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ORIGINAL PAPER

Polarization temperature effect on liquid–liquid transition and space charge detrapping behavior in atactic polystyrene by thermally stimulated depolarization current

Lunlun Gong · Xingyuan Zhang · Yuan Shi · Long Zhang

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Abstract Thermally stimulated depolarization current (TSDC) experiments were carried out to investigate the effect of polarization temperature (T_p) on liquid–liquid transition and space charge detrapping behavior in atactic polystyrene. Differential scanning calorimetry (DSC) measurement was applied as a complementary method. When T_p is 130 °C, there are four distinct peaks (α, ρ_1, LL, and ρ_2) showed in TSDC spectrum in the range of 30–200 °C. Compared with the result of DSC, TSDC spectrum show that peak α corresponds to glass transition, peak LL is related to liquid–liquid transition, and peak ρ_1 and peak ρ_2 belong to the space charge current peak. As T_p increases from 100 to 150 °C, the intensity of peak LL maximum increases and that of space charge peaks maxima decreases, which is attributed to different mechanism between liquid–liquid transition and space charge detrapping behavior. In addition, their corresponding characteristic parameters versus T_p are also analyzed in detail.

Keywords Thermally stimulated depolarization current · Atactic polystyrene · Liquid–liquid transition · Space charge detrapping behavior

Introduction

Owing to the high sensitivity and resolution, thermally stimulated depolarization current (TSDC) has been widely used to investigate transition and relaxation processes, charge storage, and transportation behaviors of polymer. In TSDC experiment, a sample electret is made firstly and then electric current releasing in outer circuit is recorded with a linearly increasing temperature. Comparing with

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L. Gong · X. Zhang (✉) · Y. Shi · L. Zhang
CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
e-mail: zxym@ustc.edu.cn

other methods, TSDC method can give not only the information of transition process, but also the properties about charge carrier storage and transportation which cannot be detected in other methods.

TSDC spectra can provide relational information on transition process and space charge detrapping behavior. Atactic polystyrene (aPS), namely commercial polystyrene (PS), which is a poor polar polymer, is one of the most important engineering materials. Investigations of aPS using TSDC have been carried out by many researchers. Kulshrestha and Srivasta [1] found three peaks, namely, β, α, and ρ peaks, located at 65, 95, and 145 °C, respectively, in the TSDC spectra of PS. Shrivastava et al. [2] observed only one peak corresponding to dipolar relaxation process in TSDC spectra of PS. Pillai and Rashmi [3] discovered one α peak at 96 °C in TSDC spectrum of pure PS but α and ρ peaks near 80 and 130 °C for polystyrene–chloranil complex. Sharma and Sagar [4] attained a similar result in the study of pure and Fe-doped PS by TSDC. Sauer and Avakian [5] found α relaxation, but no β relaxation was detected in TSDC spectrum for PS. Sheng et al. [6] discovered three peaks corresponding to β, α and liquid–liquid transitions at 23, 112.2, and 162 °C, respectively, in their TSDC experiment for PS.

However, the results of previous researches did not agree well enough with each other. Although this might be attributed to different samples that they used, the experimental conditions also play an important role in TSDC experiment, especially selected polarization temperature (T_p). Recently some efforts have been performed to illuminate the polarization temperature effect on space charge in TSDC experiment [7–10], but few people pay their attention to the influence of polarization temperature on liquid–liquid transition, which is considered as a transition of polymer from “immobile liquid” to “real liquid” and the beginning of flow as a result of movement of entire molecular chain [11].

In our previous work, we have investigated liquid–liquid transition in aPS at $T_p = 100$, 120, and 140 °C, but there is no explanation about polarization temperature effect on liquid–liquid transition [12]. This article is a continued work to reveal the behavior of liquid–liquid transition and space charge peaks under different T_p. In this article, TSDC experiments were carried out at six different polarization temperatures (100, 110, 120, 130, 140, and 150 °C) to study the effect of polarization temperature on relaxation process of liquid–liquid transition and space charge detrapping behavior in aPS. Then the correlation between characteristic parameters calculated by kinetics equation and polarization temperature was discussed in detail.

Experimental

Material

Granule samples of atactic polystyrene were produced by DOW Chemicals. The amorphous film with thickness of about 100 μm was prepared by quenching hot-pressed film between the stainless-steel templates at ambient temperature. All the film samples were coated with silver electrode of 12 mm in diameter in both side for

TSDC measurement and then placed at a vacuum drying oven at pressure of 0.1 Pa at 80 °C for 24 h in order to remove as much water as possible.

