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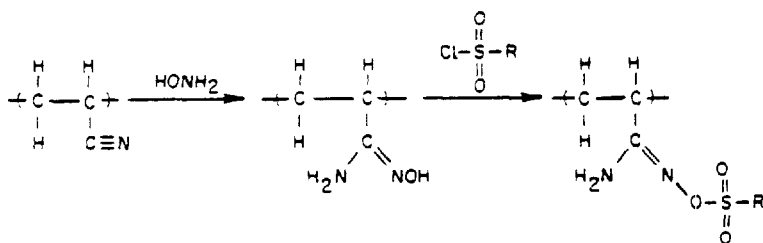
## Synthesis of Poly(-O-acylsulfonylamideoxides) from Poly(acrylonitrile)\*

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### ABSTRACT

Poly(-O-acylsulfonylamideoximes) were synthesized via the modification of poly(acrylonitrile):



Inclusion of the sulfonyl moiety is in the medium to high range. Reaction is believed to occur largely at the N-OH site and not at both the N-OH and  $\text{NH}_2$  in the same amideoxime unit.

\*Given in part at the 162nd Meeting of the American Chemical Society, Washington, D.C., September, 1971.

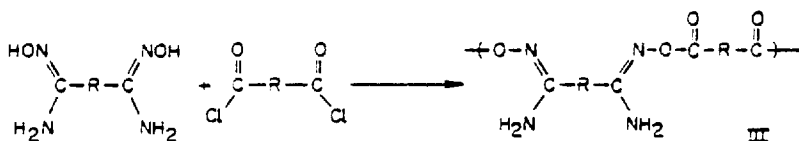
†Portions taken from the thesis of L.-S. Wang. Present address: Formosan Rubber Company, Taiwan.

## 1. INTRODUCTION

We have recently been interested in the modification of commercially available polymers [1-4]. Much of our work is based on the assumption that pendant groups on polymer chains present the same general chemical reactivity as identical groups residing in smaller molecules. In addition we have observed the similarity between (Lewis acid-base) reactions with organic acid chlorides (of Form I) and other acid chlorides such as sulfonyl acid chlorides (of Form II).



Bloomstrom [5] and Donaruma [6] reported the synthesis of poly(-O-acylamideoximes) of the form below.

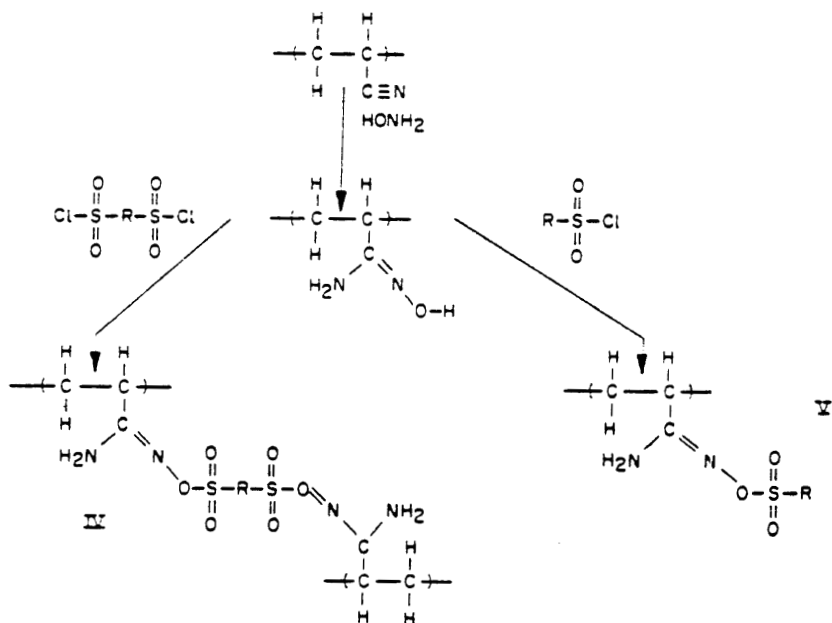


We believed that an analogous reaction should be possible via reaction at pendant amideoxime groups in a polymer chain as illustrated below. We wish to report this modification utilizing poly(acrylonitrile) which was subsequently converted to poly(acrylamideoxime).

The modification of commercial polymers is an area of active interest because of the possibility of effecting a desired modification or gross change in the chemical and/or physical properties of the polymer. This area has been capably reviewed [7] including studies involving poly(acrylonitrile).

