

Molecular Weight Characteristics of Tetrafluoroethylene–Propylene Copolymer Produced by Radiation-Induced Emulsion Copolymerization

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Synopsis

The alternating copolymers of tetrafluoroethylene and propylene produced in emulsion polymerization by radiation and by chemical initiators were fractionated and the fine structure of the molecules was examined. The correlation between \bar{M}_n and $[\eta]$ was obtained as

$$[\eta] = 3.97 \times 10^{-4} \bar{M}_n^{0.639}$$

for the fractionated samples. The molecular structure of the copolymers was not a complicated one, such as long-chain branching. There was no difference in molecular weight distribution and molecular structure between these copolymers. ^{19}F NMR measurements showed that the copolymer by radiation had a large degree of the irregularity of alternation in the sequence than that by the chemical method; the irregularity increased with increasing molecular weight in the fractionated samples. The fluorine content in the fractionated samples determined with a fluoride ion-sensitive electrode was of similar tendency as that in the results of ^{19}F NMR.

INTRODUCTION

The radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene has been studied in our laboratory.^{1–5} Amorphous, rubberlike alternating copolymers of tetrafluoroethylene and propylene with high molecular weights are obtained in the radiation process.

The physical properties of polymers in general are dependent not only on the molecular weight and the molecular weight distribution but also on the primary structure of the molecule. Therefore, in copolymers, the sequence configuration of the molecule is one of the most important characteristics.

In this report, the copolymer of tetrafluoroethylene and propylene produced by radiation is characterized in its molecular structure with regard to the long-chain branching and in its sequence configuration, as compared with the copolymer produced by a chemical method using chemical initiators.

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EXPERIMENTAL

The copolymer sample was prepared in a stainless steel autoclave of 30-l. capacity. The monomers tetrafluoroethylene and propylene were emulsified in oxygen-free water by the use of ammonium perfluorooctanate (FC-143) as emulsifier purchased from Minnesota Mining and Manufacturing Co. The emulsion was irradiated with gamma radiation originating from a ^{60}Co source, at a dose rate of 1.8×10^5 R/hr under pressure of 28 atm at 25°C. Details of the polymerization procedure were reported previously.^{1,2} The copolymer produced by a chemical method using chemical initiators from Asahi Glass Co. was used as the reference.

The number-average molecular weight \bar{M}_n and the intrinsic viscosity $[\eta]$ of the samples are shown in Table I. The sample was fractionated successively by solvent extraction using tetrahydrofuran and *n*-hexane as the solvent. About 10 g of the sample dissolved in 200 ml tetrahydrofuran was spread on a filter paper, and the solvent was evaporated under vacuum prior to fractionation. It was successively fractionated at 30°C by the mixed solvents using various ratios of tetrahydrofuran to *n*-hexane, the total volume being 200 ml. After extraction by the solvent for a specific time, the sample was precipitated by addition of methanol, followed by filtration and vacuum drying to constant weight.

The intrinsic viscosity $[\eta]$ of each fraction was measured in tetrahydrofuran at 30°C. The number-average molecular weight \bar{M}_n was determined by osmometry in tetrahydrofuran solution at 30°C, using a Hewlett-Packard high-speed membrane osmometer Model 502. Gel permeation chromatography was carried out using a high-speed liquid chromatograph Model ALC 201 of Waters Associates, with a four-column series of nominal pore sizes 10^3 , 10^4 , 10^5 , 10^6 Å of μ -Styragel. It was operated at room temperature with tetrahydrofuran as the solvent at a flow rate of 1 ml/min. The GPC calibration curve was obtained with standard polystyrene. The molecular weight conversion factor Q was calculated as $Q = 26.8/A$ from a planar zigzag conformation of the linear and alternating copolymer of tetrafluoroethylene and propylene.

NMR spectra of ^{19}F nuclei were measured at 94 MHz using a Jeol spectrometer Model PS-100, at 100°C. Benzotrifluoride was used as the solvent. The sequence of configuration in tetrafluoroethylene and propylene of the copolymer was studied from the resonance spectrum assigned by Ishigure.⁶

The fluorine content in the molecule was measured as follows⁷: The sample was imbedded in a matrix prepared from molten K_2CO_3 . It was then decomposed by heating at 600°C for 1 hr to convert the fluorine into potassium fluoride. The medium was dissolved in distilled water, and the fluorine concentration was determined using a fluoride ion-sensitive electrode.

