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## The Influence of Thermal History During Solidification of The Polyvinylidene Fluoride on The Characteristics of Dielectric Relaxation.

Andrey E. Afonkin\*, Anastasia S. Gadlevskaya, Lyana O. Shoranova.

Joint Stock Company «Federal State Research and Design Institute of Rare Metal Industry» (Institute «GIREDMET»), 119017, Moscow, Russian Federation.

### ABSTRACT

By the method of dielectric relaxation in a wide frequency range investigated relaxation process at temperatures near the melting point of two samples of polyvinylidene fluoride, which were obtained under different conditions. The observed dielectric relaxation process associated with the formation of space charge due to the presence of impurity carriers. The relaxation time and the intensity of this process decreases when the sample grows, the degree of crystallinity. This refers to the increase in the mobility of the impurity of the carriers that move in the amorphous regions. It is assumed that the isothermal crystallization can be aggregation of different kinds of chemical defects. Such defects include: end groups, branching, defects of the type "head to head, tail to tail" HHTT. Such aggregation may contribute to the higher mobility of the impurity of the carriers.

**Keywords:** polyvinylidene fluoride, films, dielectric relaxation, electric modulus

*\*Corresponding author*

**INTRODUCTION**

Poly(vinylidene fluoride) (PVDF) and its copolymers are good model objects to study mechanisms of ferro-, piezoandpyroelectricity in crystalline polymers [1,2]. Relaxation processes in PVDF have been mainly studied at low temperatures (for example, see [3]), while mobility at high temperatures [4–7], which can be related to the space charge manifestation [8], has been much less studied. For the given class of polymers such a charge may play a very important role in their electric properties. The space charge, for example, manifests itself both in pyroelectricity [9] and in the polarization processes [10, 11]. The motion of extrinsic carriers in crystalline polymers is observed in amorphous areas that make studies of their dynamics quite necessary.

In the present paper, we will demonstrate on two PVDF samples with different thermal history that the process of melting is accompanied by an intensive low-frequency relaxation process related to the space charge. The characteristics of the given process are discussed in view of the distinctions between the structures of these samples.

**EXPERIMENTAL**

A VDF homopolymer (F2E, Russia) polymerized by way of emulsion was used. The films were produced by way of crystallization from a melt under the pressure of 15 MPa. For the PVDF I the melt was held for 5min at 200 °C at given pressure, and then non-isothermally crystallized by quenching into water at room temperature. The PVDF II film was prepared by isothermal crystallization at  $T_{cr} = 150$  °C for 1.5h with subsequent cooling down to room temperature under pressure. The film thickness was 50 μm. For electric measurements, 0.1 μm thick and 5 mm diameter aluminum electrodes were evaporated onto both sides of the films.

For dielectric spectroscopy in the frequencyrange  $10^{-1} - 10^7$  Hz at 20–160 °C the Novocontrol Concept 40 system was employed. The differential scanning calorimetry (DSC) was carried out using a Perkin Elmer DSK-7 calorimeter. The heating range was 20 K/min for the samples with 20 mg hanging. Calibration was made using In. The WAXS measurements were performed in the transmission mode using X-ray diffractometer KARD-6 with a 2D-area detector [12] ( $Cu_{K\alpha}$  of  $\lambda = 1.542\text{Å}$ . and a graphite monochromator). The overlapping diffraction peaks were separated under assumption of their pseudo-Voight shape line. The crystallites' sizes were determined by the Scherrer formula

$$l_c = \frac{0.9\lambda}{\cos\theta\sqrt{\beta^2 - \beta_r^2}}, \tag{1}$$

where  $\lambda$  is the wavelength,  $\beta$  is the FWHM for the sample measured, and  $\beta_r$  is instrumental widening.

