

Network structure in poly(vinylidene fluoride–trifluoroethylene) electrostrictive films

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Recent studies of electron-irradiated copolymers of vinylidene fluoride and trifluoroethylene have demonstrated the potential for achieving a large electrostrictive response in these materials. Since the principal effect of the radiation is network formation, alternative methods of achieving improved electromechanical properties are available. In this letter, we use a two-solvent swelling technique to quantify the polymer-solvent interaction parameter for the copolymer networks. This enables determination of their crosslink densities, along with a measure of the degree of degradation accompanying radiolysis. Copolymer networks were then prepared chemically using organic peroxide. These networks were found to be similar to the radiation-crosslinked materials, both in the extent of degradation and with respect to the Curie temperature and crystalline melting behavior. The latter are crucial to the development of better electrostrictive properties. © 2001 American Institute of Physics. [DOI: 10.1063/1.1344228]

Copolymers of vinylidene fluoride and trifluoroethylene [P(VDF–TrFE)] have been the focus of recent research due to their promising electromechanical properties. Unlike poly(vinylidene fluoride) (PVDF) homopolymer, the copolymers crystallize spontaneously into the all-trans β -crystalline phase, and have Curie temperatures below their melting points. Irradiation of P(VDF–TrFE) with high energy electrons¹ or gamma rays² induces a solid state, irreversible transformation of the ferroelectric lattice to a paraelectric phase. Although such irradiation has no effect on the response to electric fields,³ it confers the capacity for a substantial electrostrictive response, in combination with a large elastic energy density.^{4,5} The mechanism is through reduction in the size of the crystallites having an all-trans conformation,⁶ yielding nanometer-sized domains within the β -crystalline phase. By interrupting the coherence length of the crystal, radiation presumably facilitates rotation (motion of the chain twist boundaries⁷) in response to an applied field. Irradiated PVDF copolymers have potential in various applications including transducers, sensors, and actuators. However, a fundamental understanding of these materials is lacking. Electron irradiation causes crosslinking, chain scission, isomerization, bond rearrangement, etc. with consequent effects on the material's chemical and physical properties. Since these properties are crucial for practical applications, a systematic study of the changes induced by ionizing radiation is of obvious importance. Such information is also necessary to develop alternative methods to achieve the desired electromechanical properties. This report describes characterization of P(VDF–TrFE) copolymer networks produced by electron irradiation, along with an assessment of a chemi-

cal method (reaction with organic peroxide) to achieve similar structures. Chemical crosslinking offers processing advantages, and can allow better control over the obtained structure.

The material was a random copolymer of 68 mole % vinylidene fluoride and 32% trifluoroethylene. The irradiated films, obtained courtesy of Q.M. Zhang of the Pennsylvania State University, were $\sim 30 \mu\text{m}$ thick. They had been irradiated with 2.6 MeV electrons at $98 \pm 3^\circ\text{C}$ while either unstretched or maintained at 450% strain. Details of the radiolysis can be found elsewhere.^{3,4} Chemical crosslinking was accomplished using 4%–10% by weight dicumyl peroxide (Varox DCP-R from R. T. Vanderbilt) added in solution. Cast films, typically 0.15 mm, were cured under pressure for 30 min at 180°C . Calorimetry experiments employed a Perkin-Elmer DSC 7.

Since networks are formed, the principal effect of radiolysis is crosslinking of the copolymers. The Flory–Rehner equation⁸ relates the number density of network chains, ν , of functionality f (cycle rank = $[1 - 2/f]\nu$) to the volume fraction of the network at equilibrium swelling, ν_R

$$\nu = -[\ln(1 - \nu_r) + \nu_r + \chi \nu_r^2] / [V_s(\nu_r^{1/3} - 2\nu_r/f)], \quad (1)$$

where V_s is the molar volume of the solvent. Applying Eq. (1) requires a value for the polymer–solvent interaction parameter, χ . To determine this, we measure networks of varying crosslink density ν_R in two solvents, and solve Eq. (1) for both simultaneously:⁹

