Transient Current Investigations in Ion Irradiated Liquid Crystalline Polyurethane

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Swift heavy ions (SHI) irradiation of Oxygen (O^{7+}) beam with different ions fluence bring the modifications in the electrical conduction behavior of liquid crystalline Polyurethane (LCPU). The persent investigation carried out under different transientconditions in the operating temperature range of 50-220°C at various selectric fields of 4.35-43.45 kV/cm. The transient currents show thehyperbolic decay character and the decay exponent Δt (one-tenth decay time) dependent on the field and temperature. Theincrease in I_0/I_svalues (where I_0 represents the current observe dimmediately after applying the voltage and $I_s$means the steady state current) and the mobility variation at high operating temperatures shows the appearance of mesophase. The transient currents originated due to the dipolar nature of carbonyl(C═O) groups in the main chain of LCPU and the trapping charge carriers.

Keywords: Electrical conduction measurement, Transient,Liquid crystalline Polyurethane

1 Introduction

liquid crystalline polymers (LCPs) have received considerable attention recently owing to their unique properties and applications[1,2]. The ion irradiation of materials can also help modify their properties to the required needs. For example, the electro-optical properties of LCPs can be adjusted using ion irradiation for their use in specific applications in non-linear optics, photonics,etc.[3-7]. However, data on modifications due to swift heavy ion irradiation in liquid crystalline polymers is minimal. So this study is very crucial. In our earlier work, we reported the synthesis of LCPU and its spectroscopic characterization[8,9]. The effect of ion irradiation on the conduction mechanism in liquid crystalline polymers (LCPs) is poorly understood. A detailed understanding of the effet of irradiation on charge transport mechanism is essential for these polymers. The present paper studiesthe electrical conduction behavior of pristine and oxygen ion irradiated liquid crystalline Polyurethane (LCPU). In this paper we report the irradiation effect on the electrical conduction behavior by studying the transient current response (Time-current characteristic)

2 Material and Methods

The liquid crystalline Polyurethane used in the present studies was synthesized using Bi-phenol and NCO- terminated polybutadiene[8]. The LCPU samples (thickness≈of 200±2 μm) were irradiated with 100 MeV O^{7+} ion beam at IUAC, New Delhi. The ion beam is deflected over the entire area of 1x1cm² using an electromagnet arrangement for uniformly irradiating the samples under a high vacuum. The conduction measurements were done at different electric fields and temperatures (243 K to 483 K) under transientconditions.To remove the stray surface charges and to attain thermal equilibrium, the sample was kept in shorted conditions at a particular temperature for 15 minutes before starting the measurement. After that an electric field is applied, and the transient currents are examined for 2mili second with the help of Keithley's digital electrometer (6517A). After each run, the electric field is switched off for 5 minutes to allow the background current to settle down, and measurements are made for the next higher field value.

3 Results and Discussion

3.1 Transient Current Investigations

Fig. 1-4 shows the transient current response for pristine and ion-irradiated LCPU samples under various step fields at different temperatures. The current decays rapidly with time after establishing an initial rise when applying field, as observed in other LCPs[10-12]. The initial surge in the current term as

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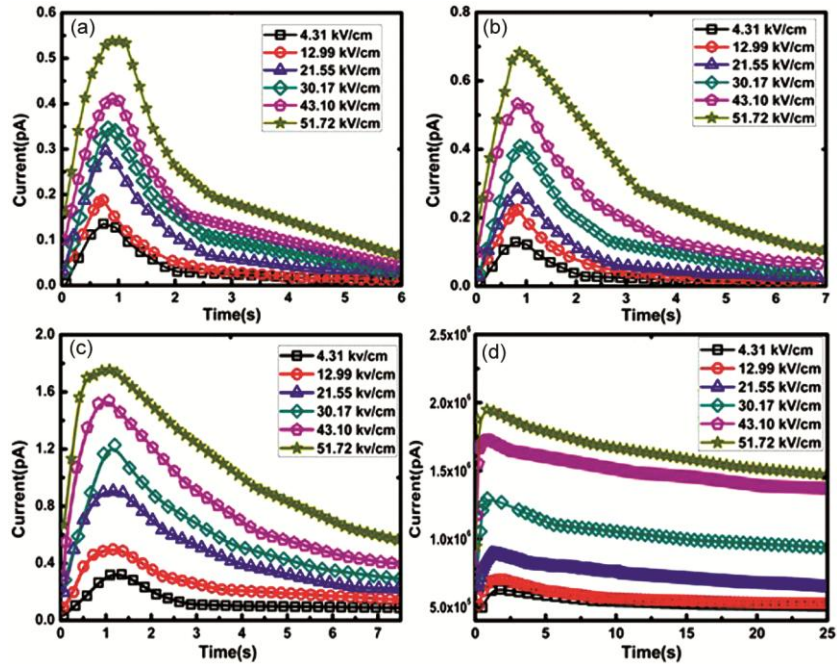*Corresponding author (E-mail: drsohanphy@gmail.com)

