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Abstract

Full Text

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ON THE COMPENSATION EFFECT FOR THE ELECTRICAL CONDUCTIVITY OF CRYSTALLINE POLYMER DIELECTRICS

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For many chemical and physical processes, variations in rates are associated with changes both in the activation energy and in the preexponential factor σ_0 in the Arrhenius equation. Moreover, in condensed bodies, changes in U and σ_0 often affect the rate of a process in opposite directions (^{1}). This compensation effect (c.e.) has been found in studies of the electrical conductivity of polymers with a system of conjugated bonds (^{2,3}), for which hole conductivity is characteristic (^{4}).

In the present work, the c.e. was observed for typical polymer dielectrics, for which an ionic mechanism of electrical conductivity is assumed (^{5}). We investigated the influence of crystallization of technically pure polyethylene terephthalate, polytrifluorochloroethylene, and pentaplast (polymer of 3—3-dimethylchloroxycyclobutane) on electrical conductivity, calculated from the value of the residual current. Samples of a given polymer with different degrees of crystallinity were prepared from the starting material by successive heat treatment. Thus, sample 5 was obtained from sample 4 by additional annealing at 170° C for 24 hours (Table 1).

Fig. 1. Dependence of the activation energy on the logarithm of the preexponential factor.
a —polytrifluorochloroethylene II; *b* —pentaplast; *v* —polytrifluorochloroethylene I; *g* —polyethylene terephthalate. The numbers at the experimental points correspond to the sample number in Table 1. Curve *II* was constructed from the data of work (^{3}).

It should be noted that the heat treatment was not accompanied by irreversible changes; for the annealed samples, after secondary "quenching," the values of electrical conductivity and density coincided with those for the initial "quenched" sample. The degree of crystallinity was estimated from the density according to (^{6}). The density was determined by the method of hydrostatic weighing with an error of no more than 0.05% (^{7}). The procedure for measuring electrical conductivity has been described previously (^{8,9}). The magnitude of the electrical conductivity was measured at temperatures above the glass-transition temperature but below the temperatures at which crystallization of the sample is noticeable during the measurement process. The heat-treatment conditions and the density and electrical-conductivity values of the samples studied are given in Table 1. The samples of polytrifluorochloroethylene II contained a smaller amount of impurities than the samples of polytrifluorochloroethylene I.

From the data of Table 1 it follows that an increase in density by 0.5 ÷ 5%

Table 1

Samples studied and some of their characteristics

Name of material	Sample no.	Heat-treatment conditions	Density at 30°C, g/cm^3	σ at 100°C, ohm^{-1} · cm^{-1}	Temperature interval in which measurements were performed, °C
Polyethylene terephthalate	1	Quenching from the melt in water with ice	1.345	$3 \cdot 10^{-13}$	70—95
Polyethylene terephthalate	2	Annealing at 105°C for 10 h	1.375	$3 \cdot 10^{-15}$	70—100
Polyethylene terephthalate	3	Annealing at 120°C for 15 h	1.378	$2 \cdot 10^{-15}$	70—115
Polyethylene terephthalate	4	Annealing at 150°C for 20 h	1.383	$1 \cdot 10^{-15}$	80—140
Polyethylene terephthalate	5	Annealing at 170°C for 24 h	1.393	$3 \cdot 10^{-16}$	80—160
Polyethylene terephthalate	6	Annealing at 200°C for 28 h	1.408	$1 \cdot 10^{-16}$	80—170

Name of material	Sample no.	Heat-treatment conditions	Density at 30°C, g/cm^3	σ at 100°C, ohm^{-1} · cm^{-1}	Temperature interval in which measurements were performed, °C
Polytrifluorochloroethylene	7	Quenching from the melt in water with ice	2.129	$5 \cdot 10^{-16}$	80—120
Polytrifluorochloroethylene	8	Annealing at 130°C for 24 h	2.131	$4 \cdot 10^{-16}$	80—125
Polytrifluorochloroethylene	9	Annealing at 150°C for 20 h	2.135	$2.5 \cdot 10^{-16}$	80—140
Polytrifluorochloroethylene	10	Annealing at 170°C for 24 h	2.138	$2 \cdot 10^{-16}$	80—160
Polytrifluorochloroethylene	11	Annealing at 200°C for 24 h	2.148	$5 \cdot 10^{-17}$	80—190
Polytrifluorochloroethylene	12	Initial quenched	2.106	$4 \cdot 10^{-17}$	80—115
Polytrifluorochloroethylene	13	Annealing at 130°C for 25 h	2.116	$1 \cdot 10^{-18}$	80—125
Polytrifluorochloroethylene	14	Annealing at 150°C for 25 h	2.122	$1 \cdot 10^{-19}$	80—140
Polytrifluorochloroethylene	15	Annealing at 170°C for 20 h	2.128	$5 \cdot 10^{-20}$	80—160
Pentaplast	16	Annealing of a pressed sample at 130°C for 10 h	1.407	$1 \cdot 10^{-16}$	80—127
Pentaplast	17	Annealing at 150°C for 40 h	1.413	$3 \cdot 10^{-17}$	80—137

Name of material	Sample no.	Heat-treatment conditions	Density at 30°C, g/cm^3	σ at 100°C, ohm^{-1} · cm^{-1}	Temperature interval in which measurements were performed, °C
Pentaplast	18	Annealing at 160°C for 30 h	1.416	$1 \cdot 10^{-17}$	80—150

is accompanied by a decrease in electrical conductivity by a factor of 10–1000. The stated increase in density corresponds to an increase in the degree of crystallinity within the range 10–50%. It is interesting to note that crystallization of polyacetylene with hole conductivity leads to an increase in electrical conductivity; in this case the activation energy decreases, but the c.e. does not occur ([10]). A similar result was also obtained in the heat treatment of polyacrylonitrile ([11]).

Figure 1 presents the dependence of the magnitude of the activation energy on the logarithm of the pre-exponential factor in the usual expression for electrical conductivity, obtained by us (curve I) and in the work ([2],[3]) (curve II). It is seen that in both cases the dependence $U - \lg\sigma_0$ can be represented by a straight line,

$$U = A + B \lg \sigma_0,$$

where the values of B, both for the samples we studied and for polymers with conjugated bonds, are 0.7 kcal/mol, while the value of A in the first case is equal to -21, and in the second to -15.

Thus, we have for the first time detected the compensation effect in studying the influence of crystallization on the electrical conductivity of polymer dielectrics.

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Note: Figure translations are in progress. See original paper for figures.