

LOW-FREQUENCY DIELECTRIC DISPERSION AND PYROELECTRIC EFFECT IN FERROELECTRIC VINYLIDENE FLUORIDE-TRIFLUOROETHYLENE COPOLYMER IN PHASE TRANSITIONS

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The investigations of the dielectric constant, the pyroelectric coefficient and thermodepolarization currents both of a pure and a rhodamine-doped copolymer of vinylidene fluoride with trifluoroethylene (P(VF-TFE)) (70/30) have been carried out over a wide range of frequencies and temperatures. The temperature relationships obtained experimentally point to the reorganization of the structure of the amorphous phase of pure (P(VF-TFE)) in the temperature range of 313-323 K. The effect of doping on the specific feature of the copolymer has been studied.

1. INTRODUCTION

The dielectric and pyroelectric methods are extensively used to study phase transitions in high-molecular compounds. The main specific feature of these methods is their sensitivity to short-range forces; this makes it possible to use these methods for the determination of structural changes caused by various effects, including temperature effects.

The authors of a number of publications [1-3] have studied the pyroelectric and dielectric properties and also the currents of thermodepolarization [4, 5] of a copolymer of vinylidene fluoride with trifluoroethylene (P(VF-TFE)). The advantages of our procedure are the rigid stabilization of temperature (not below than 0.01°C) and the possibility to carry out the required measurements at a given temperature point during a long period of time (40 min).

The goal of the present work is to study the temperature behavior of a number of electrophysical quantities (the pyroelectric coefficient, thermodepolarization currents, dielectric constant) of the P(VF-TFE) copolymer in proximity to T_C (383 K) and the effect of the copolymer doping on the characteristics indicated above.

It is known that the structure of the ferroelectric copolymer P(VF-TFE) contains a crystalline and an amorphous phase. The introduction of trifluoroethylene into vinylidene fluoride causes the crystallization of the copolymer directly into the β -crystalline phase (without orientational stretching) [3]. In the polymer chain P(VF-TFE) $-(-CH_2-CH_2-)_n-(-CF_2-CHF-)_m-$ there are n and m corresponding monomer units. Of special interest are the P(VF-TFE) units which contain from 50 to 80 mass% of vinylidene fluoride, since in them, in contrast to pure vinylidene fluoride, the phase transition from the ferroelectric to the paraelectric phase is observed at temperatures lower than the softening temperature of the polymer ($T \sim 440$ K). These copolymers are semicrystalline and are composed of crystalline lamellas mixed with regions of the amorphous phase. The phase transition from the ferroelectric to the paraelectric phase is accompanied by

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conformational changes: the molecular chain with *trans*-conformations only assumes the structure in which *trans*- and *gauche*-conformations are randomly combined. The unit cell undergoes an anisotropic expansion in phase transition, which is associated with conformational disorder of molecular chains in the paraphase. The crystalline phase undergoes a phase transition at 383 K; the structure of the amorphous phase has not yet been unambiguously determined in the literature. According to Li-Jie et al. [6], the structure of the amorphous phase displays a certain degree of ordering; on studying the piezoelectric response of the given copolymer with the aid of an atomic high-power microscope, the authors failed to detect the zero piezoelectric effect that should have been displayed by the pure amorphous phase.

2. EXPERIMENTAL

The objects of our investigations were thin films of pure P(VF-TFE) (70/30) and of the copolymer doped with rhodamine. The films were prepared from granules of P(VF-TFE) with a 70/30 content (Atochem firm, France). The sensitized films of the copolymer first prepared by Verkhovskaya [7] were fabricated by spraying a combined solution of the copolymer and the dye rhodamine 6Zh in acetone onto a glass substrate with a transparent electrode made of SnO. After gradual evaporation of the solvent, uniformly colored films of the polymer solution of the dye about 10 μm thick were obtained in P(VF-TFE). The films were then annealed at $T = 315$ K, as a result of which the degree of crystallinity of the films increased from 50 to 75% [8]. A second electrode made of Al with a surface area of 0.2 cm^2 was then sputtered onto the film in vacuum. The dye concentration in the copolymer film was about 1 mass%.

The pyroelectric coefficient and thermodepolarization currents were measured by a static method with temperature stabilization not below than 0.01°C in the temperature range of 290–390 K by means of an electrometer VA-J-51 with the current being recorded on a potentiometer.

Dielectric measurements were made using a R551 bridge in the temperature range of 270–360 K and in the frequency range of 20 Hz–20 kHz.

