

Condensation Products from Imidobis(sulfonyl Chloride)

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Synopsis

A study of model compounds and polycondensation products derived from imidobis(sulfonyl chloride) (IBSC), $\text{HN}(\text{SO}_2\text{Cl})_2$, has been carried out and their structures determined. The model compounds were reaction products of IBSC with aniline or ethyl alcohol. Polymeric products were obtained by polycondensations with (1) *p*-phenylenediamine and (2) 2,2-bis(4'-hydroxyphenyl)propane. The products were characterized by elemental analysis, infrared, NMR, DSC, TGA, and viscometry data.

INTRODUCTION

A polymer with high SO_2 and aromatic ring content in the chain backbone usually has high heat and flame resistance. Imidobis(sulfonyl chloride) was synthesized¹ in 1966, but little interest has been shown in investigating the chemistry and the nature of the products resulting from its polycondensation reactions.

The present work was undertaken with a view to extend the low-temperature solution polycondensation method pioneered by du Pont workers² to inorganic diacid chlorides such as IBSC in order to establish whether this might result in the development of a novel group of partially inorganic condensation polymers with reasonable thermal properties and acceptable hydrolytic stability. A study of the chemistry and solvent properties of IBSC itself was made by Paul et al.^{3,4} Due to the labile nature of its imido proton, IBSC reacts with inorganic halides with the elimination of HCl gas.

IBSC is highly sensitive to hydrolysis and decomposes according to



Lewis acids such as antimony(V) chloride and tin(IV) chloride do not react with IBSC and thus demonstrate the weakly basic nature of the nitrogen and the covalent nature of the chlorine present in IBSC. The following possible mode of ionization has been proposed³:



and the labile nature of the proton in IBSC has been demonstrated by preparing derivatives such as $\text{AgN}(\text{SO}_2\text{Cl})_2$, $\text{MON}(\text{SO}_2\text{Cl})_2$, and $\text{MN}(\text{SO}_2\text{Cl})_2$, where M = Li, K, or Na.

The strongly acidic properties of the imido proton of IBSC have been demonstrated by isolating adducts with pyridine *N*-oxide, 1-picolines, piperidine, triethylamine, quinoline, 8-hydroxyquinoline, and 1,10-phenanthroline. The model compounds isolated from the reaction of IBSC with aniline and with ethyl

An additional Claisen distillation was carried out so as to obtain the product free from chlorosulfonic acid residues. IBSC is best kept under dry nitrogen in predried sample bottles.

Preparation of the Model Compounds

Aniline Model Compound

A three-necked, 250-ml, round-bottomed flask fitted with a dry nitrogen inlet, a glass stirrer, and a calcium chloride drying tube was charged with a twofold excess of predistilled aniline. Dry carbon tetrachloride was then added to obtain a 20% solution of aniline (w/v), and the concentrated solution of IBSC in CCl_4 was quickly and quantitatively transferred to the aniline solution at room temperature with fast stirring.

The resinous product separated was extracted with a solvent mixture consisting of 29% chlorobenzene and 71% dichloromethane at 50°C. This afforded an effective separation of the aniline hydrochloride and imidobis(sulfanilide). After recrystallization from the same solvent mixture the white crystalline imidobis(sulfanilide) was obtained in 56% yield. Melting point 95°C. Microanalysis showed: C, 44.12%; H, 4.61%; N, 12.24%. Calculated: C, 44.03%; H, 3.97%, N, 12.8%.

Ethyl Alcohol Model Compound

A 2:1 molar mixture of absolute ethanol and IBSC was reacted at a 70% total concentration in carbon tetrachloride in a separating funnel. A stream of dry nitrogen was bubbled through the solution to assist in the removal of HCl. Separation into two layers occurred in the reaction mixture after 1 h. The top layer was transferred to an air oven at 60°C, and the reaction was allowed to continue, more HCl being evolved. The reaction proceeded at a faster rate at that temperature; gas evolution ceased after 3 h. The isolated liquid layer gradually changed to a white solid which was dried in vacuo at 45°C for 1 h. The yields were found to be low (10% theoretical) due to losses in the solvent used. Melting point 190–195°C with decomposition. Microanalysis showed: C, 20.8%; H, 3.96%; N, 5.54%. Calculated: C, 20.6%; H, 4.72%; N, 6.0%.