TABLE I
Description of Samples Used

	Radiation process	Chemical process
Producer	JAERI	Asahi Glass Co.
Intrinsic viscosity $[\eta]$ in THF at 30°C	1.03	0.84
Number-average molecular weight \bar{M}_n	14.3×10^4	19.0×10^4

TABLE II
Fractionation of Sample Produced by Irradiation^a

Fraction no.	THF, vol-%	Wt. fraction, %	$[\eta]$ in THF at 30°C	$\bar{M}_n \times 10^{-4}$	GPC peak <i>EV</i> , ml
1	20	0.63			
2	25	3.21			
3	30	2.25			
4	35	4.91	0.388	5.5	29.8
5	37.5	3.01	0.48	7.8	
6	37.5	5.41	0.615	11.5	28.5
7	40	10.03	0.53	9.1	29.3
8	42.5	7.03	0.683	13.7	27.0
9	42.5	8.32	0.80	17.5	
10	42.5	13.48	0.97	24.5	26.2
11	45	30.0	1.06	28.0	
12	45	11.73	1.17	33.0	25.6

^a Recovery 95.7%; *EV* = elution volume.

RESULTS AND DISCUSSION

The results of fractionation in the copolymers of tetrafluoroethylene and propylene produced by radiation and chemical initiator are summarized in Tables II and III. The intrinsic viscosity in each fraction increased with increasing tetrahydrofuran content of the extracting solvent, whereas the peak elution volume of GPC decreased. GPC curves of the fractionated and unfractionated samples in both radiation and chemical methods are shown in Figures 1 and 2. The feature of the molecular weight distribution curve in the unfractionated sample by radiation is that it has a shoulder peak in the vicinity of high molecular weight, about 3×10^5 , which is broader than in the sample obtained by the chemical method. The molecular weight distribution in the lower molecular weight region becomes sharp in fractionation. The GPC curve of the fraction broadens and the peak shifts to lower elution volumes (*EV*) as the fraction number increases, thus indicating that the sample is fractionated with successive solvent extractions.

Figure 3 shows the correlation between the number-average molecular weight

TABLE III
Results of Fractionation in Chemically Produced Sample^a

Fraction no.	THF, vol-%	Wt. fraction, %	$[\eta]$ in THF at 30°C	$\bar{M}_n \times 10^{-4}$	GPC peak <i>EV</i> , ml
1	25	1.01			
2	30	2.47			
3	32.5	1.85	0.33	4.2	30.4
4	35	2.73	0.36	4.9	
5	35	3.18	0.48	7.8	29.2
6	37.5	14.34	0.71	14.5	
7	37.5	8.78	0.74	15.5	27.7
8	40	12.00	0.84	19.2	
9	40	3.90	0.67	13.2	
10	42.5	24.40	1.02	26.3	26.0
11	42.5	22.64	1.13	31.0	26.5
12	45	2.73	0.83	18.7	

^a Recovery 100%.

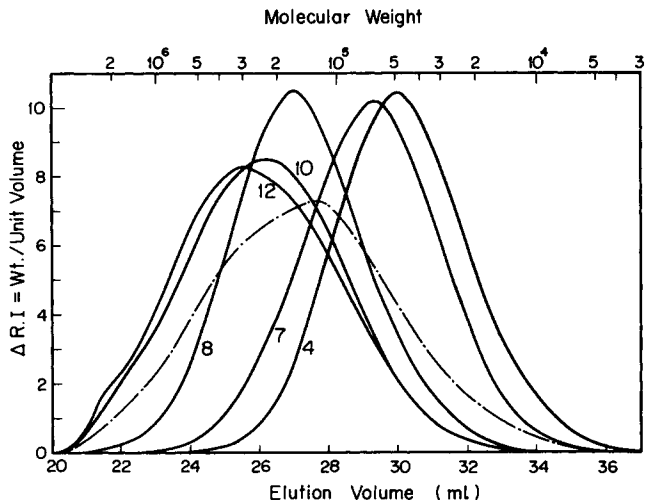


Fig. 1. GPC curves of fractionated (—) and unfractionated (---) copolymer produced by irradiation process. Numerals indicate fraction numbers in Table II.

