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Copolymers of Vinylidene Fluoride with Hexafluoropropylene And Relaxation Processes In Them.

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ABSTRACT

By the method of dielectric relaxation he studied the molecular mobility in copolymers of vinylidene fluoride and HEXAFLUOROPROPYLENE with a different attitude component. Found four of the relaxation transition and one phase transition ferroelectric – paraelectric. Low-temperature relaxation process associated with local mobility, and the transition in the glass transition region with microbrowser the cooperative movement in the amorphous phase. At temperatures above room discovered blurred relaxing phase transition-type ferroelectric – paraelectric. Finally, at the very high temperatures observed relaxation process of the space charge.

Keywords: vinylidene fluoride, hexafluoropropylene, copolymer, film of compositions, Fluorine compounds relaxation

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INTRODUCTION

Poly(vinylidene fluoride) and its copolymers have attracted considerable attention of researchers for a number of reasons. The ferroelectricity revealed in these materials [1, 2], as well as their high piezoelectric and pyroelectric activities in combination with specific properties of polymers, make it possible to recommend poly(vinylidene fluoride) copolymers for use in fabricating various types of energy converters [3, 4]. The mechanisms responsible for the manifestation of ferroelectricity and piezoelectricity in polymer materials are poorly understood [2, 5]. In this respect, it is of interest to investigate the mechanisms of molecular mobility both in the disordered phases and in crystals of the polymers under consideration. In the present work, we studied vinylidene fluoride copolymers with hexafluoropropylene.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The experiments were performed with vinylidene fluoride–hexafluoropropylene copolymers of compositions 93:7 and 86:14. The microstructure of the chains in these copolymers was previously characterized by high-resolution NMR spectroscopy [6]. The copolymer films were prepared by extrusion. The analysis of the x-ray diffraction data revealed that the copolymers predominantly crystallize in the α or α_p phase. The dielectric properties of the copolymer films were investigated under isothermal conditions on a Novocontrol spectrometer in the frequency range from 10^{-1} to 10^7 Hz at temperatures from -100 to 150°C .

RESULTS AND DISCUSSION

The temperature dependences of the dielectric loss tangent at different frequencies for both copolymers are shown in Fig. 1. It can be seen from this figure that, in the temperature range from -100 to 150°C , the copolymers exhibit three or four types of mobility. In order of increasing temperature, the processes associated with these types of mobility are designated as β , α_a , α_c , and α . The temperature dependences of the mean frequency of reorientation of the corresponding kinetic units in the Arrhenius coordinates are plotted in Fig. 2. For the processes obeying the Arrhenius equation, the mobility is characterized by the enthalpy of activation ΔH and the entropy of activation ΔS . In this case, it is expedient to use the theory of absolute reaction rates, according to which the frequency f of losses at the maximum can be written as

$$f = \frac{kT}{2\pi h} \exp(-\Delta H / RT) \exp(\Delta S / R) \quad (1)$$

The quantities ΔH and ΔS can be determined from the following relationships:

$$E_a = \Delta H + RT, \quad (2)$$

$$E_a = RT'[1 + \ln(kT' / 2\pi h)], \quad (3)$$

Here, $E_a = -Rd \ln f / d(1/T)$ and the frequency of reorientation (1 Hz) of moving units determines the defreezing temperature T' . These parameters for the observed relaxation processes are listed in the table. As follows from the table, the β process, which occurs at the lowest temperature and obeys the Arrhenius equation, is virtually insensitive to the composition of the copolymer, because the temperature T' and the activation parameters for this process turn out to be identical for both copolymers. (Table 1.)