Polycondensations

Polysulfonamide

An apparatus similar to the one used for the aniline model compound was charged with the preweighed stoichiometric quantities of *p*-phenylenediamine, triethylamine and *o*-dichlorobenzene to give a 1% amine solution. Solution of the diamine was complete after continuous stirring and heating at 90°C for 30 min. The preweighed stoichiometric amount of IBSC dissolved in carbon tetrachloride was then added in one portion, followed by 2 × 5 ml of CCl_4 rinsings. Stirring was continued for a further 5 minutes. The dark compact solid which had separated out was rinsed with a solvent mixture of 70% dimethyl sulfoxide and 30% acetone in order to remove residual hydrochloride and was finally washed with acetone and dried at 90°C. Microanalysis showed: C, 41.9%; H, 6.86%; N, 13.7%. Calculated: C, 41.1%; H, 6.28%; N, 16%.

Polysulfonate Ester of 2,2-Bis(4'-hydroxyphenyl)propane

A 5% solution of 2,2-bis(4'-hydroxyphenyl)propane was reacted with IBSC in *o*-dichlorobenzene in a 1:1 stoichiometric ratio at 90°C for 1 h until HCl evolution ceased. The brown glassy solid obtained was purified by dissolving in acetone and evaporating the solvent residues. Yield 53%. Microanalysis showed: C, 47%; H, 4.44%; N, 3.1%. Calculated: C, 48.7%; H, 4.08%; N, 3.7%.

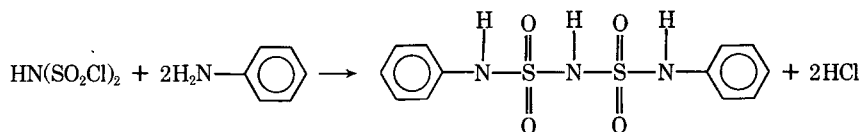
The following instruments were used for the characterization of the compounds prepared: Perkin-Elmer Infracord spectrophotometer; Perkin-Elmer R12 nuclear magnetic resonance spectrophotometer; Perkin-Elmer DSC 2 differential scanning calorimeter; and a Stanton automatic thermobalance set at a heating rate of 125°C/h.

DISCUSSION

Model Compounds

Aniline Model Compound

The structural investigations present strong evidence in favor of the following reaction:



The aniline model compound was identified as imidobis(sulfanilide) on the basis of its infrared spectrum (Fig. 1), NMR spectrum (Fig. 2), and microanalytical data.

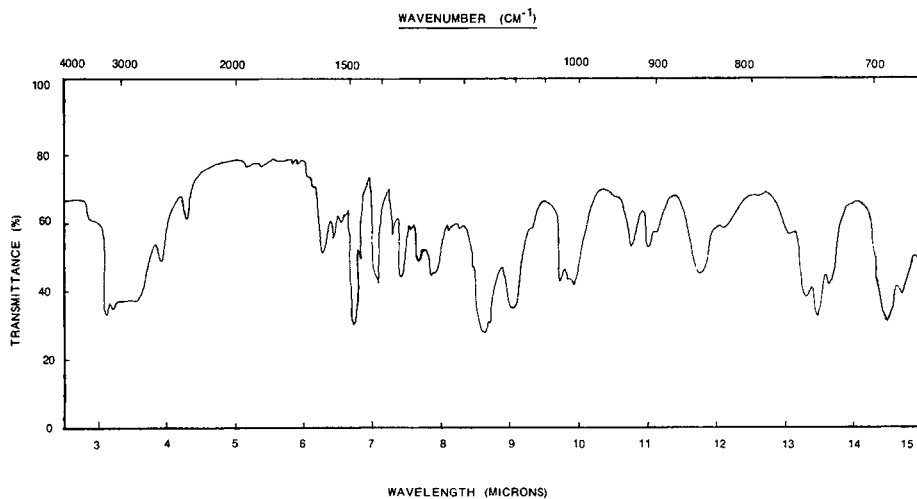


Fig. 1. Infrared spectrum of aniline model compound—imidobis(sulfanilide) (KBr disc).

