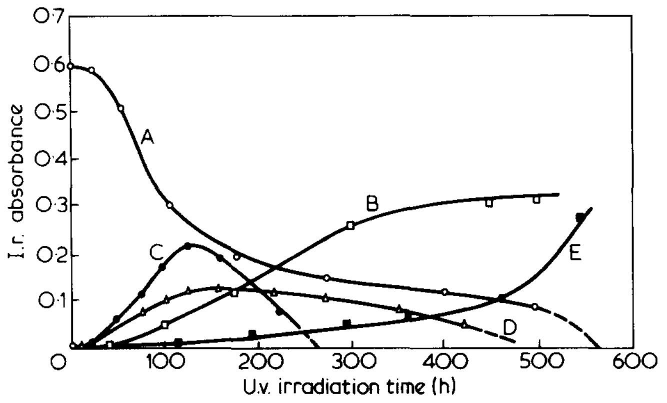

Figure 3 Effect of nitroxyl IIB (10^{-2} M) on the photo-oxidation of methyl cyclohexane. A, decay of nitroxyl, IIB; B, formation of vinylene (965 cm^{-1}); C, growth and decay of hydroxylamine (2760–70 cm^{-1}); D, growth and decay of N–O (in NOR where R=H or alkyl) (1300 cm^{-1}); E, formation of carbonyl (1715 cm^{-1})

3 compares the behaviour of nitroxyl IIB in the same substrate. The free hydroxylamine (2760–70 cm^{-1}) and associated unsaturation (965, 895 cm^{-1}) are formed in both cases at the expense of the nitroxyl radical, confirming the validity of the regenerative mechanism (reaction 3). It seems clear that the hydroxylamines act as reservoirs for the nitroxyl and the exceptional efficiency of the regenerative mechanism results from the participation of the complementary chain-breaking donor (CB–D) and chain-breaking acceptor (CB–A) antioxidant mechanisms[13].

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Copolymerization of acrylic acid with sulphur dioxide

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Numerous copolymerizations of simple aliphatic alkene monomers with liquid sulphur dioxide have been documented and established as proceeding by a free radical mechanism[1–4]. Regardless of the polymerization feed ratio, the composition of these polysulphones is that of an alternating copolymer.

In contrast, there is an overwhelming tendency for alkenes with positive values of *e* (Alfrey–Price *Q*–*e* values), to be reluctant to copolymerize with sulphur dioxide and to prefer to homopolymerize[3,5–8]. Nevertheless, acrylamide, which would be placed into the latter category, has been copolymerized with sulphur dioxide using a variety of free radical initiators[9,10]. In this communication we report the first example of the copolymerization of acrylic acid (AA) with sulphur dioxide.

Experimental

Materials. Acrylic acid (J. T. Baker Chemical Co.) was purified on a high vacuum line. Anhydrous sulphur dioxide (Union Carbide) was condensed into a jacketed burette (through which an aqueous ethylene glycol solution at –33°C was circulated) and run into the reaction vessels as needed and in the amount required. The t-butyl hydroperoxide (Aldrich Chemical Co.) was used as received. Methanol was purified by distillation. All other solvents were used as received.

Table 1 Effect of temperature on copolymerization

	Copolymer composition			
Temperature (°C)	wt% S	wt% AA	wt% SO_2	AA:SO_2 mole ratio
24	1.97	96.1	3.9	21.8
–33	2.02	96.0	4.0	21.3
–42	2.64	94.7	5.3	15.8
–52	4.20	91.6	8.4	9.7
–60	5.50	89.0	11.0	7.2

Conditions: 1 ml AA; 10 ml SO_2; 0.1 ml $(CH_3)_3COOH$; 5 min

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Table 2 Effect of temperature on the copolymerization run in methanol

Temperature (°C)	Copolymer composition wt% S	wt% AA	wt% SO_2	$AA:SO_2$ mole ratio
–33	1.02	98.0	2.0	43.6
–45	1.44	97.0	3.0	28.8
–60	1.84	96.3	3.7	23.2
–75	2.78	94.4	5.6	15.0
–90	2.88	94.2	5.8	14.5

