

Stereoselective alternating copolymerization of aliphatic acetylenes with sulphur dioxide

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A number of purified terminal aliphatic acetylenic hydrocarbons has been copolymerized with liquid sulphur dioxide in the presence of *t*-butyl hydroperoxide at low temperature. Benzoyl peroxide, hydrogen peroxide and *m*-chloroperbenzoic acid were ineffective. Neither sulphur dioxide nor *t*-butyl hydroperoxide alone was capable of polymerizing pure alkynes. Aged (impure) alkynes were copolymerized with sulphur dioxide in the absence of *t*-butyl hydroperoxide. All resulting alkyne-SO₂ copolymers were alternating with 100% *trans* configuration regardless of the nature of the alkyne, the solvent, or temperature. Several studies were performed to characterize the polysulphones, such as infra-red spectroscopy, ¹H and ¹³C nuclear magnetic resonance spectroscopy, melting point, viscosity, elemental analysis, solubility, film formation and flammability. A mechanism is proposed in which sulphur dioxide homolytically decomposes the organic hydroperoxide into free radicals which initiate the polymerization. The alkyne-SO₂ charge transfer complex is formed in solution, and the initiation and propagation steps probably involve this complex in equilibrium with its monomers.

(Keywords: stereoselective alternating copolymerization; structural characterization; reaction mechanism; aliphatic acetylenes; sulphur dioxide)

INTRODUCTION

Liquid sulphur dioxide is known¹⁻⁵ to react with terminal and internal aliphatic olefins in the presence of various radical initiators to form polysulphones. The resulting polymeric material is an alternating copolymer regardless of the copolymerization feed ratio. Conversely, styrene⁶⁻¹⁰ and some vinyl halide^{11,12} (e.g. vinyl chloride) monomers produce polysulphones with various sulphur dioxide compositions depending upon reaction temperature and feed ratio. In general, vinyl monomers with electron-withdrawing groups² resist copolymerization with sulphur dioxide, but reports have shown¹³⁻¹⁵ that with certain radical initiators and/or at low reaction temperature this type of copolymerization is possible, though the incorporation of SO₂ into the copolymer is relatively low. About half a century ago, it was reported¹⁶ that acetylenes can react with SO₂ in the presence of alcohol and paraldehyde, containing peroxides, to produce a sulphur dioxide-acetylene addition product, though structural characterization of these polymeric materials was generally poor.

A few years ago, we reported¹⁵ that *t*-butyl hydroperoxide was a highly efficient radical initiator at low temperature for the copolymerization of acrylic acid with sulphur dioxide. The objective of the present study is to use this low-temperature radical initiator system and a variety of other radical initiators to copolymerize a number of acetylenic hydrocarbons with SO₂. In addition, we carry out studies on the characterization of the resulting copolymers and the reaction mechanism.

EXPERIMENTAL

Starting materials

The following acetylenes were purchased from Farchan Chemical Company: 1-pentyne, 1-hexyne, 3-hexyne, 1-

heptyne, 1-nonyne, 1-decyne, 1-undecyne, 1-dodecyne, 1-tridecyne and 1-tetradecyne. Anhydrous sulphur dioxide was obtained from Union Carbide and used as received. Tertiary butyl hydroperoxide, benzoyl peroxide, hydrogen peroxide and *m*-chloroperbenzoic acid were obtained from Fluka.

Physical methods

The ¹H n.m.r. spectra were recorded on a Varian XL-200 spectrometer operating at a frequency of 200 MHz in the Fourier transform mode. Polymer samples were examined as 5% solutions in CDCl₃ with TMS as internal standard, at the ambient probe temperature (20°C). In addition, spectra were recorded for some samples in acetone-d₆ solvent with TMS as internal standard. The ¹³C n.m.r. spectra were recorded on a Varian XL-200 spectrometer with a carbon frequency of 50.3 MHz. Polymer samples were observed in CDCl₃ solution (0.1 g in 2.5 ml CDCl₃) at ambient probe temperature with TMS as internal standard. A single-frequency off-resonance decoupling experiment was carried out on sample AP10 (see Table 1) to differentiate the proton-bearing carbon in the olefinic region. The i.r. spectra were recorded on a Perkin-Elmer model 337 grating infra-red spectrophotometer using KBr pellets. Elemental analysis was done using a Carlo Erba Strumentazione model 1106 using a Pora Pak QS column 2 m in length for C, H analysis and 0.8 m in length for S analysis. The reduced viscosity measurements were made in an Ubbelohde type viscometer at 25°C with 0.4 wt% solution, usually in cyclohexanone. When the copolymer sample was not soluble in cyclohexanone, other suitable solvents were employed (Tables 1 and 2). All polysulphones were examined for solubility in the following solvents: acetone, cyclohexanone, dioxane, dimethylsulphoxide and dichloromethane. Each sample was tested with every

Table 1 Copolymerization of purified alkynes with sulphur dioxide in the presence of *t*-butyl hydroperoxide^a