DSC analysis

DSC analysis was carried out with DSC1 (Mettler Toledo, Switzerland) differential scanning calorimeter. Sample was heated at 25 °C/min and a flow rate of 30 mL/min under nitrogen from 25 to 200 °C for scan.

TSDC measurement

TSDC measurement was carried out on a modified thermal electric analyzer [13]. First, the film sample was polarized by a static electric field E_p at a constant polarization temperature T_p for a polarization time t_p. Then the sample was cooled from T_p to a freezing temperature T_i ($T_i = 27$ °C) with the electric field still on to freeze the orientation of dipoles. The field was cut off and the sample was short-circuited for an enough time t_c ($t_c = 30$ min) to remove surface charges and stabilize the sample temperature at T_i. The depolarization current $I(T)$ was then recorded through an electrometer from T_i to the final temperature ($T_f = 200$ °C) as the temperature increased with a linear heating rate of 4 °C/min.

In this study, six different polarization temperatures (100, 110, 120, 130, 140, and 150 °C) and only one polarization filed (50 kV/cm) were chosen. The polarization time of 30 min was selected in all cases, which was enough long to attain the equilibrium polarization.

Results and discussion

DSC curve of aPS at a heating rate of 25 °C/min is shown in Fig. 1. The curve shows two distinguished endothermal stages corresponding to two transition processes of molecular movement in the temperature range of 25–200 °C. The first stage around 94 °C corresponds with the glass transition, and the second one around 154 °C relates to the liquid–liquid transition. This result is consistent with former references [14, 15]. For some polymers, liquid–liquid transition temperature (T_{LL}) is generally found in the range of 1.1–1.3 but mostly near 1.2 T_g [15]. For aPS, Fig. 1 gives T_{LL}/T_g value of 1.16, according with the general rule of polymer.

Experimental TSDC spectrum of aPS polarized at $T_p = 130$ °C under $E_p = 50$ kV/cm is shown in Fig. 2. Four charge detrapping processes corresponding to four prominent current peaks designated as α, ρ_1, LL, and ρ_2 can be observed clearly, and the experimental observation agrees with our previous work [12]. The spectrum being compared with DSC curve of aPS, it is confirmed that peak α located at 91 °C corresponds to the glass transition process and originates from the relaxation of frozen-in dipole containing long segment [5, 6], and peak LL observed at 149 °C is related to the liquid–liquid transition and arises from the movement of entire molecular chain [6, 16]. Peak ρ_1 and peak ρ_2 belong to space charge current peak, which cannot be detected by DSC measurement. The peak ρ_1, located at

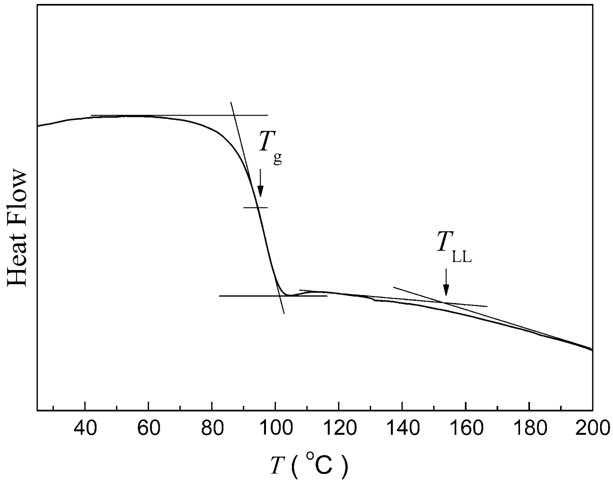

Fig. 1 DSC curve of aPS

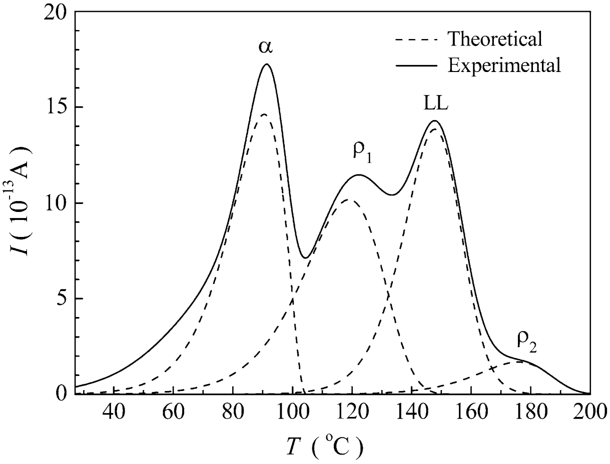

Fig. 2 TSDC spectrum of aPS ($T_p = 130$ °C)

120 °C, originates from the detrapping of charge carriers trapped in the material during formation of electret [3, 9]. The peak ρ_2 which have not be concerned in former references, located at 179 °C, may be attributed to the detrapping of trapped charge carriers in deeper trapping sites.

