

Radiation Stability of PTFE with Different Crystallinity

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SYNOPSIS

In this work, the effects of radiation on polytetrafluoroethylene (PTFE) samples with different crystallinity were studied. Using Suwa's equation for calculating the number-average molecular weight of PTFE, the radiation-induced reduction in molecular weight was followed and the G values for scission of PTFE were also obtained on the basis of the changes in molecular weight. The $G(\text{scission})$ for as-polymerized PTFE was 2.15 ± 0.01 , whereas for sintered sample, which has a relative low crystallinity, $G(\text{scission}) = 6.0 \pm 0.14$. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

PTFE is well known to be a radiation-sensitive polymer and very little irradiation was reported to cause a dramatic degradation of its molecular weight.^{1,2} Considerable research has been done on the radiation chemistry of polytetrafluoroethylene (PTFE), but because of the insolubility of the polymer, little progress has been made in elucidating G values for scission of polymer chains, i.e., the number of chain scissions per 100 eV of energy absorbed. Florin et al.³ determined the G values for the primary chemical damage caused by high-energy irradiation in PTFE to be $G(\text{damage}) = 3.3 \pm 0.3$. G values of 3.0 ± 0.1 for radiation-induced damage were also calculated by Kusy⁴ from depression of the melting temperature for PTFE samples irradiated near room temperature. It is well known that the reaction between high-energy rays and polymer molecules is a complex process; therefore, radiation-induced damage should include scission of polymer chains, cross-linking and/or branching, and the formation of unsaturated structures and end groups. The G values obtained by the above methods are based on radiation-induced changes in macroproperties of the polymer and thus can only reflect the whole effects of different radiation-induced structural changes. In

the present work, on the basis of the methods for calculating number-average molecular weight of PTFE developed by Suwa et al.⁵ radiation-induced changes in molecular weight (M_n) were observed and, thus, G values for the scission of polymer chains were obtained that are quite different from those reported in references and depend strongly on the crystallinity of the sample.

EXPERIMENTAL

The PTFE samples used in this work are from Shanghai Institute of Organicfluorine Chemistry of China, produced by polymerization in emulsion. The low crystallinity PTFE was obtained by sintering of the same PTFE powder at 380°C for 4 h and then quenching in air.

Irradiation was carried out with a 70,000 Ci Co-60 source under 0.2 Pa. The dose rate used was 0.5 Mrad/h.

DSC measurement was made on a Perkin-Elmer DSC-7 differential scanning calorimeter under nitrogen atmosphere. The heating and cooling rates are 10°C/min.

The molecular weight of PTFE was calculated by using Suwa's equation:

$$M_n = 2.1 \times 10^{10} H_c^{-5.16} \quad (1)$$

where H_c is the heat of crystallization in cal/g.

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RESULTS AND DISCUSSION

Assuming that the initial number of molecules of a high polymer per gram is $N/M_n(0)$, where N is Avogadro's number and $M_n(0)$ is the initial number-average molecular weight, then after irradiation to dose D , the number of molecules is $N/M_n(D)$. Each main chain rupture increases the number of molecules by one; hence,

$$N/M_n(D) = N/M_n(0) + DG(\text{scission})/100 \quad (2)$$

where $G(\text{scission})$ is the number of chain scissions per 100 eV of energy absorbed and D is the absorbed dose in electron volts per gram, and, then,

$$G(\text{scission}) = \frac{100N}{D} \left(\frac{1}{M_n(D)} - \frac{1}{M_n(0)} \right) \quad (3)$$

Tables I and II show the effect of radiation on some thermal properties of as-polymerized and sintered PTFE, M_n and G values for scission are calculated using eq. (3).

The data in Tables I and II indicate that the radiation sensitivity of PTFE is strongly dependent on its crystallinity. For as-polymerized samples that are highly crystalline, it can be seen that radiation has little effect on heat of fusion, indicative of polymer crystallinity, and melting temperature, which is in agreement with observed results of many researchers.^{4,6,7} For the sintered sample, which has a much lower crystallinity and melting temperature relative to as-polymerized PTFE, the heat of fusion was observed to increase with increasing irradiation dose and the melting temperature also showed the same trend. More quantitatively, it can also be found from the tables that at the same exposure dose the degradation of molecular weight for the sintered sample is much more serious than that for as-polymerized PTFE. On the other hand, on the basis of molecular weight data listed in Tables I and II, the G values for scission of PTFE $G(\text{scission})$, calculated from eq. (3), are also listed in the tables. It

is clear that the obtained $G(\text{scission}) = 2.15 + 0.01$ for as-polymerized samples is lower as compared with $G(\text{damage}) = 3.3 \pm 0.3$ reported by Kusy⁴ in which the PTFE powder used was also obtained directly from the polymerization reaction and thus should be similar to as-polymerized samples used in the present work both in crystallinity and morphology.

Taking into account differences in the calculation method and meanings involved in the values, however, this difference is easy to understand. As mentioned above, the $G(\text{damage})$ calculated on the basis of radiation-induced depression of the melting temperature represents the whole damage caused by irradiation including scission, cross-linking and/or branching, and the formation of unsaturated structures. Figure 1 gives the infrared spectra of PTFE before and after irradiation. After irradiation to a dosage of 320 and 670 kGy at room temperature, the absorption band at 1780 cm^{-1} due to $\text{CF}=\text{CF}$ — becomes much stronger than that of the unirradiated sample, especially at high dose. Therefore for as-polymerized PTFE, an allowance should be made for the contribution from radiation-induced unsaturated structures to the $G(\text{damage})$ calculated by the radiation-induced depression of the melting temperature of irradiated PTFE. From the present work, it can be seen that the $G(\text{scission})$ of as-polymerized PTFE is about two-thirds of $G(\text{damage})$.

