Radiation-Induced Copolymerization of α,β,β-Trifluoroacrylonitrile with α-Olefin

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Synopsis

Homopolymerization and copolymerization of α,β,β-trifluoroacrylonitrile (FAN) with α-olefins were carried out in bulk by γ-ray irradiation at 25°C. FAN gives very small quantities of brown and greasy low molecular weight polymer. Cyano groups in FAN polymer were found to be readily hydrolyzed to acid amide groups in the atmosphere. FAN was found to copolymerize with ethylene, propylene, and isobutylene via a radical mechanism to form equimolar copolymers in a wide range of monomer compositions. The polymerization rate increases linearly with FAN fraction in the monomer mixture. These copolymers are also hydrolyzed in the atmosphere, and the hydrolysis proceeds with more difficulty for the copolymer with higher α-olefin. The reactivity ratios r_1 (FAN) and r_2 (α-olefin) were determined to be 0.01 and 0.12 for the FAN/ethylene copolymerization and 0.01 and 0.07 for the FAN/propylene copolymerization. These results confirm that an alternating copolymerization takes place in the FAN/α-olefin system.

INTRODUCTION

α,β,β-Trifluoroacrylonitrile (FAN; $F_2C=CFCN$) is very reluctant to undergo homopolymerization reactions. It has been reported that very small quantities of polymer can be isolated in the presence of BF_3 or acetyl peroxide[1-6] and a 20% yield of an orange powder product can be obtained with as large as 200 MR of ^{60}Co γ radiation.[1,2]

Copolymerizations of FAN with various vinyl monomers have been investigated by Borders and Bovey[3-6] at the Wright Air Development Center of the United States Air Force early in the 1950s, and a brief summary was introduced by Postelnek et al.[7] in 1958. They reported that FAN copolymerized with styrene, acrylonitrile, vinyl acetate, ethylene, isobutylene, butadiene, vinyl chloride, butyl vinyl ether, and 1,1-dihydroperfluorohexyl vinyl ether. Copolymerization with styrene using cumene hydroperoxide as initiator yields a copolymer containing 20%–30% fluorine, which corresponds to approximately a 1:1 copolymer. Vinyl acetate readily gives copolymers containing 20%–28% fluorine in a monomer ratio of FAN to vinyl acetate of 1:1–12:1. Ethylene copolymer containing 20 mole % FAN is formed when 50 mole % FAN is charged. Butadiene copolymer containing 33 mole % FAN is formed from monomer of 32 mole % FAN. Butyl vinyl ether gives a plastic copolymer containing 50 mole % FAN. 1,1-Dihydroperfluorohexyl vinyl ether gives a soft plastic copolymer containing 44 mole % FAN, and vinylidene chloride gives a white powder containing 10 mole % FAN. α,β,β-Trifluoroacrylonitrile is readily hydrolyzed in the emulsion polymerization. Emulsion copolymerizations with styrene and with acrylonitrile result in low-conversion copolymers containing 10%–15% FAN.[7]

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On the other hand, fluorine-containing monomers such as 1,1-dihydroperfluorobutyl acrylate, perfluoropropene, perfluoroisobutylene, vinylidene fluoride, and chlorotrifluoroethylene did not yield the copolymers. Therefore, it can be seen that the reactivity of FAN is similar to that of perfluoroolefins in that all of the materials that form copolymers lie in the low "Q" nonconjugated region of the Price–Alfrey diagram.[7]

The authors are interested in FAN as a comonomer from the standpoint of synthesis of a fluoropolymer containing functional group, especially by means of an alternating copolymerization between an electron donor and acceptor monomers. α,β,β-Trifluoroacrylonitrile is a strong electron acceptor due to the large electron-withdrawing substituents such as fluorines and a cyano group. Consequently, it is expected that FAN will copolymerize alternatingly with an electron donor such as α-olefin. In addition, the cyano group is hydrolyzable, so that a hydrophilic fluoropolymer can be obtained by hydrolysis of the FAN copolymer. The hydrophilic fluorocopolymer has been successfully obtained in our laboratory by the alternating copolymerization of methyl α,β,β-trifluoroacrylate with α-olefin followed by hydrolysis.[8,9]

In this paper, radiation-induced homopolymerization and copolymerization of FAN with ethylene, propylene, and isobutylene in bulk were carried out at various monomer compositions. The reactivity ratios for FAN/ethylene and FAN/propylene are discussed from the copolymer composition determined by elemental analysis. The properties of the copolymers are also discussed.