3. RESULTS AND DISCUSSION

We obtained the temperature and frequency dependences of the complex dielectric constant and the temperature dependences of the pyroelectric coefficient and thermodepolarization currents for pure and rhodamine-doped P(VF-TFE).

Figure 1a shows the temperature dependence of the pyroelectric coefficient for pure P(VF-TFE). The maximum value of γ was observed at about 323 K: it was equal to 0.75 CGSE units ($2.4 \times 10^{-6} \text{C} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$). In the phase-transition region (383 K) the pyroelectric coefficient falls to zero.

Using the method of graphical integration of the $\gamma(T)$ curve, we obtained the temperature dependence of the increment of spontaneous polarization ΔP_s and its square ΔP_s^2 (Fig. 1b). According to theoretical calculations [9] performed on the assumption of 100% crystallinity of the vinylidene fluoride polymer, the value of its spontaneous polarization is 3.9×10^4 CGSE units. The introduction of trifluoroethylene into vinylidene fluoride does not diminish the degree of its crystallinity and, hence, the calculated value of spontaneous polarization does not decrease. The degree of crystallinity of the specimens studied is 75% (a higher degree of unipolarity in crystallites cannot be achieved because of the required magnitude of the field (> 1 MV/cm)), which is why the experimentally obtained value of spontaneous polarization was equal to 35 CGSE units, which is substantially lower than the calculated value.

The $\Delta P_s^2(T)$ curve clearly displays a linear portion in the region of 310–340 K, i.e., the increment of spontaneous polarization changes in this region by the law $\Delta P_s(T) \sim (T - T_C)^{1/2}$. As would be expected, in such a structurally inhomogeneous object as a semicrystalline film of P(VF-TFE), the $\Delta P_s(T)$ dependence does not vanish at T_C ; instead it falls smoothly in the paraphase region, which is always the case in nonideal crystals (see, for example, [9]). In such cases, the point of intersection of the linear portion of the $\Delta P_s^2(T)$ curve with the temperature axis is sometimes a few degrees away from T_C and for systems such as polymers it is tens of degrees away from T_C .

Figure 1c shows the temperature dependence of thermodepolarization currents for pure P(VF-TFE). From the graph we see that the $j(T)$ curve passes through zero near 320 K. The curve also exhibits a local minimal (at ~ 340 K) and a maximum (at ~ 370 K).

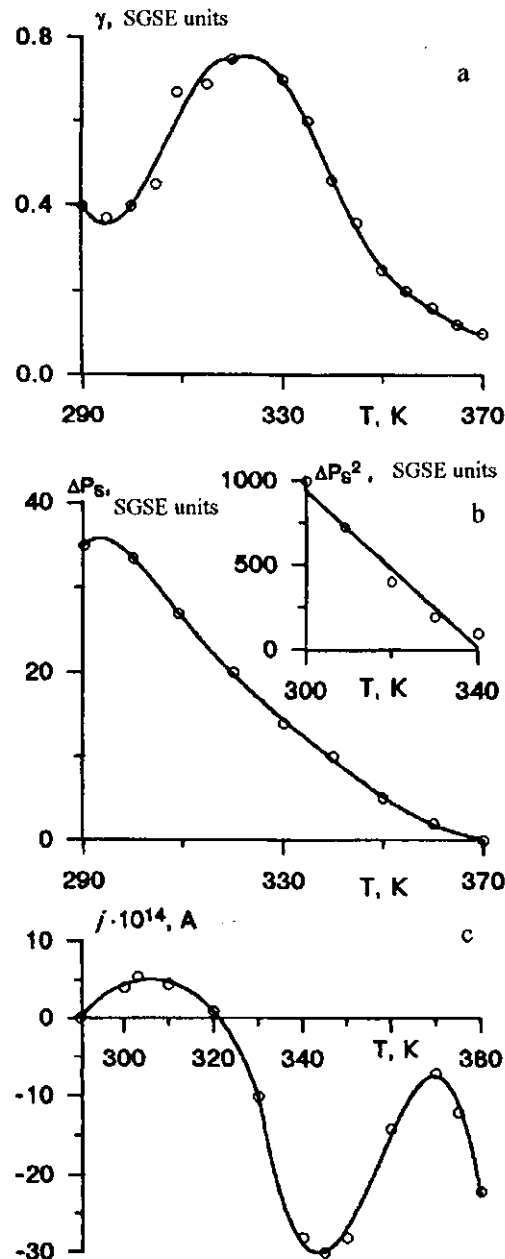


Fig. 1

Temperature dependence of the pyroelectric coefficient γ (a), spontaneous polarization increment ΔP_s , and its square ΔP_s^2 (b), and thermodepolarization currents (c) for a pure copolymer of vinylidene fluoride with trifluoroethylene.

