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CHARACTERIZATION OF ELECTROINITIATED AND RADIATION POLYMERIZED POLY(BUTADIENE SULFONE)

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ABSTRACT

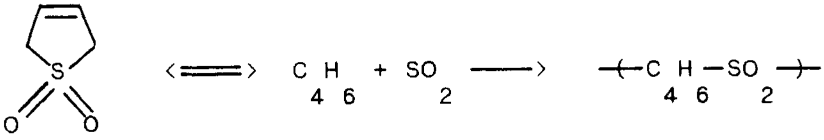
Polymerization of butadiene sulfone was accomplished by using two different methods. The first method involves electrochemical polymerization of the monomer using the constant potential electrolysis technique. Oxidation of the monomer under nitrogen atmosphere in an acetonitrile–tetrabutylammonium tetrafluoroborate system yields brown, tarry polymers. On the other hand, the second initiation method, which was radiation polymerization, yields white, powdery polymers. Structural analyses of the two polymers by various spectroscopic methods suggest a structure consisting of two different units in different proportions.

INTRODUCTION

The formation of an alternating copolymer of butadiene and sulfur dioxide (I) has been reported [1, 2].

$$C_4H_6 + SO_2 \longrightarrow -\!\!(C_4H_6-SO_2)\!\!- \quad \text{(I)}$$

The same product was also obtained by Goethals [3] in 1967 from butadiene sulfone (II, BdS) in bulk, initiated thermally by azobisisobutyronitrile (AIBN) at 100-125°C. It was suggested that BdS first decomposes to butadiene and sulfur dioxide which then copolymerize [3].



(II) (I)

No polymer was obtained in benzene solution, with AIBN, at temperatures below 75°C. Conversion at 100°C was 4%, which compares unfavorably with the 70% obtained by polymerization of an equivalent mixture of butadiene and sulfur dioxide [1, 2]. Attempts at cationic or anionic initiation of the polymerization of BdS were unsuccessful [3]. Minoura et al. [4] were unsuccessful in obtaining polymers from BdS initiated by AIBN, $(n\text{-Bu})_3B$, BuLi, BF_3, $AlEt_3$-$TiCl_4$ or by γ-irradiation at temperatures below 70°C. Low yields (1.0-7.7%) were obtained in the temperature range 80-140°C in benzene-AIBN even after long reaction times (300 h).

The electrochemical copolymerization of butadiene and sulfur dioxide was accomplished by Delamar et al. [5]. Butadiene, in liquid sulfur dioxide with benzyltrimethylammonium perchlorate as electrolyte, was oxidized at +2.8 V vs Ag/AgCl. Platinum or vitreous C anodes were used, and the polymer precipitated as a white powder during electrolysis; it was insoluble in common organic solvents. It was suggested that the copolymerization was initiated indirectly by $ClO_4^{\cdot}$ radicals. The proposed structure was the same as that described in previous studies [1-4].

We previously reported the synthesis of poly(butadiene sulfone), PBdS, by two different methods using BdS as the monomer [6]. The first method involved direct initiation of polymerization by constant potential electrolysis. Brown-colored polymers soluble only in dimethylformamide and trifluoroacetic acid were synthesized. High conversions were obtained within reasonable polymerization times. Radiation polymerization was used as the second technique for the polymerization of BdS. The experiments were performed at room temperature in bulk. White, powdery polymers were obtained which had similar solubility characteristics as those synthesized electrochemically.

In the present work the structural differences between the polymers obtained by electrolysis and irradiation are reported by utilizing FTIR, ^{1}H-NMR, 2D^{1}H COSY, positive ion mass and UV spectroscopic methods, and gel permeation chromatography.

EXPERIMENTAL

Materials

The purification of acetonitrile and tetrabutylammonium tetrafluoroborate are described elsewhere [7]. Butadiene sulfone (Aldrich Chemical Co.) was recrystallized from methanol. Chloroform and hydroquinone were used without further purification. Dimethylformamide, which was used as the solvent in molecular weight determinations, was purified by the standard method.

Instrumentation

FTIR spectra of polymers were measured as dispersed in KBr disks by using a Perkin-Elmer 1710 Model FTIR. Evolved gases from thermal degradation of polymers (in the temperature range 30-320°C) were analyzed with a Finnigan MAT 3000 Mass Spectrometer using 70 eV electron impact ionization. Details of evolved gas analysis are given elsewhere [8].

^{1}H-NMR spectra of polymers dissolved in DMF were measured at 250 MHz by using a Bruker-type AM 250 spectrometer.

A Perkin-Elmer type 552 spectrophotometer was used for the detection of UV absorption peaks of polymers dissolved in DMF.

Molecular weight determinations of the polymers were performed by a Knauer HPLC equipped with a 10^3 Å GPC column.

