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SOME NEW ASPECTS OF ALKYLENE SULPHIDES POLYMERIZATION WITH RING OPENING

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Abstract—A new possibility has been demonstrated for opening of the three-membered sulphur-containing heterocycles and formation of linear polymers under the action of charge-transfer complexes.

The polymerization of alkylene sulphides acting as donors successfully proceeds in the presence of various organic electron-acceptors, such as maleic anhydride, quinones, nitro- and CN-derivatives of hydrocarbons.

Initiation has been found to be the formation of charge-transfer complexes between the monomer and the acceptor. The formation of these complexes and their composition in solvents of various polarities have been studied by means of u.v. spectroscopy. The initiating ability of an acceptor is shown to depend not only on its affinity to the electron but also on the number of functional groups possessing acceptor properties. A sharp increase of the polymerization rate due to increase in polarity of the medium has been found. The mechanism of initiation is considered.

INVESTIGATIONS of polymerization mechanisms in the last decade have shown the essential role of the donor–acceptor (DA) interaction in the initiation and growth of macromolecular chains. In most cases, this is a relatively strong interaction where the compounds of transition metals are electron acceptors.

We have paid attention to the role of weak intermolecular interactions in the formation of DA complexes with organic compounds as electron donors and acceptors. The DA interaction between a monomer and organic electron acceptors has been used by us(1) to initiate, for the first time, polymerization of three-membered S- and O-containing heterocycles with the formation of linear polymers. So far, initiation by DA interaction has been known mainly for N-vinyl monomers, in particular, N-vinylcarbazole.(2)

Among the heterocyclic monomers the most interesting was propylenesulphide (PS), a typical *n*-donor due to $3p^2$-unshared electron pair localized on the sulphur atom. Charge transfer complexes of the $n\pi$-type have been shown to form when PS interacts with organic electron acceptors such as quinones, π-acids, polynitro-compounds, maleic anhydride (MA); this results in shifting the electron density and facilitates the fission of the C–S polar bond in the strained three-membered ring.

The formation of DA complexes is confirmed by the appearance of new absorption bands in the u.v. or the visible spectrum; these new absorption bands are absent in the spectra of the individual components (Fig. 1). As can be seen from Table 1, these new absorption bands shift to the longwave region as the electron affinity of an acceptor (E_a) increases, i.e. there is proportionality between the energy of the electron transfer $h\nu$ and the E_a value.

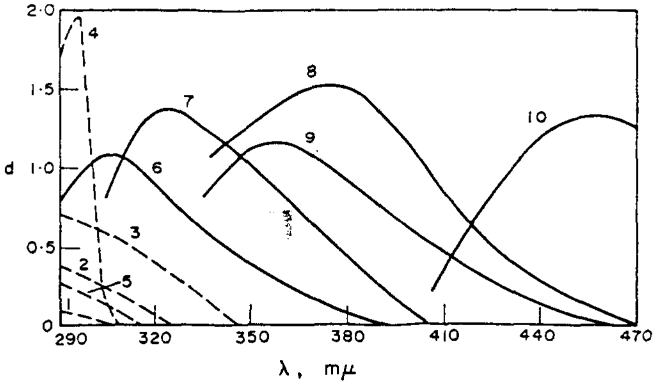

FIG. 1. Ultra-violet spectra of complexes with charge transfer and of individual components: 1—PS; 2—TNM; 3—MA; 4—chloranil; 5—trinitrobenzene; 6—PS–MA complex; 7—PS–trinitrobenzene complex; 8—PS–chloranil complex; 9—PS–TNM complex; 10—PS–tetracyanethylene complex.

TABLE 1. THE DEPENDENCE OF THE POSITION OF THE CHARGE-TRANSFER BAND ON THE ELECTRON AFFINITY OF AN ACCEPTOR (DONOR–PS). SOLVENT—CHLOROFORM, TEMP.—25°.

No.	Electron acceptor	Electron affinity E_a, (eV)	λ_{max} (mμ)	$h\nu$ (eV)
1	Maleic anhydride	0·5	305	4·06
2	Trinitrobenzene	0·69–0·76	320	3·87
3	Tetranitromethane	1·2*	358	3·48
4	Chloranil	1·37	372	3·34
5	Tetracyanethylene	2·2	455	2·73

* The E_a value is estimated according to the position of the charge-transfer band of the PS–tetranitromethane complex.

However, the initiating ability of the acceptor depends not only on its electron affinity but also on the number of functional acceptor groups (Table 2).

TABLE 2. POLYMERIZATION OF PS IN THE PRESENCE OF VARIOUS ELECTRON ACCEPTORS. ACCEPTOR CONCENTRATION—0·25 mole/l. TEMP. = 90°. THE POLYMERIZATION WAS CARRIED OUT IN BULK

No.	Electron acceptor	E_a (eV)	Polymerization time (hr)	Polymer yield (%)
1	Maleic anhydride	0·5	40	54·3
2	2,4-Dinitrophenol	0·59–0·67	40	30·4
3	2,4-Dinitrotoluene	0·76	40	20·4
4	sym-Trinitrobenzene	0·69–0·76	26	87·5
5	*m*-Dinitrobenzene	0·77–0·82	40	23·0
6	4-Chlor-1,3-dinitrobenzene	—	40	26·0
7	Tetranitromethane	1·2	26	89·5
8	Chloranil	1·37	40	66·7
9	Tetracyanethylene	2·2	5	100

The polarity of the medium is known to influence greatly the complex formation; therefore, one could expect that use of polar solvents will affect the kinetics of the polymerization initiated by the DA interaction. Indeed, sharp increase of the polymerization rate was observed with increasing solvent polarity (Table 3). In our opinion, this fact is associated both with the increase of the extent of the charge transfer and the equilibrium character of the reaction of the DA complex formation. It has been found by spectral methods that the equilibrium constant for the PS–tetranitromethane (TNM) complex formation becomes higher as the solvent polarity increases. The equilibrium constants calculated according to the Benesi–Hildebrand and Scott methods(3) were 1·1 l./mole in nitromethane (a strongly polar solvent) and 0·29 l./mole, i.e. 4 times less, in chloroform* (a weakly polar solvent).

