

# Physical and Chemical Properties of Methyl Trifluoroacrylate- $\alpha$ -Olefin Copolymer and Its Hydrolyzed Copolymer

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## Synopsis

Physical and chemical properties of alternating copolymers of methyl  $\alpha,\beta,\beta$ -trifluoroacrylate (MTFA;  $\text{CF}_2=\text{CFCO}_2\text{CH}_3$ ) with  $\alpha$ -olefins such as ethylene, propylene, and isobutylene and their hydrolyzed copolymers were investigated. The original ester-type copolymers are amorphous and hydrophobic. The copolymers, except for the MTFA-isobutylene copolymer, were found to be easily hydrolyzed in boiled NaOH-methanol aqueous solution to give hydrophilic fluoropolymers which contain nearly theoretical amounts of carboxyl groups. No chain scission takes place during the hydrolysis. The decomposition temperature of the original ester-type copolymers is in the range of 347° to 379°C in nitrogen atmosphere, and the glass transition temperature is in the range of 21° to 76°C. Two steps of weight decrease, at around 100°C due to the removal of absorbed water and around 250°C due to the decomposition, were observed in the TGA curve of the hydrolyzed acid-type copolymers. Both ester- and acid-type copolymers were crosslinked by electron beam irradiation, while the MTFA-isobutylene copolymer was degraded. The tensile strength of the copolymers is in the range of 190 to 450 kg/cm<sup>2</sup>.

## INTRODUCTION

Recently, the number of reports on functional fluoropolymer synthesis has increased because of good reported chemical and thermal stability of a fluorine-containing polymer.

In our previous works,<sup>1-3</sup> copolymerization of methyl  $\alpha,\beta,\beta$ -trifluoroacrylate (MTFA) with  $\alpha$ -olefin by gamma irradiation was studied for the purpose of preparing a functional group containing fluoropolymer. MTFA has been found to copolymerize easily with various  $\alpha$ -olefins, especially ethylene,<sup>2</sup> propylene,<sup>3</sup> and isobutylene,<sup>1</sup> via a radical mechanism to form a 1:1 alternating copolymer over a wide range of monomer composition.

In the present paper, the hydrolysis of the ester groups in these copolymers and the chemical, physical, and mechanical properties of the original copolymer (ester type) and hydrolyzed copolymer (acid type) are reported. Radiation-induced crosslinking of the copolymers is also reported.

## EXPERIMENTAL

### Preparation of Copolymer

The methyl  $\alpha,\beta$ -trifluoroacrylate- $\alpha$ -olefin copolymers used are the same as in the previous paper.<sup>1</sup>

### Hydrolysis of Copolymer

Hydrolysis of the ester groups in the copolymers was carried out by alkaline treatment. Copolymer, 3 g, was boiled in a mixed solution of 45 ml methanol, 15 ml water, and 5 g sodium hydroxide for 5 hr with stirring under reflux. After cooling, concentrated hydrochloric acid was added dropwise with stirring until the pH reached 3-4. The stirring was continued for a few hours to complete neutralization. Hydrolyzed copolymer and salt were precipitated. After the salt was dissolved by adding a large amount of water, the hydrolyzed copolymer was separated from the solution by filtration. The dried crude hydrolyzed copolymer was dissolved in tetrahydrofuran (THF) and filtered to remove the occluded salt. The purified hydrolyzed copolymer was recovered by evaporation of THF and dried completely in a vacuum oven at 60°C.

### Determination of COOH Concentration in Hydrolyzed Copolymer

The carboxyl group concentration was determined by alkalimetry. The hydrolyzed copolymers were soluble or extremely swollen in water. The polymer corresponding to about 0.1 mmole COOH was desolved in 10 ml water and titrated with 0.01N NaOH at room temperature. The endpoint was determined accurately from the titration curve in the usual way. A Hitachi-Horiba M-7 pH meter was used for this analysis.

### Measurement of Properties

The glass transition temperature of the copolymer was measured by using a Perkin-Elmer DSC-1B differential calorimeter at a scan speed of 8°C/min. Decomposition temperature of copolymer was determined in nitrogen flow by heating at a programmed rate of 5°C/min by using a Rigaku Denki TGA-1 thermogravimetric analyzer.

Infrared spectra of copolymers were obtained by the same method as described in the previous paper.<sup>1</sup>

Copolymer density was measured in a mixture of carbon tetrachloride and methanol at 25°C.

