Experimental results and relative equations are reported in *Table 1*.

The corresponding hyperboles are plotted in *Figure 1*, the corresponding values of reactivity ratios are: $r'_1 = 0.4$ and $r' = 2.35$.

Since $r'_2 = r_2$ is above 1, 1-isopropenyl naphthalene is less reactive then styrene. This corresponds to the fact that, due to the steric interference between the isopropenyl group and hydrogen in position 8, the isopropenyl group is shifted out of the plane of the naphthyl ring. This results in a decrease in the conjugation between the double bond and the ring.

^{1}H n.m.r. spectra of the copolymers shows that no cyclic dimer[1] is obtained which means that the rate of copolymerization is far above the rate of termination by cyclization. This proves that the fact that 1-isopropenyl naphthalene gives only a dimer is due to steric hindrance.

As a comparison we determined reactivity ratios by Kelen and Tudos[5,6] which does not take the penultimate effect into consideration. The values obtained are the following:

$$R_1 = \frac{k_{11}}{k_{12}} = 0.2 \quad , \quad R_2 = \frac{k_{22}}{k_{21}} = 2.3$$

It can be observed that $R_2 = r'_2$ which is reasonable since there is no penultimate effect in styrene polymerization. Moreover R_1 is between 0 (r_1) and 0.4 (r'_1) which corresponds to the fact that sequence above two units cannot be obtained.

Table 1 Copolymerization of 1-isopropenyl naphthalene (M_1) with styrene (M_2) in methylene chloride. $[M_1] + [M_2] = 0.1$ mol. l^{-1}; $[TiCl_4] = 0.002$ mol. l^{-1}. Temperature (°C) = −75

$[M_1]$	$[M_2]$	m_1	m_2	$r'_2 = f(r'_1)$
0.02	0.08	0.093	0.907	$r'_2 = 2.18 + \frac{0.6 r'_1}{0.25 r'_1 + 1}$
0.03	0.07	0.152	0.848	$r'_2 = 1.97 + \frac{1.03 r'_1}{0.43 r'_1 + 1}$
0.04	0.06	0.207	0.793	$r'_2 = 1.89 + \frac{1.74 r'_1}{0.67 r'_1 + 1}$
0.05	0.05	0.268	0.732	$r'_2 = 1.73 + \frac{2.73 r'_1}{r'_1 + 1}$
0.06	0.04	0.353	0.647	$r'_2 = 1.25 + \frac{4.12 r'_1}{1.5 r'_1 + 1}$

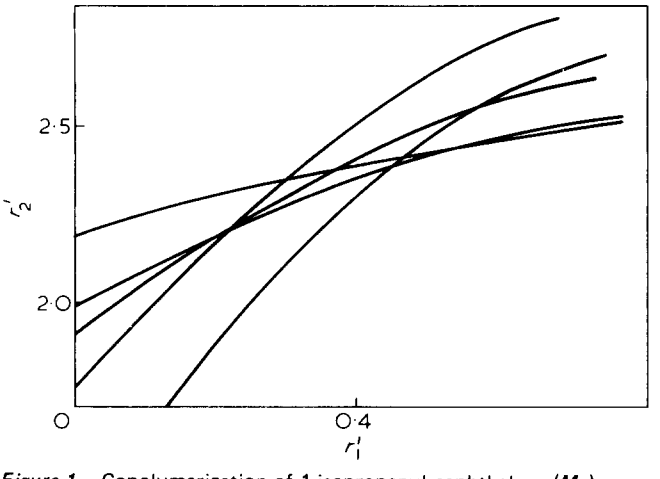

Figure 1 Copolymerization of 1-isopropenyl naphthalene (M_1) with styrene (M_2) in methylene chloride. $[M_1] + [M_2] = 0.1$ mol. l^{-1}; $[TiCl_4] = 0.002$ mol. l^{-1}; temperature (°C) = −75

REFERENCES

1 Bunel, C., Brigodiot, M. and Marechal, E. *J. Macromol. Sci. Chem.* 1978, **A12**, 1283
2 Coudane, J., Brigodiot, M. and Marechal, E. *Polym. Bull.* 1979, **1**, 465
3 Sigwalt, P. and Marechal, E. *Eur. Polym. J.* 1966, **2**, 15
4 Merz, E., Alfrey, T. A. and Goldfinger, G. *J. Polym. Sci.* 1946, **1**, 75
5 Kelen, T. and Tudos, F. *J. Macromol. Sci. Chem.* 1975, **A9**, 1
6 Kelen T., Tudos, F., Bela, T. and Kennedy, J. P. *Kem. Kozl.* 1976, **46**,