**RESULTS**

The result of WAXS analysis shows that both polymers are  $\alpha$ -polymorphs [13]. The structural characteristics of the films are listed in Table 1. The crystallinity was calculated both from theWAXS( $\phi_{X\text{-ray}}$ ) and DSC data( $\phi_{dsc}$ ). The latter case employed the value of melting heat for the  $\alpha$ -phase crystals, i.e., 104.5 J/g [14]. It follows from the Table 1 that the crystallinity is lower in the PVDF I. The WAXS data show that the crystallites are larger in the PVDF II (especially along the direction normal to planes 021 and 002).

**Table 1. Structural parameters of PVDF samples I and II**

Sample	$l_{100}$ (nm)	$l_{020}$ (nm)	$l_{110}$ (nm)	$l_{021}$ (nm)	$l_{002}$ (nm)	$\phi_{X\text{-ray}}$	$\phi_{dsc}$	$2\phi_{am}^{max}$ (grad)
PVDF I	8.1	17.3	14.7	4.3	4.1	0.36	0.43	18.77
PVDF II	11.7	19.1	13.6	7.7	6.1	0.49	0.53	18.52

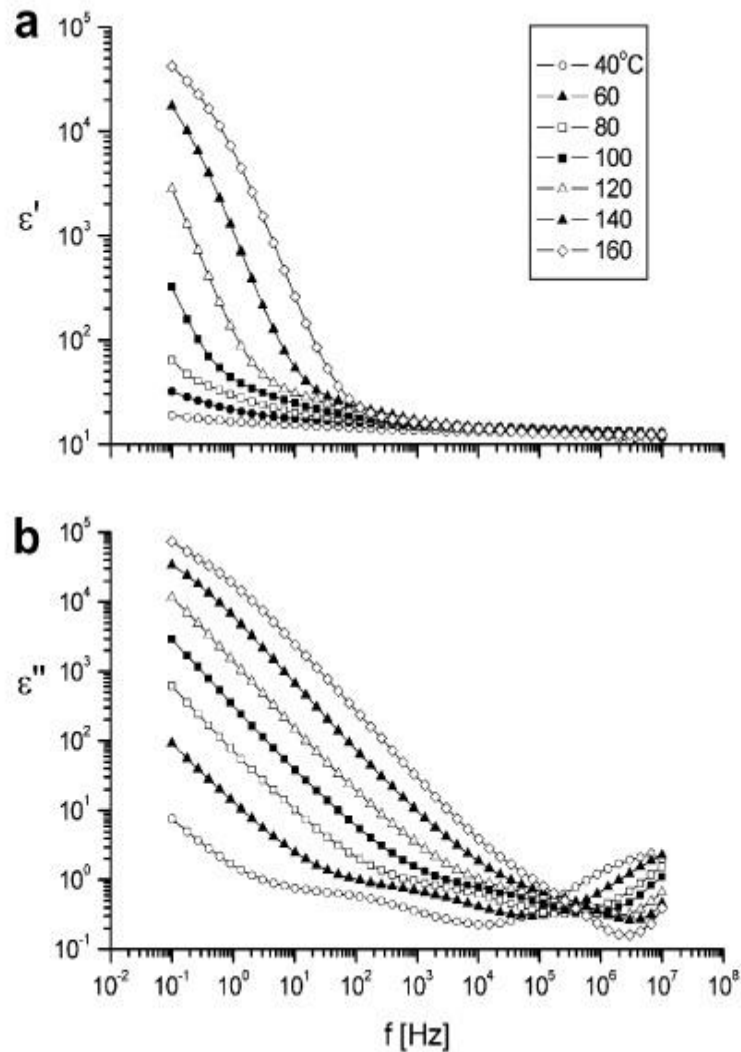


Fig. 1. log–log frequency plots of the real  $\varepsilon'(f)$  (a) and of the imaginary  $\varepsilon''(f)$  (b) parts of dielectric permittivity for the PVDF I at temperatures given on the plot. Lines are given to guide the eye.

