

## Isomerization in Olefin Formation in Radiation Degradation of Poly(Olefin Sulphone)s

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### SUMMARY

Gamma irradiation of poly(3-methyl-1-butene sulphone) in the solid state at 20°C produced a mixture of isomers, *viz.* 3-methyl-1-butene (61%), 2-methyl-1-butene (2%) and 2-methyl-2-butene (37%). Similarly, poly(1-butene sulphone) yielded 1-butene (65%) and 2-butene (35%). A hydride shift reaction in a polymer cation produced by main-chain scission is proposed to account for the isomerization.

### INTRODUCTION

Irradiation of poly(1-butene sulphone) and poly(1-hexene sulphone) by gamma rays and electrons was shown by BROWN and O'DONNELL, (1970,1972) to lead to main-chain scission with a high G(S) value (*ca.* 11) at ambient temperature. Substantial yields of SO<sub>2</sub> and olefin were also obtained, which increased rapidly with increasing temperature near the ceiling temperature. Simple depolymerization should produce equal yields of sulphur dioxide and the parent olefin according to eqn.1.



However, the ratio G(SO<sub>2</sub>)/G(olefin) was found to be considerably greater than one, although it decreased with increasing irradiation temperature. BOWDEN (1974) has also found SO<sub>2</sub> to be eliminated at a faster rate than olefin during the electron irradiation of thin films of poly(2-methyl-1-pentene sulphone).

We have confirmed that G(SO<sub>2</sub>)/G(olefin) is greater than one for four poly(olefin sulphone)s subjected to gamma irradiation in the solid state at 20°C. Moreover we have found that poly(1-butene

sulphone) and poly(3-methyl-1-butene sulphone) produce isomers of the parent olefin. The implications of this observation for the mechanism of the radiation degradation are considered.

#### EXPERIMENTAL

Poly(propene sulphone), PPS, poly(1-butene sulphone), PBS, poly(3-methyl-1-butene sulphone), P3MBS, and poly(1-hexene sulphone), PHS, were prepared from equimolar, liquid mixtures of dried, distilled SO<sub>2</sub> and the appropriate olefin at -78°C (PHS and P3MBS at 0°C) with tert-butyl hydroperoxide initiator according to the technique of CAIS and O'DONNELL (1976). Samples of dried, powdered polymer were sealed under vacuum in miniature glass ampoules and irradiated at 25°C with <sup>60</sup>Co γ-rays at 0.3 Mrad/hr to a total dose of 6-8 Mrad. The volatile radiolysis products were analysed by gas chromatography using the method developed by BOWMER and O'DONNELL (1977).

#### RESULTS AND DISCUSSION

The G values for olefin production resulting from γ-irradiation of the four poly(olefin sulphone)s are shown in Table 1. It is clear that for PBS and P3MBS there has been substantial isomerization during the olefin formation. The total yields for PBS are in accord with our previous observations of the temperature dependence (BROWN and O'DONNELL, 1972).

TABLE 1

Yields of olefins from the γ-radiolysis of poly(olefin sulphone)s at 20°C.

Polysulphone	T <sub>c</sub> (°C) <sup>a</sup>	Radiolysis Product	G value
PPS	90	propene	2.7
PBS	64	1-butene 2-butene	2.4 1.3
PHS	60	1-hexene	19.2
P3MBS	36	3-methyl-1-butene 2-methyl-1-butene 2-methyl-2-butene	4.8 0.2 2.9

<sup>a</sup> From COOK, DAINTON and IVIN (1958).

The isomerization was not observed in our previous study of PBS (BROWN and O'DONNELL, 1970,1972) on account of the lower resolution of the GC columns and the similarity of the mass spectra of the alkenes. In the present work the effluent from the gas chromatograph after the TC detector was bubbled through  $\text{CCl}_4$  in an NMR tube for each product peak and the  $^1\text{H}$  NMR spectrum obtained. 2-Butene and 1-butene were unambiguously identified from PBS. Moreover, the proportions of cis and trans isomers of 2-butene were found to be *ca.* 50:50 from the doublets at 1.62 and 1.58 ppm respectively. This indicates clearly that thermodynamic equilibrium has not been achieved, since the *trans* isomer is favoured by *ca.* 4 kJ/mol from the enthalpies of hydrogenation (HINE, 1962), corresponding to a cis:trans ratio of 15:85. The isomers from P3MBS were identified by the same technique, combined with mass spectra.

The total olefin yield and the isomerization increased with increasing irradiation temperature from 0 to 150°C as shown in Table 2.