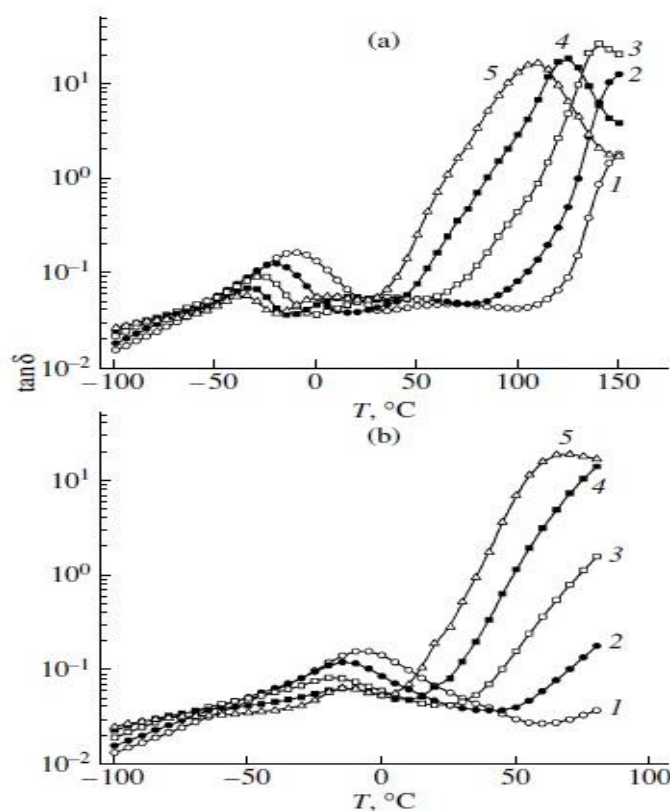


Fig. 1. Temperature dependences of the dielectric loss tangent for the vinylidene fluoride–hexafluoropropylene copolymer films of compositions (a) 93 : 7 and (b) 86 : 14 at frequencies of (1) 10^4 . (2) 1.3×10^3 . (3) 1.2×10^2 . (4) 10^1 .

Table 1. Activation parameters for mobility in vinylidene fluoride– hexafluoropropylene copolymers of different compositions

Composition	93 : 7				86 : 14		
	β	α_a	α_c	α	β	α_a	α
$\Delta H, \text{kJ/mol}$	47	78,1	111,6	151	47	97,1	80,5
$\Delta S, \text{J/mol}$	39,9		173,2	168,4	36,9		5,1
T', K	177		278	379	179		341

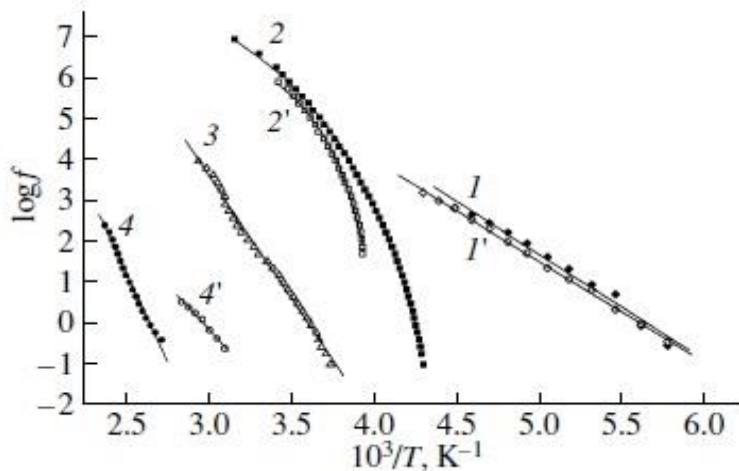


Fig. 2. Correlation diagrams for (1, 1') the β relaxation process, (2, 2') the α_a relaxation process, (3) the α_c relaxation process, and (4, 4') the high-temperature relaxation process in the vinylidene fluoride–hexafluoropropylene copolymers of compositions (1–4) 93 : 7 and (1', 2', 4') 86 : 14. Curves 2, 2', and 3 are obtained from the isochoric dependences of the dielectric loss tangent. The other curves are constructed from the isothermal dependences of the dielectric loss tangent.

It can be seen from Fig.2 that, at temperatures higher than the temperature range of the β relaxation process, there occurs another transition, namely, the α_a process, which is described by the Vogel–Fulcher equation

$$\log f = \log f_{\infty} - U / (T - T_0),$$

where T_0 is the characteristic temperature, U is a constant, and f_{∞} is the frequency at $T \rightarrow \infty$. These parameters are also presented in the table and appear to be sensitive to the composition of the copolymer. The temperatures T' for the α_a process are close to the glass transition temperature T_g of poly(vinylidene fluoride) [7]. Therefore, this process can be associated with the micro-Brownian mobility of chains in the amorphous phase in the glass transition range. The increase in the temperature T' with an increase in the hexafluoropropylene content from 7 to 14 mol % in the copolymer can be explained by the increase in the contribution of bulky fluoropropylene groups to the kinetic flexibility of the chains.