Three relaxation areas in  $\alpha$ -PVDF are mostly reported [3], that are designated as  $\beta$  – (local mobility at temperatures lower than the glass transition temperature  $T_g$ ),  $\alpha_a$  – (cooperative microbrownian motion of segments in the amorphous phase) and  $\alpha_c$  – (mobility in the crystalline areas) following the temperature increase. These transitions were also observed in both samples. In the present paper we discuss only the high-temperature relaxation ( $\alpha$ ) that is also observed in VDF/HFP copolymers [8]. Fig. 1 displays dielectric permittivity  $\varepsilon'$  and dielectric loss  $\varepsilon''$  spectra for the PVDF I (they are of the same form for the PVDF II). As seen, at low frequencies an intensive relaxation process is observed. Fig. 2 shows ac-conductivity plots,  $\sigma_{ac}(f)$ , for the same sample as in Fig. 1. The plateau value  $\sigma_{pl}$  changes with temperature. It specifies that the free charges play a dominant role in this relaxation. In this case it is convenient to present the experimental data in Fig. 1 in terms of a complex electric modulus  $M^*$  [15].  $M''(f)$  curves in Fig. 3 demonstrate a well-expressed relaxation process similar to that observed in polymers with ionogenic impurities (see Ref. [16]). Fig. 4 shows that the  $\alpha$ -process follows the Arrhenius equation (as in the case with VDF/HFP copolymers [8])

$$f = f_0 \exp(-\Delta E/RT) \quad (2)$$

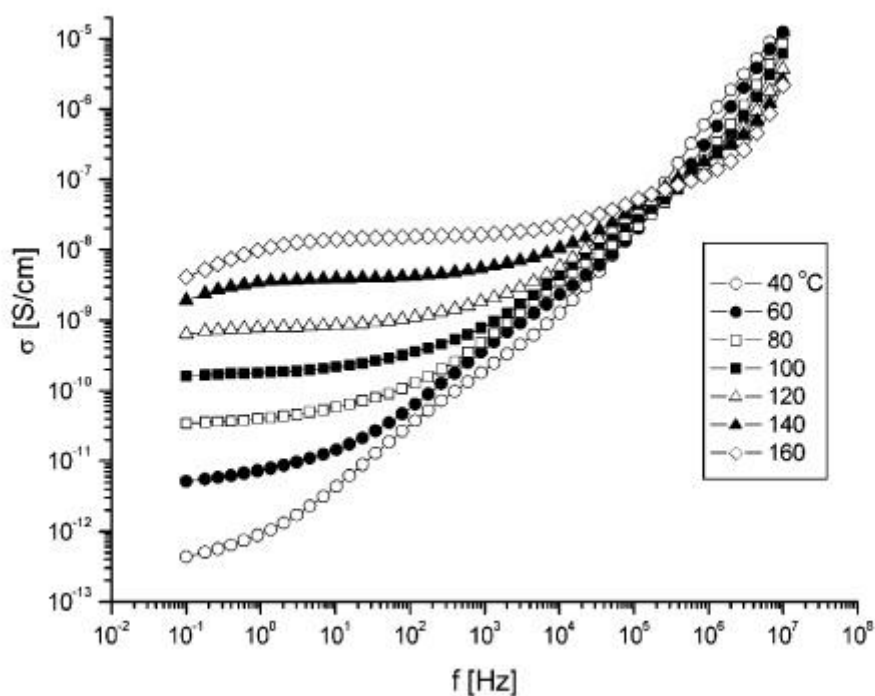


Fig. 2. Log–log frequency plots of ac-conductivity  $\sigma_{ac}(f)$  for the PVDF I at temperatures given on the plot. Lines are given to guide the eye.