## 2. EXPERIMENTAL

Poly(acrylonitrile) was prepared using a slurry method as described in Ref. 8. It had a limiting viscosity number of 8.20 (dl/g) in dimethyl formamide which corresponds to a  $\bar{M}_w$  of  $1.1 \times 10^5$  as determined by light-scattering photometry in dimethyl formamide.



Poly(acrylonitrile) was converted to poly(acrylamideoxime) via reaction at the nitrile with hydroxylamine. The procedure given by Sorenson and Campbell was initially used [8]. This procedure yielded a product which did exhibit detectable nitrile bands at  $2250\text{ cm}^{-1}$  in the IR region. The following procedure was then used to give a product which did not exhibit an IR detectable nitrile band at  $2250\text{ cm}^{-1}$ .

A solution of 50 g of poly(acrylonitrile) in 500 ml of dimethyl formamide was added to a 1-liter three-necked flask equipped with a thermometer, condenser, and mechanical stirrer. The reaction mixture was brought to  $75^\circ\text{C}$  using an external water bath. Hydroxylamine hydrochloride (105 g) and 75 g of anhydrous pulverized sodium carbonate were added to the flask and the resulting mixture stirred (with heating) for 3 hr. At the end of this time the polymer solution was filtered to remove insoluble salts. The filtrate was added to 1 liter of methanol to bring about precipitation of the product. The polymer was washed with portions of methanol and dried. The yield of product was quantitative.

Synthesis of sulfur containing poly(-O-acylamideoximes) was accomplished using the interfacial technique. Briefly, an aqueous solution of poly(acrylamideoxime) containing sodium hydroxide

[equal in molar amount to the theoretical molar amount of potential (HCl)] was added to a rapidly stirred solution composed of a solvent which is immiscible with the water containing the acid halide. The products precipitated from the reaction mixture. They were separated by suction filtration and washed repeatedly with portions of water. They were then dried and weighed. The products are white, generally, "glassy-like" in texture. Reaction was effected in a 1-pint Kimex Emulsifying Jar fitted on top a Waring Blender. A fuller description of the equipment is given elsewhere [9].

Amounts of sulfur moieties included in the products were determined for some of the products (Table 1). The aqueous phase (combined with the wash water) was evaporated using vacuum. Water was added to the solid dissolving the salt, unreacted NaOH, and hydrolyzed acid chloride but not the poly(acrylamideoxime) which takes several hours to go into solution. The mixture was filtered and the solid (unreacted polymer) weighed. From knowledge of the unreacted polymer, the amount of sulfur moiety incorporated in the products was calculated. An independent determination of the inclusion of the sulfur moiety included in the product was made by hydrolyzing the acid chloride and determining the amount of unreacted acid chloride. This value was in good agreement with the values reported in Table 1.

Softening ranges were determined utilizing a Fisher-Johns Melting Point Apparatus at a heating rate of about 5°C/min. Most of the products did not melt but changed color over the experimental range (27 to 300°C). The temperature at which change in color began is recorded in Table 1 under the heading "Color change temperature."

IR spectra were obtained utilizing KBr pellets for solids and liquids on a Beckman 237-B spectrophotometer as described elsewhere [10]. The spectra are in agreement with the inclusion of the sulfonyl moiety. Representative spectra appear in Figs. 1 to 4.

The products are generally white to light tan in color and tacky to powdery after isolation. Some form tough, flexible films when dried.

### 3. DISCUSSION AND RESULTS

The synthesis of sulfur containing poly(-O-acrylamideoximes) appears to be general (Table 1). Monochlorosulfur containing reactants produce linear products which exhibit solubility in such solvents as formic acid but is insoluble in such solvents as acetone, chloroform, carbon tetrachloride, hexane, benzene, water and 2-bromoethanol. It also dissolves in concentrated H<sub>2</sub>SO<sub>4</sub> but presently there is a question as to whether the products undergo degradation

TABLE I. Product Properties as a Function of Sulfur Reactant<sup>a</sup>

| Sulfur reactant                 | Yield<br>(20 sec<br>reaction time) | % Inclusion<br>of sulfur<br>reactant <sup>b</sup> | Color change<br>temperature<br>(°C) |
|---------------------------------|------------------------------------|---|-------------------------------------|
| p-Toluenesulfonyl chloride      | 72 <sup>c,d</sup>                  | 48  | 180                                 |
| Methanesulfonyl chloride        | 76                                 |   | 170                                 |
| Benzenesulfonyl chloride        | 67                                 | 54  | 160                                 |
| p-Bromobenzenesulfonyl chloride | 64                                 | 39  | 175                                 |
| Thionyl chloride                | 30                                 |   | 170                                 |

<sup>a</sup> Reaction conditions: The acid chloride (0.0025 mole) in 50 ml chloroform is added to stirred solutions of poly(acrylamdeoxime) (0.0025 mole) in 50 ml of water with added sodium hydroxide (0.0025 mole) at 27°C and 17,500 rpm (no load).