TABLE 3. THE EFFECT OF THE MEDIUM POLARITY ON THE POLYPROPYLENESULPHIDE YIELD. [PS] = 4·3 mole/l. TEMP. 75°

No.	Electron acceptor	Acceptor concentration (mole/l.)	Solvent	ϵ of the solvent	Time (hr)	Yield (%)
1	Tetranitromethane	0·0172	Benzene	2·27	7	0·15
2	Tetranitromethane	0·0172	Toluene	2·38	7	—
3	Tetranitromethane	0·0172	Chloroform	4·72	7	1·0
4	Tetranitromethane	0·0172	Nitrobenzene	34·75	1·5	65·0
5	Tetranitromethane	0·0172	Nitromethane	38·57	1·5	69·5
6	Maleic anhydride	0·33	Toluene	2·38	8·25	0·5
7	Maleic anhydride	0·33	Chloroform	4·72	8·25	1·1
8	Maleic anhydride	0·33	Nitrobenzene	34·75	8·25	75·5
9	Maleic anhydride	0·33	In bulk	—	8·25	7·4

In solvents of various polarity, change of complex composition is also possible. By spectral methods, the composition of the complex PS with two electron acceptors (TNM—strong; MA—weak) has been determined. Figures 2 and 3 show the dependence of the optical density of MA–PS complexes on the relation of components in

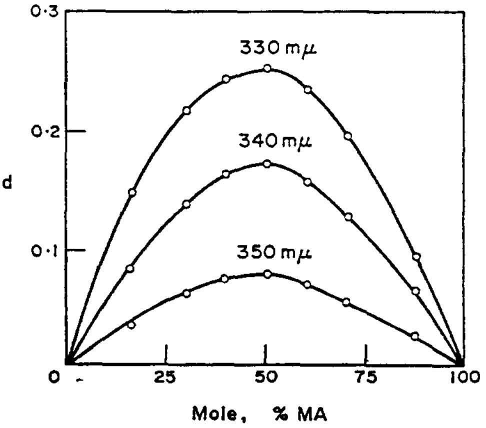

FIG. 2. The diagram of optical properties of the isomolar series of PS and MA solutions in acetone (in initial solutions [PS] = [MA] = 0·3 mole/l.)

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* The equilibrium constants were determined under the conditions for 1 : 1 complexes.

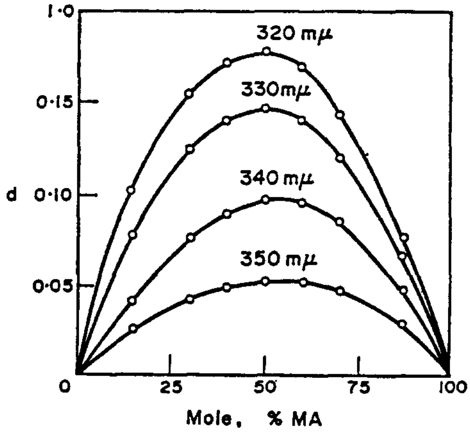


FIG. 3. The diagram of optical properties of the isomolar series of PS and MA solutions in chloroform (in initial solutions [PS] = [MA] = 0·1 mole/l.)

various solvents (the isomolar series of solutions[4]). It is seen that the 1 : 1 complex is formed in the polar solvent acetone (the absorption maximum in the whole spectrum region corresponds to the 1 : 1 PS : MA relation in the reaction mixture). In chloroform, in the region 320–330 mμ, the maximum optical density is also observed for the 1 : 1 ratio of components.

However, at about 340–350 mμ the maximum is shifted to MA : PS > 1; this indicates in the system the formation of several complexes similar in their optical properties.

Solutions, differing in concentration of one of the components, were used to establish the composition of complexes formed in chloroform (Fig. 4). The data were

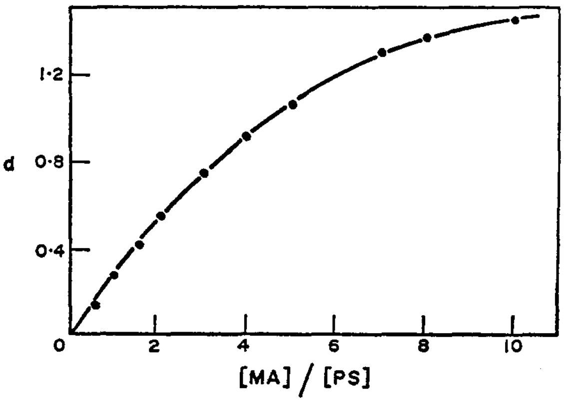


FIG. 4. The dependence of the optical density of the charge transfer band (λ = 335 mμ) on the molar MA/PS relation. [PS] = 0·15 mole/l. The solvent is chloroform.

treated according to "the method of the equilibrium shift"[4] based on the study of the equilibrium:

$$n\ \mathrm{MA} + \mathrm{PS} \rightleftarrows \mathrm{DA}\ (\text{complex})$$

with dissociation constant of the complex $K = \frac{[PS] * [MA]^n}{[DA]}$. The logarithmic form of the expression

$$\log \frac{[DA]}{[PS]} = -\log K + n \log [MA]$$

allows the value of n to be determined graphically (Fig. 5).

