

## Polymers with Pendant Isocyanate Groups. II. Dual Synthesis and Properties of Poly(acrylonitrile-co-Styryl Isocyanate)

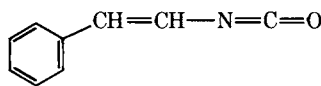
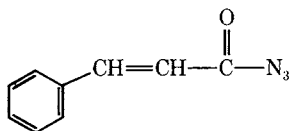
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### Synopsis

The copolymer poly(acrylonitrile-co-styryl isocyanate) was prepared directly in bulk by radical initiation either from the monomer pair acrylonitrile-cinnamoyl azide or from the pair acrylonitrile-styryl isocyanate. The copolymerization parameters, calculated by the conventional scheme, are  $r_1 = 3.5 \pm 0.5$ ;  $r_2 = 0 \pm 0.5$ , for the first pair and  $r_1 = 9 \pm 0.5$ ;  $r_2 = 0 \pm 0.5$  for the second pair. The basic physical properties (solubility, intrinsic viscosity, and thermal behavior) of the new copolymer were determined and the chemical reactions of the isocyanate group with alcohol and with dimethylformamide were investigated.

### INTRODUCTION

In the preceding paper,<sup>1</sup> after giving a short survey on the vinylhomopolymerization and copolymerization of vinyl monomers containing an isocyanate group, we reported the dual synthesis of poly(styrene-co-styryl isocyanate). Now, we wish to report the dual synthesis of poly(acrylonitrile-co-styryl isocyanate) which, similarly as with styrene, was obtained from the copolymerization of acrylonitrile (AN) with either cinnamoyl azide (CA) or with styryl isocyanate (SI):



### EXPERIMENTAL

#### Materials and Preparation of Monomers

Acrylonitrile<sup>2</sup> and the initiator  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN)<sup>1</sup> were purified as described before. Details on the syntheses of the comonomers cinnamoyl azide and styryl isocyanate are given in the preceding paper.<sup>1</sup>

TABLE I  
Copolymerization in Bulk of Acrylonitrile ( $M_1$ ) and Cinnamoyl Azide ( $M_2$ )

Experi- ment no.	$M_1$ , mole fraction of monomer 1	Time of polym- erization, min	Conver- sion, %	Nitrogen content, %	$m_1$ , mole fraction in copolymer	$[\eta]$ , dl/g	$T_g$ , °C, specimen pressed at room temp.
53/0	1.000	17	7.3	26.20	1.000	7.0	90
53/1	0.965	17	6.5	26.02	0.991	6.5	87
53/2	0.950	17	5.2	25.97	0.990		87
53/3	0.932	17	2.2	25.58	0.981	4.8	92
53/4	0.898	17	1.6	25.30	0.974		94
53/5	0.878	17	1.35	24.90	0.965		94
53/8	0.836	40	0.8	24.33	0.950		

### Copolymerization

The copolymerizations were carried out at 60°C as described before<sup>3</sup>; the reaction tubes contained, for both systems, acrylonitrile-CA or acrylonitrile-SI,  $M_1 + M_2 = 0.065$  mole, and 0.14 mole-% AIBN.

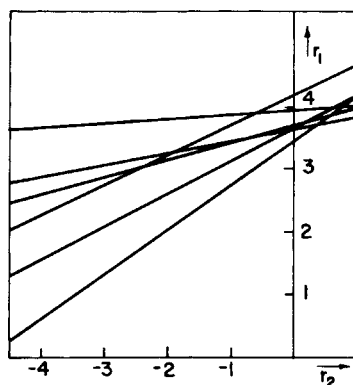


Fig. 1. Copolymerization of acrylonitrile ( $M_1$ ) with cinnamoyl azide ( $M_2$ ). Determination of  $r_1$  and  $r_2$ .

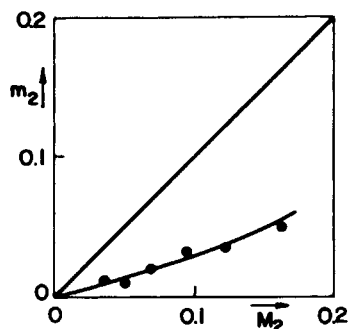


Fig. 2. Copolymerization of acrylonitrile ( $M_1$ ) with cinnamoyl azide ( $M_2$ ). Initial copolymer composition vs. composition of monomer feed.

