

# Investigation of relaxations in polystyrene–polyoxyethylene copolymer by thermally stimulated current

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## Abstract

The diblock copolymer containing 43.5 wt.% of polystyrene (PS) ( $M_w = 15\,000$ ) and polyoxyethylene (POE) ( $M_w = 19\,500$ ) was investigated by integral and by partial thermally stimulated depolarization current (TSDC) measurements in the temperature range of 173–293 K. The first peak  $P_1$ , widely distributed from 183 to 213 K, was a dipolar peak attributed to the initial stage of glass transition in POE. The second peak  $P_2$ , with a maximum at 273 K, was due to glass transition. The third peak  $P_3$ , with a maximum at about 263 K, was caused by the space charge relaxation localized at the interfaces between the ordered and nonordered phases in POE, Maxwell–Wagner relaxation, representing a precursor in melting of POE crystals. The results were supported by determination of activation energy  $E_a$  of the partial peaks, which covered the whole range of investigation, and by differential scanning calorimetry (DSC) measurements. The  $E_a(T)$  distribution showed a maximum in entropy change at  $219 \pm 4$  K. Some runs with samples containing different amounts of the PS component were considered. All the relaxations were coming from the POE block. The current due to PS slightly overlapped the total spectra without interaction. The influence of the repeated runs was observed and discussed.

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**Keywords:** Polystyrene–polyoxyethylene copolymer; Thermally stimulated current; Activation energy

## 1. Introduction

Diblock copolymers are composed of two different homopolymer chains A and B, linked together by chemical bonds [1]. Because of their block incompatibility they usually segregate and form ordered microdomains of different structures. If the volume ratio between two blocks is 1:1, segregation would lead to the lamellar microdomains A and B. When the ratio between them significantly differs from 1:1, the structure can be disturbed by the occurrence of micelles, cylinders or perforated layers. The size of

microdomains is determined by the degree of polymerization.

Thermally stimulated depolarization current (TSDC) techniques have been widely used to study the relaxation processes in organic polymers as well as in other dielectric materials [2–4]. The low frequency technique working in the range from  $10^{-2}$  to  $10^{-4}$  Hz enables high resolution and separation of the processes which would be overlapped in the high frequency procedures. Briefly, the main steps in TSDC measurements are: (a) sample poling by d.c. electric field  $E_p$ ; (b) cooling to low storage temperature  $T_0$  in order to freeze and preserve the effects of poling; (c) slow heating and measuring the depolarization current which shows the relaxation processes. The main effects of

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poling are: (a) short displacements into the sample matrix; (b) longer displacements under certain barriers or the so-called Maxwell–Wagner effects; (c) macroscopic movement of charge carriers towards sample electrodes [5,6]. The most sophisticated method in TSDC measurements is the partial polarization technique or the so-called thermal sampling [7–14].

The aim of this paper was to study the relaxation of polystyrene–polyoxyethylene (PS–POE) diblock copolymer with a volume ratio close to 1:1 (the weight ratio is similar). The study has been carried out at a low temperature from 173 to 293 K below the electric conductivity in POE. This is also well below the glass transition in PS block. The POE block is particularly prone to crystallize and this makes the PS–POE system interesting for TSDC analysis.

## 2. Experimental

PS was polymerized at a low temperature of 203 K, using phenyl isopropylpotassium as initiator. PS–POE copolymerization was carried out by anionic polymerization in solution under vacuum, using tetrahydrofuran as a solvent. The average molecular weight ( $M_w$ ) of PS–POE determined by size exclusion chromatography was 34 500, and 15 000 for PS block and 19 500 for POE block. The POE weight concentration was 56.5 wt.%. Such ratio has been approximated to 1:1 in the succeeding text. For systems with a different weight ratio between two blocks the PS of  $M_w = 15 000$  was dissolved in benzene together with a previously prepared PS–POE. The solvent was removed by freeze-drying procedure. In the experiments with homopolymer the PS of  $M_w = 15 000$  was used.

