosity measurements made with an Uberholde viscometer resulted in η values of at least 0.15 dl/g at 25°C in CH_3Cl . The polysulphides were oxidized with performic acid to yield the desired polysulphones¹.

The polysulphones gave strong, characteristic sulphur-oxygen infra-red absorptions at 1128 and 1285 cm^{-1} . The

Table 1 Melting and boiling points (mmHg) of intermediates

R_1	R_2	Ester ^a	Diol	Thietane ^b
CH_3	C_6H_{13}	95–97 (0.25)	46–49	125–130 (0.4)
CH_3	C_8H_{17}	115–117 (0.25)	55–57	74–76 (0.05)
CH_3	$\text{C}_{10}\text{H}_{21}$	125–132 (0.4)	56–58	84–90 (0.05)
CH_3	$\text{C}_{12}\text{H}_{25}$	142–146 (0.5)	63–65 ^c	106–114 (0.1)

^a No effort was made to carefully purify these intermediates

^b Elemental analyses were performed for two of the thietanes: 2-Hexyl-2-methyl thietane: 69.40% C, 11.65% H, and 18.62% S (calculated 69.60% C, 11.70% H, and 18.61% S); 2-Dodecyl-2-methyl thietane: 74.91% C, 12.57% H, and 12.58% S (calculated 74.92% C, 12.58% H, and 12.50% S)

^c Previously reported in the literature, see Ref. 10

* To whom correspondence should be directed

** Present address Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

† Present address Department of Endocrinology, The Massachusetts General Hospital and The Harvard Medical School, Boston, MA 02114

n.m.r. spectra of those sulphone polymers soluble in CDCl_3 gave peaks centred at $\delta 3.4$ for the chain backbone H, and at $\delta 1.2$ and $\delta 0.8$ for the methylene and methyl protons of the chain substituents. Elemental analysis was obtained for the poly(2-n-dodecyl-2-methyl-trimethylene sulphone) sample and gave 66.87% C, 11.21% H, and 11.08% S (calculated 66.61% C, 11.18% H, 11.11% S). X-ray powder patterns were obtained on a Norelco X-ray Unit and differential scanning calorimetry data was obtained on a Perkin-Elmer D.S.C.-1B.

RESULTS AND DISCUSSION

We had two main goals in this study. First we hoped to better understand the crystalline structure and thermal stability of this class of polymers. Secondly we wanted to pursue the goal of our earlier work and prepare a soluble trimethylene sulphone polymer for dielectric relaxation work in the hope of clarifying the anomalous dielectric relaxation results obtained on poly(olefin sulphones)^{4,12-15}. Our initial attempt was to synthesize poly(2,2-pentamethylene-trimethylene sulphone), expecting that by making the number two carbon part of a cyclohexyl ring, adjacent chains in the crystalline phase would be pushed apart sterically, thus decreasing interchain interactions. The X-ray powder pattern of the prepared polymer gave an easily detectable diffraction ring corresponding to a repeat distance of about 5.2–5.3 Å and what is probably a second order peak at 10.4 Å. This distance of 5.2 Å corresponds well with the calculated distance between sulphone groups if the chain was in a trans conformation. In our previous work on poly(n-butyl-ethyl-trimethylene sulphone) the same repeat distance was found and, in addition, a repeat distance of 4.2 Å was also observed⁴. We suggested this might be interpreted as the sulphur-sulphur distance between adjacent chains. The absence of this repeat distance in the X-ray power pattern of the poly(2,2-pentamethylene-trimethylene sulphone) is consistent with the idea that the cyclohexyl ring is pushing the chains apart as we had hoped. However, the polymer was found by d.s.c. to have a crystalline melting point of 390°C as previously reported¹ and it had negligible solubility in common organic solvents. It would appear that although there may be some increased separation between chains in the solid phase this is more than compensated for by the symmetric nature of the cyclohexyl ring resulting in a more ordered and stable crystalline material.

