Swift Heavy Ion Induced Ordering and Piezoelectric β-phase in Poly(vinylidene fluoride)

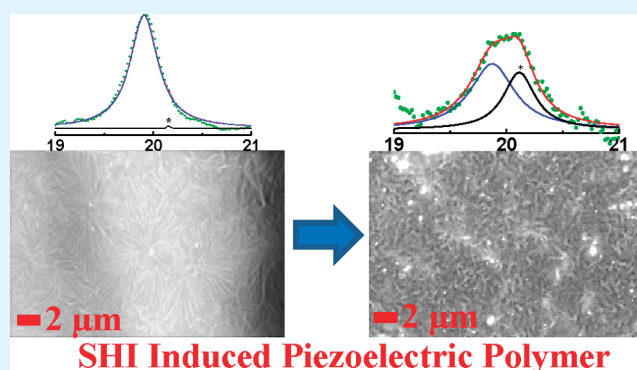Vimal K. Tiwari,[†] Devesh K. Avasthi,[‡] and Pralay Maiti*,[†]

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S *Supporting Information*

ABSTRACT: Ion flux dependent swift heavy ions (SHI) induced structural changes have been reported for pristine poly-(vinylidene fluoride) (PVDF). Ordering phenomena has been observed first followed by its transformation from α to β-form (polar metastable piezoelectric phase). The ordering of (020) plane become prominent at higher ion flux SHI irradiation and its further increase induces structural change from α to β phase as revealed by XRD and FTIR analyses. Structural changes are also supported by morphological evidence and thermal studies before and after SHI irradiation.

SHI Induced Piezoelectric Polymer

KEYWORDS: PVDF, SHI irradiation, ordering, structural change, β-phase

High energy swift heavy ions (*SHI*) irradiation on polymer thin film induce remarkable changes like chain scission, cross-linking,[1] structural changes,[2] amorphization,[3] and degradation in bulk. SHI irradiation causes residual ions, permanent dipoles, space charges, nonreactive gases, and oxidation byproduct generate violent bond stretching and segmental motion in the polymer chains.[4] Poly(vinylidene fluoride) (PVDF), a semi-icrystalline highly nonreactive thermoplastics, technologically important because of their availability in different crystalline forms, having three modes of molecular conformations, TGTG, TTTT, and TTTGTTTG, crystallizes in four types of crystalline modifications distinguished as α, β, γ, and δ forms.[5] The α phase (TGTG) is inactive with respect to piezo- and pyroelectric properties, whereas the β-form (all trans) exhibits ferroelectric activity, suitable for electroacoustic transducer applications.[6] The β-form can usually be obtained from melt crystallization at high pressure,[7] polling at high voltage,[8] recrystallization of carbon-coated highly oriented ultrathin film,[9] molecular epitaxy on the surface of potassium bromide[10] and ethylene carbonate as solvent for thermoreversible gel.[11] Addition of nanofillers like nanoclay, CNT, and graphene in PVDF, so-called nanocomposites, also shows the growth of the β-form and has been extensively utilized in an attempt to enhance the mechanical, physical, and thermal properties.[12−14] Structural change from α to metastable γ phase is reported by slow melting and recrystallization having high melting point and is characterized by 430, 776, and 810 cm^{-1} vibration bands.[15] PVDF forms polar α-phase under electric field and induced polarized molecule and is oriented in *a*-axis of lattice in the direction of applied external electric field.[16,17] PVDF-TrFE forms 60 and 180° domains during reannealing in annealed poled film.[18] The α-form PVDF shows ordering in the direction of (020) atomic plane having high intensity in XRD pattern induced by irradiation of C^{6+} with 60 MeV for 20 min.[2] PVDF film is usually degraded and amorphized upon irradiation with SHI, whereas we have reported trivial degradation and amorphization with high degree of cross-linking in PVDF in the presence of organically modified nanoclay.[19,20] But, it remains a challenge to generate piezoelectric β-phase in pure PVDF.

In the present study, we report the formation of metastable β-phase in pure PVDF and the effect of SHI irradiation on thin film at high fluence with varying ion beam current. Investigation of phase change (α to β), ordering phenomena by structural analysis (XRD and FTIR studies) has been supported by changes in surface morphology and thermal properties of the polymer thin film after SHI irradiation at different beam currents.

