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Dielectric Properties of Gamma-Irradiated
Tetrafluoroethylene-Hexafluoropropylene Copolymers

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The effect of gamma-irradiation on dielectric properties in copolymers of tetrafluoro-ethylene and hexafluoropropylene (TFE-HFP copolymer) has been investigated in connection with possible change in the structure of this copolymer. The dielectric constant and loss were measured on irradiated TFE-HFP copolymers with different irradiation doses at frequencies from 1 to 300 kHz over a temperature range of −40 to +180°C. In accordance with the dielectric constant versus temperature relation the coefficient of thermal expansion in the copolymers exhibited a small change at about 60°C, indicating the existence of a transition. The changes in both the dielectric constant and the expansion coefficient were obscured for a highly irradiated copolymer. The sizes of the α and γ relaxations found for unirradiated copolymers were influenced by gamma irradiation: With increasing the irradiation dose the magnitude of the γ loss peak increased and the α loss peak showed a considerable change at the dose of 10MR. The γ relaxation was dependent also on the degree of crystallinity. The activation enthalpy and entropy for the α relaxation were reduced with raising the irradiation dose, while these activation parameters in the γ one showed a gradual increase. The results were discussed in relation to the chain scission of the copolymer by gamma-irradiation.

INTRODUCTION

Results of precision measurements on the dielectric constant and loss of copolymer of tetrafluoroethylene and hexafluoropropylene (TFE-HFP copolymer) conducted in this laboratory[1] revealed that the copolymer showed the α and γ relaxations consistent with the mechanical behavior. A considerably higher dielectric loss of the copolymer in comparison with polytetrafluoroethylene (PTFE) was attributed to the slightly polar character of the perfluoromethyl side groups along the copolymer chain. The α and γ relaxations were ascribed to the respective molecular motions of small and large segments, as was discussed by Mc-Crum[2] and Eby and Wilson.[3] The latter authors proposed a molecular model in which the relaxation was assigned to motions of a small point defect in the crystal lattice. The present work was undertaken to investigate the effect of gamma-irradiation on the dielectric properties of TFE-HFP copolymer, since the irradiation would fracture the molecular chain and result in some change in the structure of copolymer which could be reflected by the dielectric properties. Although the

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effect of γ-irradiation on physical properties of PTFE[4,5] have been fairly extensively studied, little has been known about irradiated TFE-HFP copolymers.

This paper deals with the dielectric relaxation in the gamma-irradiated copolymers and its correlation with structural change in the copolymer by the irradiation.

EXPERIMENTAL

Physical properties of the samples used are tabulated together with the total irradiation dose in Table 1. Specimens for dielectric measurements were thin films of 70 mm dia and 0.15 mm thick. Block samples weighing about 2 g were also used for measurements of the thermal expansion coefficient. The irradiation was carried out in air by utilizing the 2 kCi ^{60}Co gamma-ray irradiation facility at this institute. The thermal expansion coefficient was evaluated from the density measured in silicone oil at temperatures from 10 to 120°C by use of the buoyancy method. The density at room temperature was measured also in n-butanol. The degree of crystallinity was determined by the X-ray diffraction method. Infrared spectra were taken of film samples of about 0.05 mm thick to examine a structural change in the copolymer by γ-irradiation. HFP concentrations were evaluated with quenched films by means of the infrared spectra.[6]

Dielectric measurements were curried out using a transformer bridge, the Type TR 10 Bridge from Ando Electric Co., Tokyo, which was equipped with a guard circuit of the Wagner type in order to obtain a higher accuracy in capacitance and conductance measurements. The bridge worked satisfactorily in the frequency range of 10 Hz to 300 kHz. The precision in capacitance measurements was within $\pm 0.02\%$, the lowest limit of dissipation factor to be found was about 2×10^{-6} between 1 and 300 kHz. The accuracy of dielectric constants was limited by the specimen thickness, being better than $\pm 3\%$. The dielectric cell was a three-terminal type and the electrical contact between the specimen and the electrode plates of the cell was ensured by use of thin aluminum electrodes which were formed on the specimen surface by vacuum evaporation process.[7]

Temperature of dielectric cell assembly was controlled thermostatically within

Table 1. List of the samples used.