TSDC method is one kind of thermally stimulated process. A kinetics equation

$$I(t) = -\frac{dn}{dt} = \left(\frac{n}{n_0}\right)^b sn_0 \exp(-E_a/kT) \quad (1)$$

was proposed to describe the released current during thermally stimulated depolarization process [17]. Here, I is depolarization current at time t, n is trapped

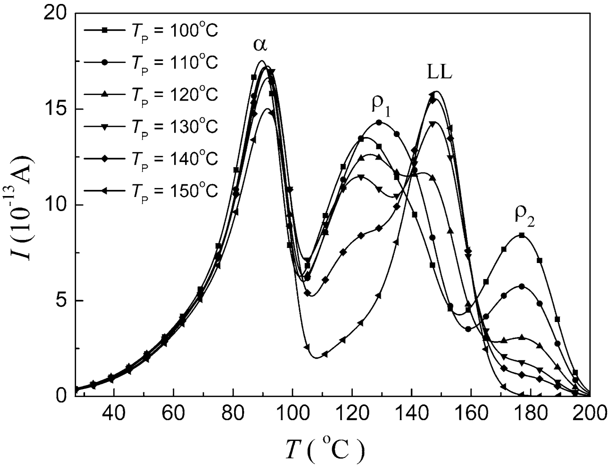

Fig. 3 TSDC spectra of aPS poled at different temperatures

charge at time t, s is frequency factor, n_0 is initial trapped charge in the trap, E_a is activation energy (trapping depth in this model), k is Boltzmann constant, T is absolute temperature, and b is kinetic order, an empirically determined parameter. In the case of a constant heating rate, T can be calculated accurately by time t. According to Eq. 1, TSDC experimental spectrum can be fitted theoretically, and then isolated current peaks and characteristic parameters, such as initial charge, activation energy, frequency factor, and kinetic order, can be obtained easily. Figure 2 also shows the result of curve fitting. The experimental curve is separated into four isolated peaks (α, ρ_1, LL, and ρ_2) which are shown in dashed line. It is found in Fig. 2 that the theoretical curves are in good agreement with the experimental spectrum.

Experimental TSDC spectra for aPS polarized at six different temperatures under $E_p = 50$ kV/cm are shown in Fig. 3. It shows that when varying polarization temperature peak α remains almost invariable but the change of peak ρ_1, peak LL, and peak ρ_2 is pronounced. When T_p is 100 and 110 °C, only three peaks (α, ρ_1, and ρ_2) can be observed and peak LL can not be found in TSDC spectra. When T_p reaches 120 and 130 °C, four distinct peaks can be observed clearly. When T_p increases to 140 and 150 °C, peak α and peak LL are remarkable, but space charge peaks (ρ_1 and ρ_2) are almost disappeared in TSDC spectra. The result indicates that the intensity of peak LL maximum increases and that of space charge peaks maxima decreases with increasing T_p. In order to further elucidate the polarization temperature effect on liquid–liquid transition and space charge detrapping behavior, experimental TSDC spectra shown in Fig. 3 are fitted theoretically by the kinetics equation. By curve fitting procedure, theoretical spectra of isolated peak LL, peak ρ_1, and peak ρ_2 with different polarization temperature can be obtained and their corresponding characteristic parameters are also calculated.

