Polymerization of acetylenic monomer with sulphur dioxide: 2. The microstructure of 1-hexyne, 1-alkenes and sulphur dioxide terpolymers

Pu Peng, Seong-Ju Kim, Yasufumi Tamai and Minoru Matsuda*
Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai 980, Japan

(Received 1 April 1988; revised 7 September 1988; accepted 12 September 1988)

Free radical terpolymerization of 1-hexyne (HY), 1-hexene (HE) (or 1-butene) and sulphur dioxide was studied with respect to the microstructure of the terpolymers by means of nuclear magnetic resonance and infrared and ultraviolet spectroscopies. The configuration of the double bond in the main chain was not affected by the presence of the ES (HE–SO_2) unit, but was always *trans* linkage. A linear correlation between $\nu_{as(S=O)}$ and YS (HY–SO_2) content in the terpolymers was observed. The mechanism of terpolymer formation is discussed.

(Keywords: 1-hexyne; 1-alkene; sulphur dioxide; terpolymer; sequence distribution; nuclear magnetic resonance; infrared)

INTRODUCTION

Although many terpolymers of sulphur dioxide and two kinds of olefins have been made[1], only two papers have dealt with the microstructure of terpolymers. Chambers *et al.*[2] determined the meso/racemic relationship of two chiral centres linked by a sulphonyl group (m_s/r_s) and that of two chiral centres within a 2-butene structure (m_c/r_c) for the terpolymer of sulphur dioxide, 1-butene and 2-butene by ^{13}C nuclear magnetic resonance (n.m.r.). Ito *et al.*[3] distinguished four sequences consisting of two kinds of olefin linked by a sulphonyl group in the terpolymers with ^{13}C labelled olefin monomer.

A study on terpolymerization of sulphur dioxide, alkyne and olefin was first done by Ivin *et al.*[4] for a sulphur dioxide, 1-hexyne and cyclohexene system at $-20°C$. They determined relative monomer reactivity from the terpolymer compositions. In previous work we prepared terpolymers of sulphur dioxide, 1-alkynes and 1-butene with the object of a new type of positive tone electron beam resist[5]. These studies revealed that the reactivity of 1-alkyne monomers to sulphur radicals is lower than that of 1-olefin monomers at $-20°C$[4,5]. However, the relative monomer reactivity at temperatures $> T_c$ (ceiling temperature) and the microstructure of these terpolymers containing 1-alkyne units have not been determined.

In this paper, the 'diad' sequence distribution of the terpolymers (PHYHES) of sulphur dioxide (S), 1-hexyne (HY) and 1-hexene (HE) or 1-butene (BE), YSYS, YSES, ESYS, ESES, and the configuration of C=C double bonds are studied. On the basis of these data, the mechanism of terpolymer formation is discussed.

EXPERIMENTAL

Terpolymerization

Free radical terpolymerization of sulphur dioxide, 1-hexyne (HY) and 1-hexene (HE) or 1-butene (BE) was carried out with 2,2′-azobis-isobutyronitrile (AIBN) at 30, 40 and 50°C in *o*-dichlorobenzene as diluent. The total monomer concentration was kept constant at 6.0 M, and liquid sulphur dioxide was always 70 mol%. Hence the molar ratio of Y and E in the feed was 30 mol% (Y and E stand for alkyne and olefin, respectively).

In each terpolymerization system, 0.2 M of bromotrichloromethane was added to control the molecular weight of the terpolymers smaller than 3×10^4. Liquid sulphur dioxide, HY, HE, BE, AIBN and solvents were purified according to standard methods[5–7].

Characterization

The molecular weight of the terpolymers was measured by gel permeation chromatography on a Toyo Soda HLC-802 UR chromatograph (eluent: THF).

The ^1H n.m.r. spectra of terpolymers were measured using three kinds of instrument in $CDCl_3$ (2% (mg/ml)) with TMS as standard at room temperature: a JEOL-FX90Q for determination of the compositions of PHYHES terpolymers (A–O in *Table 1*); a Bruker CPX-300 for determination of the compositions (P–S in *Table 1*) and assignment of the signals (*Figure 2*) of PHYBES terpolymers; and a JEOL-GX500 *FT* n.m.r. spectrometer for assignment of the signals (*Figure 1*) of PHYHES-50 terpolymers. 22.50 MHz $^{13}C\{^1H\}$ n.m.r. spectra for determination of the configurations of PHYHES-50 and PHYBES-50 terpolymers (*Figures 6* and *7*) were measured with a JEOL-FX90Q *FT* n.m.r. spectrometer in $CDCl_3$ (10–20% (mg/ml)) with TMS at 55°C.