Sample	Alkyne	Reaction temp. (°C)	Yield (%)	T _m (°C)	η_{red} (cm ³ g ⁻¹)	Copolymer composition						Repeating unit	Solubility ^b					
						Theoretical			Experimental				A	B	C	D	E	
						%C	%H	%S	%C	%H	%S							
AP1	1-Pentyne	-37	25	185-195	3.45	45.43	6.11	24.26	45.42	6.19	23.11	C ₃ H ₈ SO ₂	-	-	-	-	-	+
AP2	1-Hexyne	-37	50	115-125	2.93	49.28	6.91	21.92	50.44	7.02	22.53	C ₆ H ₁₀ SO ₂	+	+	-	-	-	+
AP3	1-Heptyne	-17	74	140-150	2.80	52.46	7.56	20.01	52.24	7.47	22.07	C ₇ H ₁₂ SO ₂	+	+	-	-	-	+
AP4	1-Heptyne	-37	60	125-135	4.17	52.46	7.56	20.01	52.43	7.38	21.68	C ₇ H ₁₂ SO ₂	+	+	-	-	-	+
AP5	1-Heptyne	-57	05	130-140	-	-	-	-	-	-	-	-	+	+	-	-	-	+
AP6	1-Nonyne	-37	51	140-150	3.48	57.40	8.58	17.02	56.85	8.59	17.59	C ₉ H ₁₆ SO ₂	+	+	-	-	-	+
AP7	1-Decyne	-37	68	135-145	3.66	59.36	8.98	15.84	59.28	9.02	14.69	C ₁₀ H ₁₈ SO ₂	+	+	-	-	-	+
AP8	1-Undecyne	-37	52	130-140	6.77	61.06	9.34	14.82	61.27	9.37	13.40	C ₁₁ H ₂₀ SO ₂	+	+	-	-	-	+
AP9	1-Dodecyne	-37	84	125-135	6.37	62.55	9.64	13.91	61.13	9.81	15.02	C ₁₂ H ₂₂ SO ₂	+	+	-	-	-	+
AP10	1-Tridecyne	-17	98	120-130	4.95	63.88	9.92	13.12	63.94	9.96	14.07	C ₁₃ H ₂₄ SO ₂	+	+	-	-	-	+
AP11	1-Tridecyne	-37	c										+	+	-	-	-	+
AP12	1-Tetradecyne	-17	68	110-120	2.42	65.05	10.16	12.40	65.86	10.44	13.01	C ₁₄ H ₂₆ SO ₂	+	+	-	-	-	+
AP13	1-Tetradecyne	-37	c										+	+	-	-	-	+
AP14	3-Hexyne	-25	0										+	+	-	-	-	+

^a Conditions: 15 ml liquid SO₂; 1.0 ml (CH₃)₃COOH; 1.5 h; no solvent

^b The letters A, B, C, D and E represent the solvents acetone, cyclohexanone, dioxane, dimethyl sulphoxide and dichloromethane respectively. The symbol + means soluble and - means insoluble. For each sample the first row represents the solubility tested at room temperature with stirring for 18 h and the second row represents the tests for 80°C for 1 h

^c Alkyne solidified and precipitated

Table 2 Copolymerization of impure alkynes with sulphur dioxide in the absence of t-butyl hydroperoxide^a

Sample	Alkyne	Reaction temp. (°C)	Conversion (%)	T_m (°C)	η_{red} (cm ³ g ⁻¹)	Copolymer composition						Repeating unit	Solubility ^b					
						Theoretical			Experimental				A	B	C	D	E	
						%C	%H	%S	%C	%H	%S							
AP15	1-Pentyne	-37	61	180-190	4.50	45.43	6.11	24.26	45.82	6.02	24.89	C ₃ H ₈ SO ₂	-	-	-	-	-	+
AP16	1-Hexyne	-17	90	110-120	3.81	49.28	6.91	21.92	48.77	6.52	20.98	C ₆ H ₁₀ SO ₂	+	+	-	-	-	-
AP17	1-Hexyne	-37	70	115-125	2.89	49.28	6.91	21.92	48.89	6.47	21.66	C ₆ H ₁₀ SO ₂	+	+	-	-	-	+
AP18	1-Heptyne	-17	96	130-140	1.99	52.46	7.56	20.01	52.15	7.36	19.89	C ₇ H ₁₂ SO ₂	+	+	-	-	-	+
AP19	1-Heptyne	-37	85	150-160	3.12	52.46	7.52	20.01	51.79	7.37	19.64	C ₇ H ₁₂ SO ₂	-	+	+	-	-	-
AP20	1-Heptyne	-57	22	135-145	4.98	52.46	7.56	20.01	51.67	7.52	20.02	C ₇ H ₁₂ SO ₂	-	+	+	-	-	+
AP21	1-Nonyne	-37	55	145-155	5.86	57.40	8.58	17.02	57.32	8.52	17.69	C ₉ H ₁₆ SO ₂	+	+	-	-	-	-
AP21	3-Hexyne	-25	0										+	+	+	+	+	+

^a Conditions: 15 ml liquid SO₂; 1.0 ml impure alkyne; 1.5 h; no solvent^b The letters A, B, C, D and E represent the solvents acetone, cyclohexanone, dioxane, dimethyl sulphoxide and dichloromethane respectively. The symbol + means soluble and - means insoluble. For each sample the first row represents the solubility tested at room temperature with stirring for 18 h and the second row represents the tests at 80°C for 1 h

solvent at room temperature with stirring for 18 h using an automatic shaker, and for 1 h in an 80°C water bath with occasional agitation.