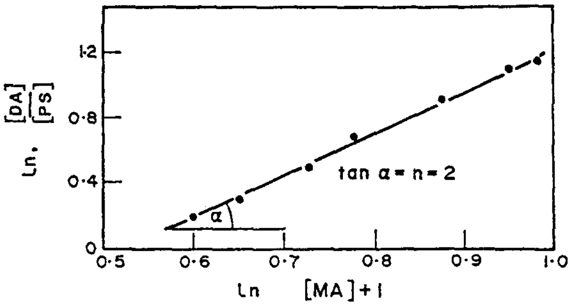


FIG. 5. Determination of the composition of the PS–MA complex by the "equilibrium shift method" (λ = 335 mμ, [PS] = 0·15 mole/l.)

The concentration of the complex [DA] was calculated from measurements of the optical density (d) of solutions differing in MA concentration, by the equation:

$$[DA] = \frac{[PS]_0 \cdot \{[MA]_j - p\,[MA]_i\}}{p \cdot \{[MA]_j - [MA]_i\}}$$

where $[PS]_0$ is the initial PS concentration;

$$p = \frac{d_j}{d_i};\ [MA]_j > [MA]_i.$$

It is seen from Fig. 5 that, in chloroform when MA is in excess, complexes of the composition MA_2–PS are mostly formed.

Due to the presence of four functional groups, TNM is capable of forming complexes of different compositions. In the curves of the dependence of the optical density of the charge transfer complex on PS:TNM in nitromethane (Fig. 6), there is a transition at the 1:1 relation of the reacting components. However, further increase of the PS concentration leads to rise of the optical density of the solution; this indicates the formation of complex compounds of various compositions. The complicated nature of the curve does not allow determination of the exact compositions of these compounds. For chloroform, the curve (Fig. 7) had to be treated according to "the method of the equilibrium shift". However, unlike the similar curve for the PS:MA complex, the curve has a horizontal part for considerable excess of PS.

Hence, the d_i/d_0–d_i relation may be substituted for the [DA]/[TNM] value, where d_0 is the optical density of the solution corresponding to the horizontal part of the curve, i.e. to the complete association of TNM with PS (Fig. 8).

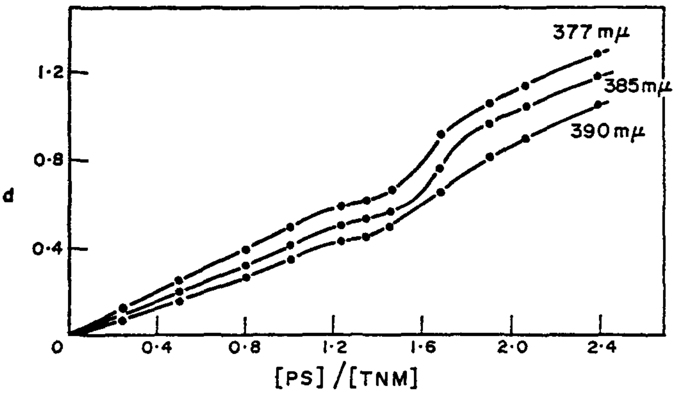


FIG. 6. The dependence of the optical density of the charge transfer band on the molar PS/TNM relation. [TNM] = 3·9 × 10^{-2} mole/l. The solvent is nitromethane.

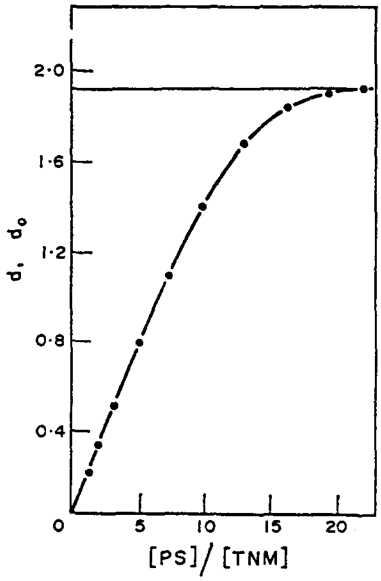


FIG. 7. The dependence of the optical density of the charge transfer band (λ = 380 mμ) on the molar PS/TNM relation. [TNM] = 3·2 × 10^{-2} mole/l. The solvent is chloroform.

The plot in Fig. 8 shows that, in chloroform when the PS concentration exceeds that of TNM, the formation of several complexes of TNM–PS$_n$ with $n \geqslant 2$ is possible.

Thus, in the case of MA, the 1:1 complex is formed in the polar solvent, and the formation of 1:1 and 2:1 complexes is possible in the weakly polar chloroform; while, in the case of TNM, in chloroform the PS:TNM $\geqslant$ 2:1 complexes are formed, and in nitromethane $\geqslant$ 1:1.

Kinetic investigation of the PS polymerization initiated by the DA interaction revealed a number of regularities of behaviour in the presence of strong and weak organic electron acceptors.

