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MOLECULAR MOTION IN POLYMERS

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I. INTRODUCTION

THE various physical properties of polymeric materials, such as the temperature-time conditions of the glass transition, the dielectric losses and dielectric constant, and the manifestation by polymers of high elasticity or low-temperature brittleness, are determined by the kinetic characteristics of the macromolecules. That is, they depend on the internal mobility of the polymer chains.^[1]

The characteristics of the molecular motion in polymers in the solid and rubbery states and in solution involve the chain structure of their molecules. The mobility of macromolecules, which is above all a function of the temperature, depends on the chemical composition of the polymer, the structure of its monomer links, and the morphology of the chains. From the standpoint of studying the relation of the structure of polymers to their properties, the thermal motion and the enumerated structural characteristics can be considered as the two sides of one general concept, that of the structure of polymers.

One can study molecular motion in polymers by using methods involving relaxation of the atomic groups that move independently, to a first degree of approximation. These atomic groups form independent kinetic units of corresponding types. The time that a kinetic unit takes to come into a statistical-equilibrium state after some force has acted on it (an external electric or mechanical field, etc.) depends on the mobility of the given kinetic unit, and is usually defined by its relaxation time. By the relaxation time τ we mean the time that it takes for the quantity characterizing the deviation from equilibrium of the given kinetic unit to decline by a factor of e owing to thermal motion, when the external force acting on it is suddenly removed (e is the base of the natural logarithms). The temperature-time (or temperature-frequency) dependence of these quantities not only determines the properties of a polymer, but also provides information on the structure of polymers, the thermal motion, and the nature of the molecular interactions.

When an electric field is applied, one can study the time-dependence of the electric moment per unit volume induced by the action of the external field. Experimentally, one directly measures the dielectric constant ϵ' and the dielectric loss angle δ .^[2]

For convenience of mathematical notation, the dielectric constant ϵ' and the dielectric losses are expressed in the form of the generalized dielectric con-

stant, which is the complex function $\epsilon = \epsilon' - i\epsilon''$. Its imaginary component, the so-called dielectric-loss coefficient, is equal to the product of the dielectric constant times the tangent of the loss angle ($\epsilon'' = \epsilon' \times \tan\delta$). The value of ϵ' characterizes the electric moment per unit volume of the dielectric at a given temperature in an electric field of a given frequency. By the dielectric losses we mean the fraction of the electric-field energy that is irreversibly dissipated in the dielectric in the form of heat during the process of establishing the macroscopic electric moment therein following any variation in the electric field. If the external electric field is periodic, the dielectric constant and the dielectric loss angle depend on the frequency of the alternating field and on the relaxation time of the given dielectric. That is, they depend on its ability to come, at a certain rate, to a statistical-equilibrium mutual arrangement of the molecules and their component parts through the process of thermal motion.

The relaxation times of polymers depend on the temperature. The dielectric loss angle passes through a maximum in a temperature-frequency range that corresponds to a first degree of approximation to the condition $\omega\tau = 1$ (ω is the circular frequency of the external field). Simultaneously, the temperature (or frequency) dependence of the dielectric constant ϵ' goes through an inflection point. Therefore, we can determine the value of the relaxation time τ of the molecular motion of a given type, or more exactly, its most probable relaxation time, from the frequency coordinate at which we observe the maximum in $\tan\delta$ or the inflection point in ϵ' as they vary with the frequency or the temperature. It has now been established that each type of kinetic unit corresponds to not just one relaxation time, but a set of them. Here the width of this set depends both on the nature of the polymer and on the temperature. A large number of theoretical and experimental papers have been devoted to studying the relaxation-time spectra of polymers of various structures. However, in this article, we shall take under discussion only the most probable τ .

The dielectric method is one of the most convenient and sensitive methods of studying molecular relaxation as determining the polymer physical properties that involve the peculiarities of structure of their macromolecules. This method is suitable both for polar and for non-polar polymers (polyethylene, polystyrene, and polytetrafluoroethylene), since polymers absolutely devoid of polar groups practically do not exist. During

the process of preparing the polymer, polar residues of the catalyst can be attached to individual non-polar links of the macromolecule, or oxidation can take place, e.g., in polyethylene. Besides, as Curtis^[3] has shown, the polarity of the CH₃ group (dipole moment $\mu = 0.4$ Debye units) proves sufficient to explain dielectric losses having $\tan \delta \leq 10^{-3}$.

The occurrence of dielectric losses and polarization is due to the orientational motion of the polar groups of various types in the macromolecule in the electric field. Hence, an important advantage of the dielectric method is the relative ease of establishing a relation between the macroscopic properties and the molecular mobility in the polymer. This distinguishes this method favorably from the study of relaxation using nuclear magnetic resonance or dynamic-mechanical properties.

In conducting studies by the mechanical method, one studies the time-dependence of the strain under a constant stress, or conversely, the time-dependence of the stress at a constant strain. The molecular relaxation can be conveniently analyzed by use of the complex compliance of the material, e.g., under shear stresses: $J = J' - iJ''$. The real component J' of this function is the compliance proper of the substance, or the reciprocal of the shear modulus. The imaginary component J'' characterizes the mechanical losses. That is, it characterizes the fraction of the energy that is dissipated in the specimen in the form of heat when a mechanical stress of the given type is applied to it. The nature of the temperature-frequency curves for J' and J'' in many ways resembles the analogous variations in ϵ' and ϵ'' .