Purification of alkynes

A solution consisting of 0.5 l previously boiled distilled water, 25 g ferrous ammonium sulphate and 2 ml concentrated sulphuric acid was placed into a one litre flask. A 15 ml alkyne sample was washed repeatedly (8 × 20 ml) with the above aqueous solution. After washing with 20 ml distilled water, the organic layer was dried over anhydrous magnesium sulphate, filtered and distilled at 0°C under high vacuum to give peroxide-free alkyne. The two alkynes tridecyne and tetradecyne were purified but were not distilled due to their high boiling point.

Copolymerization technique

All copolymerizations were carried out in essentially the same manner, the specific conditions being given in *Tables 1* and *2*. A typical run was conducted as follows: A 100 ml, one-neck round-bottomed flask was equipped with a rubber septum and was placed into a liquid nitrogen/methanol bath at the desired temperature. Approximately 15 ml of anhydrous sulphur dioxide was condensed into the cold flask, which contained 1.0 ml of purified alkyne. After mixing and allowing the two monomers to cool to the required temperature, 0.1 ml of t-butyl hydroperoxide was injected using a syringe. The mixture was allowed to react with occasional swirling and within a few minutes a white precipitate was observed for all acetylenic monomers except 1-pentyne, 1-hexyne and 3-hexyne. After 1.5 h 25 ml of cold methanol was added and the system was warmed to room temperature in the fume hood to remove the excess SO₂. The remaining reaction mixture was filtered and washed with water followed by methanol. The resulting white solid was vacuum dried to a constant weight at room temperature.

Also, when 15 ml of liquid SO₂ was mixed with 1.0 ml of impure alkyne (used as received) at low temperature (*Table 2*), the copolymerization was spontaneous, without the presence of t-butyl hydroperoxide, producing a white precipitate. The work-up of these reactions was the same as those where purified alkynes were used.

Finally, 15 ml liquid SO₂ and 1.0 ml of pure or impure 3-hexyne was allowed to react at 25°C and at -35°C with or without the presence of t-butyl hydroperoxide. In all cases, after 1.5 h, each reaction was quenched with 25 ml methanol and upon usual work-up no copolymer was obtained.

Reaction controls

Three reactions were performed under the following conditions: (a) 15 ml SO₂, 1.0 ml purified 1-heptyne; (b) 15 ml SO₂, 1.0 ml 1-heptyne, 0.1 ml t-butyl hydroperoxide; (c) 15 ml SO₂, 1.0 ml 1-heptyne used as received (unpurified). All three reactions were allowed to stand at -37°C for 1.5 h. After work-up the first reaction gave no polymeric product, whereas the second and third reactions formed alkyne-SO₂ copolymers in high yields.

RESULTS AND DISCUSSION

Copolymerization

The first experiment was the reaction of 1-heptyne with excess liquid SO₂ in the presence of t-butyl hydroperoxide

at -37°C. Surprisingly, when the alkyne was injected into the vessel containing liquid SO₂ a white precipitate was formed in seconds. There was not enough time to add the t-butyl hydroperoxide before the reaction was over. It was not clear whether the alkyne was very reactive and copolymerized with SO₂ without any radical initiator or whether some impurities caused the copolymerization. To clarify this uncertainty, the alkynes were purified by washing repeatedly with acidified ferrous ammonium sulphate solution. When the reaction was carried out using freshly distilled purified 1-heptyne, copolymerization did not occur in the presence of SO₂ without the addition of t-butyl hydroperoxide. Furthermore 1-heptyne could not be induced to homopolymerize when mixed with t-butyl hydroperoxide at -37°C without any SO₂ in the reaction mixture.

A similar phenomenon has been observed in olefins. More than half a century ago, Seyer and King¹⁷, in an attempt to obtain the freezing point of several olefin-SO₂ systems, observed that a white precipitate was always formed when SO₂ was mixed with olefins containing high concentrations of molecular oxygen. For the cyclohexene-SO₂ system, the white solid product was assigned the empirical formula (C₆H₁₀SO₂)_x. Other workers later reported that norbornene^{18,19}, cyclopentene²⁰ and 1-methylcyclopropene²¹ were copolymerized spontaneously with liquid SO₂ without the addition of a radical initiator. Recently, however, studies have revealed^{22,23} that these reactions occur because of the presence of small amounts of organic hydroperoxides when olefins or solvents had prolonged exposure to air.

All the polysulphones in the present study were synthesized by the addition of impure and pure alkynes to liquid SO₂ with or without t-butyl hydroperoxide at various temperatures. The data obtained from these experiments are shown in *Tables 1* and *2*.