TABLE 2

Temperature dependence of isomerization of olefin formation from the  $\gamma$ -radiolysis of P3MBS.

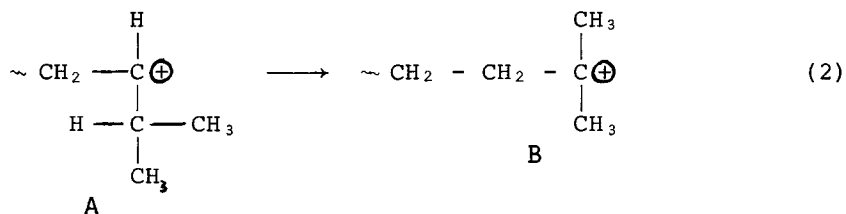
Product	G values for radiolysis at			
	0°C	50°C	75°C	150°C
3-methyl-1-butene	3.6	22.0	68.4	90
2-methyl-1-butene	0.25	1.2	4.6	50
2-methyl-2-butene	2.3	15.7	58.4	450

The first question which arises is whether isomerization has occurred during the polymerization, so that the polymer contains a mixture of structural units. This would not be expected since BACSKAI *et al.* (1969) using  $^1\text{H}$  NMR and FAWCETT *et al.* (1977) using  $^{13}\text{C}$  NMR have shown for a wide variety of poly(olefin sulphone)s that each polymer contains only one type of unit. We have also confirmed the absence of isomerization in our polymers by NMR (except for P3MBS which is insoluble). The second question which arises is whether the isomerization occurs by a rearrangement of (1) the terminal alkyl species at the position of main-chain scission or (2) the free olefin, i.e. after depropagation. If the free olefin undergoes isomerization, the reaction must proceed via an active, intermediate species. Concurrently with isomerization

there should be dimerization and some oligomerization to form higher alkanes and alkenes. Thus, studies of the radiolysis of alkenes (SPINKS and WOODS, 1976) have shown that the yields of dimeric and larger molecules are greatly increased relative to the radiolysis of alkanes. However, in the present work the yields of dimers were quite small ( $G = 0.15$  for PBS and P3MBS), from which we conclude that isomerization must proceed predominantly in alkyl units at chain ends.

The third question is whether the isomerization reaction occurs through a free radical or cationic intermediate. The literature evidence on the relative reactivity of carbonium ions and free radicals indicates that the carbonium ions undergo far more facile isomerization. Thus, BACSKAI (1967) has shown that the free radical polymerization of optically active 3-methyl-1-pentene with  $SO_2$  gives the alternating polysulphone without loss of activity whereas cationic homopolymerization of the olefin gives a polyolefin without optical activity.

Isomerization of carbonium ion polymer chain ends is well established in the cationic polymerization of various olefins. In particular, it has been shown (KENNEDY and JOHNSTON, 1975) that structural rearrangement of 3-methyl-1-butene occurs to form the tertiary carbonium ion, and this has been postulated to occur via a 1,2 hydride shift according to eqn.2,



The polymerization continues and the polymer contains a proportion of structural units of type B as well as the normal units of type A. In this case no depropagation is involved.

Rearrangement according to eqn.2 and depropagation according to eqn.3 of the olefinic residue in P3MBS by some novel mechanism could account for the production of 2-methyl-2-butene and 2-methyl-1-butene.