<sup>b</sup> Based on reactions run for 20 sec stirring time.  
<sup>c</sup> Yield increased to 75% when amount of p-toluenesulfonyl chloride was increased twofold.  
<sup>d</sup> Yield increased to 80% when amount of p-toluenesulfonyl chloride was increased threefold.

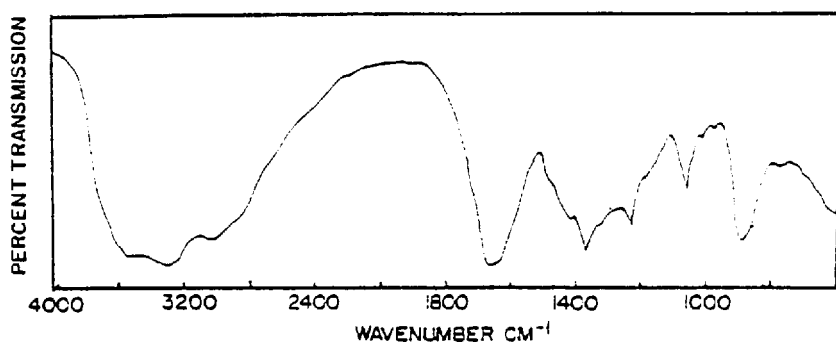


FIG. 1. IR spectrum of poly(acrylamideoxime).

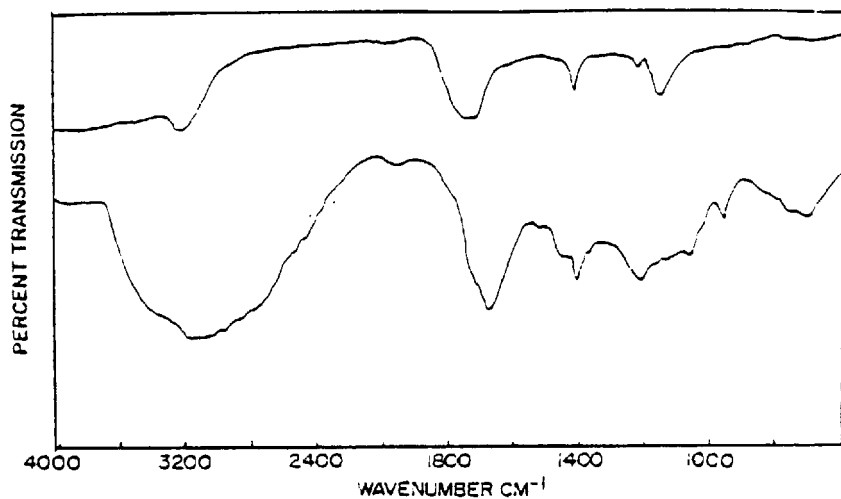


FIG. 2. IR spectra of (top) *p*-toluenesulfonyl chloride and (bottom) condensation product of poly(acrylamideoxime) and *p*-toluenesulfonyl chloride.

in this solvent. Dichlorosulfur reactants produce cross-linked products which exhibit insolubility in all solvents tried.

Previous polycondensations with acid chlorides (of Form III) were reported to occur at the N—OH rather than the NH<sub>2</sub> group [4, 5]. In the present situation we have not been able to differentiate between

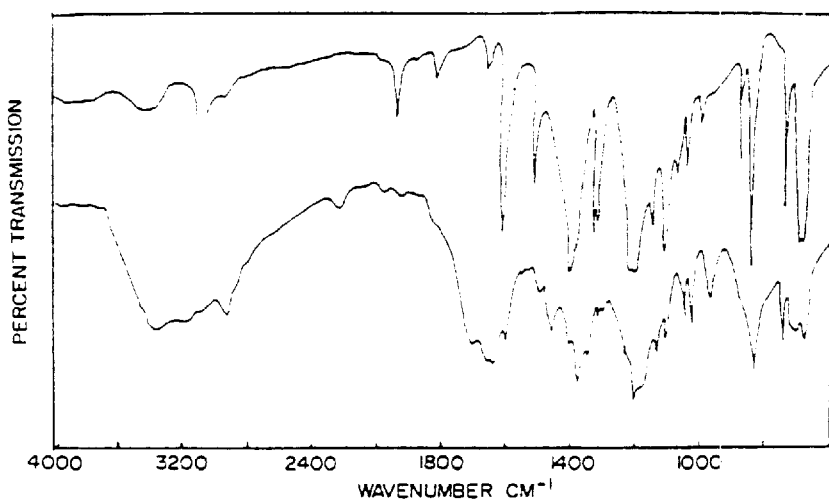


FIG. 3. IR spectra of (top) p-bromobenzenesulfonyl chloride and (bottom) condensation product of poly(acrylamideoxime) and p-bromobenzenesulfonyl chloride.