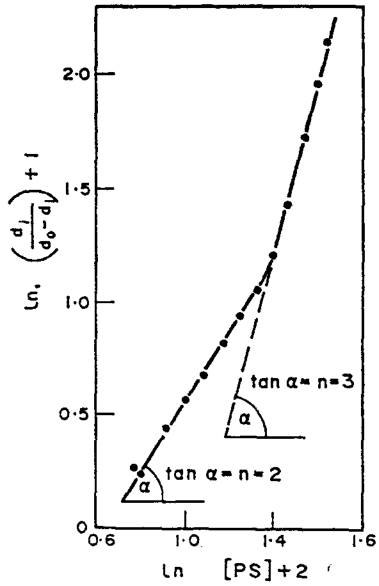


FIG. 8. Determination of the composition of the PS–TNM complex in chloroform by the "equilibrium shift method" (λ = 380 mμ, [TNM] = 3·2 × 10^{-2} mole/l.).

(1) Unlike ordinary ionic polymerization,(5) the kinetic curves of the PS polymerization (Fig. 9) initiated by the DA interaction possess a strongly pronounced *S*-shaped character. They have an induction period, the length of which depends on the strength and the amount of the acceptor as well as on the polarity of the medium, a period of acceleration, a period of the maximum stationary rate and then a gradual deceleration of the process. The existence of the induction period and the prolonged period of acceleration indicates that the concentration of the active sites increases during polymerization.

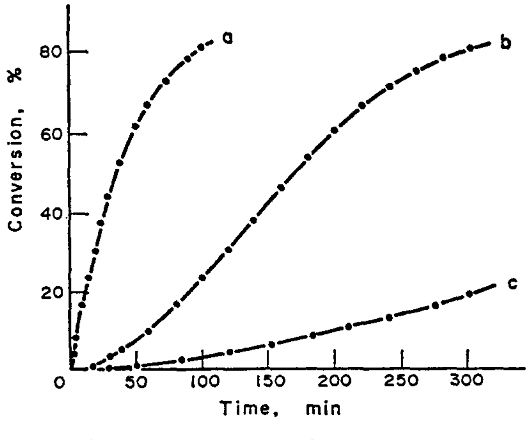


FIG. 9. The kinetic curves for PS polymerization initiated by MA and TNM: (a) [TNM] = 1·7 × 10^{-2} mole/l., [PS] = 3·5 mole/l., the solvent is nitrobenzene; (b) [MA] = 1·5 mole/l., [PS] = 4·3 mole/l., the solvent is nitrobenzene; (c) [MA] = 1·5 mole/l., [PS] = 5 mole/l., the solvent is chloroform. t = 75°.

The formation of the charge transfer complex between the monomer and the electron acceptor takes place over a period, as indicated by i.r. and u.v. spectroscopy. However, a still slower process seems to be the opening of the episulphide ring following the complexing reaction at the initiation stage, i.e. in the polymerization under consideration, the initiation rate is comparable or even less (in the case of weak acceptors) than the rate of chain growth.

If the complex of monomer and electron acceptor is prepared beforehand (at the 1:1 relation) and then the remaining monomer is added, the induction period disappears, and the acceleration period becomes 6 times shorter (Fig. 10). In this case, the acceleration period cannot disappear completely because addition of a new portion of PS, which is an electron donor, causes the equilibrium to shift towards formation of the charge transfer complex; this shift will result in an increase in the concentration of active sites.

This experimental fact strongly supports our suggestion about the increase in concentration of active sites during polymerization being responsible for the induction and acceleration periods.

(2) The molecular weight of polypropylenesulphide produced by both acceptors increases with increasing PS concentration (Fig. 11), slightly decreases with increase of the acceptor concentration (Fig. 12) and is independent of the polymerization time and temperature (Table 4). This establishes the similarity of the reactions of termination or transfer of the kinetic chain for processes initiated by TNM and MA.

TABLE 4. THE DEPENDENCE OF THE MOLECULAR WEIGHT OF POLYPROPYLENESULPHIDE ON THE POLYMERIZATION TIME [PS] = 4·3 mole/l.; SOLVENT—NITROBENZENE; t = 75°

No.	Acceptor	Acceptor concentration (mole/l.)	Polymerization time (min)	$[\eta]_{\text{int}}$ (in benzene) t = 20°
1	TNM	4×10^{-3}	10	0·30
2	TNM	4×10^{-3}	25	0·315
3	TNM	4×10^{-3}	45	0·29
4	TNM	4×10^{-3}	390	0·28
5	MA	1·0	30	0·33
6	MA	1·0	120	0·37
7	MA	1·0	180	0·35
8	MA	1·0	240	0·35

Treatment, according to the Mayo method,⁽⁶⁾ of the experimental data on the dependence of the molecular weight of polypropylenesulphide upon the monomer concentration led to important information about the mechanism of the elementary steps of the polymerization. The number-average degree of polymerization ($\overline{\text{DP}}_n$), for the case of monomolecular termination only, is given by

$$\frac{1}{\overline{\text{DP}}_n} = \frac{k_m}{k_p} + \frac{k_t}{k_p} \cdot \frac{1}{[M]} + \frac{J}{k_p[M]}$$

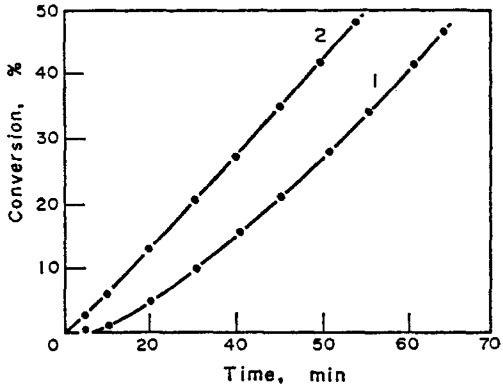


FIG. 10. The kinetic curves for PS polymerization by MA in nitrobenzene: 1—without preliminary complex formation; 2—with preliminary complex formation. [PS] = 4·3 mole/l., [MA] = 1·0 mole/l., t = 75°.