Sample No.	Form	HFP Concentration, mole %	Crystallinity, %	Density, g/cc at 25°C	Total Irradiation Dose, MR	Annealing*
1	film	11.9	35	2.132	0	no
2	,,	,,	41	2.136	1	no
3	,,	,,	45	2.151	1	yes
4	,,	,,	40	2.136	10	no
5	,,	15.5	42	2.154	0	yes
6	block	11.9		2.141	0	yes
7	,,	,,		2.151	1	yes
8	,,	,,		2.157	3	yes

* Annealed for 16 h at 200°C after irradiation.

±0.5°C. The rate of varing temperature was about 5°C/h; no hysteresis was observed in the values of capacitance and conductance measured as a function of temperature. The dielectric constant and loss were determined over a temperature range of −40 to 180°C at frequencies from 1 to 300 kHz.

RESULTS

The dielectric constant ε' at 100 kHz for TFE-HFP copolymers with different irradiation doses are plotted against temperature t in Fig. 1. There was no considerable dependence of ε' on frequency. The variation of density with tempera-
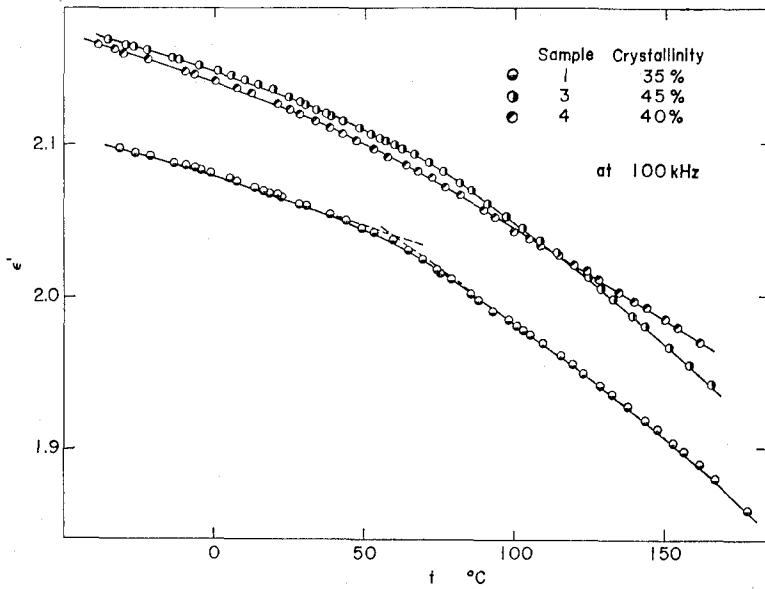

Fig. 1. Variation of the dielectric constants ε' with temperature t of irradiated TFE-HFP copolymers at 100 kHz.
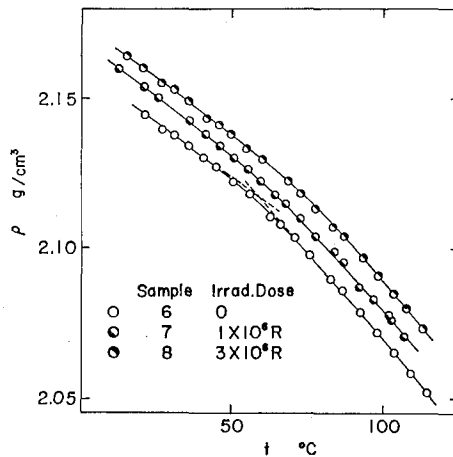

Fig. 2. Plots of the density versus temperature for irradiated TFE-HFP copolymers.

ture is shown in Fig. 2. Both the dielectric constant and the density versus temperature curves exhibited a change in the slope at 60°C. In Fig. 3 the variation of the dielectric loss ε'' with temperature is drawn with samples 1, 2, 3, and 4. The α loss peak around 110°C was not affected by the irradiation of the order of 1MR, while the magnitude of the γ loss peak below 0°C increased gradually with higher irradiation doses. Figs. 4 and 5 are the dielectric loss versus temperature curves at several different frequencies for samples 2 and 3, respectively. By comparing these figures it can be seen that the unannealed sample exhibited a very small loss peak at about 50°C.

