A POLYMERIC ANALOG OF DIMETHYL SULFOXIDE: SYNTHESIS OF CROSSLINKED POLYMERS WITH BOUND SULFOXIDE GROUPS

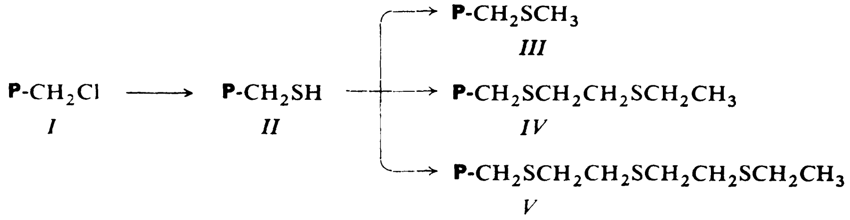
Václav JANOUT, Hana HRUDKOVÁ and Pavel ČEFELÍN

Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6

Received December 2nd, 1983

By using a sequence of functionalization reactions, a series of crosslinked polymers with pendant sulfoxide units of the $\mathbf{P}$-$(CH_2SOCH_2)_nR$ type with $n = 1, 2, 3$ and $R = H, CH_3$, where **P** is poly(styrene-co-divinylbenzene) (content of the crosslinking component 1%, 2%) were prepared. The high reactivity of the crosslinked polymeric thiol $\mathbf{P}$-CH_2SH in alkylation reactions was used in the preparation. Conditions for the selective oxidation of polymeric sulfides to sulfoxides were checked.

Possibilities of using insoluble, suitably functionalized polymers as solid cosolvents have been pointed out earlier[1-10]. These possibilities, along with the concept of three-phase catalysis[1], gave rise to a number of papers demonstrating the usefulness of polymers which contain structurally similar units, such as, *e.g.*, those present in hexamethylphosphortriamide[1-4], N,N-dimethylacetamide[5], linear polyethers derived from ethylene glycol[6-9], N-methylpyrrolidone[10], crowns, and cryptands[12,13]. Surprisingly enough, only very few papers have so far been published dealing with this subject in the case of dimethyl sulfoxide (DMSO). In the field of application of a polymeric analog of dimethyl sulfoxide as the solid cosolvent, only the activity of polymeric sulfoxide has been described in the reaction between 1-bromobutane and cyanides under the conditions of three-phase catalysis[14]. Also, quite recently, Japanese authors have synthesized an uncrosslinked soluble analog of dimethylsulfoxide and demonstrated its activity[15].



SCHEME 1

This study is a continuation of the work reported earlier and concerning crosslinked poly(1-[*p*-(methylsulfinylmethyl)phenyl]ethylene)[14]; it is dealing with the preparation and characterization of the polymer in which the crosslinked polystyrene carrier contains bound $—CH_2SOCH_3$ units and $—(CH_2SOCH_2)_nCH_3$ groupings ($n = 2$ or 3). Their preparation starts with chloromethylated poly(styrene-co-divinylbenzene) and continues according to Scheme 1.

Oxidation of polymeric sulfides gave a series of crosslinked polymeric sulfoxides of the general formula

$$\mathbf{P}\text{-}(CH_2SOCH_2)_nR$$

$$VI\text{: } n = 1,\ R = H$$
$$VII\text{: } n = 2,\ R = CH_3$$
$$VIII\text{: } n = 3,\ R = CH_3\ ,$$

where **P** is the polymeric carrier – poly(styrene-co-divinylbenzene) containing 1% or 2% divinyl benzene units as the crosslinking agent, and $—(CH_2SOCH_2)_nR$ simply denotes numerous functional groups of the given structure. Polymers *I* with various chlorine contents were used in the reactions (Table I).