Figure 2 shows a characteristic form of the frequency dependence of ϵ' and ϵ'' for pure and doped P(VF-TFE) in the temperature range from 303 to 353 K. From these data it follows that the maximum value of ϵ' for a pure copolymer varies from 8.5 (at 303 K) to 16.8 (at 353 K) and the minimum value varies from 7.9 (at 303 K) to 15 (at 353 K). The doped copolymer is characterized by a stronger scatter of ϵ' values: the maximum value varies from 50 (at 303 K) to 350 (at 353 K, not shown in the figure) and the minimum value varies from 34 (at 303 K) to 42 (at 353 K). Moreover, as the value of ω increases, the $\epsilon'(\log \omega)$ curves for the doped copolymer drop more sharply than in the case of the pure copolymer.

The maximum value of ϵ'' for the pure P(VF-TFE) varied from 0.2 (at 303 K) to 1.17 (at 353 K); for

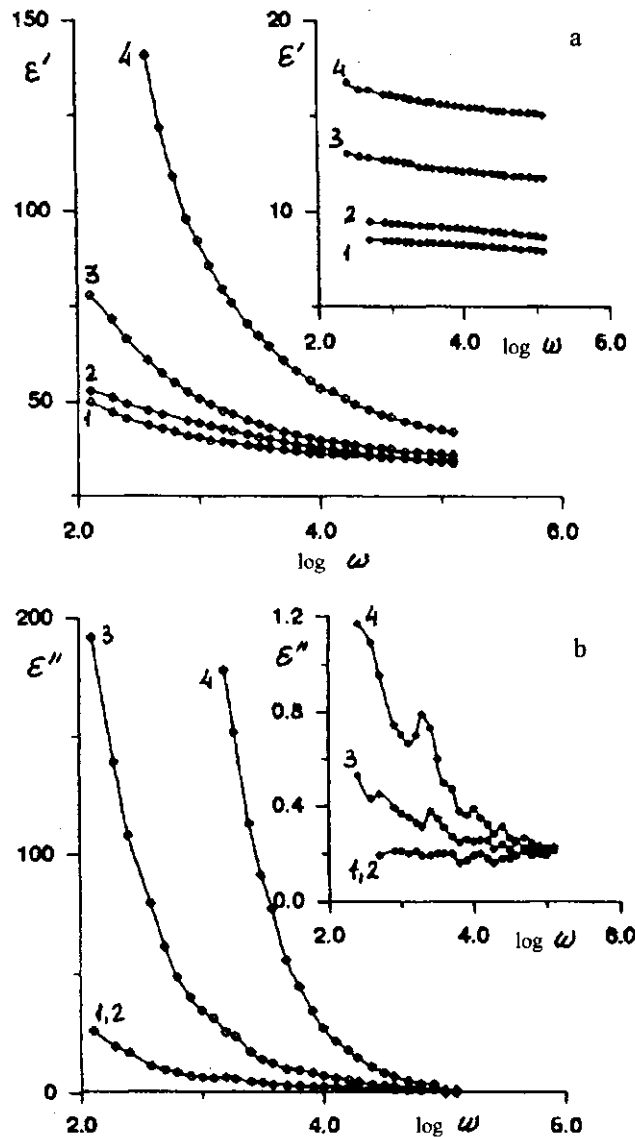


Fig. 2

Frequency dependence of the complex dielectric constant: ϵ' (a) and ϵ'' (b) for pure (insets) and doped copolymers of vinylidene fluoride with trifluoroethylene at temperatures: 303 K (1), 313 K (2), 338 K (3), and 353 K (4).

the doped copolymer it varied from 19 (at 303 K) to 400 (at 353 K, not shown in the figure). The minimum value of ϵ'' for the pure copolymer is about 0.2 (over the entire temperature range studied); for the doped P(VF-TFE) copolymer they vary from 0.2 (at 303 K) to 1.46 (at 353 K). As can be seen from Fig. 2, the quantity ϵ'' for the doped copolymer decreases with increasing frequency at all temperatures; in the case of the pure copolymer a different dependence is observed. Thus, at 295 K the value of ϵ'' increases with increasing ω (the curve is not shown in the figure); at 303 and 313 K the quantity ϵ'' does not practically change and at 338 and 353 K it decreases with increasing frequency. It should also be noted that the spread of ϵ'' values for the doped copolymer is much greater than for the pure copolymer, this being due to a small value of the measured quantity.

