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SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

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CONTENTS

I. Introduction 103
II. Methods for the experimental investigation of self-diffusion and interdiffusion in polymer systems 103
III. Mechanism of self-diffusion and interdiffusion of polymers 105
IV. Influence of time, temperature, and concentration on self-diffusion and interdiffusion in polymers 106
V. Influence of molecular structure and properties on self-diffusion and interdiffusion in polymers 107
VI. Importance of self-diffusion and interdiffusion in the processing and application of polymers 112

I. INTRODUCTION

During the past two decades the diffusion of substances of low molecular weight in high polymers has formed the subject of numerous researches by both Soviet and foreign investigators, among whom must be mentioned Reitlinger, Zhurkov, Ryskin, Malinskii, and Vasenin in the Soviet Union, and Barrer, Crank, Long, Park, Auerbach, Van Amerongen, McCall, Stamm, and many other workers abroad. In contrast, the phenomena of self-diffusion in polymers and of the diffusion of one polymer into another (interdiffusion) have remained little investigated because of the great experimental difficulties and the complexity of the theoretical interpretation. Nevertheless, these phenomena are of great scientific interest and immense practical importance. As we shall see below, very many properties of polymers are to some extent linked with the ability of flexible macromolecules or their segments to diffuse. The capacity for self-diffusion and interdiffusion of polymers is no less important for their processing and application.

The purpose of the present review is to summarise results on the self-diffusion and interdiffusion of polymers having flexible molecules (elastomers) and to outline directions for future research on this problem.

II. METHODS FOR THE EXPERIMENTAL INVESTIGATION OF SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

The first experimental investigations of self-diffusion were based on a study of the self-adhesion of polymers, which several workers have shown[1-5] to depend on the interpenetration and intertwining of flexible macromolecules under the influence of thermal motion. The method consisted in placing two specimens of the same polymer in

contact with one another for a definite time, and determining the resistance which must be overcome to separate them[6,7]. From the dependence of self-adhesion on temperature this method enables the apparent activation energy of the process to be calculated by means of an equation analogous to the Arrhenius equation, on the assumption that the strength of the bond produced by self-adhesion is a measure of the diffusibility of the polymer.

On the basis of the results obtained for self-adhesion, several qualitative hypotheses were made, at the very beginning of the past decade, concerning the mechanism of the self-diffusion and interdiffusion of polymers, as well as the dependence of these processes on particular characteristics of the polymer, such as molecular weight, the proportion of three-dimensional structures, the degree of branching of the macromolecules, and the presence of polar groups in the latter. The method used also enables the exponential temperature dependence of the self-diffusion (self-adhesion) of polymers to be established. Such a dependence is characteristic also of the diffusion of substances of low molecular weight[8].

In 1952 Bueche *et al.*[9] first reported measurements of the self-diffusion of polymers by a tracer method. Plasticised polystyrene prepared from styrene labelled with the ^{14}C isotope at the second atom in the side-chain and a copolymer prepared from 99% of n-butyl acrylate and 1% of labelled styrene were used. Measurements of diffusion were made by the method of Rayner *et al.*[10], in which a thin layer of the radioactive substance is deposited on a flat block of the same substance possessing no radioactivity. As the radioactive substance diffuses into the non-radioactive, the β-ray intensity, measured on a counter placed over the specimen, decreases through absorption of the rays by the material of the block. Thus the rate of diffusion can be assessed from the decrease in intensity of the radiation.

The above work showed that the coefficients of self-diffusion, which lay within the range 10^{-11}–10^{-12} cm^2 s^{-1}, were roughly inversely proportional to the viscosity of the polymer. The activation energy of self-diffusion calculated from these results for the n-butyl acrylate–styrene copolymer was 13.2 kcal mole^{-1}, the activation energy for viscous flow of the same copolymer being 13.8 kcal mole^{-1}. Similar results were obtained in other cases: the activation energies of self-diffusion and viscosity were the same within the limits of experimental error. Since in the opinion of Bueche *et al.* a comparatively simple relation exists between the coefficient of self-diffusion and the viscosity, and since it is far easier to measure the latter than self-diffusion, Bueche considers[11] that this relation provides a simpler method for assessing molecular motion in a solid polymer.

Quite recently Bresler *et al.*[12] have also investigated the diffusion of polymers by means of labelled atoms. By an analogous method to the above[10] they have examined the diffusion of macromolecules of tritium-labelled synthetic polyisoprene into natural rubber.

The temperature of the specimen in the diffusion measurements could be adjusted between 22° and 140°. The coefficient of diffusion into natural rubber of synthetic polyisoprene having molecular weights within the range 8×10^3–2.8×10^4 lies between 6×10^{-13} and 0.9×10^{-13} cm^2 s^{-1} at 100°. In the case of the polyisoprene fraction of molecular weight 1.1×10^4, the coefficient of diffusion into vulcanised natural rubber at 100° was determined, and found to be about 1.4×10^{-13} cm^2 s^{-1}. These values are seen to be considerably lower than those reported in Ref. 9. Nevertheless, the activation energy for macromolecules of molecular weight 11 000 was, according to the results of Bresler *et al.*, 8.7 kcal mole^{-1}, which is just as low as in the case of substances of low molecular weight diffusing into unvulcanised rubber.

