

Copolymerization of acrylamide with sulphur dioxide. Determination of the effect of copolymerization temperature on the monomer sequence distribution by ^{13}C n.m.r.

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Acrylamide was copolymerized with sulphur dioxide at temperatures from -78° to 60°C . The bulk monomer composition was fixed at 60 mol % sulphur dioxide, and both azobisisobutyronitrile and ^{60}Co gamma radiation were used as initiators. The ratio R of acrylamide to sulphur dioxide in the copolymers increased as the copolymerization temperature was raised; for example R was 1.97 at -78°C and 29.3 at 60°C . The microstructure of the copolymers was determined by $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. The carbonyl resonances were the most sensitive to structure, and they were assigned to monomer sequence pentads and configurational sequence dyads and triads. Only the backbone carbon resonance areas were quantitatively reliable under the observing conditions. The methine and methylene carbons revealed monomer sequence triad structure, and their relative areas allowed the monomer sequence distribution to be obtained as a function of temperature. A propagation-step mechanism was proposed to account for the effect of temperature on the monomer sequence distribution. No 1:1 alternating sequences were formed above 0°C , and this result suggested that depropagation of the sulphonyl radical was particularly facile when there was a pen-penultimate sulphone unit in the terminal chain sequence. The results were compared with those from other systems which form variable-composition polysulphones.

INTRODUCTION

Most polysulphones obtained by free radical copolymerization of sulphur dioxide (S) with olefinic monomers (M) have an equimolar composition with the regularly alternating $\cdots\text{SMSMSM}\cdots$ monomer sequence structure¹. This structure is independent of the usual copolymerization variables such as the monomer feed ratio, concentration, and temperature. However, a few monomers form polysulphones with variable compositions. In particular, when M is vinyl chloride²⁻⁵, vinyl bromide², styrene⁶⁻⁹ or several of its *para* derivatives¹⁰⁻¹³, chloroprene¹⁴⁻¹⁶ or acrylamide¹⁷, the M/S ratio R (which defines the macroscopic copolymer composition) can vary. Copolymerization temperature has a major effect on R , which may range from near unity at low temperatures to some large number at high temperatures.

These compositions are anomalous in the sense that R cannot be consistently related to the monomer feed ratio by the Lewis-Mayo¹⁸ (first order Markov) copolymerization model⁵. Alternative models which have been proposed involve the participation of monomer association complexes^{6,7}, penultimate effects¹⁹ and/or depropagation reactions^{9,19,20}. However, these models invariably require more than two independent parameters for complete specification (e.g. reactivity ratios and equilibrium constants). Consequently, the correct model and its associated

propagation step parameters cannot be unequivocally assigned from limited kinetic and macroscopic compositional data. Elucidation of the chain microstructure, in particular the monomer sequence distribution, can provide additional independent information which allows a better insight into the copolymerization mechanism²¹⁻²³

High-resolution n.m.r. spectroscopy has proved to be a sensitive probe of the microstructure of variable-composition polysulphones, especially when the ^{13}C nucleus is observed with broad-band proton decoupling^{24,25} ($^{13}\text{C}\{-^1\text{H}\}$ N.M.R.). For the poly(styrene sulphone) system, destructive techniques such as pyrolysis gas chromatography^{26,27} and mass spectrometry²⁸ or chemical degradation²⁹ have provided limited sequence information in the case where R was two. Often ^1H n.m.r. is not particularly revealing, owing to considerable overlap of homonuclear spin-coupled multiplets²⁹. This is not so when the comonomer M is ethylene³⁰, or when it is selectively deuterated at the double bond^{31,32}. In general though, $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. studies are superior due to the inherently greater dispersion of chemical shifts induced by different structural environments.

We have determined previously by n.m.r. the monomer sequence triad distributions (i.e. the relative proportions of all chain sequences composed of three contiguous monomer units) in poly(vinyl chloride sulphone)³² and poly(styrene sulphones)²⁵ which had been prepared at various temperatures. Both systems were characterized by respective copolymerization temperatures above which

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the probability of formation of SMS sequences was negligible. This observation led to the formulation of a copolymerization model involving depropagation steps^{25,33}, which we now believe is appropriate for the other anomalous polysulphone systems described above. The major objective of the present work is to test this conjecture for poly(acrylamide sulphones).

To our knowledge this system has not been examined hitherto by n.m.r. The only detailed report of the copolymerization of acrylamide with sulphur dioxide was published by Firth and Palmer¹⁷. These authors conducted the copolymerization with peroxide, azo and metal nitrate initiators at temperatures from ambient (~25°C) up to 100°C. Copolymer compositions were determined by elemental analysis; *R* increased as the temperature was raised, and was in the range from 2.8 to 8.8. At ambient temperature, there was little change in *R* when the monomer feed composition was varied from 50 to 89 mol % sulphur dioxide. No investigation of the chain microstructure was made.

In the present work we have varied the copolymerization temperature from -78 to 60°C, with the monomer feed composition fixed at 60 mol % sulphur dioxide. The high-resolution ¹³C-¹H n.m.r. spectra of the copolymers are reported, including the assignments of monomer sequence triads as well as some configurational and higher order monomer sequences. Quantitative analysis of the spectra allows the determination of the respective monomer sequence distributions, which are then compared with those in previous systems. In addition, we briefly report results of attempted copolymerizations of some alkyl substituted acrylamides with sulphur dioxide.

EXPERIMENTAL

Materials

Acrylamide (Eastman Organic Chemicals, electrophoresis grade) was dissolved in the minimum amount of chloroform, and the solution was filtered through a 10 μm teflon filter (Millipore Corp.). The monomer was then recrystallized twice and dried overnight in a desiccator under partial vacuum (melting point 85.1° to 85.6°C). Sulphur dioxide (Matheson Gas Products, anhydrous grade) was condensed into a glass storage ampoule on a vacuum line, and traces of air were removed by several freeze-thaw cycles. *N,N*-dimethylacrylamide and *N,N*-diethylacrylamide were purchased from Polysciences Inc. and vacuum distilled. Azobisisobutyronitrile (AIBN) was recrystallized from methanol and vacuum dried.

Polymerizations

Copolymerizations were carried out with the initiator (where required) and monomer mixtures sealed under vacuum in 100 cm³ spherical flasks. No diluents were used, except for the preparation of polyacrylamide in diethyl ether. The copolymerization at 60°C took place in a type T-316 stainless steel pressure reactor (Parr Instrument Co. model 4753). The desired amounts of acrylamide and initiator were weighed into each polymerization vessel, which was then attached to a vacuum manifold. After the vessel had been evacuated, a known quantity of sulphur dioxide (measured by the gas pressure in a calibrated volume) was condensed in at liquid nitrogen temperature to form a

monomer mixture which contained 60 mol% sulphur dioxide. A small amount of degassed chloroform was also distilled into the vessel in some cases. The vessel was then sealed and warmed to room temperature to obtain a homogeneous solution.