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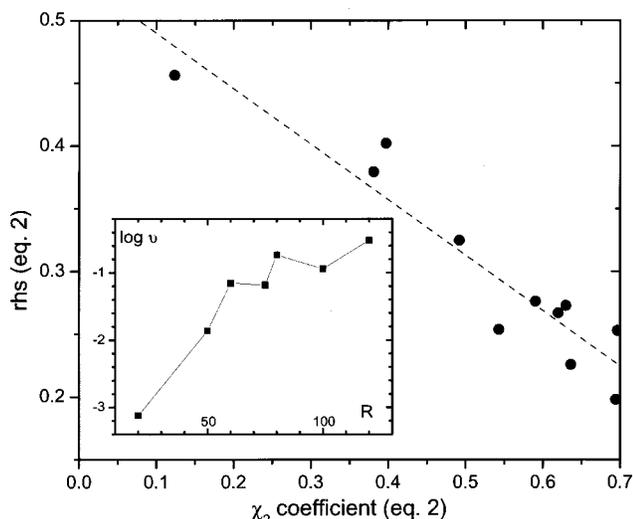


FIG. 1. Solvent swelling parameters [Eq. (2)] for radiation crosslinked P(VDF-TrFE) networks, yielding $\chi_{DMF}=0.44$ and $\chi_{MEK}=0.53$ from the intercept and absolute value of the slope, respectively. The inset shows the average network density (moles/L) calculated from Eq. (1) as a function of dose (in Mrad).

$$\begin{aligned} \chi_1 - \chi_2 & \left(\frac{V_{S,1}(\nu_{r,1}^{1/3} - 2\nu_{r,1}/f)\nu_{r,2}^2}{V_{S,2}(\nu_{r,2}^{1/3} - 2\nu_{r,2}/f)\nu_{r,1}^2} \right) \\ & = \left(\frac{V_{S,1}(\nu_{r,1}^{1/3} - 2\nu_{r,1}/f)}{\nu_{r,1}^2} \right) \\ & \times \left(\frac{\ln(1 - \nu_{r,2}) - \nu_{r,2}}{V_{S,2}(\nu_{r,2}^{1/3} - 2\nu_{r,2}/f)} - \frac{\ln(1 - \nu_{r,1}) - \nu_{r,1}}{V_{S,1}(\nu_{r,1}^{1/3} - 2\nu_{r,1}/f)} \right) \end{aligned} \quad (2)$$

in which the subscripts 1 and 2 refer to either solvent. The interaction parameters can be obtained from the slope and intercept, respectively, of a plot of the right-hand side of Eq. (2) versus the bracketed term on the left-hand side.

This relation is plotted in Fig. 1 for the radiation-crosslinked networks of varying ν , swollen in N,N-dimethylformamide ($V_{DMF}=76.9$ mL/mole) and in methyl-ethylketone ($V_{MEK}=88.9$ mL/mole). Assuming $f=4$, we obtain $\chi_{DMF}=0.44 \pm 0.05$ and $\chi_{MEK}=0.53 \pm 0.03$. Although the difference is marginal, better solubility in DMF would be consistent with the solubility parameters for these materials.¹⁰ Using these values in Eq. (1), along with the measured ν_r , we calculate the crosslink densities displayed in the inset of Fig. 1. From these results, the average number of crosslinks per 100 eV is obtained, $G_{\times}=0.75 \pm 0.17$. This is in the range reported for other PVDF copolymers.¹¹

Along with the crosslinking that leads to network formation, ionizing radiation causes side reactions in polymers, such as scissions, rearrangements, isomerization, cyclization, etc. Although most of these events are quite fast, in semi-crystalline polymers such as P(VDF-TrFE), transients (e.g., ions and radicals) can survive for hours.¹² Moreover, the high ionization potential and low polarizability of the C-F bond can lead to very long lifetimes (up to five years) for fluororadicals.¹² These side reactions affect the physical properties. For example, chain scission reduces the stiffness and strength,¹³ while cyclization and isomerization perturb the steric regularity, reducing crystallinity. Fluoropolymers

