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MOLECULAR DYNAMICS OF A POLYMER CHAIN WITH A CROSSLINK*

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The method of molecular dynamics has been used to study the behaviour of a polymer chain made up of rigid interacting links with practically free internal rotation. A single slightly deformed crosslink, whose length is equal to the length of a link, is introduced into the chain. A condensed polymeric system at high temperature is discussed. It is shown that the translational and rotational mobility of the crosslink are appreciably impeded. The impeding effect of the crosslink spreads to a small number of adjacent chain elements (one link for the orientational mobility and 4–8 links for the translational mobility). The results of a numerical experiment are compared with an analytical calculation for a viscoelastic model of sub-chains with a crosslink and with experimental data obtained using polarization luminescence, the crosslink being labelled. The ways in which certain dynamic properties of crosslinked systems depend on the mole fraction of crosslinks have been calculated.

The study of the structure and relaxation properties of crosslinked polymeric systems includes analysis of the local mobility of the nodes themselves (or bridges), formed by the crosslinking agent, and analysis of the local mobility of the chain links in the crosslinked polymeric system. The relaxation properties of

crosslinked systems have now been studied with a number of methods: NMR, dielectric relaxation and polarization luminescence. In particular, orientational mobility of crosslinks may be studied by means of "labelled" experiments (polarization luminescence, ESR) if the labelled group is introduced directly into the bridge formed by the crosslinking agent [1]. A number of papers [2, 3] have shown that there is a strong dependence of intramolecular mobility in crosslinked polymeric systems on the degree of crosslinking of the system. In connection with this, there is the problem of the mechanism by which the crosslinks affect mobility. The crosslink can exert an impeding effect on the local mobility of chain elements both through the kinematic and dynamic bonding along the chain and also through a change in the local environment of a chain element close to the node in the swollen crosslinked polymer. In order to establish the relative role played by these and other possible mechanisms, it is necessary to assess the extent of the hindrance of the crosslink and the scale of the action of the kinematic and dynamic limitations imposed by the crosslink on the mobility of the chain elements.

The mobility of the crosslink as compared with that of chain sections not forming part of the crosslink and the scale and magnitude of the limitations imposed by the crosslink on the local mobility of chain elements will depend on the structure and length of the crosslink, its flexibility and the thermodynamic and kinetic flexibility of the crosslinked chains.

The present paper discusses a simple model of a chain made up of rigid interacting links with slightly impeded internal rotation. A crosslink whose length is equal to the length of a rigid chain link is introduced into the chain (Fig. 1). The movement of the chain with a crosslink occurs at a high degree of occupation of the volume by the links of the polymeric chains, the degree of occupation being close to that for an amorphous polymer. Investigation of the local mobility of such a system may be made with the method of molecular dynamics which has been used previously to study only linear polymeric chains [4–6]. Numerical experiments made with a digital computer with the method of molecular dynamics consist in the solution of a system of equations of motion for all the particles of the chains with account taken of the limitations imposed by the crosslinks and the rigid bonds joining adjacent chain particles. An algorithm for the calculation has been set out in detail [4]: the model of the chain and the interaction parameters were selected as in [5, 6]. As in [5], a chain consisting of $N_1 = 123$ particles was considered. The interaction potential energy is given by the Lennard–Jones paired potential:

$$U(r) = 4\varepsilon_0 [(\sigma/r)^{12} - (\sigma/r)^6], \tag{1}$$

where ε_0 and σ are parameters in the potential and r is the distance between the two particles.

Adjacent particles are linked by rigid bonds with a length $l = 0.69\ \sigma$. With this selection of the length l, the average angle between adjacent bonds approxi-

mates to the tetrahedral angle. We considered a short chain with a single slightly deformed crosslink, with an average length equal to the length of the rigid bond l. A pair of particles remote from one another along the chain was selected as the crosslink, the particles being found in sequence in the initial configuration. An additional "crosslinking" potential was given between these particles:

$$U(r) = K\varepsilon_0(r^2 - l^2)^2, \tag{2}$$

where r is the distance between the particles of the crosslink, the parameter K characterizing the rigidity of the crosslink.
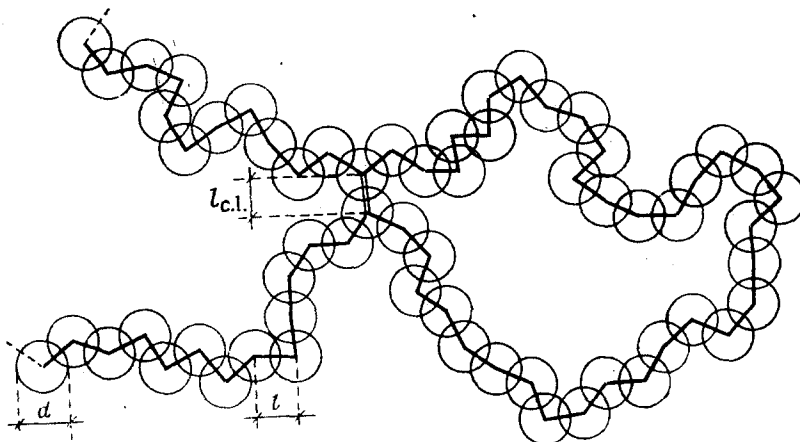

FIG. 1. Model of crosslinked chain: $l_{c.l.} = 0.69\ \sigma$ is the length of the crosslink, equal to the bond length l; $d = 1.12\ \sigma$ is the "diameter" of the chain's particles determined from the minimum of the Lennard–Jones potential (σ is the parameter of the Lennard–Jones potential $U(\sigma) = 0$).

The parameter K was selected so that the deviation of the length of the crosslink from the average value of l did not exceed 10–15%. The numerical experiments were carried out with various values of the parameter K ($K = 9$, 18 and 36). In the range of K considered, the reuslts hardly depend at all on the rigidity of the crosslink (for a specified length of the crosslink). The length of the loop formed when the crosslink is made was also varied. The results of the numerical experiments were also found not to depend systematically on the loop length. As in [5, 6], a high degree of occupation (0.82 of the maximum packing density) was achieved by imposing periodic boundary conditions. In the present work, the numerical experiments were carried out for a system temperature of $T/T_0 = 3.3$ ($T_0 = \varepsilon_0/k$, where k is Boltzmann's constant).

The translational diffusion mobility and the orientational mobility of the chain particles and the crosslink were studied. To characterize the translational mobility, the mean square displacement of the chain particles and the crosslink

$\langle \Delta r^2(t)\rangle = \langle r(0) - r(t)^2\rangle$ was calculated at time $t \ll t_{n.e}$* (here $r(0)$ and $r(t)$ are the coordinates of the particle at time $t = 0$ and t respectively). In order to characterize the local orientational mobility, the time dependence of the following quantities were calculated:

$$P_1(t) = \langle \cos \theta(t)\rangle , \tag{3}$$

$$P_2(t) = \tfrac{3}{2}\langle \cos^2\theta - \tfrac{1}{3}\rangle , \tag{4}$$

where $\theta(t)$ is the angle of rotation of a vector directed along the chain length or crosslink. We use the brackets $\langle\ \rangle$ to denote an average over the whole time of the calculation, $t_{n.e}$.

Translational mobility. The data from the numerical experiment concerning the translational mobility of chain particles and the centre of the crosslink are shown in Fig. 2; they show that the time dependence of the mean square displacement $\langle \Delta r^2(t)\rangle$ is quite clearly curved. This result is in qualitative agree-
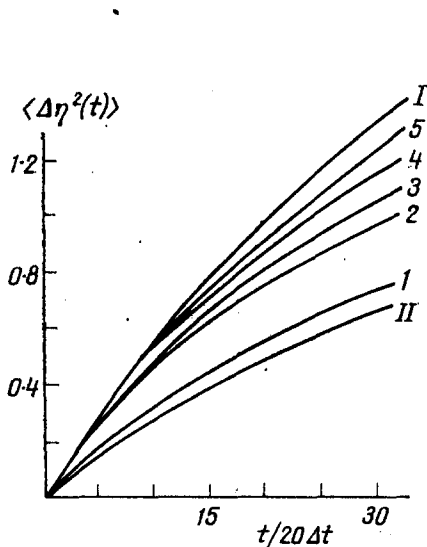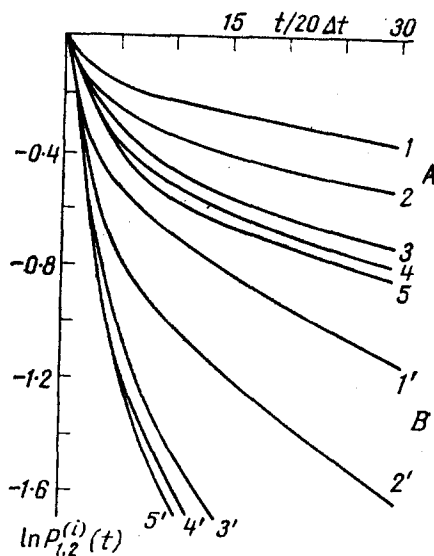