Synthesis of poly-*p*-phenylene sulphide by oxidation of thiophenol with thionyl chloride in the presence of aluminium chloride

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INTRODUCTION

The utility of the Friedel–Crafts reaction as a method for the synthesis of network polymers was drawn to attention by Phillips[1] but it was only recently that Lewis acids were applied in the synthesis of polyarylene sulphide polymers[2,3]. Polyarylene sulphides have had wide application[4] and several methods for the synthesis of the polymers are based on pressure processes[5,6].

In the present work a new method for the synthesis of poly-*p*-phenylene sulphide by oxidation of thiophenol with thionyl chloride in the presence of aluminium chloride in benzene is described. An insoluble polymer, melting at 210–215°C was isolated.

EXPERIMENTAL

Thionyl chloride (0.1 M) was added dropwise to a solution of thiophenol (0.1 M) and aluminium chloride (0.01 M) in benzene. The reaction mixture was then heated at boiling temperature for 12 h and then poured into dilute sulphuric acid. The precipitate was filtered off, washed with

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water, and extracted with toluene and *N,N*-dimethylformamide. As a result 6.5g of insoluble material m.pt. 210–215°C was obtained. Reduction of the product with $LiAlH_4$ was carried out by a procedure described in the literature[7]. Some further reactions were carried out in order to elucidate the route of the reaction studied. The results are given in *Table 1*.

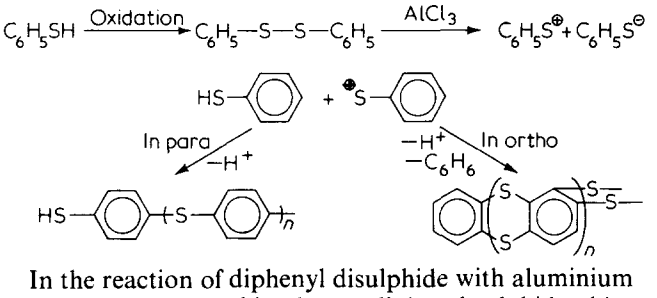
RESULTS AND DISCUSSION

The polymer obtained by the reaction of thiophenol with thionyl chloride in the presence of aluminium chloride has an elemental composition (C-59, 90%; H-3, 16%; S-36, 17%) corresponding to $C_{6.0}H_{3.8}S_{1.4}$. In this there is more than one sulphur atom per benzene ring, and this may be ascribed to the presence of mercapto groups, disulphide bonds or intramolecular cyclic sulphides.

Mercapto groups were excluded because of the absence of the band in the range 2600–2550 cm^{-1} in the i.r. spectrum (*Figure 1*). The result of reaction with $LiAlH_4$ excluded disulphide bonds since the polymer did not undergo reduction (*Figure 1*). These facts suggest the presence of sequences of cyclic sulphides besides poly-*p*-phenylene sulphide sequences. Confirmation of such a structure is difficult because of the structural similarity to both poly-*p*-phenylene sulphide and cyclic sulphide e.g. thianthrene. The mass spectrum of the polymer was recorded (*Table 2*) but analysis of the mass fragmentation does not provide any new information for the structure. The i.r. spectrum of the polymer is similar to virgin poly-*p*-phenylene sulphide (commercial material RYTON produced by Phillips Petroleum Company) except the band at 880 cm^{-1} corresponding to a four-substituted benzene ring which is not observed in the spectrum of RYTON.

X-ray diffraction makes it possible to suggest the approximate structure of the polymer. Analysis of X-ray data indicates unequivocally that in the polymer obtained, the major part of the crystalline phase is the same as in the commercial poly-*p*-phenylene sulphide RYTON (*Figure 2*).

