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Radiation-Induced Cross-linking of a Tetrafluoroethylene-Propylene Copolymer

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SUMMARY

Radiation induced cross-linking of tetrafluoroethylene-propylene copolymer with γ-rays from a ^{60}Co source and with electron beam from a Van de Graaff accelerator was investigated.

The soluble fraction of the cross-linked copolymer in tetrahydrofuran was measured to determine the G value of the cross-linking and the probability ratio between cross-linking and chain scission. It was found that the tetrafluoroethylene-propylene copolymer can be cross-linked as well as polyethylene (i.e., G = 3). Moreover, it was also found that the copolymer could be cross-linked without chain scission under the absence of oxygen.

The cross-linking occurs mainly by the abstraction of hydrogen fluoride from polymer chains. This was determined from the analysis of gases evolved from the copolymer by irradiation by means of fluorometric and mass spectrometric measurements.

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INTRODUCTION

The homopolymer of tetrafluoroethylene is a typical degradative polymer and it is difficult to produce cross-linked polymers from it. On the other hand, the homopolymer of propylene can be cross-linked by irradiation, although the G-value of the cross-linking is not high (0.1-0.3).

It was found from our experiment that this copolymer can be cross-linked by irradiation without chain scission under the absence of oxygen. The copolymer of tetrafluoroethylene and propylene obtained by the irradiation method was found to be highly alternated [1]. The high cross-linking efficiency of the copolymer may be closely related to its high alternating nature.

EXPERIMENTAL

Copolymer

The copolymer obtained by the radiation process [1] was dissolved in tetrahydrofuran in a concentration of 10 wt-% and was precipitated by methanol to remove the low-molecular weight fraction. The precipitated copolymer was dried at 80°C for 50 hr under vacuum.

The intrinsic viscosity of the copolymer in tetrahydrofuran at 30°C was 0.35, which corresponds to a number-average molecular weight of 30,000. The molecular weight distribution was measured by gel permeation chromatography, and the value of M_w/M_n was found to be 2.4, which indicates that the copolymer has almost a random molecular weight distribution.

The Huggins' constant of the copolymers was calculated from viscosity measurements, and the chlorine content in the copolymers was measured by activation analysis. These experimental results suggest that little branching structure may be included in the copolymer.

The copolymer density was 1.45.

The high alternating nature of the copolymer has been reported before [1], and it was confirmed by recent results by NMR measurements.

Irradiation

The copolymer prepared as mentioned above was pressed at 180°C to a sheet 1 mm thick. The sample sheet was introduced into a Pyrex ampoule for irradiation. Irradiation was carried out under vacuum and under atmosphere.

Measurements of Sol Fraction and Modulus of Cross-linked Copolymers

About 1 g of the irradiated copolymer was weighed and was extracted with THF for 70-80 hr through 150 mesh wire net by using Soxhlet's device to determine the sol fraction. In addition, the irradiated copolymer sheet was punched into a dumbbell shape and the elastic modulus of the sample was measured by using a tensile tester (Tensilon UTM-3).

Analysis of Gas Evolved

The sample copolymer was introduced into a Pyrex ampoule with a breakable seal and evacuated to 10^{-3} mm Hg under moderate heating. Immediately after the sample was irradiated, a certain amount of water was introduced into the ampoule through the broken seal (with care not to allow the escape of the gas evolved) to absorb the water-soluble compounds. The fluorine anion in water was titrated by thorium nitrate with the use of fluorometer [2].

The ampoule was connected to a mass spectrometer immediately after irradiation.

RESULTS AND DISCUSSION

Efficiency of Cross-linking

The changes in sol fraction are shown in Fig. 1 as a function of irradiation dose for γ-irradiation at different temperatures. The gelation doses at different temperatures were 14 (at -78°C), 6 (at room temperature), and 8 Mr (at 100°C).

It is known that the sol fraction of a cross-linked polymer with a random molecular weight distribution is related to the irradiation dose by [3].

$$S + \sqrt{S} = f + 1/qUnR \qquad (1)$$

where S. R. U_n, q, and f are the sol fraction, irradiation dose (roentgen), number-average degree of polymerization, cross-linking probability (roentgen^{-1}), and the probability ratio of chain scission to cross-linking, respectively. This copolymer has a number-average molecular weight of 30,000 and a highly alternating structure, so that we could estimate the number-average degree of polymerization to be 420 by using the molecular weight of a couple of tetrafluoroethylene and propylene. The relation be-

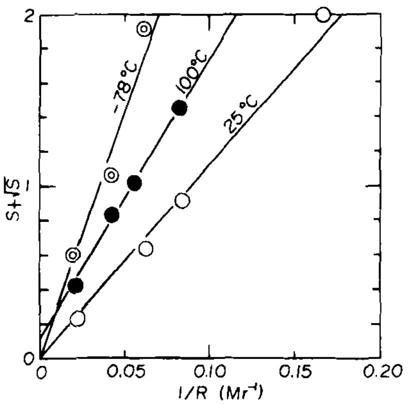

Fig. 1. Relation between sol fraction and the reciprocal irradiation dose. Irradiation was carried out at a dose rate of 10^6 r/hr at room temperature under vacuum.

tween S and R is accurately expressed by Eq. (1), as shown in Fig. 1.