As seen from the tables, the elemental analyses of C, H and S agree very well with those calculated for alkyne-SO₂ copolymer in 1:1 molar ratio regardless of the nature of the organic comonomer and the experimental polymerization conditions employed in this study.

The percentage copolymer yield decreased as the polymerization temperature decreased. For example, the reaction of purified 1-heptyne with SO₂ in the presence of equal amounts of t-butyl hydroperoxide run at three different temperatures (-17, -37 and -57°C) produced copolymers with yields of 74%, 60% and 0.5%, respectively. This may be attributed to the slow polymerization rate with a decrease in temperature, since all reactions were run for the same length of time. In general, for the purified alkynes, the percentage yield increased with increasing length of the alkyne monomer at constant reaction temperature. The two alkynes 1-tridecyne and 1-tetradecyne run at -37°C gave no copolymer with SO₂; instead the organic comonomers were solidified and precipitated. The pure or impure internal alkyne, 3-hexyne, did not copolymerize with SO₂ in the presence or absence of t-butyl hydroperoxide. The copolymer yields derived from the polymerizations of impure alkynes and SO₂ without the addition of t-butyl hydroperoxide do not show any meaningful trend. This observation is not surprising since the amount of the *in situ* organic peroxide present in the aged alkynes would not be expected to be of the same concentration in all polymerizations.

The effect of solvent on the copolymerization was also investigated. The following pure solvents were employed to copolymerize 1 ml of pure heptyne with 5 ml of SO₂ in 10 ml solvent using 0.1 ml t-butyl hydroperoxide at -37°C for 2 h. (a) Acetone produced 54% copolymer yield but the product was precipitated as it was formed. (b) Methylene chloride solvent gave 21% copolymer yield (4% yield at -17°C) and remained in solution during the reaction time. (c) Dimethyl ether caused a slight turbidity about 2 min after the injection of t-butyl hydroperoxide into the reaction mixture (copolymer yield 33%). Other solvents such as acetonitrile, methanol and dimethyl formamide gave practically no copolymer under the same conditions. The elemental analyses of the copolymers obtained in these reactions were similar to those samples presented in Table 1.

The *m*-chloroperbenzoic acid radical initiator gave dark brown solutions when 75 mg was added to a cold solution consisting of 15 ml SO₂ and 1 ml purified 1-heptyne at -37°C for 2 h. Upon work-up no copolymer was found. Benzoyl peroxide and hydrogen peroxide were also ineffective in copolymerizing 1-heptyne with liquid SO₂ under the same reaction conditions, though the reaction solutions were not coloured.

Properties and structure of polymers

In general, the introduction of polar groups into the polymers tend to decrease solubility because strong polymer-polymer bonds develop. The solubility for all alkyne/SO₂ copolymers varied. There is no clearcut correlation between solubility of the copolymers with the number of methylene groups in the aliphatic pendant group, though samples with longer R groups were generally more soluble. Branching, crystallinity and molecular weight of these thermoplastics will have some control over solubility as well. Solubility increased for some samples when they were mixed with a solvent and stirred in a water bath at 80°C for about 1 h. The samples appear to turn yellow but do not dissolve when shaken with 10% NaOH solution. When they were mixed with concentrated sulphuric acid for several hours, they gave a dark solution. They also decolourize Br₂/CCl₄ solution.

Determinations of reduced viscosity were made at 25°C with 0.4 wt% solutions, usually in cyclohexanone or in a solvent in which the particular sample was soluble at room temperature (Tables 1 and 2). There is no correlation between the type of alkyne and the reduced viscosity values of the respective copolymer.

The incorporation of an inflexible group such as phenyl, carbonyl or sulphur dioxide into a linear polymer chain backbone controls the rotation of the chemical bonds along the chain, which increases stiffness and crystallinity and hence the melting point and thermal stability of the copolymer. Thus alkyne homopolymers²⁴ are viscous materials at room temperature, whereas the alkyne-SO₂ alternating copolymers have melting points on average of 130°C. Also, the copolymer appear to be softer and more flexible as the size of the R group increases. For example, 1-pentyne-SO₂ copolymer had about 50°C higher melting point relative to those prepared from 1-decyne or 1-undecyne. Of course, crystallinity and molecular weight control the melting points of these samples as well. All the samples were films when pressed under 20 000 psi at room temperature but the films are brittle. As far as their flammability is

concerned, they are not self-extinguished when the external flame is removed in an open atmosphere.

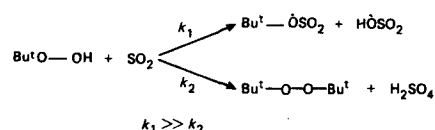
Examination of the i.r. spectra of alkyne-SO₂ copolymers show several structurally significant bands. A medium band at 1630 cm⁻¹ is for the carbon-carbon double bond stretching. The two strong bands at 1340 cm⁻¹ and 1140 cm⁻¹ arise from the asymmetric and symmetric -SO₂ stretching respectively. The weak absorption at 3020 cm⁻¹ is caused by the olefinic C-H stretch. The acetylenic C-H (3300 cm⁻¹) and C≡C (2120 cm⁻¹) stretching vibrations which appear in the i.r. spectra of 1-alkynes are absent in all polysulphone copolymer spectra.

