Studies on the copolymer composition of sulphur dioxide and phenylacetylene

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The polysulphone copolymers synthesized from the copolymerization of liquid sulphur dioxide and phenylacetylene in the presence of tert-butyl hydroperoxide at low temperature always have an alternating structure which is independent of solvent, temperature and feed ratio. At a relatively high temperature (50°C) the phenylacetylene/SO_2 system initiated by AIBN gave copolymers with a 1:1 mole ratio, whereas styrene/SO_2 under the same conditions produced copolymers with 2:1 molar ratio. The free radical initiators hydrogen peroxide, *m*-chloroperbenzoic acid, and diphenyl peroxide were inert at low temperatures. The $PhC{\equiv}CH/SO_2$ system with $(CH_3)_3COOH$ at low temperature is more reactive than $PhCH{=}CH_2/SO_2$ but with AIBN at high temperature the reactivities are reversed. These observations suggest that different mechanisms should operate on the two systems.

(Keywords: alternating copolymerization; reaction conditions; phenylacetylene; sulphur dioxide)

INTRODUCTION

Terminal and internal aliphatic olefins[1-3] copolymerize with liquid sulphur dioxide forming alternating copolymers regardless of reaction conditions. However, styrene[4-10] and vinyl chloride[11,12] react with sulphur dioxide producing copolymers whose composition depends upon reaction conditions.

We have previously reported[13] that several purified terminal aliphatic acetylenic hydrocarbons copolymerized with liquid sulphur dioxide in the presence of tert-butyl hydroperoxide. The resulting polymeric materials were stereoselective alternating copolymers and their structure was not affected by the experimental polymerization conditions employed. Internal aliphatic alkynes such as 3-hexyne were inert towards copolymerization with sulphur dioxide.

The main objective of the present investigation is to study the effect of temperature, solvent, initiator, and feed ratio on the composition of the copolymer produced from sulphur dioxide and phenylacetylene under free radical addition copolymerization conditions. In addition, comparative studies of phenylacetylene/SO_2 and styrene/SO_2 systems are made in order to provide some additional information on the copolymerization mechanism of phenylacetylene with sulphur dioxide.

EXPERIMENTAL

Materials

Phenylacetylene and styrene were purified by usual methods as reported previously[13]. Anhydrous sulphur dioxide was purchased from Union Carbide and used as received. The radical initiator α,α'-azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Tert-butyl hydroperoxide, hydrogen peroxide, phenyl peroxide, and *m*-chloroperbenzoic acid (Fluka) were used as received. All solvents used were h.p.l.c. grade.

Instrumental techniques

The elemental analyses were performed on Carlo Erba Strumentazione model 1106 using a Para Pak QS column 2 metres in length for carbon and hydrogen and 0.8 metres in length for sulphur analysis.

The infra-red spectra were recorded on a Perkin-Elmer model 337 Grating infra-red spectrophotometer using KBr pellets. The e.s.r. spectra were taken over a range of temperatures from 108 K to 203 K with a Varian E-109 spectrometer at X-band frequency (9.1 GHz) and a modulation frequency of 10 kHz. The spectra were centred in a magnetic field of 3231 G and had a scan range of 100 G. The magnetic field sweep was calibrated with a Varian E-500-2 self-tracking n.m.r. gaussmeter. Microwave frequencies were measured with a Hewlett-Packard 5342A microwave frequency counter. The temperature was controlled by a Varian E-257 variable temperature unit to within ±0.5°C. Scan speed and time constant were chosen so as not to introduce any artifact from scanning.

