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Syntheses of Polymeric Azasulfonium Salts and Iminosulfuranes

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ABSTRACT

Polymeric azasulfonium salts were synthesized by the reaction of sulfide polymers with such N-halo compounds as N-chloroacetamide, N-bromoacetamide, and ethyl N-chlorocarbamate. These polymers are soluble in CH_2Cl_2 , CHCl_3 , DMSO, and DMF, but insoluble in benzene, acetone, and water. The treatment of these polymeric azasulfonium salts with triethylamine afforded polymers containing the iminosulfurane structure in high yields. On the other hand, these iminosulfurane polymers were also synthesized by the reaction of sulfide polymers with nitrene which was generated from the photolysis of ethyl azidoformate.

INTRODUCTION

Sulfur-containing polymers have recently been attractive as functional polymers since the sulfur atom has high nucleophilicity, the ability to stabilize adjacent carbanions, and can exist in several oxidation states which show various interesting behaviors. Polymeric sulfonium salts have been used in such fields as ion-exchange resins, polymer supports of peptide synthesis, polymeric reagents, and polyelectrolytes [1]. In a series of studies of sulfur-containing polymers,

we previously synthesized several polymeric sulfonium salts such as poly(vinyl-sulfonium salts) [2], the copolymer of vinylsulfonium salt with styrene [3], and poly(dimethyl-4-vinylphenylsulfonium tetrafluoroborate [4]). However, there has been no investigation of the synthesis of a polymeric sulfonium salt containing hetero atoms adjacent to a sulfur atom.

Monomeric azasulfonium salts were first isolated by Swern et al. [5, 6] as an intermediate of iminosulfurane synthesis. Corey et al. [7] also reported the production of an unstable azasulfonium salt from the reaction of dimethyl sulfide and N-chlorosuccinimide, and they succeeded in oxidizing alcohols by the use of this azasulfonium salt under mild conditions. Their papers indicate that polymeric azasulfonium salts are interesting as polymeric reagents, but their synthetic method is limited to dialkyl sulfides. Further, most of these azasulfonium salts are not stable.

We have now found that stable azasulfonium salts could be obtained by the reaction of alkyl or aryl sulfides and N-haloacetamide in high yield.

We therefore applied this reaction to the syntheses of polymeric azasulfonium salts. Next, the conversion of these polymers to polymers containing the iminosulfurane structure was attempted.

Iminosulfurane has also been prepared by the photolysis of azide in alkyl sulfides [8]. Therefore, this reaction was also applied to prepare the iminosulfurane polymer.

EXPERIMENTAL

Reagents

Poly(ethyl vinyl sulfide), poly(methyl 4-vinylphenyl sulfide), and poly(methyl 4-vinylbenzyl sulfide) were prepared by the methods described previously [4].

N-Chloroacetamide (NCA) was prepared by the reaction of acetamide and t-butyl hypochlorite: yield, 47%; mp 109.0-109.5°C (Ref. 9, 109.0-109.5°C). Ethyl N-chlorocarbamate (NCC) was prepared by the reaction of ethyl carbamate and chloride: yield 66%; bp 44-46°C/7 torr (Ref. 10, 44.0-45.0°C/0.2 torr). Ethyl azidoformate was prepared by the reaction of ethyl chloroacetate and sodium azide: bp 30°C/7 torr (Ref. 11, 28°C/20 torr). N-Bromoacetamide (NBA) was commercially available.

Preparation of Model Compounds of Polymeric Azasulfonium Salts

All azasulfonium compounds were prepared by treatment of the corresponding sulfide and N-halo compounds. For example, N-acetyl-

iminobenzylmethylsulfonium chloride was prepared as follows. NCA (0.28 g, 3 mmol) was added slowly to a solution of benzyl methyl sulfide (0.83 g, 6 mmol) in CH_2Cl_2 (20 mL) at 0°C . The solution was further stirred for 2 h at that temperature. The reaction mixture was poured into ether (50 mL) to precipitate a white solid. The solid was filtered and recrystallized with absolute ethanol and ether. The yield was 0.31 g (45%). All other azasulfonium salts were prepared by the same method. However, azasulfonium halides prepared by the use of NCC are not stable at room temperature and the structure was confirmed only by IR and NMR spectra (in CDCl_3).