Infrared spectra showed no significant change at an irradiation dose of 1 MR. However, at 10 MR a medium absorption band appeared at 1770 cm^{-1} which was tentatively assigned to the CO vibration. As is the case with PTFE[8] the 715 and 775 cm^{-1} bands were sensitive to the degree of crystallinity.

DISCUSSION

Dielectric constants of irradiated copolymers were a little higher than those for unirradiated ones. This is likely due to an increase in the degree of crystallinity i. e. the density. It is evident that there exists a transition of the second order nature at about 60°C, since both the dielectric constant and the density versus temperature curves exhibited a change in the slope at this temperature as shown in Figs. 1 and 2. No appreciable dependence of this transition temperature on the crystallinity and the irradiation dose was found. In facts the transition was obscured in the highly irradiated copolymer sample 4.

The α and γ dielectric relaxations occurred above and below the transition temperature, respectively.[1] The γ loss peak around -20°C was dependent not only on the irradiation dose, but also on the crystallinity (Fig. 3). The magnitude
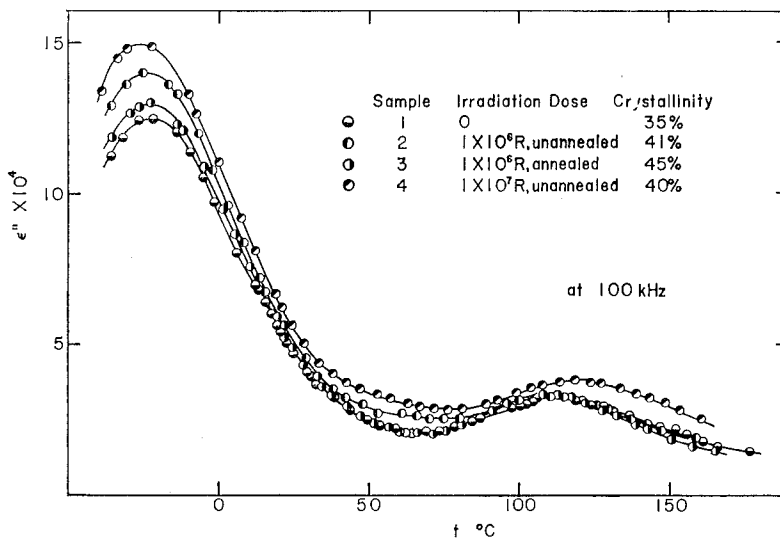

Sample	Irradiation Dose	Crystallinity
1	0	35%
2	1×10⁶R, unannealed	41%
3	1×10⁶R, annealed	45%
4	1×10⁷R, unannealed	40%

at 100 kHz

Fig. 3. Variation of the dielectric loss ε'' with temperature t of irradiated TFE-HFP copolymers at 100 kHz.

