

REFERENCES

- 1 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
- 2 Boyer, R. F. *Macromolecules* 1974, **7**, 142
- 3 Fox, T. G. Jr. and Flory, P. J. *J. Am. Chem. Soc.* 1948, **70**, 2384
- 4 Fox, T. G. Jr. and Flory, P. J. *J. Appl. Phys.* 1950, **21**, 581
- 5 Gibbs, J. H. *J. Chem. Phys.* 1956, **25**, 185
- 6 Gibbs, J. H. and DiMarzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
- 7 Rudin, A. and Burgin, D. *Polymer* 1975, **16**, 291
- 8 Richardson, M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
- 9 Turner, D. T. *Polymer*, 1978, **19**, 789
- 10 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
- 11 Williams, M. L. *J. Appl. Phys.* 1958, **29**, 1395
- 12 Fox, T. G. Jr., Kingsinger, J. B., Mason, H. F. and Schuele, E. M. *Polymer* 1962, **3**, 71
- 13 'Use of acrylic monomers in the preparation of low number average molecular weight polymers', Rohm and Haas Technical Report TMM-23, March, 1965
- 14 Sandler, S. R. and Karo, W. 'Polymer Synthesis-Vol. 1', Academic Press, New York, 1974, p. 297
- 15 Characterization Data Sheet of PMMA Cat. No. 18,225-7, Lot No. 03 from Aldrich Chemical Company, Milwaukee, Wisconsin
- 16 Ueberreiter, K. and Kanig, G. *J. Colloid Sci.* 1952, **7**, 569
- 17 Kusy, R. P., Katz, M. J. and Turner, D. T. *Thermochim. Acta* 1978, **26**, 415
- 18 Fox, T. G. Jr. and Loshaek, S. J. *Polym. Sci.* 1955, **15**, 371
- 19 Pratt, G. J. *J. Mater. Sci.* 1975, **10**, 809
- 20 Beevers, R. B. and White, E. F. T. *Trans. Faraday Soc.* 1960, **56**, 744
- 21 Thompson, E. V. *J. Polym. Sci.* 1966, **4**, 199
- 22 Kusy, R. P. and Greenberg, A. R. *J. Thermal Anal.* 1980, **18**, 117
- 23 Cowie, J. M. G. and Toporowski, P. M. *Eur. Polym. J.* 1968, **4**, 621

Poly(β -ketothioethers) by polycondensation of bis- β -dialkylaminoketones with bis-thiols

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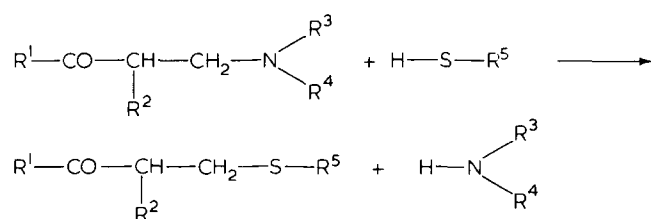
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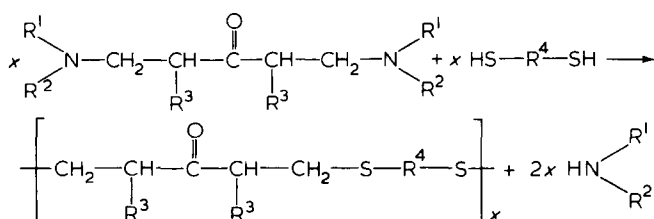
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β -Dialkylaminoketones (Mannich bases) may react with thiols to give β -ketothioethers. Substitution of an -SR group for a dialkylamino group takes place¹⁻³:



We have found that by using bifunctional compounds this reaction can open a synthetic route to a novel class of sulphur-containing polymers, the poly(β -ketothioethers):



The aim of this Report is to relate some results obtained using 2,6-bis(dimethylaminomethyl)cyclohexanone (I), and 1,2-ethanedithiol (II), oxydiethanedithiol (III) or 1,3-dimercaptobenzene (IV).

EXPERIMENTAL

¹H-n.m.r. spectra were run in CDCl₃ on a C-60 Jeol Spectrometer, with TMS as internal reference.

Bis-Mannich base I was prepared according to Barrett⁴. It was distilled just prior use, b.p. 90–92/0.4 mm.

Dithiols II and III were commercial products (Merck). They were purified by vacuum distillation just before use.

Dithiol IV (Fluka) was used without further purification.

Poly(β -ketothioether) V (Table I) was prepared by dissolving I (10.0056 g, 47.13 mmol) and II (4.4395 g, 47.13 mmol) in a 3:1 dioxane/ethanol mixture (43 ml) and maintaining the reaction temperature at 60°C by means of a thermostatic alloy-controlled bath. A slow stream of nitrogen was passed through the reaction mixture, in order to prevent oxidation of the dithiol, and to carry out all dimethylamine which was formed during the reaction. The effluent gases were bubbled into aqueous 0.1 N H₂SO₄ (700 ml), and the progress of the reaction was followed by measuring the amount of dimethylamine absorbed by the acid titrimetrically.