Fig. 1 — Transient current response for pristine LCPU samples for different biasing fields at temperatures: (i) 243 K, (ii) 303K, (iii) 353 K and (iv) 453 K.
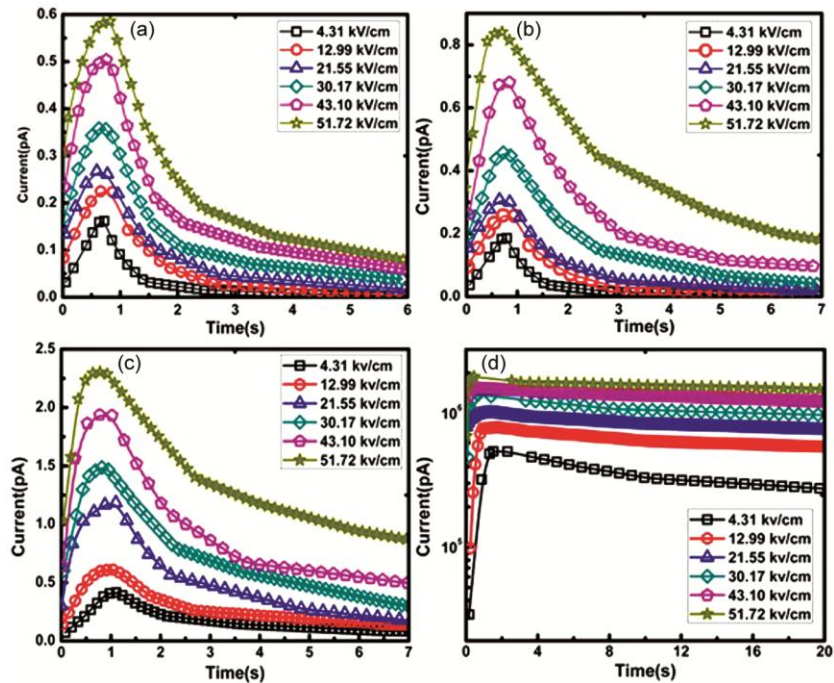

Fig. 2 — Transient current response for ion irradiated LCPU samples (fluence: 3×10^{10} ions/cm^2) for different biasing fields at temperatures: (i) 243K, (ii) 303K, (iii) 353K and (iv) 453K.