X-Ray diffraction pattern was obtained by a Rigaku Denki D-6C diffractometer with  $\text{CuK}_\alpha$  radiation.

The mechanical properties of the copolymers were measured at 20°C with an elongation speed of 166%/min by using an Instron Model 1130 tensile tester. Strips of copolymer 4 mm wide and 1 mm thick were used as specimens.

Crosslinking was carried out by electron beam irradiation from an EBG accelerator made by General Electric, using a copolymer sheet 1 mm thick. Irradiation was carried out periodically on a conveyor at room temperature and at a dose rate of 0.1 Mrad/sec. The sol parts of the irradiated samples were ex-

tracted with *N,N*-dimethylformamide at 80°C for the MTFA-ethylene copolymer, with boiled THF for the MTFA-propylene and MTFA-isobutylene copolymers, and with boiled acetone for their hydrolyzed copolymers for 48 hr through 200-mesh stainless steel net to determine the sol fractions.

Degree of swelling was determined from the weight increase of 60 Mrad-irradiated polymer sheet after immersion in water or 2*N* NaOH aqueous solution for 48 hr.

## RESULTS AND DISCUSSION

### Hydrolysis of Copolymer

Hydrolysis of the ester groups in copolymer was carried out by boiling the copolymer in alkali-methanol aqueous solution under reflux. The original ester-type copolymers have no affinity for the solution. After being boiled for 5 hr, the MTFA-ethylene and the MTFA-propylene copolymers dissolved in the alkaline solution. But the MTFA-isobutylene copolymer did not dissolve in the solution, and little change was observed after treatment of more than 5 hr.

Slightly brown, sticky polymers were recovered from the solution with regard to the MTFA-ethylene and the MTFA-propylene copolymers after alkaline treatment. These polymers show hydrophilic properties, that is, the former becomes extremely swollen with water and the latter is dissolved in water.

Infrared spectra of polymers obtained after the treatment are shown in Figures 1 to 3 in comparison with those of the original ester-type copolymers. In every spectrum of the ester-type copolymers, Figures 1(a), 2(a), and 3(a), the absorptions of C—F, C=O, and CH<sub>3</sub> from MTFA are apparently observed at 1440–1000, 1770, and 1445 cm<sup>-1</sup>, respectively. In Figure 1(a), the absorption of CH<sub>2</sub> from ethylene overlaps with that of CH<sub>3</sub> from MTFA at 1445 cm<sup>-1</sup>. In Figure 2(a), the absorptions of CH<sub>2</sub> and CH<sub>3</sub> from propylene are observed at 1470 and 1400 cm<sup>-1</sup>. In Figure 3(a), the split CH<sub>3</sub> absorptions of *gem*-dimethyl groups from isobutylene are observed at 1382 and 1410 cm<sup>-1</sup>.

In the spectra of the MTFA-ethylene and the MTFA-propylene copolymers after alkaline treatment, Figures 1(b) and 2(b), a broad absorption assigned to carboxyl OH appears newly at 3300 cm<sup>-1</sup>, and the absorption of C=O becomes very broad, while the CH<sub>3</sub> absorption at 1445 cm<sup>-1</sup> from MTFA disappears. These changes show that the ester groups of MTFA units in copolymers convert to carboxyl groups. Degree of hydrolysis of the MTFA-ethylene and the MTFA-propylene copolymers were determined by alkalimetry to be 83% and 93%, respectively. On the other hand, no change was observed in the spectrum of the MTFA-isobutylene copolymer after the alkaline treatment as shown in Figure 3. The fact indicates the MTFA-isobutylene copolymer scarcely hydrolyzed. It can be assumed that two methyl groups of isobutylene stereochemically inhibit the hydrolysis. Similar phenomenon has been observed in the hydrolysis of the isobutylene-acrylate alternating copolymer.<sup>4</sup>

The molecular weights of ester and acid type copolymers are listed in Table 1. No chain scission occurs even in the boiled alkaline solution.

