

Cross-linked sulphur-containing polymers: reaction of poly(β -ketosulphide)s with formaldehyde and bis-thiols

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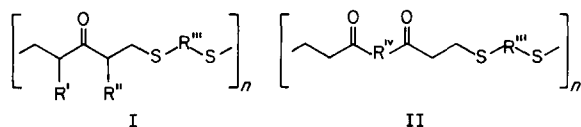
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Cross-linking of linear poly(β -ketosulphide)s has been performed by use of formaldehyde and bis-thiol in alkaline medium. The reaction results were successful depending on the nature of polymeric substrate and reactant bis-thiol. In particular, the substrate must be sufficiently stable to the concurrent dethiolation reaction, which is favoured by the alkaline medium, and the cross-linking agent should be an aliphatic bis-thiol with a suitable chain length.

(Keywords: poly(β -ketosulphide)s; cross-linking reaction; cross-linked sulphur-containing polymers)

INTRODUCTION

The synthesis of poly(β -ketosulphide)s I and II has been previously reported to occur by reacting ketonic bis-Mannich bases and bis-thiols¹⁻³. Such polymers have been tested as stabilizers for plastics⁴⁻⁶ and their behaviour towards oxidizing agents has been thoroughly investigated³.



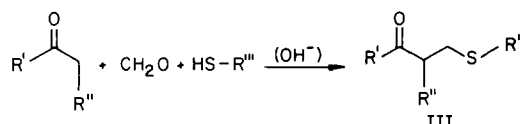
With the aim of obtaining cross-linked sulphur-containing polymers with potential applications in the field of oxidation-resistant and hydrophobic resins, the cross-linking of poly(β -ketosulphide)s I is reported in the present paper. It has been investigated, in particular, how the reaction is affected by the nature of the polymeric substrate as well as of the cross-linking agent.

Preliminary experiments carried out on polymers I in the melt by treatment with trioxymethylene, in the presence of diethanolamine as basic catalyst under similar conditions as those reported for obtaining formaldehyde resins⁷ (e.g. phenol-formaldehyde resins), generally failed. In fact, extensive depolymerization occurred with formation of vinyl-ketone and thiol-terminated fragments, probably due to the high reaction temperature. Such a process could also prevail because the formation of short linkages (methylene bridges) between the macromolecular chains is sterically hindered and the resultant cross-linking reaction depressed.

In the present study, the cross-linking reaction has been carried out under milder conditions (in solution at 70°C), but in the presence of a stronger basic catalyst (alcoholic

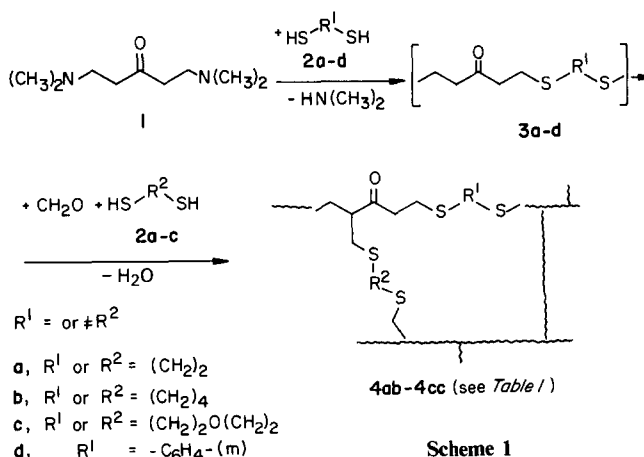
potassium hydroxide). Moreover, an equimolar amount of bis-thiol has been introduced in order to increase the length of the bridges between polymer chains as well as to reduce the undesired dethiolation reaction.

It is well known that thiols and formaldehyde in alkaline conditions can give condensation with alkyl-ketones affording thiomethyl derivatives III or polymeric β -ketosulphides when bis-thiols are used⁸.