N-Acetylaminobenzylmethylsulfonium chloride

Yield: 45%; mp, $110.0\sim 112.0^\circ\text{C}$

IR: $\nu_{\text{N-H}} = 2700\text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1710\text{ cm}^{-1}$, $\nu_{\text{S-N}} = 690, 580\text{ cm}^{-1}$

NMR: $\delta = 1.98$ (d, 3H), 3.30 (s, 3H), 4.84 (d, 2H), 7.4~7.6 (m, 5H) ppm

Calcd. for $\text{C}_{10}\text{H}_{14}\text{ClNS}$: C, 51.83; H, 6.09; N, 6.04; S, 13.83%

Found: C, 51.21; H, 6.48; N, 5.80; S, 13.46%

N-Acetylaminomethylphenylsulfonium chloride

Yield: 68%; mp, $96.0\sim 97.5^\circ\text{C}$

IR: $\nu_{\text{N-H}} = 2680\text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1690\text{ cm}^{-1}$, $\nu_{\text{S-N}} = 680, 580\text{ cm}^{-1}$

NMR: $\delta = 2.14$ (d, 3H), 3.30 (d, 3H), 7.2~8.3 (m, 5H) ppm

Calcd. for $\text{C}_9\text{H}_{12}\text{ClNS}$: C, 49.65; H, 5.56; N, 6.43; S, 14.73%

Found: C, 49.12; H, 5.95; N, 6.27; S, 14.52%

N-Acetylaminobenzylmethylsulfonium bromide

Yield: 56%; mp, $91.0\sim 92.0$

IR: $\nu_{\text{N-H}} = 2750\text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1715\text{ cm}^{-1}$, $\nu_{\text{S-N}} = 690, 650\text{ cm}^{-1}$

NMR: $\delta = 2.03$ (s, 3H), 3.27 (s, 3H), 3.5~4.2 (b, 1H), 4.85 (d, 2H), 7.3~7.6 (m, 5H) ppm

Calcd. for $\text{C}_{10}\text{H}_{14}\text{BrNS}$: C, 43.49; H, 5.11; N, 5.07; S, 11.61%

Found: C, 42.47; H, 5.38; N, 5.26; S, 11.54%

N-Ethoxycarbonyliminobenzylmethylsulfonium chloride

Yield: 20%

IR: $\nu_{\text{N-H}} = 3400\text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1735\text{ cm}^{-1}$

NMR: $\delta = 1.27$ (s, 3H), 3.62 (s, 3H), 4.05 (q, 2H), 5.40 (b, 2H), 7.38 (s, 1H), 7.6~7.8 (m, 5H) ppm

N-Ethoxycarbonyliminomethylphenylsulfonium chloride

Yield: 56%

IR: $\nu_{\text{N-H}} = 3410\text{ cm}^{-1}$, $\nu_{\text{C=O}} = 1730\text{ cm}^{-1}$

NMR: $\delta = 1.20$ (t, 3H), 2.80 (s, 3H), 4.06 (q, 2H), 5.98 (s, 1H), 7.2~7.8 (m, 5H) ppm

Preparation of Polymers with Azasulfonium Salt Structure

Poly(*N*-acetyliminomethyl-4-vinylbenzylsulfonium chloride) was prepared as follows. A solution of poly(methyl 4-vinylbenzyl sulfide) (0.187 g) in methylene chloride (4 mL) was added with stirring to a solution of NCA (0.189 g) in methylene chloride (20 mL) at 0°C. The solution was further stirred for 7 h at that temperature. Then the reaction mixture was poured into a large amount of ether to precipitate a white solid. The solid was filtered and washed with absolute ethanol. The yield was 0.281 g.

Other polymeric azasulfonium salts were prepared by essentially the same method.