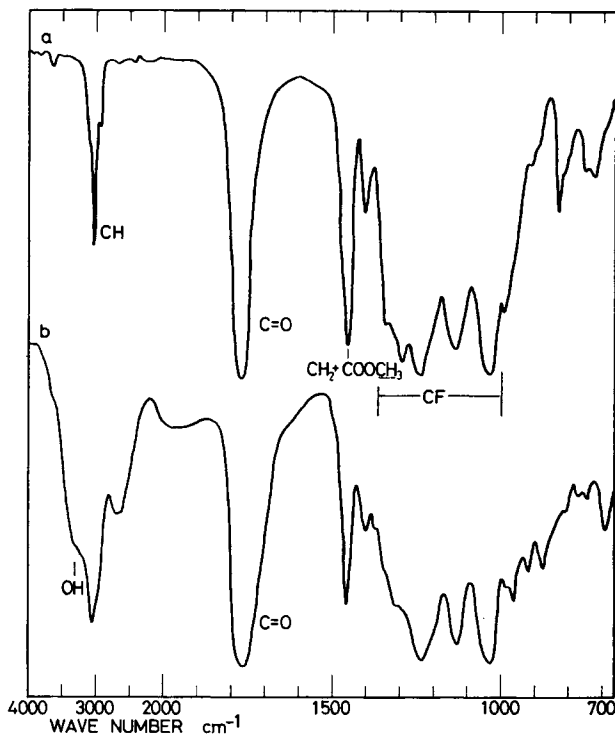


Fig. 1. Infrared spectra of MTFA-ethylene copolymers. (a) Original ester type copolymer; (b) copolymer after alkaline treatment (acid-type copolymer).

## Properties of Ester-Type and Acid-Type Copolymers

### Physical Properties

Physical properties of the ester-type and acid-type copolymers are listed in Table I. The densities of the ester-type MTFA-ethylene, MTFA-propylene and MTFA-isobutylene copolymers are 1.47, 1.41, and 1.39 g/cm<sup>3</sup> at 25°C, respectively.

X-Ray diffraction patterns indicate that all ester-type copolymers are amorphous, and the patterns did not change after hydrolysis.

The glass transition temperature  $T_g$  of the MTFA-ethylene copolymer is not clear. The  $T_g$  of the MTFA-propylene copolymer is 21°C, and this value scarcely changes upon hydrolysis. The  $T_g$  of the MTFA-isobutylene copolymer is 76°C. The ester-type MTFA-ethylene and MTFA-isobutylene copolymers are hard plastics like poly(methyl methacrylate), and the ester-type MTFA-propylene copolymer is elastic at room temperature above 25°C.

The decomposition temperatures  $T_d$  of the ester type MTFA-ethylene, MTFA-propylene, and MTFA-isobutylene copolymers are 379, 362, and 347°C, respectively. Similarly, high decomposition temperature has been also observed on the tetrafluoroethylene-propylene alternating copolymers.<sup>5</sup> Consequently, the olefin units in these copolymers are apparently protected by the neighboring fluorines. On the other hand, the thermal decomposition behavior of the acid-type copolymers is rather complex. As shown in Figure 4, two steps of weight decrease were observed in the TGA curve. The first decrease,

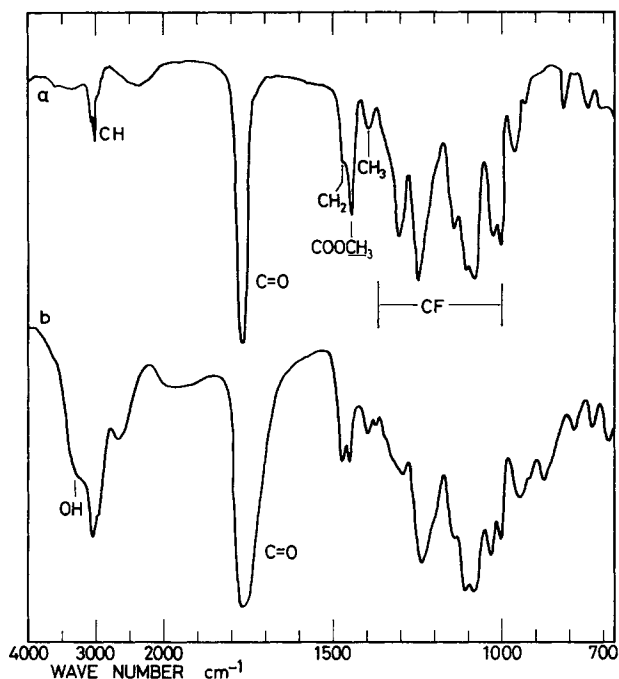


Fig. 2. Infrared spectra of MTFA-propylene copolymers. (a) Original ester type copolymer; (b) copolymer after alkaline treatment (acid-type copolymer).