After 40 h, 93.7% of the theoretical amount of dimethylamine had been evolved. The reaction was then brought to completion by raising the temperature to 90°C for 3 h. After this time, the solvents were eliminated by distillation under nitrogen, and the product was purified by dissolving the gummy residue in dichloromethane, and reprecipitating with an excess of light petroleum. The polymer was then recovered by filtration, and dried at room

Table 1 Poly(β -ketothioethers) by polycondensation of 2,6-bis(dimethylaminomethyl)cyclohexanone with bis-thiols

	Structure of the repeating unit		Analysis*			η_{sp}^{\dagger}/c (dl/g)
			C (%)	H (%)	S (%)	
V		fd	55.59	7.41	29.65	0.36
		ctd	55.51	7.45	29.63	
VI		fd	55.21	7.55	24.52	0.40
		ctd	55.35	7.74	24.62	
VII		fd	64.35	6.58	23.92	0.22
		ctd	63.60	6.10	24.25	

* In all cases, nitrogen was found to be absent by qualitative tests (Lassaigne)

 $\dagger c = 1\%$, in chloroform at 30°CTable 2 Solubility data on poly(β -ketothioethers)*

Solvent	Polymer		
	V	VI	VII
n-Heptane	i	i	i
Benzene	sh	s	sh
Toluene	sh	s	sh
Ether	i	i	i
Dioxane	sh	s	sh
Tetrahydrofuran	sh	s	sh
Methanol	i	i	i
Ethanol	i	i	i
n-Butanol	i	i	i
Acetone	i	i	sw
Ethyl acetate	i	i	sw
Chloroform	s	s	s
Dichloromethane	s	s	s
Dimethyl sulphoxide	sh	sh	sh
Dimethylformamide	sh	s	sh
Water	i	i	i

* s = soluble; sh = soluble at the b.p.; sw = swells; i = insoluble

temperature/0.1 mmHg. Yield 9.5 g (93%). The n.m.r. spectrum of V was in agreement with the proposed structure. In particular, the CH_3 peak (2.3 δ) relative to the dimethylamino group of the starting ketobase I was absent.

Poly(β -ketothioether) VI was prepared in a similar way, starting from 6.0917 g (28.69 mmol) of I and 3.9665 g (28.69 mmol) of III in 26 ml of 3:1 dioxane/ethanol. The reaction mixture was kept at 60°C for 24 h, and at 90°C for 24 h.

After this time, the solvents were eliminated as in the previous case, and the gummy product was purified by dissolving in dichloromethane, and reprecipitating with light petroleum. Yield 6.9 g (92.5%). The n.m.r. spectrum is in agreement with the proposed structure. As in the previous case, the dimethylamine peak was absent.

Poly(β -ketothioether) VII was prepared in a similar way, starting from 3.5348 g (16.65 mmol) of I and 2.3683 g (16.65 mmol) of IV in 15 ml of 3:1 dioxane/ethanol. After

standing for 5 h at 60°C, the reaction was brought to completion in 20 h at 90°C. After evaporating the solvents, the product was isolated by dissolving in hot chloroform and reprecipitating with light petroleum. Yield 4.1 g (93%). The n.m.r. spectrum is in agreement with the proposed structure. As in the previous cases, the dimethylamine peak was absent.

RESULTS AND DISCUSSION

The poly(β -ketothioethers) prepared in the present work are listed in Table 1, together with their specific viscosities, and elemental analyses. It may be noted that fairly high molecular weight products (as indicated by the viscosity values) can be obtained in high yields with both aliphatic and aromatic dithiols.

Some solubility data on the new poly(β -ketothioethers) are given in Table 2: the three polymers exhibit a similar behaviour towards solvents. As expected, polymer VI has a wider spectrum of solubilities, owing to its more flexible chain.

It may be added that some preliminary results seem to demonstrate that the above polycondensation can take place with bis-Mannich bases and bis-thiols, having a wide range of structures. Further work on this subject is presently in progress, and will be published in forthcoming papers.

REFERENCES

- Andrisano, R., Angeloni, A. S. and Tramontini, M. *Annal. Chim. (Rome)*, 1965, **55**, 652 and 1093
- Andrisano, R., Angeloni, A. S., De Maria, P. and Tramontini, M. *J. Chem. Soc. (C)*, 1967, p. 2907
- Tramontini, M. *Synthesis*, 1973, p. 703, and references therein
- Barrett, P. A. *J. Chem. Soc.* 1958, p. 330