SOME PECULIARITIES OF THE BEHAVIOUR OF HIGHLY CROSSLINKED EPOXY-AMINE NETWORKS IN THE GLASSY STATE

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Abstract – Some peculiarities of the behaviour of glassy densely crosslinked epoxy-amine networks (yield behaviour, glass transition, Young's modulus, packing density) as a function of curing reaction conditions have been studied. Networks prepared by curing diglycidyl ethers of resorcinol or bisphenol-A with aromatic amines have been considered. Experimental data, which are impossible to explain within the framework of the conventional free-volume concept, have been found. The interpretation of the observed transport properties employs a model in which the glassy state possesses holes of different sizes. Different conditions of polymer curing lead to redistribution of excess free volume over holes of different sizes. The processes of merging and dissociation of holes have been considered. It has been suggested that the properties of a polymeric glass essentially depend not only on a free-volume fraction, but also on the ratio between holes of "large" and "small" sizes as well as on the type of size distribution function of holes.

INTRODUCTION

Epoxy networks formation from rather simple diglycidyl ethers of some bisphenols and aromatic diamines has been investigated in recent years at the Institute of Chemical Physics, the USSR Academy of Sciences (1,2,3,4).
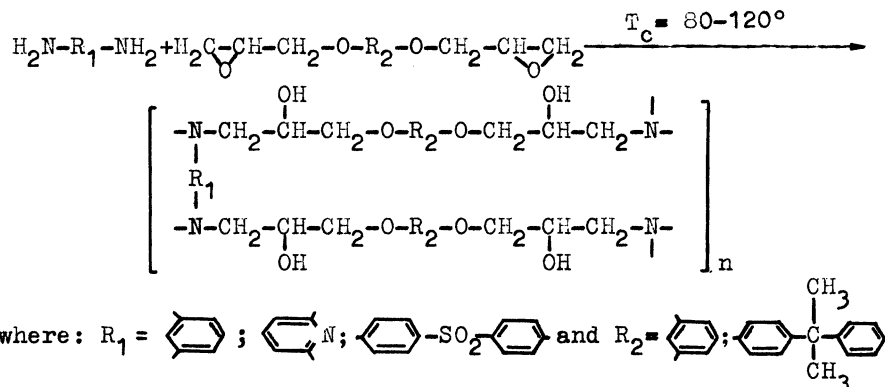
These systems, based on diglycidyl ethers of resorcinol (DGER) and bisphenol-A (DGEBA), have proved to be rather suitable from several points of view. Thus, from the chemical point of view, at moderate temperatures (T =80 – 120°C) and especially with methaphenyldiamine (m-PhDA) as a curing agent, the curing reaction proceeds practically without side-reactions, such as polymerization of epoxy groups, reactions of secondary hydroxyl groups with epoxy ones and with each other, etc.(2).

The molecular structure of the formed networks imply that the ratio of the rate constants of the first (k_1) and the second (k_2) addition reactions
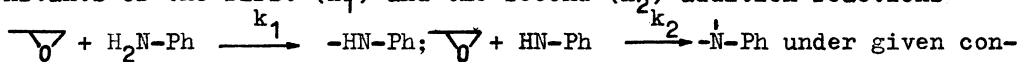
ditions is close to one: k_1/k_2 = 0.8 – 1.0.
This means that network formation reaction in this case does not proceed by formation of long linear macromolecules which then have to crosslink each other.

Statistical-topological models of the network structures describe nicely both the kinetics of their formation and equilibrium elasticity of rubbery state (4). These facts are rather important since they clearly indicate the absence of so called spatial heterogeneity of the chemical cross-links in the volume of the network. If heterogeneity exists, it may lead to weak bonding of densely crosslinked regions of networks (clusters), which, in turn, according to (5), may result in low mechanical properties of network polymers.

It has been shown (1-4) that the kinetics of epoxy-amine networks formation is nicely described by normal statistics taking into account diffusion limitations of the curing reaction. The subject of our interest in the present paper is the structure and properties of such epoxy-amine networks in the glassy state at 40 - 110°C below T_g.

We dwell at length on the above-mentioned results since they provide a good characteristic of the networks considered both from chemical and topological viewpoints.

At room temperature, network epoxy-amine polymers resulted from the curing reaction are rather dense homogeneous glasses with high mechanical characteristics (strength, rigidity). Ultimate glass transition temperatures T_g^{max} for stoichiometric networks range from 135 to 160°C.

In Table 1 are shown molecular packing characteristics of several network polymers estimated at 22°C. Mean packing density K (literature data) for a large number (about 100) of linear glassy (6,7) and some crystalline (7,8) polymers is also presented for comparison:

TABLE 1. Densities d and molecular packing coefficients K

for some polymers estimated at 22°C

Networks	$\frac{d}{(g/cm^3)}$	K	Linear polymers	$\frac{d}{(g/cm^3)}$	K
DGER-mPhDA (1:1)	1.293	0.717*	DGER-aniline	1.246	0.712
DGER-mPhDA (1:1.4)	1.299	0.727	Other linear		
DGER-mPhDA (1.4:1)	1.298	0.720	glassy polymers (6,7)	–	0.681**
DGER-DAP (1:1)	1.295	0.705	Crystalline		
DGER-DAPhS (1:1)	1.340	0.711	polymers (7,8):		
DGEBA-mPhDA (1:1)	1.280	0.708	Polyethylene	–	0.744
			Polypropylene	–	0.695
			Polytetrafluoroethylene	–	0.723

*K for stoichiometric networks are calculated for the curing reaction conversion α = 0.92. ** K=0.681 – mean value for linear polymers.

The values of K in the Table 1 are comparable since they were estimated from the same van der Waals' radii for similar atoms in different polymers. From the Table 1 it is evident that epoxy networks are markedly better packed than glassy linear polymers, i.e. the high concentration of chemical cross-links does not create noticeable kinetic obstacles for good packing of an internodular chain.

It is also of interest that fairly essential deviations of the network composition from the stoichiometric one do not affect the packing density. Undoubtedly, the dense packing of the networks is due to hydrogen bonding. This is clear from high packing density of a model linear polymer prepared by condensation of DGER with m-PhDA (see Table 1). However, chemical cross-links also lead to better packing of the networks.

As it is well-known (2,3), in the formation of dense networks curing reaction in stoichiometric mixtures cannot proceed until complete conversion of functional groups. It is connected with random character of the curing process. At rather large α unreacted monofunctional groups of the forming network cannot interact being spatially separated.