As is seen from Fig. 1, one more process occurs in the copolymer with a low hexafluoropropylene content at temperatures above the temperature range of the α_a process. According to the available data [7] and our results, the former process can be attributed to the mobility of chains in the crystalline phase (the α_c process). Taking into account the data reported in [6], this process can be caused by the $TGTG^- \rightarrow G^-TGT$ rearrangements in the crystal [8]. The α relaxation process, which is observed at the highest temperature (Fig. 1), can be associated with the manifestation of the normal relaxation mode in the polymers [9, 10]. However, the manifestation of electrode processes cannot be ruled out.

The temperature dependences of the real part of the linear permittivity for both copolymers are shown in Fig. 3. It can be seen that, at temperatures of 50–70°C, these dependences exhibit a behavior typical of ferroelectric–paraelectric phase transitions. In the polymers under investigation, there can exist ferroelectric phases of two types [2]. It should be noted that the temperature of the transition from the low-quality ferroelectric phase to the paraelectric phase lies in the above temperature range. Hence, we can assume that the low-quality ferroelectric phase is formed by regions of the polar α_p modification. However, experimental identification of this phase presents considerable difficulties [7]. A noticeable decrease in the maximum of the permittivity ϵ' with an increase in the field frequency and smearing of the phase transition are characteristic of relaxor ferroelectrics, as is the case with other copolymers. The estimates of the constant C in the expansion of the free energy in terms of polarization have demonstrated that a decrease in the

hexafluoropropylene content in the copolymer from 14 to 7 mol % leads to a decrease in the constant C. Therefore, the transition becomes less smeared and shifts toward the high-temperature range (Fig. 3). Hence, we can argue that, as the degree of perfection of the ferroelectric phase increases (as can be judged from the x-ray diffraction data), the smearing of the phase transition becomes less pronounced and the phase transition temperature increases.

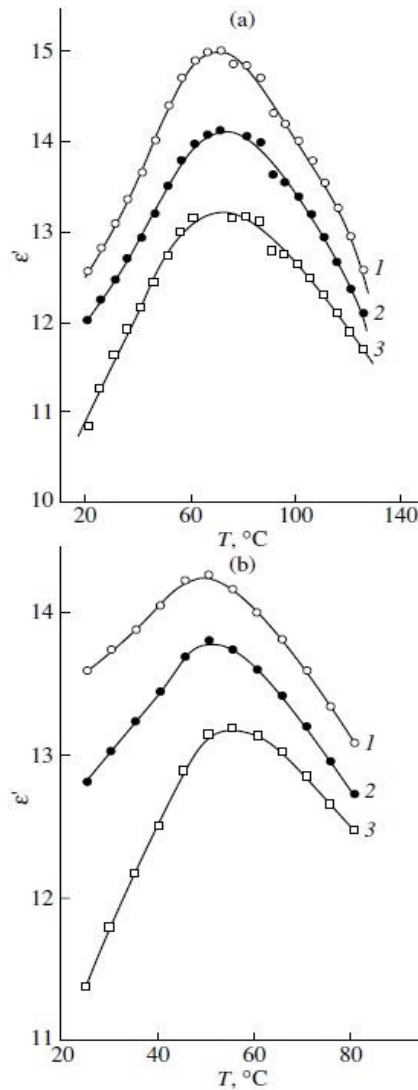


Fig. 3. Temperature dependences of the real part of the linear permittivity for the vinylidene fluoride–hexafluoropropylene copolymers of compositions (a) 93 : 7 and (b) 86 : 14 at frequencies of (1) 1.3, (2) 10.0, and (3) 120.0 kHz.

CONCLUSION

It should be emphasized that the . relaxation process occurs at temperatures above the temperature corresponding to the maximum in the dependences shown in Fig. 3, at which ferroelectric crystals of the polar α_p modification transform into the paraelectric phase. This is accompanied not only by the transformation of the polar unit cell into the nonpolar unit cell but also by a decrease in the crystal packing density [2]. It is evident that this circumstance should encourage an increase in the mobility of free carriers in the heterogeneous medium under consideration and, thus, facilitate space charge relaxation.

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