Two types of e.s.r. samples were prepared. The first sample consisted of a homogeneous solution of phenylacetylene (4.0 ml), ether (10.0 ml), and tert-butyl hydroperoxide (0.1 ml), and the second sample tube consisted of a homogeneous solution of styrene (4.0 ml), ether (10.0 ml), and tert-butyl hydroperoxide (0.1 ml). These samples were placed in e.s.r. sample tubes made of Pyrex tubing (3 mm i.d. × 4 mm o.d.). The sample tube was adapted to a 9 mm o.d. at the open end in order to fit into the quick disconnect fitting (seal structure Sargent-Welch part No. S-76639-A, size 24/40) on the Pope vacuum manifold. The sample tube was immersed in liquid nitrogen and the valve opened to the vacuum system. The sample tube was degassed by several freeze-pump-thaw cycles. A small quantity of SO_2 was allowed to fill the vacuum manifold (the pressure measured by a

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Granville-Philips vacuum gauge was 1 torr). The SO_2 gas was then condensed into the sample tube under liquid nitrogen temperature. The sample was sealed using a torch and kept under liquid nitrogen before use.

Table 1 Effect of solvent and temperature on the copolymerization of phenylacetylene with sulphur dioxide[a]

Solvent	Reaction Temperature (°C)	Copolymer[c] yield (%)	Copolymer composition[b] %C	%H	%S
$C_2H_5OC_2H_5$	+15	26	57.46	3.63	19.04
$C_2H_5OC_2H_5$	0	35	57.52	3.70	18.97
$C_2H_5OC_2H_5$	−15	87	57.58	3.62	18.29
$C_2H_5OC_2H_5$	−25	84	56.94	3.62	18.53
$C_2H_5OC_2H_5$	−35	17	55.40	3.86	18.29
CH_3COCH_3	−35	85	55.30	3.56	17.55
CH_3CN	−25	72	56.88	3.64	19.04
CH_3CN	−35	25	56.59	3.79	18.17
$C_2H_5OCOCH_3$	−25	15	56.43	3.71	17.88
$C_2H_5OCOCH_3$	−35	13	55.59	3.67	17.86
CH_3OH	−25	12	59.11	3.72	17.56
CH_3OH	−35	5	58.97	3.68	18.77
CH_2Cl_2	−25	4	58.69	3.74	18.98
Neat	−15	10	58.73	3.65	18.86
Neat	−35	4	57.89	3.80	19.02

[a] Polymerization conditions: 1 ml PhC≡CH; 5 ml liquid SO_2; 10 ml solvent; 0.1 ml $(CH_3)_3COOH$; 20 min

[b] Theoretical values for PhC≡CH:SO_2 = 1:1 copolymer: C, 57.83%; H, 3.61%; S, 19.28%

[c] Copolymer yield is based on phenylacetylene

Table 2 Effect of feed ratio on the copolymerization of phenylacetylene with sulphur dioxide[a]

Feed mole ratio (SO_2: PhC≡CH)	Copolymer[c] yield (%)	Copolymer composition[b] %C	%H	%S
12.3	87	57.58	3.62	18.29
6.14	98	56.14	3.65	18.39
2.46	77	56.24	3.63	18.68
1.23	65	57.43	3.66	18.40
0.70	66	57.31	3.68	18.84
0.49	78	58.78	3.79	17.96
0.35	59	60.95	3.73	17.87

[a] Polymerization conditions: 10 ml $C_2H_5OC_2H_5$ solvent; 0.1 ml $(CH_3)_3COOH$; −15°C reaction temperature; 20 min reaction time

[b] Theoretical values for PhC≡CH:SO_2 = 1:1 copolymer: C, 57.83%; H, 3.61%; S, 19.28%

[c] Copolymer yield is based on the limiting reactant

Copolymerization method

Synthesis of copolymers at low temperature. All copolymerizations were carried out using techniques similar to those described earlier[13]. A generalized procedure for the copolymerization of sulphur dioxide with phenylacetylene may be described as follows. In a dry flask fitted with a rubber septum the required amount of sulphur dioxide was condensed at −50°C using an ethanol/liquid nitrogen bath. The solvent with phenylacetylene was then injected and the clear homogeneous solution was brought to the reaction temperature. The system was allowed to equilibrate for a few minutes and then tert-butyl hydroperoxide (0.1 ml) was introduced into the flask using a 1 ml disposable syringe. Practically, immediate precipitation was observed in all cases since the resulting copolymers are virtually insoluble in all solvents employed in the present study. The crude polymeric material was broken up in water and filtered. The precipitate was washed with acetone, followed by dichloromethane to remove any polyphenylacetylene that might have been formed. The precipitate was subsequently dried *in vacuo* at room temperature to a constant weight.