extraction current by Geneviciuset al.[12] has been reported by several groups[10-15]. The absorption current starts after the extraction current has attained its maximum value (I_{max}) within about 0.5 seconds. The transient currents consist of two components. The first component decays vary rapidly and last only for one to two seconds, and the second component decays slowly and attains a steady state in nearly 5 to 30 seconds. For the quantitative analysis of the decay behavior, a term Δt (1/5th decay time) has been
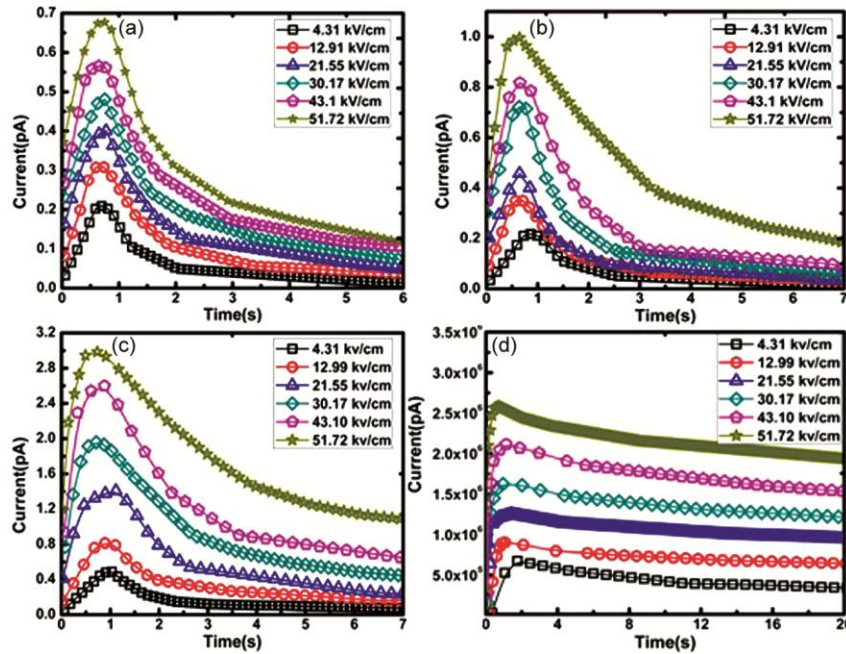
Fig. 3 — Transient current response for ion irradiated LCPU samples (fluence: 1×10^{11} ions/cm^2) for different biasing fields at temperatures: (i) 243K, (ii) 303K, (iii) 353K and (iv) 453K.
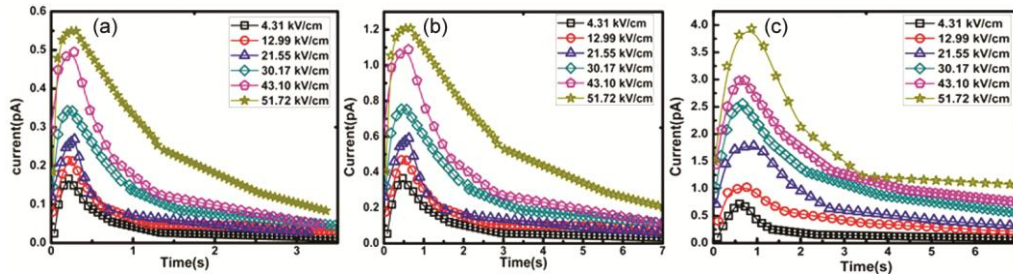

Fig. 4 — Transient current response for ion irradiated LCPU samples (fluence: 1×10^{12} ions/cm^2) for different biasing fields at temperatures: (i) 243K, (ii) 303K, (iii) 353K, and (iv) 453K.

defined as the time during which a transient current decays to $1/5^{th}$ of its peak value (I_{max}). Table (1) illustrates the Δt values for pristine and ion-irradiated LCPU samples at different fields and temperatures. The Δt for pristine and irradiated samples shows its dependence on the field.

Interestingly the Δt is also temperature dependent. It shows a moderate increase in the temperature region (243-423K) but increases significantly above 243 K, followed by a decrease at higher temperatures. For irradiated samples, except for some instances, the Δt decreases with increasingfluence.

Several mechanisms have been discussed for transient currents in polymers[16-19]. The dipolar relaxation, hopping, tunneling through empty traps, and trapped space charge are some effective mechanisms that may be responsible for these transient currents. Tunneling can't be the possible

mechanism because of Δt dependence on the temperature.

Assigning a definite agent to their transient current behavior for liquid crystalline polymers is complex. Quamara et al.[19], in the case of PET/PHB polymer liquid crystals, have shown that bulk phenomena, such as dipolar and interfacial polarization, are the governing phenomenon for transient currents. The present analysis has a similar possibility due to transient current field dominance behavior. The dipolar relaxation may be the other possible mechanism contributing towards the transient current, particularly at lower temperature regions. The LCPU exhibits polar nature (character) due to carbonyl and NH groups in the main chain. This is also supported by the TSDC data analysis that in LCPU, two dipolar relaxation processes exist, one around 160 K and the other around 210 K, owing to carbonyl and NH

Table 1 — $1/5^{th}$ decay time (in seconds) for pristine and O^{7+} ion irradiated LCPU samples