FIG. 2

FIG. 3

FIG. 2. Time dependence of the mean square displacement for particles of the chain for and the centre of the crosslink. The number of bonds separating the specified particle from the node, i, has the following values: *1*—0; *2*—1; *3*—2; *4*—3 and *5*—8; I—represents the displacement of a particle in the uncrosslinked chain and II—the displacement for the centre of the crosslink.

FIG. 3. Time dependence of the logarithm of the correlation function for the angle of rotation ln $P_{1,2}^{(i)}(t)$ of chain elements separated from the crosslink by i links. For $P_1(t)$, shown by A, and $P_2(t)$, shown by B, i has the following values: *1* and *1'*—0; *2* and *2'*—1; *3* and *3'*—2; *4* and *4'*—3; *5* and *5'*—i=8 and i= ∞.

* The suffix n.e. refers to the numerical experiment.

ment with the prediction of the analytical theory [7, 8] for the translational diffusion of an isolated element in an individual unbranched chain, the theory being based on a visoelastic model of non-interacting elements. A similar relationship corresponds to the successive involvement in the diffusional motion of increasingly larger sections of the chain adjacent to the isolated particle. It follows from the numerical experiments that the particles making up the crosslink move the most slowly. As the distance along the chain to the crosslink is increased, the dependence of $\langle \Delta r^2(t) \rangle$ for the chain particles approximates to that for particles in an uncrosslinked chain. For example, even for the particle sixth from the crosslink $\langle \Delta r_6^2(t) \rangle \approx 0.9 \langle \Delta r_{\text{free}}^2(t) \rangle$ (where $\langle \Delta r_6^2(t) \rangle$ and $\langle \Delta r_{\text{free}}^2(t) \rangle$ are respectively the mean square displacement for the sixth particle from the crosslink and for a particle in an uncrosslinked chain).

In order to obtain an expression for the mean square displacement of the crosslink $\langle \Delta r_{\text{centre}}^2(t) \rangle$ we used the results of the numerical experiment with respect to the translational diffusion of the particles of which the crosslink consisted $\langle \Delta r_0^2(t) \rangle$ and the rotational diffusion of the bridge-crosslink itself $P_1(t)$. $\langle \Delta r_{\text{centre}}^2(t) \rangle$ is expressed in terms of $\langle r_0^2(t) \rangle$ and $P_1(t)$ as follows:

$$\langle \Delta r_{\text{centre}}^2(t) \rangle = \langle \Delta r_0^2(t) \rangle + \tfrac{1}{2} l^2 (P_1(t) - 1) \tag{5}$$

For comparison with the results of the numerical experiment, the dependence of the mean square displacement of the centre of the crosslink $\langle \Delta r_{\text{centre}}^2(t) \rangle$ was obtained, as in the appendix, for a model consisting of Gaussian subchains with a crosslink; this is a generalization of the corresponding derivation for diffusion of a chain link without crosslinking [7, 8].

Rotational mobility. In investigating rotational mobility of the chain elements, the principal task consisted, as in the study of translational mobility, in establishing the scale of the action of the node. Figure 3 shows the time dependence of $\ln P_1(t)$ and $\ln P_2(t)$ for the crosslink and for chain elements variously remote from the crosslink. It may be seen that all the functions $\ln P_1(t)$ are non-linear, a fact which points to the existence of a spectrum of relaxation times. The connection $P_2(t) = P_1^3(t)$ between the functions $P_1(t)$ and $P_2(t)$ is observed in the time interval studied; this is also found for the orientational relaxation of an isolated rigid chain in a viscous fluid [9] and for a rigid link in a chain without a crosslink [6].

