The Initiation of Propylene Sulphide Polymerization by Ammonia–Zinc Carbonate

W. COOPER and M. E. TUNNICLIFFE

Propylene sulphide and aqueous ammonia in dimethyl formamide solution react slowly to give a thiol which initiates polymerization to give low molecular weight polymer. The rate of this reaction has been measured, and an approximate estimate of the composite propagation velocity constant has been made.

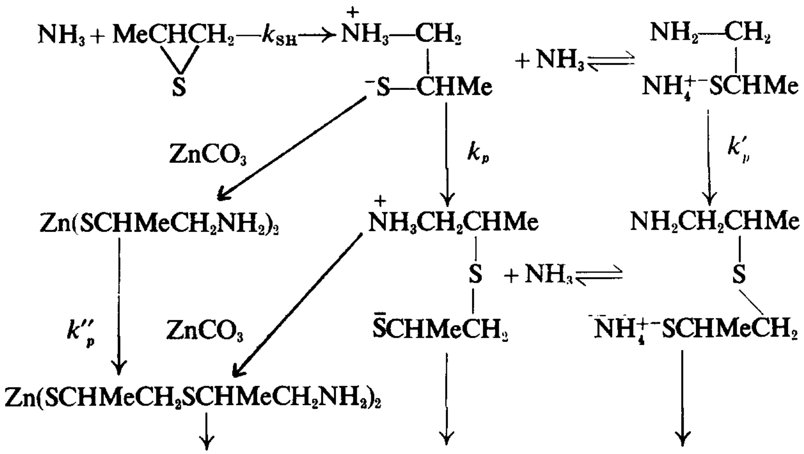
Added zinc carbonate does not affect the rate of formation of thiol significantly but dissolves to give zinc thiolates, which initiate polymerization less rapidly and so give lower molecular weight polymer.

Polymer obtained in the presence of excess zinc carbonate, although of low molecular weight, is a soft elastomer, because of intermolecular coordination bonds between zinc atoms and terminal amino groups in the polymer. These bonds can be destroyed by the addition of a stronger donor or by treatment with acid.

IN *British Patent No. 1 125 566*[1] a process is disclosed for the preparation of polyalkylene sulphides containing terminal amine and thiol groupings. Suitable initiators for these polymers, of value in the preparation of coatings by reaction with di-isocyanates[2] are compounds (usually carbonates or oxides) of zinc or cadmium and aqueous ammonia. The molecular weights of the polymers, which vary from liquids to solid rubbers, are controlled by the proportions of monomer, metal salt and ammonia, and decrease with increase in ammonia concentration[3].

The role of the initiators is not clear. Zinc and cadmium compounds alone will initiate polymerization[4], but so also will ammonia in the absence of a metal compound[5]. The rate of polymerization initiated by zinc carbonate in the absence of ammonia is very dependent on the grade of metal salt employed and on its pretreatment—heating to 150°C prior to polymerization, for example, has been found advantageous[4]. The mechanism of formation of a soluble catalytic entity from the oxide or carbonate and monomer is not clear, and although hydroxyl, in addition to thiol, terminal groups are present in the polymer, the way in which they arise is not certain[6].

In view of the known reaction of amines with alkylene sulphides to form alkylamino alkane thiols[7], and the ability of zinc and cadmium thiolates to initiate homogeneous polymerization of propylene sulphide[8], it seemed reasonable to assume that the ammonia would first open the episulphide ring to give aminopropanethiol. This could then polymerize monomer or, if zinc carbonate were present, polymerization would result from the zinc amino propane thiolate, as indicated in the following scheme*.



The importance of the different reaction paths would depend on the velocity constants for initiation and propagation and, since aqueous ammonia and metal carbonates and oxides are insoluble in the monomer, on the stirring conditions. The scheme would account for the formation of polymer with one thiol and one amino terminal group and for the solubilization of metal carbonate or oxide during polymerization.

As initiation will continue throughout the polymerization, there should be a steady increase in thiol content with time. It is the purpose of this communication to confirm this expectation, and to make estimates of the reaction velocity constants.

The two-phase systems obtained from monomer and aqueous ammonia are not convenient for analytical measurements, so a suitable common solvent, dimethyl-formamide, was also used†. The change with time in thiol content is shown for typical reaction conditions in *Figure 1*. In *Figure 2* is shown the Arrhenius plot for the rate of thiol formation (k_{SH}) over the range 0° to 30°C, from which the activation energy and frequency factor are calculated to be 14·9 kcal/mole and $1{\cdot}6 \times 10^{-5}$ respectively. (Data treated by method of least squares.)