The results shown in *Table 1* and remaining results of structural research allow us to propose the following reaction directions:



In the reaction of diphenyl disulphide with aluminium chloride in benzene, thianthrene, diphenyl sulphide, thiophenol and hydrogen sulphide are formed. This indicates the following reaction route:

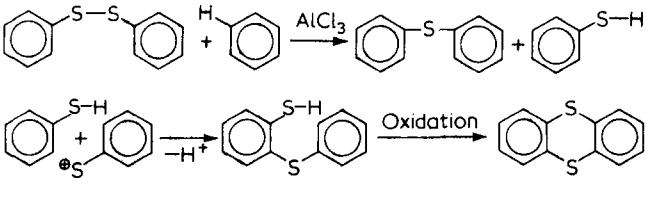


Table 1 Reaction products

Number	Starting materials	Reaction medium	Main products
1	$C_6H_5SH, SOCl_2, AlCl_3$	benzene	polymer
2	$C_6H_5SH, AlCl_3$	–	thiantrene
3	$C_6H_5SH, AlCl_3$	benzene	thiantrene
4	$C_6H_5SH, SOCl_2$	–	diphenyl disulphide
5	$C_6H_5S_2C_6H_5, AlCl_3$	benzene	thiantrene, diphenyl sulphide, thiophenol, hydrogen sulphide

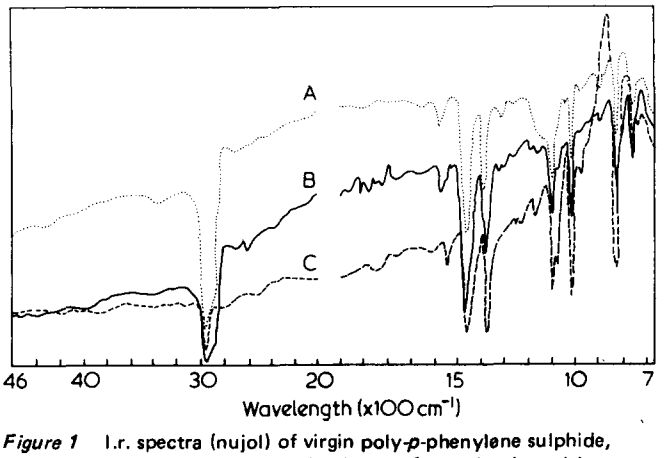


Figure 1 I.r. spectra (nujol) of virgin poly-*p*-phenylene sulphide, A; obtained polymer, B; obtained polymer after reduction with $LiAlH_4$, C

Table 2 Relative intensities of spectrum recorded at 75 eV and elemental composition of fragment ions

Number	m/z	Elemental composition	Relative intensity %
1	108	C_6H_4S	33.6
2	109	C_6H_5S	63.6
3	110	C_6H_6S	30.9
4	140	$C_6H_4S_2$	16.3
5	172	$C_6H_4S_3$	14.5
6	184	$C_{12}H_8S$	100.0
7	215	$C_{12}H_7S_2$	21.8
8	216	$C_{12}H_8S_2$	45.4
9	217	$C_{12}H_9S_2$	41.8

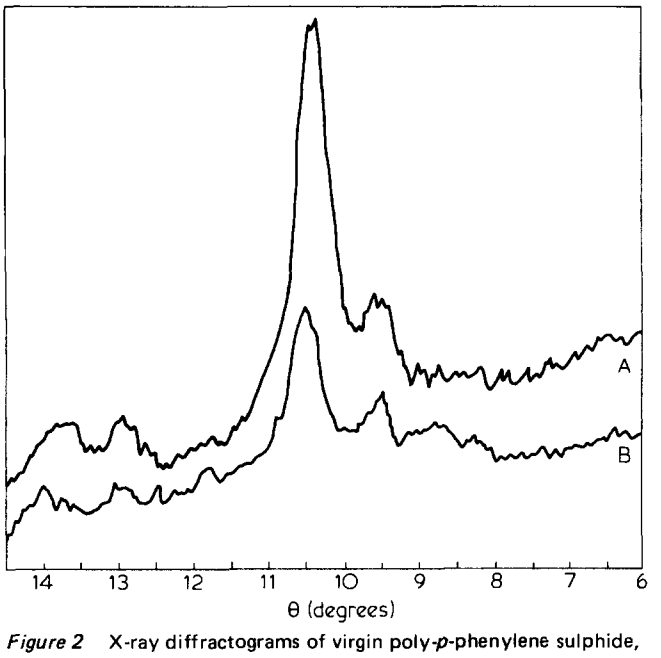
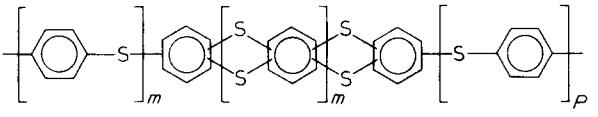


Figure 2 X-ray diffractograms of virgin poly-*p*-phenylene sulphide, A; obtained polymer, B

However, according to Behringer and co-workers[8], diaryl disulphides do not react with aromatic hydrocarbons in the presence of Lewis acids with the formation of the corresponding thiol and sulphide.