From the low activation energies found, quite unrelated to the large molecular volume of the diffusing polymer molecules, Bresler and his coworkers concluded that only a small portion of the polymer chain — probably one or a few monomer units — takes part in each elementary act of diffusion.

In the opinion of these workers[12], the comparatively slight variation in diffusion coefficient found to occur with change in the molecular weight of the diffusing species indicates that the polymer chains are not entangled, at least up to a molecular weight of 30 000. According to Bresler, this supports the bundle hypothesis of polymer structure developed by Kargin *et al.*[13,14] The observed lower coefficient of diffusion into vulcanised rubber has been explained by the formation of a three-dimensional network in the polymer on vulcanisation, which represents additional resistance to diffusion.

The interdiffusion of different kinds of polymers has been investigated by Krotova and Morozova. In their first paper[15] they had examined under the microscope sections through two-layer films of the polymers. On contact between two non-polar polymers, for example polyethylene and polyisobutylene, the interface was found to be diffuse, from which it was concluded that in this case the establishment of an adhesive bond is due to interdiffusion in the contact zone.

In later work Krotova and Morozova[16] used microscopic observation under ultraviolet radiation to study the boundary between fluorescent polymers. They found that the interface was very blurred in systems formed by non-polar polymers of similar structure. Heat-treatment of duplex films produced a sharp increase in the diffuseness of the boundary. Systems in which the components differed greatly in chemical structure (polar and non-polar) gave a narrow zone of blurring (of 1 μm and less). In contrast to the first paper, the second paper by Krotova and Morozova expresses the view that the blurring of the boundaries is due, not to the diffusion of macromolecules or their segments, but to the transfer of entire structural components from one phase to the other.

From all that has been said above, it is readily seen that investigation of the self-diffusion and interdiffusion of polymers is just beginning. The results obtained can be regarded only as crudely tentative, and a great deal of work remains to be done before the corresponding coefficients can be determined with sufficient accuracy. However, the actual fact of the diffusion of sufficiently flexible molecules, or at least of segments thereof, in the bulk of the polymer, is obviously no longer open to doubt at the present time.

Among the methods available for studying diffusion phenomena in polymers, radiometric methods seem to us especially promising. At one time such methods enabled self-diffusion to be examined in metals[17], and they are now widely employed to study the diffusion of substances of low molecular weight into polymers[18,19]. Methods based on microscopic observation of the interpenetration of polymers, in either ordinary light or ultraviolet radiation, are less suitable owing to their relatively low sensitivity. However, examination of cross-sections of duplex polymer

films under the electron microscope can undoubtedly give extremely interesting information, since in this case a resolution of 15–20 Å may be achieved. The extremely thin sections required for observation of the self-diffusion and interdiffusion of polymers are now readily obtainable with ultramicrotomes.

Infrared spectroscopy could also be used to investigate the interdiffusion of polymers. When two thin transparent films of polymers containing different characteristic groups capable of energetic interaction are brought into contact, the absorption spectrum should change as diffusion proceeds, involving both the appearance of new bands corresponding to such interaction and weakening of the old bands. This could serve as evidence of the penetration by diffusion of one polymer into the other.

Finally, nuclear magnetic resonance may be expected to provide a very useful method for studying the self-diffusion and interdiffusion of polymers. Much work has recently been done on the application of this method to the study of polymers, among which must be mentioned that of Slichter, Sauer, Wall, Woodward, McCall, and several other investigators. These workers have provided valuable information on the motion of polymer segments and on the influence of various factors on this motion. Some of their results will be discussed below.

The self-diffusion and interdiffusion of polymers are sharply distinguished by one feature from the diffusion of substances of low molecular weight into a polymer; whereas a small molecule can diffuse into a substrate completely independently of other molecules of the same substance, this is not the case with the diffusion of polymer segments, since the macromolecules can intertwine with one another, become entangled, and form loops. As a result of the stresses arising in the chains, the diffusing segments may sooner or later cease their forward movement, and the process may come to a halt. The presence of crystallites or other structural elements, for example bundles, may provide a similar obstacle to the further progress of diffusion phenomena. Several papers[20] refer to the significance of the interlacing of molecules in the viscous flow of polymers. However, such flow is caused by the application of an external stress gradient, which tends to orient, straighten out, and hence disentangle the chains[21]. This does not, of course, apply to diffusion.

Thus it may be supposed that the rate of diffusion, represented by the advance of the front formed by the ends of the diffusing polymer molecules, will not be constant, but will gradually decrease with time, and the equilibrium state of the system, corresponding to maximum entropy, will in practice never be reached. This may be the reason for the low values which have been obtained[9,12] for the coefficient of self-diffusion. For the same reason, only methods which enable the interpenetration of molecules to be measured within very short distances (electron-microscopy, radiometry) are suitable for determining the diffusion coefficient of segments of macromolecules.

