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STRUCTURE OF POLYMER NETWORKS AS A PERCOLATION SYSTEM

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With the use of the assumption that the structure of an amorphous polymer can be presented as a set of frozen locally ordered regions surrounded by a loosely packed matrix, it is shown that a structure comprising a percolation cluster is formed in epoxypolymers, and in this case the glass-transition temperature is associated with the critical percolation probability, and the glass transition itself is considered as a phase transition.

Introduction. Percolation models are widely used for the description of a number of physical problems [1], including polymer behavior [2, 3]. These models are distinguished by simplicity and clarity [1], and their application to the description of the polymer behavior makes it possible to use the well-elaborated mathematics of these models in the description and prediction of polymer properties. In the present work, the cluster model of the structure of the amorphous polymer state [4, 5], which we successfully used earlier in derivation of structure–properties relationships for epoxypolymers [6-9], is used as a quantitative model of the structure of polymer networks. It is assumed within the framework of the model that the structure of the amorphous polymer phase can be presented as a set of locally ordered regions frozen at the glass-transition temperature T_{glass} surrounded by a loosely packed matrix [4]. In turn, the locally ordered regions (clusters) consist of close-packed collinear segments of different macromolecules, being essentially an analog of stretched-chain crystallites (SCC) interconnected by passage chains comprising the supporting skeleton of the polymer. The formation of the cluster structure at T_{glass} abruptly changes the properties of the amorphous polymer, thus endowing it with the rigidity typical for a solid polymer [10]. Therefore, one can assume that in this case T_{glass} is associated with the critical probability [11] of formation of an infinite (within the limits of the sample) cluster. The objective of the work was to check this hypothesis using amine- and anhydride-solidified epoxypolymers as an example.

Results and Discussion. We investigated epoxypolymers (EP) based on bisphenol A diglycydyl ester (ED-22). Solidification was carried out by 3,3'-dichloro-4,4'-diaminodiphenyl methane (EP-1 composition) and isomethyltetrahydrophthalic anhydride in the presence of tris (dimethylaminomethyl) phenol as an accelerator (EP-2 composition). The topological structure of the EP was varied by changing the solidifier-to-oligomer molar (equivalent) ratio K_α from 0.5 to 1.5. This made it possible to change the density of nodes of the chemical bonding network ν_{n}.

Experimentally established stepwise temperature-temporal solidification regimes making it possible to achieve the most complete transformation degree were as follows: (393 K for 2 h) + (423 K for 3 hours) + (443 K for 4 h) in the case of EP-1, and (393 K for 2 h) + (423 K for 4 h) + (443 K for 12 h) in the case of EP-2. Deformation-durability characteristics were obtained in uniaxial pressing experiments at a strain rate of 5 mm/min (deformation rate $\sim 5.56 \cdot 10^{-3}$ sec^{-1}) and temperature 293 K. No less than five specimens of each composition were studied.

The glass-transition temperature of the EP was evaluated in the thermomechanical analysis carried out under conditions of uniaxial a pressing under a pressure of 1.2 MPa and a temperature variation rate of 2 K/min. Methods for calculation of the cluster structure of polymers can be found elsewhere [4, 5].

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It is evident that the percolation-theory problem as applied to the cluster structure of polymers can be considered as a bonding problem [1], since the formation of an infinite percolation cluster in polymers can be considered as the formation of a continuous chain skeleton over the entire specimen [12]. Formation of nodes (locally ordered regions) also takes place; however, it does not have a critical character. Thus, when the molecular weight is less than a certain value, no continuous skeleton emerges when the same number of nodes is formed as in a high-molecular-weight polymer, since molecular chains have length smaller than the interchain distance. Nevertheless, since we do not consider low-molecular-weight polymers, the problems of nodes and bondings become equivalent: the formation of locally ordered regions simultaneously means the formation of a continuous bonding skeleton over the entire specimen [11].