Electroinitiated Polymerization

Synthesis of PBdS was accomplished in an H-type cell by using an acetonitrile–tetrabutylammonium tetrafluoroborate solvent-supporting electrolyte system. The technique involved was constant potential electrolysis. Working and counterelectrodes were platinum (1 in.^{2}) whereas the reference electrode was Ag/Ag^+ (0.01 *M*). Polymerizations were conducted under nitrogen atmosphere. Experiments were performed with various concentrations ranging from 1.7×10^{-3} to 2.0×10^{-2} *M* by applying +2.70, +3.00, and +3.25 V (vs Ag/Ag^+). The polymers were precipitated in chloroform, filtered, and dried in vacuum at 50°C.

Radiation-Induced Polymerization

For irradiation polymerization, two Co-60 γ-ray cells were used with dose rates of 0.063 and 0.5 Mrd/h. Polymerization was accomplished in bulk and in the absence of air, and the products were isolated by precipitating in chloroform, filtering, and drying in vacuum at 50°C.

RESULTS AND DISCUSSION

Electroinitiated polymerization of BdS has yielded brown, tarry polymers from the solution and a very thin brown polymer film from the anode surface. On the other hand, white powdery polymers were obtained from γ-initiated polymerization. High conversions were obtained within a few hours in the case of electroinitiated polymerization. However, much longer irradiation times were required in the case of radiation-induced polymerization as seen in Table 1. 60% conversion was obtained within 115 min of electrolysis. At a low dose rate (0.063 Mrd/h), only 39.4% polymer was reached at the end of 210 days of irradiation. When the radiation dose rate was increased to 0.5 Mrd/h, 42 days of irradiation was required to obtain 66.2% polymer.

A probable structure for the PBdS may be either structure A or B or a mixture of both. Since the appearance of polymers obtained by electro

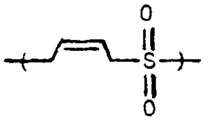
TABLE 1. Percent Conversion Obtained by Radiation-Induced and Electroinitiated Polymerization of Butadiene Sulfone

Radiation-induced polymerization[a]				Electroinitiated polymerization[b]	
Dose rate: 0.063 Mrd/h		Dose rate: 0.50 Mrd/h		$E_{pol} = 3.0$ V vs Ag/Ag^+	
Time, days	% Conversion	Time, days	% Conversion	Time, min	% Conversion
60	5.0	7	16.0	5	6.5
150	17.2	14	19.7	15	18.7
180	29.0	22	32.7	30	31.8
210	39.4	42	66.2	115	60.0

[a] In bulk at room temperature.

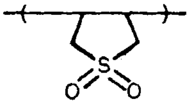
[b] $[M]_0 = 1.7 \times 10^{-3}$ *M* in acetonitrile at room temperature.

and γ-initiation were different, it is suggested that they are composed of different proportions of these units (A and B).



(A)

and



(B)

The FTIR spectra of butadiene sulfone (BdS) and the polymers obtained by γ-irradiation (GPBdS) and electroinitiation (EPBdS) are shown in Fig. 1. Besides the interferences from water in the 3500–3000 and 1700–1600 cm^{-1} regions, all three spectra have common features as well as some differences. However, not enough clues are present to aid structural elucidation of the polymers obtained by the two methods.

Analysis of the evolved gases during the pyrolysis of polymers can be used for structural elucidation [8–12]. It is known that at temperatures above 80°C, butadiene sulfone decomposes to yield SO_2 and butadiene. In fact, butadiene is commercially produced by this method. Similarly,