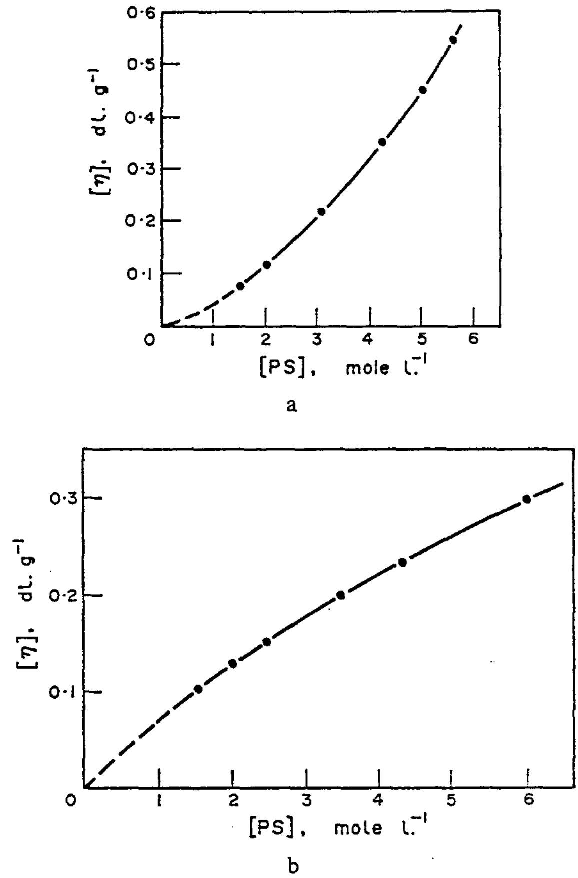


FIG. 11. The dependence of the intrinsic viscosity of polypropylenesulphide on the monomer concentration. The solvent is nitrobenzene. t = 75°. a—[MA] = 1·0 mole/l.; b—[TNM] = $1 \cdot 7 \times 10^{-2}$ mole/l.

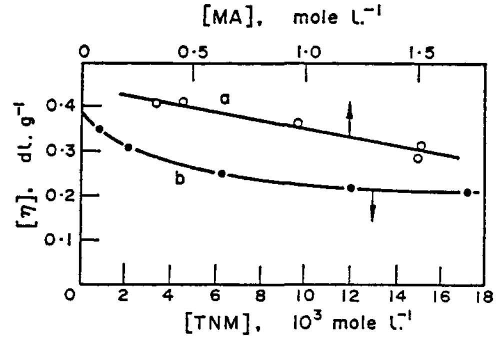


FIG. 12. The dependence of the intrinsic viscosity of polypropylenesulphide on (a) the MA concentration; (b) the TNM concentration. [PS] = 4·3 mole/l., the solvent is nitrobenzene, t = 75°.

where k_p is the rate constant of propagation,

k_t is the rate constant of monomolecular termination,

k_m is the rate constant of transfer and/or termination with monomer,

$[M]$ is the monomer concentration,

J includes all the unidentified processes of chain termination.

Figure 13 refers to polypropylenesulphide obtained by TNM; the plot is a good straight line. The increase of molecular weight with increasing monomer concentration indicates that the order of the propagation reaction with respect to monomer exceeds zero. The overall polymerization rate has order unity with respect to the monomer (from kinetic curves); the initiation rate is independent of the monomer concentration and so the propagation is first order with respect to monomer. The linear character of the plot indicates that the order with respect to monomer of chain transfer or termination by impurities is equal or close to zero, while the reactions of termination or transfer with monomer should have the same order with respect to the monomer as propagation, i.e. first.

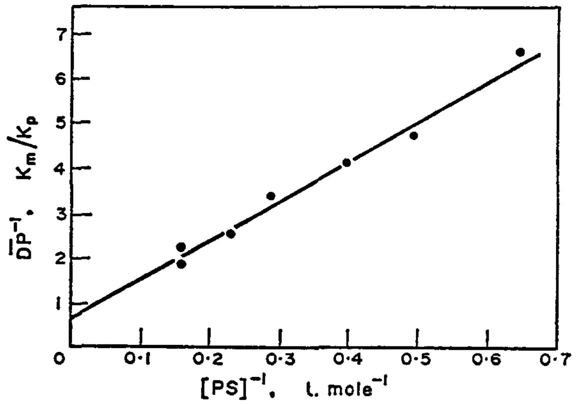


FIG. 13. The dependence of the degree of the PS polymerization on the initial monomer concentration. [TNM] = 1·7 × 10^{-2} mole/l., the solvent is nitrobenzene, t = 75°.