TABLE I  
Physical Properties of MTFA- $\alpha$ -Olefin Copolymers Before and After Hydrolysis

Property	MTFA-Ethylene		MTFA-Propylene		MTFA-Isobutylene
	Ester	Acid	Ester	Acid	Ester
Density at 25°C, g/cm <sup>3</sup>	1.47	—	1.41	—	1.39
Molecular weight $\bar{M}_n$	—	$4.6 \times 10^4$	$3.5 \times 10^4$	$3.1 \times 10^4$	$7.5 \times 10^4$
Glass transition temperature, °C	not clear	not clear	21	22	76
Decomposition temperature, °C	379	—	362	—	347
Tensile strength, kg/cm <sup>2</sup>	450	190	330	210	—
Modulus, kg/cm <sup>2</sup>	13,000	11,000	11,000	10,000	—
Elongation, %	4.0	2.5	12.0	11.0	—
COOH concentration, meg/g	—	5.4	—	5.5	—
Degree of hydrolysis, %	—	83	—	93	—
Swelling, %	—	—	—	—	—
In water	—	98	—	44	—
In 2N NaOH aq. soln.	—	1,900	—	3,300	—

around 100°C, is considered to be due to the removal of the adsorbed water, and the second decrease, around 250°C, which is about 50%, seems to be due to the decomposition.

#### Mechanical Properties

The mechanical properties of the ester-type and the acid-type MTFA-ethylene and MTFA-propylene copolymers are shown in Table I. The tensile strength of the ester type MTFA-ethylene copolymer is 450 kg/cm<sup>2</sup> at 4% elongation and

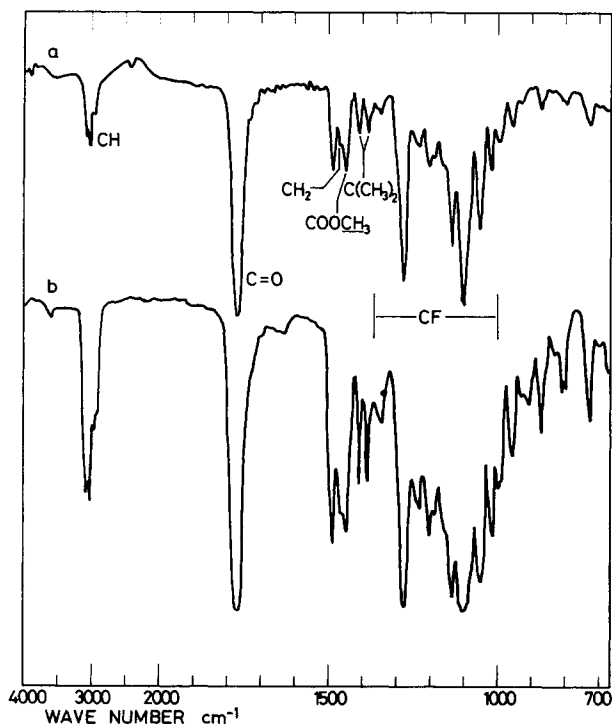


Fig. 3. Infrared spectra of MTFA-isobutylene copolymers. (a) Original ester type copolymer; (b) copolymer after alkaline treatment.

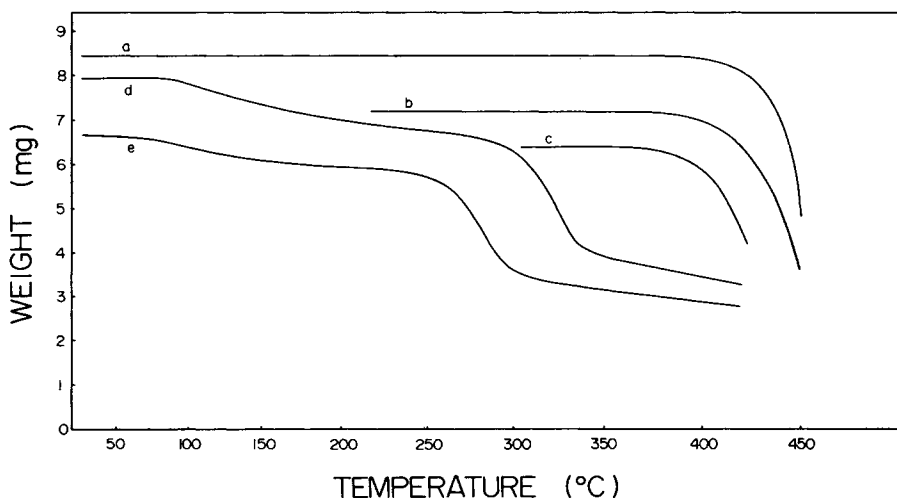


Fig. 4. Thermogravimetric diagrams of ester- and acid-type copolymers. (a) Ester-type MTFA-ethylene copolymer; (b) ester-type MTFA-propylene copolymer; (c) ester-type MTFA-isobutylene copolymer; (d) acid-type MTFA-propylene copolymer; (e) acid-type MTFA-ethylene copolymer.