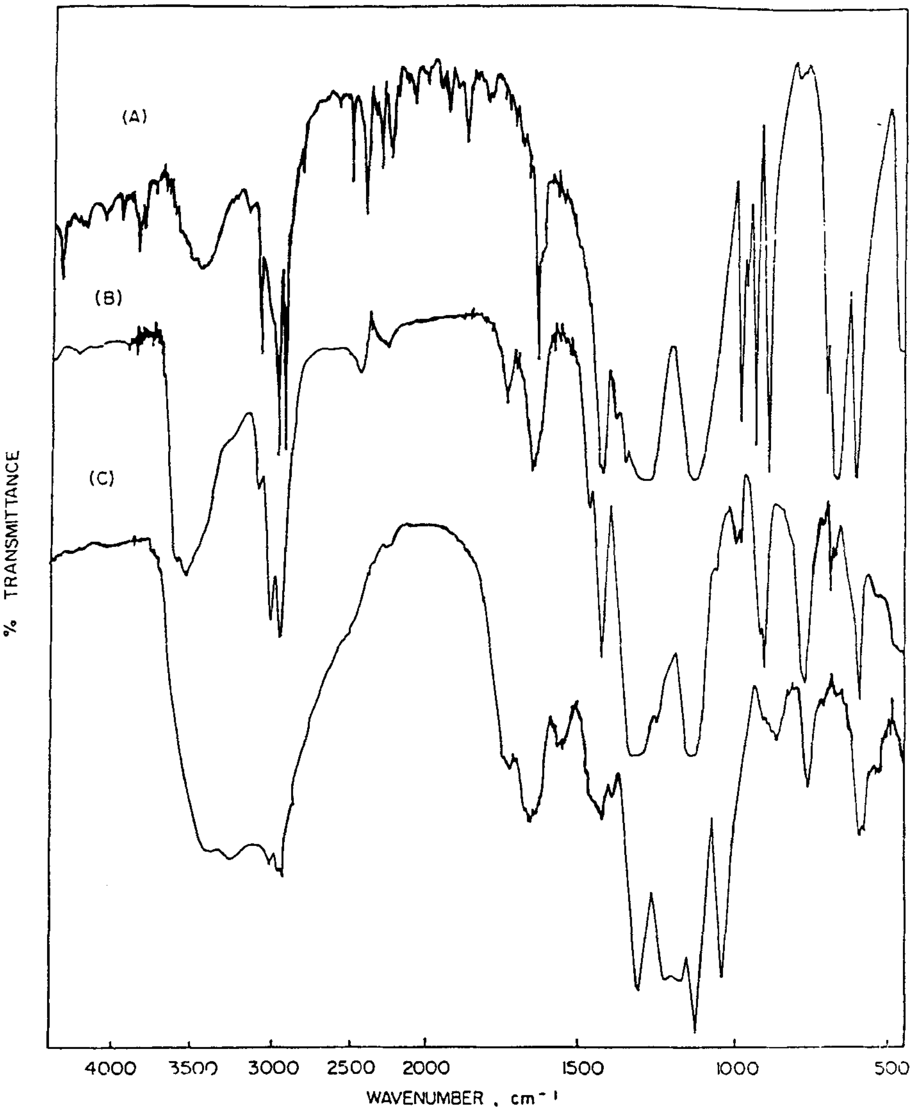


FIG. 1. FTIR spectra of (A) butadiene sulfone, and polymers obtained by (B) irradiation and (C) electrolysis at 25°C.

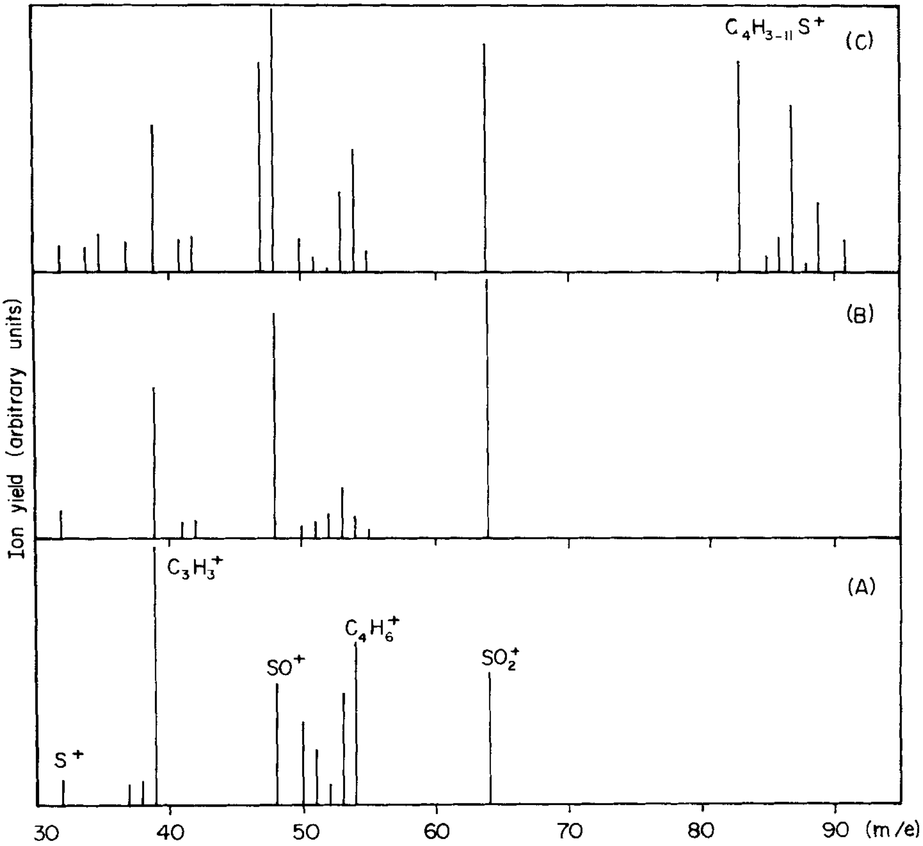


FIG. 2. Mass spectra of (A) BdS, (B) GPBdS, and (C) EPBdS, all taken at 260°C.