The generality of the observed laws is explained by the fact that both mechanical and dielectric molecular relaxation are based on the same forms of thermal motion.^[4,5] There are certain differences involving the specific action of the electric and mechanical fields on the macromolecule. Thus, the center of application of electric forces is always a polar group, which very often is part of a side chain, whereas mechanical stresses are mainly propagated along the main chain. It is precisely for this reason that flow processes in polymers, which involve the displacement of the macromolecule as a whole, are easily detected by the mechanical method, while the dielectric method is insensitive to them. A comparison of the data of dielectric and mechanical studies conducted under identical temperature-frequency conditions gives fuller information on the nature of the thermal motion and mutual arrangement of the macromolecules than either of the methods alone.

We can get very important information on the structure and molecular motion from the results of nuclear magnetic resonance studies in polymers.^[6-9]

The advantage of studies by the nuclear magnetic resonance method is its sensitivity to those types of molecular motion involving hydrogen atoms, which are contained in an overwhelming number of polymers. The

information obtained here agrees with the results of the dielectric and mechanical experiments, while in a number of cases, it permits us to study such forms of molecular mobility as do not affect the dielectric and mechanical parameters (e.g., the rotation of CH₃ groups about the C₃ symmetry axis^[11]).

We can determine the onset of molecular motion of atomic groups of certain types from the temperature-variation of the width of the resonance lines, provided that their correlation time (equivalent to the relaxation time) amounts to 10^{-4} – 10^{-5} sec.^[10] By calculating the second moment for a model structure of the given polymer and comparing it with the experimentally-observed values, we can draw direct conclusions on the molecular distances, on the orientation of the side chains with respect to the main chains, and on whether motion of a given type occurs at a certain temperature. Structural data of this sort are especially important for amorphous polymers, for which the data from x-ray studies are very limited. However, since the second moment is inversely proportional to the sixth power of the distance between the atomic nuclei, conformational changes at greater distances will not affect its value. Besides, an analysis of the second moment for polymers yields no results when studying the forms of thermal motion at high temperatures—above the glass-transition or melting point. In this case the resonance line proves to be very narrow, and its width can be affected by inhomogeneity in the magnetic field.

The study of the spin-lattice relaxation time T_1 is very promising from the standpoint of studying molecular motion in polymers. Spin-lattice relaxation is the process in which the energy taken up by a system of nuclear spins from a radiofrequency magnetic field is transferred to the structure formed by the rest of the atoms. The time T_1 is directly related to the correlation time τ_C for molecular motion of the given type, as follows:^[12]

$$\frac{1}{T_1} = \frac{c_1 \tau_C}{1 + 4\pi^2 \nu_0^2 \tau_C^2} + \frac{c_2 \tau_C}{1 + 16\pi^2 \nu_0^2 \tau_C^2}$$

Here ν_0 is the frequency of the rf magnetic field, and c_1 and c_2 are proportional to r^{-6} (r is the internuclear distance) with certain numerical coefficients. Measurements at various temperatures permit us to find the temperature-dependence of the time τ_C , and to calculate the activation energy of the process being studied over a broader range of temperatures than is allowed by the study of the second moment.

One can determine the spin-lattice relaxation time T_1 most directly by using the "spin echo" method,^[13-14] which has the advantage of a decreased sensitivity to magnetic-field inhomogeneity.

Nuclear magnetic resonance also makes it possible to study the spin-spin relaxation time T_2 . Each nuclear magnet is situated in the local magnetic field arising from a neighboring magnetic dipole. Consequently, an

interaction arises between them, resulting in a broadening of the resonance line. The local field in which the given nuclear spin is situated depends on the intensity of thermal motion, and hence, so does the spin-spin interaction. Thus, the spin-spin relaxation time T_2 also serves as a characteristic of the molecular mobility of various types of substances, including polymers.

Thus, the peculiarities of the thermal motion in polymers can be studied by use of the dielectric, dynamic-mechanical, and nuclear magnetic resonance methods. In addition to the equivalent information that we can get by the three independent methods, each of them provides specific information, mutually supplementing the others.

II. THE SEGMENTAL FORM OF THERMAL MOTION IN POLYMERS AS A COOPERATIVE PROCESS OF MOLECULAR RELAXATION

The chemical composition of the polymer, the structure of the individual monomer unit and the way that it is linked in the chain, and the morphology of the macrochains—all these factors determine the strength of the intra- and intermolecular interactions in a polymer. In other words, they determine the hindering potentials that limit the freedom of rotation of the atoms about the single valence bonds and determine the rates of conformational rearrangements. The stronger the molecular interactions are, the more hindered the internal rotation of the atoms, and thus, the farther a perturbation affecting one of the atoms (or one of the bonds, or atomic groups, etc.) will be transmitted along the chain. This segment of the chain is usually called the kinetic segment of the macromolecule. The molecular chains of cellulose and its esters can serve as an example of rigid structures,^[17] while the polyethylene ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) chain is very flexible. The mechanical dynamic studies of Willbourn^[18] have shown that the kinetic segment in this case comprises only four carbon atoms of the main chain, i.e., four methylene groups. The chains of the polysiloxanes prove to be even more flexible, as is explained by the large length of the Si-C and Si-O bonds (as compared with C-C and C-O).^[19,20]