Conditions: 10 ml CH_3OH; 1 ml AA; 10 ml SO_2; 0.1 ml $(CH_3)_3COOH$; 5 min

Table 3 Effect of various solvents on copolymerization

Solvent	Copolymer composition wt% S	wt% AA	wt% SO_2	$AA:SO_2$ mole ratio
MeOH	1.02	98.0	2.0	43.6
SO_2	2.02	96.0	4.0	21.3
DMF	3.32	93.4	6.6	12.6
DMSO	4.42	91.2	8.8	9.3

Conditions: 1 ml AA; 10 ml SO_2; 10 ml solvent; 0.1 ml $(CH_3)_3COOH$ 5 min; –33°C

Polymerizations. All reactions were conducted essentially in the same manner. Specific conditions are given in *Tables 1–4*. A typical run was as follows. 10 ml of liquid sulphur dioxide were run from the burette into a 250 ml jacketed reaction flask maintained at −33°C containing a mixing bar and closed to the atmosphere. The reaction flask was disengaged from the burette and a ground glass adapter with a rubber septum was inserted quickly. This isolated the contents of the flask from the surrounding atmosphere. 1 ml of acrylic acid was added to the liquid sulphur dioxide via a syringe and needle. After mixing of the two monomers, during stirring 0.1 ml of t-butyl hydroperoxide was added by syringe and needle. Polymer precipitated immediately and the contents of the flask solidified. Several minutes later, the adapter was removed and the system was warmed to room temperature in the fume hood to drive off excess SO_2. The remaining solid was dissolved in methanol and dialysed against several changes of distilled water. The solution from the dialysis bag was freeze dried.

Polymerization reaction controls. Three paralled reactions were carried out on the following solutions: (i) 5 ml acrylic acid and 10 ml liquid sulphur dioxide; (ii) 5 ml acrylic acid, 0.1 ml t-butyl hydroperoxide in 10 ml methanol; (iii) 5 ml acrylic acid, 10 ml liquid sulphur dioxide, 1.57 g 2,2′-diphenyl-1-picrylhydrazyl and 0.1 ml t-butyl hydroperoxide. All flasks were stirred at −33°C for 17 h. Upon workup, the starting monomers were recovered practically unchanged.

Results and discussion

Polymer yields of crude product based on the amount of acrylic acid used were quantitative. After dialysis, yields of freeze dried polymer were 50–75%. The membrane material of the dialysis bag had a cut-off of 12 000 molecular weight.

All the polysulphones prepared in this study are white solids with melting points, accompanied by some decomposition, in the 240–250°C range. The infrared spectra of the copolymers showed two absorption bands in the 1150–1300 cm^{-1} region which are associated with the stretching modes of the sulphone.

The copolymerization of acrylic acid with sulphur dioxide in the presence of t-butyl hydroperoxide is rapid and quantitative. However, when the same reaction was carried out in the presence of large amounts of 2,2′-diphenyl-1-picrylhydrazyl radical trap, the system was poisoned apparently. In the absence of t-butyl hydroperoxide, acrylic acid does not yield any polymer with liquid sulphur dioxide. Furthermore, acrylic acid could not be induced to polymerize when stirred with t-butyl hydroperoxide at −33°C for 17 h. Since neither sulphur dioxide nor t-butyl hydroperoxide alone were capable of initiating the polymerization reaction of acrylic acid, we suggest that radical formation is possible only by the redox reaction of t-butyl hydroperoxide and sulphur dioxide. SO_2 is acting in a catalytic capacity, and efficiently decomposing the t-butyl hydroperoxide at low temperature into free radicals which initiate the polymerization. This reaction as a source of free radicals has been referred to previously$^{10-12}$.

Experimental data in *Table 1* summarize the effect of temperature on the amount of sulphur dioxide incorporated into the polymer. As the polymerization temperature is increased, the amount of SO_2 incorporated decreases. Similar behaviour has been reported in acrylamide–SO_2 and vinyl chloride–SO_2 systems^{9,13}.