The samples for TSDC measurements were obtained by pressing the powder into pellets (11.4 mm in diameter) under 405 bar at room temperature (RT). The pellets were put into a teflon covered brass mold, heated to 413 K, held at 413 K for 20 min and cooled at  $2 \text{ K min}^{-1}$  to RT. The pressure applied during heating was as low as 1–2 bar. The electrodes of Ag foils of  $3 \mu\text{m}$  and 8 mm in diameter were put onto both sides of the pellets in order to get fixed during melting. The final sample thickness was 1 mm. The average sample weight, in a space between two electrodes, was 50 mg. The measurements were carried out in a cell filled with dry nitrogen. In the ordinary measure-

ments sometimes called integral, complex, or global, poling was performed by  $E_p = 10 \text{ kV cm}^{-1}$  at a temperature of  $T_p = 298 \text{ K}$ . The cooling to 173 K under  $E_p$  was at the rate of about  $2 \text{ K min}^{-1}$ . The storage in the short-circuited state (SCS) at  $T_0$  was 30 min in order to minimize the parasitic charge. Depolarization was carried out at  $4 \text{ K min}^{-1}$ . The runs with partial polarization were performed by  $E_p = 5 \text{ kV cm}^{-1}$  at various  $T_p$  for 5 min. Then the sample was cooled down to  $T_p - \Delta T_p$  under  $E_p$  for 5 min. The cooling to  $T_0$  in SCS and the storage at  $T_0$  together took 20 min.  $T_0$  was equal to 173 K or at least 30 K below  $T_p$ . The temperature window  $\Delta T_p$  was equal to 5 K and the runs were carried out from 273 to 173 K in steps of 10 K. Depolarization was performed at  $4 \text{ K min}^{-1}$ . For current measurements a Keithley 617 electrometer was used and the temperature was controlled by an LFE controller Model 2012. Differential scanning calorimetry (DSC) measurements were carried out by a Perkin-Elmer DSC 7. As regards the relation between the TSDC and DSC runs the sample weight in TSDC was five times higher but the heating rate five times lower than in DSC.

## 3. Results and discussion

### 3.1. Characterization of samples by DSC

As an introduction a routine investigation of the 1:1 diblock PS–POE material by DSC was performed. Fig. 1 shows the DSC curve obtained by 7.5 mg of powder. The heating rate was as low as  $4.0 \text{ K min}^{-1}$ . At low temperatures the curve was flat and the glass transition of PEO, which occurs at about 206 K [15] could not be observed. A significant flow of heat at 329 K was obviously caused by melting of the crystals in POE. This is close to the literature data of 342 K [16]. Other measurements carried out at a higher rate of  $20.0 \text{ K min}^{-1}$  with 9.8 mg, Fig. 2, showed the glass transition of POE in detail. Three main temperatures were recorded: the beginning of relaxation at 186 K; glass transition at  $227 \pm 0.5 \text{ K}$ ; the end of process at 260 K. The thermal lag was about 1 K. The ensuing peak of heat flow occurred at 286 K, representing a precursor to the melting events. The melting itself occurred at a higher temperature, as shown in the previous run.

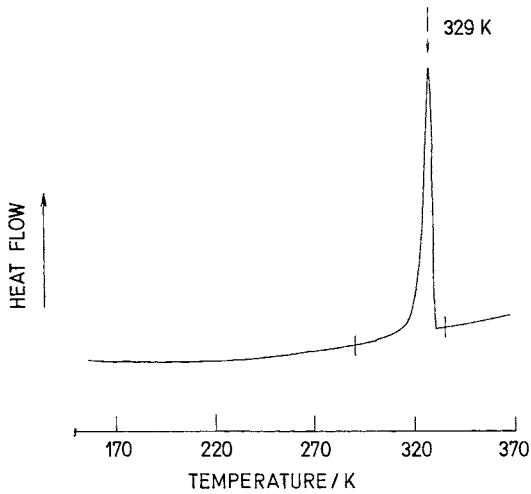


Fig. 1. DSC measurements for 1:1 PS-POE diblock copolymer. Heating rate  $4.0 \text{ K min}^{-1}$ .