Pristine PVDF crystallizes in α-phase (Figure 1a) as evident by the peak position at $2\theta = 17.6, 18.3$, and $19.9°$ corresponding to (100), (020), and (110) planes, respectively.[13] PVDF sustain its α-phase upon SHI irradiation at lower current (i.e., low flux), but the peak intensities of 17.6 and 19.9° are becoming weaker, whereas the peak at 18.3° gets stronger. In other words, the intensity of α-phase peak at 18.3° of (020) plane gradually increases with increasing ion beam current for a constant fluence (1×10^{12} ions/cm^2) with slight shifting of the peak from 18.3 to 18.4° for 4 pnA. The measured ratio of peak intensities of (020) and (100) planes (I_{020}/I_{100}) are 0.47, 1.70, 5.5, and 8.2 for pristine PVDF and irradiated PVDF with 1, 3, and 4 pnA, respectively, showing significant ordering with increasing beam current. Hence, the ordering phenomenon occurs at higher beam
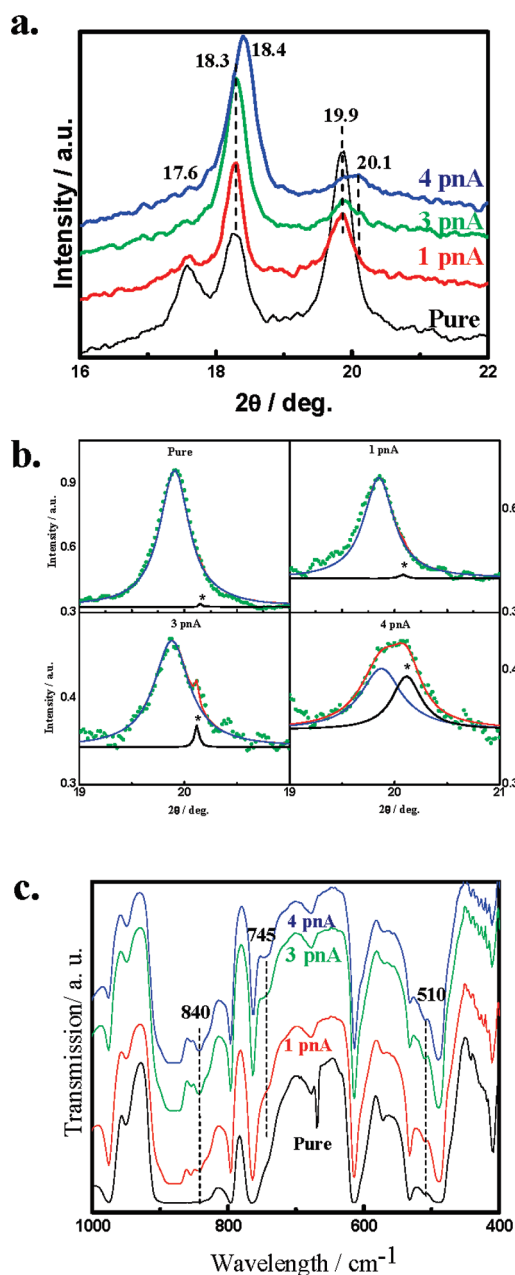
Figure 1. Comparison of pure and Irradiated PVDF having 1, 3, and 4 pnA beam current at fluence 1×10^{12} ions/cm^2: (a) XRD patterns, (b) deconvoluted peak profiles of XRD patterns showing appearance of the β peak by (*), (c) FTIR curves.
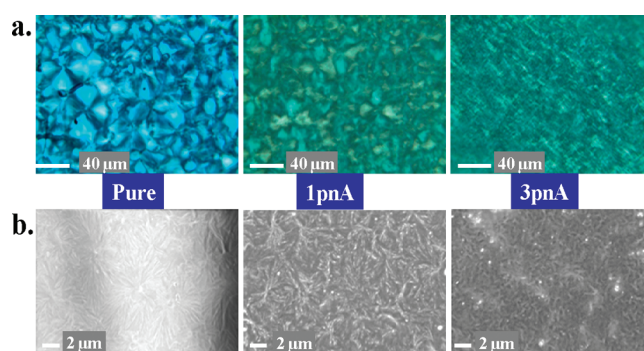
Figure 2. (a) POM images and (b) SEM images, showing crystal morphology of pure and irradiated PVDF having 1 and 3 pnA beam current at fluence 1×10^{12} ions/cm^2.

current keeping the fluence constant. Moreover, a new peak appears at higher ion beam current at 20.1° whose intensity enhances with increasing beam current indicating the formation of piezoelectric β-phase (110/200) plane. The deconvoluted peak profiles at 20.1° (indicated by * mark) clearly exhibit the increasing β-phase content with increasing ion beam current for a constant fluence (Figure 1b).[21] The deconvolution of confined powder XRD profiles has been performed from $2\theta = 19-21°$ using Lorentzian peak shape. The percentage conversion, evaluated from the respective peak area, has been shown in the Supporting Information, Figure S1. However, this is first ever instance of inducing piezoelectric β-phase in PVDF using swift heavy ions. Figure 1c shows the FTIR spectra of pure and irradiated