In Fig. 1 are shown ultimate curing conversions α_u, which may be reached in DGER-mPhDA (1:1) system at different temperatures of isothermal curing.
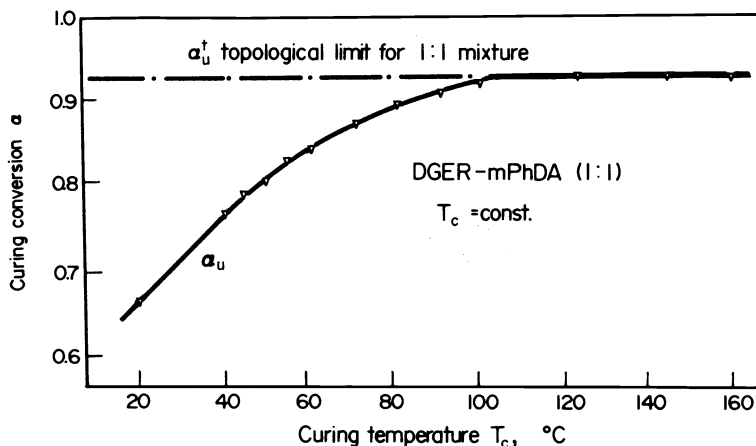
Fig. 1. Ultimate conversions α_u reached at different curing temperatures T_c (isothermal curing) by the system DGER-mPhDA (1:1). Curing time $\tau \to \infty$.

At $T_c > 110°C$ the reaction reaches its topological limit $\alpha_u^t = 0.92 \pm 0.1$ (according to our data). Increasing the T_c up to 170°C does not increase α_u^t. During isothermal curing at $T_c < 110°C$ the reaction reaches certain limits α_u determined by diffusion which depend on T_c. The reaction essentially stops when the reactant system wholly solidifies at the given T_c. In the vitrified polymer unreacted functional groups do not possess enough mobility to interact with reactive neighbours.

The polymers under consideration have rather high values of static mechanical properties. The results, testifying to this, are given in Fig.2.
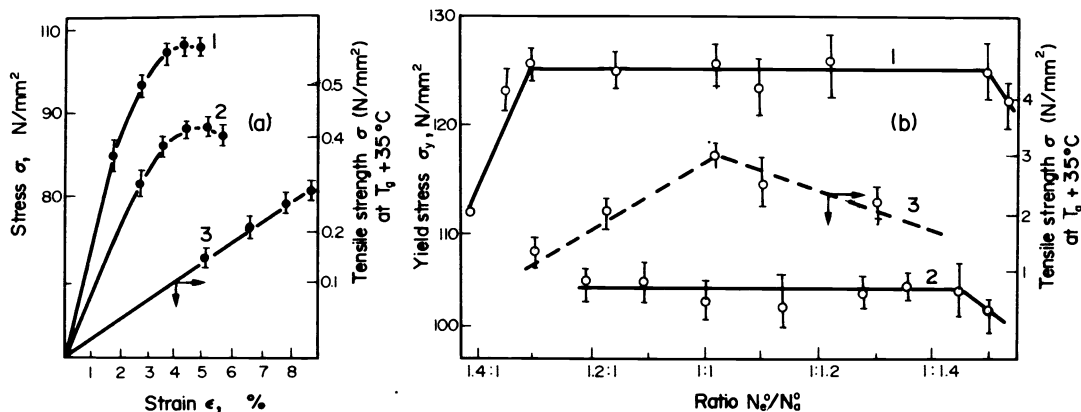

Fig. 2.

a. Typical stress-strain diagrams for ultimately cured glassy (1,2) and rubber-like (3) networks on the basis:
1 - DGER+mPhDA (1:1), 2 - DGEDPhP+mPhDA (1:1), 3 - DGER + +mPhDA (1:1). $\dot\varepsilon = 1$mm/min. N_e^0 and N_a^0 - the concentrations of epoxy and amine groups in the initial mixture.

b. The dependence of the yield point σ_y(1 and 2) and the strength σ (3) of the cured networks on the composition of initial mixture or the concentration of unreacted epoxy or amine group. 1: σ_y for DGER + mPhDA (1:1); 2: σ_y for DGEDPhP + + mPhDA (1:1); 3: σ for DGER + mPhDA ($T_{exp} = T_g + 35°C$), $\dot\varepsilon = $ = 5 mm/min.

In Fig. 2a are presented typical stress-strain diagrams (stretching) of glassy(curves 1,2) and rubber-like network polymers (curve 3) based on DGER - mPhDA (1:1). These diagrams exhibit usually yield behaviour. We have managed to prove that stress-strain behaviour of samples showing a quasi--brittle character of fracture, often observed for densely crosslinked glassy networks, is due to their macroscopic defects. As it is seen from curves 1,2 (Fig. 2a), the high concentration of chemical cross-links in a glassy

polymer does not hinder it from yielding.
These defects may be removed from the sample by means of suitable thermal
treatment (discussed later). In this case the apparent quasi-brittle frac-
ture of network glasses disappears and the yield point may be clearly seen
in the stress-strain diagrams. That is why, it was natural to choose the
yield point as a value characterizing the static mechanical behaviour of
the investigated glasses.
Values of $\sigma_y(22°C)$ for epoxy-amine networks of different compositions are
given in Fig. 2b (curves 1,2). In all cases the samples were cured up to α_u.
From Fig. 2b it is seen that σ_y of the network glasses weakly depends on the
amount of unreacted functional groups of both amine and epoxy types over
a rather wide range of their concentrations, or, in other words, σ_y of the
network glasses is practically independent of the curing conversion $\alpha_u \geq 0.83$.
It is essential that in the rubbery state* (curve 3, Fig. 2b) the ultimate
strength of the networks is proportional to the concentration of chemical
cross-links, being maximum for stoichiometric ratio.
This fact shows that in the glassy state network mechanical behaviour is
determined not by chemical factors (for example, curing conversion or net-
work composition), but by the physical structure of the glass, and most of
all by its packing. If we remember that the perfection of the molecular pac-
king of the investigated glasses is not increased in non-stoichiometric
polymers, then, the independence of the yield point $\sigma_y(22°C)$ of the concen-
tration of unreacted functional groups becomes clear.
It is obvious, that the studied glasses are well organized, the absolute
level of σ_y being fairly high, though it can be raised by another 15% more
by post-cure thermal treatment. High values of the Young's modulus, to be
discussed later, are also typical for glassy epoxy-amine networks.
Investigating the relationship between the glassy state structure and macro-
scopic properties of the studied polymers, we have found some phenomena,
which, in our opinion, cannot be even qualitatively rationalized within the
conventional free-volume concept for amorphous polymers.
Here, I would like to explain what is implied by "conventional free-volume
concept". If we speak about the kinetic properties of glassy substances,
such as, the position and the character of glass transition, yield behaviour,
diffusion coefficient etc., or, what is just the same, if we consider trans-
port processes (eg. transfer of mass, heat or electricity), we see that the
increase of free-volume fraction in the glass always leads to increasing
molecular mobility, making the transport processes easier.
This means that any increase of both T_g and σ_y is connected with a decrease
of mobility or free volume (packing improvement) and vice versa. Such a
viewpoint is, of course an oversimplification. However, it qualitatively
presents the real relationship between some macroscopic properties and the
packing structure of the glasses.
As I have already mentioned, our results do not fall within the framework
of these concepts.
So, let us proceed to some of the "unusual" results.