The studies of P. P. Kobeko had pointed out that the kinetic properties of macromolecules, i.e., the mobility of their segments, is mainly determined by interactions of the intermolecular type. When the intermolecular forces fix the positions of the links of the macromolecules, the conformation of the chain is frozen, and practically does not vary with time, and the polymer is in the glassy state. As the temperature rises, the kinetic energy of the chain increases, and finally becomes sufficient to overcome the barrier hindering the shift of a carbon atom from one equilibrium position to another. Simultaneously, all of its neighbors along the main chain within the given kinetic seg-

ment also shift. Such a shift, which entails a change in the conformation of the chain, will become more probable with rising temperature, i.e., with increasing kinetic energy of the macromolecule. Hence, the mobility of the kinetic segment increases with the temperature. As is known, the temperature at which it becomes possible to observe segmental motion of the macromolecules (during a certain period of time) corresponds to the transition of the polymer from the glassy state to the rubbery stage (T_g). The intermolecular interaction occurring between a given kinetic segment and the same type of kinetic units in neighboring macrochains causes the displacement of one segment in space to be necessarily accompanied by the spatial displacement of the others. This arises from the combination of the macromolecules through formation of supermolecular structures, even if only from the necessity of providing the moving segment with an empty space, or because of the mutual entanglement of neighboring macrochains.

Thus, the segmental motion of a macromolecule that occurs above the glass-transition temperature involves cooperation with the neighboring macrochains. This cooperative feature has the result that entire regions occupying a rather large volume are involved in the motion.^[21-27] Probably, this is the explanation of the anomalously high activation energies characterizing the segmental motion of macromolecules.

At temperatures below the glass-transition point T_g , where the kinetic energy of the main chain is insufficient to overcome the barriers hindering its motion, the shift of a segment from one equilibrium position to another becomes an event of infinitesimal probability, and the segmental motion of the macromolecule practically ceases. The relaxation times characterizing the rates of processes involving increase in size of the chain segments become very large, and considerably exceed the observation times accessible to us.

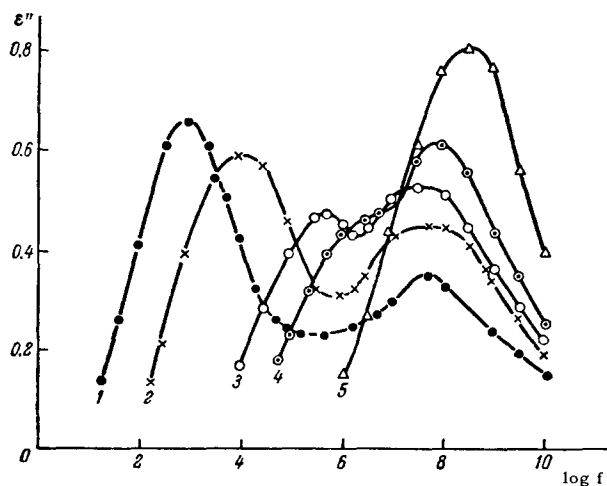


FIG. 1. Frequency-dependence of the dielectric-loss coefficient ϵ'' of polymethylacrylate.

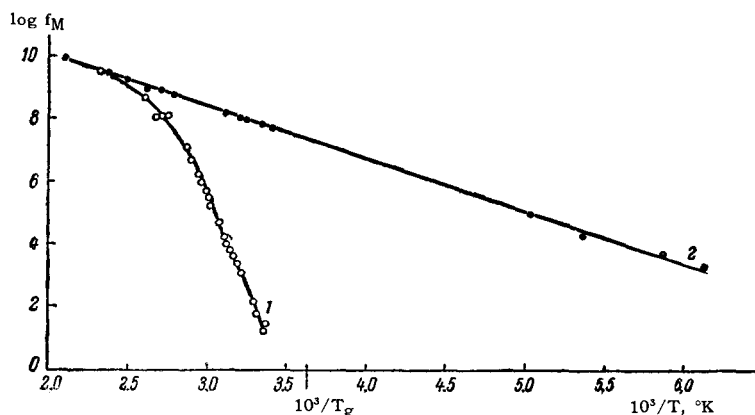


FIG. 2. Relation of the logarithm of the frequency of maximum ϵ'' of polymethylacrylate to the reciprocal of the temperature. 1 – Dipole-elastic losses; 2 – dipole-radical losses. The glass-transition temperature is noted on the horizontal axis.

III. LOCAL FORMS OF THERMAL MOTION IN POLYMERS AND PECULIARITIES OF MOLECULAR RELAXATION AT HIGH TEMPERATURES

As numerous studies of molecular relaxation in polymers conducted by the most varied methods have shown, individual groups of atoms maintain their mobility below the glass-transition temperature. Most often, these are contained in the side-chains, but they can also be bound to the main chain.^[9,28-30] The kinetic elements of this sort are considerably shorter, and their motion in space is qualitatively of a different nature. These kinetically-independent groups execute oscillations about certain fixed equilibrium positions in the process of thermal motion.^[23,31-34] Here the displacements are localized in a relatively small volume. That is, the cooperative nature and interrelation of the motion of the given group with the neighboring links of the same or other macromolecules is very small. Owing to the small volume of the relaxation unit and the relatively smaller role of the intermolecular interactions, the activation energies of the processes involving the motion of these groups are small (of the order of 5–15 kcal/mole), and the relaxation times are very short.