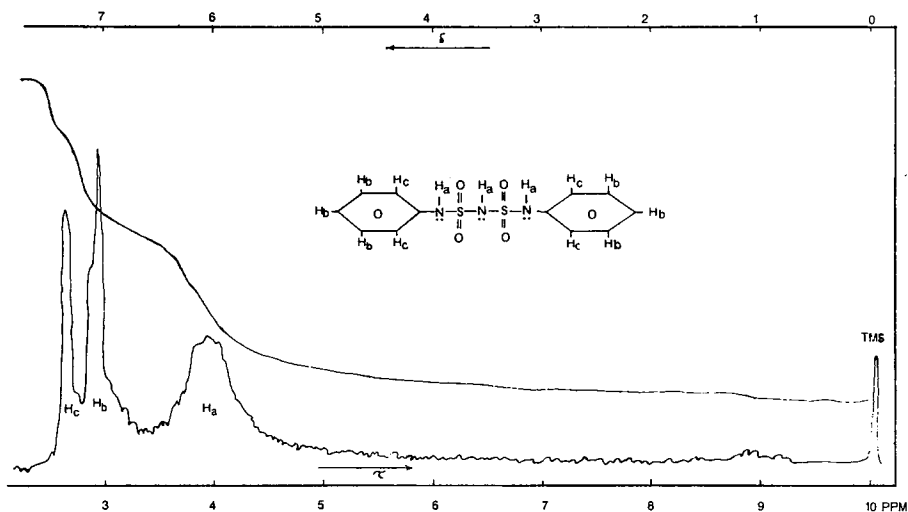


Fig. 2. NMR spectrum of aniline model compound. Solvent: DMSO d_6 ; conc., 22%; ref. std., TMS. R.F. field: 60 MHz; field shift, 53; scale, 10 PPM; sensitivity, 8; filter, 4; sweep time, 18.

The IR spectrum showed the following absorption bands: The band at 3200 cm^{-1} (observed at a much better resolution in a Nujol mull) had the characteristic shape of the N–H stretch expected at 3180 cm^{-1} for primary and secondary sulfonamides. The broadening of the band (centered around 3000 cm^{-1}) may be attributed to V(N–H) stretch of the IBSC residue as reported by Paul.³ The weak band at 1575 cm^{-1} is in the position expected for the V(N–H) deformation and is characteristic of secondary amides in the solid state.⁵

The SO_2 symmetric and the SO_2 asymmetric vibrations produce absorption bands of great diagnostic significance for sulfonamides.⁵ These have been found in the following positions: $1420\text{--}1340\text{ cm}^{-1}$ V(SO_2) asym., 1170 cm^{-1} V(SO_2) sym.; these may be compared to literature values³ given for the SO_2 groups in IBSC, namely, at $1430\text{--}1345\text{ cm}^{-1}$ V(SO_2) asym., $1208\text{--}1176\text{ cm}^{-1}$ V(SO_2) sym. The three bands centered at 1025 , 850 , and 750 cm^{-1} may be attributed to V(S–N) as given in the literature.³ Any apparent difference between the two sets of values may be due to different groups attached to SO_2 , causing the S–N bond to vibrate at a slightly different frequency.

Finally, the two strong absorptions at 740 and 690 cm^{-1} are characteristic bands denoting monosubstitution on aromatic systems⁶; these are normally expected at $740\text{--}770$ and $680\text{--}720\text{ cm}^{-1}$, respectively. The NMR spectrum of the aniline model compound gives additional diagnostic evidence and further confirms the proposed structure.

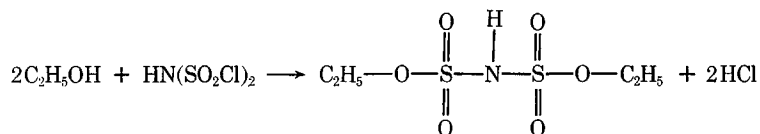
The splitting of the absorption at 7δ may be attributed to the two sets of protons H_c and H_b , the former being strongly influenced by the lone electron pair on the adjacent nitrogen atom. The formation of imidobis(sulfanilide) during the preparation of the aniline model compound indicates amines forming sulfonamides. Concentration levels of aniline of about 20% were found most effective for the preparation of the desired product in good yield.

The rapid addition of IBSC to the aniline solution (and not vice-versa) with fast stirring was another variable of importance. Dropwise addition leads to

low yields, especially when polycondensations were attempted. Surprisingly, it was found that imidobis(sulfanilide) was formed most effectively at room temperature, while a temperature of around 0°C proved unsuitable for polymerizations. The temperature range for polymerizations was 80–100°C.

Ethyl Alcohol Model Compound

The reaction of IBSC with ethyl alcohol is thought to be



The isolated product showed a number of features which one would expect to appear in imidobis(ethyl sulfonate). The microanalytic data show little disagreement with those calculated from the proposed molecular formula $\text{C}_4\text{H}_{11}\text{O}_6\text{S}_2$.