Copolymerizations at low temperatures were initiated by ⁶⁰Co gamma radiation in baths containing acetone—solid carbon dioxide, chlorobenzene slush, 1,2-dichlorobenzene slush and ice—water for the respective temperatures -78°, -45°, -17° and 0°C. At these temperatures, some acrylamide precipitated from the liquid sulphur dioxide. The reactions at 40° and 60°C were conducted in a thermostatically controlled water bath.

The vessels were rapidly chilled in liquid nitrogen after a suitable polymerization time had elapsed. Each polymer was recovered from a large excess of methanol which had been acidified with a few drops of hydrochloric acid. The polymers were then washed repeatedly with fresh methanol and dried overnight in a vacuum oven at 45°C. The copolymer prepared at 60°C contained traces of a water-insoluble black material (not characterized), which was removed by filtration of an aqueous solution. Polymerization details are given in Table 1.

N.m.r. spectra

¹³C-¹H n.m.r. spectra were obtained with a Varian XL-100 spectrometer³⁴ operating at 25.16 MHz. The polymers were examined at temperatures from 50° to 92°C with concentrations ranging from 0.20 to 0.27 g/cm³.

The copolymers with *R* less than 2.5 did not dissolve in water, acetone, chloroform, *sym*-tetrachloroethane, benzene, *p*-dioxane, glacial acetic acid or trifluoroacetic acid. The only suitable solvents were dimethylsulphoxide (DMSO) and hexafluoroacetone deuterate (HFAD). Unfortunately, the DMSO peak partly obscured some polymer resonances, particularly when this solvent was perdeuterated. Peak overlap was minimized by using (CH₃)₂SO, in which case the spectrometer frequency was locked on the resonance of D₂O, which had been placed in an internal capillary. The copolymers with *R* greater than 3.5 were soluble in water.

The primary internal reference for chemical shift was tetramethylsilane (TMS), although *p*-dioxane (D₂O solutions), DMSO and hexamethyldisiloxane (HMDS) were used in some cases as secondary references. The chemical shifts of these

Table 1 Polymerization conditions and yields

Temperature (°C)	Polymerization time (h)	[AIBN] (mol %)	[Chloroform] ^a (mol %)	Absorbed dose ^b (kGy)	Yield ^c (%)
-78	5.90	—	1.7	22.8	1.7
-45	5.18	—	1.7	20.0	18.5
-17	4.98	—	1.7	19.3	24.1
0	3.33	—	—	12.9	15.0
40	18.10	0.106	—	—	14.9
60	6.17	0.099	—	—	14.8
60 ^d	4.42	0.203	—	—	64.0

^a Chloroform was added to limit molecular weight and inhibit any ionic homopolymerization of acrylamide.

^b Effective dose rate was 1.08 Gy/sec (1 Gy = 100 rad).

^c Yield based on total weight of monomer mixture, which initially contained 60 mol % sulphur dioxide for all copolymerizations.

^d Homopolymerization of acrylamide (the monomer concentration was 22% by wt in diethyl ether)

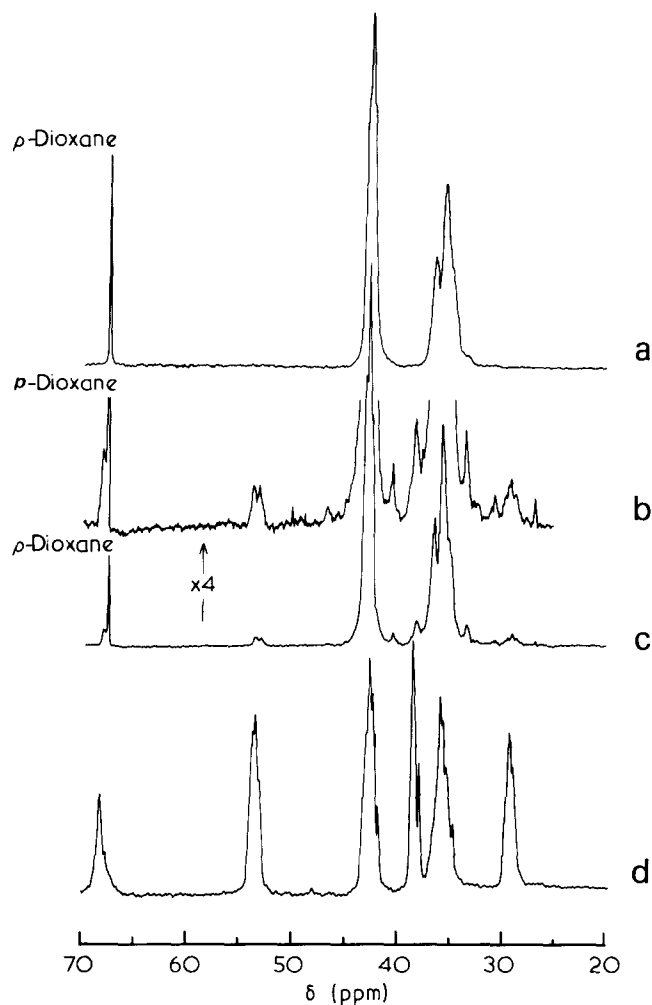


Figure 1 $^{13}\text{C}\{-^1\text{H}\}$ resonances obtained at a magnetic field strength of 2.35 T (23.5 kG) from the backbone carbons in (a) polyacrylamide, and in poly(acrylamide sulphonates) prepared at (c) 60°C; (d) 40°C. Solvent, D_2O ; *p*-dioxane (internal reference for chemical shift, $\delta = 67.40$ ppm). Spectrum (b) is a four-fold vertical expansion of spectrum (c). Observation temperature, concentration and number of scans were as follows: (a) 55°C, 0.26 g/cm³, 12 000; (c) 77°C, 0.27 g/cm³, 12 000; (d) 92°C, 0.20 g/cm³, 50 000, respectively. A $\pi/2$ flip angle (12.5 μsec pulse duration) with a pulse spacing of 1.5 sec was chosen in all cases. The spectral window and number of memory locations for storage of the free-induction decay (FID) were: (a) and (c) 5555 Hz; 16K; (d) 5000 Hz, 8K, respectively. The complete spectral window is not displayed

materials from TMS were measured on the ppm scale under the same conditions as the polymers. The following δ values were obtained: *p*-dioxane 67.40, DMSO 40.32, DMSO-*d*₆ 39.68, and HMDS 1.91. The peak positions of acrylamide were also measured in case the monomer was observed in the spectra. In DMSO solution, the olefinic peaks were at 132.05 and 125.18 ppm, and the carbonyl peak was at 166.42 ppm.