Here  $f_0$  is the constant,  $R$  is the gas constant and  $\Delta E$  is the activation energy of the underlying mechanism. Activation parameters for both samples are listed in Table 2. One can see that they increase as the degree of crystallinity grows. However, if activation enthalpy grows by 30%, the activation entropy becomes several times greater. The latter fact has been noted earlier for VDF/HFP copolymers as well [8]. As seen from Fig. 4, for the quenched sample (PVDF I) there is a certain temperature at which the activation energy increases noticeably. We relate this to the metastability of the structure, where, on heating, a process of recrystallization can proceed with formation of larger and more perfect crystals, and, as a result, raise the activation barrier for the motion of free carriers.

**Table 2** Enthalpy  $\Delta H$ , entropy  $\Delta S$  and activation energy  $\Delta E$  (Eq. (2)) for hightemperature  $\alpha$ -relaxation in PVDF I and II

Sample	PVDF I	PVDF II	
$\Delta H$ (kJ/mol)	99±5	132±6	
$\Delta S$ (J/mol K)	23±3	123±10	
$\Delta E$ (kJ/mol)		102±5	135±6

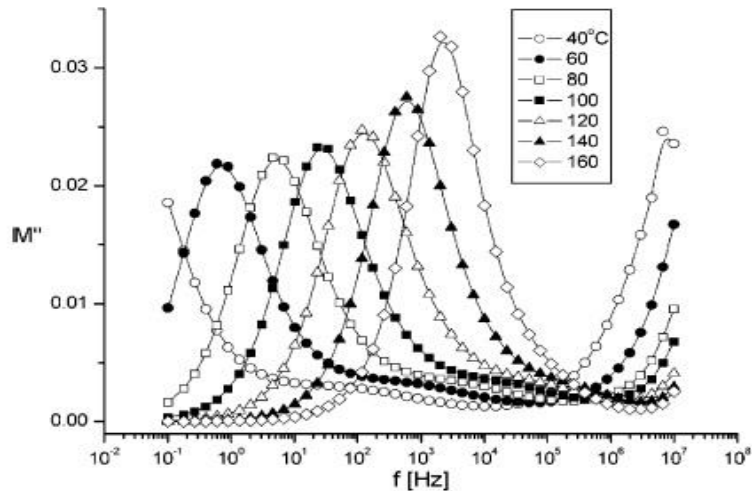


Fig. 3. Semi-logarithmic frequency plots of the imaginary part of complex electric modulus  $M''(f)$  for the PVDF I at temperatures given on the plot. Lines are given to guide the eye.

### DISCUSSION

Figs.5 and 6 show temperature dependencies of the loss tangent  $\tan\delta$  and thermal absorption (heat flow) for both films. It is seen, that in both cases, the low-frequency  $\tan\delta$  peaks fall at the temperature range in which the crystals formed at both primary and secondary crystallization processes (low-temperature and high-temperature endothermic maxima) [17] are disintegrating.

Crystalline polymers before the melting point are systems with structural and dynamic heterogeneity, since they include regions, which differ by dielectric permittivity and conductivity. This fact makes it possible to observe the Maxwell–Wagner–Sillars (MWS) relaxation in them [8]. On crystallization the ionic impurities will be ejected into the areas with larger free volume, i.e., into the amorphous phase. It should be kept in mind that at temperatures above  $T_g$  its polymer segments change their spatial positions with time. The lifetimes of such positions are determined by the relaxation times of these segments. Within the region of  $\alpha$ -dispersion they reach  $10^{-8}$ – $10^{-9}$  s [3,8]. This means the lifetime of the carrier at the impurity level must be very short and its motion is going under the multiplex trapping–detrapping mechanism.