Synthesis of copolymers at high temperature. To a solution of phenylacetylene (5.3 ml) in 4.0 ml solvent AIBN initiator was added (123 mg). The solution was cooled to −30°C with methanol/liquid nitrogen bath and then liquid sulphur dioxide (0.7 ml) was introduced. The dried system was then heated to 50°C for 2 h. The reaction mixture was homogeneous except in cyclohexane and pyridine solvents. After the elapsed time the reaction solution was cooled (−30°C) and excess methanol was poured in. The polymer was dissolved in chloroform and reprecipitated from methanol. The polymeric product was subsequently dried *in vacuo* at room temperature to a constant weight.

RESULTS AND DISCUSSION

General considerations

The bulk of this research is devoted to the study of the effect of temperature, solvent, initiator, and feed ratio on the composition of the copolymer resulting from sulphur dioxide and phenylacetylene. Specific conditions are given in *Tables 1*, *2*, and *3*.

Aged impure phenylacetylene did not copolymerize with liquid sulphur dioxide in the absence of tert-butyl

Table 3 Copolymerization of phenylacetylene and styrene with sulphur dioxide initiated by AIBN at 50°C[a]

Comonomer 1	Solvent	Comonomer 2	Copolymer[d] Yield (%)	Copolymer composition[c] %C	%H	%S	Mole ratio
Phenylacetylene	Cyclohexane	SO_2	6.5	60.10	3.76	19.11	1:1
Phenylacetylene	Dichloromethane	SO_2	5.8	60.13	3.73	17.17	1:1
Phenylacetylene	Dimethylformamide	SO_2	19.8	60.43	4.02	17.18	1:1
Phenylacetylene	Pyridine[b]	SO_2	2.6	56.08	3.41	16.97	1:1
Styrene	Cyclohexane	SO_2	61.7	69.45	5.47	10.33	2:1
Styrene	Dichloromethane	SO_2	7.2	69.37	5.54	9.82	2:1

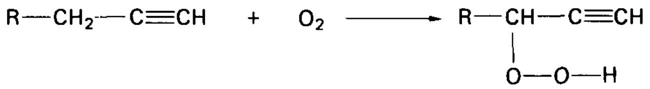
[a] Polymerization conditions: 5.3 ml organic monomer; 4 ml solvent; 0.7 ml liquid SO_2; 0.75 mmol AIBN; 2 h

[b] Conditions in pyridine solvent: 2.0 ml PhC≡CH; 1 ml pyridine; 2.5 ml liquid SO_2; 64 mg AIBN; 2 h. Excess pyridine gives no PhC≡CH/SO_2 copolymer

[c] Theoretical values for PhC≡CH:SO_2 = 1:1 copolymer: C, 57.83%; H, 3.61%; S, 19.28%. Theoretical values for PhCH=CH_2:SO_2 = 2:1 copolymer: C, 71.11%; H, 5.18%; S, 11.85%

[d] Copolymer yield is based on sulphur dioxide monomer

hydroperoxide. It was observed earlier[13] that aged terminal aliphatic alkynes, such as 1-heptyne, react spontaneously with liquid sulphur dioxide and this was attributed to the presence of the organic hydroperoxide formed *in situ* from the alkyne and molecular oxygen.



$$R{-}CH_2{-}C{\equiv}CH + O_2 \longrightarrow R{-}\underset{\displaystyle O{-}O{-}H}{\underset{|}{CH}}{-}C{\equiv}CH$$

The fact that aged phenylacetylene did not copolymerize with sulphur dioxide could be due to the absence of organic hydroperoxide in solution. There are no α-Hs present in phenylacetylene for abstraction by molecular oxygen.