decreases to 190 kg/cm<sup>2</sup> at 2.5% elongation upon hydrolysis. The tensile strength of the ester-type MTFA-propylene is 330 kg/cm<sup>2</sup> at 12% elongation and decreases upon hydrolysis similarly to the case of the MTFA-ethylene copolymer. These

mechanical properties are comparable to those of poly(vinyl chloride) but will be improved, for example, by increasing the molecular weight and by cross-linking.

### Chemical Properties

The solubilities of the ester-type and the acid-type MTFA-ethylene, MTFA-propylene, and MTFA-isobutylene copolymers are listed in Table II. N,N-Dimethylformamide (DMF) was found to be a common solvent for all copolymers.

The MTFA-ethylene copolymer is soluble only in DMF, but the solubility is low at room temperature. The hydrolyzed MTFA-ethylene copolymer is soluble in THF, acetone, methanol, and dimethyl sulfoxide (DMSO). In addition, the hydrolyzed copolymer is soluble in 0.01N NaOH solution and swollen in water.

The MTFA-propylene copolymer is soluble in benzene, xylene, ethyl ether, THF, dichloromethane, chlorobenzene, benzotrifluoride, acetone, and DMF. However, the hydrolyzed copolymer becomes insoluble in these solvents, except for THF, acetone, and DMF, and soluble newly in methanol, DMSO, water, and 0.01N NaOH solution. The change in solubility strongly suggests that the ester groups in the MTFA-ethylene and the MTFA-propylene copolymers are converted to the carboxyl groups by the alkaline treatment mentioned above. Contrary to this, it is apparent that the MTFA-isobutylene copolymer cannot be hydrolyzed because the solubility of the copolymer does not change by the alkaline treatment.

Figure 5 shows the titration curves of the hydrolyzed copolymer aqueous solutions by 0.01N NaOH solution. The curves are characteristic of a strong acid rather than a weak acid like a poly(acrylic acid). The apparent dissociation constants  $pK_a$  of carboxyl groups in the hydrolyzed MTFA-ethylene and the MTFA-propylene copolymers are determined to be approximately 3 at 25°C

TABLE II  
Change of Solubility of MTFA- $\alpha$ -Olefin Copolymers Before and After Alkaline Treatment<sup>a</sup>

Solvent	MTFA-ethylene		MTFA-propylene		MTFA-isobutylene	
	Before (ester type)	After (acid type)	Before (ester type)	After (acid type)	Before (ester type)	After
<i>n</i> -Hexane	I	I	I	I	I	I
Benzene	I	I	S	I	S	S
Xylene	I	I	S	I	SW	SW
Ethyl ether	I	I	S	I	SW	SW
Tetrahydrofuran	I	S	S	S	S	S
Dichloromethane	I	I	S	I	S	S
Chlorobenzene	I	I	S	I	S	S
Benzotrifluoride	I	I	S	I	S	S
Acetone	I	S	S	S	S	S
Methanol	I	S	I	S	I	I
Dimethylformamide	S	S	S	S	S	S
Dimethyl sulfoxide	SW	S	SW	S	I	I
Water	I	SW	I	S	I	I
0.01N NaOH aq. soln.	I	S	I	S	I	I

<sup>a</sup> Solubility was measured at 20°C. S = soluble; I = insoluble; SW = swelling.