PVDF films at the same fluence (1×10^{12} ions/cm^2) with varying ion beam current. The characteristics α-phase peaks[22] are present in unirradiated PVDF spectra at 490, 615, 763, and 976 cm^{-1}, whereas the presence of 510, 745, and 840 cm^{-1} peaks for irradiated PVDF confirms the conversion of α to β-phase[22] at higher beam current. Further, the intensity of the β peaks increases gradually with increasing ion beam current suggesting larger β-fraction for higher beam current. Nonetheless, XRD and FTIR studies confirm the structural change from usual α to piezoelectric β-phase induced by swift heavy ions at higher beam current.

It has been calculated that the time taken for the bombardment of 1×10^{12} ions/cm^2 at 0.5 pnA is 320 s, whereas it is 160, 80, 53, and 40 s for 1, 2, 3, and 4 pnA beam current, respectively, for the same fluence. So, the time taken is getting shorter for the higher beam current for the same number of ions irradiation. It is obvious that the ion flux is high for higher beam current, whereas the energy remains the same. The time scale of molecular vibration is $\sim 1 \times 10^{-14}$ s, whereas the diffusion process of polymer chain starts at a time scale of $\sim 1 \times 10^{-12}$ s.[23] So, it is presumed that high ion beam current (≥ 1 pnA), i.e., at high ion flux, is not providing enough time to relax polymer chain as subsequent SHI particle appears and compel the polymer chains to align in the direction of irradiation and, thereby, causing ordering followed by structural change to β-phase. On the other hand, at lower ion flux (beam current ≤ 0.5 pnA) the polymer chain can relax before the arrival of next incident ion in the same region causing the crystallization of usual α-phase.[19] Within a narrow cylindrical zone (ion track), the material expands because of transient melting as expected by thermal spike model,[24] causing high pressure in the region and thereby promoting the phase transition.[7]

The structural change is often commensurate with morphological alteration. Images a and b in Figure 2 show the polarized optical microscopy (POM) and scanning electron microscopy (SEM) images of unirradiated PVDF and irradiated at same fluence (1×10^{12} ions/cm^2) with varied ion beam currents. Unirradiated PVDF shows a compact spherulitic structure due to α-crystalline phase having birefringence in POM, which is also observed in the surface morphology (SEM image).[12] The dimension of spherulite has drastically been reduced after SHI irradiation and it becomes meshlike at higher beam current (3 pnA). The meshlike morphology, characteristics of β-phase,[12] is evident in SEM micrographs for higher current (3 pnA). The conversion of α- to β-phase under the influence of high-flux SHI irradiation of same fluence has also been confirmed from the morphological
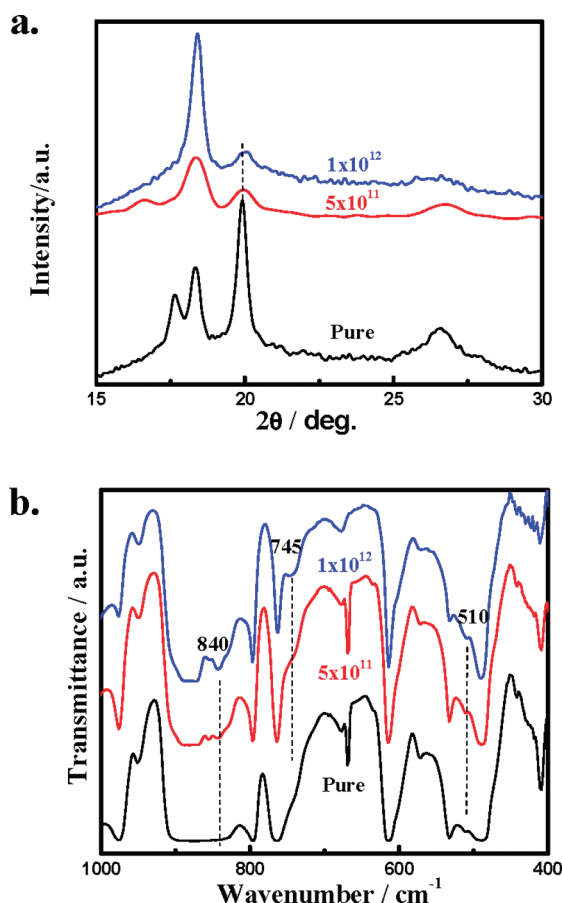
a.

b.