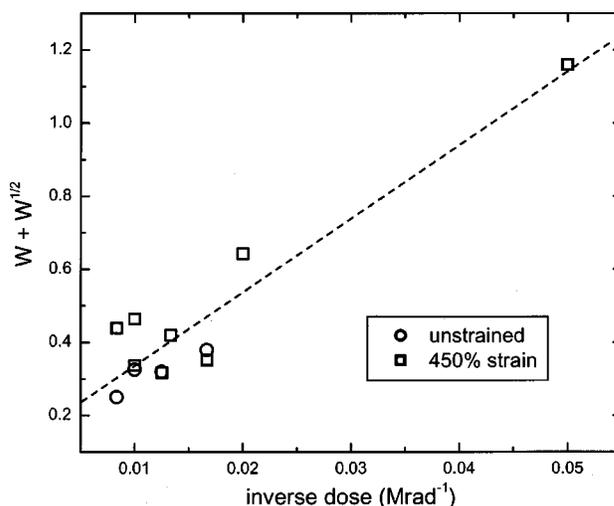


FIG. 2. Charlesby-Pinner plot for films irradiated unstretched (\circ) and while strained to 450% (\square). Averaging all samples, the intercept yields 0.27 for the ratio of scissions to crosslink reactions.

are particularly susceptible to degradation when exposed to ionizing radiation,¹² primarily through homolytic cleavage of the C-F and C-C bonds.¹³

This degradation can be quantified by analyzing the soluble fraction of the P(VDF-TrFE) after network formation. The production of an insoluble gel means that the yield of crosslinks, G_{\times} , is high compared to the rate of chain scission, G_s . To quantify the competing effects of crosslinking and scission, the Charlesby-Pinner relation can be employed¹⁴

$$W + \sqrt{W} = (G_s/2G_{\times}) + (2 - G_s/2G_{\times}) \frac{R_{gel}}{R}, \quad (3)$$

where R is the dose, R_{gel} the gel dose (incipient gel point), and W the soluble weight fraction (equal to unity for $R < R_{gel}$). A plot of the left-hand side of Eq. (3) versus inverse dose yields the scission to crosslinking ratio, G_s/G_{\times} , an indicator of the degradation efficiency of the radiation. This

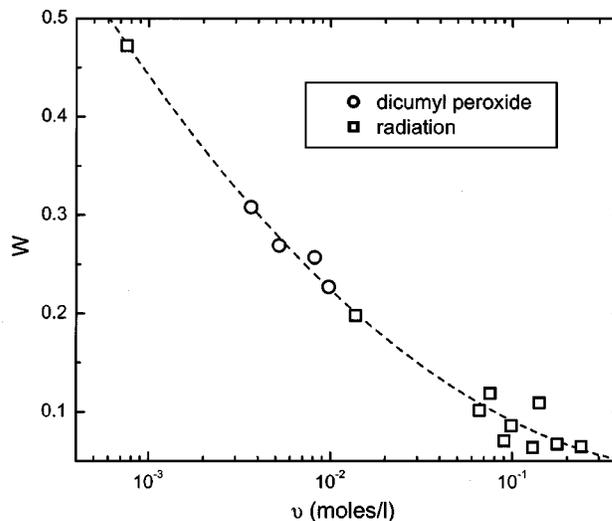


FIG. 3. The soluble fraction, reflecting chain scission at high levels of crosslinking, as a function of the crosslink density for irradiated (\square) and peroxide cured (\circ) P(VDF-TrFE).

TABLE I. Differential scanning calorimetry result.

	ν (moles/L)	Curie transition		Crystal melting	
		T (C)	ΔH (J/g)	T (C)	ΔH (J/g)
Crosslinking					
None	0	111	21	154	28
Irradiated (20 Mrad)	7.6×10^{-4}	99	6.2	137	13
Peroxide (10%)	9.8×10^{-3}	103	16	137	13

approach has been successfully employed to study degradation in various fluoropolymers,¹² including PVDF copolymers.¹⁵

The results for the electron irradiated copolymers are presented in Fig. 2. From the value of W equal to unity, $R_{\text{gel}}=10.8$ Mrad. The amount of soluble material for $R > R_{\text{gel}}$ reflects the degree of degradation. In fluoropolymers, radiation-induced degradation is reputed to be amplified by strain.¹⁶ While there is some indication in Fig. 2 of more chain scission in the stretched samples, the effect is less than the scatter in the data. The average G_s/G_x for all samples is 0.27 ± 0.09 . This is on the low side of the range of literature values for other PVDF copolymers,¹² although the relative rates of scission and crosslinking are sensitive to copolymer content.¹⁷