The reaction of chloromethylated groups on the polymeric carrier with thiourea followed by hydrolysis leads without complications to polythiols *IIa*–*IId* (ref.[16,17]), even though it may be assumed that the formation of the isothiouronium salt would be accompanied by considerable steric requirements and a strong ionic effect, especially

TABLE I

Conversion of chloromethylated poly(styrene-co-divinylbenzene) (*I*) to polythiol *II*. M_2 denotes monomeric units of divinylbenzene

I	M_2 %	Chlorine content %	Chlorine content mmol/g	Substitution %	*II*	Sulfur content calc./found	Sulfur content mmol/g	Substitution %
Ia	1	23·70	6·68	100	*IIa*	21·05 20·85	6·52	98
Ib	2	23·66	6·66	100	*IIb*	21·05 20·78	6·49	97
Ic	2	16·90	4·76	63	*IIc*	15·16 14·77	4·62	61
Id	2	10·50	2·95	36	*IId*	9·32 8·84	2·76	33

in cases *Ia*,*b*, It has been found earlier[16] that polymer *IIa* may be transformed into the thiolate form by equilibration with anhydrous sodium methoxide. The process is accompanied by a strong swelling of the polymer, which also makes thiolate groups inside the crosslinked polymeric matrix readily accessible to reactions. This is why this polymer offers further opportunities for performing a number of functionalization reactions[18].

Crosslinked polymers *III*–*V* (polymeric sulfides) are obtained by Williamson's alkylation of the salt of thiol *II* with dimethyl sulfate or 2-chloroethyl derivatives of the type $ClCH_2(CH_2SCH_2)_nCH_3$, $n = 1, 2$, prepared by using a sequence of known reactions from 2-mercaptoethanol; the results of alkylation reactions are summarized in Table II. The reactions with dimethyl sulfate proceed comparatively smoothly, while those with 1-chloro-3-thiapentane and with 1-chloro-3,6-dithiaoctane do not lead to complete conversions. A strong influence of network density in the polymeric matrix can be seen in this case (*cf.* entry 5 *vs* 6 and entry 9 *vs* 10). The degree

TABLE II

Conversion of crosslinked polythiols *II* to polymeric sulfides *III*

Entry	*II*	*T* °C	Time h	*III*	Sulfur content, % calc.	Sulfur content, % found	Conversion %
			Reaction of *II* with $(CH_3O)_2SO_2$				
1	*IIa*	40	27	*IIIa*	19·51	19·20	98
1	*IIa*	40	68	*IIIa*	19·51	19·50	100
2	*IIb*	40	69	*IIIb*	19·51	19·13	98
3	*IIc*	40	69	*IIIc*	14·40	14·31	100
4	*IId*	40	24	*IIId*	9·05	8·97	100
			Reaction of *II* with $ClCH_2CH_2SCH_2CH_3$				
5	*IIa*	45	70	*IVa*	26·89	24·15	52
6	*IIb*	45	70	*IVb*	26·89	22·25	19
7	*IIc*	45	70	*IVc*	21·60	19·62	86
			Reaction of *II* with $ClCH_2CH_2SCH_2CH_2SCH_2CH_3$				
8	*IIa*	55	190	*Va*	32·20	26·28	46
9	*IIa*	55	215	*Va*	32·20	26·78	51
10	*IIb*	55	215	*Vb*	32·20	24·68	31
11	*IIc*	55	215	*Vc*	27·00	23·68	70

of ring substitution also seems to be an important factor, because compared with *IIb*, the starting thiol *IIc* can be alkylated very readily (*cf.* entry 6 *vs* 7 and entry 10 *vs* 11), although the network density of the polymeric matrix is the same. Due to further uses of the polymers as polymer catalysts with pendant sulfoxide units, the formation of sulfonium groupings bound to the polymer had to be ruled out. For this reason, drastic reaction conditions (elevated temperature, large excesses of the low-molecular weight reagent) must be avoided in such alkylation reactions. Polymers *IV*, *V* thus formed have absorption bands at 2 500 cm^{-1} in the IR spectra corresponding to the unreacted —SH groups, while there is no band of the —SH vibration in the spectra of polymers *III*.