pyrolysis products of the two different polymers (EPBdS and GPBdS) are expected to be different. Polymers of type A would decompose in equivalent amounts of SO_2 and butadiene. However, for type B the amount of SO_2 evolved should be in excess of the butadiene. Figure 2 displays mass spectra recorded using positive ion 70 eV electron impact ionization of the pyrolysis products of the monomer, BdS, and the polymers obtained by γ-irradiation (GPBdS) and by electroinitiation (EPBdS), all taken at 260°C. Each spectrum is normalized to the most intense ion peak, hence only relative intensities can be meaningfully compared. As can be seen from the figure, BdS yields ions derived mainly from SO_2 (SO^+ at 64 amu, SO^+ at 48 amu, and S^+ at 32 amu) and butadiene ($C_4H_6^{2+}$ at 54 amu, $C_3H_3^+$ at 39 amu, and other ions having fewer hydrogens). Intensities of the hydrocarbon ions are comparable or even larger than those of SO_2 ions. Mass spectrum of GPBdS yields more or less the same spectrum as the monomer but with much larger SO_2 ion yield, indicative of a larger proportion of type B polymers.

The mass spectrum of EPBdS conveys a very different gas composition. In addition to the ions derived from SO_2 and butadiene, ions from another major gaseous species with a molecular weight of around 90 amu are present. This is most probably due to degradation from polymers consisting of mainly linear segments (type A) yielding $C_2H_x{-}S{-}C_2H_y$ type of moieties.

More information can be extracted from mass spectra if the yields of certain ions are examined as a function of temperature. The so-called ion/temperature profiles are very useful for structural elucidation [8–12]. Figure 3 shows such profiles for ions derived from SO_2 and butadiene for the two polymers. Thermal histogram of SO^+ and SO_2^+ and $C_3H_3^+$ and $C_4H_6^+$ pairs are closely correlated in GPBdS, but no such correlation exists for EPBdS. It is also evident from the figure that SO_2 evolution in GPBdS increases rapidly above 240°C whereas this increase is not so pronounced in EPBdS.

These observations further support the hypothesis that the polymers obtained by irradiation are mainly composed of cyclic segments whereas the polymers obtained by electroinitiation contain linear segments as the major constituent.

The 250 MHz ^{1}H-NMR spectra of EPBdS and GPBdS are shown in Figs. 4 and 5, respectively. The spectra were measured in d_7-DMF solution. The individual peak assignments are made by comparing ^{1}H-NMR and 2D^{1}H COSY spectra of each polymer. In ^{1}H-NMR spectra of polymers, the peaks at $\delta = 6.2$ ppm and $\delta = 3.8$ ppm are correlated with the peaks labeled as P and Q, respectively, in related 2D^{1}H COSY spectra. In Figs. 6 and 7, P and Q are assigned to the olefinic protons and methylenic protons of segment A. These protons are clearly resolved, and olefinic-methylenic cross correlations are observed in COSY spectra. The methine protons at $\delta = 1.8$–2.6 ppm and methylene protons at $\delta = 3.2$–3.6 ppm in segment B are not well-resolved in the ^{1}H-NMR spectra of polymers. These protons are labeled as regions R and S, respectively. The 2D^{1}H COSY spectra indicates that the methinic protons are coupled to the methylenic protons. Deshielding of the methylene protons can be