Poly(*N*-acetyliminomethyl-4-vinylbenzylsulfonium chloride)

IR: 660, 830, 990, 1105, 1210, 1360, 1420, 1510, 1605, 1710, 2750, 3400 cm^{-1}

Poly(*N*-acetyliminomethyl-4-vinylphenylsulfonium chloride)

IR: 550, 590, 830, 1000, 1080, 1220, 1420, 1490, 1590, 1690, 2800, 3400 cm^{-1}

Poly(*N*-ethoxycarbonyliminomethyl-4-vinylphenylsulfonium chloride)

IR: 550, 820, 955, 1040, 1140, 1300, 1405, 1595, 1715, 3320 cm^{-1}

Poly(*N*-ethoxycarbonyliminomethyl-4-vinylbenzylsulfonium chloride)

IR: 660, 840, 1020, 1260, 1420, 1510, 1605, 1700, 2920, 3400 cm^{-1}

Preparation of *N*-Ethoxycarbonyliminobenzylmethylsulfurane

N-Ethoxycarbonyliminobenzylmethylsulfurane was prepared by the method described previously [12].

IR: 1610 cm^{-1} (C=O), 820 and 780 cm^{-1} (S=N)

NMR: δ = 1.27 (t, 3H), 2.50 (s, 3H) 4.06 (q, 2H), 4.21 (q, 2H), 7.33 (s, 5H) ppm

Preparation of *N*-acetyliminobenzylmethylsulfurane

To a solution of *N*-acetyliminobenzylmethylsulfonium bromide (0.460 g, 1.7 mmol) in methylene chloride (15 mL) was added triethylamine (0.253 g, 2.5 mmol) at 0°C. The solution was stirred for 2 h at that temperature, and further for 2 h at room temperature. Then the reaction mixture was poured into ether and the precipitated triethylamine hydrochloride was filtered off. The solvent was removed under reduced pressure to afford an oily compound (0.209 g, 65%).

N-Acetylaminobenzylmethylsulfurane

Yield: 65%

IR: $\nu_{\text{C=O}} = 1570 \text{ cm}^{-1}$, $\nu_{\text{C-N}} = 1310 \text{ cm}^{-1}$, $\nu_{\text{S-N}} = 790 \text{ cm}^{-1}$ NMR: $\delta = 2.00$ (s, 3H), 2.40 (s, 3H), 4.20 (q, 2H), 7.3 (s, 5H), ppmCalcd. for $\text{C}_{10}\text{H}_{13}\text{NS}$: C, 61.51; H, 6.71; N, 7.17; S, 16.42%

Found: C, 61.21; H, 6.88; N, 7.19; S, 16.89%

N-Acetylaminomethylphenylsulfurane

Yield: 91%

IR: $\nu_{\text{C=O}} = 1570 \text{ cm}^{-1}$, $\nu_{\text{C-N}} = 1310 \text{ cm}^{-1}$, $\nu_{\text{S-N}} = 800 \text{ cm}^{-1}$ NMR: $\delta = 2.10$ (s, 3H), 2.80 (s, 3H), 7.3~7.9 (m, 5H) ppmCalcd. for $\text{C}_9\text{H}_{11}\text{NS}$: C, 59.64; H, 6.12; N, 7.73; S, 17.69%

Found: C, 59.39; H, 6.38; N, 7.31; S, 17.53%

Preparation of Poly(N-acetylaminomethyl-4-vinylbenzylsulfurane)

To a solution of poly(N-acetylaminomethyl-4-vinylbenzylsulfonium chloride) (0.187 g) in methylene chloride (25 mL) was slowly added triethylamine (0.152 g, 1.5 mmol). The solution was stirred for 2 h at 0°C and further stirred for 2 h at room temperature. The reaction mixture was poured into a large amount of ether to give a solid. The solid was washed with absolute ethanol (50 mL). The yield was 0.124 g.

