

DIFUSION PROCESSES IN COPOLYMER SYSTEMS USED FOR ELECTRICAL INSULATION PURPOSES

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Abstract: This research is connected with receiving information about diffusion processes in copolymer systems of statistical copolymers type: ethylene + styrene and ethylene - propylene in hexane diffuses molecules.

The chemical synthesis today allows the implementation of various co-polymer systems, used as polymer dielectrics. This refers, most of all, to the mass usage in the modern electronics and electrical engineering of polyene materials, such as polyethylene and polypropylene.

A research has been conducted of diffusion processes in co-polymer systems of the type ethylene + styrene and ethylene + propylene, which allows the obtaining of valuable information about: the sizes, form and flexibility of the macro-molecule chains; physical characteristics related to the thermal kinetics of the diffusion processes and the mechanism of thermal movement of the diffused molecules in co-polymer systems.

Key Words: diffusion processes, copolymer systems, mechanism of thermal movement of the diffused molecules in co-polymer systems, thermal kinetics of the diffusion processes

1. Introduction

Expansion of the area of using synthetic polymers in engineering is closely related to great requirements demands for operational use of modern electrical insulating materials. Modern chemical synthesis allows to obtain different copolymer systems used as polymer dielectrics. A vast range of copolymer systems is obtained, at the change of number and type of monomeric components and the conditions under which the processes take place-statistically constructed and block copolymer systems

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[1]-[6].

Diffusion processes are of interest because through them we can examine the diffusion of molecules of low molecular substances in the nano domain of free volume in copolymer systems. You can obtain valuable information about: size, shape and flexibility of macromolecular chains, unsteady mechanism of the thermal movement of the diffused molecules in copolymer systems, physical characteristics [8]-[12] related to the thermal kinetics of diffusion processes.

This research is connected with receiving information about diffusion processes in copolymer systems of statistical copolymers type: ethylene + styrene and ethylene - propylene in hexane diffuses molecules.

Experimental results [8] are used, where the temperature dependence of the coefficient of diffusion (D) in a limited temperature range $\Delta T \rightarrow (T_1 \div T_2)$ is given.

2. Theoretical and Experimental Part - Physical Interpretation of the Received Information

The processes of transmission of matter or energy from an area with a higher concentration to an area with a lower concentrations occur at a molecular level and is determined by the random nature of molecules movement. The coefficient of diffusion D depends on temperature. In the study of $D = f(T)$ for diffusion processes in different types of substantial systems (and polymer, in particular) in limited temperature range (ΔT^*) the Boltzmann-Arrhenius dependence type (1) is valid:

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right), \quad (1)$$

$$D_0 = D_C \exp\left(\frac{E}{k_B T_{,,}}\right), \quad (2)$$

where: (D_0) is preexponential factor, (E) is the activation energy of diffusion processes (k_B) is the Boltzmann constant. Having experimental information about $D = f(T)$ we make the dependence $\ln D = f(1/T)$ and for the obtained linear parts in the temperature range (ΔT^*); (1) is valid, via (3) and (4) we determine the corresponding numerical rates of (E) and (D_0),

$$E = (K_B T_1 T_2)(T_2 - T_1)^{-1} \ln(D_2/D_1) \quad (3)$$

$$\ln D_0 = \frac{1}{2} [\ln(D_1 D_2) + (T_1 + T_2)(T_2 - T_1)^{-1} \ln((D)_2/D_1)]. \quad (4)$$

The obtained results for (D_0) and (E) of the two types copolymer systems that have been studied are in Table 1 and Table 2.

After obtaining the numerical rates about (D_0) for all intervals (ΔT^*) and types of samples of one type copolymer systems that have been studied the dependence

copolymer systems – (ethylene + styrene) + hexane								
mas. % styrene	$T_1 \div T_2$ κ	$D_1 \div D_2$ $(\mu m^2)/s$	$\ln D_0$	E eV	τ_c as	V_c m/s	l_c ρ_m	μ $\mu m^2/Vs$
8	296 \div 329	0,15 \div 2,64	9,25	0,76	1,76 \div	293 \div	0,52 \div	5,90 \div
	372 \div 411	233 \div 545	-3,94	0,29	4590	345	1580	15400
22	297 \div 329	0,24 \div 4,81	10,60	0,79	2,85 \div	293 \div	0,84 \div	9,67 \div
	357 \div 411	88,3 \div 400	-2,48	0,35	3350	345	1160	11200
35	297 \div 329	0,62 \div 9,98	9,84	0,74	71,8 \div	293 \div	21,0 \div	241 \div
	340 \div 411	41,7 \div 284	-3,54	0,33	2390	345	824	8010

Table 1

$\ln D_0 = f(E)$ is made. If it is linear, dependence (2) is valid, where (D_C) and (T_C) are respectively diffusional and temperature constants. From the linear parts of $\ln D_0 = f(E)$ we take extreme points and by dependences (5) and (??) we define, (D_c) and (T_c).

$$\ln D_c = \frac{1}{2} [\ln (D_{01} \cdot D_{02}) - (E_1 + E_2) (E_2 - E_1)^{-1} \ln \left(\frac{D_{02}}{D_{01}} \right)], \quad (5)$$

$$T_c = (E_2 - E_1) \left[k_B \ln \left(\frac{D_{02}}{D_{01}} \right) \right]^{-1}. \quad (6)$$

The presence of linear dependence of $\ln D_0 = f(E)$ in the temperature range $\Delta T > \Delta T^*$ shows that research diffusion process is cooperative in nature. With the increase of (T) consecutive thermo activation occurs of monomolecular processes with different numerical rates of (E) and (D_0) occurs. Dependence (2) represents compensational law for diffusional processes, as the united compensational law is of the type (??) for the whole range ($\Delta T > \Delta T^*$),

$$D = D_C \exp \left[\frac{E}{k_B} \left(\frac{1}{T_C} - \frac{1}{T} \right) \right]. \quad (7)$$

In [13] they connect the temperature constant (T_C), also called thermal diffusional pole, with the change of enthalpy (ΔH) and entropy (ΔS_E) of activation of the relevant diffusion process by dependence (??):

$$\Delta H (T) = T_C \Delta S_E (T) + \Delta G (T_C), \quad (8)$$

where $\Delta G(T_C)$ is the change of free enthalpy (ΔG) at (T_C) – the potential of Gibbs.