Infrared (i.r.) spectra were measured with a KBr disc (1 wt%) using a JIR-100 *FT*i.r. spectrometer, and electronic absorption spectra were measured with a Cary 14UV spectrometer in dioxane in a 2 mm quartz cell with a 1.6 mm spacer.

---

* To whom correspondence should be addressed

0032–3861/89/040756–06$03.00

Table 1 Radical terpolymerization of 1-hexyne (HY), 1-hexene (HE) and SO_2

Terpolymer no.	In feed HY	In feed HE (mol%)	In feed SO_2	Molecular weight $10^{-3}\bar{M}_w$	Molecular weight $10^{-3}\bar{M}_n$	Molecular weight $\bar{M}_w/\bar{M}_n$	In terpolymer HY + HE (mol%)
PHYHES-50A[a]	25	5	70	43.6	24.3	1.8	51
B	20	10	70	18.7	11.6	1.6	51
C	15	15	70	10.7	7.7	1.4	50
D	10	20	70	8.8	6.3	1.4	50
E	5	25	70	2.9	2.2	1.3	50
PHYHES-40F[a]	25	5	70	56.0	29.0	1.9	49
G	20	10	70	32.1	12.5	2.6	50
H	15	15	70	24.4	10.7	2.3	50
I	10	20	70	12.5	7.4	1.7	49
J	5	25	70	6.4	5.1	1.3	49
PHYHES-30K[a]	25	5	70	59.8	29.0	2.1	50
L	20	10	70	46.2	17.9	2.6	49
M	15	15	70	43.0	18.1	2.4	47
N	10	20	70	38.8	21.0	1.9	50
O	5	25	70	39.6	20.5	1.9	50
PHYBES-50P[b]	20	10	70	24.0	11.1	2.2	50
Q	15	15	70	14.6	6.8	2.1	49
R	10	20	70	6.0	3.8	1.6	49
S	5	25	70	4.2	2.8	1.5	48

[a] For example, PHYHES-50A stands for HY–HE–SO_2 terpolymer obtained at 50°C
[b] HY–BE(1-butene)–SO_2 terpolymer obtained at 50°C

Table 2 Assignment of ^1H n.m.r. spectra of PHYS, PHES and PBES copolymers[a]

Assignment	^1H n.m.r. chemical shifts (ppm) PHYS	PHES	PBES
$-CH_3$	0.96	0.96	1.17
$-CH_2-$ (γ)	1.45	1.55	—
$-CH_2-$ (β)	1.70	1.85	—
$-CH_2-$ (α)	2.86	2.10	2.10
$-CH_2-CHR-$	—	3.04–4.02	3.04–4.02
$-CH{=}CR-$	7.19	—	—

[a] PHYS, PHES and PBES stand for HY–SO_2, HE–SO_2 and BE–SO_2 copolymers, respectively