Poly(N-acetylaminomethyl-4-vinylbenzylsulfurane)IR: 660, 820, 1110, 1260, 1360, 1420, 1510, 1560, 1610, 1700, 2920, 3400 cm^{-1} **Poly(N-acetylaminomethyl-4-vinylphenylsulfurane)**IR: 550, 720, 820, 1040, 1140, 1300, 1490, 1560, 1590, 1680, 2900, 3450 cm^{-1} **Preparation of Poly(N-ethoxycarbonyliminomethyl-4-vinylbenzylsulfurane)**

To a solution of poly(methyl-4-vinylbenzyl sulfide) (1.04 g) in chloroform (20 mL) was added slowly NCC (1.20 g, 9.7 mmol) at 0-5°C, and further allowed to react for 2 h with stirring. Then triethylamine (1.0 g, 10 mmol) was added slowly to the solution at that temperature. After stirring for 2 h, about half of the solvent was removed in vacuum and the reaction mixture was poured into ether (50 mL) to precipitate a white solid, triethylamine hydrochloride. The solid was filtered off and the filtrate was poured into a large amount of petroleum ether to give a polymer in 0.77 g yield. The IR spectrum of this compound is shown in Fig. 3.

Preparation of Poly(N-ethoxycarbonyliminomethyl-4-vinylbenzylsulfurane) by Photochemical Method

A solution of poly(methyl-4-vinylbenzyl sulfide) (1.78 g) and ethyl azidoformate (1.13 g, 12.4 mmol) in benzene (10 mL) was placed in a quartz tube. Under nitrogen atmosphere the solution was irradiated for 8 h with a high pressure mercury lamp (RIKO-100 W). After the reaction the solvent was distilled off under reduced pressure and the residue was reprecipitated three times with chloroform and petroleum ether. The yield was 1.25 g. The IR spectrum of this polymer is shown in Fig. 3.

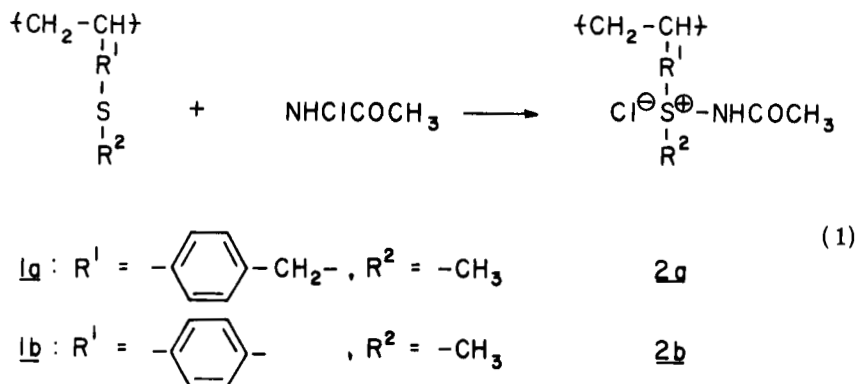
Instrument

IR spectra were recorded on a JASCO IRA-2 spectrometer. NMR spectra were recorded in CDCl_3 on a 60 MHz HITACHI R-20B spectrometer using tetramethylsilane as the internal standard.

RESULTS AND DISCUSSION

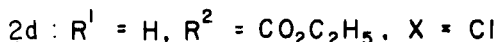
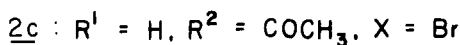
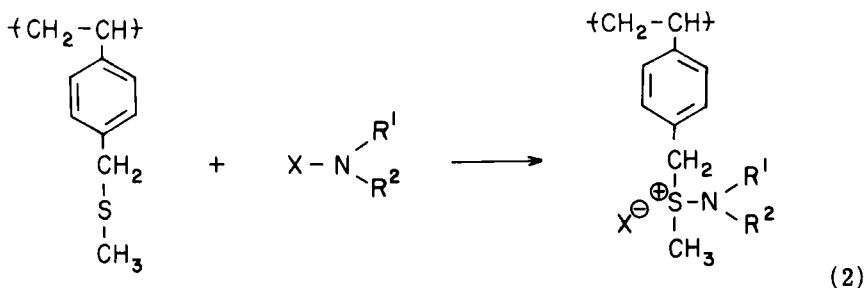
Preparation of Polymers with Azasulfonium Salt Structure

Azasulfonium polymers (2a, 2b) were prepared from the reaction of N-chloroacetamide (NCA) with the corresponding sulfide polymers at 0°C as shown in Eq. (1). The sulfide polymers used here were prepared from the radical polymerization of the corresponding vinyl monomers.