TABLE II  
Copolymerization in Bulk of Acrylonitrile ( $M_1$ ) and Styryl Isocyanate ( $M_2$ )

Experi- ment no.	$M_1$ , mole fraction of monomer 1	Time of polym- erization, min	Conver- sion, %	Nitrogen content, %	$m_1$ , mole fraction in copolymer
77/1	0.839	15	6.2	25.43	0.978
77/2	0.777	15	4.4	25.0	0.967
77/3	0.674	15	3.1	24.0	0.942
77/4	0.626	15	3.5	24.2	0.947
77/5	0.847	15	5.3	24.4	0.952

The weighing in of the starting mixture of the pair acrylonitrile-SI and the working up of the solid products from both monomer pairs were carried out in a dry-box. The polymerizations were stopped by transferring the reaction tubes into a cooling bath of Dry Ice in acetone ( $-78^\circ\text{C}$ ). Then the tubes were opened and the copolymer, which is insoluble in the monomer mixture, was

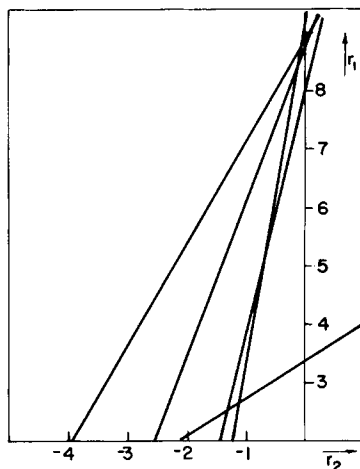


Fig. 3. Copolymerization of acrylonitrile ( $M_1$ ) with styryl isocyanate ( $M_2$ ). Determination of  $r_1$  and  $r_2$ .

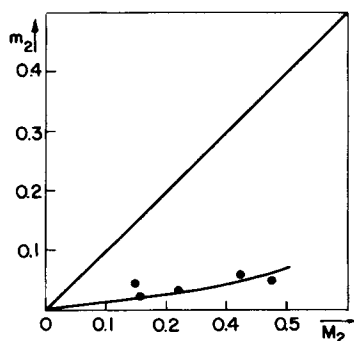


Fig. 4. Copolymerization of acrylonitrile ( $M_1$ ) with styryl isocyanate ( $M_2$ ). Initial copolymer composition vs. composition of monomer feed.

filtered off. The reaction products were purified by washing with several portions of dry benzene and drying at  $\sim 80^\circ\text{C}/0.1$  mm Hg.

The copolymers were obtained as white powders. Their compositions were calculated from the elemental analysis of their nitrogen contents.

Details on the reaction conditions and results for the copolymerization of the pair acrylonitrile-cinnamoyl azide are summarized in Table I and in Figures 1 and 2 and for the pair acrylonitrile-styryl isocyanate in Table II and in Figures 3 and 4.

### Physical Test Methods

The infrared analyses, melting range, glass transition temperature, and thermogravimetric analyses were determined as described in the preceding paper.<sup>1</sup> The intrinsic viscosity of the copolymers was obtained from viscosity measurements of their DMF solutions in an Ubbelohde viscometer at  $25 \pm 0.05^\circ\text{C}$  (see "Reaction with Dimethylformamide" and "Discussion").

### Chemical Reactions

**Reaction with Ethanol.** By dispersing the copolymer in ethanol even at room temperature, part of the isocyanate groups react to form carbamate groups, as confirmed by infrared spectra (Fig. 6), showing the appearance of the carbamate absorption at  $1740\text{ cm}^{-1}$  and the simultaneous weakening of the isocyanate band at  $2260\text{ cm}^{-1}$  (compare Fig. 5).

**Reaction with Dimethylformamide.** The copolymer was dissolved in dimethylformamide at room temperature. After evaporation of the solvent at  $80^\circ\text{C}/0.1$  mm Hg, a film was obtained whose infrared spectrum shows three new absorption bands at  $1670\text{ cm}^{-1}$ ,  $1390\text{ cm}^{-1}$ , and  $1100\text{ cm}^{-1}$ , while the absorption band of the isocyanate group at  $2260\text{ cm}^{-1}$  has disappeared (Fig. 7). Identical spectra were obtained by precipitating the copolymer from its solution in DMF with methanol.

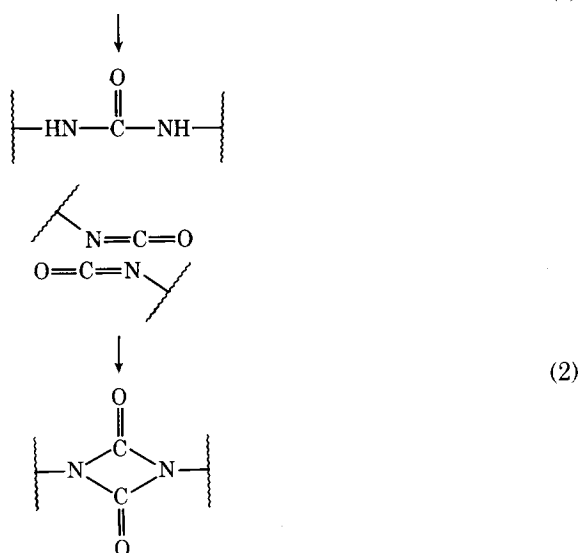
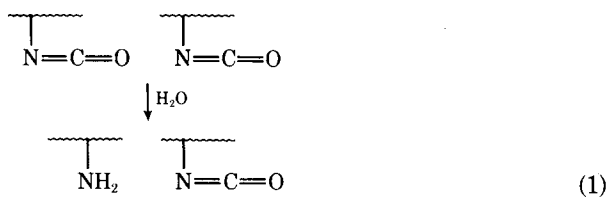
### DISCUSSION