The persistence of the mobility of atomic groups at very low temperatures is of great scientific and practical significance. At present, the idea is being experimentally confirmed that the low brittleness of polymers such as the polycarbonates, the polyamides, the polyurethanes, polyethylene, polytetrafluoroethylene, and their copolymers with other components is explained by the presence of a strong peak in J'' having a small relaxation time. All these polymers have the capability of rapid relaxation of stress at low temperatures, which prevents the onset of fracture. The opposite properties are shown by polystyrene, a brittle material in which the damping at low temperatures is very small.^[35,36] Polystyrene under tension becomes less brittle, and at the same time the dielectric and mechanical methods mark the appearance of new peaks in the mechanical and dielectric loss angles at low temperatures.^[39,38]

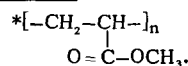
The motion of any atomic group constituting an in-

dependent kinetic unit can be studied by the method of dielectric losses and polarization over a very broad range of frequencies, from 10^{-4} to 10^{10} cycles/sec. As an example, Fig. 1 shows the frequency-dependences of the dielectric-loss coefficient ϵ'' of polymethylacrylate^[39]. * We can see here two regions where this quantity passes through a maximum. At low frequencies ϵ''_{\max} (the region of the so-called dipole-elastic losses) arises from the polarization in the electric field of the dipole group COO, which is established through the thermal motion of the segments of the macromolecule. The high-frequency region of ϵ''_{\max} shows relaxation times at 37°C five orders of magnitude smaller than τ of the dipole-elastic process (see Fig. 1). This region is not due to the orientational polarization of the same COO dipole, but arises from the vibrational motion of the small kinetic radical characteristic of the glassy state.

As we see from Fig. 2, which shows the relation of the logarithm of the frequency for maximum ϵ'' to the reciprocal of the temperature, practically only the small kinetic units are in motion below the glass-transition temperature T_g in this polymer (T_g is 3°C). In other words, below 3°C in the studied frequency range, we are in a position to observe only the region of dipole-radical losses. Above T_g , this form of molecular motion coexists with the segmental motion, in which large cooperative regions participate. Somewhat earlier, the coexistence of the segmental and radical types of motion at the same temperature had been observed in copolymers of methyl methacrylate and styrene.^[40]

With increasing temperature, the relaxation times of both processes decline exponentially, but at different rates. This is explained by the fact that the corresponding relaxation processes have different activation energies. Usually the activation energy is calculated from the slope of the graph of the relation**

$$\lg f_M = \lg f_0 + \frac{U}{RT},$$



** $\lg = \log$.

where f_M is the frequency of maximum ϵ'' at the given temperature T , f_0 is the number of vibrations per second executed by the given kinetic unit when occurring in an equilibrium position, and U/RT is the Boltzmann factor for activation energy U .

We see from Fig. 2 that at temperatures below T_g and somewhat above it, the relation

$$\lg f_M = \varphi\left(\frac{1}{T}\right)$$

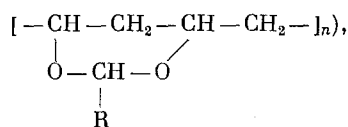
is linear for both processes. The constancy of slope is evidence that the activation parameters do not vary with temperature. Hence we can conclude that the volumes in which the corresponding dipole-elastic and dipole-radical relaxation processes take place remain constant, as does the nature of the inter- and intramolecular interactions.

Further temperature increase leads to qualitative changes in the motion of the macromolecules. The slope of the curve

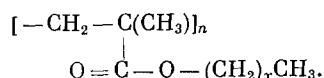
$$\lg f_M = \varphi\left(\frac{1}{T}\right)$$

for the dipole-elastic process begins to diminish, and this continues until this curve completely merges with the straight line for the dipole-radical process. Thereafter the activation energy (i.e., the slope of the coincident straight lines) remains constant.

This phenomenon had been observed even earlier, both by the dielectric method (for the homologous series of polyvinylacetals^[41]



and by measurement of the real and imaginary components of the complex compliance of polyalkylmethacrylate homologs^[42-46]



However, there has been no satisfactory treatment of this phenomenon. The group of studies conducted by different methods permits us at present to draw some conclusions on the nature of the thermal motion in polymers at temperatures far above T_g .

The decrease in the activation energy of the segment-relaxation process with increasing temperature is evidence that the kinetic energy of the main chain becomes great enough to overcome the effect of the intermolecular interaction responsible for the involvement of large cooperative regions in the segmental motion. In the cited studies of Ferry and his associates, the idea is developed that at high temperatures the cooperative motion is short-range in nature.