\bar{M}_n and the intrinsic viscosity $[\eta]$ in tetrahydrofuran solution at 30°C. The correlations in fractionated and unfractionated samples differ from each other in the radiation-polymerized sample. Equation (1) was obtained for the fractionated sample produced by radiation:

$$[\eta] = 3.97 \times 10^{-4} \bar{M}_n^{0.639} \quad (1)$$

On the other hand, the unfractionated sample by radiation follows formula (2), reported by Kojima⁸:

$$[\eta] = 2.5 \times 10^{-4} \bar{M}_n^{0.70} \quad (2)$$

The effect of fractionation is remarkable in the sample produced by radiation. The difference may be mainly due to the change in molecular weight distribution

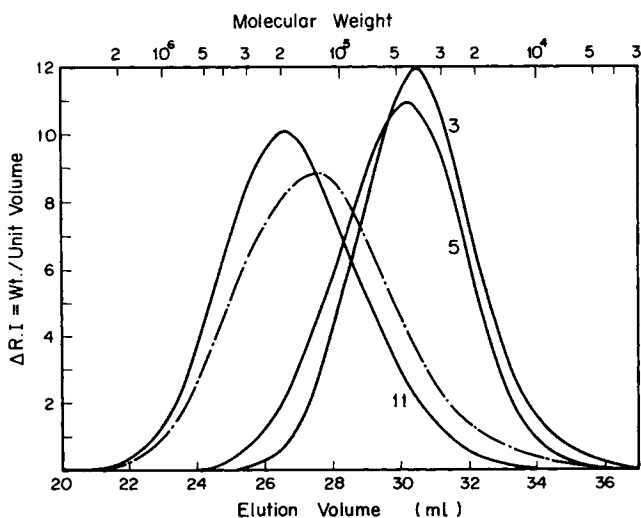


Fig. 2. GPC curves of fractionated (—) and unfractionated (---) copolymer produced chemically. Numerals indicate fraction numbers in Table III.

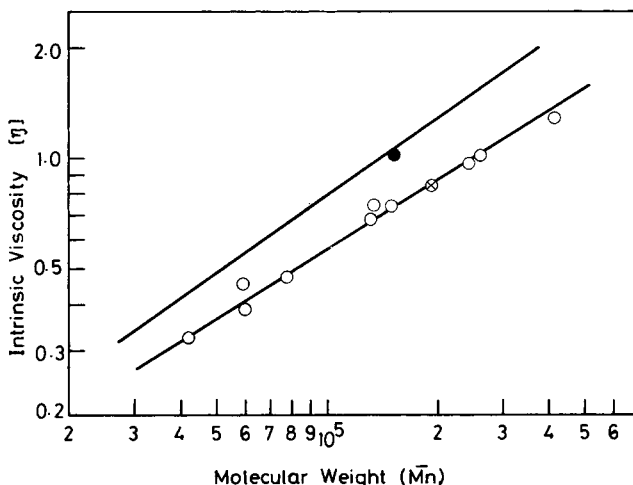


Fig. 3. Correlation between number-average molecular weight \bar{M}_n and intrinsic viscosity $[\eta]$: (O) fractionated samples in both irradiation and chemical methods; (●) unfractionated radiation copolymer; (⊗) unfractionated copolymer obtained chemically.

by fractionation. Similar results were reported for the polyethylene produced by radiation-induced polymerization.⁹ In contrast, the fractionated and unfractionated samples obtained by a chemical method fit eq. (1), as shown in Figure 3. There is, therefore, no fractionation effect on the molecular structure and molecular weight distribution in the sample obtained by the chemical method.