Similar to the copolymer poly(styrene-co-styryl isocyanate),<sup>1</sup> also the copolymer poly(acrylonitrile-co-styryl isocyanate) was obtained from two different starting systems, i.e., from the copolymerization of the pair acrylonitrile-cinnamoyl azide with rearrangement of the acyl azide to the isocyanate and also by copolymerization of the pair acrylonitrile-styryl isocyanate. The monomer reactivity ratios, determined by the graphic method, are  $r_1 = 3.5 \pm 0.5$  and  $r_2 = 0 \pm 0.5$  for the first pair (Fig. 1) and  $r_1 = 9 \pm 0.5$  and  $r_2 = 0 \pm 0.5$  for the second one (Fig. 3). Like in the copolymerization with styrene, cinnamoyl azide reacts also with acrylonitrile more readily than styryl isocyanate, yet both comonomers copolymerize rather reluctantly with acrylonitrile and enter only to a small extent into the copolymer (Figs. 2 and 4). Also here, as in previously reported copolymerizations of acrylonitrile with  $\alpha,\beta$ -disubstituted<sup>2</sup> and  $\alpha,\beta,\beta'$ -trisubstituted<sup>2,4</sup> vinyl monomers, the rate is reduced by steric hindrance of both comonomers and further by giving resonance-stabilized radicals after being attacked by a free radical. Identical in-

frared spectra were obtained for the copolymers, prepared from either comonomer pair. There appears one wider absorption band which is composed of the absorption bands of the nitrile and of the isocyanate group at  $2240\text{ cm}^{-1}$  and at  $2260\text{ cm}^{-1}$ , respectively (Fig. 5). This fact was confirmed by the infrared spectra of the copolymer after reaction with alcohol (Fig. 6) or DMF (Fig. 7), where the isocyanate absorption at  $2260\text{ cm}^{-1}$  becomes weaker or it disappears at all, whereas the nitrile band at  $2240\text{ cm}^{-1}$  remains.

Regarding their thermal behavior, the copolymers melt with simultaneous degradation at about  $175^\circ\text{C}$ . The glass transition temperature and their thermal stability are quite similar to those of polyacrylonitrile.

The obtained copolymers are very sensitive to humidity and tend to cross-link quite readily. According to Butler and Monroe,<sup>5</sup> crosslinking can be due to two possible ways. One possibility is by hydrolysis of part of the isocyanate groups to amines, which by reaction with the residual isocyanate groups form disubstituted ureas.<sup>1</sup> Reaction between two isocyanate groups is the second way to obtain crosslinking<sup>2</sup>:



In our case, the formation of a disubstituted urea seems to be the main cross-linking reaction, as shown by the typical absorption at  $1650\text{ cm}^{-1}$  in the infrared spectrum,<sup>5</sup> whereas the absorption for the isocyanate dimer between  $1800$  and  $1700\text{ cm}^{-1}$  is hardly detectable<sup>6</sup> (Fig. 8). Regarding the reaction with ethanol, the carbamate formation was not complete, because the copolymer was in powder form and not in solution; and thus, in addition to the infrared absorption band of the carbamate group at  $1740\text{ cm}^{-1}$ , there remains also the now weaker band of the isocyanate group at  $2260\text{ cm}^{-1}$  (Fig. 6). The

high reactivity of the isocyanate in the acrylonitrile copolymer with water and alcohol is contrary to the behavior of the isocyanate group in the styrene copolymer, as described in the preceding paper.<sup>1</sup> This difference of the reactivity of the isocyanate group can be explained by the presence of the electron-withdrawing nitrile groups on the chain.

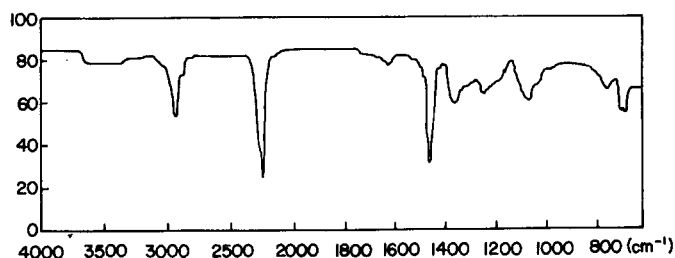


Fig. 5. Infrared spectrum of poly(acrylonitrile-co-styryl isocyanate) obtained from acrylonitrile ( $M_1$ ) with cinnamoyl azide ( $M_2$ ).