The ¹H n.m.r. spectra of the copolymers show a single signal with a linewidth of 8 Hz in the olefinic region. This strongly suggests a highly stereoregular structure for the polymer, either in all-*trans* or an all-*cis* structure. The allylic CH₂ protons also show a singlet having a linewidth of 18 Hz, indicating a stereoregular structure. The ¹³C n.m.r. spectra of the copolymers (Figure 1) show only two fairly sharp peaks in the olefinic region, corresponding to the two olefinic carbons in the copolymer. The single-frequency off-resonance decoupled ¹³C n.m.r. spectrum showed the splitting of the high-field olefinic signal into a doublet, indicating that this signal is due to the carbon bearing the proton. The fact that each carbon in the copolymer shows a single sharp signal further confirms the stereoregularity of the polymers. No substituent parameters for SO₂ in the alkene system have been reported and it is not possible to get an idea of the carbon chemical shifts in the *trans* and *cis* systems for comparison.

The calculated chemical shifts for the olefinic proton, using the polyisoprene data²⁵ and alkene substituent parameters²⁶ for SO₂ and alkyl groups, are 6.75 and 6.58 ppm for *trans* and *cis* respectively. This favours a *trans* structure for the copolymers under study, showing a chemical shift of 7.3 ppm. However, the difference in the calculated shifts is not large enough to rule out a *cis* structure on the proton n.m.r. data alone. The data for the other samples (prepared at different temperatures and solvents) show identical chemical shifts (Table 3), indicating identical structures for the copolymers prepared under different experimental conditions.

Reaction mechanism

The copolymerization of terminal acetylenic hydrocarbons with liquid SO₂ in the presence of t-butyl hydroperoxide is very rapid. However, neither SO₂ nor t-butyl hydroperoxide alone were able to induce polymerization of pure alkynes. This probably suggests that SO₂ reacts with the organic peroxide, producing free radicals which initiate the polymerization. In fact, this redox reaction as a source of free radicals has been demonstrated previously²⁷ and studies show²⁸⁻³⁰ that t-butyl hydroperoxide undergoes induced homolytic decomposition in the presence of SO₂ and competes effectively with the side reaction that forms di-t-butyl peroxide and sulphuric acid.