Polysulphone copolymers are always formed when tert-butyl hydroperoxide is used as a free radical initiator at low temperature. At relatively high temperatures AIBN was employed for the copolymerization of phenylacetylene and sulphur dioxide. The well-known free radical initiators hydrogen peroxide, metachloroperbenzoic acid, and diphenyl peroxide were not effective in copolymerizing phenylacetylene with sulphur dioxide under the conditions used for tert-butyl hydroperoxide.

The solubility of the phenylacetylene/SO_2 copolymers, prepared at low temperature using tert-butyl hydroperoxide, was tested at room temperature and in a 80°C bath for about 24 h using the solvents acetone, cyclohexanone, dioxane, dimethyl sulphoxide, chlorobenzene, and toluene. All these copolymers were completely insoluble. The copolymers prepared at high temperature using AIBN were easily soluble in common organic solvents.

The incorporation of sulphur dioxide into the polyphenylacetylene backbone increased the stiffness and crystallinity and hence the melting point of the polymer. Thus polyphenylacetylene has a melting point of about 140°C–150°C and the phenylacetylene/SO_2 copolymers prepared with tert-butyl hydroperoxide had a melting point of 280°C–300°C range. Naturally crystallinity and the size of the polymer chain control the melting points of these copolymers.

To obtain some information about the structure of phenylacetylene/SO_2 copolymers the infra-red spectrum was examined. It shows several bands of significant importance. Two strong bands at 1340 and 1150 cm^{-1} stem from the asymmetric and symmetric $-SO_2$ stretching, respectively. Absorption arising from the stretching vibration of C=C appear in the 1560–1620 cm^{-1} region. The peaks at 1080, 1035, 750, and 700 cm^{-1} are characteristic of monosubstituted benzene. Actually, in the absence of elemental analyses the copolymer composition of these polysulphones can be estimated if one of these monosubstituted benzene absorptions is divided by one of the sulphur dioxide vibration bands. The skeletal vibrations, involving C–C stretching within the ring, absorb in the 1590–1600 cm^{-1} and in the 400–500 cm^{-1} region. The acetylenic CH (3300 cm^{-1}) and C≡C (2100 cm^{-1}) stretching vibrations which appear in the infra-red spectrum of phenylacetylene are absent in the spectra of these copolymers. The band at 3020 cm^{-1} is due to the aromatic and olefinic CH stretching modes.

Effect of temperature and solvent

As can be seen from *Table 1*, a number of different temperatures and solvents were used to copolymerize phenylacetylene with sulphur dioxide in the presence of tert-butyl hydroperoxide. In general, the copolymer yield increases substantially with increasing reaction temperature keeping all other reaction conditions constant. For example, excess sulphur dioxide was mixed with phenylacetylene and the two comonomers were dissolved in diethyl ether containing tert-butyl hydroperoxide. The resulting homogeneous solution was run at five different temperatures (+25°C, 0°C, −15°C, −25°C, −35°C) and gave copolymer percent yields of 26, 35, 87, 84, and 17, respectively. At the two higher temperatures (i.e. 25°C and 0°C) most of the SO_2 (b.p. −10°C) would be in the gas phase making these runs of a different nature. The highest yields were obtained with acetone or diethyl ether solvents, whereas solvents such as methanol and methylene chloride had a detrimental effect on the copolymer yields. It is of interest to note that phenylacetylene with sulphur dioxide in the presence of tert-butyl hydroperoxide without any solvent present produced a copolymer of relatively very low yield. This behaviour could be due to the electron donating property of the phenyl group that makes phenylacetylene to homooligomerize cationically in the presence of SO_2 and traces of H_2O present in solution. In fact styrene in SO_2 and tert-butyl hydroperoxide at −15°C without solvent produced exclusively polystyrene homopolymer as a result of cationic polymerization[14]. At any rate, the consumption of phenylacetylene in the above reaction system was examined by gas chromatography, the result revealed that 80% of the phenylacetylene remained unreacted. From the 20% consumed phenylacetylene approximately 15% was used to make polysulphone and only 5% was found by n.m.r. to be converted to polyphenylacetylene homopolymer. This homopolymer was isolated by extraction of crude polymer with methylene chloride.