On the other hand, as shown in Table II, for sintered PTFE, which has a low crystallinity relative to the as-polymerized sample as indicated by the heat of fusion, irradiation is seen to cause a gradual increase in the heat of fusion, which is consistent with the observations reported by many investigators about a radiation-induced increase in crystallinity of PTFE.^{4,8} The driving force for the radiation-induced increase in crystallinity results from the relief of stress built up in the amorphous phase formed during the nonequilibrium crystallization caused by scission of polymer chains, which permits further crystallization. In the past several decades, much research work has been carried out on the region where the radiation-induced scission of polymer

Table I Radiation-Induced Changes in Thermal Properties of As-polymerized PTFE

Dose (kGy)	H_m (J/g)	T_m (°C)	H_c (J/g)	T_c (°C)	$M_n \times 10^6$	G (scission)
0	59.1	338.9	25.3	315.6	1.95	
0.5	60.9	339.5	26.24	315.8	1.61	2.16 + 0.01
2.3	59.6	339.2	28.9	315.5	0.99	2.15 + 0.01
4.0	60.7	338.9	30.6	315.1	0.73	2.14 + 0.01

Table II Radiation-Induced Changes in Thermal Properties of Sintered PTFE

Dose (kGy)	H_m (J/g)	T_m (°C)	H_c (J/g)	T_c (°C)	$M_n \times 10^6$	G (scission)
0	35.4	333.2	25.3	312.4	1.95	
0.5	37.9	333.3	27.7	312.8	1.22	6.12 + 0.01
2.3	38.2	333.6	32.5	313.1	0.53	6.00 + 0.01
4.0	44.9	334.4	35.3	312.5	0.35	5.86 + 0.01

chains occurs. On the basis of observations of radiation-induced depression of the transition temperature and deterioration of mechanical properties, some thought the scission to occur mainly in the crystalline phase.⁹ The "cage effect" of radiation-induced macromolecular radicals,⁸ studies on dynamic mechanical properties,¹⁰ and infrared spectra studies of irradiated PTFE,⁸ however, encouraged others to conclude that most of scissions occurred in the amorphous region. The observed marked decrease in molecular weight of the low crystallinity sample and high G (scission) value for sintered PTFE relative to the as-polymerized sample in the present work clearly demonstrate that the molecular weight of low crystallinity PTFE is more sensitive to irradiation than is high crystallinity PTFE, which, we think, makes it possible that radiation-induced

scission of PTFE occurs predominantly in the amorphous region.

The G (scission) = 6.0 ± 0.14 for sintered PTFE observed here seems too high relative to that for as-polymerized PTFE and G (damage) reported in the references. Taking into account the difference in crystallinity of examined PTFE samples, however, this value seems acceptable and reasonable. In Kusy's work,⁴ the PTFE samples used were directly from the polymerization reaction that has a crystallinity as high as 20 cal/g and about 2.5 times that of sintered PTFE used in our work; therefore, owing to the dependence of radiation sensitivity on crystallinity,¹¹ more scissions of polymer chains are expected to occur in low-crystallinity samples and thus lead to high G (scission) values. Moreover, as shown in Tables I and II, the G (scission) values could be

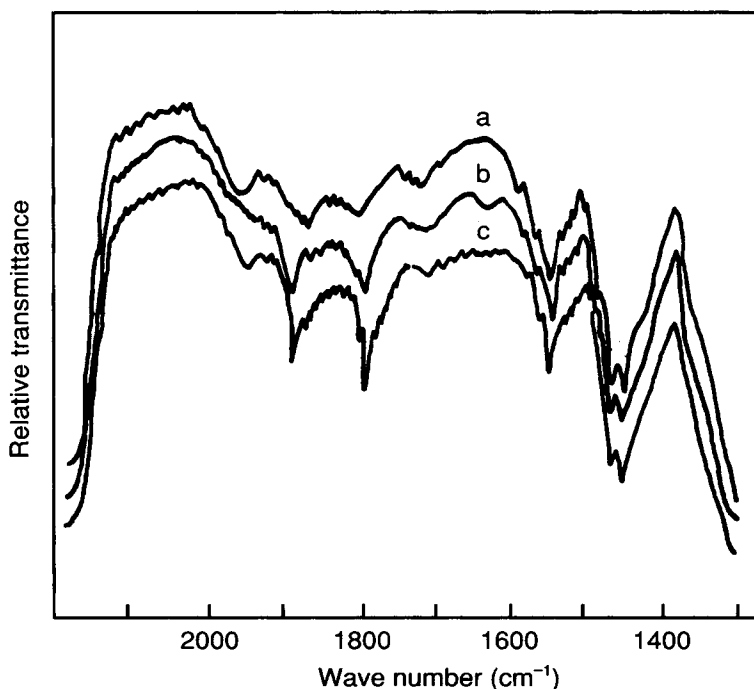


Figure 1 The infrared spectra of PTFE irradiated to dosage of (a) 0, (b) 320, and (c) 670 kGy at ambient temperature.

observed to decrease slightly with increasing irradiation dose, which, we think, might result from the accelerating effect of residual oxygen in the irradiation system on the scission of macromolecules.

On the basis of the above discussion, it can be concluded that the radiation-induced scission of polymer chains of PTFE strongly depends on the crystallinity of samples. The low-crystalline PTFE was observed to have high G values for scission relative to high-crystalline PTFE.

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Received January 22, 1992

Accepted May 7, 1992