The monomer sequence distributions were determined from the relative areas of the backbone carbon resonances. These areas were measured by weighing peaks which had been traced onto drawing paper. This method proved more reliable than the digital integration routine available from the spectrometer software, since most of the polymer resonances had broad, asymmetric lineshapes.

RESULTS AND DISCUSSION

Copolymerization temperature has a significant effect on the structure of poly(acrylamide sulphonates), as revealed by the positions and relative intensities of the various ^{13}C resonances. Figures 1 and 2 show all $^{13}\text{C}\{-^1\text{H}\}$ resonances observed in the range from 25 to 70 ppm. These resonances are due to the polymer backbone carbons. In some cases, peaks due to solvent and reference also fall in this range. The polymers have basically two types of backbone carbon, the methine or α -carbon which bears the amide substituent, and the methylene or β -carbon. The resonance positions depend on carbon type (i.e. α or β) and local structural environment, whereas the corresponding intensities depend on the frequency of occurrence of the different environments.

Assignment of backbone ^{13}C resonances

Polyacrylamide gives the simplest spectrum (Figure 1a). The peak at 42.76 ppm is due to the α -carbon, and the one

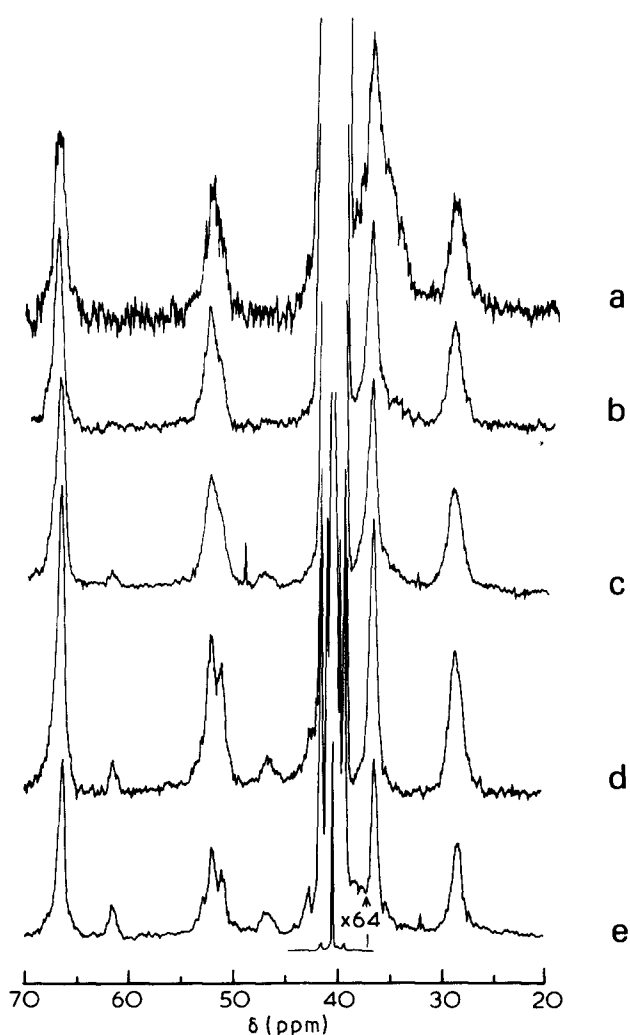


Figure 2 $^{13}\text{C}\{-^1\text{H}\}$ resonances observed for the backbone carbons in poly(acrylamide sulphonates) prepared at (a) 40°C; (b) 0°C; (c) -17°C; (d) -45°C; (e) -78°C. The intense peak at 40.32 ppm (with spinning side bands) is due to the solvent, which was DMSO. Temperature, concentration, and number of scans were (a) and (b) 60°C, 0.25 g/cm³, 6400; (c) 55°C, 0.25 g/cm³, 12 000; (d) 55°C, 0.25 g/cm³, 8000; (e) 55°C, 0.20 g/cm³, 12 000, respectively. Other conditions were the same as those given in the caption to Figure 1

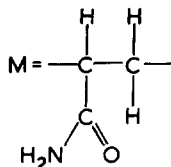
at 35.62 ppm corresponds to the β -carbon. These assignments were made by observation of the proton-coupled ^{13}C spectrum, in which $^1\text{J}_{^{13}\text{C}-^1\text{H}}$ was 129 Hz for both the α -carbon doublet and β -carbon triplet.

A total of eight characteristic resonance positions may be distinguished from the various copolymer $^{13}\text{C}-\{^1\text{H}\}$ spectra. These are centred at 66.5, 62.1, 52.1, 46.9, 41.0, 36.6, 34.4 and 28.7 ppm in DMSO solutions (Figure 2). We attribute these to four dissimilar monomer sequence environments for each backbone α - and β -carbon. This multiplicity of environments must be derived from monomer sequence triads. If the backbone ^{13}C resonances were sensitive to chain structure at the monomer sequence dyad level, only six resonance positions would result (from the α - and β -carbons in the three dyads MM, MS and SM). On the other hand, the peak multiplicity would be far greater than observed if monomer sequence tetrads were resolved.

The copolymers do not contain sequences of the type S_n , where n exceeds unity, because sulphur dioxide does not add to the sulphonyl radical during chain propagation¹. Consequently, only five monomer sequence triads exist, MMM, MMS, SMM, SMS and MSM. The last sequence (MSM) is not observable by ^{13}C n.m.r. (*vide infra*), so there are four monomer sequence triads to be assigned in the spectra.

It is possible to assign immediately the α (MMM) and β (MMM) resonances by reference to the homopolymer spectrum (Figure 1a). These occur at 42.7 and 35.8 ppm respectively in D_2O solution, and the corresponding positions in DMSO solution are shifted slightly upfield to 41.0 and 34.4 ppm.