The broadening of some bands observed in its infrared spectrum (Fig. 3) may be attributed to a combination of factors such as: (a) overlapping of vibrational frequencies expected in the same frequency range, (b) hydrogen bonding between the polar

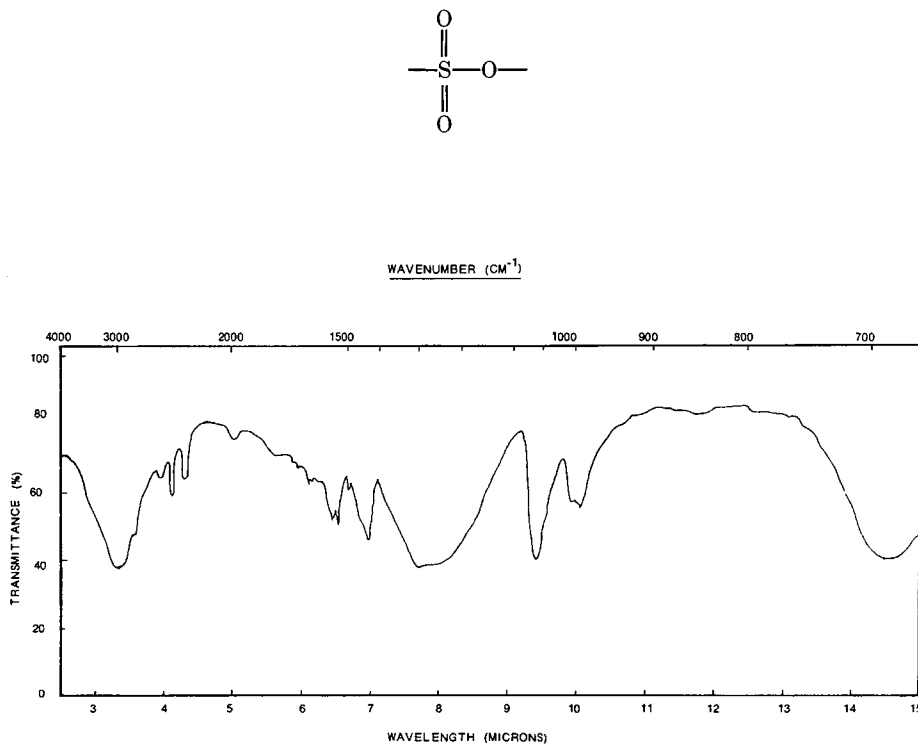


Fig. 3. Infrared spectrum of ethyl alcohol model compound (KBr disc).

groups and electropositive protons, (c) residual solvent traces in the sample.

The NMR spectrum of the ethyl alcohol model compound (Fig. 4) shows three absorption regions of 1.8, 3.5, and 5.0 δ , respectively. The first two are typical of methylic and methylenic protons, respectively. The absorption at 5 δ is due to H₂O in D₂O. The N-H proton of the IBSC residue is also expected to appear as a broad peak at 5 δ . It is therefore possible that the environment of this single proton is screened by the H₂O protons. The low yields obtained may be due to the isolation of this compound by means of a phase separation. The solvent dissolves most of the liquid phase formed in the early stages of the reaction and leaves only a small amount of liquid to separate. The subsequent heating of this liquid phase gave rise to imidobis(ethyl sulfonate).

Polycondensation experiments with 2,2-bis(4'-hydroxyphenyl)propane gave a 53% yield of what is thought to be the polysulfonate ester II. The ethyl alcohol model compound was found to be more heat stable than the aniline model compound.

DSC runs indicated that decomposition commenced at around 150 \pm 2°C, whereas the aniline model compound started to decompose at 120°C. The somewhat greater thermal stability of the ethyl alcohol model compound is analogous with the greater thermal stability of the polysulfonate ester II (220°C by TGA measurements, see Fig. 5), while the corresponding polysulfonamide I started to decompose at about 200°C. On purely chemical and resonance considerations, it is anticipated that the phenol model compound will be more stable and should be obtained in higher yields.

Polycondensation Products

Polysulfonamide I

The reaction of IBSC with *p*-phenylenediamine gave polymeric products only when a tertiary amine was employed as an acid acceptor. Compounds with