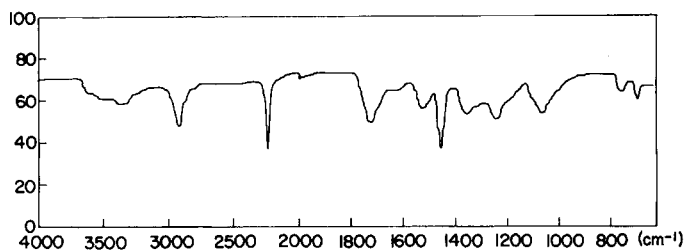


Fig. 6. Infrared spectrum of poly(acrylonitrile-co-styryl isocyanate) after reaction with ethanol.

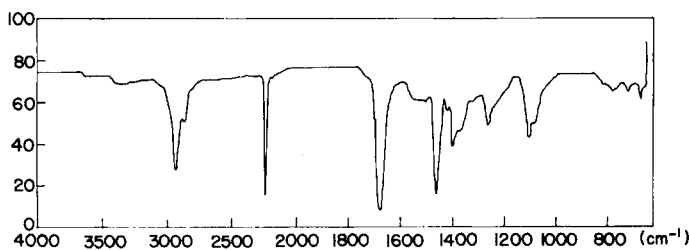


Fig. 7. Infrared spectrum of poly(acrylonitrile-co-styryl isocyanate) after reaction with dimethylformamide.

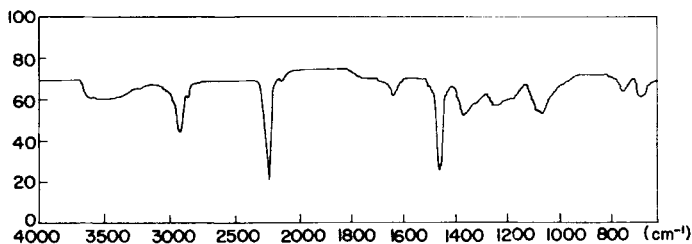
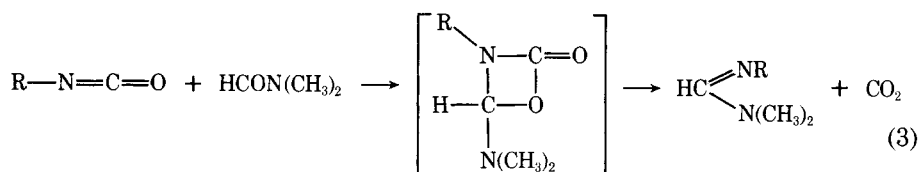
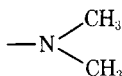


Fig. 8. Infrared spectrum of poly(acrylonitrile-co-styryl isocyanate) after reaction with water (humidity of air).

When the copolymer was dissolved in DMF, a different copolymer was recovered either by its precipitation after addition of methanol to the DMF solution or as film after evaporation of the DMF. Thus, contrary to the original poly(acrylonitrile-co-styryl isocyanate), the copolymers, obtained after dissolution in DMF, soften without decomposition and their melting range decreases with increasing isocyanate content in the original copolymer. Comparing the infrared spectra, there appear some striking changes in comparison to the original copolymer (Fig. 7). Thus, the absorption band of the isocyanate group at  $2260\text{ cm}^{-1}$  disappeared in all cases and three new absorptions at  $1670\text{ cm}^{-1}$ ,  $1390\text{ cm}^{-1}$ , and  $1100\text{ cm}^{-1}$  can be observed. As the solution of the original copolymers were carried out under dry conditions, the possibility of a chemical reaction of the isocyanate groups with the solvent dimethylformamide and the subsequent formation of an amidine reaction (3) as described by Weiner,<sup>7</sup> had to be considered,



where the absorption at  $1670\text{ cm}^{-1}$  belongs to the double bond  $>\text{C}=\text{N}-$ ,<sup>7,8</sup> whereas the other new absorption bands at  $1390\text{ cm}^{-1}$  and at  $1100\text{ cm}^{-1}$  belong to the



group.<sup>9</sup> This reaction between the isocyanate groups and DMF can also be ascribed to the activation of the isocyanate by the presence of the electron-withdrawing nitrile groups in the chain.

From the technological point of view, the introduction of the very reactive isocyanate groups into the polyacrylonitrile chain could facilitate its modification in order to improve fabrication behavior, dyeing properties, etc. Regarding dyeing, the formation of the basic amidine group by reaction with DMF should be of special interest. Consequently, the chemical behavior and the physical properties of the parent copolymers and of its various modifications are to be now further investigated.

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