A note on nomenclature is in order here. We adopt the convention that M always represents the acrylamide unit in the directional sense having the α -carbon on the left and the β -carbon on the right, as written below:



The α (SMM) resonance, for example, is due to central monomer unit M in the SMM triad. It specifically pertains to the α -carbon which, because of the directional sense of M as defined above, must be bonded directly to the sulphone unit. This resonance is not equivalent to that from the α -carbon in the 'reversed' sequence MMS, in which the α -carbon of the central (observed) unit is two main-chain bonds distant from the sulphone unit, which is now bonded directly to the β (MMS) carbon. It is also evident that the monomer sequence triad MSM has no resonance observable by ^{13}C n.m.r. from the central monomer unit.

We find that both the α (MMM) and β (MMM) resonances are clearly resolved only in D_2O solutions (Figure 1). In DMSO solutions (e.g. see Figure 2a) the β (MMM) peak is a broad shoulder on the peak at 36.6 ppm, which we assign below to the α (MMS) resonance. The DMSO peak occurs almost directly on top of the α (MMM) peak. The latter peak is also obscured in $\text{DMSO}-d_6$ solution, but may be seen clearly at 41.04 ppm when HFAD is employed as solvent, as shown in Figure 3.

The α - and β -carbon resonances from the three monomer sequence triads MMS, SMM and SMS remain to be assigned. A measurement of ^{13}C spin-lattice relaxation times (T_1) was carried out to make the assignment to carbon type (α or β). The standard inversion-recovery procedure was used

(involving a $\pi-\tau-\pi/2-T$ sequence of pulses and delay times), with a 2.3 sec waiting period (T) to allow the backbone ^{13}C magnetization to fully relax after the $\pi/2$ sampling pulse. The experiment was performed at 60°C with a DMSO solution of the copolymer prepared at 0°C (spectrum shown in Figure 2b).

The peaks at 66.4 and 36.6 ppm each had a T_1 value of 75 msec, whereas those at 52.1 and 28.7 ppm both relaxed more rapidly, with a T_1 value of 40 msec. The nearly exact 2:1 ratio of these values indicates that these ^{13}C nuclei relax by a dipolar interaction with their directly-bonded proton(s), so the former pair are α -carbons and the latter pair are β -carbons³⁵. The T_1 experiment was more convenient for obtaining these assignments than alternative procedures involving either specific deuterium labelling of the chain backbone²⁵, or an off-resonance decoupling experiment³⁶.

The final evidence we used for assigning peaks was based on the report¹⁷ that poly(acrylamide sulphones) prepared above room temperature ($\sim 25^\circ\text{C}$) have R values greater than 3. Therefore the non-alternating sequences, MMM, MMS and SMM, should predominate in the copolymers synthesized at 60° and 40°C (Figures 1c and 1d). Carbons directly bonded to a sulphone unit will be substantially deshielded by an inductive effect, which allows us to assign the peaks at 68.1 and 53.4 ppm to α (SMM) and β (MMS), respectively (e.g. see Figure 1d). The deshielding from the corresponding peak positions in the MMM sequence amounts

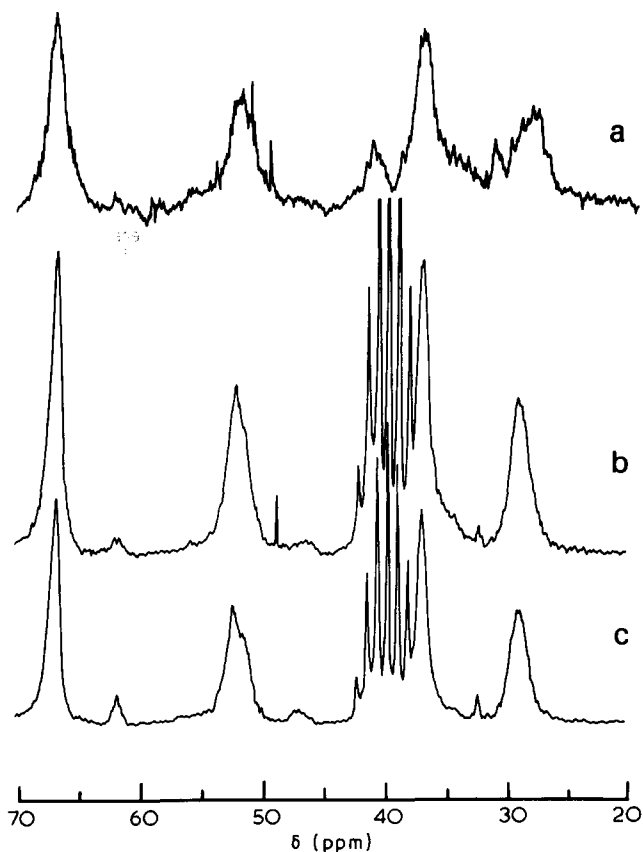


Figure 3 Backbone $^{13}\text{C}-\{^1\text{H}\}$ resonances for poly(acrylamide sulphones) prepared at (a) and (b) -17°C ; (c) -45°C . Solvents: (a) HFAD; (b) and (c) $\text{DMSO}-d_6$. Spectra obtained at 55°C with 0.25 g/cm^3 concentration and the following number of scans; (a) 8000; (b) 24 000; (c) 15 000. Other conditions were the same as those given in the caption to Figure 1a

Table 2 Peak positions for the methine (α) and methylene (β) backbone ^{13}C resonances from the monomer sequence triads in poly(acrylamide sulphones)

Solvent	Temperature ($^{\circ}\text{C}$)	Monomer sequence triad and ^{13}C resonance position (ppm) ^a							
		SMS		SMM		MMS		MMM ^b	
		α	β	α	β	α	β	α	β
DMSO	55	62.1	46.9	66.5	28.7	36.6	52.1	41.0	34.4
D ₂ O	92	—	—	68.1	29.2	38.4	53.4	42.7	35.8

^a Chemical shift of the centre of the peak from TMS

^b M denotes the acrylamide unit in the directional sense $-\text{CH}(\text{CONH}_2)\text{CH}_2-$