The effect of temperature on the acrylic acid–SO_2 copolymerization in methanol was also investigated (*Table 2*). With this solvent, it was possible to extend the temperature study to −90°C and yet maintain solubility of the acrylic acid. Unfortunately, the presence of methanol has a detrimental effect on the incorporation of SO_2 into the copolymer. At −60°C without methanol (*Table 1*), the $AA:SO_2$ mole ratio is 7 whereas under the same conditions in methanol (*Table 2*) the $AA:SO_2$ mole ratio rose to 23. In methanol, there is a linear relationship between temperature and SO_2 incorporation. In the neat copolymerization, such a relationship appears to exist for the temperature range −60°C to −30°C. At higher temperatures (e.g. 24°C), most of the SO_2 (b.p. −10°C) would be in the gas phase making such runs of a different nature. Focussing on the four runs between −30°C and −60°C, it would appear that there is a linear relationship between SO_2 incorporation and temperature whether the copolymerization be run undiluted or in solution.

Solvent appears to have an effect on SO_2 incorporation. *Table 3* lists a number of polymerization solvents, together with the sulphur content of the polymers prepared in them. Solvents with a high dielectric constant and weak hydrogen bonding (DMF, DMSO) apparently facilitate SO_2 incorporation into the copolymer. Strong hydrogen bonding by the

Table 4 Effect of feed ratio on copolymer composition

$AA:SO_2$ mole ratio	Copolymer composition wt% S	wt% AA	wt% SO_2	$AA:SO_2$ mole ratio
0.0614	1.90	96.2	3.8	22.6
0.0204	2.16	95.7	4.3	19.8
0.0122	2.66	94.7	5.3	15.9

Conditions: 0.1 ml $(CH_3)_3$ COOH; –33°C; 5 min methanol solvent could cause some inactivation of the acrylic acid, thereby depleting the effective polymerization concentration of this monomer.

The feed ratio of the copolymerization affects the incorporation of SO_2 into the copolymer very slightly. For a feed ratio variation factor of 5, the copolymer composition increased by a factor of 1.4 with respect to SO_2 (*Table 4*). We suggest that the copolymerization reaction between acrylic acid and sulphur dioxide is somewhat different from the vinylic copolymerization reaction.

To test whether any adverse side reactions may be complicating the copolymerization, the components in a solution polymerization were mixed in various sequences. The results indicate that sequence has no influence essentially on SO_2 incorporation.

A more detailed investigation must be carried out to obtain a better understanding of this system. Studies are continuing.

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Preparation and application of functional polymers. Preparation of carbodiimides, ketenimines and imidoyl bromides using a poly(styryl diphenylphosphine dibromide)

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The utilization of insoluble functionalized polymers was first developed by Merrifield for polypeptide synthesis[1]. After the successful application of solid phase peptide synthesis was reported, the synthesis and utilization of insoluble functionalized polymers as reagents and catalysts in other organic synthesis wide application[2–4].

Because of the advantages of using insoluble resins, polymer-supported organophosphorous reagents were used recently in the preparation of polymeric Wittig reagents[5–8]. Treating cross-linked polymeric triarylphosphines with alkyl halides gave polymeric phosphonium salts which, after treatment with strong base, reacted with carbonyl compounds to form various olefins. The olefins were separated from the cross-linked polymeric triarylphosphine oxide by simple filtration, thus removing the main problem of Wittig reactions.

However, polymeric trisubstituted phosphines were also used in the preparation of various transition metal catalysts[9–12] and in the preparation of polymeric trisubstituted phosphine dihalides[13,14]. Moreover, the polymeric triarylphosphine–carbon tetrachloride system was used as a mild and efficient reagent for conversion of alcohols or carboxylic acids to the corresponding alkyl chlorides or acid chlorides[15–18]. This technique removes the difficulty of separation by column chromatography which is not possible with acid chlorides. In addition, since the conditions are essentially neutral i.e. no HCl is evolved, the system is convenient for substrates which are sensitive to the presence of HCl.

In this communication, we report the synthesis and successful application of 2% cross-linked poly(styryl diphenylphosphine dibromide) (IV) for the preparation of carbodiimides, ketenimines and imidoyl bromides.

Polymeric phosphine resin (III) was prepared by brominating 2% cross-linked polystyrene (I), then treating the brominated product (II) with lithium diphenylphosphine[13]. The resulting polymeric phosphine resins (III) were treated with bromine to give the polymeric reagent (IV):

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