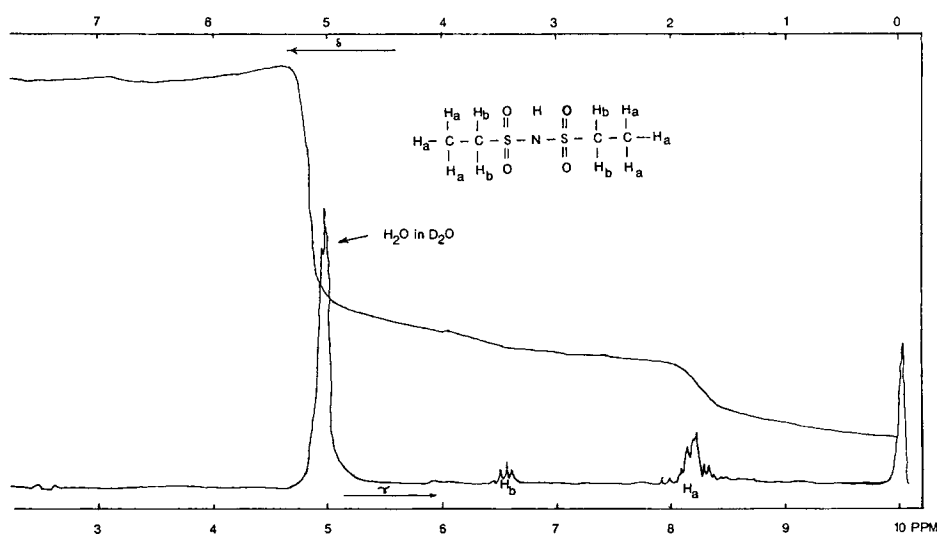


Fig. 4. NMR spectrum of the ethyl alcohol. Solvent: D₂O 98%; conc., 10%; ref. std., TMS. R.F. field, 60 MHz; field shift, 541; scale, 10 PPM; sensitivity, 4; filter sweep time, 18.

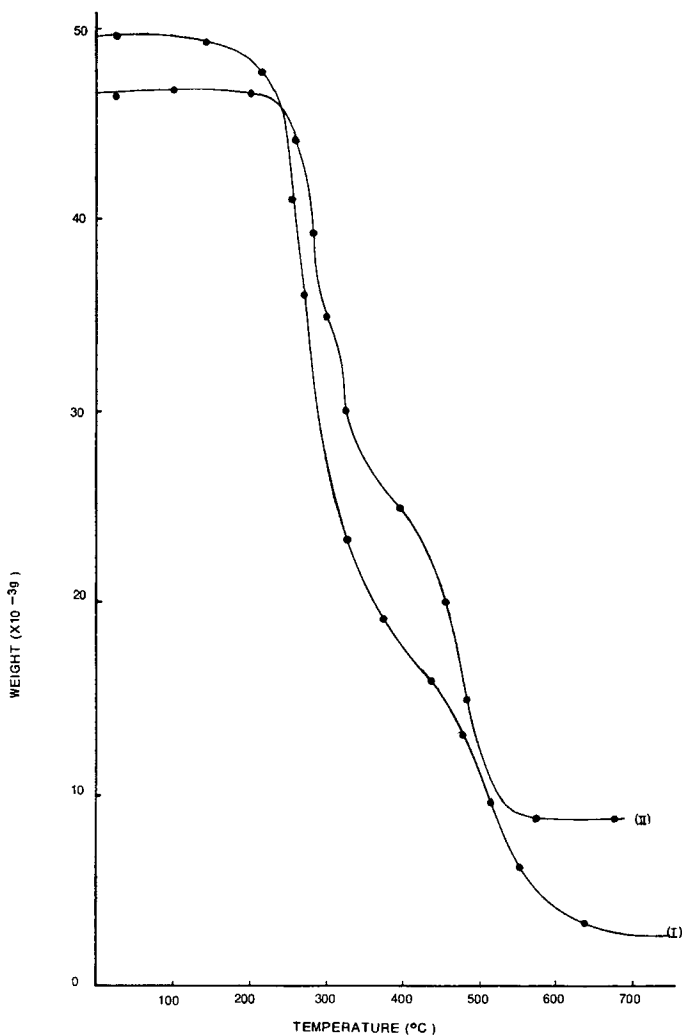
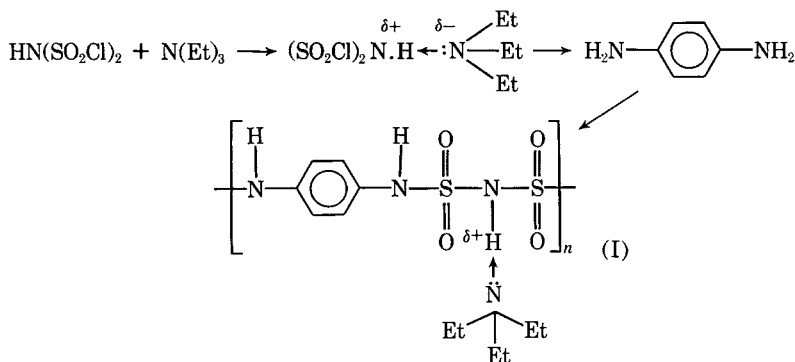


Fig. 5. Thermogravimetric analysis plot of products: I and II.

acid-accepting properties such as NaHCO_3 , $\text{Ca}(\text{OH})_2$, and excess diamine were found to be unsuitable for the purpose of obtaining polymeric materials.