As is known [1], the critical behavior of the power P_∞ of an infinite cluster (probability that the node belongs to the cluster) upon approaching the percolation threshold x_p is described by the scaling relationship

$$P_\infty \sim (X - X_p)^\beta . \tag{1}$$

If the glassy polymer is considered as a set of N_{seg} statistical segments with length l_{seg} (this is the length of segments in clusters [4]), then the parameter P_∞ is associated with the number of segments of the type entering into the locally ordered regions or clusters N_{cl} (the quantities N_{seg} and N_{cl} per unit volume are assumed there):

$$P_\infty = N_{cl}/N_{seg} = \varphi_{cl} , \tag{2}$$

where φ_{cl} is the fraction of statistical segments entering into the locally ordered regions, or the relative fractions of clusters.

The estimate of the quantity φ_{cl} can be evaluated using the following simple method. It is assumed in the model [4, 5] that, to a first approximation, N_{cl} equals the density of the cluster network of macromolecular linkages V_{cl} determined from results of mechanical tests [13]. Then the segment length per unity polymer volume L_{cl} in locally ordered regions is determined as follows:

$$L_{cl} = V_{cl}\, l_{seg} , \tag{3}$$

where l_{seg} is assumed to be determined as follows [14]:

$$l_{seg} = l_0 C_\infty , \tag{4}$$

with l_0 being the length of the skeleton bonding of the main chain [14] and C_∞ being the characteristic ratio indicating the statistical rigidity of the chain. For the EP under investigation, C_∞ values can be found elsewhere [15].

The total length L of macromolecules per unity volume of the polymer is [16]

$$L = S^{-1} , \tag{5}$$

where S is the area of the molecular cross section whose value for the EP under investigation can be found in [15].

Now we can determine the quantity φ_{cl} from the obvious relationship [5]

$$\varphi_{cl} = L_{cl}/L = V_{cl} S l_0 C_\infty . \tag{6}$$

Then, we consider the proposed treatment of T_{glass} as the percolation threshold. First of all, it should be noted that the connectivity of the molecular chain skeleton is determined by locally ordered regions, and the skeleton of continuous bondings is formed at the temperature T_{glass} [11] with the corresponding value $\varphi_{cl} = 0$. It seems at first glance that the formation of a continuous bonding skeleton under the condition of $P_\infty = \varphi_{cl} = 0$ has no physical meaning. However, at $T > T_{glass}$ a local order also exists, but this is the dynamical order, i.e., with a substantially smaller lifetime, which does not allow one to associate it with the "frozen" local order characterized

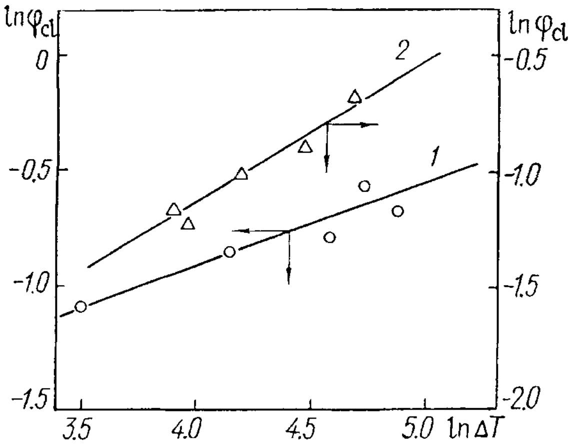

Fig. 1. Dependences of relative fraction of clusters φ_{cl} on temperature difference $(T_{glass} - T) = \Delta T$ in double logarithmic coordinates for epoxypolymers EP-1 (1) and EP-2 (2).

TABLE 1. Characteristics of Percolation Clusters

Parameter	Experimentally evaluated parameters		Theoretically calculated parameters [1]
	EP-1	EP-2	
β	0.36	0.58	0.40
γ	1.28	2.28	1.84
ν	0.67	1.15	0.88
β/ν	0.537	0.504	0.455
d_f	2.46	2.50	2.545

by V_{cl} or φ_{cl}. Upon passing T_{glass}, the local order becomes "frozen," which corresponds to a jump in all parameters characterizing the polymer thermodynamics at T_{glass}. Nevertheless, we consider approaching the percolation threshold only from the side of $T < T_{glass}$, since for $T > T_{glass}$ the condition $\varphi_{cl} = 0$ is satisfied automatically.