All the polysulphones that appear in *Table 1* have an elemental analysis for C, H, and S that supports a 1:1 alkyne/SO_2 copolymer. The calculated values for an alternating copolymer structure ($C_8H_6SO_2$) are C, 57.83%; H, 3.61%; and S, 19.28%. For these polysulphone samples to have a copolymer composition of 2:1 (PhC≡CH/SO_2) their elemental analysis must be ($C_{16}H_{12}SO_2$), C, 71.64%; H, 4.48%; S, 11.94%. A copolymer structure of 2 moles of sulphur dioxide per mole phenylacetylene is not possible since SO_2 is not known to homopolymerize.

Effect of feed ratio

The effect of feed ratio on the copolymer composition of phenylacetylene/SO_2 system run in diethyl ether at −15°C using tert-butyl hydroperoxide radical initiator was also investigated and the results obtained are shown in *Table 2*. In the feed column the 12.3 mole ratio represents 12 molecules of SO_2 per molecule of PhC≡CH in solution. Going down the column the mole ratio becomes practically 6 and 2, then it reaches about 1:1. Finally it drops to 2 and 3 molecules of phenylacetylene for every sulphur dioxide molecule present in solution. These copolymerizations were allowed to proceed for about 20 min and after the usual workup and purification their elemental analysis was determined. The results that appear in *Table 2* reveal that, despite this wide difference in the feed mole ratio, the copolymer composition is always alternating.

Effect of initiator

The effect of radical initiator on the copolymerization of phenylacetylene and sulphur dioxide was also investigated. To four reactions each containing liquid sulphur dioxide (15 ml) and phenylacetylene (1.0 ml) kept at −35°C the following initiators were added: tert-butyl hydroperoxide (0.1 ml), *m*-chloroperbenzoic acid (0.075 g), 5 drops hydrogen peroxide (conc. 30%) and diphenyl peroxide (0.1 g). These reactions were allowed to react for about 20 min. After workup only tert-butyl hydroperoxide gave a copolymer product.

Comparative studies of $PhC{\equiv}CH/SO_2$ and $PhCH{=}CH_2/SO_2$

In order to see how phenylacetylene behaves with SO_2 at high temperature we ran several copolymerizations of phenylacetylene/SO_2 in the presence of AIBN at 50°C in various solvents and compared them with the styrene/SO_2 system. The radical initiator tert-butyl hydroperoxide is decomposed by the catalytic action of SO_2 producing free radicals at very low temperature; therefore it is not suitable for high temperature applications.

The systems were designed to have SO_2 as the limiting reactant and the length of time was kept short in order to examine the copolymers formed at relatively low conversions. The copolymerizations are relatively slow for both systems with AIBN initiator at 50°C but the styrene/SO_2 copolymerization was faster than that of the phenylacetylene/SO_2. In contrast, the phenylacetylene/SO_2 system at low temperature using tert-butyl hydroperoxide is instantaneous but styrene/SO_2 copolymerizes at a much slower rate under the same conditions.

As shown in *Table 3*, cyclohexane solvent for styrene/SO_2 and dimethylformamide for phenylacetylene/SO_2 produced the highest polysulphone yields. The presence of pyridine appears to suppress the copolymerization process. In fact excess pyridine poisons the copolymerization; presumably the pyridine complexes with SO_2 and inhibits its participation in the copolymerization with phenylacetylene.