RESULTS AND DISCUSSION

The polymers (**3a**, **3c**, **3d**, Scheme 1) deriving from the bis-Mannich base **1** and the corresponding bis-thiols **2a**, **2c**, **2d** have already been reported², whereas **3b** has been



Scheme 1

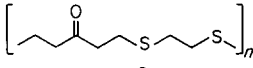
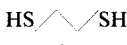


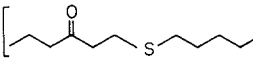
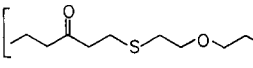
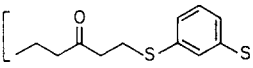
synthesized in the present work in order to cover a wide range of structural units in the starting material.

Poly(β -ketosulphide)s **3a–d**, dissolved in benzyl alcohol at $\sim 70^\circ\text{C}$ under nitrogen atmosphere, have been allowed to react with bis-thiols **2a–c**, formaldehyde and potassium hydroxide ($\sim 2\text{M}$ solution in benzyl alcohol) using molar ratios 1:2:1 with respect to the repeating unit of the polymer in that order. After few minutes, with only two exceptions (see below), the reaction product precipitates in good yields (*Table 1*) proving insoluble in all the solvents in which the polymeric substrate can be dissolved (*Table 2*). I.r. spectra do not show any substantial variation with respect to the corresponding starting materials as far as the position of the bands is

concerned, thus indicating the presence of unchanged β -ketosulphide structure. Elemental C, H, S analyses (*Table 1*) confirm the introduction of nearly one $-\text{CH}_2-\text{S}-\text{R}^2-\text{S}-\text{CH}_2-$ group for each repeating unit of the starting polymer, as expected.

The d.s.c. behaviour of the insoluble products, as compared with the corresponding starting linear polymers (*Table 2*), shows the absence of endothermic melting peaks and displays an appreciable thermal stability up to 220°C or more, after which degradation reaction starts to occur. In some cases exothermic processes also begin to take place at the above temperatures, probably due to aldol-type condensation reactions occurring into the polymer mass. *Figure 1*

Table 1 Cross-linking of poly(β -ketosulphide)s **3a–d** with formaldehyde and bis-thiols **2a–c**

Polymer (%, C, H, S)	Cross-linking agent HS-R ² -SH	Product 4 (yield %)	Elemental analysis (%)					
			Calc. ^a			Found		
			C	H	S	C	H	S
 3a (C, 47.69; H, 6.86; S, 36.37)	 2a	<i>b</i>						
	 2b	4ab (55)	48.44	6.88	39.71	48.70	7.10	37.59
	 2c	4ac (54)	46.15	6.56	37.83	47.03	6.70	37.72
 3b (C, 52.90; H, 7.89; S, 31.38)	2b	4bb (81)	51.42	7.48	36.53	52.19	8.14	36.65
	2c	4bc (87)	49.17	7.15	34.94	50.66	7.87	34.88
 3c (C, 49.06; H, 7.32; S, 29.10)	2b	4cb (86)	49.17	7.15	34.94	49.21	7.92	35.12
	2c	4cc (80)	47.08	6.85	33.52	47.88	7.43	31.87
 3d	2b	<i>b</i>						

^a Calculated for a product having one additional $-\text{CH}_2\text{S}-\text{R}^2-\text{SCH}_2-$ group per each repeating unit of the starting polymer

^b No cross-linking occurs; see text and experimental

Table 2 Thermal and solubility properties of starting polymers **3** and cross-linked products **4**

Compound	Thermal data ($^\circ\text{C}$)		Solubility data ^a	Notes
	Initial modification temperature	Melting peak temperature		
3a	95 ^{bc}	119 ^c	(A, B, C, D, E, F, G, H) ^d	
4ab	270 ^e	–	Insoluble	Yellow powder
4ac	222 ^f	–	Insoluble	Yellow powder
3b	97 ^b	103	E, F, (A, B, C, D, G, H)	
4bb	232 ^e	–	Insoluble	White powder
4bc	267 ^f	–	Insoluble	White powder
3c	35 ^{bc}	50 ^c	A, B, C, D, E, F, (G, H) ^d	
4cb	269 ^f	–	Insoluble	White powder
4cc	280 ^e	–	Insoluble	White powder