We next prepared and studied a series of trimethylene sulphone polymers with chain substituents varying from n-hexyl to n-dodecyl. All of these polymers melted in the range 248–254°C with some yellowing. In each case the X-ray powder pattern of these polymers showed a repeat distance of 5.2 Å, and in the case of $\text{R}_2 = \text{C}_6\text{H}_{13}$, C_8H_{17} , $\text{C}_{10}\text{H}_{21}$, a repeat distance of 4.4 Å was observed. The X-ray data for the polymer with $\text{R}_2 = \text{C}_{12}\text{H}_{25}$ did not show a

repeat distance at 4.4 Å but rather one at 4.9 Å suggesting that perhaps the bulky dodecyl substituent had effected a separation of the chains in the solid phase. To complement these measurements, enthalpies of fusion were measured by d.s.c. for the polymers with $\text{R}_2 = \text{C}_6\text{H}_{13}$, C_8H_{17} , and $\text{C}_{12}\text{H}_{25}$, and found to be 6.0, 5.4, and 7.8 kJmol^{-1} repeat unit respectively. The reliability of these values is suspect due to the slight yellowing which accompanied the melting transition. The solubilities of the polymers in a variety of solvents increased as the length of the substituents increased. All the polymers were insoluble in diethyl ether or mixed hexanes. Only the polymers with decyl and dodecyl groups showed any solubility in benzene, toluene, tetrahydrofuran or chloroform, with the dodecyl polymer having the maximum solubility. In light of the constant crystalline melting points of the four polymers and X-ray data it would appear that the increase in solubility is due not to a decrease in crystallinity but rather to the entropic effect of the longer aliphatic substituents.

ACKNOWLEDGEMENTS

We are grateful to Dr Robert Newland for numerous helpful suggestions on the synthetic aspects of this work and to Mr Stevin Zorn for assisting with the preparation of one of the monomer thietanes. In addition, the help of Mr James Bonn of J. T. Baker Chemical Company in obtaining the d.s.c. data is appreciated. This work was supported in part by a grant from the United States Steel Foundation Inc., Grant of Research Corporation.

REFERENCES

- 1 Foldi, V. S. and Sweeny, W. *Makromol. Chem.* 1964, **72**, 208
- 2 Brode, G. L. *Polym. Prepr.* 1965, **6**, 626
- 3 Stille, J. K. and Empen, J. A. *J. Polym. Sci. A* 1967, **5**, 273
- 4 Cook, R. J. *Polym. Sci. Polym. Chem. Edn.* 1978, **16**, 3001
- 5 Pavia, D. L., Lampman, G. M. and Kriz, G. S., 'Introduction to Organic Laboratory Techniques', Saunders, Philadelphia, 1976, pp 342–343
- 6 Nystrom, R. F. and Brown, W. G. *J. Am. Chem. Soc.* 1947, **69**, 1197
- 7 Shortridge, R. W., Craig, R. A., Greenlee, K. W., Derfer, J. J. and Boord, C. E. *J. Am. Chem. Soc.* 1948, **70**, 946
- 8 Searles, S., Hummel, D. G., Nukina, S. and Throckmorton, P. C. *J. Am. Chem. Soc.* 1960, **82**, 2928
- 9 Searles, S., Hays, H. R. and Lutz, E. F. *J. Org. Chem.* 1962, **27**, 2828
- 10 Joshi, V. S. and Bhide, B. V. *J. Ind. Chem. Soc.* 1960 **37**, 461
- 11 Empen, J. A. and Stille, J. K. *Macromol. Synth.* **3**, p 53
- 12 Cais, R. E. and Bovey, F. A. *Macromolecules* 1977, **10**, 757
- 13 Stockmayer, W. H., Jones, A. A. and Treadwell, T. L. *Macromolecules* 1977, **10**, 762
- 14 Fawcett, A. H., Heatley, F., Ivin, K. J., Steward, C. D. and Watt, P. *Macromolecules* 1977, **10**, 765
- 15 Much of the initial concern due to the absence of a high frequency dielectric response for poly(olefin sulphones) has now been resolved by new measurements. However, certain questions still remain concerning the magnitude of the longitudinal dipole of these polymers. K. Matsuo and W. H. Stockmayer, private communication