### 3.2. TSDC measurements

The results of integral measurements of PS-POE (1:1), without poling in the range from 170 to 298 K, are shown in Fig. 3a. The depolarization current is very small, of an order of  $10^{-13} \text{ A}$ , showing nonconductive behavior up to 270 K. The run after poling is shown in Fig. 3b. At least three relaxations can be distinguished. The first  $P_1$ , is relatively small and widely distributed in the temperature range from 183 to 213 K. This relaxation is a precursor to the glass transition in POE block. The second  $P_2$ , is better defined with a maxi-

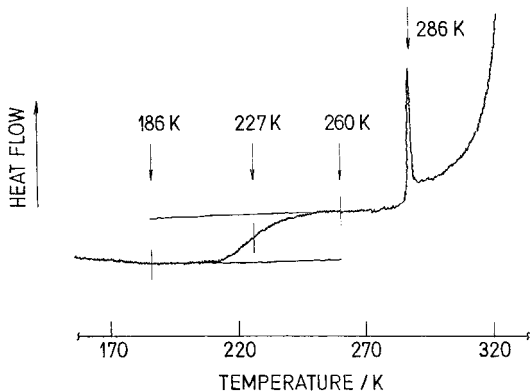


Fig. 2. DSC measurements of the same material. Heating rate  $20 \text{ K min}^{-1}$ .

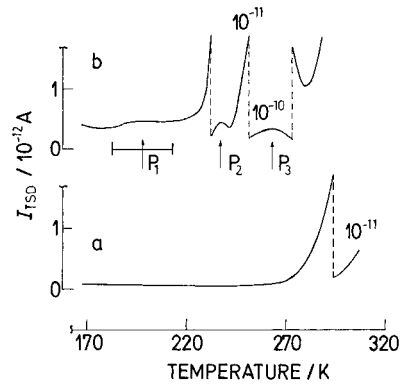


Fig. 3. TSDC measurements for 1:1 PS-POE: (a) without poling; (b) poling  $10 \text{ kV cm}^{-1}$  at 293 K.  $P_1$ ,  $P_2$  and  $P_3$  are the relaxation maxima.

mum at 237 K. The third  $P_3$ , is very large, about two orders of magnitude larger than  $P_1$ , with a maximum at 263 K.

### 3.3. Partial measurements

The integral runs are useful for a general insight. However, more details can be obtained only by partial measurements. The partial runs are drawn in Fig. 4. The first group of peaks, related to  $P_1$  from integral measurements, consists of four peaks (1–4). The next relaxation,  $P_2$ , is presented by three peaks (5–7). The final group (8–11) covers the relaxation  $P_3$ . Except

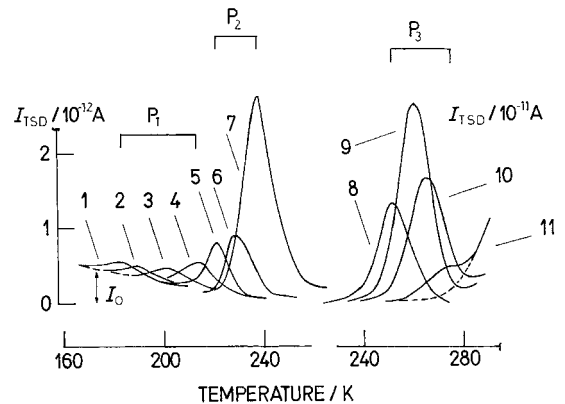


Fig. 4. TSDC peaks obtained by partial poling for 1:1 PS-POE.  $E_p = 5 \text{ kV cm}^{-1}$ . Horizontal lines show the group of peaks related to the relaxations from Fig. 3.

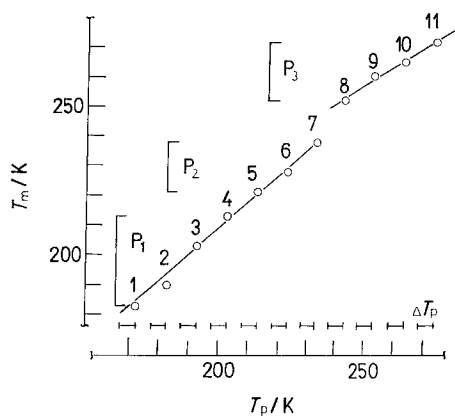


Fig. 5. Temperature of the peaks maxima  $T_m$  vs. temperature of poling  $T_p$ , related to the partial peaks from Fig. 4. Horizontal lines,  $\Delta T_p$ , show temperature windows in which poling is applied.

for the current caused by relaxations, an additional background or parasitic current  $I_0$  appears mainly due to the homocharge introduced during poling [17]. For any kind of analysis the peaks are normalized by subtraction of  $I_0$  [18].