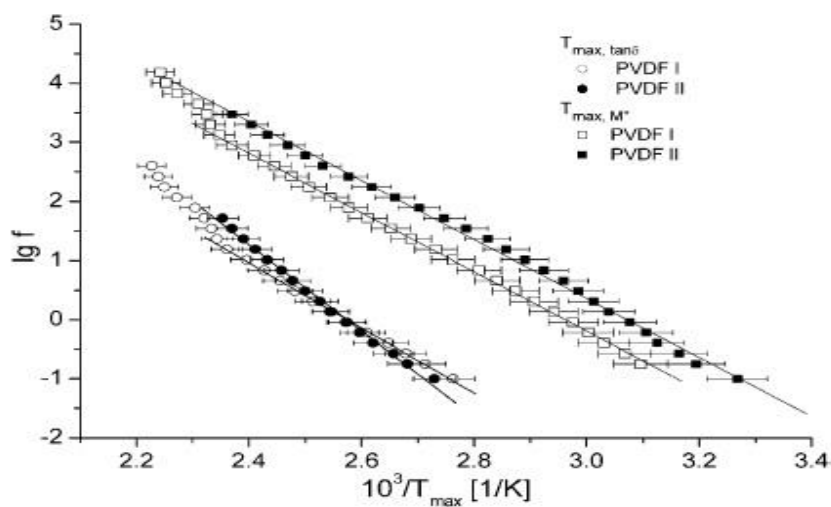


Fig. 4. Arrhenius plot for loss tangent,  $\tan\delta$ , and the imaginary part of electric modulus,  $M''$ , for PVDF I and II. The error bars describe errors in determination of  $T_{max}$ , the straight lines are least-squares fits to the data.

The process of melting may change the characteristics of the mentioned heterogeneity. In particular, it may lead to an increase of conductivity in the amorphous phase due to the release of the carriers with their traps located on the surfaces of these crystals. We will assume the equation for the macroscopic relaxation time  $\tau$  as

$$\tau = \frac{\epsilon_a \epsilon_0}{A\sigma}, \tag{3}$$

where  $\epsilon_0$  is the electric constant and  $\epsilon_a$  is the dielectric permittivity of the matrix with a volume fraction  $v$  of inclusions with conductivity  $\sigma$  and form-factor  $A$ . At a certain stage of melting the condition  $\omega\tau = 1$  is met, which means a relaxation peak has appeared. The  $\sigma_{pl}$  increase with temperature (Fig.2), according to (3), should lead to the reduce of  $\tau$  that corresponds to the relaxation peak shift to higher frequencies (Fig.3).

The nature of ionic impurities is usually associated with remains of the polymerization process products, which is emulsion in our case. However, one should take into account that in such systems (particularly at high temperatures) dehydrofluorination reactions accompanied by formation of HF molecules are possible [18,19]. It is also known that similar products can be formed in PVDF in fields of high strength [20,21].