The rotational mobility of the crosslink is appreciably limited as compared with the mobility of chain links but the effect of the crosslink on adjacent links falls off rapidly with distance from the node (the functions $\ln P_1^{(t)}(t)$ and $\ln P_2^{(t)}(t)$ where i is the number of the chain element reckoned from the node). A characteristic relaxation time $\tau_{1,2}^{(t)}$ may be introduced as a quantitative characteristic of the rotational mobility; this is the time for the corresponding functions $\ln P_1^{(t)}(t)$ and $\ln P_2^{(t)}(t)$ to fall by an amount Δ. Since $t \leqslant t_{\text{cor}}$ during the calculation of the correlation functions (3, 4) and the value of $\ln P_1^0(t)$ for the crosslink falls by only $\Delta = 0.4$, the time $\tau_1^{(t)}(0.4)$ was selected as the characteristic of the decrease in $\ln P_1^{(t)}(t)$. In $P_2^{(t)}(t)$ decreases much more rapidly with time and therefore the

generally adopted time of decrease of a function by a factor e, $\tau_2^{(i)}(1)$ may also be used as its characteristic.

Figure 4 shows the quantities $\tau_1^{(i)}(0.4)$, $\tau_2^{(i)}(0.4)$ $\tau_2^{(i)}(1)$ for the crosslink and for links close to it along the chain. In the range of variation of $P_1^{(i)}(t)$ and $P_2^{(i)}(t)$ considered, the effect of the node on orientational mobility appears only in the case of links directly adjoining the crosslink ($i=1$). Even for the next links along the chain ($i=2$), the orientational mobility is practically the same as that for chain links in the absence of a crosslink.

Thus the introduction of a bridge whose length approximates to the length of a rigid chain section exerts an appreciable effect on the local diffusional and relaxation properties of chain particles close to the crosslink. The mobility of the crosslink itself differs substantially from that of particles in the chain. Thus the
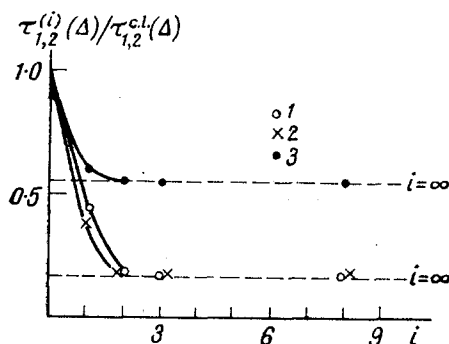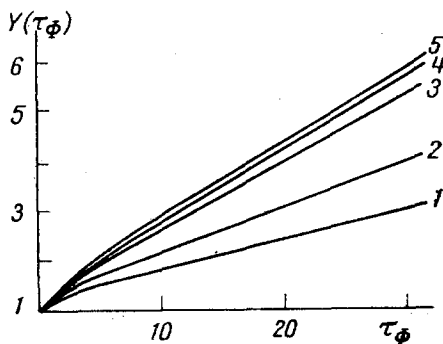

FIG. 4   FIG. 5

FIG. 4. Ratio of the relaxation time for a chain element separated by i links from the crosslink to the relaxation time for the crosslink. The relaxation time is determined from the decrease in the logarithm of the appropriate autocorrelation function, $\ln P_{1,2}(t)$ by an amount Δ:
$$1 - \tau_1^{(i)}(0,4)/\tau_1^{c.1.}(0.4), \quad 2 - \tau_2^{(i)}(1)/\tau_2^{c.1.}(1), \quad 3 - \tau_2^{(i)}(0.4)/\tau_2^{c.1.}.$$

FIG. 5. Dependence of the reduced luminescence polarization $Y = \dfrac{1/P + 1/3}{1/P_0 + 1/3}$ on τ_φ for the crosslink ($i=0$, curve 1) and for chain elements, separated from the crosslink by the following values of i: $2-1$; $3-2$; $4-3$; $5-8$ and ∞.

mean square displacement of the centre of the bridge-crosslink is only half that of a particle along the chain remote from the crosslink. The same result is also obtained with a model of Gaussian subchains for a crosslink joining two chains (eqn. (16) in the Appendix). The rotational diffusional mobility of the bridge-crosslink differs even more markedly from the mobility of links in the chain. The times $\tau_1^{(0)}(0.4)$ and $\tau_2^{(0)}(1.0)$ are almost six times greater than the corresponding times for links in a chain without a crosslink $\tau_1^{(free)}(0.4)$ and $\tau_2^{(free)}(1.0)$.