Figure 13 shows that the value of k_m/k_p is rather high, viz. $0{\cdot}7 \times 10^{-3}$, so evidently reactions of termination and chain transfer with monomer play an appreciable role in this system. The independence of the molecular weight upon conversion (Table 4) indicates the existence of kinetic chain transfer. These results indicate that, in the PS polymerization initiated by electron acceptors, chain transfer with monomer but not termination is important.

There is also the fact that the average concentration of the polymer chains at the end of the reaction is about 4–6 times higher than the initial acceptor concentration.

(3) The activation energy for the PS polymerization is practically independent of the acceptor strength and the solvent polarity (for TNM in nitrobenzene $E = 16{\cdot}1$ kcal/mole; for MA in nitrobenzene $E = 15{\cdot}7$ kcal/mole and in bulk $E = 14{\cdot}8$ kcal/mole). At the same time, the acceptor strength and the polarity of the medium are known to affect strongly the energetics of the complex formation. Hence, the fundamental contribution to the activation energy of the PS polymerization initiated by organic acceptors is from the activation energy of the heterocycle opening and the propagation reactions but not from that of the charge transfer complex formation.

In addition, the increase of the total polymerization rate with increasing polarity of the medium is characteristic of processes initiated by both strong and weak acceptors (see Table 3).

However, there are essential differences in the kinetics of processes initiated by strong and weak organic acceptors.

Firstly, when using MA, polymerization is preceded by a rather long induction period the length of which depends on the solvent polarity, the component concentrations and the temperature. In our opinion, the existence of this period is associated with the formation of the PS–MA complex over a period and with the slow formation of active sites. For processes initiated by TNM in nitrobenzene or in bulk, the induction period is practically absent because the TNM–PS complex is formed instantly.

Secondly, reactions initiated by TNM and MA are of different orders in monomer and acceptor. Thus, in nitrobenzene the polymerization initiated by MA is first order in acceptor (Fig. 14), and second order in monomer (Fig. 15). The reaction initiated by TNM is of a variable order with respect to the acceptor—from 0·5 to 0·2 (Fig. 16)

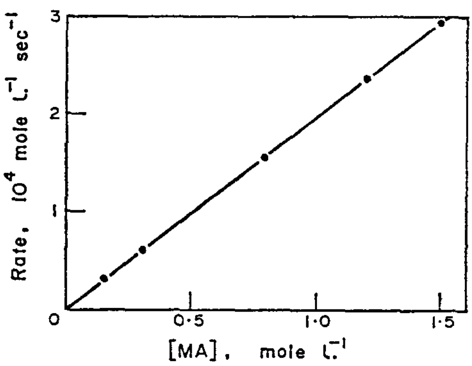


FIG. 14. The dependence of the PS polymerization rate on the MA concentration. [PS] = 4·3 mole/l., the solvent is nitrobenzene, $t = 75°$.

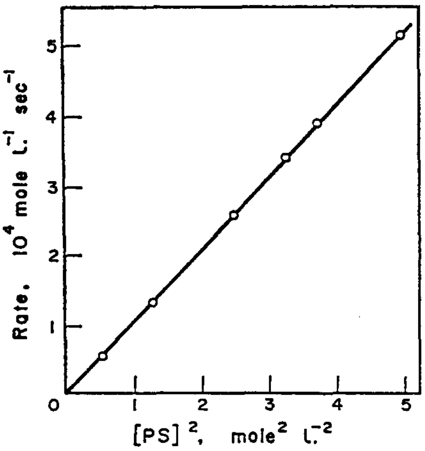


FIG. 15. The dependence of the PS polymerization rate on the monomer concentration. [MA] = 1·0 mole/l., the solvent is nitrobenzene, t = 75°.

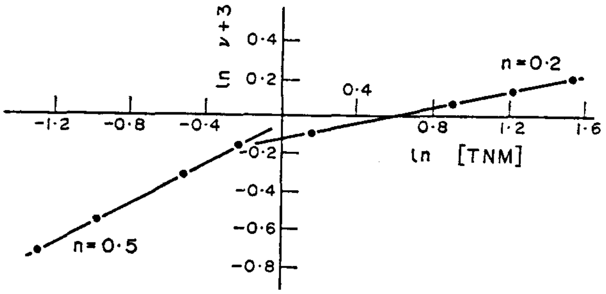


FIG. 16. The determination of the reaction order of the PS polymerization with respect to TNM. [PS] = 4·3 mole/l., the solvent is nitrobenzene, t = 75°.

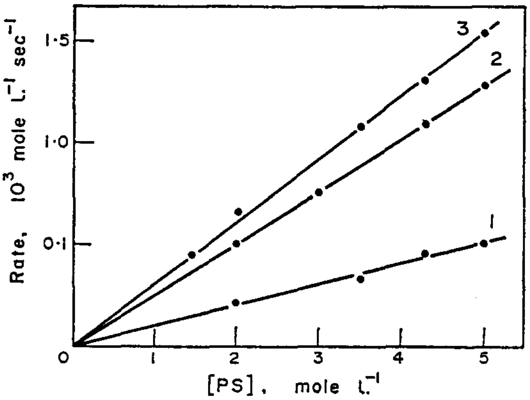


FIG. 17. The dependence of the PS polymerization rate on the monomer concentration. [TNM] (1)—0·3 × 10^{-3} mole/l., (2)—8 × 10^{-3} mole/l., (3)—17·2 × 10^{-3} mole/l. The solvent is nitrobenzene. t = 75°.