^a A, Benzene; B, toluene; C, dioxane; D, tetrahydrofuran; E, chloroform; F, dichloromethane; G, dimethylsulphoxide; H, dimethylformamide (letters in parentheses indicate solubility near the boiling point)

^b Initial melting temperature

^c From reference 9

^d From reference 2

^e Initial exothermic transformation (see, e.g., curve D in *Figure 1*)

^f Initial decomposition temperature (see, e.g., curve C in *Figure 1*)

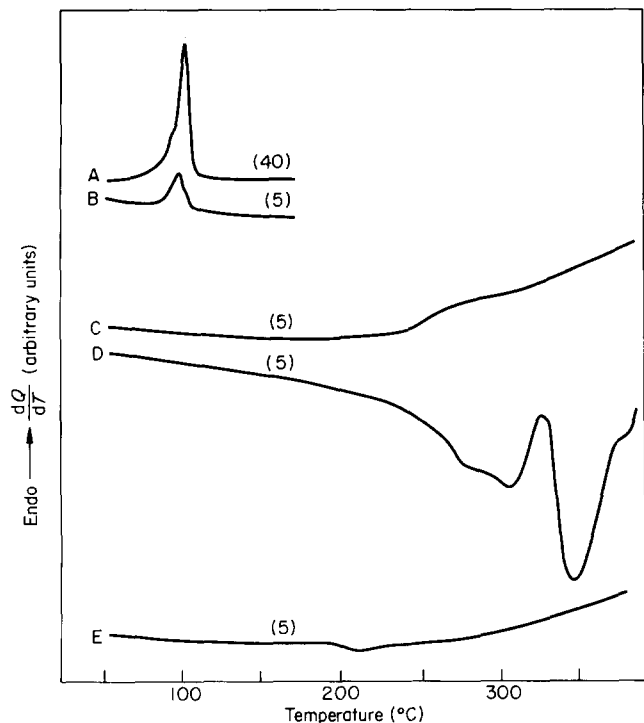


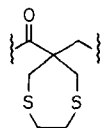
Figure 1 D.s.c. of polymer **3b** (curves A, B) and of the cross-linked products **4ac**, **4bb** and **8b** (curves C, D and E, respectively). Heating rates (in °C min⁻¹) are reported in brackets

shows the d.s.c. curves of polymer **3b** together with two typical examples of the thermal behaviour of the insoluble products.

All the collected data allow reasonable assignment of the cross-linked structure **4** (Scheme 1) to the above-mentioned products.

Polymer **3a**, which was found to give, with bis-thiols **2b** and **2c**, cross-linked products **4ab** and **4ac** in lower yield with respect to polymers **3b** and **3c** (Table 1), does not afford any cross-linked product with ethanedithiol **2a**. By contrast, a quite complex broadly melting material, having higher solubility and lower S content than the starting polymer, is obtained in 45% yield.

Elemental analysis, solubility, i.r. and n.m.r. data (see Experimental) do not allow the easy assignment of a well-defined structure to this material. However, the presence of $-S-CH_2-$ and/or $-CH_2OH$ groups on the C atom in α position with respect to carbonyl as well as the occurrence of unsaturated groups, produced by depolymerization of **3a** (due to thiol elimination), are observed. The seven-membered cyclic structures of the type depicted below, originated by intramolecular thiomethylation already described^{8,10} in analogous reactions on alkylketones, cannot be excluded.