Figure 4 gives theoretical spectra of peak LL with different polarization temperature based on fitting result of Eq. 1 and relevant characteristic parameters

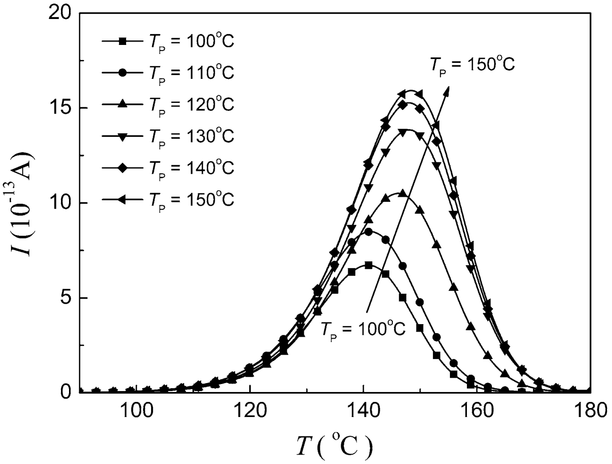

Fig. 4 Theoretical spectra of peak LL poled at different temperatures

Table 1 Characteristic parameters of peak LL

T_p (°C)	T_m (°C)	I_m (10^{-13}A)	E_a (eV)	n_0 (10^{-10}C)	b	s_0 (s^{-1})
100	140.8	6.73	1.94	2.598	1.28	3.65×10^{21}
110	141.2	8.48	1.91	3.314	1.31	1.24×10^{21}
120	146.1	10.50	1.85	4.431	1.33	1.51×10^{20}
130	148.0	13.85	1.81	5.340	1.33	3.49×10^{19}
140	148.0	15.28	1.79	6.666	1.31	2.09×10^{19}
150	148.4	15.92	1.78	6.891	1.27	1.43×10^{19}

T_m is the peak temperature at which maximum takes place

I_m is the maximum value of peak current

are listed in Table 1. It is found in Fig. 4 that peak temperature T_m moves from 140.8 to 148.4 °C and peak maximum value I_m increases from 6.73 to 15.92 (10^{-13} A) with T_p increasing from 100 to 150 °C. Table 1 also shows that the activation energy E_a decreases from 1.94 to 1.78 eV and initial trapped charge n_0 increases from 2.598 to 6.891 (10^{-10} C) with increasing T_p. This result is ascribed to the mechanism of liquid–liquid transition. The liquid–liquid transition is considered as a transition of polymer from "immobile liquid" to "real liquid" as a result of movement of entire molecular chain. When the selected polarization temperature is below the polymer's liquid–liquid transition temperature (T_{LL}), the peak LL may be significantly smaller due to incomplete polarization. In other words, only a portion of molecular chains possess enough mobility to be poled in the electric field when lower polarization temperature is chosen. As polarization temperature is increased, due to the increase of molecular chain mobility more ones can be aligned in polarization process, so peak LL becomes more intense. On the other hand, if the chosen polarization temperature is below the polymer's glass

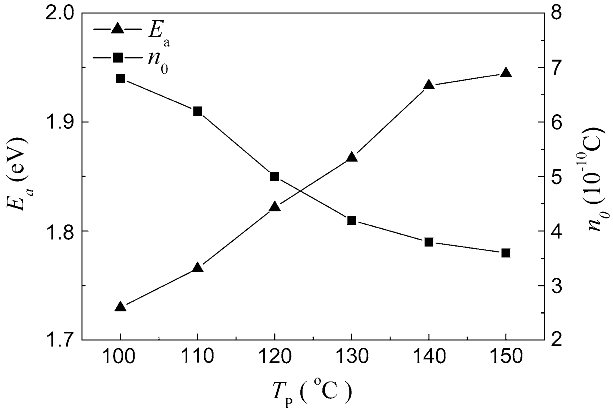

Fig. 5 Values of E_a and n_0 of peak LL versus polarization temperature

transition, the peak α may be significantly smaller and the peak ρ may not be visible at all [18]. Therefore, it is important to select proper polarization temperature for ensuring that desired current peak can be obtained in TSDC experiment. In our experiments, only when T_p is 120 and 130 °C, peak LL, peak ρ_1, and peak ρ_2 can be observed clearly.

To further explore the polarization temperature effect on liquid–liquid transition, the plot of activation energy E_a and initial trapped charge n_0 of peak LL versus polarization temperature T_p is shown in Fig. 5. The value of E_a decreases with increasing T_p, suggesting that molecular chain moves more freely with increasing T_p. For a single dipolar relaxation, T_m is independent of T_p. But actually peak LL is associated with a distribution of molecular chain relaxation process. As T_p is increased, molecular chain which is not active at lower temperature can be poled at higher T_p, and this gives rise to T_m of peak LL toward to higher temperature. The value of n_0 increases with increasing T_p, and tends to saturation when T_p is higher than 140 °C. This reflects the fact that when T_p is higher than 140 °C the effect of T_p on liquid–liquid transition is not significant.