The G-values of the radiation-induced cross-linking can be estimated by the following relationship between G and q:

$$G = 100\ qUnN/E \tag{2}$$

where N and E correspond to the average number of polymers in 1 g of sample and the energy absorbed by 1 g of sample with the irradiation of 1 roentgen (eV/r g-sample). Although the exact value of the absorption coefficient of this copolymer for γ-irradiation is not known, we can roughly estimate the value to be 6.25×10^{13} eV/r g-sample [4].

The G-values obtained from the slope of the lines in Fig. 1 and the f values in Table 1 indicate that the cross-linking proceeds with no or very little chain scission at these temperatures. The G-values show that cross-linking occurs most efficiently at room temperature. In this case, the G-value is about the same as that of polyethylene.

The cross-linking of homopolymers of propylene is not easily accomplished. Atactic polypropylene, for example, did not produce gell with as much as 50 Mr of irradiation. On the other hand, polytetrafluoroethylene is a typical degradative polymer. It is therefore implied that the copolymer would be degradative if it had some block sequences of either monomer. The high cross-linking efficiency, in consequence, should be interpreted as due to the

Table 1. Cross-linking efficiency[a]

Irradiation temperature (°C)	G	f
-78	1.2	0
25	2.9	0
100	1.9	0.1

[a] Irradiation was carried out in a dose rate of 10^6 r/hr under vacuum at different temperatures.

high alternating nature of the copolymer structure. This is one example of the interesting cases in which an alternating copolymer possesses utterly different properties than the homopolymers of either monomer. The low G-value of cross-linking below the glass transition temperature may be due to the low mobility of the polymer chain. The low G-value at 100°C, on the other hand, cannot be explained yet.

The results of cross-linking of the copolymer with both γ rays and electron beams in the presence of air are shown in Fig. 2. G-values were 2.6 and

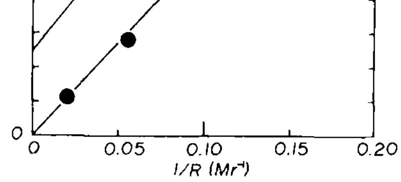

Fig. 2. Relation between sol fraction and reciprocal irradiation dose. Irradiation was carried out at room temperature in the presence of air. (○): Co γ-ray, 10^6 r/hr. (●): electron beam, 0.48 μA/cm^2, 1.5 Mv.

2.9, respectively, which are about the same as in the case of irradiation under vacuum. There is a difference in the *f* value in the presence and absence of air for the γ-ray irradiation. The *f* value in air was 0.5. It remained at zero, however, when irradiation was carried out with electron beams. In the latter case the time required for the same irradiation dose is of the order of 1/100 compared to that of γ rays. For that reason the oxygen, which seems to cause chain scission under irradiation, diffuses into the sample in such small quantities that the copolymer could be cross-linked without a marked effect of the oxygen.

It was observed that the copolymer specimen foams when it is exposed to a high-intensity electron beam. This is due to the evolution of certain kinds of low-molecular weight substances such as hydrogen fluoride and hydrogen molecules.

The stress-strain curves of the copolymer specimen irradiated with electron beams at room temperature in the presence of air are shown in Fig. 3. The elastic modulus is related with the cross-linking density by

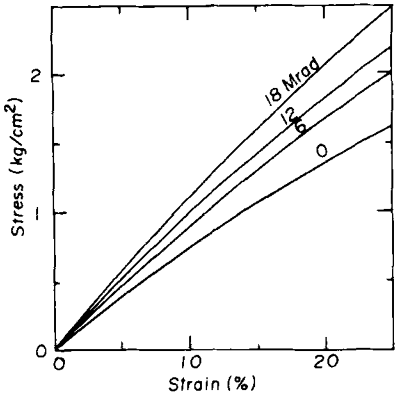

Fig. 3. Stress-strain behavior of irradiated copolymer specimen. Irradiation was carried out with electron beam (0.48 μA/cm^2, 1.5 Mv) at room temperature in the presence of air.

$$\tau = \mathrm{RgT}\nu\psi(\alpha) \qquad (3)$$

where τ, ν, Rg, T, α, and $\psi(\alpha)$ are elastic modulus (kg/cm^2), cross-linking density (mole/cm^3), gas constant (kg cm/mole deg), absolute temperature, ratio of length of strained sample to initial length, and a function of α, respectively. Equation (3) can be transformed to Eq. (4) when α is small:

$$\tau = \mathrm{RgT}\nu(\alpha - \alpha^{-2}) \qquad (4)$$

When RgTν is expressed by A, Eq. (4) becomes

$$A = \tau\alpha^2/(\alpha^3 - 1) \qquad (5)$$

The values of A at different doses can be estimated from the results shown in Fig. 3. "A" values are plotted against irradiation dose in Fig. 4. The increase in cross-linking density per rad ($\Delta\nu$) is expressed by