The need for a solvent which can solvate both reactants and products was apparent. Solvents such as dimethyl sulfoxide, dimethylacetamide, *N*-methylpyrrolidone, and dimethylformamide were found unsuitable due to the high reactivity of IBSC. It is thought that the latter is due to the highly acidic nature of the imido proton and that potassium-substituted derivatives⁴ may not cause any major problems in the selection of a suitable solvent system. *o*-Dichlorobenzene was found to be the best solvent for the polycondensations. Chlorinated hydrocarbons were of little value because of the formation of $-\text{SO}_2\text{Cl}$ -terminated products due primarily to the low solvating power of these solvents.

The prepared polysulfonamide was structurally identified as I, and the following reaction sequence attempts to describe the mechanism:



Calculations for the repeating unit show good agreement with the microanalytical data.

The infrared spectrum (Fig. 6) can be interpreted using similar arguments as those put forward for the formation of the aniline model compound. Additional evidence supporting the suggested reaction sequence is given by the NMR spectrum of the product (see Fig. 7). The spectrum shown is self-explanatory and provides clear evidence that the proposed adduct has been formed. The DSC trace for the polysulfonamide I showed an endothermic transition at 89°C. This temperature corresponds to that observed as a softening point during hot stage microscopy studies of the material. It is therefore reasonable to consider that this temperature is the glass transition temperature. The polymeric nature of the compound cannot be supported on the grounds of the above transition alone. Additional evidence is provided from the inherent viscosity in dimethyl sulfoxide ($\eta_{\text{inh}} = 0.182$) although this is rather low.

The low inherent viscosity value may be explained on structural grounds, quite apart from the fact that the degree of polymerization is low. The proposed structure contains a sequence of —C—S—N—S—N—C— bonds which pre-

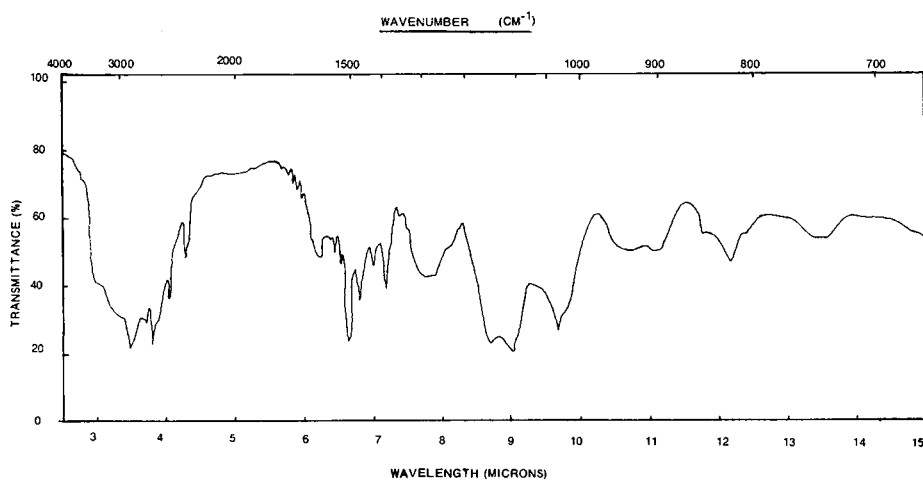


Fig. 6. Infrared spectrum of product I (KBr disc).