of the γ peak increased with the irradiation dose but decreased with higher crystallinities. These results suggest that the γ relaxation is related to motions of short segments at or near the ends of the copolymer chain in amorphous regions, because the irradiation process increases the number of shorter segments owing to the chain scission. In the α relaxation the loss peak depended on neither the irradiation nor the crystallinity at the dose of 1 MR. But a considerable change in the α peak took place at 10 MR.
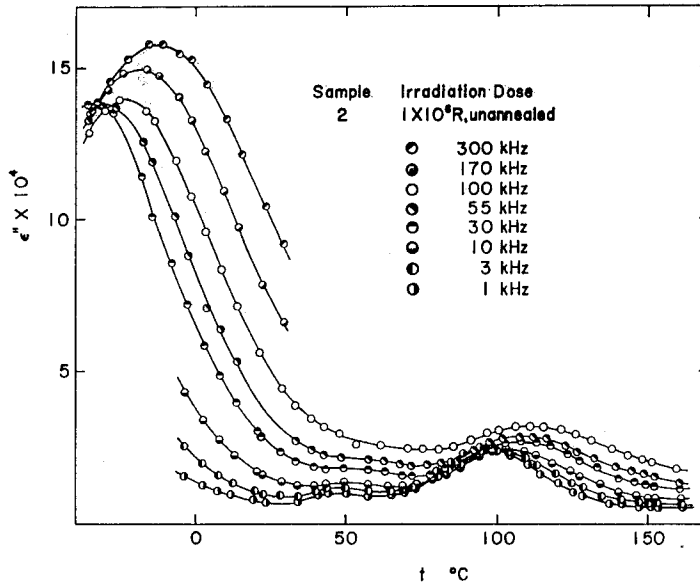

Fig. 4. Plots of the dielectric loss ε'' versus temperature t for unannealed copolymer sample 2 at different frequencies.
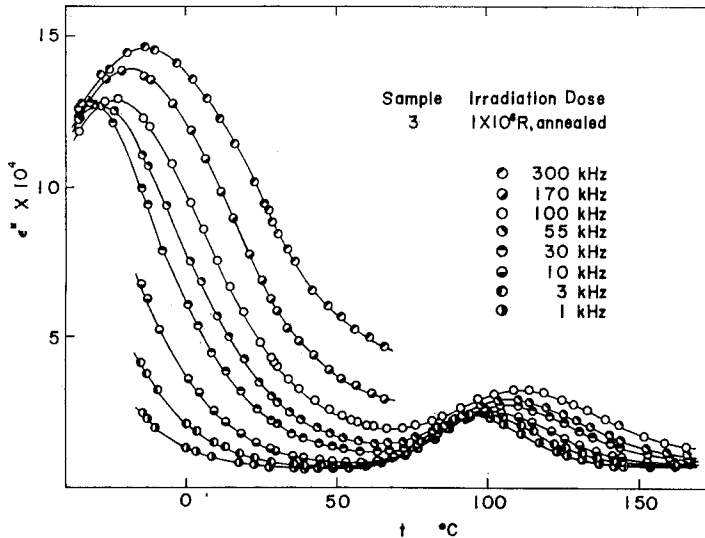

Fig. 5. Plots of the dielectric loss ε'' versus temperature t for annealed copolymer sample 3 at different frequencies.

A very small loss peak at 50°C in the unannealed copolymer sample 2 diminished in the case of the annealed one as seen from Figs. 4 and 5. This small peak would be associated with the molecular motion in amorphous regions, since the infrared spectra showed no difference between sample 2 and 3 except for that in intensitites of amorphous bands at 715 and 775 cm⁻¹.