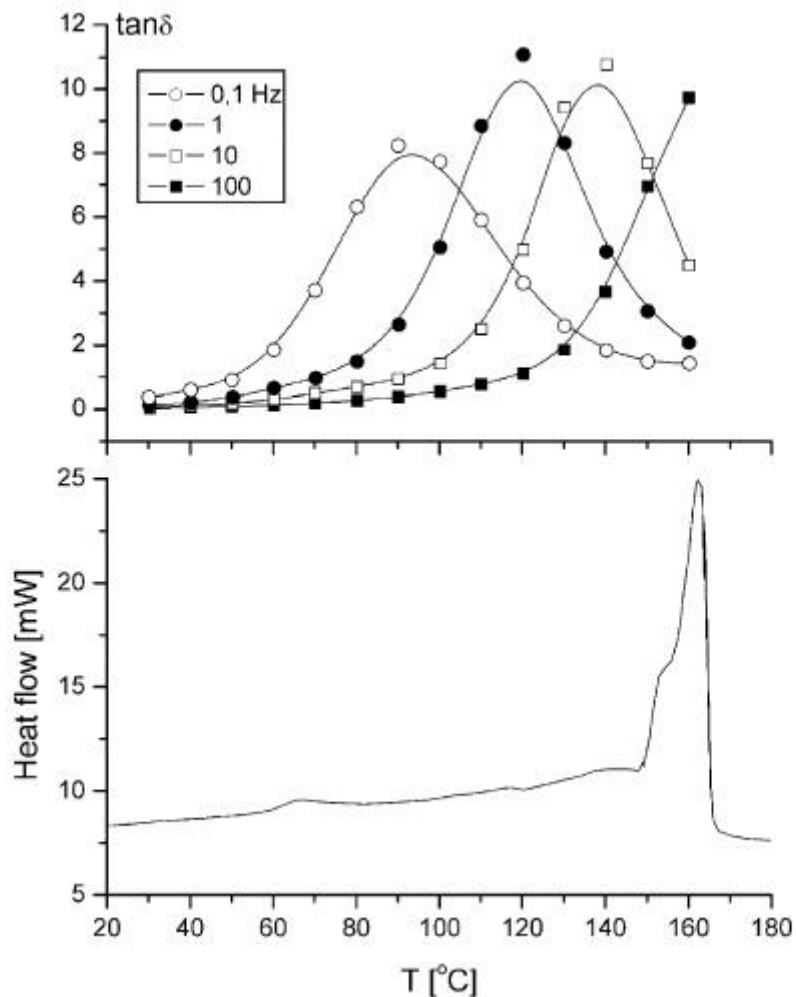


Fig. 5. Temperature dependencies of loss tangent  $\tan\delta(T)$  (at frequencies given on the plot) and DSC scan (first heating cycle) for the PVDF I in the region of the  $\alpha$ -relaxation.

It is of interest to see how the characteristics of the  $\alpha$ -process may be affected if we change the structure of

the initial PVDF film. For that, let us compare the frequency dependencies  $\sigma_{ac}(f)$  for both films at the same temperature (Fig. 6).

It is seen that in the PVDF II  $\sigma_{pl}$  is several times higher than in the PVDF I. We shall suppose there is only one type of carriers with charge  $q$ . Then the conductivity we noted –  $\sigma_{pl}$

$$\sigma_{pl} = nq\mu, \tag{4}$$

will be determined by the product of the mobility  $\mu$  and the concentration  $n$ . The larger value of  $n\mu$  in the PVDF II (Fig. 7) is due to the different thermal history of the samples. Since at crystallization the PVDF II film was kept at high temperatures for a longer period of time, the reactions of dehydrofluorination are more possible here. If such a reaction is the main source for accumulating of extrinsic carriers (of  $H^+$  and  $F^-$  type at HF molecules dissociation), then  $n$  is higher in the PVDF II. Besides, the mobility of carriers may be higher in this film as well. Indeed, longer high-temperature crystallization time of the PVDF II lead to a growth of crystals in all directions (Table 1). This can be achieved because of displacement of various sorts of defects (end groups, branches, HHTT-type defects) into disordered inter-lamellar areas [22]. This is schematically shown in Fig. 8. Thus, the inter-lamellar intervals in the PVDF II are characterized by a lower packing density of polymeric segments. It is qualitatively supported by some shift of the angle position of the amorphous halo in the PVDF II against film I (Table 1). The validity of this model is supported by our tentative SAXS data as well. To our mind, the given fact can lead to an increase of the carrier mobility in this sample, since  $\mu$  is controlled by the local free volume.