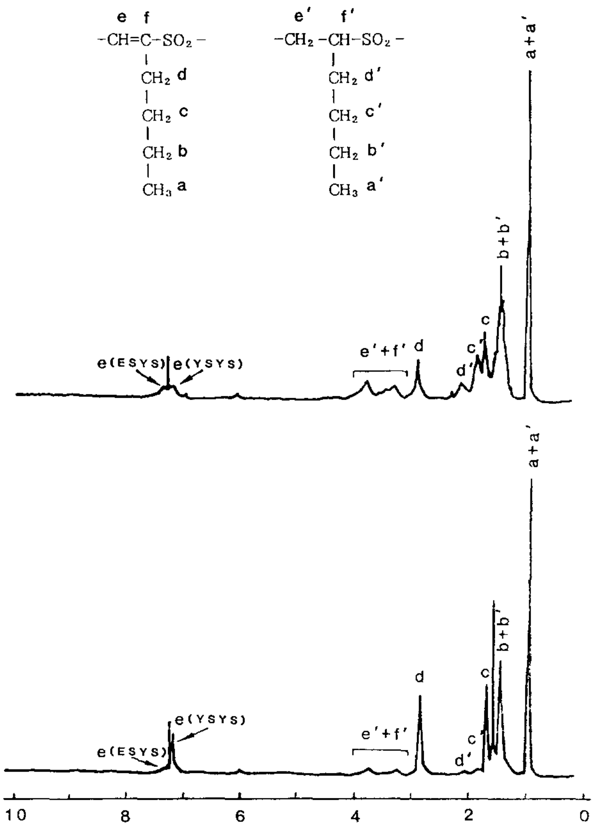


Figure 1 500 MHz ^1H n.m.r. spectra of (above) PHYHES-50D ($I_Y:I_E = 0.55:0.45$) and (below) PHYHES-50B ($I_Y:I_E = 0.85:0.15$)

RESULTS AND DISCUSSION

Terpolymer composition

The mole fractions of HY + HE (or HY + BE) and/or SO_2 in PHYHES (or PHYBES) terpolymers prepared under the conditions shown in *Table 1* were determined by elemental analysis of carbon. Terpolymers consisting of HY + HE (or HY + BE):SO_2 = 1:1 were formed, irrespective of terpolymerization conditions:

$$-(HY-SO_2-)_p-(HE-SO_2)_q-$$

The mole fraction of HY in HY + HE (or HY + BE) (p:q) was determined by ^1H n.m.r. with reference to the assignment of PHYS, PHES and PBES copolymers (*Table 2*). Ratios of HY to HE in PHYHES terpolymers were determined from the integrated intensity ratio of I_Y ($= I_{-CH_2-(HY)}/2$) to I_E($= I_{-CH_2CHR-(HE)}/3$) ($\delta_{-CH_2-(HY)} =$ 2.86 ppm (signal d in *Figure 1*) and $\delta_{-CH_2CHR-(HE)} =$ 3.04–4.02 ppm (signals e' + f' in *Figure 1*)) and those of HY to BE in PHYBES terpolymers were determined from the integrated intensity ratio of I_Y ($= I_{-CH_3(HY)}$) to I_E ($= I_{-CH_3(BE)}$) ($\delta_{-CH_3(HY)} = 0.96$ ppm (signal a in *Figure 2*) and $\delta_{-CH_3(BE)} = 1.17$ ppm (signal a' in *Figure 2*)). The composition curves for PHYHES-50 series and PHYBES-50 series are depicted in *Figure 3*.

A linear correlation between alkyne–SO_2 (YS) units in the terpolymers and the asymmetric stretching vibration frequency of S=O is observed (*Figure 4*); with increasing YS units ($-CH{=}C(C_4H_9)-SO_2-$) in the terpolymers, the $\nu_{as(S=O)}$ shifts to a higher wavenumber region:

$$\text{YS (mol\%)} = 3.64(\nu_{as(S=O)} - 1308)$$

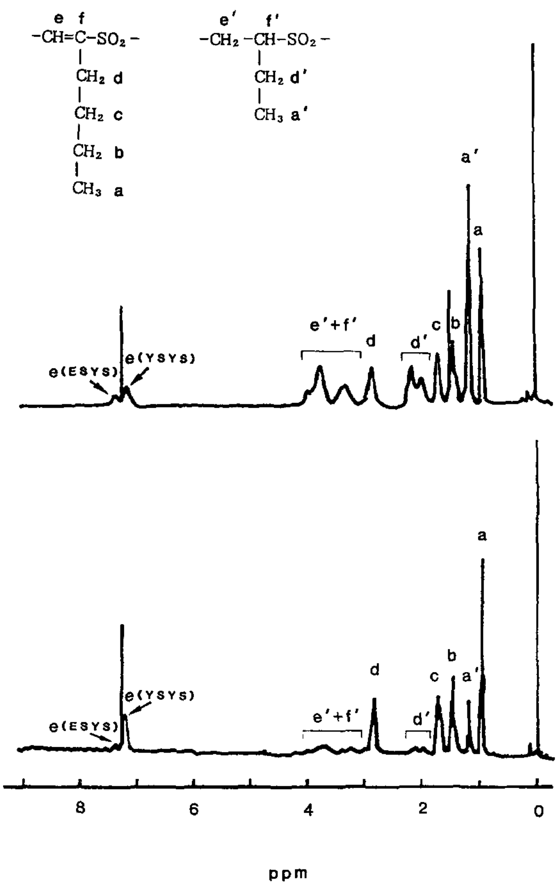


Figure 2 300 MHz ^{1}H n.m.r. spectra of (above) PHYBES-50R (I_Y:I_E = 0.42:0.58) and (below) PHYBES-50P (I_Y:I_E = 0.73:0.27)

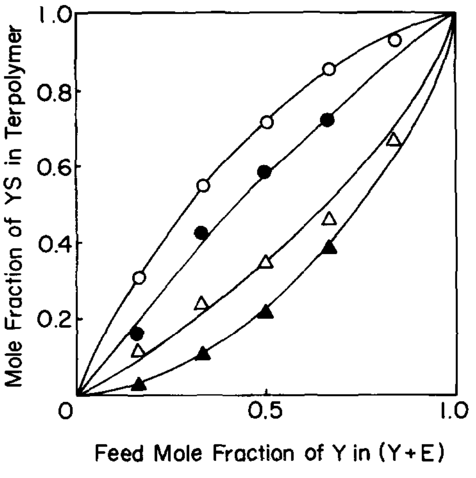


Figure 3 Relationship between feed and terpolymer composition: ○, PHYHES-50; △, PHYHES-40; ▲, PHYHES-30; ●, PHYBES-50. Y, 1-hexyne; E, 1-hexene or 1-butene. YS, $-CH=C(CH_2CH_2CH_2CH_3)-SO_2-$

The lowest stretching frequency of 1308 cm^{-1} was observed with PHES and PBES copolymers of sulphur dioxide and olefin (HE or BE), and the highest stretching frequency of 1335 cm^{-1} was observed with PHYS copolymer of sulphur dioxide and HY. The shift of $\nu_{as(S=O)}$ with the change of neighbouring substituents for many sulphone compounds has been studied extensively[8–10]; a linear relationship between S=O stretching frequencies with many sulphone compounds and bond order (n) of the S=O bond has been reported ($\nu_{(S=O)} = 642n + 95$)[10]. The $\nu_{as(S=O)}$ of 1335 cm^{-1} observed with PHYS corresponds to a bond order of 1.78 on the basis of the linear equation[10]. This may be attributable to the inductive effect of the SO_2 group through the neighbouring olefinic double bond[9]. Contrary to this, for the olefin copolymers (PHES and PBES) in which the double bond is absent the bond order is estimated to be 1.75. Thus, in the terpolymers, it follows that the S=O bond orders in YSYS and ESES sequences are 1.78 and 1.75, respectively, and the bond orders for YSES and ESYS sequences in the terpolymers lie between them.

Sequence distribution

1-Alkyne (Y), 1-olefin (E) and sulphur dioxide (S) do not homopropagate under our terpolymerization conditions, and radical polymerizations of Y with S and E with S always give alternating copolymers, indicating that YYS, YES and EES sequences in the copolymers due to the penultimate unit effect are negligibly small. This means that YY, EE, and SS sequences do not exist in the terpolymer chain. Consequently, the 'diad' sequence distribution of the terpolymers, i.e. YSYS, YSES, ESYS and ESES, was determined from the ^{1}H n.m.r. spectra as shown in *Figures 1* and *2*. The ^{1}H n.m.r. signal at 7.19 ppm corresponds to that appearing with PHYS copolymer, and on increasing the HE (or BE) unit the intensity of the signal at 7.40 ppm increased. Therefore, the former signal is assigned to the YSYS 'diad' sequence and the latter to ESYS 'diad' sequence:

$$-CH=CR-SO_2-CH=CR-SO_2-$$
(YSYS)

$$-CH_2-CHR-SO_2-CH=CR-SO_2-$$
(ESYS)

Denoting the unconditional probability of occurrence of the 'diad' sequences by p(YSYS), p(YSES), p(ESYS) and p(ESES), the following relation is applied:

$$p(\text{YSYS}) + p(\text{YSES}) + p(\text{ESYS}) + p(\text{ESES}) = 1 \quad (1)$$

