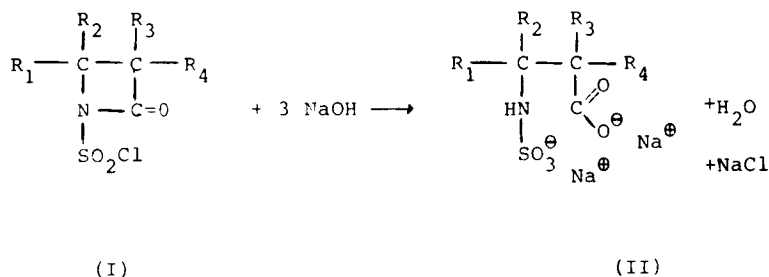


**POLYELECTROLYTES OBTAINED BY REACTION OF
β-LACTAM-N-SULFONYLCHLORIDE GROUPS
WITH AQUEOUS AMMONIA**

The reaction between $R_1R_2C=C R_3R_4$ and N-chlorosulfonyl isocyanate, resulting in a β-lactam-N-sulfonylchloride has been studied in the past for small molecules (1-3) as well as for unsaturated polymers (4-6). For polyisoprene it has been shown (4) that the addition product, containing β-lactam-N-sulfonylchloride groups, reacts with NaOH at 100-110°C to form a polyelectrolyte, according to the following scheme:



This reaction does not proceed at room temperature. Graf (1,2) studied the reaction between low molecular weight derivatives (I) and organic bases like aniline and p-chloroaniline at room temperature. The uncharged reaction products had as a general formula structure D (Fig. 2), with $-NR_5R_6$ instead of $-NH_2$.

In none of these investigations has the reaction of (I) with aqueous ammonia been reported. The use of ammonia offers the possibility of a reaction with NH_3 as well as with OH^- . We investigated therefore this reaction with the addition products of styrene, polyisoprene, and a styrene-isoprene block copolymer (S-I-S) with N-chlorosulfonyl isocyanate.

Experimental

We prepared (I) from cis-1,4-polyisoprene (Cariflex IR 307), according to Van der Does, Hofman, and Van Utteren (4). This polymer was treated with aqueous ammonia (in a range of 0.8 to 6.6 M) at room temperature (20°C) with stirring. Within about 1 hr a highly viscous solution developed, indicating the formation of an ionic reaction product. The polymer was isolated by evaporation of the water. In the infrared spectrum of this reaction product the very strong absorption from the $>C=O$ group in the lactam ring at 1810 cm^{-1} had disappeared (Figs. 1A-B).

There was a new absorption at 1655 cm^{-1} (Fig. 1B) which can be assigned to carbamoyl absorption.

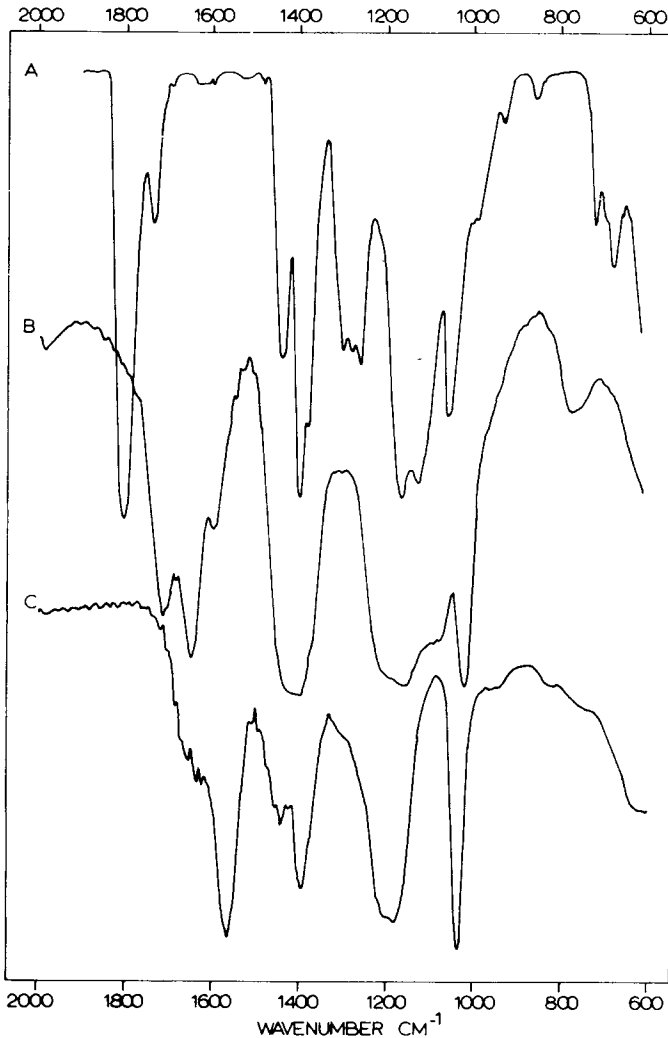


Fig. 1. Infrared spectra from the addition product of polyisoprene with N-chlorosulfonylisocyanate (A), its reaction product with ammonia at room temperature (B), and with NaOH at 100°C (C).

The structural units which can be present in the reaction product are shown in Figure 2. In Figure 1 the infrared spectrum of the polyisoprene analogue of (II) is also given (Fig. 1C).