In the initial part of the function $P_2(t)$, the difference is rather less: $\tau_2^{(0)}(0.4)/$ $/\tau_2^{(free)}(0.4) \approx 2$. The difference between the orientational mobility of the bridge and of free chain links can be established experimentally with labelled dynamic

experiments, for example, by polarization luminescence if the luminescence label is included in the crosslink of the bridges [1]. The functions $P_2^{(t)}(t)$ obtained in the numerical experiment were used to calculate the quantity $Y = (1/P + \frac{1}{3})/$ $/(1/P_0 + \frac{1}{3})$ which is directly measured in experiments with polarization luminescence (here $1/P$ is the reciprocal of the polarization and $1/P_0$ is the reciprocal of the limiting polarization). The theory [10] shows that:

$$Y = \cfrac{1}{\cfrac{1}{\tau_\varphi} \int\limits_0^\infty e^{-t/\tau_\varphi} P_2(t)dt} , \qquad (6)$$

where τ_φ is the lifetime of an oscillator in the excited state, t is time and $P_2(t)$ is determined by eqn. (4). The dependence of Y on T/η (where T is the temperature and η the viscosity of the solvent) is generally obtained in experiments with polarization luminescence. The characteristic time τ_w is thus determined from the slope of the straight-line section of the curve $Y(T/\eta)$ at large T/η. Similar information may also be obtained from $Y(\tau_\varphi)$ at a fixed value of T/η.

Figure 5 shows the $Y(\tau_\varphi)$ obtained in the numerical experiment for a labelled group included in the crosslink and for labelled groups positioned in links variously remote from the node along the chain. The usual experimental range of variation is from $Y = 1$ to $Y = 5-6$ [10]. The $Y(\tau_\varphi)$ obtained in the numerical experiment in this range are practically linear, except for a small initial region. The slopes of the linear sections of $Y(\tau_\varphi)$ for a labelled group in the crosslink and for a labelled group remote from the crosslink differ by a factor of 2–3. The average "luminescent" time τ_w for a crosslink is thus 2–3 times greater than that for a labelled group in the main chain. The value obtained for the ratio of the times approximates to values obtained for a luminescent labelled group at the nodes of a crosslinked system based on PMMA [1].

Since the impeding effect of the bridge is also distributed to chain links not included directly in the crosslink, the presence of crosslinks can also appear in the local dynamic characteristics averaged over the entire specimen. The features of the relaxation times for chain elements obtained in the numerical experiment for a chain with a single crosslink can be used to assess the way in which certain average characteristics of the local mobility in network systems depend on the number of links positioned between nodes of the network or on the mole fraction of crosslinks.

We assume that, in the case of a chain section between crosslinks, the local diffusional mobility of the elements depends on the distance from the nearest crosslink in the same way as that obtained in the numerical experiment for a chain with a single crosslink. Hence the following averaged characteristics may be calculated for a chain element: $\bar\tau_{1,2}$—the average time; $\overline{(1/\tau_{1,2})}$—the average reciprocal time; $\sqrt{\overline{\tau_2^2}}$—the mean square time and $\overline{\tau_2^2}/\bar\tau_2 = \tau_w$—the weighted mean time (the averaging is here carried out over all the n elements of the chain in-

cluded between crosslinks, the bridge itself also being included with an appropriate weighting). The quantities $\bar{\tau}_2$ and $\overline{(1/\tau_2)}$ are related to the spin-lattice relaxation time T_1 in NMR [2]. In fact, if there is a distribution $G(\tau_2)$ of the relaxation (correlation) times, the expression for $1/T_1$ has the form (see, for example, [11]):

$$\frac{1}{T_1} = A \int\limits_0^\infty \left(\frac{\tau_2}{1+(\omega_0\tau_2)^2} + \frac{4\tau_2}{1+(2\omega_0\tau_2)^2} \right) G(\tau_2)/d\tau_2, \qquad (7)$$

where A is a constant and ω_0 is the working frequency of the NMR. At sufficiently high temperatures, where τ_2 fulfils the condition $\tau_2 \ll 1/\omega_0$ for the major region,

$$\frac{1}{T_1} \sim \int\limits_0^\infty G(\tau_2)\tau_2 d\tau_2 = \bar{\tau}_2, \qquad (8)$$

by contrast at low temperatures when $\tau_2 \gg 1/\omega_0$

$$\frac{1}{T_1} \sim \int\limits_0^\infty \frac{G(\tau_2)}{\tau_2} d\tau_2 = \left(\overline{\frac{1}{\tau_2}}\right) \qquad (9)$$

The quantities $\overline{(1/\tau_2)}$ and $\bar{\tau}_w$ can also be determined from experiments on polarization luminescence from the initial slope $\left(\dfrac{\tau_\varphi T}{\eta} \to 0\right)$ and from the asymptotic behaviour (at large values of $\dfrac{\tau_\varphi T}{\eta}$) of the curves for the reciprocal polarization $1/P$ as a function T/η respectively if the labelled groups are distributed at random along the chain (here T is the temperature and η the viscosity).