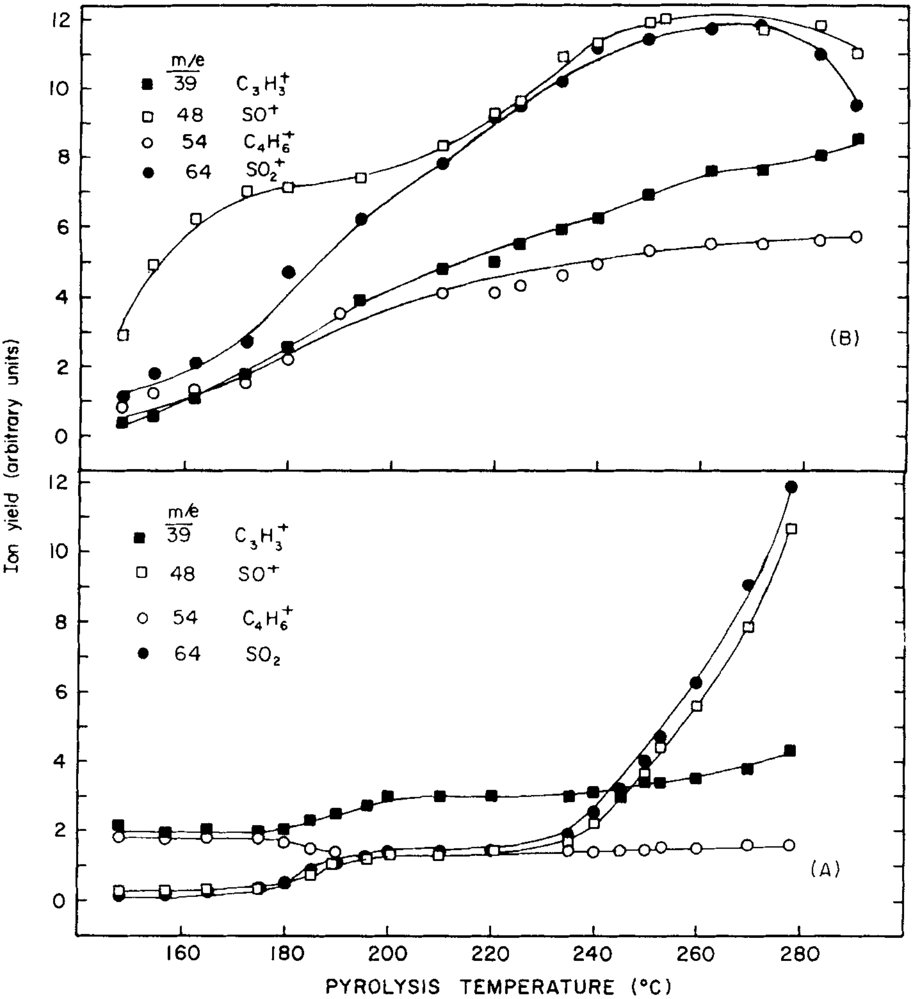


FIG. 3. Ion yield-prolysis temperature profiles for (A) GPBdS and (B) EPBdS.

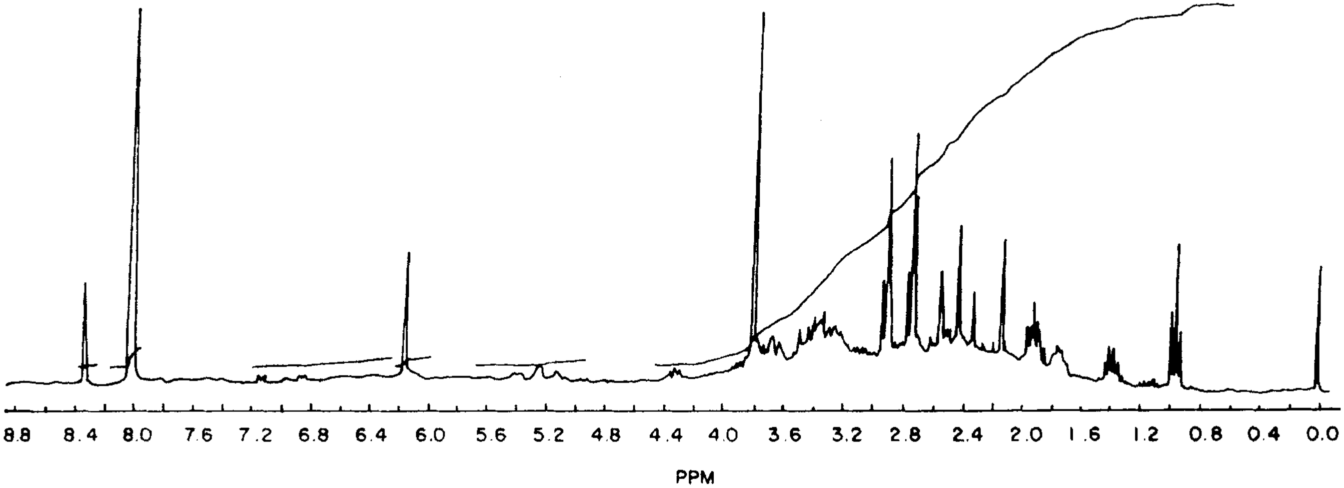


FIG. 4. ^{1}H-NMR spectrum of EPBdS obtained at 25°C.