EXPERIMENTAL

α,β,β-Trifluoroacrylonitrile (purity above 99%) was synthesized from hexafluoropropylene by the method described in a U.S. Patent.[10] The α-olefins were the same as in the previous paper.[11]

A stainless steel autoclave of 10 ml capacity was used as a reactor. All polymerizations were carried out in bulk by irradiation of γ rays from a ^{60}Co source.

The polymer composition was determined by elemental analysis. The infrared spectra of polymers were measured by the same method as described in the previous paper.[8] The molecular weight of the polymer was determined from the reduction in vapor pressure of the polymer–methanol solution at 30°C by using a Hitachi vapor pressure osmometer, Model 115, and benzil as standard material.

The decomposition temperature of the polymer was measured using a Rigaku Denki TGA-1 thermogravimetric analyzer at a heating rate of 5°C/min in nitrogen atmosphere. The glass transition temperature was measured using a Perkin–Elmer DSC-1B differential calorimeter at a scan speed of 8°C/min.

RESULTS AND DISCUSSION

Homopolymerization of FAN

Time–conversion curves of FAN irradiated at a dose rate of 1.0 Mrad/hr and temperatures of −78, 0, and 25°C are shown in Figure 1. Brown, greasy low molecular weight polymers were obtained. The molecular weight of the polymer with irradiation of 100 Mrad at 25°C was 2700.
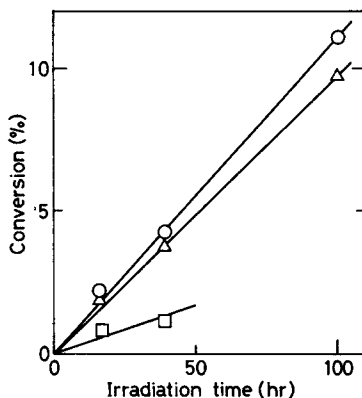
Fig. 1. Time–conversion curves for various polymerization temperatures. Reaction conditions: dose rate, 1×10^6 rad/hr; polymerization temperature (O) 25°C, ($\triangle$) 0°C, and ($\square$) −78°C

The time–conversion curves are approximately shown as linear relationships through the origin. Ballantine's result (20% at 196.4 MR)[2] fits well the straight line at 25°C. The polymerization rate of FAN is very slow, and the G-value at 25°C is only 11. The activation energy was calculated to be 1.9 kcal/mole, which is reasonable for radiation-induced polymerization.

The polymerization is slightly accelerated in trichlorotrifluoroethane (Freon R-113) and is not affected by the addition of water, as shown in Table I. This shows that the polymerization reaction proceeds via a radical mechanism.

The infrared spectrum of the polymer obtained in bulk after irradiation of 100 Mrad at 25°C is shown in Figure 2, together with that of FAN. The spectrum of the product is apparently different from that of FAN. The relatively weak absorption at 2255 cm^{-1} assigned to the C≡N stretching vibration shows only a small frequency shift to 2250 cm^{-1}. The C=C stretching absorption observed in the spectrum of monomer apparently disappears. The strong and sharp absorptions at 1370, 1280, and 1140 cm^{-1} assigned to the C—F stretching absorption are broadened in the spectrum of the product. The broadening of the C-F absorption is usually observed in the spectrum of polymers with continuous perfluorinated carbon sequences at the main chain such as polytetrafluoroethylene. Therefore, the product is a polymer of FAN formed by opening of the double bond.

Relative strong and broad absorptions newly appear at 3300 and 1710 cm^{-1}, which are assigned to the N—H stretching vibration and the C=O stretching vibration, respectively, due to the acid amide group formed by hydrolysis of the cyano group during the storage. They are not observed in the spectrum of FAN

TABLE I
Homopolymerization of FAN[a]

Solvent	Conversion, wt %	Polymerization rate, wt %/hr
None	4.30	0.11
H$_2$O[b]	3.22	0.08
Freon R-113	7.99	0.21

[a] Reaction conditions; in monomer/solvent molar ratio, 1/1; temperature, 25°C; dose rate, 1×10^6 rad/hr; irradiation time, 39 hr.
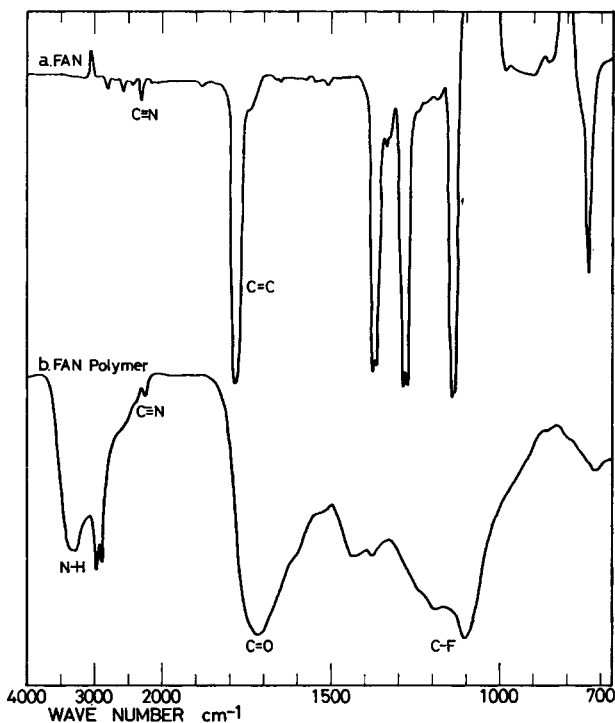
Fig. 2. Infrared spectra of (a) monomer and (b) polymer of FAN.