Fields (kV/cm)	Temperature (K)	Fluence (ions/cm^2)			
		Pristine	3×10^{10}	1×10^{11}	1×10^{12}
4.32	243	0.34	0.12	0.2	0.19
	323	0.36	0.11	0.36	0.26
	353	0.42	0.36	0.22	0.29
	453	23.57	4.23	3.49	5.77
	483	**21.36**	**4.20**	**3.35**	**2.34**
12.91	243	0.21	0.13	0.32	0.21
	323	0.22	0.11	0.35	0.35
	353	0.63	0.37	0.42	0.34
	453	8.31	7.76	8.12	9.75
	483	**7.3**	**7.61**	**7.40**	**8.4**
21.55	243	0.31	0.42	0.3	0.1
	323	0.32	0.42	0.29	0.1
	353	0.78	0.34	0.43	0.47
	453	12.53	10.4	9.34	8.24
	483	**10.28**	**9.73**	**8.75**	**6.5**
30.17	243	0.46	0.46	0.32	0.44
	323	0.45	0.48	0.36	0.44
	353	0.6	0.65	0.77	0.47
	453	11.13	6.68	11.44	9.38
	483	**10.31**	**6.53**	**10.23**	**7.87**
43.1	243	0.51	0.4	0.4	0.38
	323	0.52	0.37	0.45	0.23
	353	0.86	0.47	0.51	0.57
	453	19.203	9.48	10.8	9.21
	483	**17.43**	**8.7**	**9.62**	**8.64**
51.72	243	0.61	0.8	0.45	0.65
	323	0.65	0.8	0.46	0.72
	353	1.26	1.01	1.13	0.51
	453	15.91	19.36	11.75	12.75
	483	**13.41**	**18.34**	**11.00**	**8.72**

groups, respectively[20]. These relaxations can be held responsible for the fast decay of transient current. The high-temperature secular decline of the current may be associated with the space charge polarization and the formation of the Schottky layer near electrodes which results in the electric field reduction. Pushkar al.[20] have shown the presence of space charge polarization around 443 K in liquid crystalline Polyurethane (LCPU) due to the trapping of charge carriers. Interestingly we observe a considerable enhancement in the transient current at higher temperatures above 453 K. Pushkar et al.[8] have shown the presence of mesophase in LCPU around this temperature region. The segmental movements associated with mesophase may be responsible for this enhancement in the transient current.

In ion-irradiated LCPU samples, we observe a decrease in decay time at low fluence, while an increase in decay time is observed at higher fluence. This behavior may be because at low fluence chain secessions due to ion irradiation dominated, facilitating the movement of large segmental groups and reducing the decay time. At higher fluence, the increase in decay time may be due to cross-linking effect.

Sawa et al.[21] have given the following theoretical equations for transient current step forsingle relaxation time on the application of step fields for a small given time t:

$$I(t) = \frac{P_0}{\tau} \exp\left[-t/\tau\right] \qquad \ldots(1)$$

Where τ and P_0 are the relaxation time and relaxed electric polarization, respectively. The relaxed polarization P_0 is given as

$$P_0 = \frac{\varepsilon_0 \Delta\varepsilon_r SV}{d} \qquad \ldots(2)$$

Where ε_0 is the absolute permittivity of free space, S is the area under consideration of the sample, d is the thickness of the piece, V is the applied voltage, and $\Delta\varepsilon_r$ is the relative permittivity, which is given as:

$$\Delta\varepsilon_r = \varepsilon_{r0} - \varepsilon_{r\infty} \qquad \text{...(3)}$$

Where $\varepsilon_{r\infty}$ and ε_{r0} are the high and low-frequency limitspermittivity, respectively. From eq. (1) and (2):

$$I(t) = \frac{\varepsilon_0 \Delta\varepsilon_r SV}{\tau d} \exp\left[-t/\tau\right] \qquad \text{...(4)}$$

Debye equation[22] gives single relaxation time complex relative permittivity (ε_r^*):

$$\varepsilon_r^* = \varepsilon_{r\infty} + \frac{\Delta\varepsilon_r}{1 + j\omega\tau} \qquad \text{...(5)}$$

But we have distributed relaxation times in polymeric materials instead of single relaxation time. So ε_r^* can be given as:

$$\varepsilon_r^* = \varepsilon_{r\infty} + \frac{\Delta\varepsilon_r}{1 + (j\omega\tau)^{1-\alpha}} \qquad \text{...(6)}$$

where α is constant $(0 \leq \alpha \leq 1)$. For $\alpha = 0$, equation (6) reduces to equation (5)

Applying Laplace transformation to equation (6), we can estimate the step response $I(t)$ of equation (3) as

$$I(t) = \frac{\varepsilon_0 \Delta\varepsilon_r SV}{\tau d} f(t/\tau) \qquad \text{...(7)}$$

where

$$f\left(\frac{t}{\tau}\right) =$$
$$(1-\alpha)\left(\frac{t}{\tau}\right)^{-\alpha} \sum_{n=1}^{\infty} \frac{-1)^{n-1} n}{\Gamma[1+n(1-\alpha)]}\left(\frac{t}{\tau}\right)^{(n-1)(1-\alpha)} \qquad \text{...(8)}$$

$$I(\tau) = \frac{\varepsilon_0 \Delta\varepsilon_r SV}{\tau d} A_\alpha \qquad \text{...(9)}$$

Where $A_\alpha = (1-\alpha)\sum_{n=1}^{\infty}\frac{-1)^{n-1} n}{\Gamma[1+n(1-\alpha)]}$

We can use equation (9) to determine the value of current $I(t)$ at $t = \tau$. We can use known values to

calculate the dipolar relaxation strength. By choosing the appropriate values of τ and α (0.1 for irradiated and 0.2 for pristine LCPU samples), the $f(t/\tau)$ values are numerically calculated to fit the experimental data points best. The practical data points and theoretical points based on equation (8) are illustrated in Fig. 5.