Under certain conditions, both the concentration and other variables can be used as X. For example, when describing gelation within the framework of percolation models, the reaction time is used [18]. It is evident that for a system undergoing thermally induced fluctuations, such as the cluster network, the temperature is such a variable. The necessary condition of this substitution is the monotonic behavior of the function used in the vicinity of the percolation threshold, which is satisfied for $\varphi_{cl} = f(T)$ in the neighborhood of T_{glass} for $T < T_{glass}$ [4].

Under the conditions considered, relationship (1) can be written as follows [3]:

$$\varphi_{cl} \sim (T_{glass} - T)^{\beta}, \tag{7}$$

where T and T_{glass} are interchanged due to the inequality $T_{glass} > T$. It should be noted that, inasmuch as all the tests were carried out at $T = 293$ K, Eq. (7) in essence yields a dependence of φ_{cl} on T_{glass} for the EP. Figure 1 presents log-log plots of φ_{cl} vs $(T_{glass} - T)$ for EP-1 and EP-2. The plots are linear, which makes it possible to calculate the exponent β from their tangent. The value of β equals 0.36 for EP-1 and 0.58 for EP-2 (see Table 1), which is quite close to the theoretical "geometrical" value $\beta = 0.40$ [1]. Therefore, the cluster structure of the epoxypolymers under consideration is a percolation cluster with percolation threshold T_{glass}. This means that the glass transition in polymer networks is a phase transition, and φ_{cl} is the order parameter [1]. The same circumstance implies that general regularities of the percolation theory [1] can be applied to the description of the structure of epoxypolymers. Thus, the number of nodes n of a finite cluster depends on the dimensionless deviation of the concentration C for the critical value ($C = (X - X_p)/X_p$ [1]) when $C \to 0$ in the following manner:

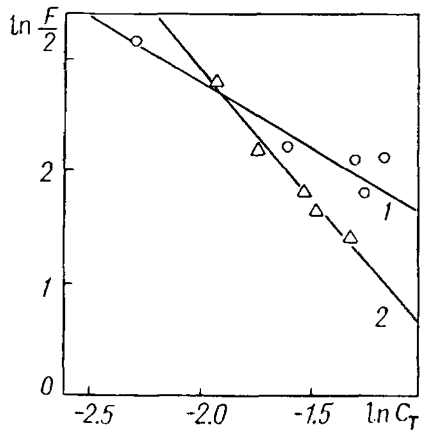

Fig. 2. Dependences of number of nodes (segments) in a finite cluster $F/2$ on dimensionless temperature deviation $C_T = (T_{\mathrm{glass}} - T)/T_{\mathrm{glass}}$ in double logarithmic coordinates for epoxypolymers EP-1 (1) and EP-2 (2).

$$n \sim (C_T)^{-\gamma}. \tag{8}$$

For a cluster structure, the number of segments per cluster, which equals $F/2$ (F being the cluster functionality) as this is an analog of the stretched-chain crystallite [19], should be taken as n, and the parameter $(T_{\mathrm{glass}} - T)/T_{\mathrm{glass}}$ should be taken as C_T. Figure 2 presents corresponding dependences in double logarithmic coordinates, and values of the quantity γ calculated for a three-dimensional percolation cluster [1] from the tangent are presented in Table 1.

Quantitative deviations of values of the exponents β and γ obtained in the present work from their theoretical values [1] should be noted. In addition to the usual statistical error, objective reasons for the deviations exist. First, the theoretical values of the exponents obtained in model calculations do not take into account a number of factors affecting actual systems (e.g., steric hindrances [18]). However, the main reason for the deviation is the fact that in the case of percolation on fractals the value of the exponents depends strongly on the fractal geometry [20], i.e., on their fractal dimensionality [12].