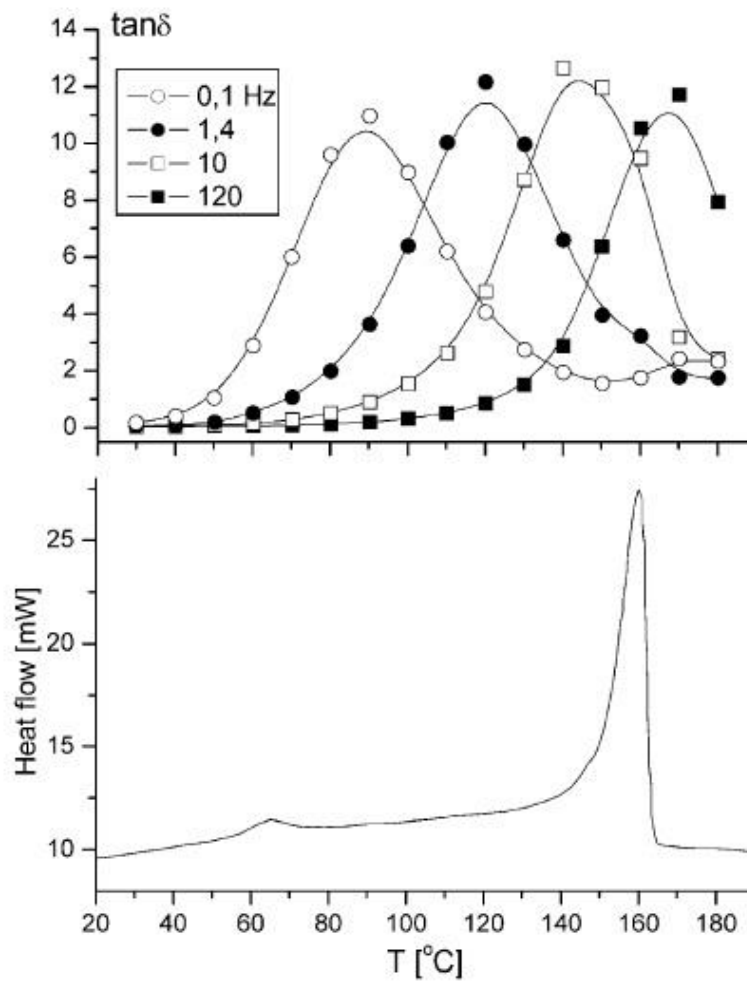


Fig. 6. Temperature dependencies of loss tangent  $\tan\delta(T)$  (at frequencies given on the plot) and DSC scan (first heating cycle) for the PVDF II in the region of the  $\alpha$ -relaxation.

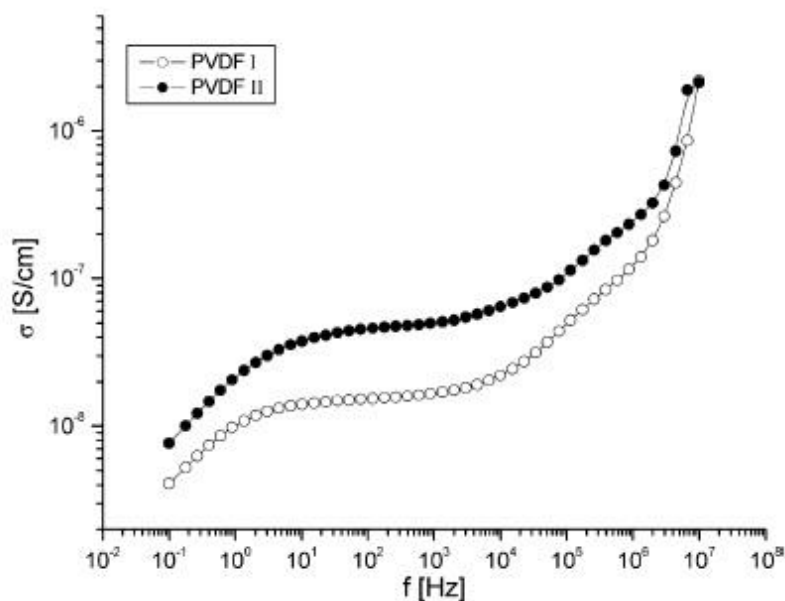


Fig. 7. Comparative log–log frequency plots of ac-conductivity  $\sigma_{ac}(f)$  for the samples I and II at 160 °C