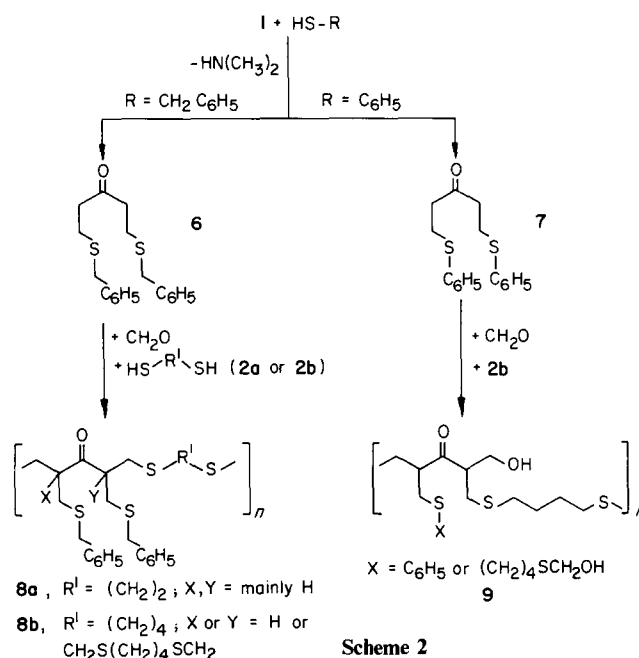


Indeed, the n.m.r. signal at 3.2 ppm (see Experimental) can be assigned¹⁰ to the ring $-CH_2-S-$ groups in β position to the carbonyl.

The above results suggest that in this case the combined effects of polymer degradation and cyclization reactions are prevailing on the cross-linking process, thus preventing any formation of insoluble material.

Polymer **3d** with butanedithiol **2b** does not yield cross-linked products. From this reaction only a small amount of an oily product has been isolated, which results from depolymerization of **3d** and replacement of the arylthiol by the aliphatic one.

The capability of giving cross-linked products by polymers **3a-d** in the reaction with formaldehyde and bis-thiols has been further studied employing bis-thiol **2b** and keto-sulphides **6** and **7** as models of the alkyl- and arylthio polymers **3a-c** and **3d**, respectively (Scheme 2). The



Scheme 2

shorter ethanedithiol **2a** has been also allowed to react with model **6** to test how the chain length of the cross-linking agent affects the reaction.

The thioalkylation has been carried out with molar ratios keto-sulphide/formaldehyde/bis-thiol/KOH 1:2:1:1.

From the reaction between **6** and **2a** an oligomeric product **8a** ($n=3$) having X and Y mainly equal to H precipitates in low yield. The presence of the seven-membered cyclic structures of the type described above is also possible in such a product.

On the contrary, **6** with **2b** gives, in a shorter reaction time, a gummy material **8b** having the properties of a cross-linked product, as it appears insoluble in the most common organic solvents which are usually able to dissolve the corresponding linear polymers **3** and swells in chloroform and dichloromethane. Moreover, elemental analysis indicates the presence of slightly less than two $-CH_2S(CH_2)_4SCH_2-$ groups per repeating unit of **8b**, thus suggesting a considerable substitution of H-atoms in the α position to the carbonyl group.

The d.s.c. analysis of **8b** (Figure 1, curve E) does not show any melting peak and exhibits a similar trend as observed for the cross-linked products **4**, with the appearance of a weak exothermic process around 200°C before the degradation reaction begins.

All the collected data indicate an extensive cross-linking of **8b**, X or Y in Scheme 2, thus representing the $-CH_2S(CH_2)_4SCH_2-$ group as binding moiety between the polymer chains.

Keto-sulphide **7** in reaction with **2b** behaves similarly to polymer **3d**, giving rise in a low yield to product **9**, characterized by a low molecular weight ($M_n \approx 2000$). For this material the partial substitution of phenyl-thio groups by the alkyl-thio groups of butanedithiol can be proposed. On the basis of n.m.r. analysis (see Experimental) a 3:1 alkyl-thio/phenyl-thio molar ratio per repeating unit is evidenced. Moreover, the presence of S-CH₂OH and C-CH₂OH groups is observed by i.r. and ¹H n.m.r. The general structure depicted in Scheme 2 can be assigned to product **9**, where X represents C₆H₅ or (CH₂)₄SCH₂OH groups, having similar probability of occurrence.