The structure of these polymers was confirmed by IR and NMR spectra in comparison with those of authentic model compounds which were prepared according to Saika's method [6]. These polymers showed a characteristic absorption band of carbonyl group at 1690-1710 cm^{-1} and N-H stretching at 2750-2800 cm^{-1} . IR spectra of 2a and acetyliminobenzylmethylsulfonium chloride as a model compound of 2a are shown in Fig. 1. The conversion of divalent sulfur to trivalent sulfur was measured by the integral of the NMR spectrum.

Other types of azasulfonium salt polymers were prepared by the reaction of 1a with several N-halo compounds such as N-bromoacetamide (NBA) and ethyl N-chlorocarbamate (NCC) by the same method as in the case of 2a and 2b.



These polymers are very hygroscopic and soluble in chloroform, dimethylsulfoxide, and dimethylformamide.

Conversion of Polymeric Azasulfonium Salts to Polymers with Iminosulfurane Structure

Swern et al. [5] reported that the treatment of azasulfonium salts with triethylamine gave iminosulfuranes in good yield. We altered this to aryl sulfides or other N-halo compounds by changing the reaction condition [12]. These reactions were adopted to polymer reactions.

The polymer prepared from 1a and NCA was allowed to react with triethylamine and gave a polymer with iminosulfurane structure (3a). The IR spectrum shows a characteristic absorption band at 820 cm^{-1} (S=N) and 1560 cm^{-1} (C=O). However, a weak absorption band at 1700 cm^{-1} based on the carbonyl group of the azasulfonium salt is

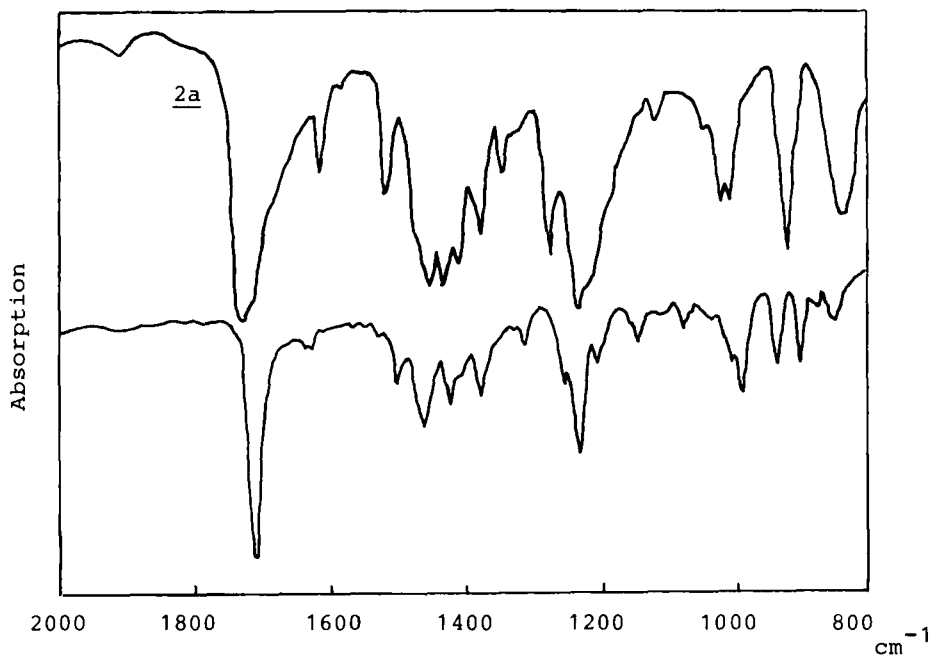


FIG. 1. IR spectra of poly(N-acetyliminomethyl-4-vinylbenzyl sulfonium chloride) (2a) and N-acetyliminobenzylmethylsulfonium chloride.