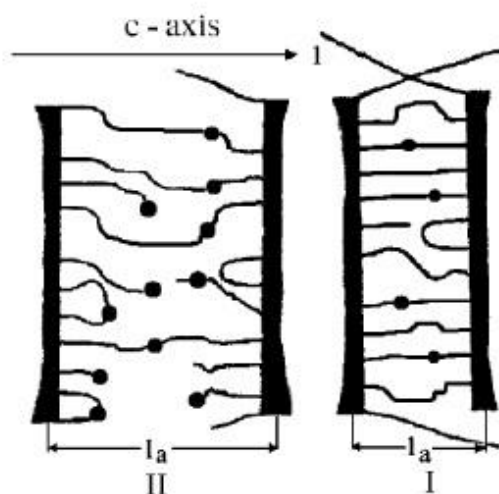


Fig. 8. Schematic representation of the amorphous inter-lamellar intervals formation in the PVDF I and II. • – chemical defects (end groups, chain branches, chain defects HHTT, etc.).

If  $\sigma_{pl}$  in the PVDF II is higher (Fig.7), then in accordance with Eq. (3), the relaxation time for the isothermally crystallized film (PVDF II) must be shorter vs. the quenched one (PVDF I). It is seen in Fig. 9, where the frequency plots of imaginary part of the electric modulus  $M''$  are shown. As seen, the peak for the PVDF II is shifted to higher frequencies. It means that the relaxation time for the PVDF II is longer, that is defined by Eq. (3) for the MWS polarization. From Fig.9 it also follows that besides longer relaxation time, the intensity of the  $\alpha$ -transition (the area under curve) is higher as well. This indirectly confirms the important role of the amorphous phase in space charge carriers' migration processes. As follows from Table 1, the fraction of the amorphous phase is higher in the PVDF I according to both methods. So when the carriers are located in the amorphous phase, any increase of its fraction, with other things being equal, will result in intensifying the given process. For the purpose of its more detailed description, the process of electrode polarization should be taken into account [8]. In the case of Al electrodes, one should not exclude chemical interactions forming new compounds at the polymer-metal boundary [19, 23].



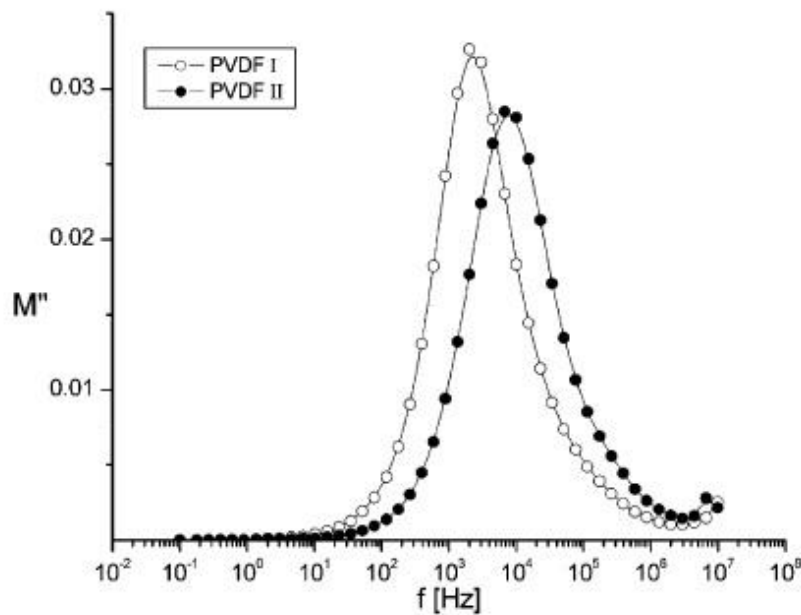


Fig. 9. Comparative semi-logarithmic frequency plots of the imaginary part of complex electric modulus  $M''(f)$  for the PVDF I and II at 160 °C.

### CONCLUSION

In the melting range of crystallites formed during the primary and secondary crystallization, an intensive relaxation process has been observed. This process is attributed to the manifestation of a space charge formed by extrinsic charge carriers. The relaxation time of this process is sensitive to the microstructure of the inter-lamellar regions. Increasing the chemical defect concentration in them due to a longer period of high-temperature crystallization leads to the decrease of the relaxation time.

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