Figure 6 shows how these quantities depend on the number of links in the model chain "between the crosslinks". It may be seen that the values of $\overline{(1/\tau_{1,2})}$ rapidly go to a level corresponding to the "uncrosslinked" chain. The value of τ_w is the last of all to reach this level. An appreciable difference (by more than a factor of 2) between the average characteristics of crosslinked and uncrosslinked chains is observed when the number of links between the crosslinks N is less than 3 in the case of $\overline{(1/\tau_{1,2})}$, the corresponding figures being 6 for $\bar{\tau}_{1,2}$, 8 for $\sqrt{\bar{\tau}_2^2}$ and 15 for τ_w. For a tetrafunctional node, the mole fraction of crosslinks $\nu/c = \frac{1}{2}N$, where N is the number of links between crosslinks, γ is the concentration of nodes and c the concentration of the polymer. For example, a doubling of $\bar{\tau}_2$, as calculated from the results of the numerical experiment, occurs when ν/c is greater than $1 \cdot 5 - 2 \cdot 5\%$, the corresponding figure for τ_w being $0 \cdot 6 - 1\%$.

With the chain model considered, the rotation of the links around the bonds is practically free. In real chains, the rotation is impeded and this must lead to a more marked lack of freedom of the rigid crosslink and a greater extension of the action of the node to the chain links. As an example, Fig. 7 shows the way in

which $1/T_1$ was found experimentally to depend on the number of links N between crosslinks for a crosslinked polybutadiene [3] at high temperature (90·5°C). The same Figure also shows the dependence of $1/T_1 \sim \bar{\tau}_2$ (8) on N, found in the numerical experiment. It may be seen that the impeding effect of the crosslink is experimentally more pronounced [3].

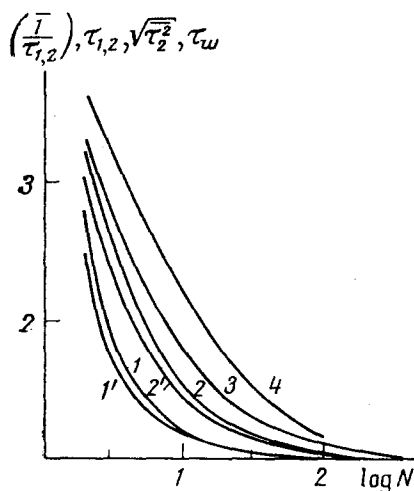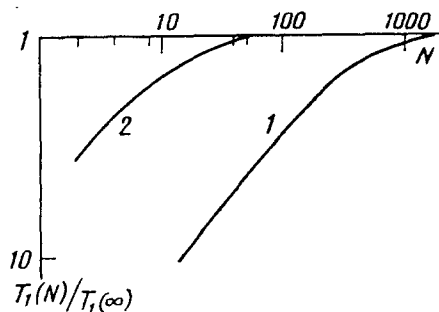FIG. 6   FIG. 7

FIG. 6. Ratios of the various characteristic times, averaged over the entire N elements between the two crosslinks, to the characteristic time of the uncrosslinked chain, as a function of N. 1, $1'-(\overline{1/\tau_1})$ and $(\overline{1/\tau_2})$ respectively, mean reciprocal values, 2, $2'-\bar{\tau}_1$ and $\bar{\tau}_2$, mean values, $3-\sqrt{\tau_2^2}$, room mean square value, $4-\tau_w$, weighted-mean value.

FIG. 7. Dependence of $\log[T_1(N)/T_1(\infty)]$ on $\log N$ for crosslinked polybutadiene [3] at 90·5°C (1); dependence of $\log \dfrac{\bar{\tau}_2(\infty)}{\bar{\tau}_2(N)} \approx \log \dfrac{T_1(N)}{T_1(\infty)}$ at $t \to \infty$ on $\log N$, obtained in a numerical experiment (2). $T_1(N)$ is the spin-lattice relaxation time corresponding to N links between the crosslinks and $T_1(\infty)$ is the corresponding time for the uncrosslinked system.