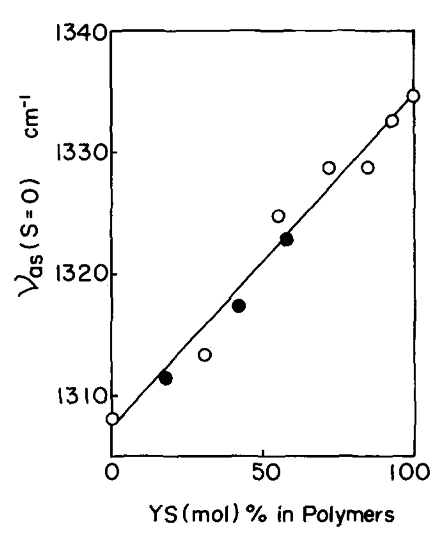


Figure 4 Relationship between S=O asymmetric stretching vibration frequencies and composition of terpolymers. ○, PHYHES-50; ●, PHYBES-50. YS, $-CH=C(CH_2CH_2CH_2CH_3)-SO_2-$

Table 3 Sequence distribution and run number of PHYHES and PHYBES terpolymers

Terpolymer	p (YSYS)	$\frac{1}{2}[p\ (YSES)+p\ (ESYS)]$[a]	p (ESES)	Run number
PHYHES-50A	0.862	0.069	0.000	14
B	0.709	0.143	0.005	27
C	0.533	0.184	0.099	39
D	0.351	0.197	0.255	40
E	0.118	0.192	0.498	38
PHYHES-40F	0.511	0.154	0.181	31
G	0.269	0.189	0.353	38
H	0.186	0.160	0.494	32
I	0.110	0.127	0.636	25
J	0.028	0.084	0.804	17
PHYHES-30K	0.452	0.212	0.124	42
L	0.176	0.209	0.406	42
M	0.066	0.151	0.632	30
N	0.020	0.082	0.816	16
O	0.000	0.029	0.942	6
PHYBES-50P	0.505	0.191	0.113	38
Q	0.321	0.196	0.287	39
R	0.208	0.180	0.432	36
S	0.040	0.103	0.754	20

[a] p (ESYS) = P (YSES)

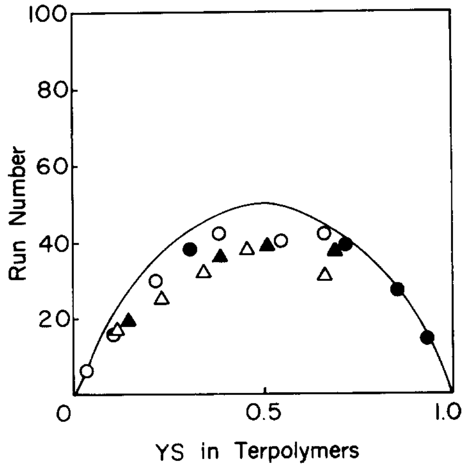


Figure 5 Relationship between run number and composition of terpolymers. ○, PHYHES-50; △, PHYHES-40; ▲, PHYHES-30; ●, PHYBES-50. YS, $-CH{=}C(CH_2CH_2CH_2CH_3)-SO_2-$

From a basic theory of statistical analysis of the monomer sequence distribution[11]

$$\begin{aligned} p(\mathrm{YSES}) &= p(\mathrm{ESYS}) \\ p(\mathrm{ESES}) &= 1 - p(\mathrm{YSYS}) - 2p(\mathrm{YSES}) \end{aligned} \tag{2}$$

Therefore, the unconditional probabilities of occurrence of the four possible 'diad' sequences can be derived as listed in *Table 3* from the assignments of ^1H n.m.r. signals[12].

The run number R was calculated from the following equation:

$$R = 100[p(\mathrm{YSES}) + p(\mathrm{ESYS})] \tag{3}$$

The R values of PHYHES and PHYBES terpolymers are listed in *Table 3*, and are plotted against the contents of YS in the terpolymers in *Figure 5*. The calculated R values deviate from a line drawn for a copolymer with random diad sequence distribution. Thus the terpolymers have a slight block tendency.