It has been verified earlier that oxidation of sulfide groups in polymer *IIIa* with an equivalent amount of 30% H_2O_2 in an aqueous medium in presence of acetic acid at −10°C gives rise selectively to sulfoxide units, and that polymer *VIa* (the letter suggests that the polymer is related to the starting polymer, *cf.* Table I) does not contain detectable —SO_2— groups[14]. If, however, near the centre undergoing multistage oxidation there is another centre which can be oxidized similarly, the reaction in the latter centre may be both favoured and disfavoured by transfer of new stereoelectronic effects[19]. The difference in the reaction mechanisms is also of importance. It was observed in the oxidation of low-molecular systems containing mutually close —SO— and —S— groups in one molecule that in the case where a nucleophilic mechanism (HOO^-, $R^1R^2CHOO^-$, R—COO^-) is operative, the attack of the positively charged sulfur atom is preferred, and the sulfone–sulfide system is exclusively formed[19–21]. If the nucleophilic oxidation mechanism is not operative, selective oxidation can be performed in both centres, leading to the formation of bis(alkylsulfinyl) derivatives[19]. This is also confirmed by our results of the oxidation of cross-linked polymeric sulfides. The procedure used for cases of the oxidation of polymers *IV* and *V* and verified earlier did not reveal any sulfonic groups in products *VII* and *VIII* (ref.[14]). Oxidation of *IV* and *V* which contain free —SH groups gives rise to polymers with no absorption at 2 550 cm^{-1}; it may be assumed, therefore, that —SH groups were oxidized with formation of disulfidic groups. Of course, the presence of —SO_2H groups (the absorption of which lies in the absorption in range of sulfoxides) in these polymers cannot be excluded either[22].

EXPERIMENTAL

Chemicals

2-Mercaptoethanol (Fluka) was used without previous purification. Samples of chloromethylated poly(styrene-co-divinylbenzene) were obtained by the chloromethylation of poly(styrene-co--divinylbenzene) (Spolchemie, Ústí nad Labem) (extracted for 24 h with benzene) with chloromethyl methyl ether using $SnCl_4$ as the catalyst according to ref.[23]; their reaction with thiourea (reagent grade, Lachema) and alkaline hydrolysis of isothiouronium salts[14] gave rise to the respective polythiols.

Preparation of Low-Molecular Weight Sulfides

1-*Chloro*-3-*thiapentane* was prepared from 3-thiapentan-1-ol and $SOCl_2$. ^1H NMR spectrum C^2HCl_3, δ, ppm): 3·60 (t, 2 H, $ClCH_2$), 2·50—2·90 (m, 4 H, S—CH_2), 1·20 (t, 3 H, CH_3). The starting 3-thiapentan-1-ol was prepared by reacting 2-mercaptoethanol with ethyl bromide according to ref.[24].

3,6-*Dithiaoctan*-1-*ol*: To sodium ethoxide prepared from 1·29 g Na (56 mg-atom) and 30 ml ethanol, 4·380 g (3·93 ml, 56 mmol), 2-mercaptoethanol was added, and after that, 7·000 g (56 mmol) 1-chloro-3-thiapentane was added dropwise with stirring at 40°C. The mixture was stirred at 40°C for 7 h. After the solvent was distilled off, 20 ml water was added to the residue, and the mixture was extracted three times with 50 ml CH_2Cl_2. The organic layer was dried with Na_2SO_4, the solvent was distilled off, and the raw product was distilled *in vacuo*. Yield 6·805 g (41 mmol, 73%) of the product, b.p. 101—105°C/0·20 kPa, n_D^{20} 1·5355. ^1H NMR spectrum (C^2HCl_3, δ, ppm): 3·70 (t, 2 H, CH_2—O), 2·42—2·78 (m, 9 H, CH_2—S, O—H), 1·22 (t, 3 H, CH_3).

1-*Chloro*-3,6-*dithiaoctane*: To 4·68 g 3,6-dithiaoctan-1-ol (28·2 mmol), 3·60 g (2·2 ml, 30 mmol) $SOCl_2$ was added with stirring and cooling. The mixture was maintained at 70°C for 3 h, on cooling added to 20 ml of 10% $NaHCO_3$, extracted with CH_2Cl_2, the extract was washed twice with 50 ml of 10% $NaHCO_3$ and 50 ml water and dried over Na_2SO_4. Distillation gave 3·40 g (18·4 mmol, 65%) of the product, b.p. 74—76°C/0·07 kPa. ^1H NMR spectrum (C^2HCl_3, δ, ppm): 3·60 (t, 2 H, Cl—CH_2), 2·50—2·90 (m, 8 H, CH_2—S), 1·20 (t, 3 H, CH_3).