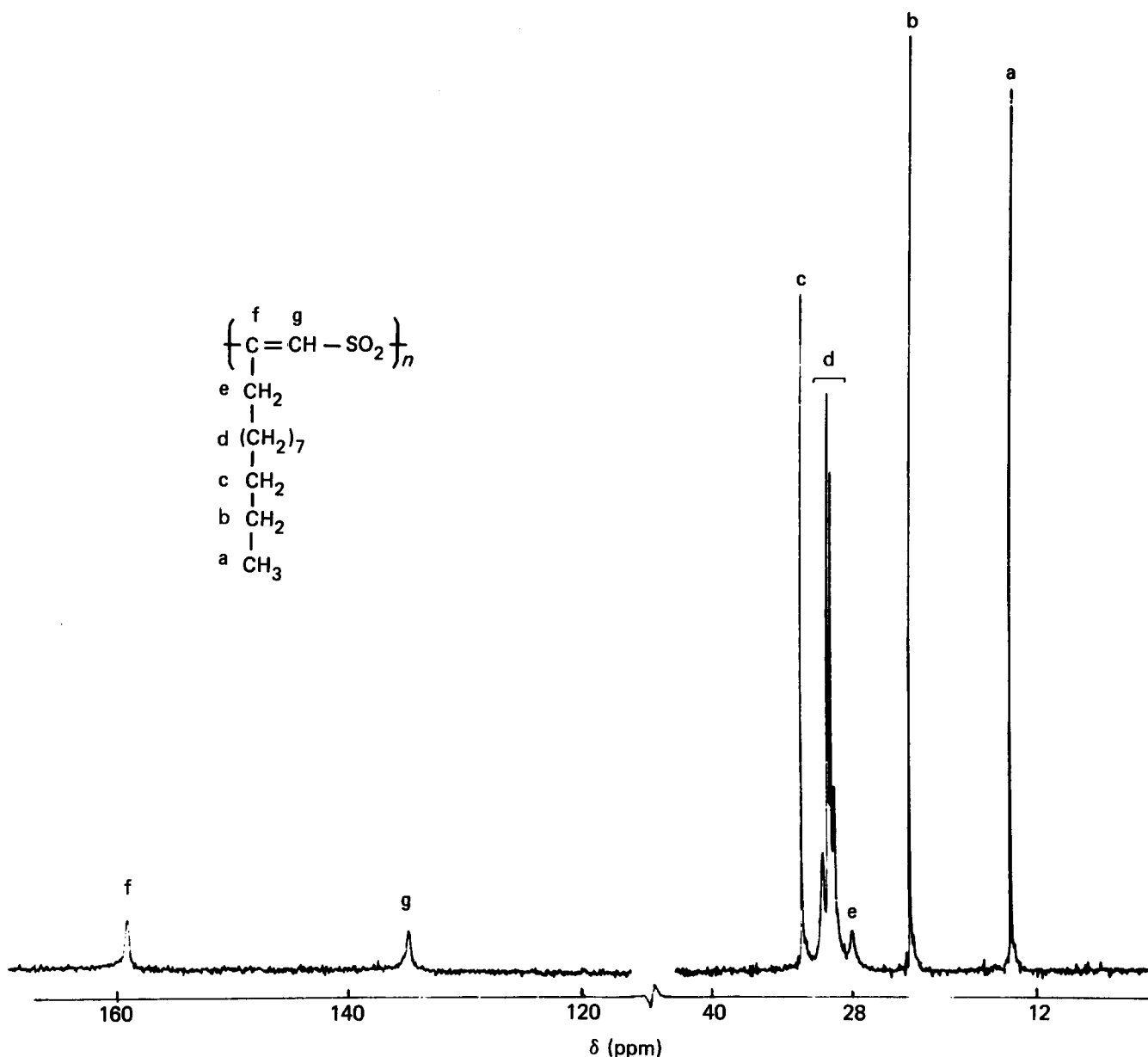


Figure 1 Proton-decoupled ^{13}C n.m.r. spectrum of 1-tridecyne- SO_2 copolymer

Table 3 The n.m.r. chemical shifts^a of the copolymers $\{\text{RC}=\text{CH}-\text{SO}_2\}_n$

Sample	Solvent	^1H chemical shifts			^{13}C chemical shifts		
		CH_3	Allylic CH_2	$\text{HC}=\text{C}$	Allylic CH_2	$\text{HC}=\text{C}$	$-\text{C}=\text{C}$
AP1	Acetone- d_6	1.00	2.90	7.55	^b	^b	^b
AP2	CDCl_3	0.96	2.86	7.28	^b	^b	^b
AP4	CDCl_3	0.92	2.88	7.26	^b	^b	^b
AP6	Acetone- d_6	0.94	2.88	7.54			
AP6	CDCl_3	0.90	2.85	7.24	31.8	135.0	157.8
AP7	CDCl_3	0.90	2.87	7.24	31.8	135.2	157.9
AP7	Acetone- d_6	0.90	2.88	7.55			
AP8	CDCl_3	0.90	2.86	7.23	31.8	135.0	159.0
AP9	CDCl_3	0.90	2.86	7.23	31.8	133.7	158.0
AP10	CDCl_3	0.90	2.86	7.23	31.9	135.0	159.4
AP12	CDCl_3	0.90	2.86	7.23	31.9	135.4	159.7

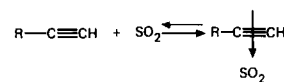
^aIn ppm relative to internal TMS

^bOwing to low solubility, ^{13}C n.m.r. was not obtained

These radicals (denoted by I^*) can initiate the copolymerization of the alkyne- SO_2 system. The question then arises as to how the system propagates to form a stereoselective alternating copolymer. There is a general belief³¹ that radical-initiated alternating copolymerization will probably occur if a strong electron acceptor monomer is mixed with a powerful electron donor. For example, the comonomer pair maleic anhydride-styrene³²⁻³⁴ form a donor-acceptor charge transfer which leads to alternating copolymerization. The powerful electron acceptor SO_2 is also known⁵ to form alternating copolymers with aliphatic olefins. It should be pointed out, however, that the exact nature and degree of participation of the charge transfer complex in the copolymerization is not clear.

In the present work, the elemental analyses and the n.m.r. data show that the alkyne- SO_2 copolymers are alternating regardless of the experimental polymerization conditions. Furthermore, an experiment was carried out where an equimolar mixture of 1-heptyne and SO_2 was introduced into an n.m.r. sample tube at -35°C and the spectrum recorded. As shown in Figure 2, the acetylenic

proton is shifted downfield compared to the corresponding proton resonance in neat 1-heptyne and all the other resonance positions are unchanged. This suggests that there is formation of a charge transfer complex, though in equilibrium.



All the above experimental evidence strongly suggests that the charge transfer complex is the species that participates in the alternating copolymerization.

At low temperature, the copolymerizations of olefins with SO_2 by a radical mechanism are known³⁵ to be stereospecific, giving preferential *trans* addition. However, at higher temperatures the intermediate radical can equilibrate to the stable radical by inversion of configuration, thus giving rise to both *cis* and *trans* addition products. Since the starting alkyne cannot show stereoisomerism, its addition to SO_2 may be stereoselective but never stereospecific. The polymerization of terminal alkynes with SO_2 is found to be