Note in *Figure 5* that the 'diad' sequence distribution is not changed by terpolymerization temperature when the terpolymer compositions are similar.

Configuration

It has been determined, by ^{13}C n.m.r. chemical shift of the side chain carbons[13], that the C=C double bond in the SO_2–HY–SO_2 unit in PHYS copolymer is a linkage of E (*trans*) configuration. The ^{13}C n.m.r. spectra are shown in *Figure 6* for PHYHES and *Figure 7* for PHYBES terpolymers. The signals due to the side chain carbons of Y units in both the terpolymers are very similar to those in PHYS copolymer and do not change with sequence distribution. That is, each signal attributable to four side chain carbon atoms does not split. The chemical shift of allylic $-CH_2-$ (signal d in *Figures 6* and *7*) is obviously different between E and Z forms for a number of C=C bond-containing compounds and polymers[13–16]. For example, it has been reported that for dialkyl substituted ethylenes $\delta_{-CH_2-(E)} - \delta_{-CH_2-(Z)}$ (the difference in ^{13}C n.m.r. chemical shift of allylic methylenes in the E and Z forms) is about 5 ppm[14], and that for 1-alkyne homopolymers, $\delta_{-CH_2-(Z)} - \delta_{-CH_2-(E)}$, is about 2 ppm[15]*. Therefore, the signals of side chain carbons are safely assigned to E configuration, i.e. the C=C configuration is not changed by introducing the ES unit into the polymer chain.

Mechanism of terpolymer formation

Participation of a monomer charge transfer complex formed between 1-alkyne or 1-olefin and sulphur dioxide in the propagation step of the terpolymerization does not need to be considered, on the basis of the results obtained with the sulphur dioxide–styrene radical copolymerization[6–7].

It has been revealed from the terpolymer compositions that the reactivity of 1-alkyne radical to sulphur dioxide is lower than that of 1-olefin radical at −20°C[4,5], at

---

* The difference in the ^{13}C n.m.r. chemical shift between E and Z forms has been explained by the γ-effect[16]. In α,β-disubstituted olefins ($X-CH{=}CH-(\alpha)CH_2-(CH_2)_x-CH_3$), the allylic carbon atom ($\alpha-CH_2-$) is shielded by X when X is located on the same side with respect to $\alpha-CH_2-$ (Z form). On the other hand, in the E form $\alpha-CH_2-$ is not shielded by X, leading to $\delta_{-CH_2-(Z)} < \delta_{-CH_2-(E)}$. Similarly, in 1-alkyne homopolymers ($\sim CH{=}C(-(\alpha)CH_2-(CH_2)_x-CH_3)\sim$), $\alpha-CH_2-$ is shielded by the polymer main chain (E form), but not in the Z form, leading to $\delta_{-CH_2-(E)} < \delta_{-CH_2-(Z)}$

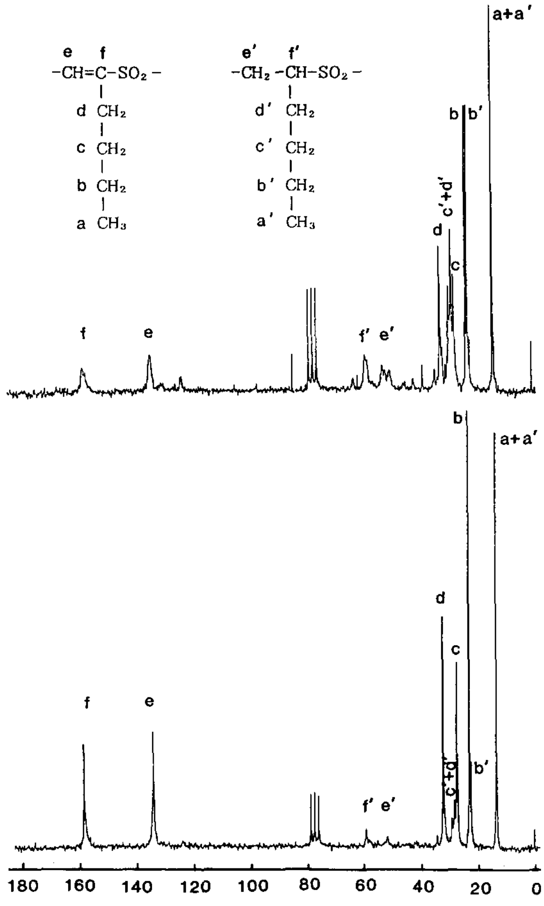


Figure 6 22.50 MHz $^{13}C\{^1H\}$ n.m.r. spectra of (above) PHYHES-50D and (below) PHYHES-50B