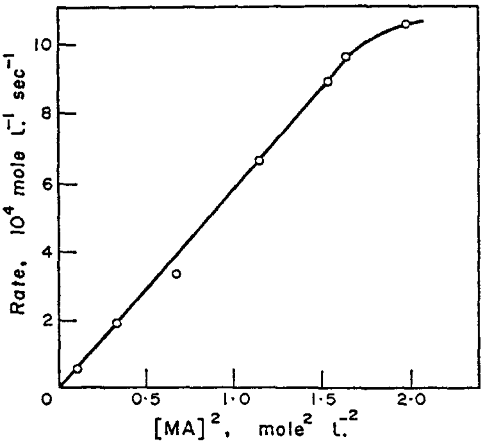


FIG. 18. The dependence of the polymerization rate on the MA concentration in bulk. $t = 75°$.

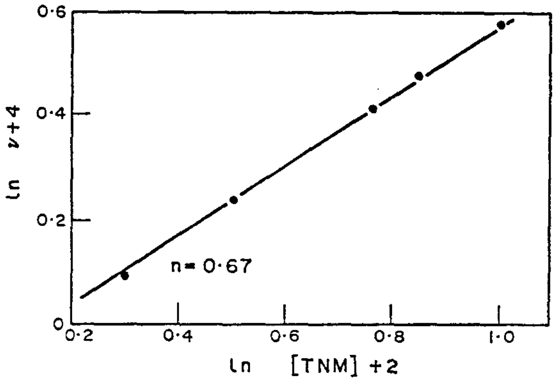


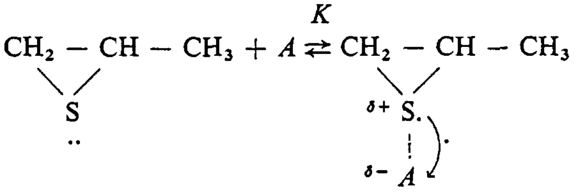
FIG. 19. The determination of the reaction order of the PS polymerization with respect to TNM in bulk. $t = 75°$.

and of the first order in monomer (Fig. 17). In a weakly polar solvent, the reaction order in MA becomes 2 (Fig. 18) and in TNM–0·67 (Fig. 19).

The results of the investigation of the DA complex compositions explain the unusual orders with respect to acceptor and monomer as well as their change with the polarity of the medium.

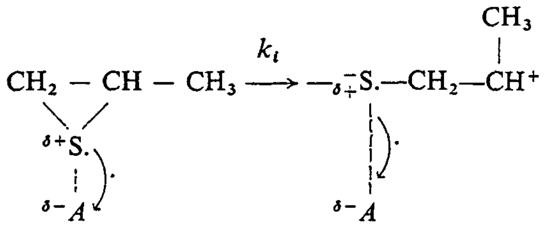
The following example will be an illustration. The PS polymerization in nitrobenzene is first order in acceptor (as mentioned above, the complex composition in the polar medium is 1 : 1); in chloroform the reaction is second order in the acceptor (in this case the complex composition is 1 : 2).

The following mechanism of the initiation of alkylenesulphide polymerization by organic electron acceptors is proposed on the basis of the experimental results. The first stage is formation of the DA complex between the monomer molecule and the electron acceptor:



(1)

the degree of the electron transfer in the complex depending on the acceptor strength and the polarity of the medium. The electron density shift results in additional polarization of the C—S bond and decreases the activation energy for opening of the three-membered heterocycle:



(2)

One question to be discussed in connection with the polymerization mechanism is the location of the opening of the mono-substituted episulphide ring. From the chemistry of episulphides, it is known(7,10) that, under the influence of anionic catalysts, there is "normal" cycle opening in PS (at the primary C atom).

In the presence of acids, the ring opening is the result of the attack at both carbon atoms, although to different extents. The organic acceptors, which form DA complexes with electron transfer from the monomer, will be similar to cationic catalysts, i.e. ring opening will occur at both the primary and secondary carbon atoms.

Thus, the new possibility has been proved of opening the three-membered sulphur-containing heterocycle, with the formation of linear polymers, by the DA interaction between the monomer and organic-electron acceptors.

The initial step of the polymerization is the formation of the charge transfer complex, where the degree of electron transfer depends on the acceptor strength and the polarity of the medium. By u.v. spectroscopy, the formation of these complexes and their compositions have been studied.

A correlation has been found between the kinetic parameters of the PS polymerization and the composition of the corresponding DA complexes as well as the equilibrium constants of their formation in media of various polarities. The most probable mechanism of the initiation by organic electron acceptors is discussed.

EXPERIMENTAL

Materials

Propylenesulphide, chromatographically pure, was dried for 24 hr and distilled repeatedly over CaH_2. The monomer purified in this way had $n_D^{20} = 1{\cdot}4750$ and b.p. = 74·5–75·0° (at 760 mm Hg). PS for polymerization was stored in argon at about 0°.

Maleic anhydride was recrystallized twice from chloroform with subsequent sublimation *in vacuo* m.p. = 53°).

Tetranitromethane was dried and distilled *in vacuo* over barium oxide, using only the middle fraction ($n_D^{20} = 1\cdot4341$). The other organic acceptors were recrystallized from suitable solvents (chloroanil—from toluene, benzene; nitroderivatives—from a mixture of water and ethyl alcohol).