Figure 3. (a) XRD patterns and (b) FTIR curves of pure PVDF and irradiated at fluence 5×10^{11} ions/cm^2 and 1×10^{12} ions/cm^2 having 4 pnA beam current.

Figure 4. Heat of fusion as a function of beam current for irradiated PVDF at fluence 5×10^{11} ions/cm^2 and 1×10^{12} ions/cm^2. The dashed lines are the value for the corresponding pristine samples indicated as "0 fluence". The arrow indicates β-phase Heat of fusion taken from ref 19.

point of view and supports the phase change demonstrated by XRD and FTIR results.

To understand the mechanism of structural change over, it is proposed that the ordering takes place initially followed by its transformation to β-phase. The ordering phenomena has been established by comparing the XRD patterns of unirradiated PVDF and irradiated at fluences of 5×10^{11} and 1×10^{12} ion/cm^2, keeping 4 pnA ion beam current constant, as shown in Figure 3a. It is clear that (020) plane intensity gradually increases with fluence, whereas the (100) and (110) peak intensities reduce. Additionally, with the degree of ordering, signature of peak at 20.1° (due to β-phase) enhances with increasing fluence at the same beam current (4 pnA). The influence for ordering and subsequent structural change is greater at higher fluence (at 1×10^{12} ion/cm^2) presumably due to larger bombardment (double) as compared to 5×10^{11} ion/cm^2 fluence for same ion beam current. Moreover, the absence of any signature of ordering and transformation to β-phase at lower fluence ($<1 \times 10^{11}$ ion/cm^2) and at lower beam current (<1pnA) further strengthen the significance of higher flux and number density of ion beam for the ordering process followed by its transformation to β-phase (see the Supporting Information, Figure S2). Figure 3b compares the FTIR spectra of pure and irradiated samples having similar results in XRD data (Figure 3a). Only the signature (510, 745, and 840 cm^{-1} peaks) has just appeared at 5×10^{11} ion/cm^2 fluence for β-phase while sufficient peak intensities have been observed for 1×10^{12} ion/cm^2 fluence for identical ion beam current.

Figure 4 represents the heat of fusion (ΔH) for irradiated samples at 5×10^{11} and 1×10^{12} ions/cm^2 at different beam currents measured by using differential scanning calorimeter (DSC). The dashed line represents ΔH of unirradiated PVDF. There is significant reduction in ΔH for irradiated samples mainly because of amorphization and chain cleavage under SHI, which further increases with higher fluence.[19] However, a decrease in ΔH has been observed with increasing beam current for both the fluences. This reduction might be associated with the transformation to β-phase at higher beam current as the ΔH of pure β-phase[19] (as shown by the arrow) is smaller as compared to α-phase PVDF. For the higher beam current at same fluence, the chain cleavage should be less as the time of bombardment is considerably low. This is further corroborated with the quality of the irradiated samples, evident by more flexible exposed film for high beam current as compared to lower beam current at the similar fluence. It is noteworthy to mention that β-PVDF is more flexible (tough) as compared to α-PVDF.[19] Hence, both physical appearance and heat of enthalpy confirm yet again the transformation from α to β-phase under the influence of high flux SHI.

New phenomenon of inducing piezoelectric β-phase by high flux swift heavy ions has been revealed in PVDF. Ordering of particular plane and subsequent transformation to β-phase has been demonstrated primarily due to kinetic effect of the swift heavy ions in high viscous liquid polymer. Structural changes have been supplemented by the morphological evidence both in optical and electron microscopes. The decreasing heat of fusion with increasing ion beam current also supports the transformation to β-phase in PVDF induced by swift heavy ions.

■ EXPERIMENTAL METHODS

SOLEF 6008 PVDF supplied by Ausimont, Italy, was melt-pressed into thin film of ~30 μm thickness of size 1×1 cm^2 for irradiation of swift heavy ions. PVDF thin film was irradiated using 80 MeV Si^{7+} ion in a vacuum of ~1×10^{-6} Torr at the Inter University Accelerator Center, New Delhi, India. The ion beam currents of 1, 2, 3, and 4 pnA (particle nanoampere) were taken to vary the ion flux, where 1 pnA = (6.25×10^9)/(charge state of the ion). The electronic energy loss (Se) was ~2.44 keV/nm, whereas the nuclear energy loss was ~1.8 eV/nm, as estimated

by SRIM simulation. The structural details of samples (before and after irradiation) were measured by using XRD, FTIR, FE-SEM, and DSC.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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