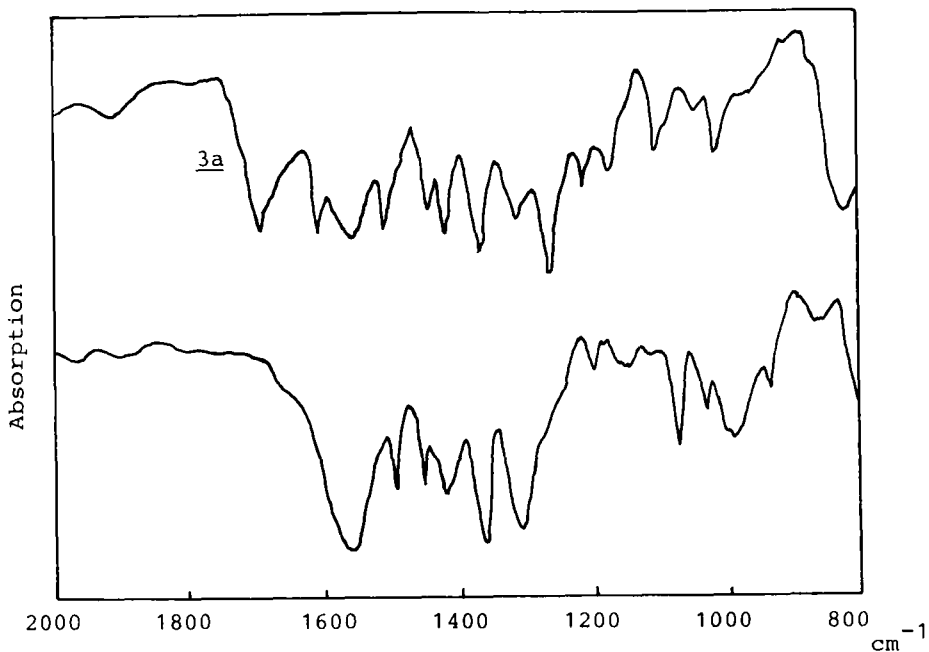
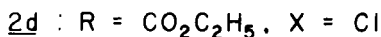
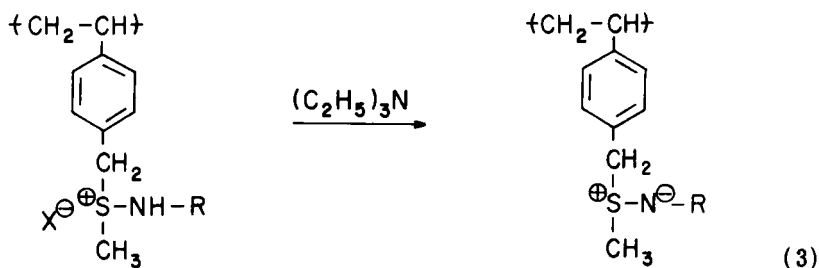


FIG. 2. IR spectra of poly(N-acetyliminomethyl-4-vinylbenzylsulfurane) (3a) and N-acetyliminobenzylmethylsulfurane.

observed. The IR spectra of this polymer and acetylaminobenzylmethyl sulfurane as the model compound are shown in Fig. 2.

Similarly, an iminosulfurane polymer was obtained by the use of NBA and NCC:



Preparation of Iminosulfurane Polymers by Photochemical Method

Ando et al. [8] reported that photodecomposition of methyl azidoformate in dialkyl sulfides gave iminosulfuranes in 40-60% yield. This method is excellent for the preparation of sulfilimine because of the ease of the work-up procedure. Therefore, we adopted this reaction to the preparation of polymeric iminosulfurane and compared the polymer with that obtained through an azasulfonium salt intermediate.