Logarithm of the relaxation frequency ω_m are plotted against the reciprocal of absolute temperature $1/T$ for the α and γ relaxations in Fig. 6. The activation enthalpy and entropy, $\varDelta H$ and $\varDelta S$, for these relaxations were obtained from the slope of $\log \omega_m$-$1/T$ plots and listed in Table 2. Evedently the values of these activation parameter for the α relaxation are much greater than those for the γ one. The values of $\varDelta H$ and $\varDelta S$ for the α relaxation decreased with higher irradiation doses. From these results it is obvious that the size of segments involved in the α relaxation was reduced owing to the chain scission by the irradiation so that activation parameters showed a considerable decrease.
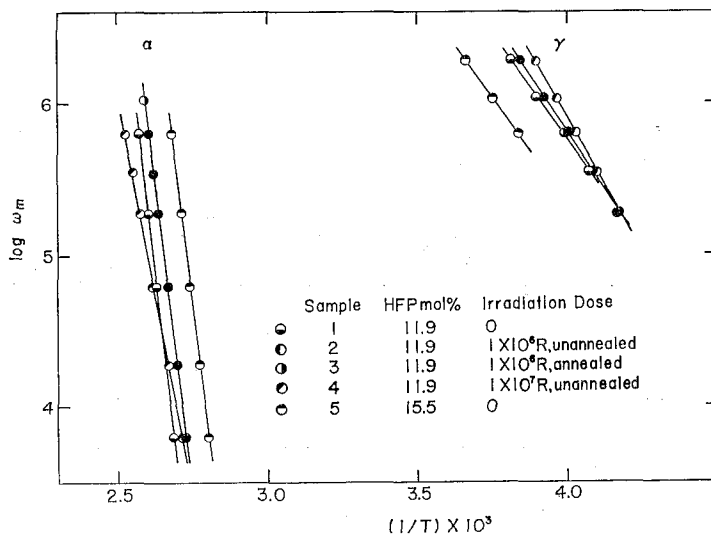

Fig. 6. Plots of logarithm of the relaxation frequency versus reciprocal of absolute temperature for the α and γ relaxations.

Table 2. Activation parameters for the α and γ relaxations in irradiated TFE-HFP copolymers.

Sample No.	Crystallinity %	α relaxation				γ relaxation				Irradiation dose, MR
		$\varDelta H$, kcal /mole	$\varDelta S$, eu	$(\varDelta S/12\varDelta H)$ $\times 10^4$, degree⁻¹	$\beta \times 10^4$ (100°C), degree⁻¹	$\varDelta H$, kcal /mole	$\varDelta S$, eu	$(\varDelta S/12\varDelta H)$ $\times 10^4$ degree⁻¹	$\beta \times 10^4$ (30°C), degree⁻¹	
5	42	78	177	1.89	1.74	12	13	0.90	1.17	0
1	35	82	178	1.81	1.83	12	16	1.11	1.13	0
2	41	76	164	1.80	1.86	13	21	1.35	1.29	1
3	45	74	160	1.80	1.83	13	21	1.35	1.18	1
4	42	48	89	1.51	1.46	16	31	1.62	1.21	10

In the diffusion process of several amorphous polymers the ratio of ΔS to ΔH is related to the volume expansion coefficient α by the equation.[9]

$$\Delta S/\Delta H = 4\alpha.$$

Also in Table 2 the value of $\Delta S/12\Delta H$ are shown and compared with the linear expansion coefficient β. In accordance with Eby and Wilson's results,[3] the values of $\Delta S/12\Delta H$ in the α relaxation above the transition temperature are very close to those of the linear expansion coefficient of the copolymers, although this relation dose not necessarily hold for the γ relaxation below the transition temperature. It is noteworthy that a considerable decrease in $\Delta S/\Delta H$ for the α relaxation in the highly irradiated copolymer corresponds to a small value of the expansion coefficient even at higher temperature and thus obscures the transition temperature in the dielectric constant and the density versus temperature curves.

Also in the copolymer sample 4 there might be a possibility of the contribution to dielectric polarization and relaxation of the polar groups produced by the irradiation process, whereas infrared spectra showed an absorption band at 1770 cm^{-1}. The details concerning this point have not been made clear yet.

CONCLUSION

From the present work on the dielectric relaxation in gamma-irradiated TFE-HFP copolymers the following was concluded : The dielectric constant and the density data indicated the existence of a transition of the second order nature at 60°C in this copolymer. No appreciable change in the α relaxation was observed at the irradiation dose of 1 MR, but with a higher dose a marked increase in the magnitude of the α loss peak occurred, which was attributed to the scission of the main chain by irradiation. The size of the γ relaxation associated with motions of short segments in amorphous regions of the copolymer depended on both the irradiation dose and the degree of crystallinity. A very small loss peak at 50°C observed for an irradiated copolymer would be assigned to the molecular motion in amorphous regions.

ACKNOWLEDGMENTS

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