Fig. 5 contains the temperature of the peaks maxima  $T_m$  versus  $T_p$  for the partial runs. The numbers are related to the curves in Fig. 4. The horizontal lines show the temperature windows in which  $E_p$  is applied. Such a diagram allows observation of a difference between various processes [19]. The ratio between the effects ( $T_m$ ) and the causes ( $T_p$ ) is not equal for all runs. The low temperature peaks (1–4) and (5–7) are a results of short displacements of the atoms in POE block. The shift of the (1–2) points can be due to the uncertainty involved in normalizing the extremely low current peaks. As regards the higher temperature peaks (8–11), show a difference in the  $T_m/T_p$  slope and a significant increase in the released charge. It is evident that the polarization mechanism is changed. These peaks are attributed to a space charge motion at the interfaces between the POE crystals and the amorphous phase, i.e. the Maxwell–Wagner polarization [4, p. 165].

### 3.4. Activation energy

For determination of the activation energy of the partial peaks two different methods were used. First was the well known initial rise method [20] in which

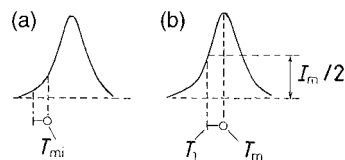


Fig. 6. Approximate description of the temperature ranges used in determining the activation energy by different methods: (a) initial rise method where,  $T_{mi}$  indicates the maximum temperature of the initial rise; (b) is the peak shape method where,  $T_1$  indicates the temperature related to one half of the current maximum, and  $T_m$  denotes temperature of the peak maximum.

an arbitrary initial rise temperature range plays a role. It has to be high enough to ensure sufficient accuracy in reading the current but below the point of inflection of the peak. Fig. 6a shows an arbitrary  $I(T)$  peak with a marked initial rise range and its maximum temperature  $T_{mi}$ . The other method was the peak shape method [21,22]. The activation energy  $E_a$  is determined by

$$E_a = \frac{T_1 T_m}{7940(T_m - T_1)} - \frac{T_1}{14866}, \quad (1)$$

where  $T_1$  is the temperature related to  $I_m/2$  at low temperature side and  $T_m$  is the temperature of the peak maximum. Fig. 6b shows an arbitrary  $I(T)$  peak with the temperature points in question.

Fig. 7 shows the activation energy  $E_a$  of the partial peaks. The numbers correspond to the curves in Fig. 4.  $E_a$  (Fig. 7a) (now on designated as  $E_a$  (a)) are determined by the initial rise method and are drawn versus the maximum temperature of the initial rises,  $T_{mi}$ . Horizontal lines show the temperature in which calculation of  $E_a$  takes place. The vertical arrow shows the temperature of glass transition obtained by DSC.

Fig. 7b shows  $E_a$  (now on designated as  $E_a$  (b)) obtained by the peak shape method. Horizontal lines show the  $T_m - T_1$  range used in calculation of  $E_a$  (b). The  $E_a$  (b) are smaller than  $E_a$  (a) and shifted towards higher temperatures, because the determination of  $E_a$  (b) takes place close to the peak maxima where the lower values of  $E_a$  can be expected. In spite of variations, the main course of  $E_a(T)$  function in a and b is the same.

Considering the results for  $E_a(T)$  the following ranges can be distinguished as (1)  $P_1$  relaxation, introduction to glass transition in POE. (2) The beginning of  $P_2$  relaxation (partial peaks 5–6) at  $219 \pm 4$  K, the maximum in entropy change and the point of real

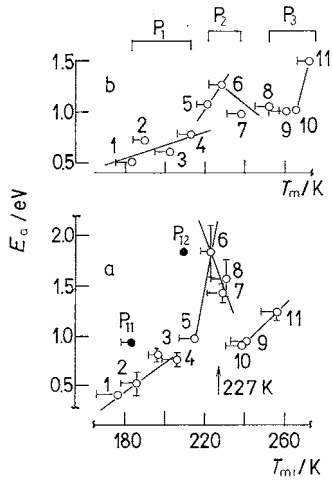


Fig. 7. Activation energy  $E_a$ , of the partial peaks from Fig. 4. (a) Determined by the initial rise method. Vertical lines indicate deviation. Horizontal lines indicate temperature in which calculation takes place.  $T_m$ , is the maximum temperature of the initial rise. Vertical arrow shows the temperature of glass transition obtained by DSC. Filled circles  $P_{11}$  and  $P_{12}$  are obtained at samples with imperfections. (b) Shows  $E_a$  obtained by the peak shape method.

glass transition. The results of  $E_a(T)$  are in line with DSC results. The end part of  $P_2$  with the negative entropy change represents a post-transition state. (3) Finally, the very broad and intensive relaxation process  $P_3$  can be understood as a precursor to the melting process in POE block. It is a result of the events coming from the crystal–amorphous interphases.