Selecting the suitable values of τ and A_α using equation (9), the dipolar relaxation strength $\Delta\varepsilon_r$ for pristine and irradiated LCPU samples has been estimated and are given in Table 2. We have also experimentally measured the importance of dielectric strength using a precision LCZ meter. The experimental values of dielectric strength estimated from dielectric data are higher than those calculated from transient current data. This nature is because, in transient current data, high electric fields are used compared to small electric fields applied in the measurement of dielectric data using the bridge method. In addition, the transient current data are obtained at very low frequencies as compared to the bridge method data, which have been obtained at very high frequencies (1 kHz – 5 MHz). Similar observations have also been made by some other
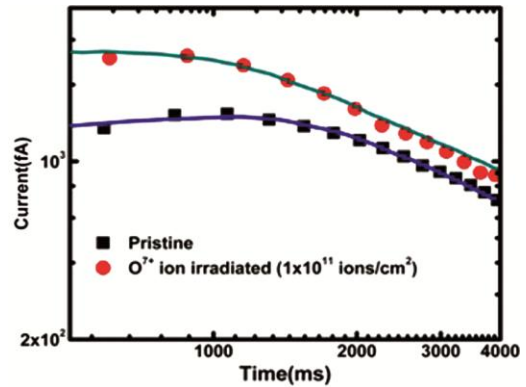

Fig. 5 — Transient current response (data point) and theoretically calculated values (lines) for pristine and ion-irradiated LCPU samples.

Table 1 — Estimated value of dipolar relaxation strength ($\Delta\varepsilon_r$) from the bridge method and transient current data for pristine and ion-irradiated LCPU samples.

Temperature (K)	Bridge method				Transient current data			
	Fluence (ions/cm^2)				Fluence (ions/cm^2)			
	Pristine	3×10^{10}	Pristine	1×10^{12}	Pristine	3×10^{10}	1×10^{11}	1×10^{12}
243	3.21	3.13	4.12	3.25	1.02	1.14	1.21	1.19
353	5.12	4.56	5.48	5.22	2.09	1.37	2.69	1.78
453	5.39	5.12	5.79	5.62	3.25	3.12	3.09	3.17
483	5.01	5.03	5.7	5.20	3.13	4.04	4.93	4.25

groups also in different polymers[23-25]. Ion-irradiated LCPU samples also show identical variations in relative permittivity value from both methods. A decrease in $\Delta\varepsilon_r$ values for low, low irradiation fluence, whereas an increase is observed for higher irradiation fluencies compared to the pristine sample. The crystallinity change with fluence may be responsible for this behavior[13]. Geetika et al.[13]have discussed the effect of loss in carbonyl groups because of dimerization in irradiated polyetheramide on dipolar relaxation strength ($\Delta\varepsilon_r$). In the present analysis, the decomposition of the carbonyl group because of irradiation may be responsible for the decrease in $\Delta\varepsilon_r$ at low fluencies. However, some new sub-polar groups formed on ion irradiation may be accountable for increased dipolar strength at higher fluencies. This observation conforms with the work reported by Geetika[13].

3.2 Mobility Calculation from Transient Data

The step field applied to the sample takes some time to reach its operating value (maximum value). During this time, the extracted charge carriers produce an extraction current (Δj):

$$\Delta j = j(t) - j(0) \quad \ldots(10)$$

When the step field is applied, j(t) is the maximum current value, and j(0) is the current value. Genevicius et al.[12] have given the relation between charge carrier mobility (μ) and sample thickness for $\Delta j \le j(0)$:

$$\mu = \frac{2d^2}{3At_{max}^2\left[1+0.36\dfrac{\Delta j}{j(0)}\right]} \quad \ldots(11)$$

Where A represents the voltage change rate, Table 3 illustrates the μ values for the pristine and ion-irradiated LCPU samples at various temperatures