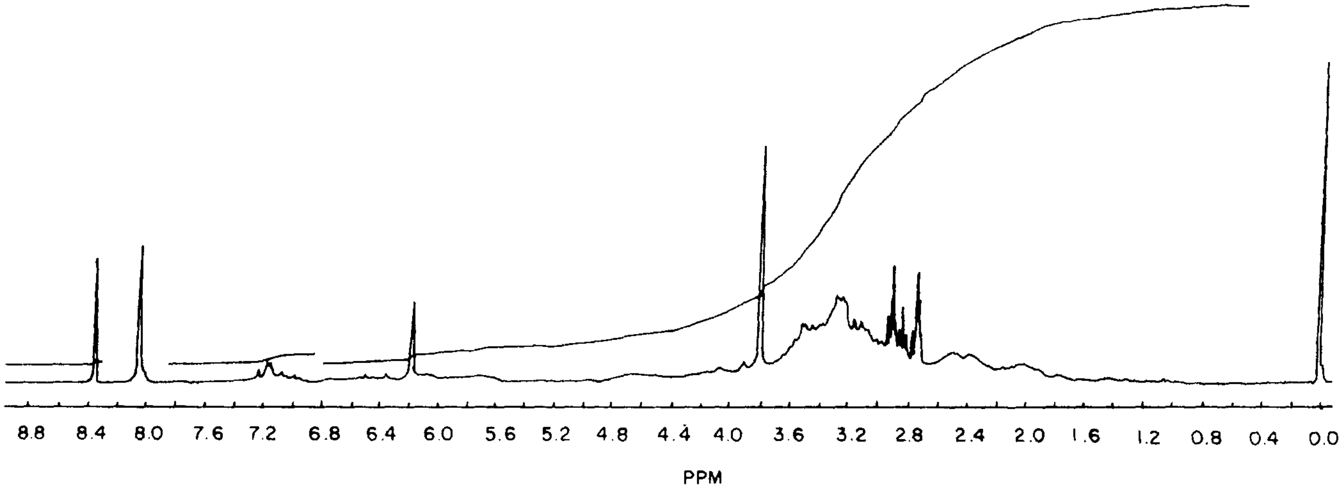


FIG. 5. ^{1}H-NMR spectrum of GPBdS obtained at 25°C.

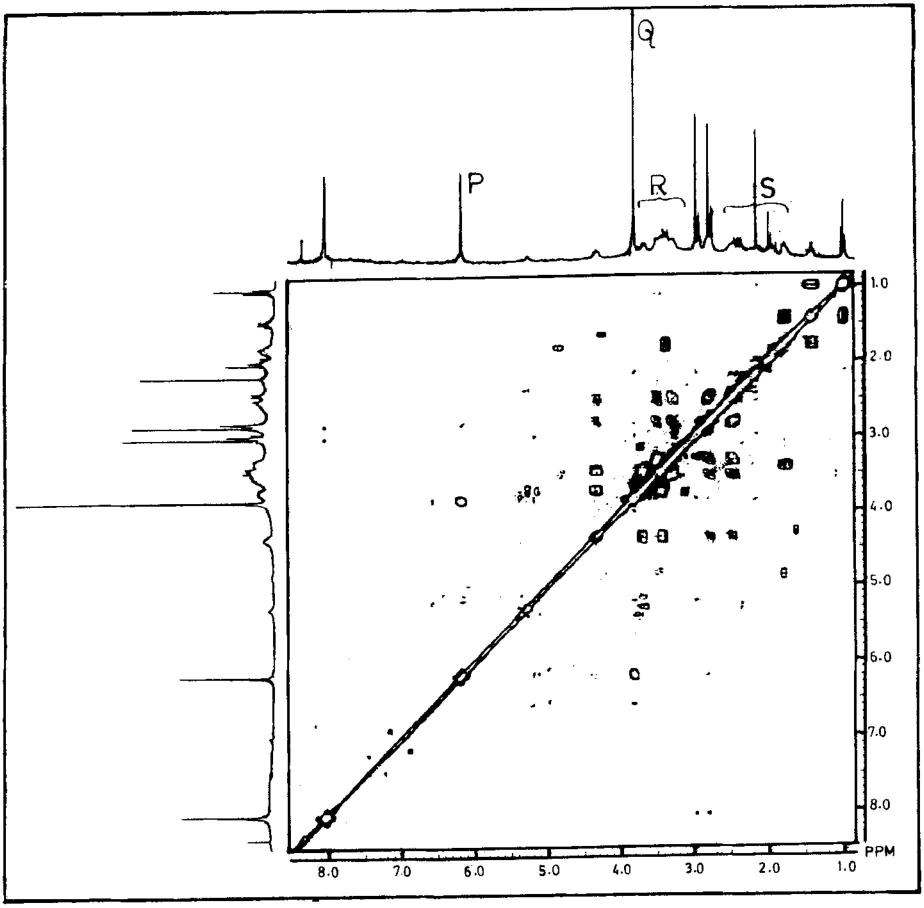


FIG. 6. 2D^{1}H-COSY spectrum of EPBdS obtained at 25°C.

due to the presence of a nearby sulfone group. The presence of the proton peaks at $\delta = 2.7$, 2.9 ppm and 8.0, 8.4 ppm are assigned to *N*-methyl and aldehyde protons of the solvent, d_7-DMF.

In the spectrum of EPBdS there are two extra signals at $\delta = 1.0$ ppm as a triplet and at $\delta = 1.4$ ppm as a quartet, which indicate the presence of an ethyl group in the structure. These signals may result from impurities in the reaction medium or may arise from the isomerization of the terminal segment A, depending on the acidic character of the α-methy-