The velocity constants, $2{\cdot}3 \times 10^{-7}$ and $3{\cdot}6 \times 10^{-6}$ l. mole^{-1} sec^{-1} at 0°C and 30°C respectively, are very similar to those for the ring-opening of

---

*Initiation from hydroxyl ions derived from ammonium hydroxide (or ammonia hydrates) is also possible, but clearly this is not a major reaction otherwise the polymer would be predominantly hydroxyl-thiol rather than amine-thiol. In this investigation even under the conditions most likely to give side reactions, namely high conversion and the presence of excess zinc carbonate, the polymer had a ratio of amine to thiol groups near to unity (SH/N=1/0·86).

Velocity constants have been calculated on the total ammonia concentration, but in the presence of water the effective concentration of ammonia acting as NH_3 may well be less than this. However, a constant ratio of ammonia to water was employed throughout. In the heterogeneous systems the ammonia concentration would be determined by its partition coefficient between monomer, which dissolves very little water, and the aqueous phase.

†It is appreciated that the solvent, in addition to changing the concentrations of active species, could also change the propagation velocity constants, but the main features of the reaction should not be affected.

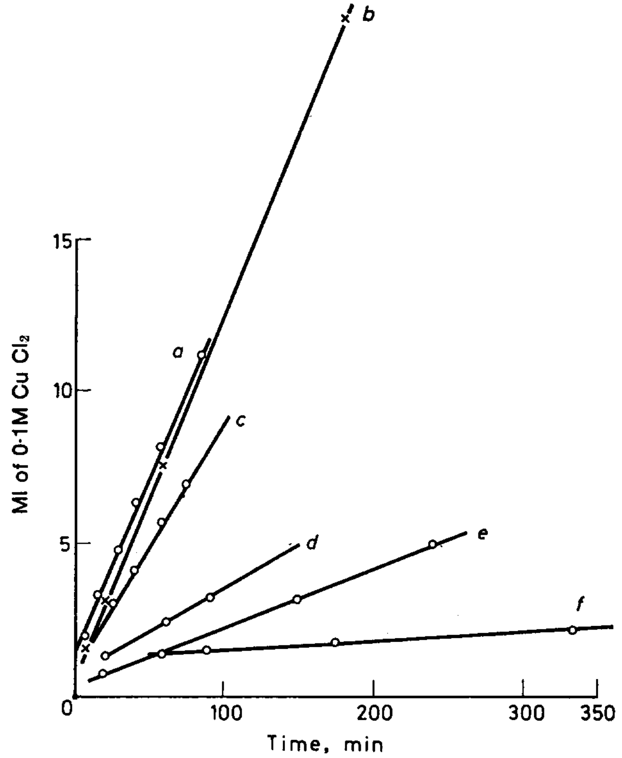


Figure 1—Thiol formation in the reaction of propylene sulphide with ammonia

	Temp., °C	*Mole ratio* $PS/NH_3/ZnCO_3$
a	30·5	8·25/1/0
b	30	8·25/1/0·041
c	25	8·25/1/0
d	20	8·25/1/0
e	20	16·5/1/0
f	0	16·5/1/0

Reactions as 50 per cent solution in DMF

propylene oxide by bases, calculated from the data of Gee *et al.*[9]. The activation energy and temperature-independent factors are somewhat different (17·4 kcal/mole, and 10^{-7} respectively, are quoted for the HO^-–propylene oxide reaction), but not greatly so.

From measurements of the yield of polymer at the end of the reaction and knowledge of the concentration of thiol groups, the degree of polymerization (DP) can be calculated. This varies from 19 to 38 in the absence of zinc carbonate and from 6 to 15 in its presence, at the reagent concentrations and temperatures used (*Table 1*).

As concentrations of growing chains and monomer are varying with time, the overall propagation velocity constant cannot be obtained directly from k_{SH} and yield of polymer. However, an approximate value can be