EXPERIMENTAL

Molecular weights were determined by a Knauer vapour pressure osmometer. I.r. spectra were recorded on a Perkin Elmer 1750 FT-IR spectrophotometer and ¹H n.m.r. spectra (in CDCl₃) on a Varian EM 360 L spectrometer; chem. shifts are given in δ ppm, using TMS as internal reference. Elemental analyses were obtained on a Carlo Erba CHN/S elemental analyser mod. 1106. A Perkin Elmer differential scanning calorimeter mod. DSC-2C was used for the calorimetric measurements.

Bis-thiols **2a** and **2c** (Merck) and **2b** (Aldrich) were purified by vacuum distillation just before use.

Poly(β -ketosulphide) **3b**

This polymer was prepared according to ref. 2 from 3.04 g (17.6 mmol) of bis-Mannich base **1** in benzyl alcohol (34 ml) and 2.16 g (17.6 mmol) of 1,4-butanedithiol **2b**. The mixture was kept under a slow nitrogen stream at a temperature gradually rising from 60 to 120°C during 4 days. Polymer **3b** precipitated on cooling in 84% yield and was purified by repeated washings with diethylether (76% yield). Analysis: calculated for C₉H₁₆OS₂: C, 52.90; H, 7.89; S, 31.38%. Found: C, 52.71; H, 8.18; S, 31.40%. $[\eta] = 0.165$ (dl/g, in CHCl₃ at 30°C); $M_n = 2600$. I.r.: 1708 cm⁻¹ (C=O). ¹H n.m.r.: δ p.p.m. 1.63 (4H, m, C-CH₂-CH₂-C); 2.52 (4H, m, CO-CH₂); 2.80 (8H, m, S-CH₂).

General procedure of cross-linking of polymers **3** by formaldehyde and bis-thiols **2**

To a solution of polymer **3** (2.4 mmol of repeating units) in benzyl alcohol (4 ml) at 67°C, under nitrogen atmosphere, 2.4 mmol of bis-thiol **2**, 4.8 mmol of paraformaldehyde and 2.4 mmol of potassium hydroxide (1.27 ml of a 1.93 M solution in benzyl alcohol) were added. The temperature was kept constant and a precipitate was generally formed after a few minutes. The reaction mixture was then poured into a large excess of water and neutralized with diluted hydrochloric acid. The solid product was finally filtered, thoroughly washed with water and dried under vacuum. The i.r. spectra (KBr disc) were in agreement with the expected structure. In particular, increased intensity of CH bands at 2920 and 1410 cm⁻¹ was observed. An example is shown in Figure 2. Yields and other characteristic data are shown in Tables 1 and 2.

The reaction of **3a** with 1,2-ethanedithiol **2a** did not give any precipitate after one hour and a yellowish product was obtained by addition of an excess of water (45% yield). Such a product, melting from 105 to 230°C,