We also measured ϵ' as a function of the temperature at a frequency of 1 kHz for both copolymers. It was found that the value of ϵ' smoothly increases with increasing temperature: from 7 (at 290 K) to 25 (at 360 K) for the pure copolymer and from 25 (at 290 K) to 280 (at 360 K) for the doped copolymer.

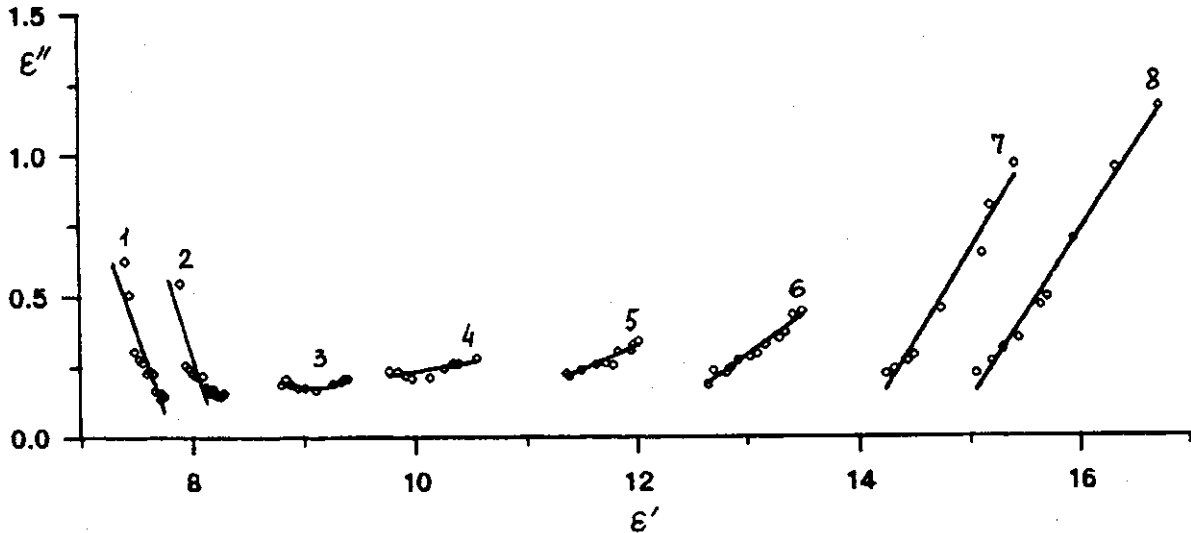


Fig. 3

Graphs of $\epsilon''(\epsilon')$ for a pure copolymer of vinylidene fluoride with trifluoroethylene at temperatures: 293 K (1); 303 K (2); 313 K (3); 323 K (4); 338 K (5); 343 K (6); 348 K (7); 353 K (8).

Figure 3 shows the dependence $\epsilon''(\epsilon')$ for the pure copolymer. We notice that in the region of 293–303 K the dependence $\epsilon''(\epsilon')$ has linear portions with a negative slope; in the region of 313–323 K the value of ϵ'' does not practically change and the curve is almost parallel to the ϵ' -axis, and at 338–353 K the slope of the linear portions is reversed.

Such a behavior may reflect a certain structural ordering of the copolymer, which in this case is, evidently, associated with the amorphous phase since it occurs far from the phase transition in the crystalline phase (383 K). The temperature dependence of the pyroelectric coefficient and thermodepolarization currents also exhibits anomalous behavior in the region of 313–323 K (see Fig. 1). The $\gamma(T)$ curve displays a maximum in this temperature range and the $j(T)$ curve passes through zero. The coincidence of the temperature regions of anomalies of the three quantities confirms the possibility of a structural change of the amorphous phase. Moreover, it is well known that it is precisely the region of 313–323 K that is most convenient for stretching the polyvinylidene fluoride polymer, which is also an indication of a certain special state of its structure.

Such graphs were also obtained by us for the doped copolymer (not given here), but in this case no change of the slope of the linear portions of the $\epsilon''(\epsilon')$ curves was detected; the curves themselves exhibit most likely a quadratic dependence. This suggests that the doping of the copolymer under consideration alters, in a way, the configuration of the copolymer and because of this no phenomena associated with the structural change of the amorphous phase are observed in the region of 313–323 K in contrast to the case with the pure copolymer.

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