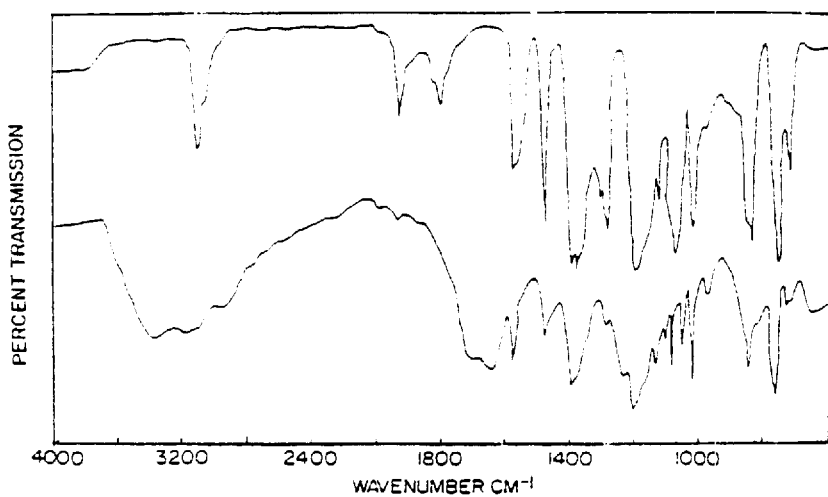
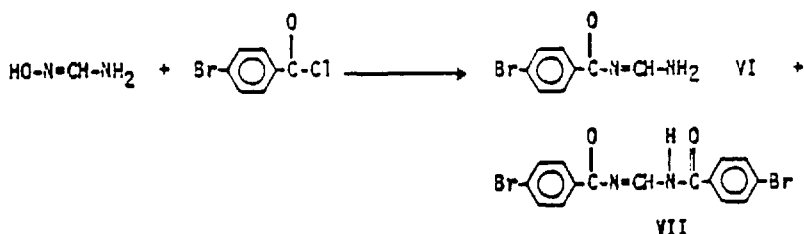


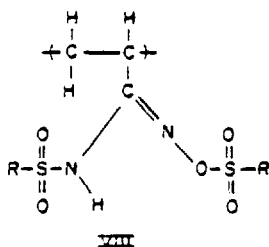
FIG. 4. IR spectra of (top) thionyl chloride and (bottom) condensation product of poly(acrylamideoxime) and thionyl chloride.



reactions at either site. The poor solubility properties have made it difficult to conduct NMR studies of the products. At least two definite possibilities exist. First, reaction occurs at the  $\text{NH}_2$  and NOH group, but not both at the same amideoxime group. The interfacial reaction of diamines with sulfonyl chlorides is well known [11-13] and reaction could occur at the  $\text{NH}_2$  as well as the NOH group. Eloy and co-workers [14] reported the formation of both acylated products in the study of acyl derivatives of formamideoxime. Under one set of reaction conditions the ratio of VI/VII was about 3/1. Thus it is proper to consider that the products contain a mixture of NOH and  $\text{NH}_2$  products.



The second possibility is that reaction occurs at both the NOH and  $\text{NH}_2$  in the same unit as described by Form VIII. A model of VIII was



constructed using Fisher-Hirschfelder-Taylor models where  $\text{R} = \text{CH}_3$ . A large amount of steric hindrance was found to be predicted from the model. The importance of products of Form VIII is believed to be (via experiment) unimportant since even a threefold increase in the amount of *p*-toluenesulfonyl chloride results in a yield of less than 100% based on a theoretical yield assuming monoreaction at any single amideoxime group\* (Table 1). Also per cent inclusion of sulfur reactants is not in any case significantly greater than 50 mole %. (An inclusion of one

\*Because of the poor and limited solubility of the products, such useful techniques as NMR were not of use in differentiating between possible structures.

sulfur moiety per repeating amideoxime unit would give a 50% sulfur moiety inclusion value.)

There appears to be a fair to good inclusion of the sulfur moiety in the polymer as indicated by the fair to high inclusion values experimentally determined. This, along with the fair to high yield of products, attests to the great reactivity between the amideoxime and sulfur acid chlorides.

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