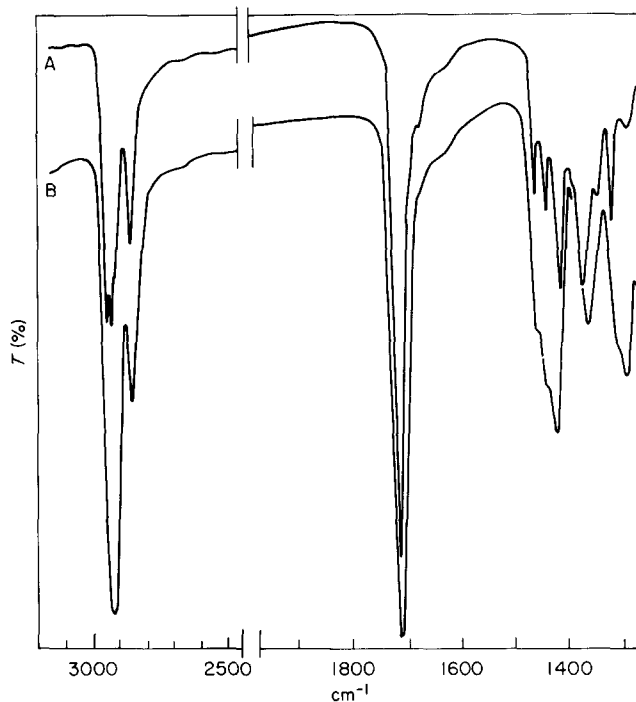


Figure 2 FT-i.r. spectra of polymer **3b** (A) and cross-linked product **4bb** (B)

proved completely soluble in benzyl alcohol and warm dimethylsulphoxide, whereas it was partially soluble in cold acetone, dimethylsulphoxide and chloroform. Analysis: found C% 44.08, H% 6.70, S% 31.30. I.r. of the crude product showed bands at 3435 (OH), 1705 (C=O), 1656 and 1632 (C=C), 1407 and 832 (C=CH₂) 1058 (C-OH) cm⁻¹. The i.r. spectrum of the fraction soluble in acetone displayed bands at 3397, 1705 and 1058 cm⁻¹ and its ¹H n.m.r. spectrum exhibited peaks from 2.53 to 3.22 ppm, attributable to S-CH₂-CH₂-S, CO-C-CH₂-S, CH₂-CO and CH-CO groups.

The reaction of **3d** with **2b** was carried out at 120°C due to the low solubility of the starting polymer. No precipitation of product was observed after one hour. By addition of excess water an ether-soluble yellow oil (15% yield) was obtained which was not further purified. Its i.r. spectrum showed in particular the presence of bands at 2560 (SH) and 1710 (C=O) cm⁻¹. ¹H n.m.r.: peaks at δ ppm 1.32 (s, SH), 1.75 (m, SCH₂CH₂CH₂CH₂S), 2.48–3.04 (m, S-CH₂, CO-CH₂, CO-CH) and 7.61 (s, arom. H). Analysis: found C% 63.41, H% 7.62, S% 22.48.

1,5-Bis-benzylthio-pentan-3-one **6**

To 2.82 g (1.64 mmol) of bis-Mannich base **1** in toluene (10 ml), 4.25 ml (36.1 mmol) of benzylthiol were added. The mixture was kept at 70°C for 24 h under a slow stream of nitrogen until all the dimethylamine was evolved. The solution was then washed with 10% aq. sodium hydroxide and water, dried (Na₂SO₄) and finally evaporated under vacuum. An oily product (3.7 g, 68% yield) was obtained. After crystallization with pet. ether at 0°C the product had m.p. 10.5–12°C. Analysis: calculated for C₁₉H₂₂OS₂: C, 69.04; H, 6.71; S, 19.40%. Found: C, 68.57; H, 6.90; S, 19.09%. I.r.: bands at 3040–3100 (arom. CH), 1720 (C=O), 770 and 710 (arom. CH) cm⁻¹. ¹H n.m.r.: δ ppm 2.65 (8H, m, SCH₂CH₂ and CH₂-CO), 3.73 (4H, s, S-CH₂-C₆H₅) and 7.34 (10H, s, arom. H).

1,5-Bis-phenylthio-pentan-3-one 7

The same procedure as for **6** was followed employing 5.67 g (32.9 mmol) of **1** in toluene (85 ml) and 7.97 g (72.4 mmol) of thiophenol. The crude product (8.6 g) was crystallized from 4:1 pet. ether/benzene, thus giving 6.28 g (63% yield) of pure **7**, m.p. 42–43°C. Analysis: calculated for $C_{17}H_{18}OS_2$: C, 67.51; H, 6.00; S, 21.20%. Found: C, 67.71; H, 6.01; S, 21.68%. I.r.: bands at 3060 (arom. CH), 1710 (C=O), 745 and 695 (arom. CH) cm^{-1} . 1H n.m.r.: δ p.p.m. 2.68 (4H, t, CH_2 -CO), 3.12 (4H, t, CH_2 -S) and 7.33 (10H, m, arom. H).