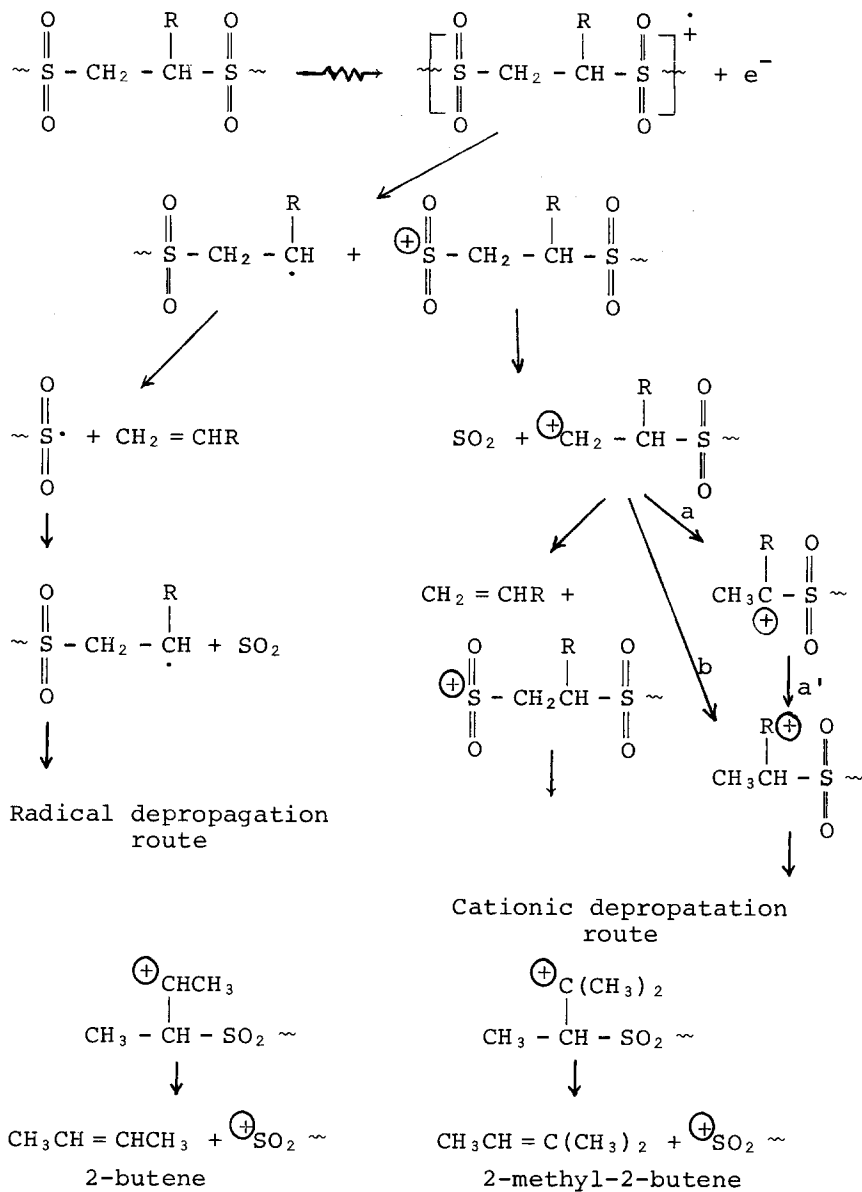


FIGURE 1: Proposed mechanism for the radiolysis and isomerization of P3MBS and PBS.

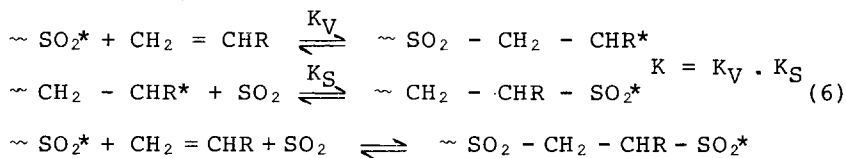
carbonium ion to give the more favourable secondary or tertiary species from which 2-butene or 2-methyl-2-butene can arise (FRY and KARABATSOS, 1970).

"Original" olefin ( $\text{CH}_2 = \text{CHR}$ ) arises through both the radical and cationic depropagation routes, but competitively with isomerized olefin in the latter case.

Supporting evidence for a carbonium ion mechanism for isomerization also comes from the radiolysis of alkenes where the dimerization and oligomerization proceed predominantly by non-radical mechanisms; for example more than 90% of the dimer from the irradiation of liquid hexene is unaffected by radical scavengers, and the reaction has been shown to involve carbonium ions. Similarly, AYSCOUGH and EVANS (1964) have concluded from ESR studies on olefins irradiated at low temperatures that straight-chain terminal olefins react by carbonium ion-molecule reactions. We also have obtained some preliminary results which indicate that cationic scavengers suppress the isomerization; these will be reported in a subsequent paper.

The difference between PBS and PHS is surprising; in the latter case no significant isomerization was observed. Also, note from Table 1 that PHS has an exceptionally high G value for olefin production indicating some special phenomenon. These observations must be related to the high rate of vapour development of PHS relative to PBS found by BOWDEN and THOMPSON (1973) using a technique of irradiation of thin films under vacuum.

A possible interpretation lies in the relative values of the two equilibrium constants involved in the depropagation.



If  $K_V$  is small then depropagation of the olefin could occur before isomerization can occur. The ceiling temperature is directly related to the overall equilibrium constant  $K$ , but the individual values of  $K_V$  and  $K_S$  may be quite different for olefins with similar values of  $K$  (and hence similar  $T_C$ ).

## CONCLUSIONS

We have shown that substantial isomerization occurs in the formation of olefin during the  $\gamma$ -radiolysis of PBS and P3MBS. The most probable mechanism is via rearrangement of the carbonium ion produced on an olefin unit in the polymer by C-S scission in the main chain.

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