Preparation of Polymeric Sulfides (General Procedure)

To 1·5 g of the given polythiol, a corresponding amount of 1M-CH_3ONa in CH_3OH was added with exclusion of moisture, and the mixture was kept 2 h at 50°C. After that, a corresponding amount of the alkylating agent was added at once (*cf.* Table II), and the mixture was left to stand under the given conditions under nitrogen. The polymers were first washed with water and methanol and then by stirring with 50 ml of methanol and ether for 24 h, and dried at 50°C/0·13 kPa for 48 h.

Oxidation of Polymeric Sulfides (General Procedure)

A mixture of 1 g polymeric sulfide and 2 ml 99% CH_3COOH was maintained at room temperature for 12 h. On cooling to −10°C, an equivalent amount of 30% H_2O_2 and 1 ml glacial acetic acid were added at once. The mixture was left to stand at −10°C for 8 h. The strongly swollen polymers were then washed on the glass filter successively with 50% CH_3COOH, water, methanol and ether and dried at 50°C/0·13 kPa for 48 h. IR spectra (7·2 mg/0·37 g KBr) have a common band at 1 020 cm^{-1}, but not bands at 1 300—1 340 and 1 150 cm^{-1} corresponding to antisym. or sym. vibrations of the sulfonic group.

The determined sulfur content (%) in the polymeric sulfoxides thus obtained: *VIa* 17·48, *VIb* 17·05, *VIc* 13·00, *VId* 8·82; *VIIa* 19·73, *VIIb* 19·45, *VIIc* 17·45; *VIIIa* 23·15, *VIIIb* 21·64, *VIIIc* 20·22.

REFERENCES

1. Tomoi M., Takubo T., Ikeda M., Kakiuchi H.: Chem. Lett. *1976*, 476.
2. Regen S. L., Nigam A., Besse J. J.: Tetrahedron Lett. *1978*, 2757.
3. Tomoi M., Ikeda M., Kakiuchi H.: Tetrahedron Lett. *1978*, 3757.

4. Nee G., Leroux Y., Seyden-Penne J.: Tetrahedron *37*, 1541 (1981).
5. Regen S. L., Mehrotta A., Singh A.: J. Org. Chem. *46*, 2182 (1982).
6. Regen S. L., Dulak L.: J. Amer. Chem. Soc. *99*, 623 (1977).
7. Regen S. L., Heh J. C. K., McLick J.: J. Org. Chem. *44*, 1961 (1979).
8. Kimura Y., Regen S. L.: J. Org. Chem. *48*, 195 (1983).
9. Kimura Y., Regen S. L.: Syn. Commun. *13*, 443 (1983).
10. Nee G., Seyden-Penne J.: Tetrahedron *38*, 3485 (1982).
11. Regen S. L.: Angew. Chem., Int. Ed. Engl. *18*, 421 (1979).
12. Cinquini M., Colonna S., Molinari H., Montanari F., Tundo P.: J. Chem. Soc., Chem. Commun. *1976*, 394.
13. Tomoi M., Kihara K., Kakiuchi H.: Tetrahedron Lett. *36*, 3485 (1979).
14. Janout V., Čefelín P.: This Journal *47*, 1818 (1982).
15. Kondo S., Ohta K., Tsuda K.: Macromol. Chem., Rapid Commun. *4*, 145 (1983).
16. Janout V., Čefelín P.: Polymer, in press.
17. Fréchet J. M. J., de Smet M. D., Farral M. J.: Polymer *20*, 675 (1979).
18. Kalch P., Poiblanc R., Gaset A., Rovera A., Martin R. P.: Tetrahedron Lett. *21*, 459 (1980).
19. Ogura K., Suzuki M., Tsuchibashi G.: Bull. Chem. Soc. Jap. *53*, 1414 (1980).
20. Curch R., Modena G.: Tetrahedron Lett. *1965*, 863; *1963*, 1749.
21. Ogata Y., Suyama S.: J. Chem. Soc., Perkin Trans. 2, *1973*, 755.
22. Detoni S., Hadži D.: J. Chem. Soc. *1955*, 3163.
23. Hodge P., Sherrington D. C.: *Polymer-Supported Reactions in Organic Synthesis.* Wiley, Chichester, New York, Brisbane, Toronto 1980.
24. Albertson F., Tullar B. F.: J. Amer. Chem. Soc. *67*, 502 (1945).

Translated by L. Kopecká.