Figure 4 shows \bar{M}_n versus the GPC peak elution volume (EV) in each fraction of both samples yielded by radiation and chemical methods. Because there is no well-characterized linear copolymer of tetrafluoroethylene and propylene, the molecular weight and intrinsic viscosity of a linear copolymer were calculated from the standard polystyrene calibration curve, assuming $Q = 26.8/A$ in eq. (1). The results are summarized in Table IV and shown by the solid line in Figure 4. The plots of the fractions as observed for the GPC peak elution volume do not much deviate from the calculated line for the linear sample. Furthermore,

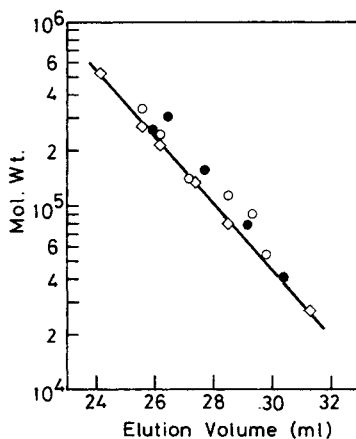


Fig. 4. Plots of molecular weight vs peak elution volumes of GPC: (O) radiation copolymer; (●) copolymer chemically obtained; (□) calculated from standard polystyrene.

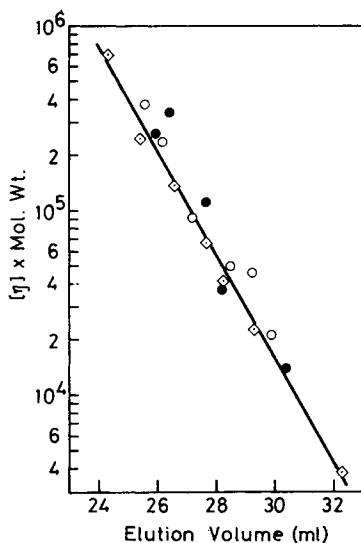


Fig. 5. Plots of $[\eta] \times$ molecular weight vs peak elution volume. Symbols as in Figure 4.

there is little difference between the samples originating from radiation or chemical methods. The peak elution volume of each fractionated sample fits the universal calibration curve,¹⁰ as shown in Figure 5. The calculated values for the linear copolymer, from the GPC elution behavior of standard polystyrene (in Table IV), are shown by the solid line in Figure 5. The results in the present experiment fit approximately the calculated line for the linear copolymer.

The intrinsic viscosity of a linear polymer is generally larger than that of a branched polymer of the same molecular weight.¹¹ The values in the present experiment are not lower than the calculated values for a linear polymer. It suggests that few long chain branchings do exist in the copolymer of tetrafluoroethylene and propylene. Furthermore, the difference in preparation methods does not affect much the molecular weight, the molecular weight distribution, and the amount of long-chain branching.

The fractionated samples were examined by high-resolution ¹⁹F NMR measurement to measure the irregularity of the sequence. The regular sequence of the copolymer will be an alternative linkage of tetrafluoroethylene and propylene units having head-to-tail configuration for propylene.^{1,8,12} The ¹⁹F NMR spectrum was reported to be complicated because of its fine structure due to vicinal fluorine nuclei (F-F) coupling.⁶ However, the two types of irregular sequence, i.e., (a) and (b) below, would be formed when the regular alternation

TABLE IV
Calculation of The Theoretical Values of TFE-PP Copolymer

$[\eta]$	$\bar{M}_n \times 10^{-4}$	$[\eta](\bar{M}_n \times 10^{-4})$	EV, ml
0.2	1.9	0.38	32.3
0.4	5.8	2.32	29.3
0.5	8.3	4.15	28.3
0.6	11.1	6.66	27.7
0.8	17.5	14.0	26.6
1.0	25.0	25.0	25.5
1.5	48.0	72.0	24.4

TABLE V
Irregularity of Alternation and Fluorine Content

Sample	$\bar{M}_n \times 10^{-4}$	Irregularity of alternation RFFR/RFRF	Fluorine content measured by ion electrode, %	Fluorine content calculated from irregularity of alternation, %
Irradiation process	5.5	15.5	54.1	54.6
	13.7	16.0	55.1	54.6
	24.5	17.5	55.6	54.7
Chemical process	7.8	13.0	54.0	54.5
	15.5	14.0	53.9	54.6
	26.3	14.5	53.1	54.5

is broken during the copolymerization process:

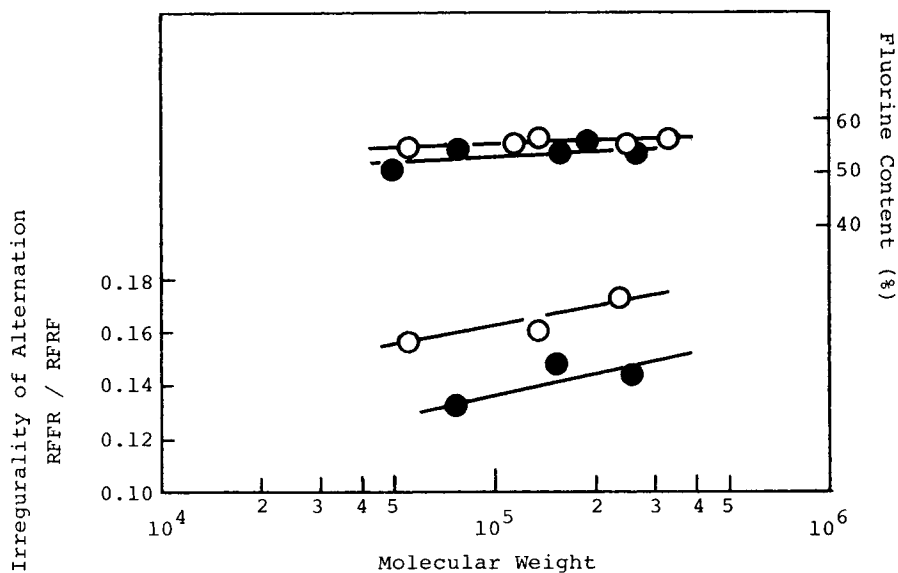
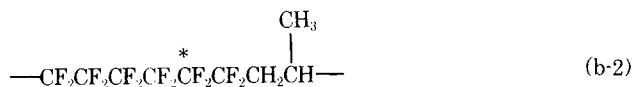
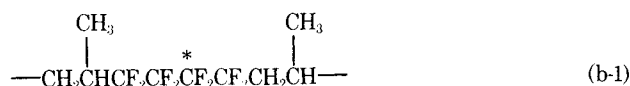
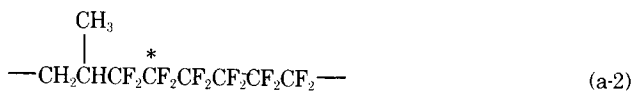
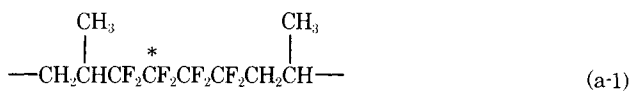


Fig. 6. Plots of "irregularity of alternation" and fluorine contents vs molecular weight. Symbols as in Figure 4.

The CF_2 groups with an asterisk give resonance peaks which are enough separated from the spectrum of the regularly alternating sequence. The resonance peak of CF_2 groups far away from the propylene unit without an asterisk in (a-2) and (b-2) will be weak, since resonance peaks corresponding to these groups are not observed. Therefore, structures (a-1) and (b-1) may be the main configurations of the irregular sequences in the alternating copolymer. The sequence irregularities described as (a) and (b) were calculated from the integrated peak areas of the spectra which are shown in Table V and Figure 6 as "irregularity of alternation." We mean by this expression the number of sequence irregularities concerning tetrafluoroethylene (F) and propylene (R) units (RF units), i.e., the ratio RFFR/RFRF . As shown in Figure 6, the "irregularity of alternation," RFFR/RFRF , slightly increases with increasing molecular weight in the fractionated samples of both radiation and chemically obtained samples.

The fluorine contents in the fractionated samples measured with a fluoride ion-sensitive electrode are also shown in Table V and Figure 6. The little dependence on the molecular weight is similar to the small dependence of the irregularity of alternation in ^{19}F NMR. The calculated value of the fluorine content in an alternating copolymer of tetrafluoroethylene and propylene is 53.6% by weight. The values found for the sample produced by the chemical method almost correspond with the value calculated for the alternating copolymer. On the other hand, the values found for the sample produced using radiation are slightly above the calculated ones.

The fluorine contents in both the fractionated samples were calculated from the "irregularity of alternation" determined by ^{19}F NMR. These values are shown in Table V for purpose of comparison with the experimental ones obtained with an fluoride ion-sensitive electrode; both are in agreement. Formulae (a-1) and (b-1) will thus be the main configurations in the irregular sequences of the copolymers.

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