monomer and do not disappear by drying the polymer under vacuum for a long time. The elemental analysis of FAN polymer shows that 97% of its cyano groups are hydrolyzed to acid amide groups.

The decomposition temperature of the polymer in nitrogen atmosphere is 145°C, and the glass transition temperature is about 30°C.

Copolymerization of FAN

Table II shows the copolymerization results of FAN with ethylene, propylene, and isobutylene at 25°C with an equimolar monomer composition. Brown plastic products were obtained in the FAN/ethylene and the FAN/isobutylene systems, and brown, greasy product was obtained in the FAN/propylene system. The G-value of the copolymerization is 10 to 15 times larger than that of the homopolymerization of FAN. A relatively high yield was obtained in the FAN/isobutylene system.

The infrared spectra of these products are shown in Figure 3. The spectra are apparently different from those of both monomers and homopolymers of FAN and α-olefins. The relatively weak absorptions assigned to the C≡N stretching vibration are clearly observed at 1200–1000 cm^{-1} in every spectra of those products, which show the existence of FAN unit in them. The absorptions at 1460 and 1400 cm^{-1} in the spectra of the products obtained in the FAN/ethylene and the FAN/propylene systems are assigned to methylene and methyl groups from ethylene and propylene, respectively. The absorptions at 1410 and 1382 cm^{-1} in the spectrum of the product obtained in the FAN/isobutylene system
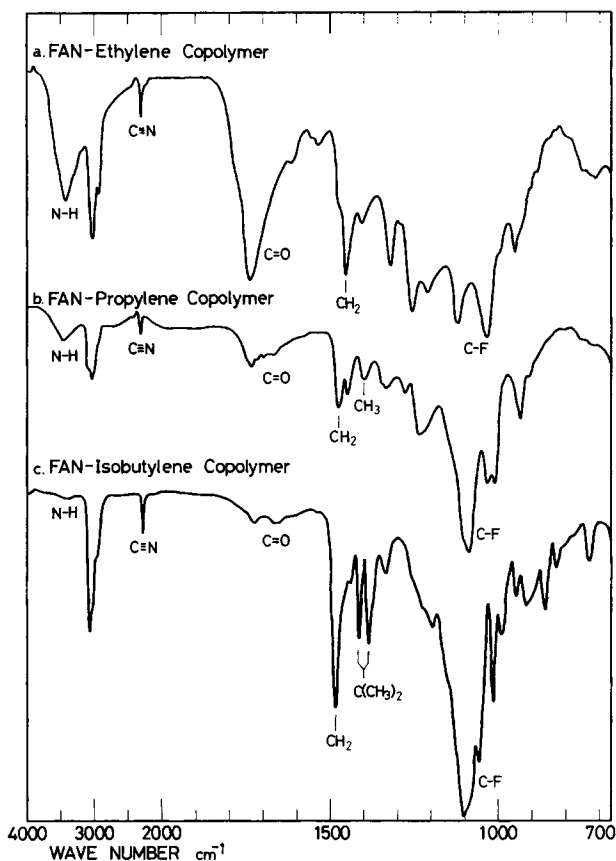
Fig. 3. Infrared spectra of copolymers of FAN with (a) ethylene, (b) propylene, and (c) isobutylene obtained under equimolar monomer composition at 25°C.