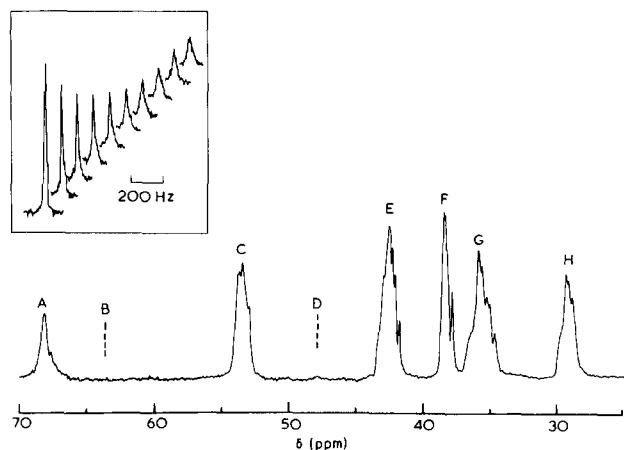


Figure 4 Assignments of the backbone carbon resonance in poly(acrylamide sulphone) to monomer sequence triads. The spectrum of the copolymer prepared at 40°C is used as an example (instrumental details are given in the caption to *Figure 1d*). An explanation of the monomer sequence notation is given in the text. The SMS sequence was not observed in this copolymer, but its relative resonance positions are indicated. The inset spectra show on a different scale the $\alpha(\text{SMM})$ peak after intervals of 2.08 h (5000 scans for each peak). This peak changes with time owing to hydrogen-deuterium exchange involving the solvent (D_2O). A, $\alpha(\text{SMM})$; B, $\alpha(\text{SMS})$; C, $\beta(\text{MMS})$; D, $\beta(\text{SMS})$; E, $\alpha(\text{MMM})$; F, $\alpha(\text{MMS})$; G, $\beta(\text{MMM})$; H, $\beta(\text{SMM})$

to 25.7 ppm for the α -carbon and 17.6 ppm for the β -carbon.

By a process of elimination, the peak at 38.41 ppm in *Figure 1d* must be due to the $\alpha(\text{MMS})$ carbon, and the one at 29.22 ppm then corresponds to the $\beta(\text{SMM})$ carbon. It is significant that these resonance positions are 4.10 and 6.59 ppm, respectively, upfield from their MMM sequence counterparts. This shielding occurs when there is a sulphone unit in place of a carbon atom in the position which is removed from the observed carbon by two main-chain bonds. It may be attributed to a three-bond *gauche* interaction of the observed carbon with one of the oxygen atoms on the sulphone unit. The effect was observed also in the $^{13}\text{C}-\{^1\text{H}\}$ spectra of poly(vinyl chloride sulphones)²⁴ and poly(styrene sulphones)²⁵, and has been noted by others^{37,38}.

We identify the two weak peaks in *Figure 2e* at 62.78 and 46.53 ppm with the alternating SMS sequence. They are assigned to $\alpha(\text{SMS})$ and $\beta(\text{SMS})$ respectively, on the basis of their corresponding upfield shifts of 3.45 and 5.51 ppm from $\alpha(\text{SMM})$ and $\beta(\text{MMS})$. This shielding is again due to the presence of a sulphone oxygen atom in the γ -position to the observed carbon, as described above. It is most sig-

nificant that SMS sequences are not observed in copolymers prepared above 0°C , and this point will be taken up subsequently in more detail.

The resonance positions of the α - and β -carbons from the four monomer sequence triads are listed in *Table 2*. These positions were not affected to any extent by the overall copolymer composition or observation temperature. However, solvent had some effect. The resonances are shifted by about 0.5 to 1.8 ppm to lower field in D_2O from their positions in DMSO solution.

The backbone resonances of the copolymer prepared at 40°C are shown with their assignments on an expanded scale in *Figure 4*. The $\alpha(\text{SMM})$ resonance was observed to decrease in intensity and broaden during spectrum accumulation from D_2O solution, as shown by the inset spectra. This is due to exchange of the labile proton on the methine carbon bonded directly to a sulphone unit with deuterium from the solvent. The nuclear Overhauser enhancement (NOE) of the $\alpha(\text{SMM})$ carbon is lost when its proton is replaced by deuterium, resulting in a reduced peak intensity. The peak is also broadened somewhat by deuterium coupling, although this may be incomplete due to scalar relaxation of the second kind³⁹.

Fine structure

Peak broadening is present in the $^{13}\text{C}-\{^1\text{H}\}$ spectrum of polyacrylamide due to configurational isomerism (tacticity). This is shown in *Figure 1a*. The α -carbon resonance is partly resolved into a fairly symmetrical triplet, which corresponds to the three stereosequence triads: *rr*, *rm* (*mr*) and *mm*. It appears that the homopolymer is nearly perfectly atactic, provided we make the reasonable assumption that the stereosequence distribution conforms to Bernoullian statistics⁴⁰. If there were any strong bias in the stereosequence distribution, then the α -carbon triplet would be distinctly asymmetric.

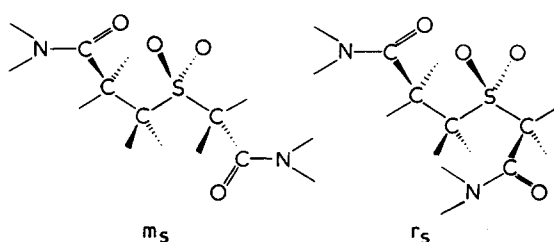
The β -carbon resonance is not resolved into any obvious stereosequential pattern. It is principally a doublet (at 36.54 and 35.62 ppm), with a broad shoulder on the high field (low frequency) side of the resonance. The overall pattern is most likely a composite of overlapping tetrads.

We have found that the primary influence on backbone ^{13}C resonance positions in the copolymer spectra is due to the identity of the monomer sequence triad environment. Configurational isomerism and longer monomer sequence structure also have some effect. However, this effect is comparatively small, and is manifest mainly as peak broadening. In general, the α -carbons give narrower peaks than the β -carbons (e.g. see *Figure 2*). This may be due to in part a reduced sensitivity of α -carbons to environment, but

their resonances also must be inherently narrower than those from β -carbons, due to their longer spin-spin relaxation times (T_2)³⁵.

Both MMM sequence resonances have more fine structure in the spectrum of the copolymer prepared at 40°C (Figure 4) than in the homopolymer spectrum. These extra features may be assigned to the monomer sequence tetrad resonances α (MMMM), α (SMMM), β (MMMM) and β (MMMS), where the observed unit is underlined.

The only other resolved structure appears on the β (MMS) peak, which is primarily a doublet in spectra of the copolymers prepared at 60°, -45° and -78°C (Figures 1b, 2d and 2e, respectively). The copolymer prepared at 60°C has predominantly only one monomer sequence environment for this carbon, . . . MMMSMMM . . . , so the splitting must be due to dyad tacticity. The asymmetric centres involved are the two α -carbons in the sequence MSM, and the spectra show that these have an approximately equal chance of being in both the m_S and r_S relative configurations, which are represented by the planar zig-zag (Natta) projections below.



The subscript S is used above to distinguish these dyad configurational structures from those in MM sequences, for which the notation m_C and r_C will be used.