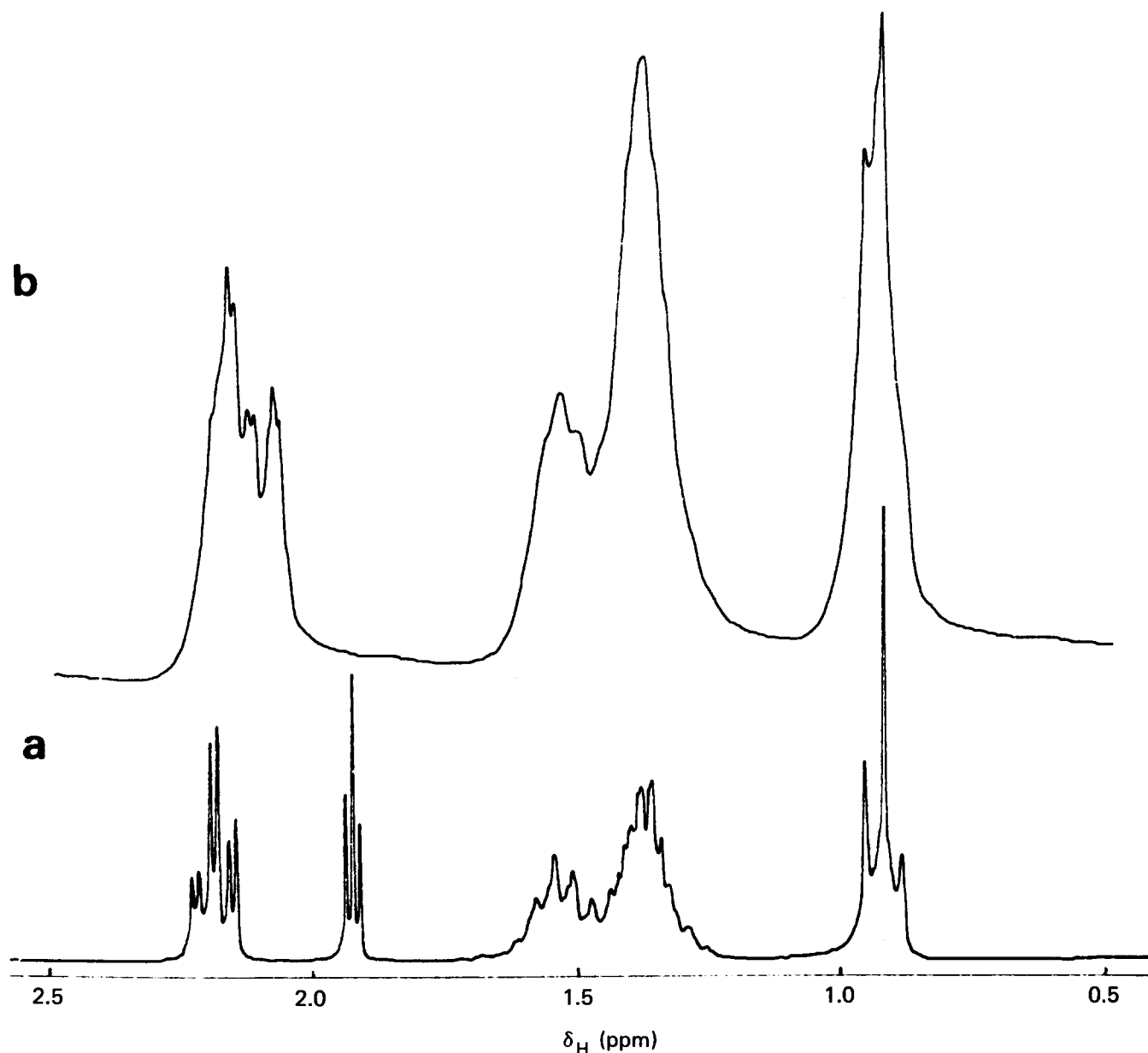


Figure 2 (a) Proton n.m.r. spectrum of neat heptyne. (b) Proton n.m.r. spectrum of the 1:1 mixture of heptyne and SO_2

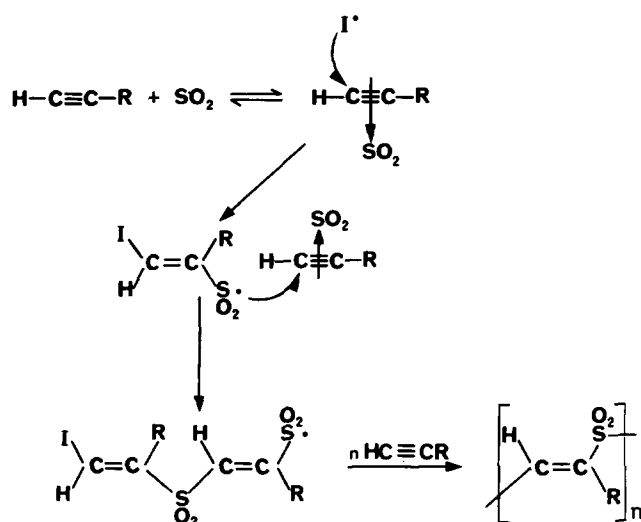


Figure 3 Proposed mechanism for the copolymerization of 1-alkyne with SO_2 , in the presence of a radical initiator

stereoselective. Only one kind of double bond is observed (*cis* or *trans*) in the n.m.r. spectra for the copolymers produced in the range -55 to -17°C . Copolymerizations of terminal alkynes with SO_2 are slower than those of alkenes. In our experiments no polymeric products are formed below -60°C , while olefins are known³⁵ to copolymerize with SO_2 at -78°C . Though the alkynes have higher electron density, the electrons are tightly held in the sp hybrid orbitals. The internal alkyne, 3-hexyne, failed to copolymerize with SO_2 , presumably due to steric hindrance in the transition state leading to the tetrasubstituted double bond.