THE DESCRIPTION OF SOME "UNUSUAL" EXPERIMENTAL RESULTS

Curing at lowered temperatures. As we have already stated, during isother-
mal curing at $T_c < 100 - 110°C$ the reaction stops at $\alpha_u < \alpha_u^*$ due to poly-
mer vitrification. It is natural to suggest that at heating such a polymer
it will soften at $T_g \approx T_c$ if measurements of T_g are taken at the frequencies
corresponding to the effective frequency of the chemical reaction ($\nu_{eff} \sim 10^{-4} s^{-1}$)
This is confirmed experimentally.
In Fig. 3 are shown the results of heat capacity measurements for the net-
works obtained by isothermal curing at $T_c = 80, 100, 130°C$ respectively. T_g
for each of them was rather close to the corresponding T_c. The somewhat
higher values of T_g in comparison with T_c are due to the effective fre-
quency of the scanning calorimetry ($\nu_{eff} \sim 10^{-3} s^{-1}$), which is a little bit
higher than the effective frequency of the curing reaction. Polymers resul-
ting from isothermal curing at each T_c are not only of different composi-
tion (different α_u), but also have a different structure of the glassy
state. Both different T_g and different values of endothermic peaks of C_p

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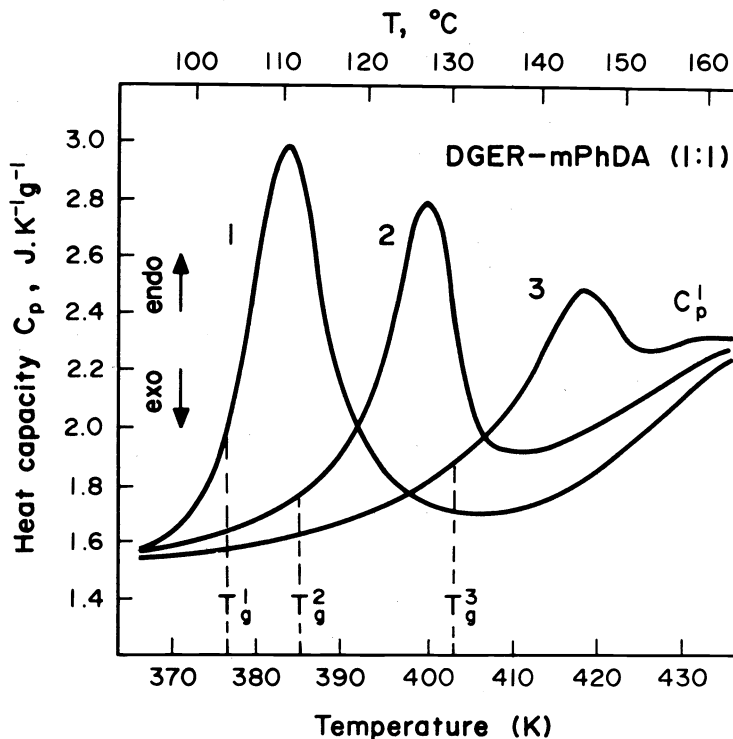* T_g for the networks of each composition was measured separately.

Fig. 3. Heat capacity for networks DGER-mPhDa (1:1) prepared under
different T_c . T_c :1 - 80; 2 - 100; 3 - 130°C. T_g (1,2,3) -
- the glass transition temperature of each sample. C_p^l - the
heat capacity of networks at T_c > 110°C.

indicate this. It is well-known that the larger the area under an endother-
mic peak of C_p , the larger is the energy absorbed by the glass for the
formation of new holes   during the glass-rubber transition.
From Fig. 3 it is clear that the lower T_c , the higher is the endo-peak of
C_p , i.e. the structure of glass obtained at low T_c is more perfect than
of the glass obtained at high temperatures (enthalpy of such glass is lower).
To a certain extent this fact is in itself contradictory. On the one hand,
at low T_c we obtain a glass with more perfect structure, but, on the other
hand, this glass softens at lower temperature
We have managed to establish that the glass structure is being formed when
the reacting system vitrifies in the course of curing (so called liquid -
glass transition). The lower the rate of vitrification, the better is the
structure of the glass (low enthalpy) forming in the process.
Let us examine another important kinetic property of glasses, namely,
the yield point.
In Fig. 4 are shown the values of σ_y (22°C , stretching, $\dot{\varepsilon}$ = 1mm/min) for
polymers with different T_g (that is, for polymers, obtained at different T_c).
In spite of the fact that the networks cured at a lower T_c have smaller T_g ,
their mechanical properties (σ_y) are essentially higher.
In Fig. 5 we assemble some other results. In this Figure is shown the de-
pendence of the Young's modulus on the testing temperature for a number of
network polymers. The curves correspond to polymers obtained at T_c equal
to: 43°C (1); 90°C(2) and 110°C (3). From Fig. 5 it is clear that the poly-
mers with higher modulus in the glassy state have the lowest T_g . These re-
sults also require special explanation.