In this section we remark finally on the presence of several small, unassigned peaks in the spectrum of the copolymer prepared at 60°C (Figure 1b). These peaks occur at 46.70, 40.44, 33.38, 30.60 and 26.73 ppm, and were not observed for the other polymers. They may be due to some impurity related to the side reaction which produced the water-insoluble black material, or to end-group structures. If the latter assumption is correct, then the copolymer prepared at 60°C must have a molecular weight which is lower than that for the other polymers. Firth and Palmer¹⁷ detected sulphate groups in poly(acrylamide sulphones) prepared at high temperatures in stainless-steel reactors, but not in copolymers prepared below 50°C.

Assignment of carbonyl resonances

Often the resonances of non-protonated carbons reveal considerable fine structure in polymer spectra because of their intrinsically narrow linewidths (long T_2 values). This is the case for poly(acrylamide sulphones), where the carbonyl resonances show extensive structural detail (Figure 5).

The carbonyl resonance positions occur from 163 to 180 ppm, and are affected little by temperature and overall copolymer composition. However the nature of the solvent has some effect, as in the case of the backbone carbon resonances. In D_2O solution, the carbonyl resonances are shifted by about 2.2 ppm to lower field from their corresponding positions in DMSO solution (e.g. compare Figures 5d and 5e).

The carbonyl resonance in polyacrylamide is at 180.18 ppm in D_2O solution (Figure 5a), and is insensitive to tacticity. We can distinguish two resonance regions in the

copolymer spectra, one at high field (centred around 165 ppm), and one at low field (centred around 175 ppm). Therefore the primary effect on carbonyl chemical shift is due to monomer sequence dyads. The MM dyad region is at low field, where the resonance from the homopolymer occurs, and the SM dyad region is at high field. The upfield shift of the latter region from the former is consistent with our previous observation of the effect of a *gauche* interaction of the observed carbon with a sulphone oxygen atom.

Given the multiplicity of carbonyl resonances, and the trend in their relative intensities with copolymerization temperature, we interpret the fine structure in terms of monomer sequence pentads, upon which a small tacticity splitting is superimposed. The monomer sequence assignments are shown in Figure 6, where the carbonyl resonances from the copolymer prepared at 40°C provide a convenient illustration.

A carbonyl resonance from the central M unit in the alternating MSMSM sequence is observed at 163.45 ppm in DMSO solution, but only for the copolymers prepared below 0°C (Figures 5g, 5h and 5i). This observation confirms our finding from the backbone carbon spectra, and is

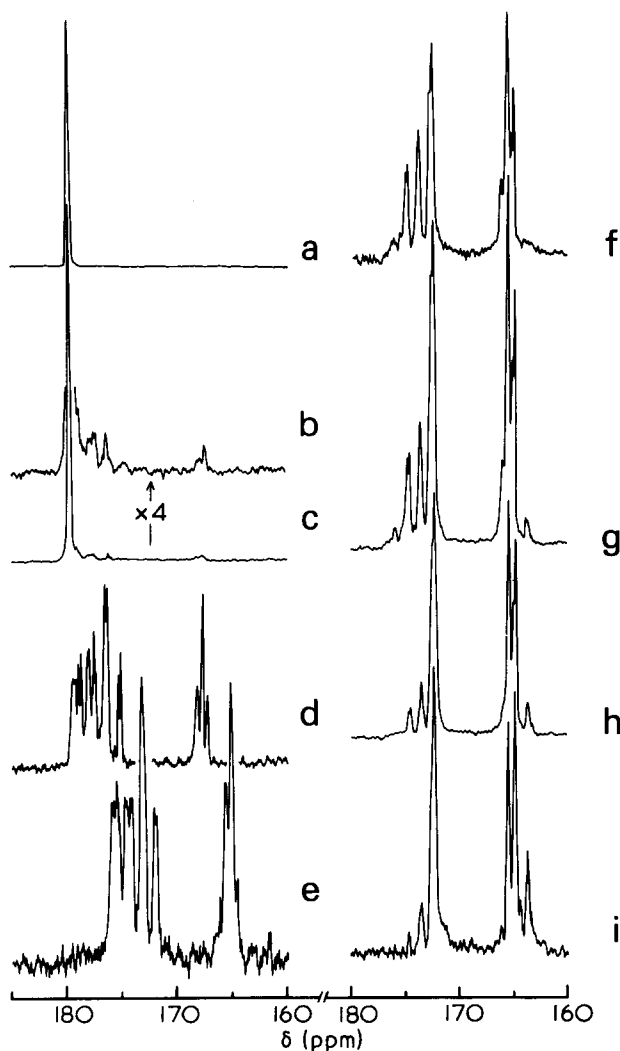


Figure 5 Carbonyl resonances for (a) polyacrylamide, and poly(acrylamide sulphone) prepared at: (c) 60°C; (d) and (e) 40°C; (f) 0°C; (g) -17°C; (h) -45°C; (i) -78°C. Solvents; (a) to (d) D_2O ; (e), (f), (i) DMSO; (g), (h) DMSO- d_6 . Instrumental details are given in the captions to Figures 1, 2 and 3

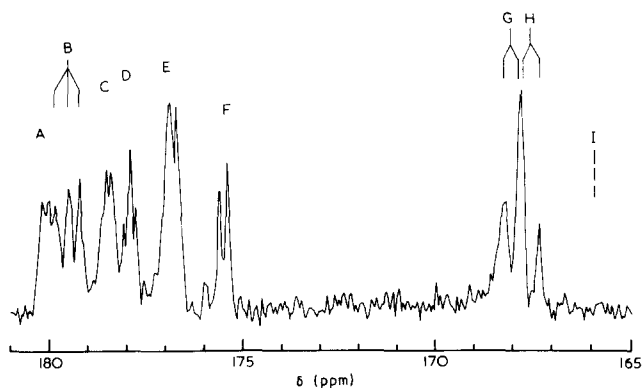


Figure 6 Assignments of the carbonyl resonances to monomer sequence pentads. The spectrum of the copolymer prepared at 40°C is used as an example (instrumental details are given in the caption to Figure 1d). The MSMSM sequence was not observed in this copolymer, but its carbonyl resonance position is indicated relative to the resonances from other sequences. A, MMMMM; B, MMMMS; C, SMMMM; D, SMMMS; E, MMMSM; F, SMMSM; G, MSMMM; H, MSMMS; I, MSMSM

central to our subsequent discussion of the copolymerization mechanism.