Theoretical spectra of peak ρ_1 poled at different temperature are shown in Fig. 6 and corresponding characteristic parameters are listed in Table 2. It is found in Fig. 6 that T_m located around 120 °C remains unchanged and I_m decreases from 11.68 to 2.07 (10^{-13} A) with T_p rising from 100 to 150 °C. Table 2 also shows that E_a is constant and n_0 decreases form 5.977 to 1.05 (10^{-10} C) when T_p changes form 100 to 150 °C. This can be explained by the mechanism of space charge peak. The space charge peak originates from the detrapping of charge carriers trapped in the material during polarization. With the increase of T_p the mobility of charge carriers increases during polarization, which can not only result in a greater probability per unit time for a carrier to be trapped, but also cause loss of trapping sites and detrapping behavior of trapped charge carriers. Which effect will play a dominant role depends on polarization temperature in polarization process.

In order to explore this further, the plot of E_a and n_0 of peak ρ_1 versus T_p is shown in Fig. 7. The value of E_a corresponding to trapping depth remains constant

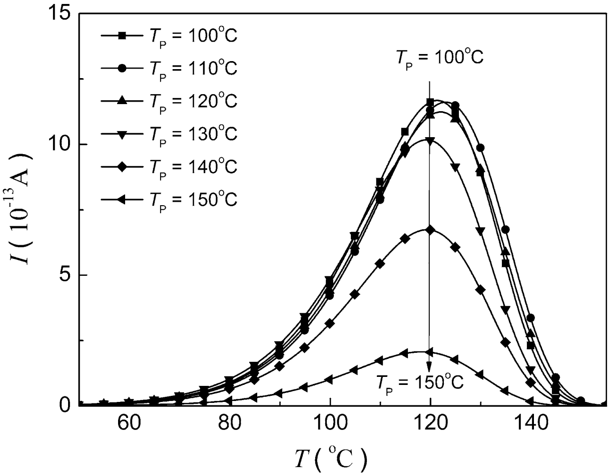

Fig. 6 Theoretical spectra of peak ρ_1 poled at different temperatures

Table 2 Characteristic parameters of peak ρ_1

T_p (°C)	T_m (°C)	I_m (10^{-13}A)	E_a (eV)	n_0 (10^{-10}C)	b	s_0 (s^{-1})
100	121.3	11.68	1.01	5.977	1.00	3.50×10^{10}
110	123.0	11.61	1.00	6.020	1.00	2.63×10^{10}
120	122.0	11.24	0.99	5.847	1.00	2.17×10^{10}
130	119.2	10.17	0.97	5.327	1.00	1.42×10^{10}
140	119.3	6.74	0.98	3.495	1.00	1.92×10^{10}
150	118.2	2.07	1.00	1.050	1.00	3.86×10^{10}

with increasing T_p, and T_m shows a trend similar to E_a. The value of n_0 decreases with increasing T_p, and this result is consistent with Pillai's research [3]. But the decreasing rate of n_0 changes significantly around 130 °C. Obviously, the curve of $n_0 \sim T_p$ can be divided into two parts. The n_0 decreases slowly until T_p reaches 120 °C, and n_0 decreases rapidly when T_p above 120 °C. This result indicates that n_0 is approximately constant until T_p reaches 120 °C as a result of the equilibrium state of the two effects on space charge introduced above, but decreases rapidly when T_p above 120 °C due to the dominant effect of losing trapping sites and detrapping of trapped charge carriers at higher T_p.

Figure 8 and Table 3 give theoretical spectra and characteristic parameters of peak ρ_2 poled at different temperature. The peak ρ_2 has never been reported in previous literatures and appears to be a release of space charge due to not being detected in DSC measurement. Compared with peak ρ_1, peak ρ_2 shows a behavior similar to peak ρ_1 with increasing T_p. So it can be expected that the mechanism of peak ρ_2 may be the detrapping of trapped charge carriers in deeper trapping sites. It can be found that the peak ρ_2 decreases more rapidly than peak ρ_1 with increasing T_p, which implies that the deeper trapping sites are unstable at higher temperature.