As is well known [1], structures behaving as fractals on small-length scales and as homogeneous objects on large-length scales are known as homogeneous fractals. It has been shown experimentally [21] that the fractal behavior in amorphous polymers is observed on scales from several to ~50 Å. It should be noted that this linear scale exactly corresponds to the limits of the cluster structure. For this structure, the length of the statistical segment l_{seg} is the lower linear scale, and the intercluster distance R_{cl} corresponds to the upper linear scale. For the epoxypolymers under investigation, the quantity l_{seg} varies within the limits of 4.23–6.59 Å, and R_{cl} varies within the limits of 16.7–35.3 Å. [9], which corresponds well to the linear limits of the fractal behavior presented in [21]. Percolation clusters are homogeneous fractals when $X \neq X_{\mathrm{p}}$ (i.e., the epoxypolymer structure has a fractal behavior when $T_{\mathrm{glass}} \neq T$ or, with regard to the above considerations, when $T_{\mathrm{glass}} < T$). In other words, the combination of the data under consideration assumes that the well-known fractal nature of the polymer structure (including polymer networks [22]) is determined by the presence of a cluster structure or, more precisely, by the frozen local order. However, there is some disagreement on the value of the fractal dimension d_{f} of the polymer structure under the general constraint $2 < d_{\mathrm{f}} < 3$ [23]. Thus, in [21], based on theoretical propositions by Alexander and Orbach [24], a conclusion has been drawn that the quantity d_{f} equals 2 for an ideal linear disordered polymer, and lies within the limits of 2.0–2.2 for real polymers. Let us derive several simple estimates of d_{f} for the epoxypolymers under investigation. The following relationship holds for a percolation cluster [1]:

$$d_{\mathrm{f}} = d - (\beta/\nu), \tag{9}$$

where d is the dimensionality of the Euclidean space in which the fractal is embedded, ν is one of the critical exponents of the percolation cluster defined from the relationship [1]

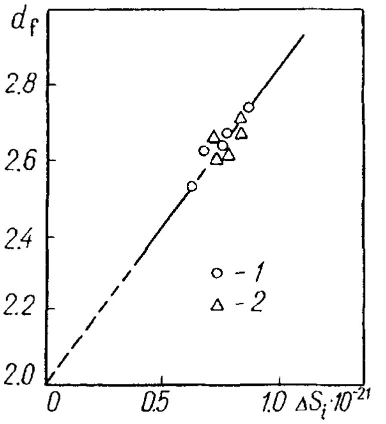

Fig. 3. Dependence of fractal dimensionality d_f of structure on entropy change ΔS_i for epoxypolymers EP-1 (1) and EP-2 (2).

$$d\nu = 2\beta + \gamma . \tag{10}$$

The estimate from Eq. (10) with the use of the earlier derived values of β and γ (for $d = 3$) yields $\nu = 0.67$ for EP-1 and $\nu = 1.15$ for EP-2, which also agrees well with the theoretical value $\nu = 0.88$ [1] (see Table 1). The parameters calculated by Eq. (4) are listed in Table 1 and equal $d_f = 2.46$ and 2.50 for EP-1 and EP-2, respectively (for the percolation cluster, $d_f \sim 2.545$ [1]).

Balankin [25] proposed the following formula for estimation of d_f:

$$d_f = (d - 1)(1 + \mu) , \tag{11}$$

where the Poisson coefficient μ can be estimated from mechanical tests using the following relationship [5]:

$$\sigma_{\text{creep}}/E = (1 - 2\mu)/[6(1 + \mu)] . \tag{12}$$

Quantities d_f evaluated from Eq. (11) for epoxypolymers EP-1 and EP-2 are within the limits of 2.56 to 2.73, which agrees rather well with estimates obtained in the present work but substantially exceed the earlier estimates [21, 24].

In [21], the following relationship for percolation clusters has been presented:

$$d_{sl} = d_f/\tilde{d} > 1 . \tag{13}$$

By using values of d_{sl} and $\tilde{d}$ for the epoxydian polymer, from [21], we calculated the value of d_f for the polymer, which appeared to be equal to 2.25. The quantity is again close to the above estimates, and it should be noted that the application of Eq. (13) to epoxypolymers became possible owing to the identification of their structure as a percolation system.