Elemental analysis shows that phenylacetylene/SO_2 initiated by AIBN at 50°C gives copolymers whose composition is always one mole of phenylacetylene and one mole of sulphur dioxide. However, the styrene/SO_2 system under the same conditions produced copolymers with 2:1 molar ratio (styrene/SO_2 = 2:1). We did not investigate the copolymerization of styrene with sulphur dioxide using AIBN because the system has been studied extensively elsewhere[8,10]. As seen in *Table 3*, the theoretical values of C, H, S analyses agree with the analyses found for the proposed polysulphone copolymer compositions. The elemental analysis of carbon is more consistent and hence more dependable than that found for hydrogen and sulphur.

E.s.r. studies

The e.s.r. sample tube was placed in the variable temperature controller maintained at −165°C and e.s.r. spectra were taken as a function of increasing temperature. The variable temperature e.s.r. spectra of the copolymerization of phenylacetylene and styrene were shown in *Figures 1a* and *1b*, respectively. It can be seen that copolymerization of phenylacetylene started at −90°C while the copolymerization of styrene started at

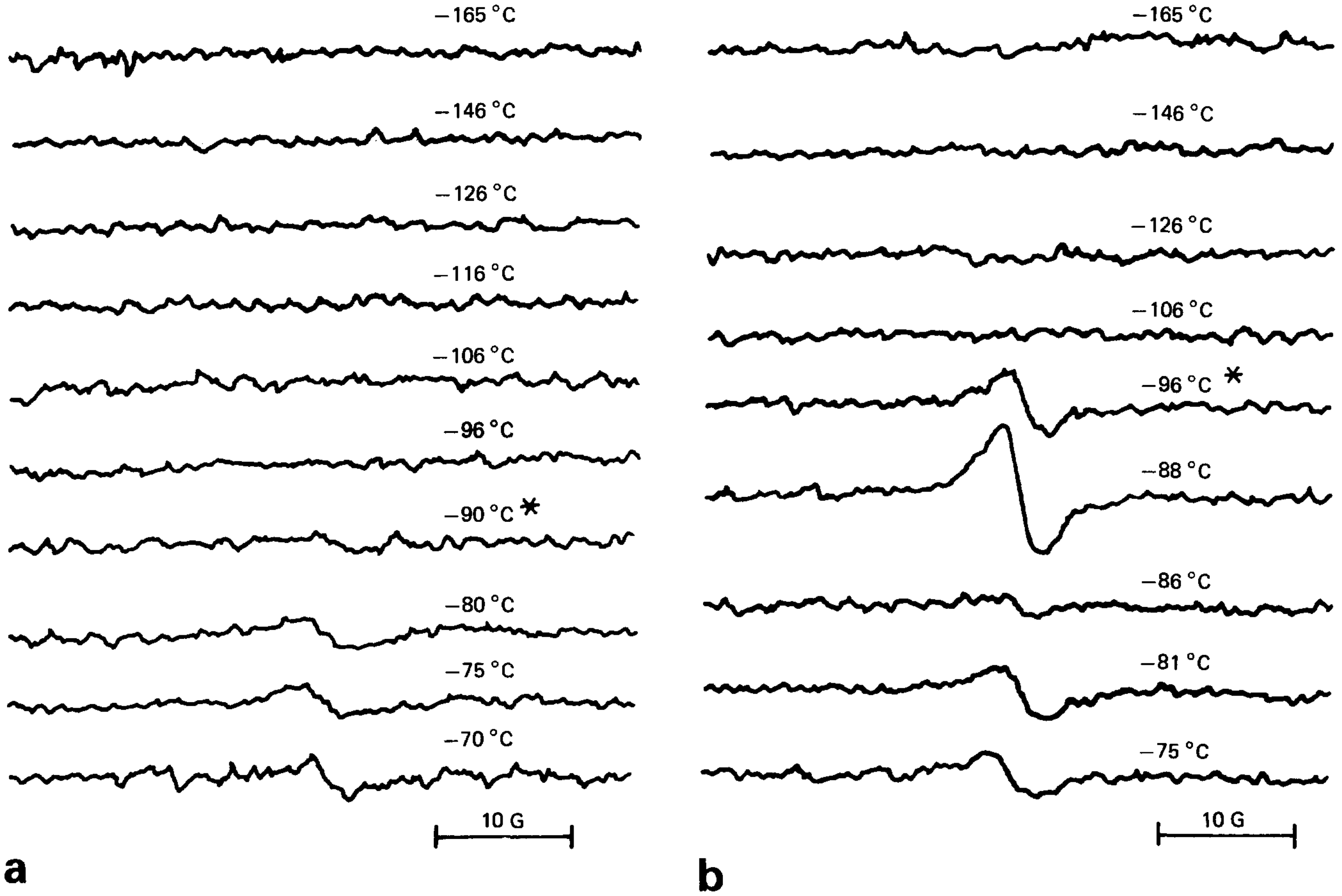


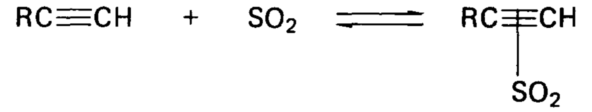
Figure 1 (a) E.s.r. spectra of phenylacetylene, ether, tert-butyl hydroperoxide and SO_2 taken at various temperatures. (b) E.s.r. spectra of styrene, ether, tert-butyl hydroperoxide and SO_2 taken at various temperatures. The asterisk denotes the temperature at which free radicals were detected