Koppelman considers that the "true" activation energy of the segmental motion is near to that which is

observed at very high temperatures, where it no longer varies with further temperature increase.^[24] According to Bueche, the decrease in activation energy observed upon introducing a plasticizer (at not too high temperatures) is explained by the screening of segments of the macrochains, resulting in a decrease in the size of the cooperative regions.^[25]

We can assume that at temperatures considerably above the glass-transition temperature, the macromolecule becomes seemingly "independent" of the surrounding adjacent chains in its motion, though this "independence" is not complete. In studying the thermomechanical relations of polymethylmethacrylate and the elastic properties of melts of polyethylene and polypropylene, it has been shown^[48] that with rising temperature one can observe two regions of completely reversible rubbery deformation sharply differing in modulus, provided that the stresses are not too great. The molecular picture of the same phenomenon, as discussed in the studies of Bueche,^[25,49] includes two more types of rubbery deformation, besides purely elastic deformation and viscous flow. On the basis of the network structural model of polymers, Bueche considers that the high-modulus rubbery deformation involves the change in conformation of regions of the macrochain included between entanglements. These entanglements can be formed by various sorts of kinks, loops, and contacts between the chains (Fig. 3).^[51]

At sufficiently high temperatures, small-modulus rubbery deformation sets in, and the author ascribes this phenomenon to the effect of slippage of the knots of the network. Studies of concentrated polymer solutions, in particular poly-*n*-butylmethacrylate, directed toward investigating the behavior of this sort of knots have confirmed that with rising temperature they can dissociate and permit the chains to slip through.^[50]

Small-modulus rubbery deformation can involve the breakdown of the long-range cooperative interaction, however this interaction has been effected. The possibility of existence of small-modulus rubbery deformation indicates that the state of the macromolecule in the bulk material at high temperatures can be likened to that in a concentrated solution of the polymer at moderate temperatures, where a very great mobility of the macrochains exists alongside a strong intermolecular interaction.

Bearing in mind the widely-demonstrated analogy

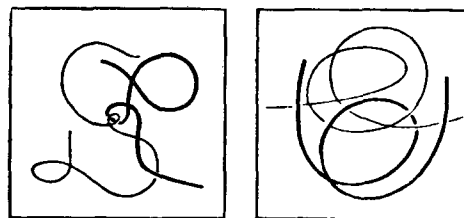


FIG. 3. Diagram of possible examples of kinks and loops of the macrochains of polymers.

between the mechanical and dielectric properties, which are based on the same molecular-motion processes in polymers, we can compare the high-temperature region of rubbery deformation with the process of dielectric relaxation at very high temperatures.

At high temperatures far above T_g , the value of ϵ''_m in the temperature or frequency-dependence begins to decline with increasing temperature.^[39,52] At the same time, the maximum of the dielectric-loss coefficient of the dipole-radical type usually sharply increases with the temperature, and becomes somewhat narrower in shape.^[53] This gives us grounds to suppose that in the high-temperature region, where we observe one merged process of dielectric molecular relaxation (see Figs. 1 and 2), the predominant fraction of the dielectric losses can be ascribed to a process of the dipole-radical type.

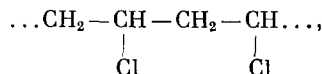
The use of the shear mechanical compliance of polyethylmethacrylate^[42] and polybutylmethacrylate^[43] leads to the opposite conclusion: in the high-temperature region, the unified molecular-relaxation process almost entirely involves the segmental motion of the chain, and is ascribed to the so-called α -dispersion, an analog of the dipole-elastic losses.

However, these conclusions, while contradictory at first glance, can easily be reconciled if we bear in mind the fact that the increase in kinetic energy of the chain with rising temperature permits it to overcome not only the intermolecular interactions responsible for the cooperative segmental motion, but also the intramolecular interactions. The result of the latter is an increase in the kinetic flexibility of the chain and a consequent shortening of the kinetic segment.

The mechanical deformation of polymer materials involves the properties of the main carbon chain considerably more strongly than it does the structure of the side attachments of the monomer unit. Above all, the increase in flexibility of the main chain at high temperatures must entail an increase in the number of realizable conformations, and hence, an increase in the extent of rubbery deformation, as obtained under a constant stress and given time conditions. Consequently, at temperatures far above T_g , rubbery deformation under an alternating mechanical load involves the kinetic properties of the main chain, which performs its conformational transformations through the motion of short segments.

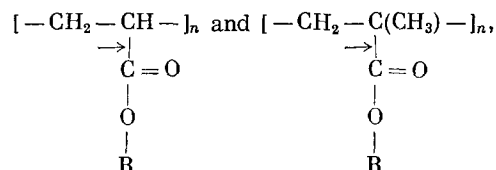
A peculiarity of the dielectric method of studying relaxation processes is the fact that the centers of application of the external influence (i.e., the electric field) are the polar groups contained in each monomer unit. The polar groups can be rigidly bound to the main chain (e.g., in polyvinylchloride), or can be joined indirectly to the main chain (C=O in polyethylene or in the polyalkylacrylates and polyalkylmethacrylates), but sometimes the polar group is at the end of a longer or shorter side chain, i.e., the polar group proves to be rather far from the main chain. Depending on the

position of the dipole with respect to the main chain, the correlation with the main chain of the orientational motion of the side polar group in the electric field varies. Obviously, the CCl dipole in polyvinylchloride



which involves a carbon in the main chain, can move only with the participation of a certain segment of the main chain, even in the glassy state. Naturally, such a dipole-radical relaxation process has certain features characteristic of the laws governing the dipole-elastic losses (e.g., the relaxation times decrease when a low-molecular-weight plasticizer is added^[54]). However, it can be observed considerably below the glass-transition temperature. Hence, this process does not involve the thermal motion of the chain segments.