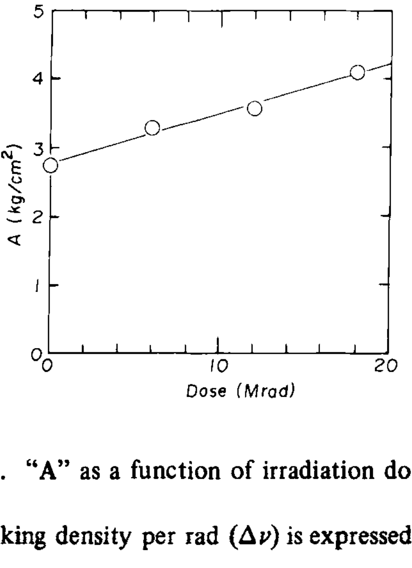

Fig. 4. "A" as a function of irradiation dose.

$$\Delta\nu = \mathrm{m/RgT} \qquad (6)$$

in which m expresses the slope of the line in Fig. 4. For Rg = 82, T = 298, and m = 7×10^{-8}, the value of $\Delta\nu$ is 2.9×10^{-12} (mole/cm^3 rad). This means that 1 rad of irradiation produces cross-links with a probability of about 6×10^{-8} in a polymer chain.

The probability of cross-linking, on the other hand, evaluated from the results of gel formation shown in Fig. 1 and Table 1, yields the value of 9×10^{-8} per roentgen. These two values show fairly good agreement. The small difference may be due to the fact that the whole number of cross-links does not contribute to the elasticity of the irradiated copolymer specimen.

Mechanism of Cross-linking

The mechanism of cross-linking of the copolymer is interesting. The gases evolved when the copolymer was irradiated were identified by the use of a fluorometer and a mass spectrometer.

Fluorine anions detected by the fluorometer are ascribed to hydrogen fluoride since the water solution of the substances evolved from the irradiated copolymer was acidic. It was also shown from the mass spectrum of gaseous products that hydrogen fluoride is the main component of the evolved gas. The quantity of HF thus given by fluorometry is plotted against the irradiation dose in Fig. 5, in which the cross-linking density is shown for comparison. The quantity of HF increases linearly with irradiation dose and is nearly half of the cross-linking density.

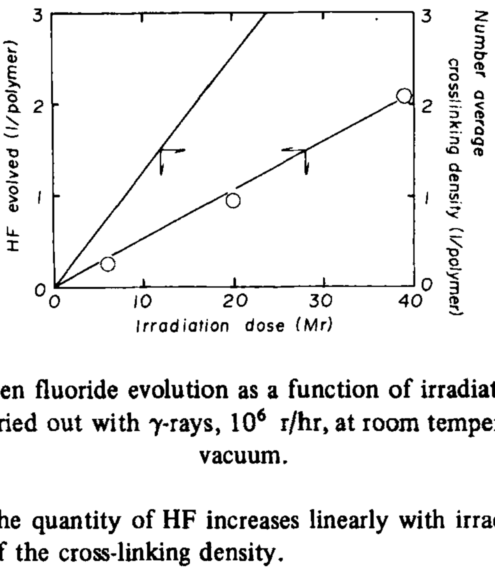

Fig. 5. Hydrogen fluoride evolution as a function of irradiation dose. Irradiation was carried out with γ-rays, 10^6 r/hr, at room temperature under vacuum.

There may be two possible changes in the polymers due to hydrogen fluoride evolution from the irradiated copolymers. One is cross-linking (via mainly intermolecular elimination); the other is double bond formation in the polymer chain. The infrared measurement made clear that there are no observable double bonds in the irradiated copolymers. Therefore, the evolution of the hydrogen fluoride contributes to the formation of cross-linking between polymer chains. This agrees with the small amount of hydrogen fluoride evolved compared to the amount of cross-linking. Thus about one-half of the cross-linking may be caused by the intermolecular elimination of hydrogen fluoride.

This is supported by the relatively weak bondage of hydrogen to the tertiary carbon of propylene and the large heat of formation of hydrogen fluoride. A similar mechanism of cross-linking was proposed in the case of vinylidene fluoride-hexafluoropropylene copolymer [5].

Analysis of evolved gas by mass spectrometry showed that hydrogen and methane are also generated from the irradiated copolymer.

CONCLUSION

The efficiency and mechanism of radiation-induced cross-linking of a highly alternating copolymer of tetrafluoroethylene and propylene with almost random molecular weight distribution were elucidated.

The G-value of cross-linking of the copolymer was 2.5-3.0 at room temperature, with little or no chain scission when the oxygen was absent. This high efficiency of cross-linking was ascribed to the high alternating structure of the copolymer.

Cross-linking was presumed to be due mainly to the intermolecular abstraction of hydrogen fluoride and partly to that of hydrogen and methane.

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