Figure 2 (A) E.s.r. spectrum of *Figure 1a* taken at slower scan speed and longer time constant. The broad background which overlaps with the second peak is due to the e.s.r. spectrum of polyphenylacetylene itself. (B) E.s.r. spectrum of *Figure 1a* taken at slower scan and longer time constant. The single peak in the spectrum has a g value of 2.0150

−96°C. The e.s.r. spectra shown in *Figure 2* were those in *Figure 1* examined under slow scan speed and long time constant. *Figure 2a* has two peaks with g values of 2.0040 and 2.0155, respectively, the later superimposed on a broad peak, while *Figure 2b* has only one peak with a g value of 2.0150. Both of these spectra confirmed the presence of free radicals in the copolymerization of phenylacetylene and styrene.

Mechanism

Recently[13], we examined the copolymerization of a series of aliphatic terminal acetylenes with sulphur dioxide in the presence of tert-butyl hydroperoxide at low temperature and the resulting polysulphones had a stereoselective alternating structure regardless of the conditions used. We attributed this phenomenon to the formation and participation of a 1:1 alkyne/SO_2 complex



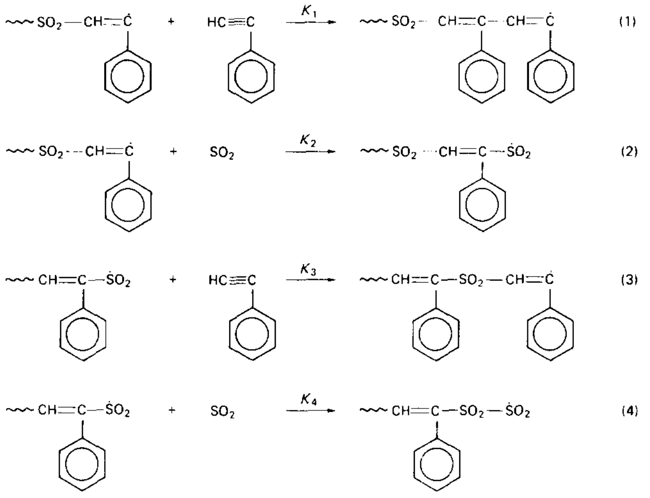
$$RC{\equiv}CH + SO_2 \rightleftharpoons \underset{\displaystyle SO_2}{RC{\equiv}CH}$$

If the alkyne/SO_2 pi complex is the one that controls the copolymer composition by reducing its concentration we should be able to prepare phenylacetylene/SO_2 copolymers of various composition. The solvents used (diethyl ether, acetonitrile, and methanol) are good Lewis bases and complex effectively with liquid SO_2 (a good Lewis acid) thus reducing the effective concentration of the alkyne/SO_2 complex. The results shown in *Table 1* do not support this hypothesis since the copolymer composition appears to be independent of the nature of the solvent employed.