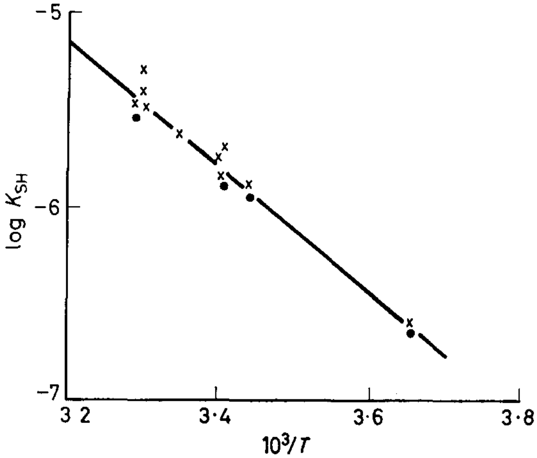


Figure 2—Variation of k_{SH} with temperature. PS/NH_3: ●, 16·5/1; ×, 8·25/1

calculated assuming the monomer removed by the propagation reaction is large in comparison with that involved with initiation, and that in the early stages of reaction, initiation is of constant rate at a given ammonia concentration. These assumptions are reasonable, since in a typical experiment employing 0·63 mole of propylene sulphide and $8{\cdot}7 \times 10^{-2}$ mole NH_3, only $7{\cdot}9 \times 10^{-3}$ mole of thiol was produced during the consumption of 0·3 mole monomer; the lines in *Figure 1* are essentially straight.

$$-\mathrm{d}M/\mathrm{d}t = k_p[I]\,[M] \simeq k_p k_{SH}[A]_0[M]t$$

where $[A]_0$ is the initial concentration of ammonia. Hence

$$\ln(M_0/M) = k_p k_{SH}[A]_0 t^2/2$$

Table 1. Polymer and thiol yields in reaction of propylene sulphide with ammonia/zinc carbonate

Temp. (°C)	*Time (min)*	*SH* × 10^2 *(mole)**	*Polymer (mole)**	*DP (calc.)*
4	370	1·08†	0·24	22*
20	110	1·21	0·46	38‡
	105	1·26	0·49	33‡
	180	1·85	0·14	7·5§
30	85	2·08	0·40	19‡
	85	1·78	0·11	6·2‖
	180	3·52	0·40	11‖
	240	4·65	0·60	13‖
	245	4·60	0·68	15‖

*Calculated per mole of propylene sulphide initially present.
†Interpolated.
‡PS/NH_3=8·25/1.
§PS/NH_3/$ZnCO_3$=8·25/1/0·025.
‖PS/NH_3/$ZnCO_3$=8·25/1/0·041.

From the polymer yields at the end of the reaction, and taking the appropriate units for k_{SH}, values for k_p[*] were calculated to be in the range 2 to 3×10^{-3} l. mole^{-1} sec^{-1} at 20°C. Propagation is much faster than initiation in spite of the fact that the reactions are of similar type, but this is in accord with the observation that in the polymerization of alkylene sulphides by amines alkyl substitution on the nitrogen has a pronounced effect in increasing polymerization rate[10].

Zinc carbonate, which dissolved in the course of the reaction, reduced both the rate of polymerization and the molecular weight of the polymer but not the rate of thiol formation (*Figure 1* curve *b*). The overall velocity constants were in the range 1·5 to 3×10^{-4} l. mole^{-1} sec^{-1} at 20° to 30°C and although these cannot be ascribed to any specific propagating centre, since there must be several of them, the range is close to the published value of 4×10^{-4} l. mole^{-1} sec^{-1} at 30°C for homogeneous polymerization using zinc thiolate initiators[8].

The amount of zinc carbonate used can only react with a small proportion of the total initiating sites produced and it is surprising that it should have so marked an effect on rate and DP. Rapid transfer is to be expected between the amino-thiols and the zinc thiolates[8], but it is not obvious why this should have any effect on the polymerization rate. With excess of zinc carbonate the polymerization was comparable in rate and low molecular weight products were formed, showing the primary reaction still to be that between the monomer and ammonia. However, the physical appearance of the polymer produced was very different, being a soft deformable rubber, resilient on the application of a rapid stress, instead of a viscous liquid. This is undoubtedly due to inter-molecular coordination between the zinc atoms and terminal amino groups in the polymer, which has been shown at sufficiently high molecular weights to result in insoluble 'crosslinked' products[8]. Removal of the zinc by treatment with hydrochloric acid converted the rubbery polymer to a liquid material with a viscosity appropriate to its molecular weight. From the amount of combined zinc (3·73 per cent) and the thiol content of the acid-treated polymer (1·68 per cent) it appears that only one polymer chain of DP 23–26 is attached to the metal, which might be expected when the zinc carbonate is in large excess.

Molecular weights (by GPC) on this polymer showed some unusual features (*Table 2*). The zinc-containing polymer gave an apparent DP of 34, suggesting that coordination bonds persist in the THF solvent. Treatment with ethylene diamine, which would not remove zinc, but which by preferential coordination with the metal would break any internal or external coordination bonds, caused a fall in DP to ten while the acid-treated (zinc-free) aminothiol polymer gave a value of 14.

