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Aromatic Polyfluoronitroso Polymers

Joseph Green^{ab}; Nathan Mayes^a; Ernest Cottrill^a

^a Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey ^b Columbia Carbon Co., Princeton, N.J.

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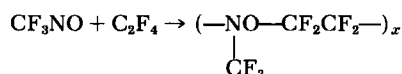
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LETTER TO THE EDITOR

Aromatic Polyfluoronitroso Polymers

The reaction of trifluoronitrosomethane and tetrafluoroethylene yields a 1:1 alternating copolymer referred to as nitroso rubber (1,2):



The copolymer gum can be cured only through the use of polyfunctional amines and the resultant products exhibit low tensile strength and lose their resistance to strong oxidizers. It is therefore of interest to prepare nitroso polymers that contain functional groups through which stable cross-links may be obtained. One means of doing this is through terpolymerization of polyfluoroaromatic nitroso compounds which may act as carriers of functional groups.

The copolymerization of trifluoronitrosomethane with tetrafluoroethylene has been studied extensively by Crawford et al. (2), and the reaction is postulated to take place via a free-radical mechanism. These workers also reported the preparation of terpolymers involving the reaction of various perfluoroaliphatic nitroso compounds with C_2F_4 and CF_3NO . We have prepared copolymers of C_2F_4 with pentafluoronitrosobenzene (I), 4-nitrosotetrafluorobromobenzene (II), and 4-nitrosotetrafluorobenzoic acid (III), as well as terpolymers of these aromatic compounds with CF_3NO and C_2F_4 . The aromatic nitroso monomers were prepared by the performic acid oxidation of the appropriately substituted anilines (3). The polymerization reactions were conducted in sealed tubes in bulk or in solution at -25°C for 24 hr. The resultant copolymers were hard resinous materials and the terpolymers were resilient rubbers. The results of some of these experiments are summarized in Table 1.

TABLE I

Solution Polymerization Studies with Polyfluoroaromatic Nitroso Compounds

X	Monomer feed ratio, moles			Conversion, %	Results
	<i>p</i> -XC ₆ F ₄ NO	CF ₃ NO	C ₂ F ₄		
F	1.0	—	1.0	50	Resin
Br	1.0	—	1.0	42	Resin
COOH	1.0	—	1.0	80	Resin
F	0.1	0.9	1.0	76	Rubber
Br	0.1	0.9	1.0	82	Rubber
COOH	0.1	0.9	1.0	80	Rubber

EXPERIMENTAL

Bulk Polymerization

A 7-ml Carius tube was charged with 0.22 g (0.0010 mole) of freshly prepared 4-nitrosotetrafluorobenzoic acid (III). The tube was evacuated and 0.89 g (0.0090 mole) of trifluoronitrosomethane and 1.00 g (0.010 mole) of tetrafluoroethylene were condensed in at -196°C from a calibrated vacuum system. After the tube was sealed under vacuum, it was shaken at -25°C for 24 hr. The tube was allowed to warm to room temperature and the resultant polymer plug was washed several times with acetone to remove unreacted monomer and dried overnight in a vacuum oven at 50°C . A yield of 1.7 g (80.5%) of a tan gum was obtained. A strong absorption at 1530 cm^{-1} in the infrared spectrum of the product indicated the presence of the aromatic ring in the polymer.

Solution Polymerization

A solution of 0.22 g (0.0010 mole) of (III) in 4:1 methylene chloride-acetone was charged into a 7-ml Carius tube. The polymer tube was alternately evacuated and flushed with dry nitrogen three times. After the final evacuation 0.89 (0.0090 mole) of trifluoronitrosomethane and 1.00 g (0.010 mole) of tetrafluoroethylene were condensed in at -196°C . The tube was sealed under vacuum and shaken at -25°C for 24 hr. After allowing the mixture to warm to room temperature, the precipitated polymer was filtered, washed several times with acetone, and dried overnight in a vacuum oven

at 50°C to yield 1.68 g (80%) of yellow rubber. An absorption at 1530 cm^{-1} in the infrared spectrum confirmed the presence of the aromatic ring in the polymer.

Copolymerization of (I), (II), and (III) with Tetrafluoroethylene

The copolymerization of (I), (II), and (III) with tetrafluoroethylene was conducted in solution and the results of the experiments are shown in Table I. Each of these products was a hard, resinous material.

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JOSEPH GREEN^{*}
NATHAN MAYES
ERNEST COTTRILL

*Thiokol Chemical Corporation
Reaction Motors Division
Denville, New Jersey*

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^{*} Present address: Columbia Carbon Co., Princeton, N.J.