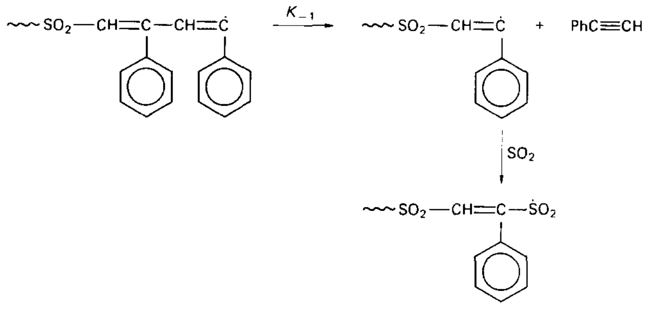
In the feed ratio effect (*Table 2*), if the alkyne/SO_2 complex operates the copolymer composition should depend upon its concentration, and this concentration varies with the total concentration of the comonomers. Again *Table 2* clearly shows that the copolymer composition is alternating regardless of the feed mole ratio.

There exists evidence in the literature[15,16] which suggests that, during copolymerization of aliphatic olefins with sulphur dioxide, depropagation occurs in the growing olefinic radicals with elimination of an olefin molecule and that allows the formation of an alternating copolymer. However, vinyl systems of the styrene or vinyl chloride type copolymerize with sulphur dioxide and give copolymers of various composition depending upon the experimental conditions employed.

In the copolymerization of phenylacetylene with sulphur dioxide let us consider another alternative where copolymerization does not involve an alkyne/SO_2 complex but proceeds in a conventional copolymerization manner. There are four possible propagation reactions.



The $K_4 = 0$ since SO_2 is not known to homopolymerize. The $PhC{\equiv}CH/SO_2$ always forms alternating copolymers regardless of the conditions used in the present study. This might suggest that $K_1 < K_2$ or K_3 even though phenylacetylene is known to homopropagate by a radical mechanism. If propagation 1 operates in the copolymerization but does not give a 2:1 $PhC{\equiv}CH/SO_2$ copolymer this could be explained by the depropagation process where a phenylacetylene molecule is released from the growing copolymer chain allowing the SO_2 to compete effectively forming always an alternating copolymer.



However, it is very unlikely that this depropagation takes place at such low temperatures used in the present study with the tert-butyl hydroperoxide initiator since the overall copolymerization rate increases with increasing temperature. Depropagation should not take place at all in the phenylacetylene/SO_2 system even at relatively high temperature where the styrene/SO_2 system was examined and reported[10] that there was evidence for the occurrence of the depropagation of growing styryl radicals. The three possible propagations in the $PhC{\equiv}CH/SO_2$ system have their growing radicals stabilized by delocalization and makes the C–C or C–S bonds much stronger than those in the styrene/SO_2 system. The propagations 2 and 3 are more likely to occur in the phenylacetylene/SO_2 copolymerization, since both give an alternating polysulphone copolymer. However, the e.s.r. spectrum (*Figure 2A*) suggests that propagation 3 is most likely to occur because of the large doublet typical for α-styryl radical attached to the polymer. The styrene/SO_2 system appears to follow propagation 2 because of the asymmetric e.s.r. spectrum (*Figure 2B*) with a g value of 2.0150 typical for hydrocarbon-sulphonyl radical. The asymmetry in the e.s.r. spectrum is due to the anisotropy in the g-factor arising from an incomplete quenching of the orbital angular momentum.

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