The carbonyl resonances from all monomer sequence pentads, except MMMMM, are clearly split into either doublets or triplets. It appears that this splitting must be due to tacticity, since the relative intensities of the multiplets from a given monomer sequence pentad are fairly consistent throughout the composition range. The resonances in the high-field SM region have configurational dyad fine structure, most likely from m_S and r_S placements of the asymmetric centres in the sequence MSM . The doublets from the MSMMM and MSMMS sequences overlap, and give the appearance of a single triplet (Figure 6).

In the low field MM region, m_C and r_C dyad tacticity is observed for the sequences MMMSM and SMMSM. The SMMMS, SMMMM and MMMMS sequences each have at least three resonances, which suggests that the central carbonyl of the MMM part of these sequences is sensitive to triad tacticity. It is noteworthy that this is not the case for the MMMMM sequence in either the homopolymer or the copolymers, so it follows that the presence of at least one sulphone unit in the monomer sequence pentad is a prerequisite for stereosensitivity of the central carbonyl resonance.

Derivation of the monomer sequence distribution

The relative areas of peaks from the various monomer sequences were measured to obtain the monomer sequence distribution. However, in certain cases these areas do not correspond directly to the probability of occurrence of the related polymer structure. For example, if there is a differential NOE between carbons in different sequences, or if the delay time separating $\pi/2$ pulses during data acquisition is not at least three times the longest ^{13}C T_1 value, peak intensities can be distorted.

The former situation arises from the $\alpha(\text{SMM})$ backbone resonance when it is observed in D_2O solution at elevated temperatures. We found that the NOE of this carbon was reduced, owing to exchange of its methine proton with deuterium. The $\alpha(\text{SMM})$ resonance was not used for quantitative purposes under these circumstances.

In principle, the local segmental mobility in the backbone of a copolymer can depend on fairly short range monomer sequence structure. A reduced NOE for carbons

in stiff sequences, compared to those in more flexible sequences, may result. We could not detect any difference in the dynamic behaviour of SMS and SMMS sequences (as monitored by T_1 values) in poly(styrene sulphones)⁴¹, and by analogy we assume the same is true for poly(acrylamide sulphones).

The delay time between pulses was 1.5 sec during data acquisition. During this time, the magnetization of all backbone carbons will be fully restored to equilibrium. This will not be the case for the carbonyls, which have T_1 values greater than 1 sec due to the inefficiency of dipolar relaxation with distant protons (e.g. in PMMA, the carbonyl T_1 is 1.25 sec under similar conditions⁴²). The time required to obtain a reasonable signal-to-noise ratio from our spectra, while allowing complete relaxation of the carbonyl magnetization between pulses, was prohibitive.

We have measured exclusively the backbone ^{13}C resonance areas, which give the monomer sequence triad distribution. The pentad distribution, potentially available from the carbonyl resonance areas, would allow a deeper insight into the copolymerization mechanism. However, for the reasons given, these areas are unreliable.

The unconditional probabilities of finding the five possible monomer sequence triads, and the single acrylamide unit, were derived according to our previous procedure²⁵. The values are given in Table 3. We have deduced from these results the number fractions of SM_nS sequences²⁵, $N_M(n)$, where n is 1, 2 and 3. These values, as well as the probability of finding a sulphone chain unit, $p(\text{S})$, are plotted with respect to copolymerization temperature in Figure 7.

Mechanism of the propagation step

There are two characteristic temperatures for the formation of poly(acrylamide sulphones) from a bulk monomer mixture which contains 60 mol % sulphur dioxide. These can be distinguished in Figure 7. The first is approximately 0°C, above which all alternating SMS sequences are excluded from the copolymers. The second appears to be slightly above 60°C, where the sulphur dioxide content of the polymer extrapolates to zero.

The existence of these temperatures strongly suggests that the monomer sequence distribution is regulated by depropagation steps. These steps compete with normal chain propagation, to an extent determined by temperature, pressure and monomer concentration¹. Temperature was the only significant variable in the present system, and the results will be discussed in terms of its effect.

We refer to a model of the propagation step which was formulated previously for the copolymerization of styrene with sulphur dioxide²⁵:

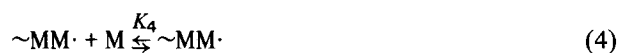


Table 3 Effect of polymerization temperature on the macroscopic composition and the monomer sequence triad distribution in poly (acrylamide sulphones)

Temperature (°C)	Macroscopic composition		Unconditional probabilities of monomer sequence triads				
	$\rho(M)^a$	R^b	$\rho(SMS)$	$\rho(MSM)$	$\rho(MMS)$	$\rho(SMM)$	$\rho(MMM)$
-78	0.663	1.97	0.041	0.337	0.296	0.296	0.031
-45	0.670	2.03	0.027	0.330	0.303	0.303	0.037
-17	0.701	2.34	0.011	0.299	0.288	0.288	0.115
0	0.712	2.47	0.0	0.288	0.288	0.288	0.136
40	0.780	3.54	0.0	0.220	0.220	0.220	0.341
60	0.967	29.3	0.0	0.033	0.033	0.033	0.900

a The unconditional probability of a single acrylamide unit (equivalent to the mole fraction of acrylamide in the copolymer).

b $R = \rho(M)/\rho(S)$

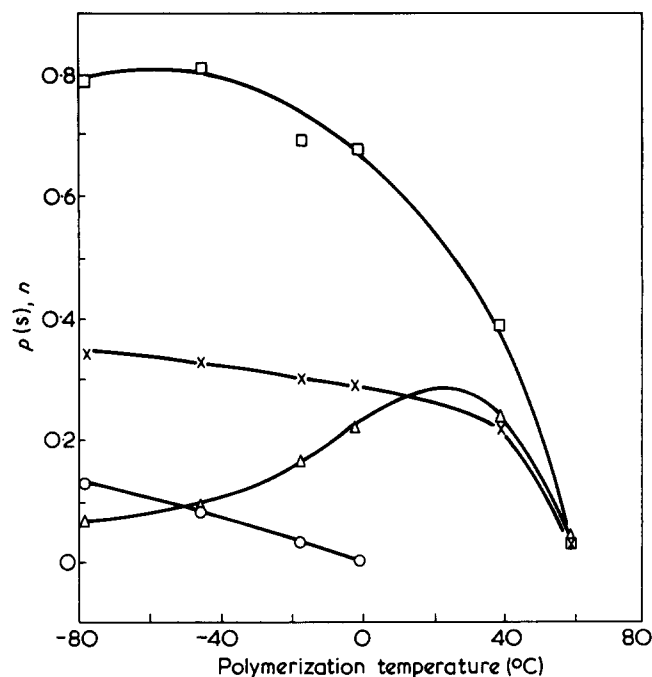


Figure 7 Effect of polymerization temperature on the unconditional probability of a sulphone chain unit, $p(S)$, and the number fraction of SM_nS sequences, with the following n values: \circ , 1; \square , 2; and \triangle , 3; \times , $p(S)$

The equilibrium constant K for each step is equal to the propagation rate constant k_p divided by the depropagation rate constant k_d . These K values decrease with increasing temperature, since the propagation reaction has a lower activation energy than the depropagation reaction.