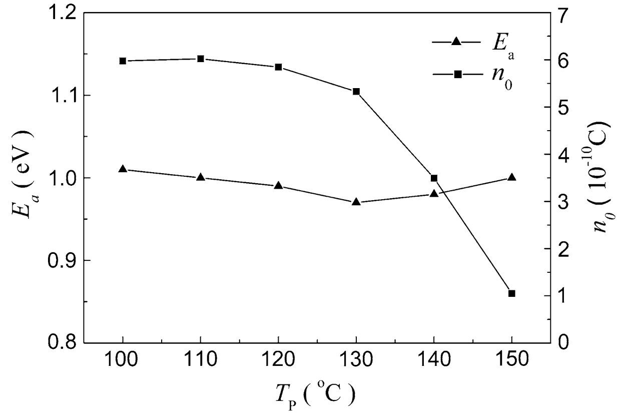

Fig. 7 Values of E_a and n_0 of peak ρ_1 versus polarization temperature

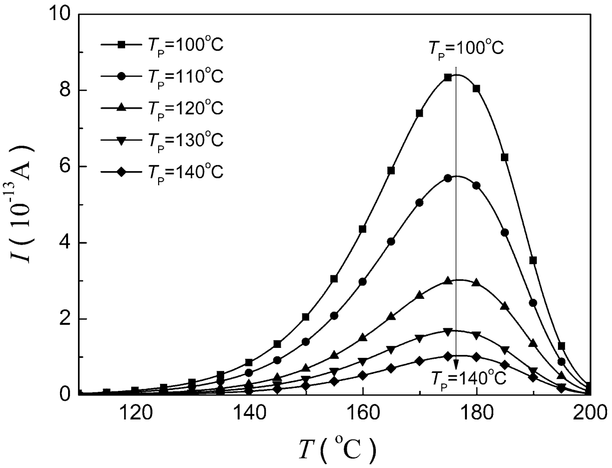

Fig. 8 Theoretical spectra of peak ρ_2 poled at different temperatures

Table 3 Characteristic parameters of peak ρ_2

T_p (°C)	T_m (°C)	I_m (10^{-13}A)	E_a (eV)	n_0 (10^{-10}C)	b	s_0 (s^{-1})
100	176.6	8.41	1.40	4.586	1.00	2.64×10^{13}
110	177.0	5.74	1.40	3.136	1.00	2.55×10^{13}
120	176.9	3.02	1.40	1.629	1.00	4.38×10^{13}
130	175.9	1.68	1.40	0.906	1.00	2.80×10^{13}
140	177.5	1.03	1.41	0.561	1.00	3.18×10^{13}

It is worth noting that when T_p reaches 150 °C, the peak ρ_2 is missing. There are three possible trapping sites: (1) single molecule, (2) chain folds, and (3) interfaces between crystalline and amorphous regions, reported for most polymers [19]. When above T_{LL} molecular chain is in the viscous flow state, and chain fold is disappeared for linear polymer. The peak ρ_2 missing when T_p above T_{LL} may deduce that the trapping sites of peak ρ_2 could be related to chain fold.

Conclusion

The effect of polarization temperature on liquid–liquid transition and space charge detrapping behavior in aPS was investigated by means of TSDC. Four distinct peaks (α, ρ_1, LL, and ρ_2) are observed in TSDC spectrum in the range of 30–200 °C when T_p is 130 °C. Compared with DSC curve of aPS, it is confirmed that peak α corresponds to glass transition process and originates from the relaxation of frozen-in dipole containing long segment, peak LL is related to liquid–liquid transition and arises from the movement of entire molecular chain, and peak ρ_1 and peak ρ_2 belong to the space charge current peak and originate from detrapping of charge carriers trapped in the material. As polarization temperature increases from 100 to 150 °C at intervals of 10 °C, peak α remains almost constant, but the other three peaks change significantly. By curve fitting procedure of the kinetics equation, theoretical spectra of isolated peak LL, peak ρ_1 and peak ρ_2 with different polarization temperature can be obtained and their relevant characteristic parameters are also calculated. Analysis of theoretical spectra indicates that peak LL moves toward higher temperature and the intensity of peak LL maximum increases and that of space charge peaks (peak ρ_1 and peak ρ_2) maxima decreases with the increase of polarization temperature due to the different mechanism between liquid–liquid transition and space charge detrapping behavior. Therefore, it is important to select proper polarization temperature in TSDC experiment for obtaining desired current peak. In addition, calculated results versus T_p show that: (1) the polarization temperature effect on liquid–liquid transition is not significant when T_p above 140 °C; (2) peak ρ_1 is almost constant until T_p reaches 120 °C and decreases rapidly when T_p above 120 °C; and (3) peak ρ_2 decreases more rapidly than peak ρ_1 with increasing T_p and is missing when T_p is above T_{LL}.

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