The Linear dependence $\ln D_0 = f(E)$ can be presented in the type (9):

$$\ln D_0 = \kappa E + a, \quad (9)$$

where: (κ) is the angular coefficient, $a = \ln D_C$ is a free member.

For copolymer systems of the type ethylene + styrene: $\kappa = 29,14$; $a = \ln D_C = -12,39$ and $T_C = 398^\circ \text{K}$.

For copolymer systems of the type ethylene + propylene: $\kappa = 16,20$; $a = \ln D_C = -6,81$ $T_C = 716^\circ \text{K}$.

According to [14] $[D]$ is functionally linked with other physical characteristic of diffusion processes: (τ_c)- duration of the diffusion jump with length (l_c) and speed (V_c); (μ) - mobility of the molecules.

For this purpose we use the ratio of Einstein (10)

$$D = V_c l_c = V_c^2 \tau_c = 3k_B T \tau_c (m)^{-1} = k_B T \mu (q)^{-1}, \quad (10)$$

where (m) is the mass of the diffused molecules, and (q) is its electric charge. We assume $q = q_0 = 1,6 \cdot 10^{-19} \text{ C}$. The determination of numerical values of τ_c, V_c, l_c and μ is carried out by relevant dependences (11 ÷ 14) as the obtained results for the two types of copolymers systems are in Table 1 and Table 2.

$$\tau_c = m D (3k_B T)^{-1} \quad (11); \quad V_c = [D(\tau_c)^{-1}]^{1/2}, \quad (12)$$

$$L_c = V_c \cdot \tau_c \quad (13); \quad \mu = q D (k_B T)^{-1}, \quad (14)$$

Small numerical values of (τ_c) and (l_c) confirmed the jumping mechanism of realization of the diffusion processes from the diffused molecules in copolymer systems. It is accompanied with a super short residence of diffuses molecules in the instantaneous out of conformal state.

The obtained numerical rates (V_c) are compared to the RMS (\bar{V}) (??) from the molecular statistics of Maxwell about the unreal gas and very good matches are obtained.

$$\bar{V} = [3k_B T (m)^{-1}]^{\frac{1}{2}}. \quad (15)$$

There is a dependence of $V_c = f(T, m)$. Speed (V_c) doesn't depend on mass percentage (mass %) content of one of monomer components in the studied copolymer systems.

For the size of (l_c) numerical rates are obtained $l_c < 1 \text{ \AA} = 10^{-10} m$. This confirms the conclusion made in [14], [15] in studying the diffusion of antioxidants, sulphur, accelerators of vulcanization in elastomers. These results show that when diffused molecules are moved from one conformal state to another in copolymer systems thermo fluctual volumes participate less than the critical. Even a small fluctuation in the volume contributes to intermittent translational movement of the diffused molecules [16].

copolymer systems - (ethylene + styrene) + hexane								
mas. % propylene	$T_1 \div T_2$ κ	$D_1 \div D_2$ $(\mu m^2)/s$	$\ln D_0$	E eV	τ_c as	V_c m/s	l_c ρ_m	μ $(\mu m^2)/Vs$
5	297 ÷	0,56 ÷	1,87	0,54	6,53 ÷	293 ÷	1,92 ÷	21,9 ÷
	352	14,16	-1,03	0,36	138	320	44,1	464
	390 ÷							
	413							
10	297 ÷	1,59 ÷	2,13	0,52	17,4 ÷	293 ÷	5,11 ÷	58,4 ÷
	352	35,54	-1,3	0,36	348	319	111	1170
	390 ÷							
	413							
15	297 ÷	2,10 ÷	-0,88	0,43	24,3 ÷	293 ÷	7,13 ÷	81,4 ÷
	352	28,24	-1,03	0,36	276	319	88,1	925
	390 ÷							
	413							
25	297 ÷	12,56 ÷	-1,03	0,43	145 ÷	293 ÷	42,6 ÷	487 ÷
	352	61,85	-1,03	0,36	662	309	204	2220
	390 ÷							
	413							

Table 2

For the first copolymer system of ethylene + styrene with the increase of mass % content of styrene (at $T = T_{max}$) the numerical rates of (τ_c), (l_c) and (μ), is decreased, which is due to the presence of large lateral phenylene nuclear group ($-C_6H_5$) in styrene monomer.

3. Conclusions

Study of the diffusion processes in copolymer systems of the type ethylene + styrene and ethylene - propylene is carried out:

- numerical values of physical characteristics are obtained, associated with thermal kinetics of diffusion processes;
- the validity of the compensation law is shown, representing $D_0 = f(T, E, D_c, T_c)$;
- the hopping mechanism of thermal motion of the diffused molecules in copolymer systems is confirmed;
- the obtained numerical values of (V) almost coincide with those of (\bar{V}) of

molecular Maxwell statistics for non ideal gases. Speed V doesn't depend on the mass percentage of monomer components in the copolymer systems;

e) the numerical rates of $l_C < 1 \text{ \AA} = 0,1 \text{ nm}$ confirmed the obtained results in [14], [15] as the thermo fluctuational free volume is less than the critical one.

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