As is known [26], the dimensionality spectrum (e.g., d_f, d_s, and $\tilde{d}$) is required to provide a description of fractals. Dimensionalities proposed for characterization of fractal objects can, to a first approximation, be divided into two groups, with dimensionalities derived purely from geometrical considerations related to one of the groups, and characteristics related to the information theory related to another group. The latter reflects the degree of inhomogeneity of the fractal under consideration [26]. The Lyapunov exponent λ, which increases with the degree of fractal inhomogeneity and is connected with the information dimensionality of a multifractal D_1 [27], can be related to this group. The quantity d_f is connected with λ by the following relationship [28]:

$$d_f = S_i/\lambda . \tag{14}$$

where S_i is the entropy of the system. The change in the entropy ΔS_i can be estimated by the following simple formula [29]:

$$\Delta S_i \approx 3f_{\text{free}} \ln f_{\text{free}} k\,. \tag{15}$$

The quantity f_{free} is calculated in turn as follows [5]:

$$f_{\text{free}} \approx 0.017\,(1+\mu)/(1-2\mu)\,. \tag{16}$$

Figure 3 presents the quantity d_f calculated by Eq. (11) as a function of ΔS_i as determined from Eq. (15) for the epoxypolymers under consideration. The plot has a number of interesting features. First, extrapolation of the linear plot of $d_f(\Delta S_i)$ to $\Delta S_i = 0$ yields the value of δ_f. It follows from Eq. (15) that the condition $\Delta S_i = 0$ corresponds to $f_{\text{free}} = 0$. This condition corresponds to the close-packed epoxypolymer structure, i.e., in the case of an amorphous polymer, $d_f = 2$ is reached in the case of close packing, but not for an ideal disordered polymer, as has been assumed in [24]. Second, the value of $d_f = 3$ is reached at the value of ΔS_i corresponding to $f_{\text{free}} \approx 0.157$. To the authors' knowledge, this is the maximum theoretically predictable value of the relative free volume at T_{glass} [30]. In other words, the value of $d_f = 3$ corresponds to the devitrified polymer state, i.e., the breakdown of the local frozen order [10]. This circumstance again points to the relationship of the local order and fractal nature of amorphous polymers. Third, the linear behavior of $d_f(\Delta S)$ means that, according to Eq. (14), the condition $\lambda = \text{const}$ is satisfied. This assumes the necessity of applying multifractal analysis methods to the description of the structure of glassy polymers, since each epoxypolymer is characterized by a different set of dimensionalities: the constant D and variable d_f. In addition, it follows from Eq. (14) that the fractal dimensionality of the epoxypolymer structure is uniquely determined by the disorder degree (ΔS_i).

Thus, the results obtained in the present work have shown that at the glass-transition temperature, a structure that is a percolation cluster and well described within the framework of the model [4, 5] is formed in epoxypolymers. This circumstance assumes that the glass transition in epoxypolymers is a phase transition of the second kind, and the quantity φ_{cl} is the order parameter. In addition, this serves as an additional substantiation of the fractal character of polymer networks (at $T \neq T_{\text{glass}}$) within the linear-dimension region ~3–50 Å. The fractal dimensionality of the epoxypolymer structure is substantially higher than has been assumed earlier and is determined by its disorder degree. The loss of the fractal character by the epoxypolymer structure (at $d_f = d$) is achieved at the glass-transition temperature.

NOTATION

T_{glass}, glass-transition temperature; K_α, oligomer/solidifier ratio; ν_n, density of chemical bonding network; P_∞, power of infinite cluster; X_p, percolation threshold; β, exponent of the scaling relationship; φ_{cl}, relative fraction of clusters; n, number of nodes of a finite cluster; $C = (X - X_p)/X_p$, concentration; F, cluster functionality; γ, exponent; σ_{creep}, yield limit; E, elasticity modulas; d_{sl}, superlocalization index; f_{free}, relative free volume; k, the Boltzmann constant; d, spectral dimensionality. Indices: glass, glass transition; n, network; p, percolation; seg, segment; f, fractal; s, spectral, sl, super localization.

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