Nonuniform energy distribution is a problem inherent to the radiation processing of polymers.¹² Indeed, the copolymer films herein exhibited substantial curling during swelling, indicating nonuniform crosslink density through the thickness. For this reason among others, it is desirable for practical applications to explore alternatives to radiation crosslinking. The low chemical reactivity of fluoropolymers has led to development of copolymers containing reactive monomers.¹³ However, these disrupt the crystal lattice and thus diminish the electromechanical properties. PVDF copolymers can be chemically crosslinked using amines or organic peroxides. Systematic studies are lacking, although the reaction with organic peroxides is reputed to give similar physical properties to those obtained by radiation.¹⁸

The copolymers were crosslinked with dicumyl peroxide to yield networks of varying crosslink density, the latter determined by solvent swelling, in the manner described above. The higher levels of radiation crosslinking were not achieved using dicumyl peroxide. To compare the degradation associated with the two methods, Fig. 3 compares the soluble fraction to the degree of crosslinking. Clearly, over this range of crosslink density, there is no substantial difference in the degree of chain scission accompanying network formation by the respective methods.

The objective of crosslinking P(VDF-TrFE) is the development of better electromechanical properties. Electron-beam irradiated samples have shown the capacity for large electrostrictive strains (4%).^{3,4} Large electromechanical coupling factors are possible because the crosslinks reduce the interaction between dipoles in the crystalline domains. However, crosslinking also suppresses the degree of crystallization, which reduces the polarization capacity of the material.

From DSC measurements, we can compare the crystallinity of P(VDF-TrFE) networks prepared by peroxide crosslinking to those obtained by radiation. These results are displayed in Table I. The crystalline melting point and the heat of fusion, while less than the values in the absence of crosslinking, are identical for the two networks. Moreover, we see in Table I that the Curie point is likewise reduced in both intensity and temperature. Conversion of the ferroelectric phase into a paraelectric-like phase is a key feature of the copolymer networks formed by irradiation.⁵ These results suggest that peroxide crosslinking can provide an alternate means for achieving high electromechanical conversion efficiencies. Moreover, the processing flexibility of a chemical approach may prove crucial for the development of devices based on such materials. Additionally, the absence of many of the side reactions (e.g., isomerization and cyclization) plaguing radiolysis may allow the basic mechanisms responsible for property enhancement to be isolated.

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¹A. J. Lovinger, *Macromolecules* **18**, 910 (1985).

²T. T. Wang, *Ferroelectrics* **41**, 213 (1982).

³V. Bharti, H. S. Xu, G. Shanthi, Q. M. Zhang, and K. Liang, *J. Appl. Phys.* **87**, 452 (2000).

⁴Q. M. Zhang, V. Bharti, and X. Zhao, *Science* **280**, 2101 (1998).

⁵V. Bharti, Z.-Y. Cheng, S. Gross, T.-B. Xu, and Q. M. Zhang, *Appl. Phys. Lett.* **75**, 2653 (1999).

⁶B. Daudin, M. Dubu, and J. F. Legrand, *J. Appl. Phys.* **62**, 994 (1987).

⁷D. H. Reneker and J. Mazur, *Polymer* **26**, 827 (1985).

⁸P. J. Flory and J. Rehner, *J. Chem. Phys.* **11**, 521 (1943).

⁹R. A. Hayes, *Rubber Chem. Technol.* **59**, 138 (1986).

¹⁰E. A. Grulke, in *Polymer Handbook*, 4th ed., edited by J. Brandrup, E. H. Immergut, and E. A. Grulke (Wiley, New York, 1999), p. 675.

¹¹G. G. A. Bohm and J. O. Tveekrem, *Rubber Chem. Technol.* **55**, 575 (1982).

¹²J. S. Forsythe and D. J. T. Hill, *Prog. Polym. Sci.* **25**, 101 (2000).

¹³P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953), Chap. 11.

¹⁴A. Charlesby and S. H. Pinner, *Proc. R. Soc. London, Ser. A* **249**, 367 (1959).

¹⁵T. Yoshida, R. E. Florin, and L. A. Wall, *J. Polym. Sci., Part A: Gen. Pap.* **3**, 1685 (1965).

¹⁶F. A. Makhlis, G. Gubanov, and V. Popova, *Vysokomol. Soedin.* **15**, 1995 (1973).

¹⁷A. S. Novikov, V. L. Karpov, F. A. Galil-Ogly, N. A. Slovokhotova, and T. N. Dyumaeva, *Vysokomol. Soedin.* **2**, 485 (1960).

¹⁸D. K. Thomas, *J. Appl. Polym. Sci.* **8**, 1415 (1964).