STRUCTURAL AND PROPERTY CHANGES OF HIGH ENERGY PROTON-IRRADIATED POLY(VINYLDENE FLUORIDE-TRIFLUOROETHYLENE) 56/44 MOL.% COPOLYMER

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Abstract
High-energy proton irradiation with a broad range of dosages has been carried out to investigate the potential for modifying the properties of poly(vinylidene fluoride-trifluoroethylene) 56/44 mol.% copolymer films. The relative permittivity, polarization hysteresis, electric field induced strain, lattice spacing and phase transition behavior of the irradiated copolymer films were studied. With regards to the dielectric and polarization behaviors, the copolymer film can be converted from a typical ferroelectric to a relaxor ferroelectric upon irradiation. This implies that the high-energy protons can break up the coherent polarization domains in the normal ferroelectric copolymer into nano-sized regions. Besides, the XRD data showed that the solid-state phase transition from the polar phase to nonpolar phase is induced in the copolymer during irradiation in which the lattice spacing increases significantly. The electric field induced phase transformation of the nano-sized regions between the polar and nonpolar phase leads to a high electrostrictive strain observed in the irradiated copolymers.

Introduction
Ferroelectric polymers have generated much interest in the past ten years because of their potential as functional materials for energy transduction and information recording. Current interest in poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) copolymers arises because these materials have high electromechanical response and large ferroelectric polarization [1-2]. Besides, copolymers with VDF content of 60-82% spontaneously crystallize into the ferroelectric β phase without the need of mechanical stretching. These features make them useful in transducer, actuator and sensor applications. Recent report indicates that the field-induced strain response of the copolymers can be improved significantly under irradiation treatment [3-5]. From our previous paper [5], P(VDF-TrFE) 80/20 mol.% copolymer shows high electrostrictive strain after proton irradiation (up to 200 Mrad). It is interesting to further study the influence of irradiation on copolymer with lower VDF content. In this paper, the ferroelectric behavior and electric field induced strain response of the irradiated 56/44 mol.% copolymers are investigated. To understand the property modification upon irradiation treatment, the microstructure and the phase transition behavior of the irradiated copolymer are also studied.

Experimental
The P(VDF-TrFE) copolymer with composition of 56 mol.% VDF, supplied in pellet form by Piezotech Co., France, was used in the present study. Films with a thickness of 60 μm were fabricated by compression molding at 210°C under a load of 3 metric tonnes. To increase the crystallinity of the copolymer films, they were annealed at 120°C for 2 hours and then slowly cooled to room temperature. The proton irradiation process was carried out in an accelerator (High Voltage Engineering Europa B.V., Netherlands) located at the Chinese University of Hong Kong. Low beam current (< 0.01 mA/m²) was maintained to prevent excessive temperature increase in the films during irradiation. The films were irradiated by 3 MeV protons (H⁺ ion) at ambient temperature in a vacuum. The proton dosage used was in the range of 43 – 200 Mrad. To study both the electrical and electromechanical properties, circular shape aluminum electrodes were evaporated on the surfaces of both unirradiated and irradiated samples. The dielectric properties of the films were evaluated using an impedance/ gain-phase analyzer (HP 4194A) from 1 kHz to 10 MHz. The measurement of the polarization–electric field (P-E) hysteresis loop was carried out using a modified Sawyer-Tower circuit at a frequency of 10 Hz. The electric-field induced strain along the thickness direction was measured at a frequency of 10 kHz using a heterodyne

11th International Symposium on Electrets, 2002
0-7803-7560-2/02/$17.00 © 2002 IEEE
laser interferometer [6]. The X-ray diffraction pattern was obtained at room temperature using an X-ray diffractometer with nickel-filtered CuKα radiation (X′pert System, Philips Electronic Instruments). The thermal measurement was carried out using a differential scanning calorimeter (Perkin Elmer DSC 7) at a scanning rate of 10 °C/min under nitrogen atmosphere.

Results and discussion

Property modification in irradiated copolymers
The temperature dependence of the relative permittivity at 1 kHz for the irradiated copolymers as a function of proton dosage is presented in Fig. 1. Consistent with early observations in irradiated 80/20 copolymer [5], the relative permittivity peak of the irradiated copolymer shifts to lower temperature. When the dosage is increased, the peak broadens and its height falls. Also, the irradiated 56/44 copolymer shows strong dielectric dispersion even at low proton dosage (Fig. 2). The peak temperature \( T_m \) of the relative permittivity moves to a higher temperature as the measurement frequency increases. As shown in Fig. 3, the dielectric data obtained from the irradiated copolymers can be described well by the Vogel-Fulcher (V-F) law which holds for relaxor ferroelectrics [7] which is given by: \( f = f_o \exp[-U/(k(T_m-T_j))] \) where \( U \) is the constant related to the activation energy, \( k \) is the Boltzmann constant and \( T_j \) is the freezing temperature. Hence, the irradiated copolymers exhibit characteristic properties of the relaxor ferroelectrics.

![Fig. 1](image1.png)  
Fig. 1 Relative permittivity measured at 1 kHz as a function of temperature for unirradiated copolymer and copolymer irradiated with different proton dosages.  