Table 2 — Estimated values of charge carrier mobility (μ in 10^{-8} cm^2 V^{-1} s^{-1} $\pm$ 0.05) for pristine and ion-irradiated LCPU samples

Fields (kV/m)	Temperature (K)	Pristine	Fluence (ion/cm^2)		
			3×10^{10}	1×10^{11}	1×10^{12}
	243	5.89	142.69	120.55	22.76
	323	52.76	111.37	70.00	171.89
4.32	353	55.11	88.18	20.15	142.26
	453	132.49	26.31	13.49	121
	483	120	25.15	13.35	16.52
	243	29.85	80.41	59.84	19.84
	323	31.88	78.34	37.48	113.24
12.91	353	33.24	43.75	28.2	77.10
	453	52.21	25.03	18.12	68.26
	483	57.3	27.61	18.0	58.25
	243	16.26	64.06	45.57	1.09
	323	16.06	62.31	6.44	56.66
21.55	353	21.48	24.47	34.86	36.99
	453	38.44	58.02	9.34	36.15
	483	10.28	56.20	10.28	38.12
	243	10.81	43.12	37.50	22.76
	323	9.34	36.04	34.97	54.21
30.17	353	14.41	30.29	39.04	35.76
	453	33.45	30.09	11.44	32.64
	483	43.25	29.30	12.35	33.25
	243	13.96	24.72	28.70	19.84
	323	12.61	20.56	19.18	33.24
43.1	353	10.41	19.94	4.66	26.69
	453	24.06	46.25	10.8	31.30
	483	25.30	45.26	11.62	28.50
	243	13.31	20.42	22.76	1.09
	323	10.94	20.76	19.84	21.07
51.72	353	13.34	19.94	1.089	16.22
	453	19.10	22.90	11.75	12.75
	483	15.26	19.65	10.26	12.35

andfields. The Crystallinity, conjugation in polymeric chains, defects, their density, operating temperature, and in some cases, the operating electric field are the prime factors that affect the charge carrier mobility in polymers. The shallow, deep, and delocalized trapping sites affect mobility differently. The value of µ is less for shallow or deep traps than for delocalization. The electrons that move between delocalized states mainly exist deep into the conduction band, requiring no thermal energy to move between traps. For delocalized conditions, the order of mobility (µ) is ~ 10 cm^2 V^{-1} s^{-1}, whereas 10^{-3} cm^2 V^{-1} s^{-1} and 10^{-1} to 10^{-17} cm^2 V^{-1} s^{-1} for electrons captured and shallow and deep traps, respectively[15]. We observed the estimated mobility values (Table 3) decreased significantly at a higher field in pristine LCPU samples. The charge carrier mobility values suggest that shallow traps mainly govern the low-field transient currents, whereas deep traps govern the high-field transient current.

Further, the mobility data also shows that in the low-field region (< 30.6 kV/cm), the mobility generally decreases with temperature. However, in high-field areas, we do not observe any particular behavior, which confirms that in polymer liquid crystals, the reaction of moieties towards the field is associated with a threshold voltage. An enhancement in mobility with temperature from 453 K to 483 K is due to the liquid crystalline phase transition in LCPU in this temperature region. Interestingly except for high fluence (1×10^{12} ions/cm^2) irradiated samples where µ increases with temperature, we observe a decrease in µ with temperature for other irradiation fluences. Certain factors cause an increase in mobility, while others have the opposite effect. The rise in mobility may be due to increasing crystallinity or cross-linking, whereas the increase in deep trap density decreases mobility. The dominance of a particular process governs the resultant mobility of charge carriers. The formation of deep traps in high fluence ion irradiated samples may be responsible for the decreased mobility values, this behavior is also evident from the temperature dependence of mobility values at higher fluence. So, the deep trap formation in ion-irradiated LCPU may be responsible for the low mobility values.

4 Conclusions

The transient current behavior has been investigated in pristine and O^+ ion-irradiated LCPU samples. This behavior cannot be associated with the bulk phenomenon, as the field has no significant effect (except at higher electric fields) on the half-decay time. The nature of trapping sites and trap density, Crystallinity, backbone conjugation, and operating temperature mainly govern the nature of fast transient currents in irradiated LCPU. These are reflected in the charge carrier mobility measurements. The variation in the dipolar relaxation strength estimated from transient current data has been associated with the demerization of carbonyl groups and the formation of radiation-induced subpolar groups. The occurrence of the Poole-Frenkel type of mobility confirms the enhancement of conjugation due to irradiation.

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