Reaction of **6** with ethane- and butanedithiols **2a** and **2b**

To a mixture of **6** (1 g, 3.03 mmol), bis-thiol **2** (3.03 mmol) and paraformaldehyde (0.18 g, 6.06 mmol) a 1.78 M solution of potassium hydroxide in ethanol (1.7 ml, 3.03 mmol) was added under nitrogen atmosphere and the reaction mixture was heated at 40°C.

In the reaction with **2a** an oily product (**8a**) was obtained after 1 h; it was dissolved in dichloromethane and then reprecipitated with pet. ether (0.29 g, 22% yield). $\bar{M}_n = 1400$. Analysis: calculated for $C_{23}H_{28}OS_4$: C, 61.56; H, 6.29; S, 28.58%. Found: C, 60.65; H, 6.71; S, 29.20%. I.r.: bands at 3026–3083 (arom. CH), 1710 (C=O) cm^{-1} . 1H n.m.r.: δ p.p.m. 2.69–3.21 (14H, m, CH_2 -S, CH -CO), 3.78 (4H, s, C_6H_5 - CH_2 -S) and 7.48 (10H, s, C_6H_5).

In the reaction with **2b** a gummy insoluble product (**8b**) was formed after 20 min (0.55 g, 38% yield). The product swelled in dichloromethane and chloroform, being insoluble in the other solvents listed in Table 2. Analysis: calculated for $C_{31}H_{43}OS_6 \cdot H_2O$: C, 57.58; H, 7.06; S, 29.96%. Found: C, 57.51; H, 6.93; S, 29.18%. I.r.: bands at 3400 (OH), 3083–3025 (arom. CH), 1709 (C=O), 1418 and 2914 (CH_2) cm^{-1} .

Reaction of **7** with butanedithiol **2b**

To a mixture of **7** (2.0 g, 6.6 mmol), bis-thiol **2b** (0.81 g, 6.6 mmol) and paraformaldehyde (0.4 g, 13.2 mmol) a 1.78 M solution of potassium hydroxide in ethanol (3.7 ml, 6.6 mmol) was added under nitrogen atmosphere. The reaction mixture was heated at 40°C for 1 h and at 60°C for an additional hour. As no precipitate was formed, the solution was poured into a large excess of water until an oily product was formed. This was extracted with dichloromethane, the resulting solution washed with water, dried (Na_2SO_4) and finally evaporated under vacuum. 0.48 g (16% yield) of product **9** were obtained after further purification by dissolution in dichloromethane and reprecipitation with pet. ether. $\bar{M}_n = 2000$. Analysis: found: C% 50.72, H% 7.12, S% 27.93. I.r.: bands at 3424 (OH), 3070–3018 (arom. CH), 1708 (C=O), 1025 (C-OH) cm^{-1} . 1H n.m.r.: δ p.p.m. 1.67 (12H, m, $SCH_2CH_2CH_2CH_2S$), 2.50–2.83 (28H, m, S- CH_2 , CH_2 -CO and CH -CO), 3.82 (4H, m, C- CH_2 OH), 4.71 (2H, s, S- CH_2 OH) and 7.34 (5H, s, C_6H_5). Deuterium exchange with D_2O revealed the presence in the sample of about two mobile hydrogen atoms in the region 2.5–2.8 ppm.

CONCLUSION

All the results obtained show that the capability of bis-thiols and formaldehyde to give cross-linking reactions on poly(β -ketosulphide)s under alkaline conditions is

strongly related to the nature of both polymer substrate and bis-thiol reactant.

The cross-linking reaction occurs provided that the starting polymer is sufficiently stable towards the degradation caused by the strongly alkaline medium.