Young's modulus. The other "unusual" experimental fact is connected with the
polymer glass rigidity, which may be characterized either by the effective
Young's modulus E or by shear modulus G. It is well-known that the Young's
modulus of glasses essentially depends on the excess of free volume in
them.Recent theoretical calculations (9,10) (computer simulation) have re-
vealed that the Young's moduli of densely packed amorphous and crystalline
solids, composed of similar particles, satisfy as E_{am}(amorphous) = 0.57 E_{cr}
(crystalline). This ratio nicely agrees with experimental results available
in literature. The estimation of the magnitude of the Young's modulus for
molecular crystals from van der Waals' interactions of molecules gives
$E_{cr} \approx$ 5.5-6.0 GN/m^2(10,11). This means that real moduli for polymer glasses
have to be about 3.0 GN/m^2. In Table 2 are assembled the values of Young's
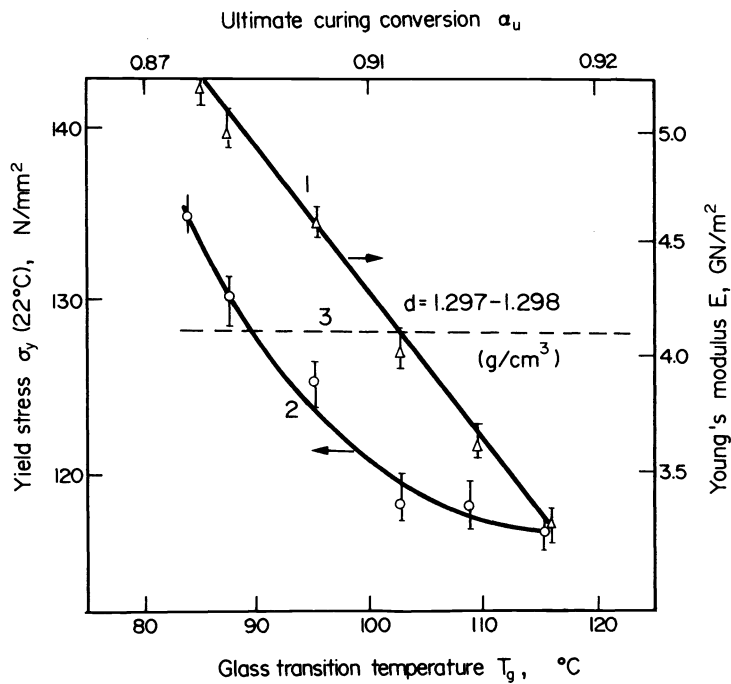moduli for some glassy polymers at room temperature.

Fig. 4. Changes of yield point σ_y (22°C) (1),Young's moduli E (22°C)
(2) and density d (22°C) (3) for glassy networks DGER-mPhDA (1:1),
cured under different T_c and having different T_g (T_g were deter-
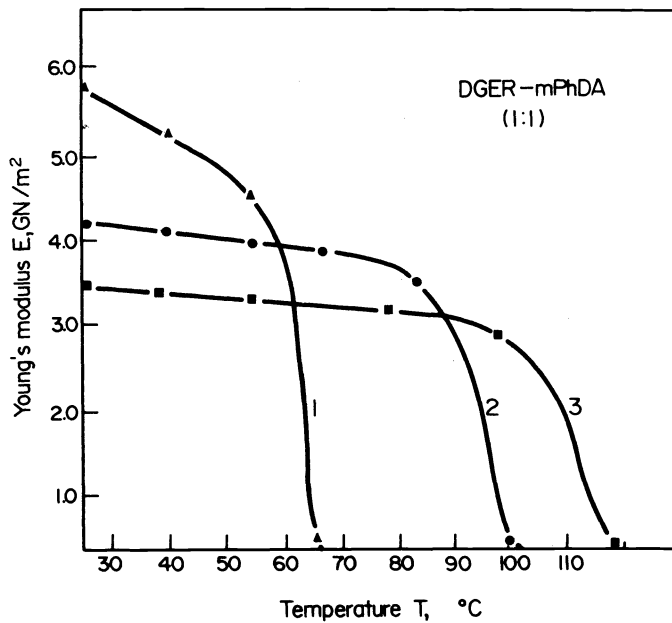mined from Fig.3).

Fig. 5. Changes of Young's moduli of networks DGER-mPhDA (1:1) with
temperature. The samples (1,2,3) were cured at different tem-
peratures of isothermal curing T_c up to corresponding α_u.
T_c for the samples: 1 – 43°C; 2 ≃ 90°C; 3 – 110°C.

TABLE 2. Effective Young's moduli for some polymers (stretching)

Polymer	E, GN/m^2	Polymer	E, GN/m^2
Polystyrene (atactic)	2.8 - 3.32	Delrin	2.85
Polymethyl-metacrylate	2.95 - 3.21	"Capton" (aromatic polyimide)	3.1
Polycarbonate	1.89 - 2.09		
Polysulfone (aromatic)	2.6	Polyethylen-terephthalate	3.9
Polycrystal of polyethylene (9)	5.05	Network DGER-m-PhDa (1:1)	3.3
Polyphenelene oxide	2.6 - 2.8	Network DGER--mPhDA (1:1) obtained by low-temperature curing	5.5
		Polyethylene chain flexure	2.6 x 10^2

Although the modulus depends on the temperature and frequency of measurement, in all the cases, given in Table 2, glass transition temperatures are rather high and the temperature dependence of E (stretching) in this cases may be neglected. As far as the frequency of measurements is concerned, all the values of E correspond to deformational rates, at which the frequency (rate) dependence becomes insignificant.
Two facts are of interest in Table 2.

1.All the values of E are really close to 3,0 GN/m^2,   which nicely agrees with theoretical estimates.

2.The moduli of all the polymers are very close to each other.
In Table 1 we quote also a modulus for a network based on DGER-mPhDA (1:1), E (22°C) =3.3-35 GN/m^2. First of all, this value shows that the rigidity of glassy networks is determined not by chemical bonds, but by van der Waals' interactions between chains, i.e. it is dependent on the packing density. Secondly, the network has an elevated modulus, as compared to linear polymer glasses, which is due to its higher dense packing. The independence of the moduli of linear polymers on their chemical structure can be easily explained within the framework of a packing concept. Thus, it is well-known that packing density for a large number of linear polymers is K (22°C) = = 0.681±0.01. This fact is macroscopically reflected in the similar values of the glass moduli.
In Fig. 4 (curve 2) are shown the values of E (22°C) for some glassy net - works (DGER-mPhDA, 1:1) prepared at different T_c From this Figure it is clear that E (22°C) linearly grows with the decrease of T_c, and at T_c = 43°C it reaches E (22°C) = 5.5 GN/m^2. This value is close to the theoretical one of molecular crystals. How can this be understood? Polymer remains amorphous with approximately the same quantity of excess free volume in it. It is absolutely obvious that this result cannot be explained within the framework of conventional concepts, it requires a new approach.