As demonstrated in Figure 3, SO_2 (a Lewis acid) would probably form some kind of π complex with alkynes. Either the π complex or the alkyne (or a mixture of both) could possibly undergo copolymerization. The formation of a π complex may indeed make it more receptive towards incoming free radicals, thus resulting in the stereoselective *trans* addition as shown in Figure 3.

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REFERENCES

- Dainton, F. S. and Ivin, K. J. *Q. Rev.* 1958, **12**, 61
- Tokura, N. *Encycl. Polym. Sci. Technol.* 1968, **9**, 460
- Ivin, K. J. and Rose, J. B. 'Advances in Macromolecular Chemistry', Vol. 1, Academic Press, New York, 1968, Vol. 1
- Tsuruta, T. and O'Driscoll, K. F. 'Structure and Mechanism in Vinyl Polymerization', Marcel Dekker, New York, 1969
- Sandler, S. R. and Karo, W. 'Polymer Synthesis', Academic Press, New York, 1980, Vol. 3
- Tokura, N., Matsuda, M. and Ogawa, Y. *J. Polym. Sci. (A-1)* 1963, 2965
- Tokura, N., Matsuda, N. and Arakawa, K. *J. Polym. Sci. (A-2)* 1964, 3355
- Matsuda, M. and Ino, M. *Macromolecules* 1969, **2**, 216
- Herz, J., Hummel, D. and Schneider, C. *Makromol. Chem.* 1963, **63**, 12
- Herz, J., Hummel, D. and Schneider, C. *Makromol. Chem.* 1963, **64**, 95
- Marvel, C. S. and Glavis, F. J. *J. Am. Chem. Soc.* 1938, **60**, 2622
- Suzuki, H., Ito, M. and Kuri, Z. *Kogyo Kagaku Zasshi* 1968, **71**, 764
- Frith, W. C. Jr and Palmer, L. E. *Macromolecules* 1971, **4**, 654
- Cais, R. E. and Stuk, G. L. *Polymer* 1978, **19**, 179
- Tsonis, C. P. and Pasika, W. M. *Polymer* 1980, **21**, 253
- Ryden, L. L. and Marvel, C. S. *J. Am. Chem. Soc.* 1936, **58**, 2047
- Seyer, W. F. and King, E. G. *J. Am. Chem. Soc.* 1933, **55**, 3140
- Zutty, N. L. and Wilson, C. W. *Tetrahedron Lett.* 1963, **30**, 2181
- Zutty, N. L., Wilson, C. W., Potter, G. H., Priest, D. C. and Whitworth, C. J. *J. Polym. Sci. (A-3)* 1965, 2781
- Iwatsuki, S., Okada, T. and Yamashita, Y. *J. Polym. Sci. (A-1)* 1968, **6**, 2451
- Iwatsuki, S., Kobubo, T. and Yamashita, Y. *J. Polym. Sci. (A-1)* 1968, **6**, 2441
- Sartori, G. and Lundberg, R. D. *J. Polym. Sci., Polym. Lett. Edn.* 1972, **10**, 583
- Raetzsch, M. and Borman, G. *Plaste Kautsch.* 1973, **20**, 600
- Wazeer, M. I. M. and Tsonis, C. P. *Polymer* 1986, **27**(Commun.), 145
- Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972
- Silverstein, R. M., Bassler, G. C. and Morrill, T. C. 'Spectrometric Identification of Organic Compounds', 4th Edn., John Wiley, Chichester, 1981
- Mazzolini, C., Patron, L., Moretti, A. and Campanelli, M. *Ind. Eng. Chem., Prod. Dev.* 1970, **9**, 504
- Chien, J. C. W. and Boss, C. R. *J. Polym. Sci. (A-1)* 1970, **10**, 1579
- Oster, B. and Lenz, R. W. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 2479
- Husbands, M. J. and Scott, G. *Eur. Polym. J.* 1979, **15**, 249
- Cowie, J. M. G. 'Alternating Copolymers', Plenum Press, New York, 1985
- Tsuchida, E. and Tomono, T. *Makromol. Chem.* 1972, **141**, 265
- Tsuchida, E., Tomono, T. and Sano, H. *Makromol. Chem.* 1972, **151**, 245
- Dodgson, K. and Ebdon, J. R. *Makromol. Chem.* 1979, **180**, 1251
- Fawcett, A. H., Heatly, F., Ivin, K. J., Stewart, C. D. and Watt, P. *Macromolecules* 1977, **10**, 765