The second type of attachment of a polar group to a side chain is exemplified by the polyalkylacrylates and polyalkylmethacrylates (the structural formulas of their molecular units are respectively:



where R = $-\text{CH}_3$ (methyl), $-\text{CH}_2\text{CH}_3$ (ethyl), $-(\text{CH}_2)_2\text{CH}_3$ (propyl), etc.). This type shows a lesser dependence of the motion of the dipole on the main chain. The addition of a plasticizer no longer affects the τ of the dipole-radical losses.^[55] Nevertheless, the correlation of the motion of the side radical with the main chain remains rather great. The mutual influence of a carbon atom in the main chain and the carbon atom of the carbonyl group C=O bound to it is quite obvious from the fact that rotation about the C-C bond (indicated by the arrow) is not free even at high temperatures (above T_g). Otherwise, we could not observe any appreciable region of dipole-elastic losses, since the main chain does not contain polar groups joined directly to it. The onset of motion of the segments could not bring about an additional orientational polarization of the side-group dipole, the latter being already fully attained at lower temperatures and shorter times.

The dipole-radical process in polymethylmethacrylate (the region of $\tan \delta_{\text{max}}$) occurs at temperatures higher than is usually observed in polymers of the vinyl series. Hence, its relaxation times are relatively long. The activation energy amounts to 21 kcal/mole, also an unusually high value for dipole-radical losses or the analogous mechanical losses. For polymethylacrylate, whose structure differs only in the replacement of the CH_3 group joined to the main

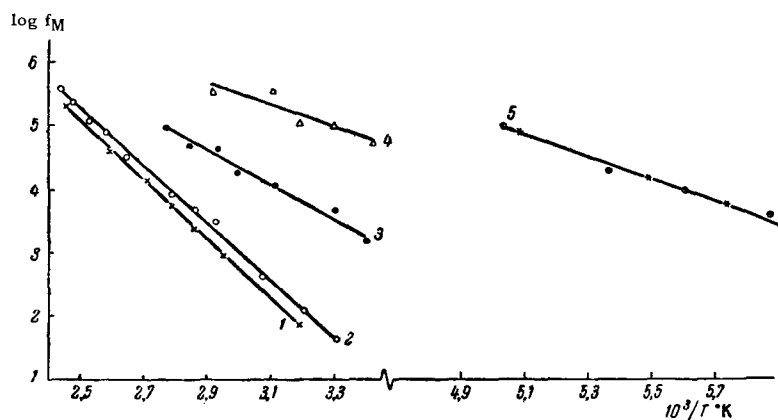


FIG. 4. Relation of the logarithm of f_M to the reciprocal of the temperature for the dipole-radical losses for copolymers of styrene with methyl methacrylate (MMA) and methyl acrylate (MA). 1 – 100% MMA; 2 – 80.5% MMA; 3 – 55.5% MMA; 4 – 40.5% MMA; 5 – 100% MA and 49% MA. (The weight content of the polar component is given.)

chain by a hydrogen atom, both the activation energy and the relaxation times^[52,56] have far lower values. Hence, we can conclude that the methyl group exerts a hindering action on the vibrational motion of the kinetic radical bearing the side-chain dipole.

The copolymerization of methyl methacrylate with methyl acrylate, i.e., the replacement of a certain portion of the CH_3 groups of the main chain by hydrogen, increases the mobility of the side radical of methyl methacrylate. This is evidenced by the decrease in the values of the activation energy and τ .^[28] The copolymerization of methyl methacrylate with styrene gives exactly the same result,^[40] since here we "replace" part of the methyl groups of the main chain with hydrogen atoms. The introduction of the heavy side attachments of the benzene rings does not exert a hindering action on the motion of the side radicals of the methyl methacrylate. Hence, the kinetic radical is formed by the side group of methyl methacrylate and the nearest groups along the chain. Here, its flexibility is determined by the local flexibility of the main chain, which is altered by the steric hindrance introduced by the methyl group, rather than by the interaction of the side groups. This conclusion is confirmed by the fact that the introduction of styrene links into a methyl acrylate chain affects neither the relaxation times of the dipole-radical losses nor their activation energy.^[57,49] What has been said is illustrated by Fig. 4, which shows the variation

$$\lg f_M = \varphi\left(\frac{1}{T}\right)$$

($f_M = 1/2\pi\tau$) of the dipole-radical losses of polymethylmethacrylate, polymethylacrylate, and their copolymers with styrene.

Such a great effect of the methyl group attached to the main chain on the kinetic properties of the latter can be demonstrated by the example of a study of the dipole-elastic losses of copolymers of methyl methacrylate with styrene.^[40] Figure 5 (1) shows the relations of $\tan \delta$ of the dipole-elastic losses of the copolymers to the weight fraction of methyl methacrylate. We see from Fig. 5 that the copolymerization of styrene with methyl methacrylate increases

the maximum value of $\tan \delta$ for the dipole-elastic losses, in spite of the decrease in the concentration of dipoles. In the copolymer containing 60% methyl methacrylate, $\tan \delta_{\max}$ attains its upper limit and then declines again. The increase in the value of $\tan \delta_{\max}$ at small styrene contents involves the decrease in the number of CH_3 groups on the main chain, which reduces the hindrance of the orientational motion of the dipole in the electric field during the process of segmental motion of the macromolecule. At a high styrene content, the decrease in concentration of polar groups begins to manifest its effect, and $\tan \delta_{\max}$ decreases. The analogous variation for the copolymers of methyl acrylate with styrene [Fig. 5 (2)] shows that the decrease in the value of $\tan \delta_{\max}$ for the elastic-dipole losses is a linear function of the concentration of the polar component alone, while the flexibility of the main chain does not vary appreciably. According to Adam's conclusions,^[21,58] the fact that variation of concentration of the benzene rings does not exert a hindering effect could be due to the great freedom of rotation about the $\text{C}_{\text{phenyl}}-\text{C}_{\text{main chain}}$ bond.