A solution of polymer (1a) and ethyl azidoformate in benzene was placed in a quartz tube and irradiated by a high pressure mercury lamp as the light source. The polymer obtained has a characteristic absorption band at 1630 cm^{-1} , based on the carbonyl group of this kind of ylide. The IR spectrum is shown in Fig. 3. As can be seen, the IR is in good agreement with that of 4a. However, conversion of iminosulfurane was only 17%.

On the other hand, the reaction of poly(ethyl vinyl sulfide) with nitrene derived from photolysis of ethyl azidoformate gave an iminosulfurane polymer (5a) in 30% yield (Fig. 4).

The utilization of these azasulfonium salt and iminosulfurane polymers will be reported in the near future.

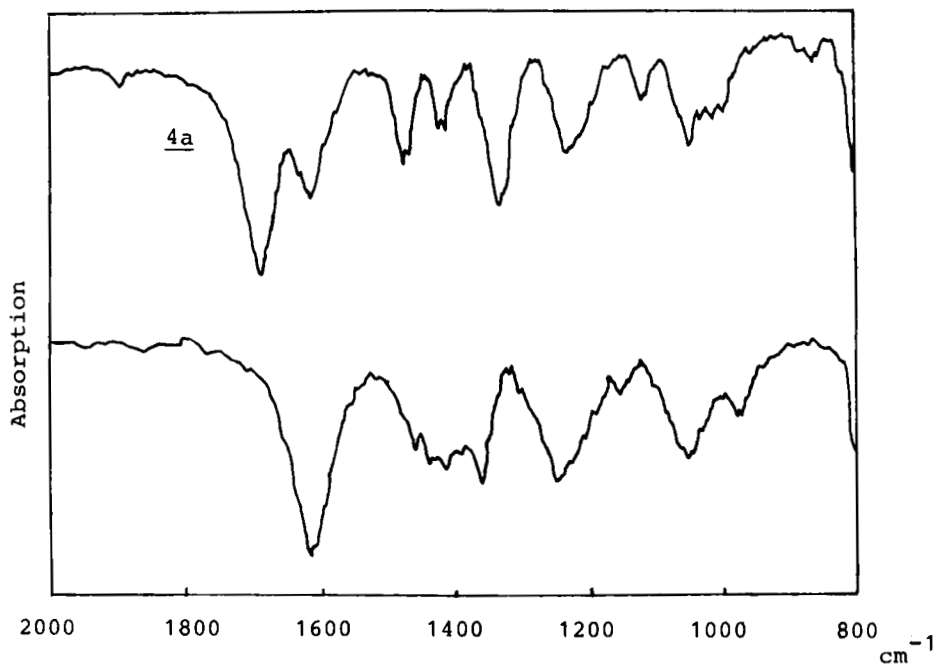
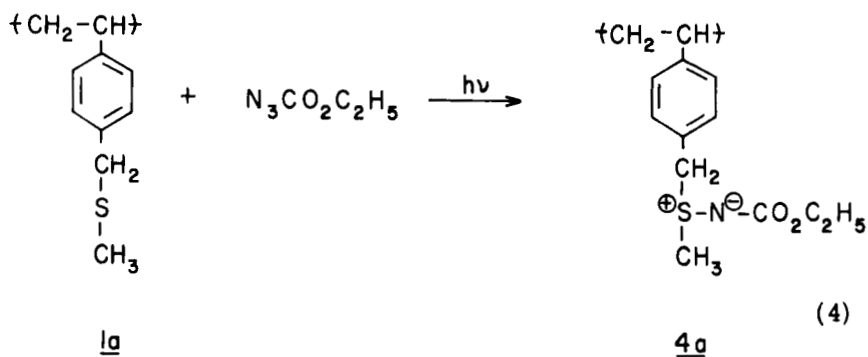


FIG. 3. IR spectra of poly(N-ethoxycarbonyliminomethyl-4-vinylbenzylsulfurane) (4a) and N-ethoxycarbonylimino methylbenzylsulfurane.



FIG. 4. IR spectra of poly(N-ethoxycarbonyliminoethylvinylsulfurane) (5a) and N-ethoxycarbonylimino diethylsulfurane.

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