The result of the present work thus gives a lower boundary for the impeding effect of a node on the local mobility in a crosslinked condensed polymeric system with rigid crosslinks. On the other hand, less pronounced loss in freedom is to be expected for a long and flexible crosslink. In connection with this, it would be of interest to carry out numerical experiments in which the length and flexibility of the crosslink and also the kinetic chain flexibility were varied.

APPENDIX

Let us consider two chains consisting of Gaussian springs with a spring constant K and beads, forming centres of viscous friction with a coefficient of friction ζ (the Kargin–Slonimskii–Rouse model), joined by a "crosslink", namely a Gaussian spring with a spring

constant K_0. The equation of motion of the beads making up the crosslink have the form:

$$\dot{x}_0 = \frac{K}{\zeta}(2x_0 - x_{-1} - x_1) - K_0(x_0 - y_0) \tag{10}$$

$$\dot{y}_0 = \frac{K}{\zeta}(2y_0 - y_{-1} - y_1) - K_0(y_0 - x_0), \tag{11}$$

and the equations of motion for these beads not forming part of the crosslink are:

$$\dot{x}_i = -\frac{K}{\zeta}(2x_i - x_{i-1} - x_{i+1}) \tag{12}$$

$$\dot{y}_i = -\frac{K}{\zeta}(2y_i - y_{i-1} - y_{i+1}) \quad i = \pm 1, \pm 2, \dots \tag{13}$$

Here x_i and y_i are the coordinates of beads in the first and second chain respectively. The numbering is carried out from the beads forming part of the crosslink ($i=0$). The equations for the coordinates of the centres of mass of the i-th beads $z_i = \dfrac{x_i + y_i}{2}$ are obtained by the paired addition of the equation (10) and (11), (12) and (13) and have the same form as do the equations for the beads in an isolated chain

$$\dot{z}_i = -\frac{K}{\zeta}(2z_i - z_{i-1} - z_{i+1}) \quad i = 0, \pm 1, \pm 2, \dots \tag{14}$$

It should be noted that the spring constant K_0 does not enter into the equation for the centre of mass of the crosslink ($i=0$). On the other hand, it is readily shown that the coefficient of friction ζ_1 of the centre of mass of the i-th beads (including also the crosslink) is double that of an isolated beads, ζ. It follows from this that the spring constant K_1 of the effective spring linking two adjacent centres of mass is also twice the value of the spring constant of the subchain K (since the ratio $K/\zeta = K_1/\zeta_1$) is found in equation (14). Hence it may be shown from this [7] that the time dependence of the mean square displacement of the centre of mass of the particles forming the crosslink $\langle \Delta r^2_{centre}(t) \rangle$ has the form:

$$\langle (\Delta r^2_{centre}(t) \rangle = \frac{6kT_a|t|}{\zeta_1} e^{-at}[I_0(\alpha|t|) + I_1(\alpha|t|)], \tag{15}$$

where $\alpha = \dfrac{K_1}{\zeta_1} = \dfrac{K}{\zeta}$, $I_0(x)$ and $I_1(x)$ are Bessel functions of the imaginary argument x. Since the expression for $\langle \Delta r^2(t) \rangle$ in the case of beads in an isolated (uncrosslinked) chain differs in that the value of ζ is halved, it follows that:

$$\langle \Delta r^2_{centre}(t) \rangle = \tfrac{1}{2}\langle \Delta r^2(t) \rangle \tag{16}$$

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RADICAL-CHAIN PHOTO-REACTIONS IN POLYETHYLENE*

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Radical-chain photo-reactions take place in polyethylene containing alkyl side groups when exposed to UV light at 77°K; their continuation (progress) involves the photochemical reactions of the central and terminal alkyl macro-radicals. Crosslinkages, double bonds and gaseous products (mainly N_2, CH_4, C_2H_4) are produced in these reactions, but also macromolecular degradation. The chain length of these reactions depends on the exposure time to UV light and can be 30 or more. The products content will be 2–5 times larger than average. The quantum efficiency of the C—H bond fracture photo-sensitized by the radicals is 10–100 times above that of photo-dissociation of the macro-radicals at the C—C bond. The hot H-atoms forming in the photochemical reaction can penetrate to a distance of 10–15 Å. The photo-recombination kinetics of the alkyl macro-radicals can be qualitatively explained by a free valency migration caused by the hot H-atoms.

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