The hindering effect of the main-chain methyl group can explain the difference in properties between the kinetic radicals of polymethylmethacrylate and poly-

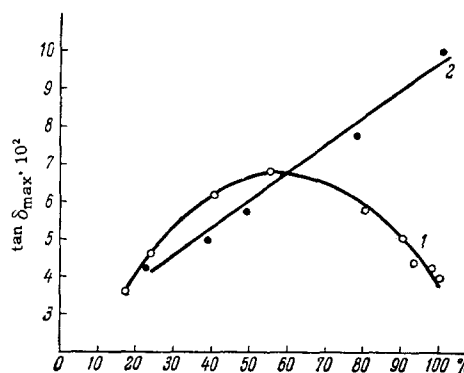
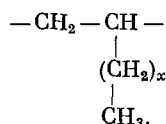


FIG. 5. Relation of $\tan \delta_{\max}$ for the dipole-elastic losses in copolymers of styrene with methyl methacrylate (1) and methyl acrylate (2) to the weight content of the polar component.

methylacrylate as the side chain is lengthened, i.e., as we go to the higher homologs of these series.^[28,52,55,59-60] In the polymethylmethacrylate series, lengthening of the side chain by 2-3 methylene units (i.e., on going to polybutylmethacrylate) does not appreciably affect the relaxation time and the activation energy of the dipole-radical losses. An analogous change in the side chain in the polymethylacrylate series, conversely, considerably shifts the region of $\tan \delta_{\max}$ of the dipole-radical losses to lower temperatures, owing to the decrease in the most probable relaxation time, and it decreases the activation energy. Apparently, the lengthening of the side chains separates the main chains by increasing the free volume,^[61] and diminishes the intermolecular interaction. The decrease in T_g is evidence of an increase in mobility of the main chain. If we assume that the kinetic radical includes a small segment of the main chain, the conditions for its motion must also be made easier. This is precisely what causes the decrease in τ and in the activation energy of the dipole-radical losses in the polymethylacrylate series. The absence of this effect among the first members of the polymethylmethacrylate series should be ascribed to the predominance of the chain-hindering effect of the main-chain CH_3 group, which determines its kinetic properties. This effect is obscured upon increase in the homolog number, since among the higher homologs the temperature-frequency coordinates of the dipole-radical loss region obviously do not coincide with the same for the first three members of the series.

On the basis of the presented experimental facts, we can conclude that the boundary of the kinetic radical in the glassy state extends beyond the limits of the side chain, and includes a certain number of carbon atoms of the main chain. In generalizing the results of the dielectric and dynamic-mechanical studies of the homologous series of polymethylmethacrylate, Ferry also concluded that one must postulate the cooperation of the regions of the skeleton of the macromolecule adjacent to the side chain to explain the observed laws obeyed by the dipole-radical losses, especially when the side chain is short.^[4]

An analogous conclusion has been drawn in a study of the relaxation process (by the dynamic-mechanical method) involving the mobility of the side groups in the glassy state in the polyolefins, for which the structural formula of the monomer unit has the following form:



In the polyolefins, the presence of the peak in $\tan \delta$ (or J'') at 150°K cannot be explained by a change in the configuration of the side groups alone, treating the main chain as being completely excluded from the molecular motion in the glassy state.

Thus, we must recognize that even in the glassy state, in which the overall conformation of the main chain is frozen, it retains local mobility, and participates in the molecular motion along with the adjacent portion of the side chain. However, the amplitude of vibrations of such a kinetic radical with respect to the equilibrium position will be small. On going over to the rubbery state, this type of motion will persist, but a second type will be superimposed on it: the motion of chain segments in cooperation with the segments of neighboring molecules. Here, when one uses the method of dielectric losses and polarization, the polar group can perform certain rotations about an axis along the main-chain direction, in addition to being oriented in the process of vibrational motion.^[28] This type of transition, which is accompanied by a change in the configuration of the main chain, is responsible for the appearance of the peak of the dipole-elastic losses or the α -process in the dynamic-mechanical losses.

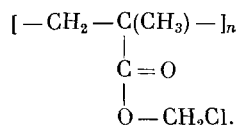
At high temperatures, the kinetic energy of the chain becomes sufficient to overcome the intermolecular interactions and to break down the long-range cooperative interaction. At the same time, the flexibility of the main chain grows, owing to the increase in freedom of internal rotation. This entails a shortening in the kinetic segment. Here conditions can arise under which the length of the kinetic segment of the main chain becomes comparable with the length of the kinetic radical (counting the number of carbon atoms of the main chain alone), i.e., they become identical. Under these conditions, which arise only at temperatures considerably above T_g , one observes the merging of the characteristics of the dipole-radical and dipole-elastic relaxation processes, as was shown in Fig. 2. This is also corroborated by the merging of the relaxation processes observed by the method of mechanical-dynamic losses.