Relaxation of endothermic peak of heat capacity. It is well-known that the perfection of the structure of glasses, including polymer glasses, depends on the thermal prehistory, and in particular on the rate of cooling. The structure of a polymer glass may be improved, that is, its specific volume or enthalpy may be decreased by slow cooling of the melt or by prolonged isothermal annealing near T_g .
Figure 6. shows such results for linear (Fig. 6a) and network (Fig. 6b) polymer glass. During isothermal annealing of linear polymers the improvement of glass packing takes place, which is reflected in the growth of the endothermic peak of C_p with annealing time. The growth of the endothermic peak of C_p is also observed for networks. It is obvious that, from the point of view of the free volume concept, only densification process may proceed spontaneously.
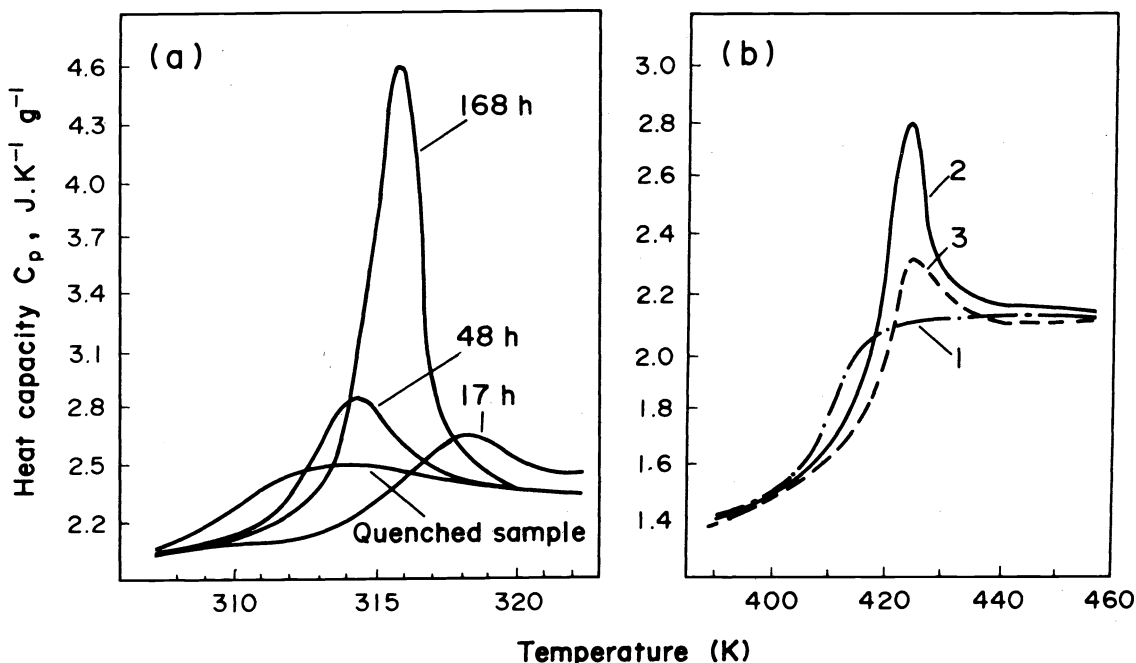
Fig. 6.Change of the heat capacity C_p (a) of polyvinylacetate(Ref.
17) and (b) network DGER-mPhDA (1:1),annealed at different time.
Annealing temperature T_a for PVA is equal to 21°C; for DGER-mPhDA:
(1) the quenched sample; (2) T_a = 120°C; annealing time 90 h.; (3)
the sample cooled from 110°C to room temperature for 9 hours.

Figure 7 demonstrates the data on C_p relaxation for the network on the ba-
sis of DGER-mPhDA (1:1) prepared at T_c = 90°C. After curing the sample has
been exposed to physical ageing at room temperature in an atmosphere of dry
argon (curve 2) and air (curve 3).
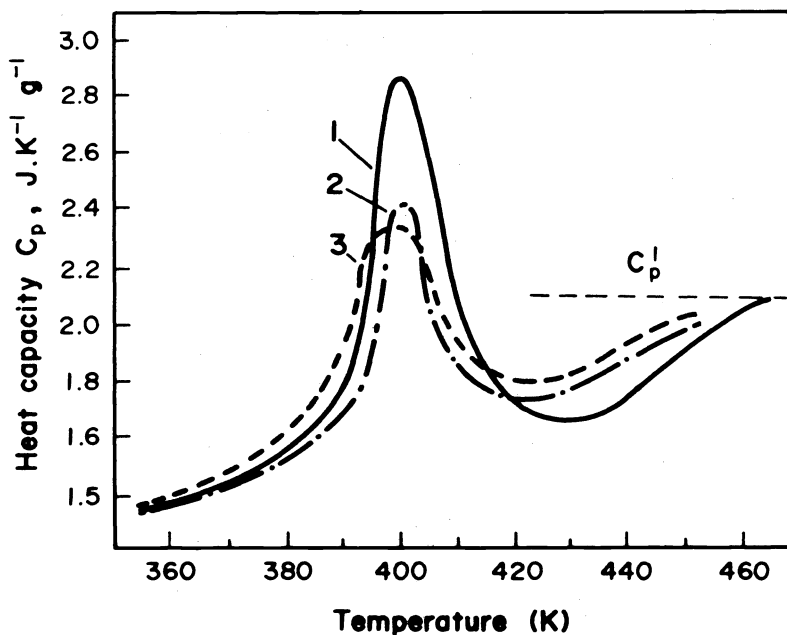

Fig. 7. Relaxation of endo-peak of heat capacity for the network
    DGER-mPhDA (1:1) cured at T_c=90°C. Time of storage at tem-
    perature 23°C:(1) 0 h.; (2) 350h.(argon); (3) 350 h.(air);
    C_p^l - the level of C_p of the rubbery network cured at T_c = 120°C
    up to α_u^t.

From Fig. 7 it is seen that the endo-peak of C_p decreases with ageing time. This does not agree with the densification processes which have to proceed under these conditions.