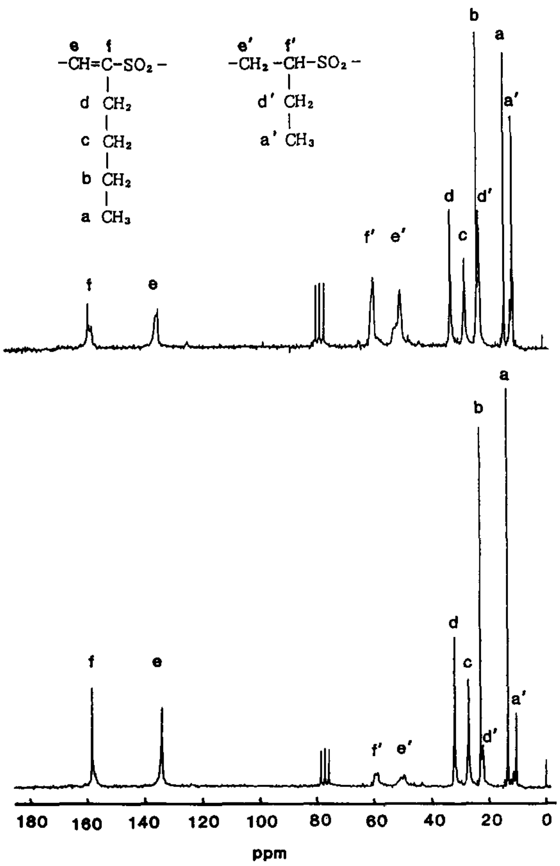
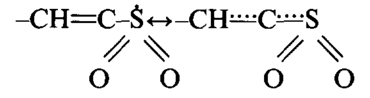


Figure 7 22.50 MHz $^{13}C\{^1H\}$ n.m.r. spectra of (above) PHYBES-50R and (below) PHYBES-50P

which temperature the depropagation does not occur. The lower reactivity of 1-alkyne suggests that the carbon centred vinyl radical (sp^2 σ-radical)[17,18] is more stabilized than alkane radical.

At temperatures (30–50°C) studied in this paper, depropagation must be taken into consideration for the terpolymer formation processes. In particular, the growing radical endings involving 1-olefins ($\sim CH_2\text{-}CHR\text{-}\dot{S}O_2$ and $\sim SO_2\text{-}CH_2\text{-}\dot{C}HR$) may depropagate under the terpolymerization conditions ($T_c = 47°C$ for HE–sulphur dioxide and 51°C for BE–sulphur dioxide copolymerization at $[HE] = [BE] = 1.8$ and $[SO_2] = 4.2$ M; T_c estimated using thermodynamic data[19]). As for a 1-alkyne–sulphur dioxide copolymerization system, we have determined the T_c for a 1-octyne (OY)–sulphur dioxide radical copolymerization[20], and estimated $T_c = 156°C$ at $[OY] = 1.8$ and $[SO_2] = 4.2$ M. A higher T_c for the OY–sulphur dioxide system than the T_c for 1-olefin–sulphur dioxide systems again suggests that $\sim SO_2\text{-}CH{=}\dot{C}R$ radicals are more stabilized than $\sim SO_2\text{-}CH_2\text{-}\dot{C}HR$. Furthermore, when we pay attention to the sulphonyl radical endings the $\sim CH{=}CR\text{-}\dot{S}O_2$ may be more stabilized than $\sim CH_2\text{-}CHR\text{-}\dot{S}O_2$ radicals, since in the former an electron may spread over a penultimate double bond owing to conjugation:



$$-CH{=}C\text{-}\underset{O\;\;O}{\dot{S}} \leftrightarrow -CH{\cdots}C{\cdots}\underset{O\;\;O}{S} \qquad (4)$$

The bathochromic shift of ultraviolet absorption of PHYS, PHYHES and PHYBES relative to the olefins and even divinyl sulphone is indicative of such electron delocalization[21–23].