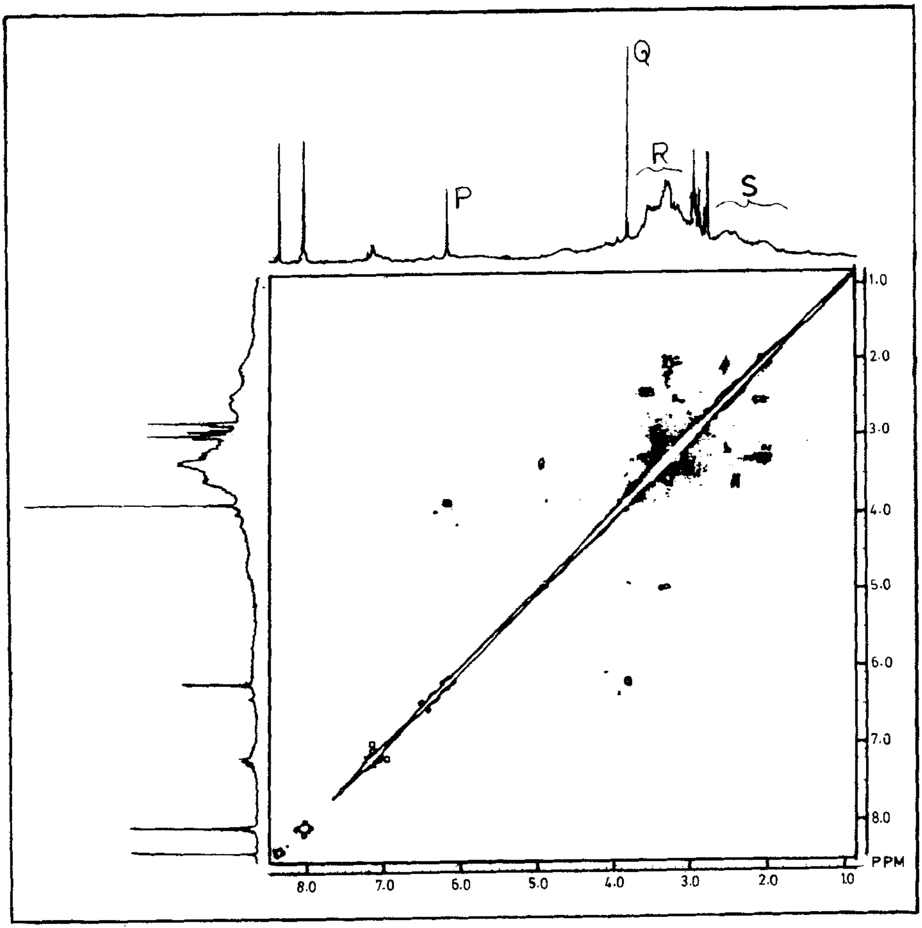


FIG. 7. 2D^{1}H-COSY spectrum of GPBdS obtained at 25°C.

lene protons. The related COSY spectrum indicates that the protons at $\delta = 1.0$ ppm are coupled to the protons at $\delta = 1.4$ ppm. Although the protons at $\delta = 1.4$ ppm are coupled to methine protons at $\delta = 1.8$ ppm in region S, this coupling may result from another group which may be hidden under the peak at $\delta = 1.4$ ppm.

The UV spectra of polymers obtained in DMF are given in Fig. 8. GPBdS shows a maximum absorption at 240 nm and EPBdS has a maximum at 254 nm. The red shift in EPBdS may be explained in terms

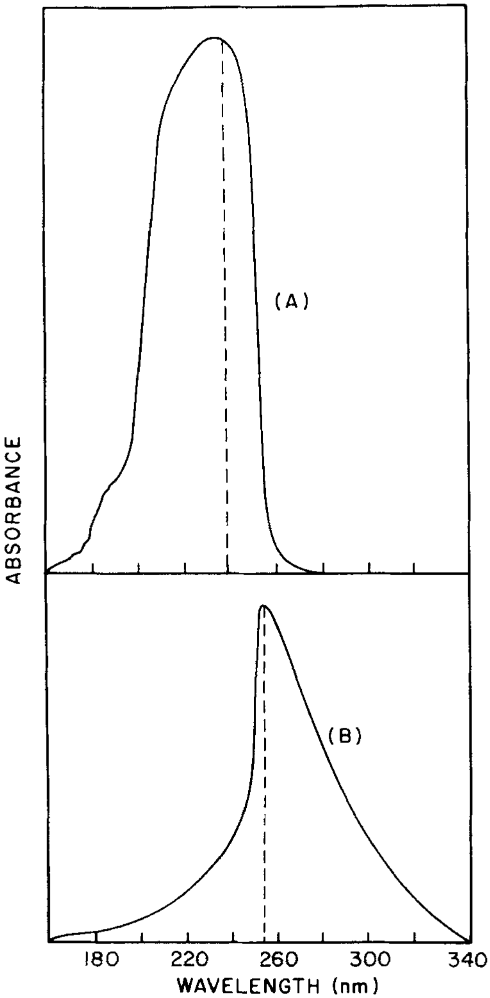


FIG. 8. UV spectra of polymers obtained by (A) irradiation and (B) electrolysis.