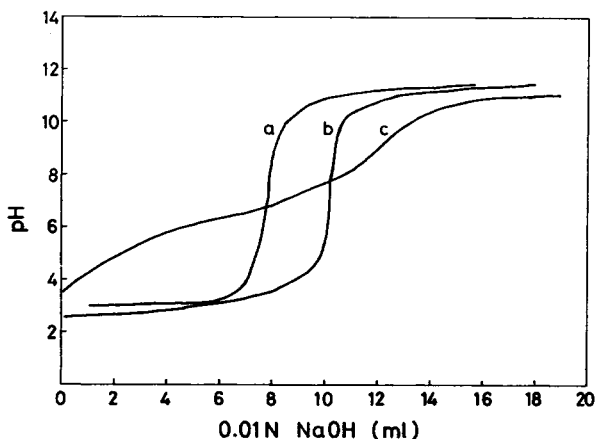


Fig. 5. Titration curves of acid-type MTFA-ethylene and MTFA-propylene copolymers aqueous solutions by 0.01N NaOH at 25°C. (a) Acid-type MTFA-ethylene copolymer; (b) acid-type MTFA-propylene copolymer; (c) poly(acrylic acid). Polymer aqueous solutions corresponding to about 0.01N COOH were prepared.

by using the Katchalsky equation.<sup>6</sup> The observed  $pK_a$  value smaller than 6 of poly(acrylic acid) is reflected by the strong electron-withdrawing effect of the neighboring fluorines.

### Radiation-Induced Crosslinking and Properties of Crosslinked Copolymer

It is known that the sol fraction of crosslinked polymer with a random molecular weight distribution is related to the dose by

$$s + \sqrt{s} = p_0/q_0 + 1/q_0uR \quad (1)$$

where  $s$  is the sol fraction,  $R$  is the irradiation dose (Mrads),  $u$  is the number-average degree of polymerization, and  $p_0$  and  $q_0$  are the probabilities of scission and crosslinking.<sup>7,8</sup> The  $G$  values of scission and crosslinking can be calculated from the probabilities.

The changes in sol fraction as a function of absorbed dose are shown in Figure 6. Both the ester-type and the acid-type MTFA-ethylene and MTFA-propylene copolymers can be crosslinked in air by electron beam irradiation, but the MTFA-isobutylene copolymer is degraded even under vacuum. The gelation dose and the  $G$  values of scission and crosslinking are listed in Table III. The probabilities were calculated on the assumption that the number-average molecular weight of the monomer unit in the copolymer is an average of those of MTFA and  $\alpha$ -olefin. The  $G$  value of crosslinking of the hydrolyzed MTFA-ethylene copolymer is larger than that of the original copolymer. This tendency is reversed in the case of the MTFA-propylene copolymer. The  $G$  value of scission of the ester-type MTFA-propylene copolymer is very small.

The degrees of swelling in water and in 2N NaOH aqueous solution of the acid-type copolymers crosslinked by 60 Mrads electron beam irradiation are listed in Table I. The degrees of swelling of the acid-type MTFA-ethylene and MTFA-propylene copolymers in water are 98% and 44%, respectively. These



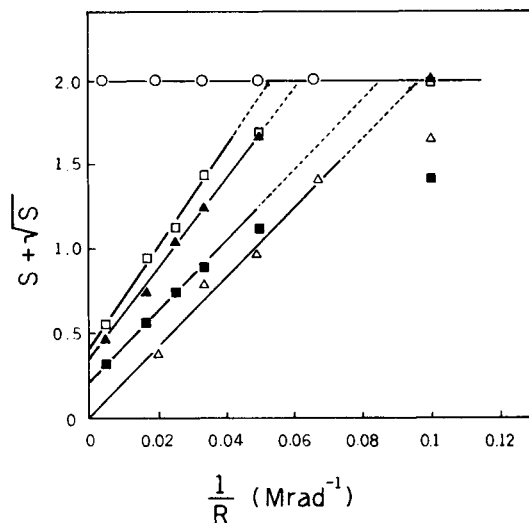


Fig. 6. Charlesby-Pinner plots for ester- and acid-type copolymers: ( $\square$ ) ester-type MTFA-ethylene copolymer; ( $\blacksquare$ ) acid-type MTFA-ethylene copolymer; ( $\triangle$ ) ester-type MTFA-propylene copolymer; ( $\blacktriangle$ ) acid-type MTFA-propylene copolymer; ( $\circ$ ) ester-type MTFA-isobutylene copolymer.

TABLE III  
Radiation-Induced Crosslinking of MTFA- $\alpha$ -Olefin Copolymers in Air

	MTFA-ethylene		MTFA-propylene	
	Ester type	Acid type	Ester type	Acid type
Gel dose, Mrads	18.9	12.0	14.0	16.1
$G$ (crosslinking)	0.33	0.51	0.30	0.36
$G$ (scission)	0.25	0.22	0.00	0.24

copolymers are swollen in 2*N* NaOH aqueous solution to 1900% and 3300% to form so-called hydrogel.

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