Table 1  
Parameters of partial TSDC peaks<sup>a</sup>

Range	Curve number	$T_m$ (K)	$I_m \times 10^{-12}$ (A)	$T_p$ (K)	$E_a$ (a) (eV)	$E_a$ (b) (eV)
P <sub>1</sub>	1	183	0.17	173–168	0.40	0.51
	2	190	0.13	183–178	0.51	0.72
	3	203	0.18	193–188	0.81	0.61
	4	213	0.36	203–198	0.73	0.78
P <sub>2</sub>	5	221.5	0.63	213–208	0.98	1.08
	6	228	0.79	223–218	1.84	1.26
	7	238	2.73	233–228	1.44	0.97
P <sub>3</sub>	8	252	13.1	243–238	1.58	1.05
	9	260.5	26.3	253–248	0.96	1.02
	10	265	16.3	263–258	0.91	1.02
	11	272	3.17	273–268	1.25	1.50

<sup>a</sup> Activation energy  $E_a$  (a) is obtained by the initial rise method, and  $E_a$  (b) by the peak shape method. Uncertainties:  $I_m$  for  $P_1$  and  $P_2$  is  $\pm 5\%$ ; for  $P_3$  is  $\pm 2\%$ ; for  $T_m$  is  $\pm 1$  K; for  $T_p$  is  $\pm 1$  K. Deviations for  $E_a$  (a) are shown in Fig. 7. Deviations for  $E_a$  (b) are  $\pm 0.05$  eV. The numbers are related to curves in Fig. 4.

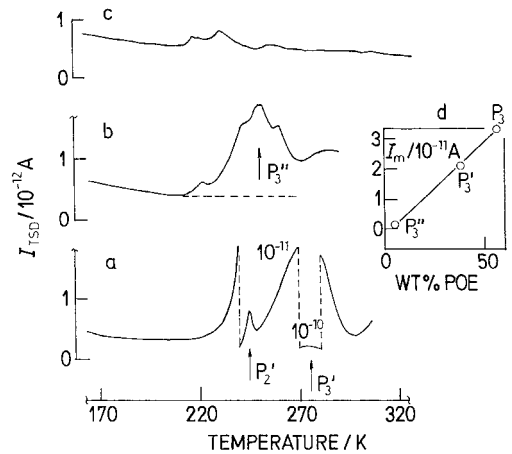


Fig. 8. TSDC measurements for samples with different concentrations: (a) 38 wt.% of POE and 62 wt.% of PS; (b) 5 wt.% of POE and 95 wt.% of PS; (c) 100 wt.% of PS; (d) maximum current  $I_m$  of high temperature peaks  $P_3$ ,  $P_3'$  and  $P_3''$  vs. wt.% of POE.  $E_p = 10$  kV cm<sup>-1</sup> at 293 K.

The numerical data related to the partial peaks are listed in Table 1.

### 3.5. The influence of concentration

In order to confirm the origins of  $P_1$ ,  $P_2$  and  $P_3$ , some runs at samples with different concentrations were performed. Fig. 8a shows the TSDC curve of sample containing excess PS, i.e. 62 wt.%. In

comparison with the standard curve from Fig. 1b it is obvious that  $P_1$  practically disappears.  $P'_2$  which corresponds to  $P_2$  is increased and shifted towards a higher temperature. This is in opposition to the decrease in POE concentration, which means that some perturbation in the structure is at work. The curve b in Fig. 8 is related to a sample containing only 5% POE. Only one peak  $P''_3$  appeared corresponding to  $P_3$ , but decreased and shifted towards a lower temperature. If we make a comparison among  $P_3$ ,  $P'_3$  and  $P''_3$  (inset d in Fig. 8), in spite of the shift in temperature, the related current maxima strictly follow the POE concentration, which confirms that  $P_3$  is coming from the POE block. TSDC curve of pure PS in Fig. 8c shows a relatively small signal at about 230 K, which can be attributed to the  $\beta$  relaxation in PS.