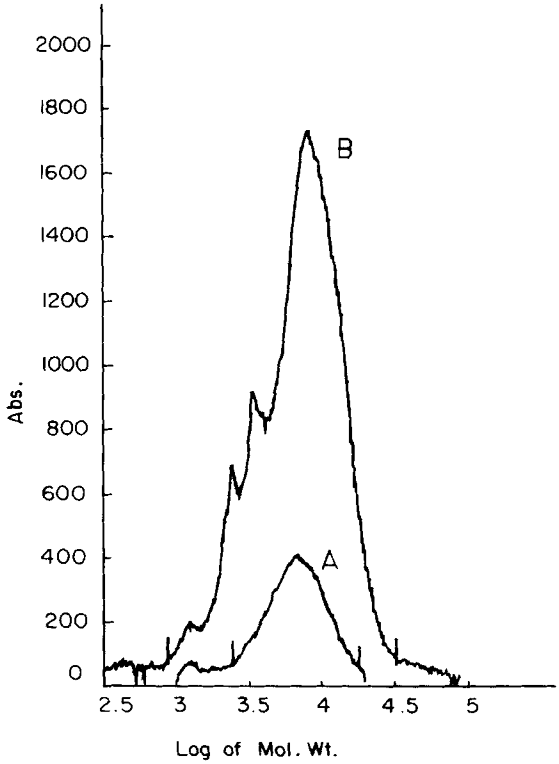
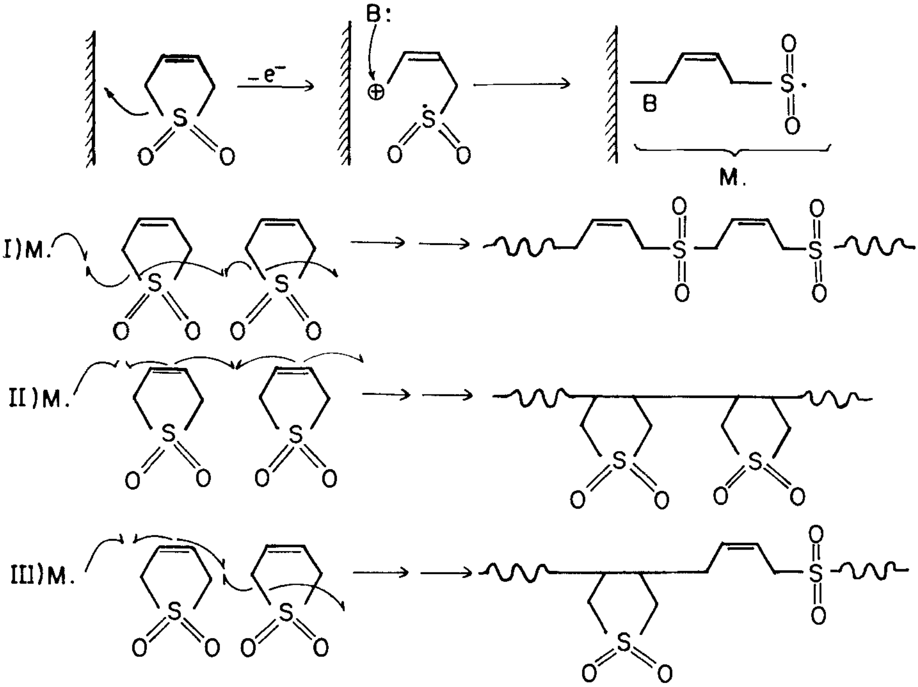


FIG. 9. Molecular weight distribution curve of polymer obtained by (A) irradiation and (B) electrolysis.

of structure A having a higher degree of conjugation than structure B.

Molecular weight distribution curves of EPBdS and GPBdS are given in Fig. 9. From the figure, the weight-average molecular weights ($\overline{M}_w$) and the number-average molecular weights ($\overline{M}_n$) can be determined. For GPBdS, $\overline{M}_w$ and $\overline{M}_n$ were found to be 7300 and 6300, respectively, and for EPBdS 7950 and 5500, respectively. The heterogeneity index ($HI = \overline{M}_w/\overline{M}_n$) was calculated as 1.15 for GPBdS whereas it was 1.44 for EPBdS. Comparison of *HI* values of these two polymers showed that polymers obtained by irradiation are significantly more homogeneous than electroinitiated polymers.

On the surface of the anode, an electron is removed from the C—S bond of the monomer to yield a radical cation ($M^{+\cdot}$). The cation end is



SCHEME 1.

not stable enough to initiate polymerization and thus can be deactivated easily. The radical end of the oxidized monomer can initiate polymerization which can propagate either by opening of the ring or the double bond. Addition of hydroquinone to the electrolysis solution completely stopped the polymerization, indicating that polymerization proceeds via a radical mechanism. Scheme 1 represents the possible initiation and propagation mechanism for electroinitiated polymerization.

The monomer is expected to form radicals upon irradiation by the cleavage of either C—S or C=C. The polymerization can be initiated by M, similar to electroinitiation. Since radiation-induced polymerization mainly yields polymers with cyclic segments, it can be concluded that ring opening is less probable in the solid state (in bulk). On the other hand, ring-opening polymerization must be favored in solution since polymers obtained by electrolysis mainly consist of linear segments.

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