![Fig. 2](image2.png)  
Fig. 2 The relative permittivity as a function of temperature for copolymer irradiated with a dosage of 43 Mrad. The frequency is (from top to bottom): 1 kHz, 10 kHz, 100 kHz, 1 MHz and 10 MHz.  

![Fig. 3](image3.png)  
Fig. 3 Fitting of Vogel-Fulcher law for copolymer irradiated with a dosage of (a) 43 Mrad and (b) 200 Mrad. The symbols are the experimental data and the solid line is the fitting data.
Presented in Fig. 4 is the polarization hysteresis loops of both unirradiated and irradiated copolymers. The unirradiated copolymer exhibits a well-defined ferroelectric hysteresis loop with a coercive field of 55 MV/m and remanent polarization of 6.5 μC/cm². For the irradiated copolymer, it shows a slim hysteresis loop with a much reduced polarization level. Based on the dielectric and polarization measurements, it is seen that proton irradiation can break up the coherent polarization domains in the normal ferroelectric copolymer into nano-sized regions, thereby converting the ferroelectric copolymer to a relaxor ferroelectric.

The longitudinal strain $S$ induced by the applied field $E$ is measured and the electrostrictive coefficient $M$ can then be determined by the equation $S = ME^2$ [8]. Figure 5 demonstrates the change in $M_{33}$ constant of the copolymer with different proton dosages. Upon irradiation, the $M_{33}$ constant increases and reaches a maximum value of $1.5 \times 10^{-18}$ m²/V² at the dosage of 75 Mrad. However, at higher dosage, $M_{33}$ constant decreases. The degree of crystallinity of the crystalline phase may reduce significantly under high proton dosage, leading to low lattice strain.

**Fig. 4** Polarization hysteresis loops at 10 Hz for unirradiated copolymer and copolymer irradiated with different proton dosages.

**Fig. 5** Electrostrictive coefficient $M_{33}$ of the copolymer as a function of proton dosage.

**Structural changes in irradiated copolymers**

The X-ray diffraction patterns of the (200)/(110) reflection peak obtained from the copolymers irradiated with different proton dosages are shown in Fig. 6. The unirradiated copolymer exhibits two partially overlapping peaks at 18.8° and 19.2° which corresponds to the presence of the 1/3-helical and the disordered trans conformations in the crystalline phase (polycrystalline phase) respectively [9]. Upon 43 Mrad irradiation, a peak at 18.5° appears which corresponds to a lattice spacing close to that of the paraelectric phase (nonpolar phase) of the copolymer [10]. Therefore, by applying an electric field to the irradiated copolymers, the local phase transformation between polar and nonpolar phase is induced, leading to a slim polarization hysteresis loop. Besides, this phase transformation also leads to a high electrostrictive strain observed in the irradiated copolymers because the lattice spacing of the nonpolar phase is greater than that of the polar phase. However, at high proton dosage (≥ 150 Mrad), the diffraction peak becomes lower. This implies a decrease in the volume fraction of crystalline regions, resulting in the low strain response.

A DSC measurement was carried out to investigate the transition behavior of the irradiated copolymers and the data are presented in Fig. 7. The unirradiated copolymer shows a typical DSC curve for copolymer of this composition. The endothermic peak at lower temperature (~ 65°C) upon heating is attributed to a structural transition from the ferroelectric phase to paraelectric phase in the crystallites. The other peak at higher temperature corresponds to the melting of crystallites. Upon irradiation, both peaks shift to lower temperature and finally disappear at high proton dosage. Besides, the peaks become broader and their height decreases with increase in proton dosage, indicating a reduction in the crystal ordering in the irradiated copolymer.
Fig. 6 X-ray diffraction patterns for the 56/44 copolymer irradiated with different proton dosages.

Fig. 7 DSC thermogram for the 56/44 copolymer irradiated with different proton dosages.

Conclusions
The structural and property changes in high energy proton-irradiated P(VDF-TrFE) 56/44 mol.% copolymers have been investigated. The irradiated copolymers exhibit a slim polarization hysteresis loop with a much reduced polarization level. Besides, a strong dispersion is observed in the relative permittivity of the irradiated copolymer with frequency, which follows the Vogel-Fulcher law. Those features are the characteristic properties of relaxor ferroelectrics, suggesting that the proton irradiation breaks up the coherent polarization domains into nano-sized region and transforms a normal ferroelectric copolymer into a relaxor. From our previous report, high proton dosage (200 Mrad) is required to convert 80/20 mol.% copolymer into a relaxor. However, for 56/44 mol.% copolymer, a lower proton dosage is sufficient for this conversion. The XRD measurements indicate that the nanosize regions exist in the nonpolar phase. By applying an external field, a local phase transformation between polar and nonpolar phase is induced and a slim hysteresis is observed. Since the lattice spacing of the nonpolar phase is greater than that of the polar phase, this phase transformation also leads to high electrostrictive response. At 75 Mrad, the irradiated copolymer shows the highest $M_{33}$ value of $1.5 \times 10^{-18}$ m²/V². However, if the proton dosage is further increased, the volume fraction of the crystalline regions in the irradiated copolymer decreases, resulting in a low strain response.

Acknowledgements
Financial supports from the Centre for Smart Materials (CSM) of The Hong Kong Polytechnic University, and from the Hong Kong Research Grants Council are acknowledged.

References