TABLE II
Copolymerization of FAN with α-Olefins[a]

Olefin	Polymerization rate, wt %/hr	G-value of polymerization	Copolymer composition, FAN mole %	Degree of hydrolysis, mole %
None	0.11	11	100.0	—
Ethylene	1.3	1177	50.0	80.4
Propylene	0.8	103	49.5	43.0
Isobutylene	1.7	250	49.6	7.9

[a] Reaction conditions: monomer composition, FAN/olefin = 1/1 (molar ratio); temperature, 25°C; dose rate, 1 × 10^6 rad/hr.

are assigned to *gem*-dimethyl groups from isobutylene.[12] These results indicate that each α-olefin is also certainly contained in these products. Every product was soluble in tetrahydrofuran. Therefore, an ethylene homopolymer is not contained in the product of the FAN/ethylene system. Ethylene, propylene, and isobutylene scarcely homopolymerize under these reaction conditions. From these results, it is concluded that these products are copolymers of FAN with α-olefins.
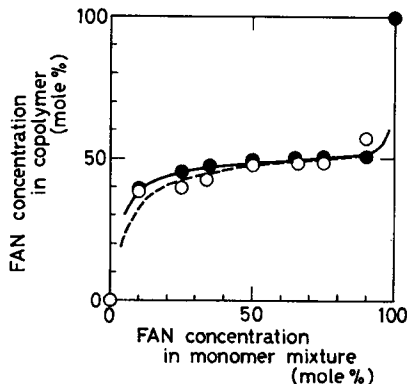
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Fig. 4. Relationship between initial FAN concentration in monomer mixture and FAN concentration in copolymer obtained in FAN–ethylene (○) and FAN–propylene (●) copolymerizations. Reaction conditions: polymerization temperature, 25°C; dose rate, 1 × 10⁶ rad/hr; irradiation time, 4 hr (ethylene) and 6 hr (propylene).
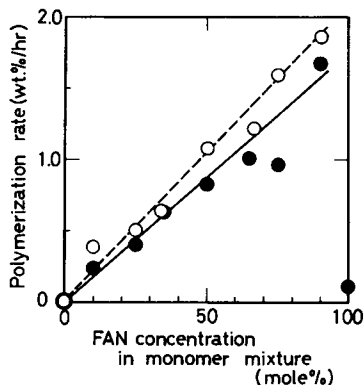

Fig. 5. Relationship between initial FAN concentration in monomer mixture and polymerization rate observed in FAN–ethylene (○) and FAN–propylene (●) copolymerizations. Reaction conditions: polymerization temperature, 25 °C; dose rate, 1 × 10⁶ rad/hr.

The strong and broad absorptions assigned to acid amide groups due to hydrolysis of cyano groups in the copolymer are apparently observed at 3400–3000 and 1800–1600 cm⁻¹. The strongest absorptions of the acid amide groups are observed in the FAN-ethylene copolymer. The higher the α-olefin, the weaker is the intensity of these absorptions. This shows that the hydrolysis proceeds with more difficulty for the higher α-olefin. Hydrolysis scarcely occurs for the FAN–isobutylene copolymer. This tendency is similar to that observed in the case of methyl trifluoroacrylate–α-olefin alternating copolymers.[9]

The copolymer compositions and the degree of hydrolysis calculated form the elemental analysis are shown in Table II, where it can be seen that all copolymers contain nearly 50 mole % FAN. This suggests that all copolymers are alternating copolymers. In the FAN–ethylene, the FAN–propylene, and the FAN–isobutylene copolymers, 80%, 43%, and 8% of the cyano groups are hydrolyzed, respectively.

The effects of initial FAN concentration in the monomer mixture on the copolymer composition and the copolymerization rate in the FAN/ethylene and

the FAN/propylene systems are shown in Figures 4 and 5. The FAN content in the copolymer is 50 mole % over a wide range of FAN concentration in the monomer mixture. The polymerization rates increase with the fraction of FAN in the monomer mixture up to 90 mole % FAN in both systems.

The monomer reactivity ratios for FAN/ethylene and FAN/propylene were determined by the curve fitting method; r_1 (FAN) = 0.01, r_2 (ethylene) = 0.12 and r_1 (FAN) = 0.01, r_2 (propylene) = 0.07. The values of $r_1 r_2$ are nearly zero. These results confirm alternating copolymerization.

The Q and e parameters for FAN were estimated to be 0.073 and +2.39 and 0.004 and +1.92, respectively, from the monomer reactivity ratios for the FAN/ ethylene and the FAN/propylene copolymerizations, assuming that the Q and e values are 0.015 and -0.20 for ethylene and 0.002 and -0.78 for propylene.[14] The e value of FAN is largely positive due to the large electron-withdrawing effect of the substituents F and CN. Therefore, FAN has an alternating tendency toward α-olefin with the negative e value. The small Q value shows that the resonance stability of FAN radical formed by addition of monomer is small and that the copolymerization reactivity is rather low. There is a large difference between the two Q values of FAN. This is partially due to the alternating co-polymerization and partially to the fact that the theoretical composition curves which fitted well with the experimental plots cannot be obtained for the FAN/ ethylene system.

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