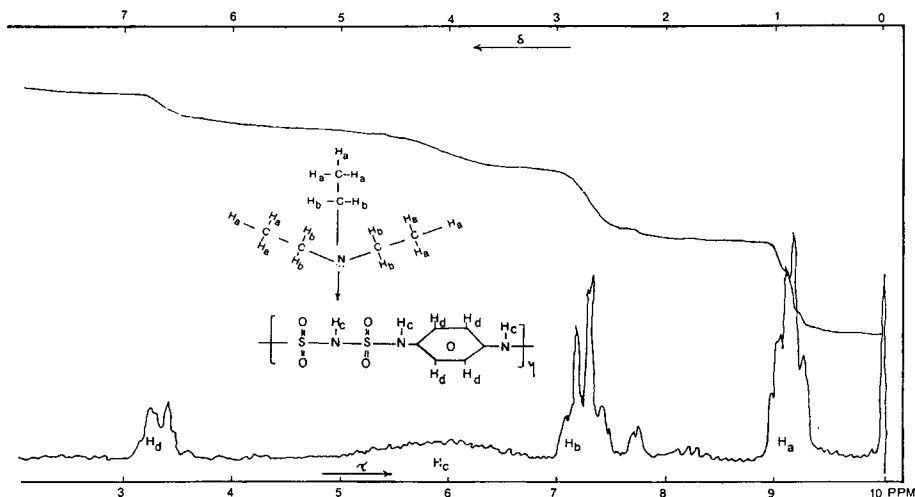


Fig. 7. NMR spectrum of product I, showing the adduct formation between triethylamine and the acidic proton on the IBSC residue. Solvent: DMSO d_6 ; conc., 20%; ref. std., TMS. R.F. field, 60 MHz; field shift, 501; scale, 10 PPM; sensitivity, 8; filter, 4; sweep time, 18.

sumably confers considerable backbone flexibility to the chain with a consequent lowering of inherent viscosity values.

The thermogravimetric analysis plots obtained for I at a heating rate of $125^\circ\text{C}/\text{h}$ showed the sigmoidal trace characteristic for many polymeric materials; the onset of decomposition was at about 200°C .

Hot stage microscopy enabled one to observe the separation of a crystalline material from the melt of product I. The crystals formed are apparently a reaction product between the main chain and the triethylamine residue with the formation of a quaternary ammonium salt of a crystalline nature. One may conclude that such a reaction may lower the thermal stability of the compound and that higher thermal stabilities may be expected for products which do not involve tertiary amine adducts in their structure. The molten product was,

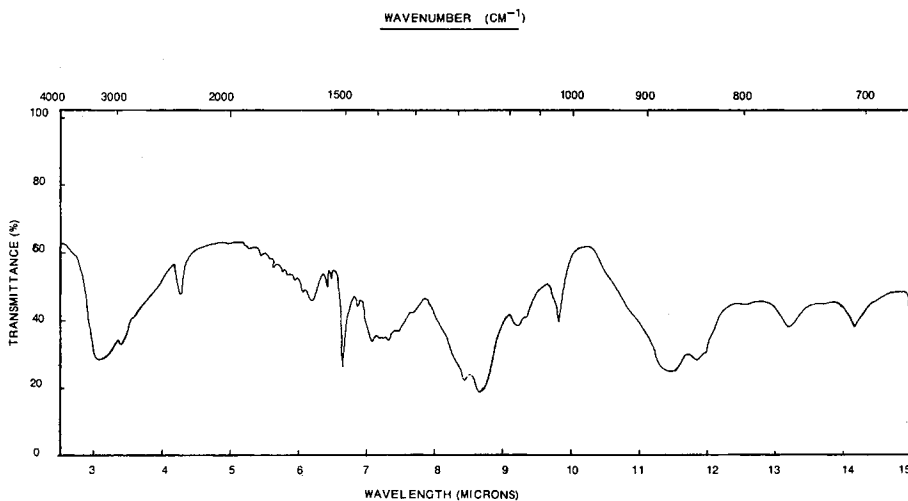
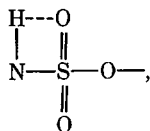


Fig. 8. Infrared spectrum of product II (KBr disc).

however, found to behave as a thermoplastic and long (though weak) fibers could be drawn.

Polysulfonate Ester II

The reaction product of IBSC and 2,2-bis(4-hydroxyphenyl)propane is thought to be a low-molecular-weight polysulfonate ester of repeating unit II. The microanalytical data obtained for this compound were in agreement with the proposed repeating unit although the carbon values were some 1.6% low. This may be due to end group error contributions which can be significant in polymeric compounds of low molecular weight. The infrared spectrum of II (Fig. 8) shows a series of broad bands which may be due to residual solvent and to the amorphous and polymeric nature of the sample. The broadening of the band centered at 3000 cm^{-1} may be assigned to a combination of two vibrations, namely $V(\text{N-H})$ str. (expected at 3000 cm^{-1}) and aromatic (C-H) str. (expected at 3030 cm^{-1}). Intramolecular hydrogen bonding



may also significantly contribute to this broadening. The medium-sized absorption at 1080 cm^{-1} has been attributed to a $V(\text{C-O})$ vibration expected at this wavelength. The doublet for the isopropyl part of the molecule expected at $1390\text{--}1360\text{ cm}^{-1}$ has in fact been found within the broad band centered at 1360 cm^{-1} . Furthermore, absorptions due to SO_2 and S-N may similarly be assigned (see the aniline model compound). The NMR spectrum of product II (Fig. 9) strongly supports the structure of the proposed repeating unit. Once again the presence of H_2O in the D_2O gave rise to a peak at 4.7δ . The presence of the two water spinning side bands is apparent, and this is accompanied by a phase change of the spectrum line. The absorption at 1.1δ is typical of methylic and that at