It is apparent that there is a lack of consistency between the values calculated from chemical determinations and those from GPC. This could

---

[*] This will be a composite of k_n and k_p', since although ammonia is a weaker base than an alkylamine it is present in much higher concentration. Polymerization from sites resulting from the attack of the primary amino group on propylene sulphide is also possible. Such a reaction would produce a dithiol and a secondary amine group in the polymer (i.e. a ratio of SH/N greater than unity). This reaction does occur, particularly at high conversions and at high reaction temperatures or when zinc compounds are used as catalysts, but does not seem to be significant under the conditions used here.

Table 2. Molecular weights of polypropylene sulphide initiated by ammonia or ammonia + zinc carbonate

Initiator $PS/NH_3/ZnCO_3$		$\overline{M}_w$	$\overline{M}_n$
8·25/1/0		4160	1250
8·25/1/0·041		1780	760
	*	1950	735
8·25/1/0·410		4025	2510
	†	2520	770
		1880‡	740‡
	*	2560	1050
		2480‡	1040‡

*Treated with hydrochloric acid.
†Treated with $(CH_2NH_2)_2$. Excess reagent was not removed but was readily resolved from the polymer.
‡Averages calculated on the main distribution of the polymer, omitting a very small (five per cent) and separate higher molecular weight fraction. This latter probably results from independent initiation by the zinc carbonate.

arise from changes in the retention time in the GPC columns resulting from differences in the chemical structure of the end groups or from the presence of low molecular weight species of different structure from those analysed and, although the observed values are in the range calculated from the kinetic data, it would be prudent to use the molecular weight data for purposes of comparison rather than as absolute values.

Experimental

Purified propylene sulphide (50 ml) and aqueous ammonia (2·5 or 5 ml) were obtained as a 50 per cent homogeneous solution in DMF; zinc carbonate (99·5 per cent purity, with a particle size of 20–30 μm) was added where appropriate. The reaction mixtures were thermostatically controlled at the appropriate temperature and aliquots taken at intervals titrated by 0·1 M $CuCl_2$ in DMF—the end point was given by the blue cuprammonium colour. The polymer, which is sparingly soluble in the solvent mixture, caused the mixture to separate into two phases later in the reaction. Yields of polymer were determined by removal of excess monomer, solvent, etc., under vacuum, or by gas chromatography; results by the two procedures were concordant. Molecular weights were by gel permeation chromatography in THF.

Dunlop Research Centre,
Kingsbury Road,
Birmingham 24

(*Received March 1969*)

REFERENCES

[1] Dunlop Co. Ltd (1965)
[2] *Brit. Pat. No. 1 109 165* Dunlop Co. Ltd (1965)
[3] *Brit. Pat. No. 1 109 164* Dunlop Co. Ltd (1965)
[4] *Brit. Pat. No. 1 042 149* Dunlop Co. Ltd (1963)
[5] Delepine, M. and Jaffene, P. *C. R. Acad Sci.*, 1920, **171**, 36, found ammonia to polymerize ethylene sulphide to a low molecular weight nitrogen-containing polymer

[6] Woodhams, R. T., Adamek, S. and Wood, B. B. *J. Rubb. Plast. Age,* 1965, **46,** 56

[7] Wineman, P. J., Collis, M. H., James, J. C. and Pompini, A. M. *J. Org. Chem.* 1962, **27,** 4222

[8] Cooper, W., Morgan, D. and Wragg, R. T. *European Polymer J.* 1969, **5,** 71

[9] Gee, W., Higginson, W. C. E., Taylor, K. J. and Trenholme, M. W. *J. chem. Soc.* 1961, 4298

[10] Dunlop Co., Forthcoming publications

Note added 2 October 1969

The velocity constants for thiol formation and rate of polymerization at 30°C in dry 50/50 propylene sulphide/DMF solution containing ammonia gas (0·225M) were $2{\cdot}3 \times 10^{-6}$ and 4×10^{-4} l mole^{-1} sec^{-1}. The rate of initiation is therefore comparable to that found using aqueous ammonia and supports the view that the mechanism is the same. The main difference between the two systems was a lower ratio of combined nitrogen to thiol in the polymer obtained in the absence of water ($SH/N = 1{\cdot}59$) which would imply a proportion of chains with two terminal thiol groups, although the experimental DP of 19·7 was close to the value of 21·5 calculated from polymer yield and thiol content assuming one thiol group per polymer molecule.