The above stability mainly depends on the nucleophilic character of the bis-sulphide moiety present in the repeating unit of the polymer chain. In fact **3d**, which derives from a poor nucleophile (good leaving group) such as the aryl bis-thiol **2d**, readily decomposes before giving any cross-linking.

Analogous behaviour is shown by the corresponding low molecular weight analog **7**, which undergoes extensive removal of the aryl bis-thiol by the more nucleophilic aliphatic butanedithiol **2b**.

Polymer **3a** also shows a similar trend towards degradation, even if to a rather low extent. In this case, besides the nature of the main chain ethane-bis-sulphide moiety, which is a good leaving group due to the presence of an electron-withdrawing atom in the β -position with respect to S, an important role is played by the cross-linking capability of the bis-thiol reactant. As a consequence, either low yields of the cross-linked products (**4ab**, **4ac**) or no cross-linking at all in the reaction with **2a** occur. In fact, the chain length of reactants **2b** and **2c** is long enough to allow that cross-linking reaction occurs before an extensive polymer degradation takes place. By contrast, the shorter and less nucleophile **2a** appears unable to link together at close distance the macromolecular chains of the starting materials. However, the chain length of the bis-thiol reactant seems to play a more important role than its nucleophilicity, as supported by the results obtained in the reaction of **3a** with oxydiethanedithiol **2c** which, although it has a comparable nucleophilicity as **2a** (due to the O-atom in the β -position to S), affords cross-linked products in the same yield as butanedithiol **2b**.

Accordingly, **6**, the low molecular weight analog of polymers **3a-c**, gives rise only to an oligomeric material in the reaction with **2a**, whereas with **2b** no cross-linked products are obtained.

In conclusion, the bis-thiol/formaldehyde reagent is to be considered a convenient cross-linking agent for poly(β -ketosulphide)s, provided that the substrate is sufficiently stable under alkaline conditions and the bis-thiol has a suitable chain length.

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REFERENCES

- 1 Andreani, F., Angeloni, A. S., Angiolini, L., Costa Bizzarri, P., Della Casa, C., Fini, A., Ghedini, N., Tramontini, M. and Ferruti, P. *Polymer* 1981, **22**, 270
- 2 Andreani, F., Angiolini, L., Costa Bizzarri, P., Della Casa, C., Ferruti, P., Ghedini, N., Tramontini, M. and Pilati, F. *Polym. Commun.* 1983, **24**, 156
- 3 Angiolini, L., Ghedini, N. and Tramontini, M. *Polym. Commun.* 1985, **26**, 218
- 4 Andreani, F., Angeloni, A. S., Angiolini, L., Costa Bizzarri, P.,

- Della Casa, C., Ferruti, P., Fini, A., Ghedini, N., Manaresi, P., Pilati, F. and Tramontini, M. Italian Patent Application 20305 A/82
- 5 Andreani, F., Costa Bizzarri, P., Della Casa, C., Ferruti, P. and Ghedini, N. Italian Patent Application 22180 A/82
- 6 Ferruti, P., Angiolini, L., Ghedini, N., Manaresi, P. and Pilati, F. Italian Patent Application 23166 A/83
- 7 Saunders, K. J. 'Organic Polymer Chemistry', Chapman and Hall, London, 1977, p. 291
- 8 Dronov, V. I., Nikitin, Y. E., *Usp. Khim.* 1985, **54**, 941 and refs. cited therein; *Ch. Ab.* 1985, **103**, 214237
- 9 Pilati, F., Andreani, F., Angiolini, L., Costa Bizzarri, P., Della Casa, C., Ferruti, P., Ghedini, N. and Tramontini, M. *Polym. Commun.* 1983, **24**, 309
- 10 Dronov, V. I., Nigmatullina, R. F., Khalilov, L. M. and Nikitin, Y. E. *Zh. Org. Khim.* 1979, **15**, 1709; *Ch. Ab.* 1980, **92**, 5662