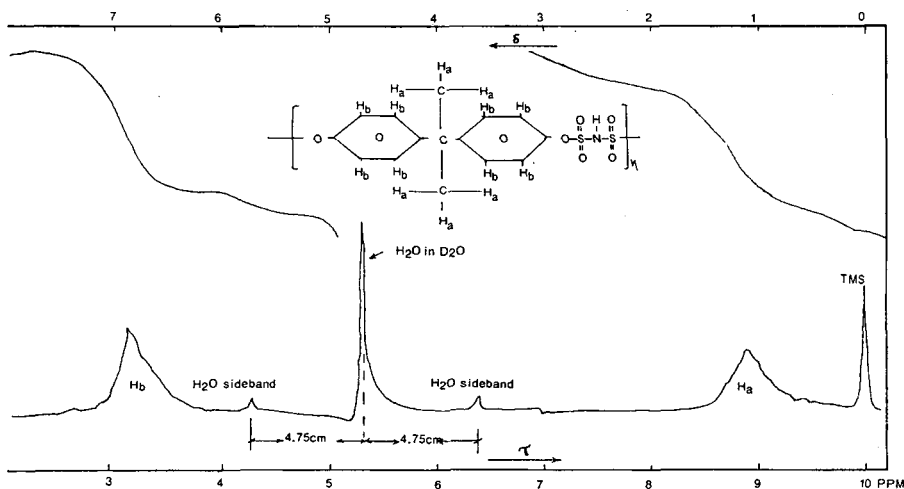
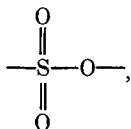


Fig. 9. NMR spectrum of product II. Solvent: D_{20} 98%; conc., 28%; ref. std., TMS. R.F. field, 60 MHz; field shift, 541; scale, 10 PPM; sensitivity, 4; filter, 4; sweep time, 18.

6.75 δ of aromatic protons. The ratio of the integrals for these absorptions is close to 6/8 within the allowed $\pm 2\%$ error.

Solution viscometry in acetone at 0.1% concentration gave an inherent viscosity of 0.153. This low value once again indicates that the chains are short, although chain flexibility also tends to reduce the viscosity.

Thermogravimetric analysis indicated the onset of decomposition at 220°C; above this temperature the compound lost weight and followed a sigmoidal trace. The water solubility of II may be explained on the basis of the polar interactions between



N—H δ^+ groups,

and water molecules as well as on the basis of its esteric nature.

Conix and Laridon⁷ prepared polysulfonates from aromatic diacid chlorides and bisphenols quoting crystalline melting points. Photomicrographs of the slowly cooled melt of product II show no signs of crystallinity.

SUMMARY

The reactivity of IBSC toward compounds containing aminic and hydroxylic protons was demonstrated by isolating the corresponding model compounds, i.e., imidobis(sulfanilide) and imidobis(ethyl sulfonate). The high reactivity of IBSC presented considerable problems in solvent and acid acceptor selection. Aromatic hydrocarbons were found to be suitable solvent media for the polycondensation reactions. Triethylamine and tribenzylamine were suitable acid acceptors. Due to the high acidity of its imido proton, IBSC forms adducts with the Lewis bases (e.g., triethylamine) that were used in the polycondensations.

It is of considerable interest that polymeric products could be obtained at all. These were of low molecular weight, but the aromatic polysulfonamide and the polysulfonate ester did exhibit fiber-forming properties and were stable up to 200 and 220°C, respectively. No commercial outlets for the polymeric products are envisaged at this stage, but the present study provides information about the chemistry of the process and the structures and properties of the compounds obtained.

References

1. M. Becke-Goehring et al., *Inorganic Synthesis*, Vol. VIII, 1966, p. 105.
2. P. Morgan and S. Kwolek, *J. Polym. Sci., Part A-2*, **181**, 2001 (1964).
3. R. C. Paul et al. *Indian J. Chem.*, **13**, 619, 1184 (1975).
4. R. C. Paul et al., *J. Inorg. Nuclear Chem.*, **39**, 441, (1977); **40**, 2001, 2005 (1978).
5. A. Vogel, *Textbook of Practical Organic Chemistry*, 4th ed. Longman's, London, 19xx.
6. W. Kemp, *Organic Spectroscopy*, 1st ed., Macmillan, New York, 1975, pp. 40–52.
7. A. J. Conix and C. L. Laridon, *Angew. Chem.*, **72**, 116, 272 (1960).

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