Although T_c for HY–sulphur dioxide copolymerization was not determined, the length of the alkyl group of HY is similar to that of OY, and the yield of the copolymerizations of HY and OY with sulphur dioxide was very similar under the same copolymerization conditions[20]. Thus it is most likely that T_c of HY–sulphur dioxide copolymerization is close to that of OY–sulphur dioxide copolymerization.

On the basis of the comparison of T_c of OY, HE and BE, the change in the terpolymer composition with terpolymerization temperature shown in *Figure 3* could be explained as follows. When the terpolymerization temperature is close to the T_c of the HE–sulphur dioxide pair, the mole fraction of YS units in the terpolymers becomes higher than that of ES units due to the difference in the ease of depropagation. On the other hand, the mole fraction of ES units is higher than that of YS units in the terpolymers at 30°C, which is well below the T_c of the HE–sulphur dioxide pair.

REFERENCES

1 Sandler, S. R. and Karo, W. 'Polymer Synthesis', Vol. 3, Academic Press, New York, 1980

2 Chambers, S. A. and Fawcett, A. H. *Macromolecules* 1985, **18**, 1710

3 Ito, H., Pederson, L. A., MacDonald, S. A., Cheng, Y. Y., Lyerla, J. R. and Wilson, C. G. 'Preprints of Regional Technical Conference, Photopolymers: Principles, processes and materials', 1985, p. 127

4 Ivin, K. J. and Walker, N. A. *J. Polym. Sci. A-1* 1971, **9**, 2371

5 Matsuda, M., Kim, S.-J., Peng, P., Kobayashi, Y. and Yokobori, K. 'Preprints of 2nd SPSJ International Polymer Conference', The Society of Polymer Science, Japan, 1986, p. 157

6 Matsuda, M., Iino, M., Hirayama, T. and Miyashita, T. *Macromolecules* 1973, **5**, 240

7 Bae, H.-J., Miyashita, T., Iino, M. and Matsuda, M. *Macromolecules* 1988, **21**, 26

8 Gillespie, R. J. and Robinson, E. A. *Can. J. Chem.* 1963, **41**, 2074

9 Bellamy, L. J. and Williams, R. L. *J. Chem. Soc.* 1957, 863

10 Szmant, H. H. 'Sulfur in Organic and Inorganic Chemistry', Vol. I (Ed. A. Senning), Marcel Dekker, New York, 1970

11 Ito, K. and Yashita, Y. *J. Polym. Sci. A-1* 1965, **3**, 2165

12 Peng, P., Kim, S.-J., Tamai, Y. and Matsuda, M. 'Preprints of Chem. Soc. Jpn Tohoku Division Symposium', Morioka, 1986, p. 4P220

13 Peng, P., Tamai, Y. and Matsuda, M. 'Preprints of 54th Annual Meeting of Chem. Soc. Jpn', Tokyo, 1987, p. 4IVD34

14 de Haan, J. W. and van de Ven, L. J. M. *Org. Magn. Resonance* 1973, **5**, 147

15 Wazzer, I. and Tsonis, C. P. *Polymer Commun.* 1986, **27**, 145

16 Bovey, F. A. and Cais, R. E. 'Carbon-13 NMR in Polymer Science', *ACS Symp. Ser.* 1979, **103**, 1

17 David, G. and Ingold, K. U. *Acc. Chem. Res.* 1976, **9**, 13

18 Ito, O., Omori, R. and Matsuda, M. *J. Am. Chem. Soc.* 1982, **104**, 3934

19 Cook, R. E., Dainton, F. S. and Ivin, K. J. *J. Polym. Sci.* 1958, **29**, 579

20 Kim, S.-J. and Matsuda, M. *J. Polym. Sci., Polym. Chem. Edn* submitted for publication

21 Waight, E. S. *J. Chem. Soc.* 1952, 2440

22 Koch, H. P. and Moffitt, W. E. *Trans. Faraday Soc.* 1951, **47**, 7

23 Peng, P., Tamai, Y. and Matsuda, M. unpublished results