Nitrobenzene was recrystallized from itself three times. About 50 per cent of the initial amount was collected, dried over barium oxide for 24 hr and distilled *in vacuo*; a fraction with b.p. = 63–65°/5 mm Hg was collected. The purified solvent had $n_D^{20} = 1\cdot5524$. Nitrobenzene was stored in a dark glass bottle under argon.

Nitromethane, spectrally pure, was dried over $CaCl_2$ and distilled over P_2O_5 *in vacuo* ($n_D^{20} = 1\cdot3813$); it was stored in a dark glass bottle under argon. The remaining solvents were purified and dried according to techniques already described.(8)

Polymerization procedure

All experiments were carried out *in vacuo* (10^{-3}mm Hg). Polymerization was performed in sealed glass ampoules or dilatometers. The order of the component charge was as follows. The solid acceptor was introduced into the ampoule or into the charging arm of the dilatometer. Then the ampoule or the dilatometer was evacuated until the vacuum was steady (10^{-3} mm Hg). PS and all solvents, except nitrobenzene and nitrocyclohexane, were recondensed *in vacuo* from measuring tubes. In experiments carried out with nitrobenzene or nitrocyclohexane, the solvents were run into a special reservoir where they were degassed simultaneously with the acceptors; after that, they were poured into the frozen dilatometer or the ampoule.

After charging of all components, the ampoules or dilatometers were sealed off in vacuum and put in the thermostat.

When the polymerization was over, the reaction mixture was dissolved in benzene and poured into excess methanol. The polymer was reprecipitated twice and dried in vacuum at 61° to constant weight.

The kinetics of the PS polymerization were studied dilatometrically (capillary diameters, from 1·6 to 2·1 mm).

Spectrophotometric measurements

The u.v. spectra were run on the SF-4A spectrometer with 1 cm silica cells. All solutions were prepared by means of the double dissolution.

Molecular weight determination

Molecular weights of polypropylenesulphide were determined from intrinsic viscosities, measured in benzene at 20°, by the equation: (9)

$$[\eta] = 0\cdot33 \times 10^{-4}\ M^{0\cdot86}.$$

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Résumé—On a montré l'existence d'une nouvelle possibilité pour ouvrir les hétérocycles à 3 atomes contenant du soufre et provoquer la formation de polymères linéaires sous l'action de complexes de transfert de charges.

La polymérisation de sulfures alkyléniques, se comportant comme des donneurs, se produit convenablement en présence de divers accepteurs électroniques organiques, comme l'anhydride maléique, les quinones et les dérivés hydrocarbonés contenant des groupements nitrés ou CN.

On a trouvé que l'amorçage se produit par l'intermédiaire d'un complexe de transfert de charges. La formation de ces complexes et leur composition dans des solvants de différentes polarités ont été étudiées par spectroscopie u.v. On a montré que la capacité d'amorçage d'un accepteur dépend non seulement de son affinité électronique mais aussi du nombre de groupements fonctionnels possédant les propriétés acceptrices. On a trouvé que l'accroissement de la polarité du milieu provoquait un accroissement rapide de la vitesse de polymérisation. On étudie le mécanisme d'amorçage.

Sommario—Si è dimostrato che, sotto l'azione di complessi trasferitori di cariche, esiste una nuova possibilità di aprire eterocicli costituiti da tre membri e contenenti zolfo con formazione di polimeri lineari.

La polimerizzazione di solfuri di alchilene, in funzione di donatori, procede con successo in presenza di vari accettatori di elettroni organici, come anidride maleica, chinoni, derivati nitro e CN di idrocarburi.

Si è trovato che l'iniziazione è dovuta alla formazione di complessi trasferitori di cariche tra il monomero e l'accettatore. La formazione di tali complessi e la loro composizione in solventi di diversa polarità è stata studiata per mezzo di spettroscopia all'ultravioletto. Si mostra che il potere iniziatore di un accettatore non solo dipende dalla sua affinità rispetto gli elettroni ma pure dal numero di gruppi funzionali in possesso di proprietà accettatrici. Si è trovato un forte aumento della velocità di polimerizzazione in seguito all'aumento di polarità del veicolo. Si prende in considerazione il meccanismo di iniziazione.

Zusammenfassung—Es wird eine neue Möglichkeit zur Öffnung der dreigliedrigen Schwefel-haltigen Heterocyclen und der Bildung von linearen Polymeren unter der Einwirkunf von chargetransfer Komplexen aufgezeigt.

Die Polymerisation von Alkylensulfiden, die als Donatoren wirken, verläuft erfolgreich bei Gegenwart verschiedener organischer Elektronen-Akzeptoren wie Maleinsäureanhydrid, Chinonen, Nitro- und CN-Derivaten von Kohlenwasserstoffen.

Ee wurde festgestellt, daß der Initiatierungsschritt in der Ausbildung von charge-transfer Komplexen zwischen dem Monomeren und dem Alzeptor besteht. Die Bildung dieser Komplexe und ihre Zusammensetzung in Lösungsmitteln unterschiedlicher Polarität wurde durch u.v.-Spektroskopie untersucht. Es wird gezeigt, dass die Initiatierungsfähigkeit eines Akzeptors nicht nur von seiner Elektronenaffinität abhängt, sondern auch von der Anzahl funktioneller Gruppen, die Akzeptoreignschaften besitzen. Es wurde eine scharfe Zunahme der Polymerisationsgeschwindigkeit mit zunehmender Polarität des Mediums gefunden. Betrachtungen zum Mechanismus der Iniatierung werden angestellt.