In order to get more information on the reaction product we synthesized as a model compound 4-phenylazetidinone-2-N-sulfonylchloride (1,2). This compound (III) was reacted with aqueous ammonia (6.6 M) for 24 hr at room temperature.

After addition of an excess of a hydrogen chloride solution white crystals

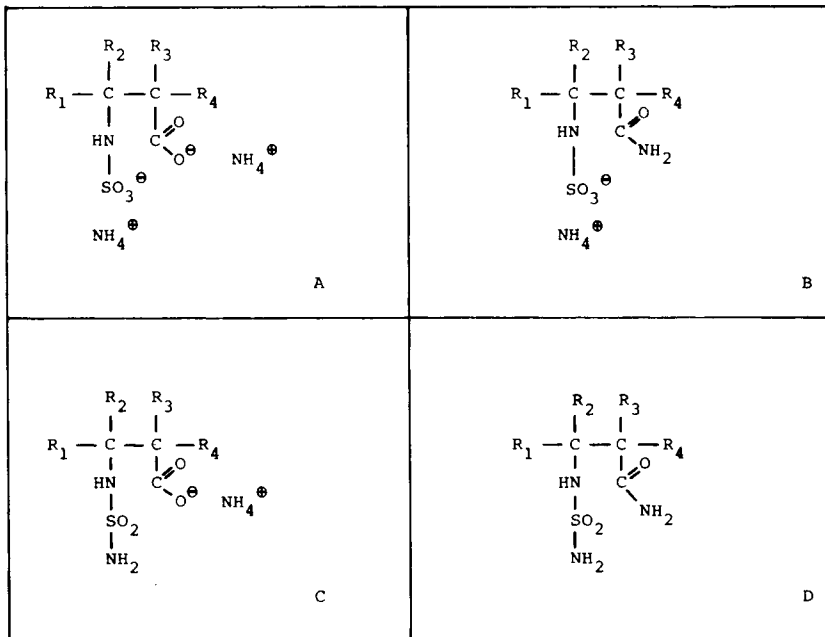
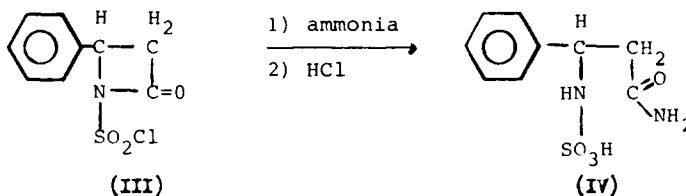


Fig. 2. Possible products of the reaction between ammonia and β -lactam-N-sulfonylchloride groups at room temperature.

appeared (IV). The absorption at 1655 cm^{-1} in the infrared spectrum of (IV) clearly indicates the presence of carbamoyl groups. After subtraction of NH_4Cl content the following elemental analysis was obtained:

C	H	N	O	S
44.33	5.11	11.93	25.54	13.09

which can be written as $\text{C}_{9.0}\text{H}_{12.4}\text{N}_{2.1}\text{O}_{3.9}\text{S}_{1.0}$. These results can be interpreted assuming the following reaction sequence:



The assumption that the crystals (IV) have the proposed structure was checked by titration. It was found that the yield of the ammonia reaction was about 95%. An equivalent weight of 249 was found (calc. 244).

From these results it seems reasonable to assume that in the polyisoprene ana-

TABLE I

Ion Exchange Capacities of SISS-57 Polymers Synthesized with Ammonia at Room Temperature

ammonia	time of hydrolysis	ion exchange capacity
(Mole/l)	(hours)	(meq/g dry polymer)
6.6	24	1.98
3.3	24	1.64

logue structure B (Fig. 2) is present. Hence the reaction with ammonia makes it possible to synthesize a polyelectrolyte from cis-1,4-polyisoprene at room temperature.

Since we were more interested in block copolymers with an ionic middle block, we continued our experiments with a S-I-S block copolymer (Cariflex TR 1108) with 29% polystyrene, which had been modified (6) to give the analogue of (I) and by reaction during 24 hr with aqueous ammonia to give the analogue of (IV) (SISS-X); X is the molar ratio N-chlorosulfonyl isocyanate/isoprene in percentages.

Ion exchange capacities were determined by the following procedure: A large excess of 2.0 N hydrogen chloride solution was passed through a column filled with SISS - 57 polymer. The excess acid was removed by washing, and afterwards the sodium salt was formed using 50 ml of 0.1 N NaOH solution. Finally the excess NaOH was titrated with 0.1 N HCl solution. The ion exchange capacities found are shown in Table I. The calculated ion exchange capacities for these polymers are: zero for structure D, 2.94 meq/g dry polymer for structures B and C, and 5.88 meq/g dry polymer for structure A. Infrared spectra of these polymers are in agreement with the preceding results.

Conclusions

The results from our experiments indicate a simultaneous reaction of the β -lactam-N-sulfonylchloride groups with NH_3 and OH^- . Contrary to similar reactions with NaOH, a polyelectrolyte can be synthesized at room temperature. From model studies on 4-phenylazetidinone-2-N-sulfonylchloride we conclude that during the reaction between a β -lactam-N-sulfonylchloride group and aqueous ammonia, a reaction product with structure B was formed.

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