It is highly probable that the obtained polymer has a poly-*p*-phenylene sulphide structure the sequences of which are separated by cyclic sulphide type sequences.



Such a structure supposes its potential high thermal stability confirmed by the results of thermal gravimetric analysis (*Figure 3*).

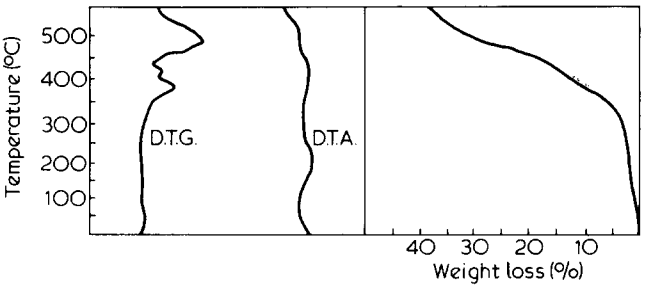


Figure 3 DTA and DTG curves of the obtained polymer

REFERENCES

1 Phillips, L. N. *Trans. Plastics Inst.* 1964, **32**, 298
2 Sergeyev, W. A., Shitikov, W. K. and Nedelkin, W. I. *Vysokomol. Sojed.* 1977 **A19**, 2754
3 Sergeyev, W. A., Lepilin, W. A. and Nedelkin, W. I. *Vysokomol. Sojed.* 1979, **B21**, 252
4 Smith, H. A., 'Encyclopedia of Polymer Science and Technology' Interscience Publishers, New York, 1969, p 653
5 Macallum, A. D. *J. Org. Chem.* 1948, **13**, 154
6 U.S. Patent 3,354,129 to Phillips Petroleum Company Co., November 21, 1967
7 Cook, J. W., London, J. D. and McCloskey, P. *J. Chem. Soc.* 1952, 3904
8 Behringer, H. and Kuchinka, K. *Angew. Chem.* 1960, **72**, 348

Rheological study of particle interaction in a concentrated polymer dispersion

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INTRODUCTION

The influence of the purification procedure on the viscosity of polymer dispersions has been investigated[1,2]. However, data on particle interaction and the formation of the ordered structure of dispersed particles in well-defined systems are still not available[2,3]. Ferguson *et al.*[4] have suggested that the formation of an ordered structure of dispersed particles can adequately be followed by measuring the development of shear stress with time at constant shear. They also suggested that a dispersed system with ordered particle structure is characterized by a peak stress (static yield value) found at the onset of steady shear.

Here, we have used a Couette-type viscometer to study a well-characterized polystyrene latex. The formation of structure by the dispersed particles after purification has also been studied. In addition, we have attempted to calculate the Hamaker constant for particle interaction by using an equation developed by Albers and Overbeek[5].

EXPERIMENTAL

A monodisperse polystyrene dispersion (latex 206–2) was prepared by the direct polymerization of styrene by using potassium persulphate as initiator and an emulsifier (Aerosol MA, American Cyanamid CO., Wayne, NY, USA). The characteristics of the latex were as follows: particle arithmetic mean diameter 177.2 nm; standard deviation of distribution 4.7 nm; polydispersity ratio 1.006; electrophoretic mobility -5.50 nm $s^{-1}V^{-1}cm$; and zeta potential -77.5 mV. The preparation procedure, as well as all these parameters were defined and computed as described elsewhere[6].

The samples were extensively dialysed against distilled water (procedure, ref 7). The deionization procedure for the dialysed latex suspensions was carried out by the method of Vanderhoff *et al.*[2]. Initial concentrations were about 20% for the dialysed and about 5% the deionized latex. The concentration of the dialysed dispersions was increased to 50%, and that of the deionized samples to 30%, respectively, by vacuum evaporation. These concentrations were chosen as the upper limits, for above these limits considerable amounts of thick, dry film are found which prevent further study. Evaporation of deionized samples is somewhat simpler due to the absence of emulsifier which generally causes foaming. Solutions of sodium hydroxide, hydrochloric acid and sodium chloride were added instead of redestilled water in experiments where the variation of pH or ionic strength was needed.

A Haake–Rotovisko Couette-type rotational viscometer (Gebruder Haake, Berlin, BRD) and NV head were used. In order to ensure that all samples had been subjected to the same shear history the same loading procedure was employed in all experiments. Samples were