Effect of post-cure thermal treatment on the yield behaviour of glassy networks; In Fig.8 are shown stress-strain ($\sigma - \epsilon$) curves (σ is the actual stress) for the networks based on DGER-DAP (1:1) cured at 100°C and then heated up to 170°C. Starting at 170°C the samples were either slowly (≈ 10°C/h) cooled (annealing) or quickly cooled to low temperature (0 - 10°C) (quenching).
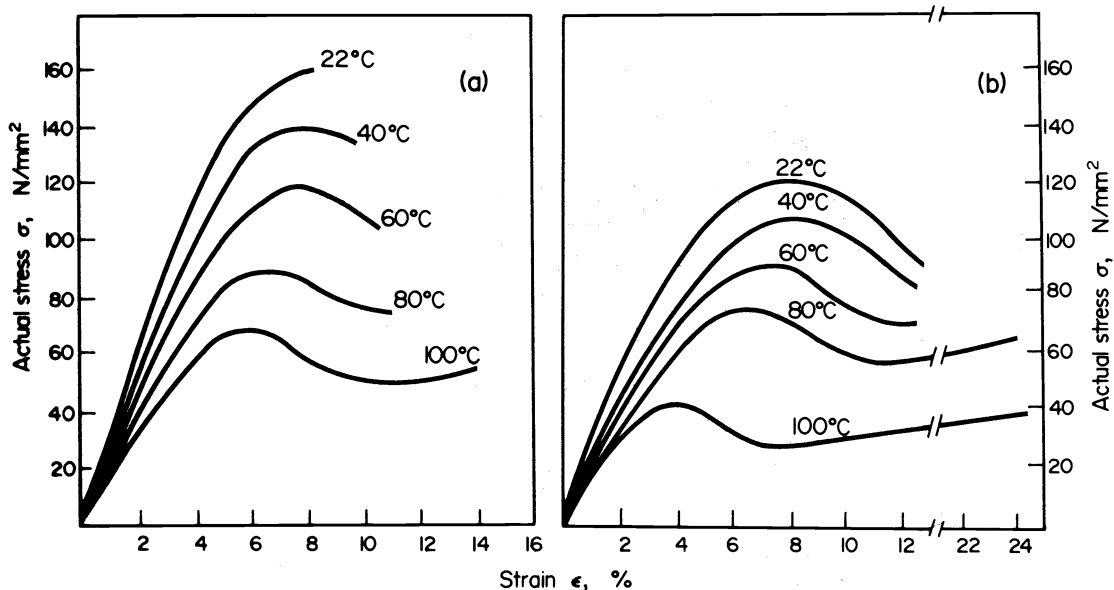

Fig. 8. Stress-strain curves (stretching) for the network DGER-DAP (1:1) at different temperatures. (a) the annealed samples. (b) the quenched samples;strain rate = 10^{-2}min^{-1} .

Figure 8 shows that the sets of samples behave in a different way (different $\sigma_y, \epsilon_{break}$), the difference remaining up to rather high temperatures. Different curves, undoubtedly, reflect the different structures of the quenched and annealed samples. The annealed samples are characterized by a large rigidity, elevated σ_y and relatively small ϵ_{break}.The quenched samples are essentially more plastic with far larger break elongations.

It is essential that this phenomenon is reversible. The 5-7 -fold repetition of annealing-quenching operations leads to reversible $\sigma - \epsilon$ diagrams. It turned out that the observed yield of the studied network polymers was not connected with the breaking of chemical bonds, i.e. this was not a chemically controlled yield. Thus, repeated loadings of relaxed samples, preliminarily loaded up to elongations slightly larger than ϵ_y , show the diagrams of the first loading (with the shift on the value ϵ_0)and a stable level of σ_y values. If annealing causes the growth of a glassy polymer density, this always leads to the above-mentioned changes of the mechanical properties. Annealing-quenching thermal treatment always result in typical changes of stress-strain curves. However, such changes are not always accompanied by the changes of polymer density.

Two facts, in our opinion, are noteworthy here.

1.In a number of cases network polymers change their mechanical properties (stress-strain curves) without marked changes in macroscopic density; Even when the density of glassy polymers was practically constant, we found rather large changes in σ_y level.

2.Lowering of isothermal curing temperature (for DGER-mPhDa 1:1) leads to a markedly larger increase of σ_y (see Fig. 5.)than the process of annealing. However, the density d (22°C) of networks DGER-mPhDA, cured in the range of T_C from 100 to 55°C, is practically constant for all T_C . Both these facts suggest to us that the changes of σ_y during the thermal treatment of these polymer glasses are not necessarily connected with the change of the total free volume in the polymer.

Thus, concluding this part of the paper, we would like to emphasize once

more that all the above-mentioned experimental results, obtained while investigating densely crosslinked epoxy-amine network glasses, are difficult to explain solely from the point of view of differences in free volume fractions.

INTERPRETATION OF THE GIVEN EXPERIMENTAL RESULTS WITHIN THE FRAMEWORK OF A HOLE MODEL OF POLYMER GLASSES

Since liquids, including polymer ones, keep in their structure a short-range order, typical for a corresponding crystalline body, it is logical to come to the following conclusion about the hole structure of glassy bodies. As a matter of fact, there is at present no other structural alternative for the the description of such subjects.

Frenkel introduced the hole concept into solid state physics (12). This concept was further developed for polymers in the works of Eyring (13) and other authors (14).

The holes of an amorphous body concentrate the total excess free volume of a polymer glass, i.e., the volume which is excess in relation to a polymer crystal composed of macromolecules of the same chemical structure.*

Two classes of holes, configurational and fluctuational, should be distinguished in an amorphous polymer. The former are connected with the existence of configurational (stereochemical) defects in a regular structure of macromolecules. These defects arise at the moment of a monomer (oligomer) "erroneous" addition to the growing species. The experience indicates that the following types of addition: "head-to head", "tail-to-tail" heterotactic addition etc., lead to defects in a configurational sense.

The other class of holes — fluctuational holes, have a kinetic nature, being due to the "freezing-in" in the glass of a certain amount of relatively high-energy conformational sequences of macromolecular fragments.

In principle, the large fraction of fluctuational holes may be removed from an amorphous polymer by infinitely slow cooling. At the same time configurational holes cannot be removed from a polymer without breaking chemical bonds in macromolecules.

Proceeding from this classification of holes, the total volume of a polymer body, unoccupied by atoms may be presented as

$$V_{am} = V_{cr} + N_{fl}\overline{V}_{fl} + N_{sf}\overline{V}_{sf}$$

where V_{cr} the unoccupied volume of a corresponding crystal; N_{fl}, N_{cf} the the number of fluctuational and configurational holes in the body; $\overline{V}_{fl}$, $\overline{V}_{cf}$ the average volumes of holes of both classes.

In relation to transport processes in the glassy state the holes have different properties. Thus, configurational holes at any dynamic transitions, occuring in a polymer, cannot separate from their parent chain and migrate in the space of the sample. Migrations of such holes occur only with the parent chain to which they are attached. At the same time fluctuational holes may migrate in the sample due to consequent conformational transformations in macromolecules and disappear at the free surface of the sample. In this sense and from the point of view of transport processes in polymer, fluctuational holes may be called dynamic, and configurational ones — static.