The TSDC spectra of PS described by other authors varied due to variation among samples. PS ( $M_w$  about 368 000) showed a maximum in  $\beta$  relaxation at 338 K [23]. PS ( $M_w = 160\,000$ ) showed  $\beta$  relaxation at 298 K [24]. In a recent paper  $\beta$  relaxation for PS ( $M_w = 60\,000$ ) has been found at 260 K [25]. It is obvious that  $M_w$  is a factor that influences the temperature of  $\beta$  relaxation. Therefore it is acceptable that in this investigation  $\beta$  relaxation of PS,  $M_w = 15\,000$  appears at about 230 K. In PS blends the TSDC spectra can show a strong interaction between the components [24,25] or a simple overlapping [24]. In our case, a comparison of b and c curves in Fig. 8, shows that  $P''_3$  is simply overlapped by a current, on both shoulders, caused by PS spectra. Such overlap shows that the components are mutually incompatible at the study temperature.

### 3.6. Aging effect

For TSDC measurements the samples were freshly prepared. An attempt was made to check possible effects of repeating runs at the same sample. One run is defined by poling at 293 K, cooling to 173 K and heating up to 300–310 K. The results are presented in Fig. 9. Curve 9a was obtained after nine previous runs. In comparison with the first run in Fig. 3, the results are practically identical and only a small shift in  $P_3$  occurs. After 17 runs, Fig. 9b, a new peak  $P_{11}$  appears in the  $P_1$  region,  $P_2$  is overlapped by the initial part of  $P_3$  and  $P_3$  is increased. The observation after 33 runs, Fig. 9c, shows one more peak,  $P_{12}$ .  $P_3$  has

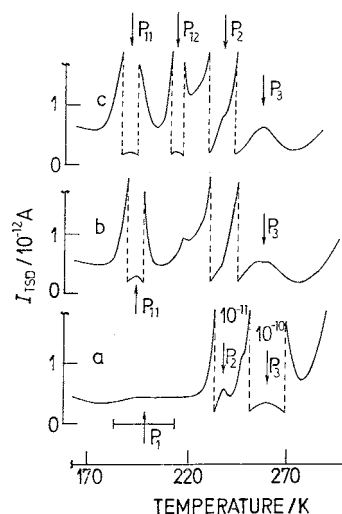


Fig. 9. TSDC measurements for 1:1 PS-POE samples with a different history of repeating runs: (a) 10 runs; (b) 18 runs; (c) 34 runs.  $P_{11}$  and  $P_{12}$ , new peaks in the  $P_1$  region, caused by imperfections.  $E_p = 10\text{ kV cm}^{-1}$  at 293 K.

been additionally increased. The  $E_a$  of new processes are shown in Fig. 7 (filled circles). The related  $E_a$  are completely out of the main course of  $E_a(T)$ . Both processes are relatively narrow with high  $E_a$ . They are due to sample imperfections caused by repeated runs. They are similar to the approximately single relaxation time processes described in [19]. The increase in  $P_3$  is attributed to the increased number of traps at the interfaces between the amorphous and the crystalline phases in a sample.

## 4. Conclusions

By the use of integral and partial TSDC measurements in combination with DSC and by determination of  $E_a$  in the 173–293 K range three main relaxations were observed. The first,  $P_1$ , widely distributed from 183 to 213 K, is attributed to short distance displacements of atoms as an introduction to the glass transition in the POE block.

The second relaxation,  $P_2$ , with the current maximum at 237 K, is also caused by short displacements, but the distance of motions is increased.  $P_2$  is a result of glass transition. The  $E_a(T)$  function shows the maximum in entropy change at  $219 \pm 4\text{ K}$ .

$P_3$  in comparison with  $P_1$  is increased by two orders of magnitude. It is attributed to the motions of the charge localized at the interface between the amorphous and the crystalline phase, i.e. the Maxwell–Wagner relaxation.  $P_3$  is caused by the events going on as precursors to the melting process. Investigation at higher temperatures is unfeasible due to an increase in POE electric conductance.

The TSDC caused by a PS component is very small and simply overlaps the POE component spectra without interaction.

During the repeated experiments some new peaks appeared at low temperature due to imperfections in POE blocks caused by successive heating and cooling treatments.

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