Thus, throughout the attainable temperature range, the motion of a group occurs in correlation with local displacements of the main chain whenever it is directly linked to the main chain. At very high temperatures, the laws that it obeys will coincide with the kinetic properties of the main carbon chain.

In conclusion, we should discuss a third type of molecular motion in polymers: a motion of the dipole-radical type, which is inherent in kinetic radicals distant from the main chain. An example of such a kinetic unit might be the end group of a sufficiently long side chain. Sinnott^[30] has observed the motion of CH_3 and C_2H_5 groups at the ends of the side chains of polymethylmethacrylate and polyethylmethacrylate, by the methods of mechanical-dynamic losses and nuclear magnetic resonance, respectively. This type of molecular relaxation has been observed in a study of the mechanical-dynamic losses in polyalkylmethacrylates.^[29]

It has been established that independent motion of the end group of a side chain is possible when the

OC=O group, whose motion is highly correlated with the main chain, is followed by a chain of at least three methylene groups. Thus, this type of relaxation was observed in the higher homologs of the series, starting with polypropylmethacrylate. The dielectric method was used in studying the polyhalogenated derivatives of the alkyl methacrylates, the ends of the side chains being "marked" by the polar CCl group. This made it possible to establish the fact that this form of molecular motion can be observed by the dielectric method even for poly- α -chloromethylmethacrylate, which is a structural analog of polyethylmethacrylate:^[65]



Hence, the side chain of the polymers of the alkyl methacrylate series having one methylene group is flexible enough for it to participate in the molecular motion in two ways. This entails the appearance of two regions of dielectric losses of the dipole-radical

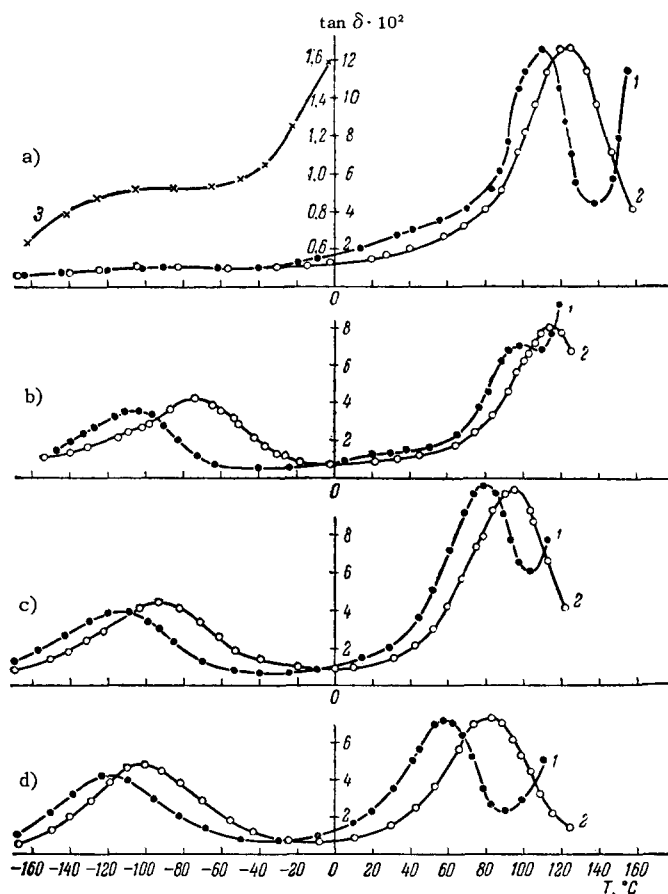


FIG. 6. Temperature-dependence of $\tan \delta$ for: a) poly- α -chloromethylmethacrylate, b) poly- β -chloroethylmethacrylate, c) poly- γ -chloropropylmethacrylate, and d) poly- δ -chlorobutylmethacrylate. 1 - 400 cycles/sec; 2 - 10 Kc; 3 - 400 Kc. The scale for curve 3 is given on the left-hand side of the axis of ordinates.

type (Fig. 6) (at -100 – 120° and at $+20$ – 40°C). However, as we see from Fig. 6, the value of $\tan \delta_{\max}$ for the low-temperature losses for poly- α -chloromethylmethacrylate is almost four times smaller than for the subsequent homologs of this series. In addition, as the homolog number increases, the peak in $\tan \delta$ shifts to lower temperatures. This means that the relaxation times of the process being studied are decreasing. Consequently, lengthening of the chain of methylene groups in the side radical weakens the intramolecular correlation existing between the end portion of the side chain and the C=O group, whose motion in turn is correlated with that of the main chain. Thus, in poly- α -chloromethylmethacrylate, a motion occurs in a kinetic radical formed by the terminal polar group, and its mobility increases with lengthening of the aliphatic portion of the side chain.

The aim in what has been said above is to show that molecular motion in polymers is a very complex process. Both the segmental motion of macromolecules and the local conformational motion, which take place within relatively small volumes, and occur at temperatures either below or above the glass-transition temperature, depend on the chemical composition and structure of the monomer link, on the mode of packing of the chains, and on the temperature. For low-molecular-weight substances, changes in the form of thermal motion involve only the temperature, and occur at phase-transition points; for polymers, in distinction, the time factor is of paramount importance, together with the temperature. A change in the form of thermal motion in a polymer is not accompanied by a change in the state of aggregation, but is entirely determined by the temperature-time conditions of the experiment.

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