Steps (1) and (2) are the only ones which can occur when M is a simple olefin, as the homopropagation rate constant for M is zero under the copolymerization conditions. A strictly alternating 1:1 poly(olefin sulphone) is the result¹. In the present case, the rate of homopropagation of acrylamide must be significant even at -78°C , where the value of $N_M(2)$ is considerably greater than $N_M(1)$.

Only those depropagation reactions which involve homolysis of the relatively weak carbon-sulphur bond are probable over the present temperature range. Hence k_d for steps (3) and (4) will be vanishingly small, and these reactions will proceed entirely in the forward direction. We see no reason to expect a penultimate-unit effect on the rate of addition of M , so the propagation rate constants for steps (3) and (4) should be equal.

Several trends can be discerned as the copolymerization temperature is raised. The value of $N_M(1)$ decreases monotonically to zero at about 0°C . Accordingly, the product

K_1K_2 must be less than unity at this temperature. If acrylamide did not homopropagate, 0°C would be a ceiling temperature for polymerization. However, k_p for steps (3) and (4) is finite, and its value will increase according to the usual Arrhenius equation. Chain growth can then continue by the addition of successive acrylamide units.

The cross-propagation step (5) competes with the homopropagation step (4) to limit the average length of acrylamide blocks. However, at sufficiently high temperatures, $p(S)$ is reduced to zero. This trend reflects the concomitant decrease in K_5 to values less than unity above 60°C . In consequence, the average length of acrylamide blocks increases with temperature as the sulphonyl radical becomes more susceptible to depropagation.

The magnitudes of the respective equilibrium constants at a given temperature may be ranked in the following order: $K_1K_2 < K_5 \ll K_3 \approx K_4$. It should be noted that the equilibria represented by equations (1) to (5) may not be established in all cases. For example, steps involving chain transfer or termination, or the addition of monomer, can convert a chain radical which would otherwise depropagate into a stable structure. This makes the two characteristic temperatures somewhat indistinct, in that the values of $N_M(1)$ and $p(S)$ approach zero asymptotically.

We conclude this section with some comments on an apparent contradiction. Firth and Palmer found they could prepare a poly(acrylamide sulphone) at 100°C which contained 11.2 mol % sulphur dioxide¹⁷. The monomer composition was initially 84.7 mol % sulphur dioxide. For a moment mixture which has 60 mol % sulphur dioxide, our data suggest that no polysulphone will be formed above 60°C . This temperature will depend on the monomer concentration just like a regular ceiling temperature¹, and it will be slightly higher for the monomer mixture which is richer in sulphur dioxide.

Even allowing for this difference, it is hard to reconcile the two independent results. However, Firth and Palmer also found that the compositions of their poly(acrylamide sulphones) prepared at 80° and 100°C were inconsistent. According to their published experimental procedure¹⁷, they allowed the polymerization reactor to stand overnight before it was opened, during which time it had cooled to room temperature. It is possible that some copolymerization took place during this period.

Comparison with other systems

The results of this study are very similar to those obtained for poly(vinyl chloride sulphones)³³ and poly(styrene sulphones)²⁵. The monomer sequence distributions in all three systems depend markedly on copolymerization temperature. The absence of SMS sequences in copolymers pre-

pared above certain characteristic temperatures is particularly striking. This temperature is 0°C when M is acrylamide and vinyl chloride, and it is 40°C for styrene.

Two differences are worth noting. Both vinyl chloride and styrene form essentially 1:1 polysulphones ($N_M(1) \approx 1$) at -78°C. Also, at the respective characteristic temperatures where $N_M(1)$ becomes zero in these systems, 2:1 polysulphones are formed with a very regular monomer sequence structure, for which $N_M(2)$ is almost unity. However, poly(acrylamide sulphones) do not have monomer sequence structures which are as regular at comparable temperatures. The differences are attributable mainly to the relatively rapid rates of homopropagation of acrylamide (steps 3 and 4) at these temperatures.

Substituted acrylamides

Only the homopolymer was formed at 25°C when a mixture of 1-methylacrylamide and sulphur dioxide was exposed to ⁶⁰Co gamma radiation⁴³. A similar result has been reported for α -methylstyrene⁴⁴, which homopolymerized under conditions where styrene forms the polysulphone. The failure of these monomers to copolymerize may be attributed to the presence of a second substituent on the α -carbon. The methyl substitution must lower the ceiling temperature for copolymerization substantially.

Rather surprisingly, neither *N,N*-dimethylacrylamide nor *N,N*-diethylacrylamide produced any polymer from mixtures containing 60 mol % sulphur dioxide during gamma irradiation at 0°C. Traces of oily residues were the sole products. We have no obvious explanation for the negative results. It appears that an amide proton may be necessary for the monomer to copolymerize with sulphur dioxide. This proton could stabilize the sulphonyl radical by forming a six-membered cyclic transition state involving a hydrogen bond to the sulphone oxygen atom.

CONCLUSIONS

The binary copolymerizations of sulphur dioxide with unsaturated monomers M of the type CH₂ = CHX result in variable-composition polysulphones, provided M can compete effectively with sulphur dioxide for addition to the carbon-centred radical. This is possible in the cases where X is a chlorine, phenyl or amide substituent, and we have shown here that the sulfonyl radical is much more likely to depropagate when there is a pen-penultimate sulphone unit in the terminal sequence. Depropagation of this sequence relieves the strain arising from steric and electrostatic repulsion between the oxygen atoms on adjacent sulphone units. It results in a particular temperature above which the SMS sequence does not form. This temperature depends on the nature of X.

At present, we are investigating by ¹³C-{¹H} n.m.r. the microstructure of the polysulphones obtained from 2-chloro-1,3-butadiene. Here adjacent sulphone units in SMS sequences are separated by four carbon atoms (discounting 1,2 or 3,4 modes of addition), so there is little reason to expect any difference in the rates of depropagation of \sim SMS \cdot and \sim MMS \cdot terminal sequences. Our results will be presented in a future publication.

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