As it is known, the rate of transport processes depends on the moving rate of holes (frequency of jumps) in the sample. That is why, in the remainder we shall be mainly interested in fluctuational holes, although configurational holes can make certain contributions to kinetic properties of a glassy body. This phenomenon will be considered later.

Brownian motion of fluctuational "holes" in the sample proceeds by the mechanism of "exchanging places" (by analogy with the movement of vacancies in an atomic lattice with defects). Usually, the holes move in the sample due to conformational transitions of the corresponding chain fragments. The vector of this transition, on the average, is directed perpendicularly towards the chain axis. The movement of holes along the chain is possible only in rare cases. Thus, the movement of holes is a process characteristic of an ensemble of chains, but not of one chain.

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* For epoxy-amine networks we can imagine only hypothetic crystal since constituent chains are unable to crystallize because of stereochemical defects statistically distributed through N-atoms.

The number N_h and size V_i of holes of i-th type are determined by

$$N_h = N_0 \exp(-\Delta G/kT) = N_0 \exp S/k \exp[-(W_h + p\bar{V}_i)/kT]$$

where N_0 is the number of segments in the system; ΔG is the free energy; ΔS is the entropy of the mixture of holes with segments, and W_h is the energy of one hole, which consists of elastic energy of the hole environment W_{el} and of the surface energy of the hole W_{sf}

$$W_h = W_{el}(\bar{V}_i) + W_{sf}(\bar{V}_i)$$

Within the framework of the dislocation theory (18) and taking into consideration only elastic terms, it may be written as

$$W_{el}(\bar{V}_i) = \frac{\mu b^2}{4\pi(1-\nu)} \cdot \ln(r_1/r_0)$$

where μ is the shear modulus, b is the Burgers' vector, ν is the Poisson's ratio, r_0 is the radius of the dislocation nucleus, and r_1 is the distance from the centre of the nucleus (hole).
For W_{sf} it may be presented as

$$W_{sf} = 4\pi r^2 \gamma_0 \left(1 - \frac{\delta^2}{r^2}\right) = 4\pi \gamma_0 (r^2 - \delta^2)$$

where r is the radius of a hole, γ_0 is the coefficient of surface tension and δ is the minimum possible distance between the walls of a "nucleus" hole. It is appropriate to mention here that the calculation of $W_{sf}(\bar{V}_i)$ is a complex problem. Naturally, W_{sf} has to be essentially different from macroscopic surface tension. To estimate this magnitude one should take into consideration the real structure of the macromolecular fragment with appropriate conformation and configuration on the surface of this hole. At present, such calculation is probably possible only with the help of a computer within the frame of molecular dynamics methods.
The values of W_{el} are assumed to be estimated in terms of a purely elastic approach as it is seen from the equation. However, in reality, the viscoelastic behaviour of the material near the hole should be taken into account. Unfortunately, this has not yet been done for polymer bodies.
The literature on the study of molecular mobility in polymers by different methods (15) shows that practically all the polymers have a temperature-discrete spectrum (at $\nu = $ const) of molecular motions, whose nature is similar for all polymers. This fact allows us to suggest that in the range of dynamic molecular transitions the mobility of the corresponding holes unfreezes. At each transition (α, β, γ etc.) we have defreezing of the corresponding holes. It means that the total fluctuational free volume of a polymer is discretely distributed through the holes of different types - $V_\gamma, V_\beta, V_\delta$ and V_α, where indices correspond to the conventional classification of molecular motions in polymers (15). Such holes have the following size hierarchy $\bar{r}_\alpha \gg \bar{r}_\beta > \bar{r}_\gamma > \bar{r}_\delta$.
On heating an amorphous polymer in a certain range of temperatures ΔT_i ($i = \delta, \gamma, \beta, \alpha$) there usually appear mechanical or dielectric losses. And it is in this range, ΔT_i, that unfreezing of i-th type holes motions takes place. Starting at low temperatures δ, γ, β holes and, finally, α-type holes gradually unfreeze.*
As soon as fluctuational holes begin to move in the sample, they interact, merging into multiplets, which, in their turn, split into singlets and smaller multiplets.
Merging of holes is an advantageous process since the specific energy on a unit surface of a hole decreases with increasing hole size. Such a decrease is caused by the decrease of surface tension with the growth of the hole radius. Merging of holes into multiplets proceeds until the decrease of mixing entropy of holes exceeds the energetic term resulting from the increase of the hole size.
According to this, we have suggested that <u>for each temperature of an amor-</u>

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*Strictly speaking, in each region of ΔT_i is being observed a slight increase of free volume of a polymer due to the origination of new holes. However, for δ, γ and β processes the increase of volume is insignificant. The account of newly appearing holes should be undertaken only in the glass transition region.

phous polymer there is a corresponding thermodynamically equilibrium size distribution of holes. Such a suggestion means that in any amorphous polymer glass in non-equilibrium state there exist at least two relaxation processes, i.e. the tendency towards decreasing of excess free volume of a polymer (densification) and the tendency towards the equilibrium hole size for the relaxation temperature.

The rate of the first process is determined by the amount of excess free volume ΔV_f and by ΔT – the difference between the temperature of relaxation and the temperature of unfreezing of the corresponding molecular motions. The rate of the second process depends not only on the difference in temperatures, but also on the time history of the sample, which influences the deviation of the system from the equilibrium structure at the preceding temperature.

Since the movement of holes is a kinetic process, it is logical to suggest that the frequency of the hole jumps is a function of their sizes r_i

$$\tau = \tau_0 \exp \left[-u \, (r_i)/kT \right]$$

where u is the barrier, which the hole has to overcome to change a place. The larger the hole, the longer is the time τ of its settled life. It means that holes merge into multiplets, but merging always "slows down" the velocity of motions (jumping frequencies) in the sample.

Configurational holes cannot move on their own (they move only together with the chain, to which they are "attached"). However, they can capture fluctuational holes merging with them. That is why, configurational holes, in average, limit the mobility of the fluctuational ones, i.e. they are traps for the latter.

Since macromolecules or their fragments cannot migrate in the space unoccupied by other molecules, any "mass redistribution" in a polymer may occur only in the presence of holes, or in other words, all the processes of mass transfer in polymers are due to directed transition of holes.

Let us consider some properties of the studied polymers in the framework of a hole model. As an example we shall consider only the holes of V(d)-type since these are the holes of this type, that make the greatest influence upon the properties under consideration. For other holes the analysis is similar.

Shear viscosity and plasticity. It is well-known that the rate of viscous shear flow is determined by the rate of hole jumps at the constant concentration of holes. In accordance with the above , shear viscosity for the given body will be smaller, the smaller is the average size of holes responsible for shear flow, other things being equal. When the mechanical straining of a glassy polymer reaches the yield point, than a process similar to shear flow occurs in a local zone of the polymer (shear band). It means that "splitting" of holes in the polymer to smaller ones takes place in the shear band. This is the change of the material structure at yielding. The energy for such a process W (τ) appears due to the work of effective shear stress

$$W(\tau) \sim V_{sh} \, \tau_{eff}$$

where V_{sh} is the shear activation volume.

It is such a transformation of a polymer glass structure which takes place at its plastic deformation.

Fig. 9 shows the changes of the shear activation volume V_{sh} during deforma-
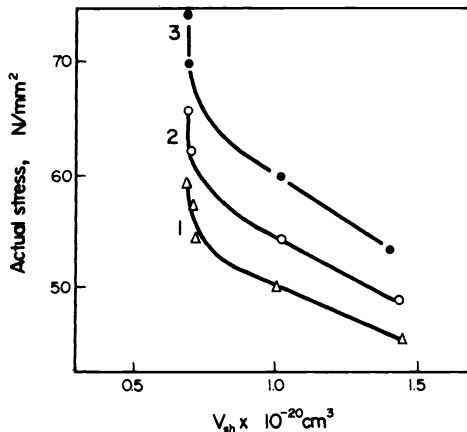

Fig. 9. The change of V_{sh} at stretching DGER-mPhDA (1:1, 3) network. $T_{exp.} = 343°K$. Strain rates $\dot{\varepsilon}$, min^{-1}: 1-10^{-5}; 2 – 10^{-2}; 3 – 10^{0}.

tion of a glassy network based on DGER-mPhD[A] (1:1,3). The shear activation
volume V_{sh} was calculated on the basis of the model of thermally activated
stress-biased viscous flow given by Eyring (16). It is seen that V_{sh} dec-
reases with increasing stress and deformation, and, when the stress in the
sample approaches $\approx \sigma_y$, V_{sh} becomes constant. The result shows that the
average volume of the "molecular flow fragment" near σ_y decreases by a
leap, which favours yielding.

Fracture. For yielding the great role is played by the width of the hole
size distribution function. If F(r) is wide, small holes begin to move at
rather small σ (low proportionality stress). However, this process quick-
ly stops due to the capture of small holes by large ones. Too large stres-
ses are needed for the movement of large holes, and fracture process, which
is parallel to deformation, "outruns" yielding. Such processes probably oc-
cur in the "plastic zones" of the polymer before cracks begin to grow.
Annealing and quenching of polymer glasses. The rise in temperature always
favour the decrease of an average size of holes, surface tension γ_0 redu-
cing with temperature as

$$d \gamma_0 /dT \sim - B (d/M_i)^{2/3}$$

where d is the density and M_i is the molecular weight of a fragment, which
transforms through the i-th type hole. Large holes are entropically not
favoured in the polymer melt, that is why, fast cooling of high-temperature
polymer melts leads to freezing-in a larger fraction of small holes, which
makes the process of plastic deformation easier (small σ_y, large ε_{br}).
On annealing the average size of holes increases, which results in large σ_y.
These phenomena may occur both with a change of the total free volume of
the system and without it. The latter is possible only because in a glassy
polymer there always exist pores, whose surface is the source of nucleation
or trapping of holes. However, the process of pore loss in the sample (the
decrease of a polymer specific volume) is, apparently, a permanent process
because of their great size. The dynamic exchange between pores and holes
may lead to the fact that such properties of the sample as σ_y and T_g can
change at almost constant density of the polymer.

Formation of polymer properties in the course of curing reaction. As it has
been shown the properties of glassy polymers essentially depend on the rate
of vitrification in the course of curing. It is natural to assume that at
vitrification of the reacting system the hole structure formation takes
place, and at slow vitrification F(r) has time to come nearer to equilibri-
um. Fast vitrification (high T_c) leads to a glass with very non-equilibrium
hole size distribution, resulting in rather low σ_y.
The softening temperature of the sample depends, in the first place, on the
concentration of large holes since only large holes permit the transitions
of large segments. At low T_c (slow vitrification) of the sample the for-
mation of large holes takes place in the process of curing, which leads to
reduced T_g. However, large holes cannot move easily under stress, and the
mechanical behaviour of the sample is defined by another "tail" of the size
distribution function F(r), i.e. by small holes. These considerations explain
the concurrent behaviour of T_g and σ_y. F(r) of holes may influence kine-
tic parameters of a glass transition process. Thus, a certain increase of
activation energy of the α-transition with temperature may be caused by
a gradual involvement of larger hole motions.
This means that the size of segments, whose mobility
heating of polymer glasses, is determined not by the property of a single
macromolecule (its rigidity), but by the sizes of holes exosting in the
glass. In this case the size distribution of holes is the physical basis
of the usually observed distribution of relaxation times.

   CONCLUSIONS

Densely crosslinked epoxy-amine polymers appeared to be rather interesting
objects of study from the point of view of the structure of the polymer
glassy state. This is due not only to the fact that networks form fairly
homogeneous closel. packed glasses, but also because of the possibility of
change in the structure and properties of glasses under isothermal condi-
tions. In usual studies of the glass-transition phenomenon in a polymer,
the investigator has to change the temperature of the sample to observe
this transition. On curing the networks considered in this work one can
observe the glass transition under isothermal conditions, and kinetic para-
meters of this transition depend on the rate of the molecular weight increase
of a polymer in a chemical reaction. Since the rate of the chemical reaction
may be changed by introducing catalysts into the system, at the same tempe-

rature one can obtain glasses with different structures and thus with different properties. We think that, using this approach, we can receive new information on the nature of the glass transition and the changes of the polymer structure in this transition. As far as the above-mentioned hole model is concerned, it is necessary to have experimental data on the sizes of holes in a polymer to answer the question concerning the real value of the model. Unfortunately, these data have not been available in literature. There are as yet no good experimental methods of defining hole sizes. We hope this can be done by the analysis of the form (width) of the endothermic peak of heat capacity. However, this work is still to be done.

Theoretical analysis of the energy of different types of holes requires reliable information on the hole physical structure. Unfortunately, such data are also not available.

It is impossible to give a general solution of the problem here, and in this sense the situation is similar to that in the theory of dislocations (18), in which the structure of a dislocation core is still unknown. However, in spite of this, the theory of dislocations has greatly contributed to the understanding of the nature of the mechanical behaviour of solids. That is why, the development of hole concepts for polymer glasses does not seem hopeless to us.

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