III. MECHANISM OF SELF-DIFFUSION AND INTERDIFFUSION OF POLYMERS

Present-day views on the mechanism of viscous flow and diffusion in liquids are based on the so-called "hole" theory of liquids put forward by Frenkel'[22–24] and independently by Eyring[25]. Their views on viscous flow and diffusion in liquids of low molecular weight are now widely known[26,27], and we shall not discuss them further. The mechanism of the diffusion of macromolecules in liquids of low molecular weight, and especially the mechanism of self-diffusion and interdiffusion in incompletely vitrified amorphous polymers, the flexible molecules of which are capable of thermal motion, are far less clear and have been far less studied. Nevertheless, it is already possible, on the basis of general considerations, analogies with diffusion in systems formed by simple molecules, and certain experimental results, to visualise roughly the molecular pattern of self-diffusion and interdiffusion in polymers.

In amorphous polymers having flexible molecules, just as in liquids of low molecular weight, short-range order is present but long-range order absent. As in ordinary liquids, holes or microvoids occur in such systems. However, these microvoids are not large enough to contain an entire molecule. Furthermore, in a high polymer the position of each monomer unit is determined not only by interaction with units in neighbouring molecules but also by adjacent and more remote units in the same chain. Therefore the simultaneous displacement of the whole macromolecule to a new position is impossible: it would require too high an activation energy.

With sufficiently flexible macromolecules, however, individual segments may move, forming in this case the kinetic units. As a result, any segment of the molecular chain which is close to a microvoid can be displaced without producing a change in the arrangement of the other parts of the macromolecule. Such movement obviously does not require too great energy to overcome the activation barrier. Thus the elementary process in the self-diffusion or interdiffusion of elastomers is an intermittent transition to a fresh equilibrium position, not of the whole macromolecule but only of a segment thereof, comprising a comparatively small number of carbon atoms. The activation energy for displacement of a molecule approaches asymptotically a definite value as the number of carbon atoms in the linear molecule increases to 25–30. Moreover, it has been shown by an extrapolation method that the activation energy of viscous flow in linear hydrocarbons of high molecular weight is equal to the activation energy required for the viscous flow of segments consisting of about 20 carbon atoms[28,29]. On this basis Eyring considers that, for sufficiently long chains, the mean size of a segment which can move in the above way is a chain length comprising 20–30 atoms. Flory reached similar conclusions[30].

The size of segment representing the kinetic unit is not, of course, constant, being determined primarily by the flexibility of the molecular chain, the intensity of molecular interaction, and the temperature. It is also obvious that segments of different sizes can take part in self-diffusion and interdiffusion.

The movement of segments of a macromolecule always produces some change in conformation of a chain molecule. As a result, a large number of successive movements of segments will lead not only to a change in shape of the macromolecule (Kuhn's micro-Brownian motion) but also to a shift in its centre of gravity, *i.e.* to a "wandering" of the macromolecule in the mass of polymer (macro-Brownian motion). Of course, owing to the very high viscosity of the system, movement of the whole molecule in the mass of polymer will be extremely slow, and in some cases, when sufficiently strong intermolecular bonds are formed, may be completely absent.

In the absence of external forces, the micro-Brownian and macro-Brownian motion of a polymer chain molecule is completely random, in any direction. The action of external forces, for example a shear stress, affects both types of motion. Macro-Brownian motion will then take place irreversibly, and a process of flow will start. Micro-Brownian motion, if unaccompanied by relative movement of whole molecules, will produce orientation of the molecules in the direction of the force. After the force has ceased to act, however, the molecules will again adopt the thermodynamically most probable conformations as a result of the action of conformational (entropy) elasticity caused by the micro-Brownian motion.

The effect of temperature on the self-diffusion and interdiffusion of polymers is similar to that on the diffusion of simple liquids. With rise in temperature, thermal expansion of the polymer results in the appearance of further microvoids with an increased probability of activation of segments lying close to holes. As a result, the segments will overcome more easily the energy barrier to movement into a microvoid, and diffusion will be more rapid[31].

Brandt[32] has recently put forward the hypothesis that the elementary act of diffusion in polymers consists in two activated polymer chains parting to allow a small molecule (or segment of a macromolecule) to pass through. He considers that the activation energy of diffusion in polymers is made up of an intermolecular component E_i due to mutual repulsion between molecules and their neighbours (*i.e.* internal pressure) and an intramolecular component E_b due to the forces tending to inhibit internal rotation in the macromolecules.

As the temperature is raised, increasing numbers of segments of an individual macromolecule will obviously take part in diffusion phenomena, with an ever increasing kinetic energy. Finally, a point is reached, at a definite temperature, at which the sum of the activation energies for the individual segments exceeds the energy barrier for the whole macromolecule, which will make it possible for the latter to take part in diffusion as a whole. This can obviously take place only if this temperature is below that at which the polymer decomposes.

Quite recently Vasenin[33] has attempted a quantitative approach to the self-diffusion of polymers. On the assumptions that only the terminal portions of molecules are capable of diffusion and that short branches impede diffusion, while sufficiently long branches can themselves act as free ends, he derived an equation linking the strength of the self-adhesion bond with such factors as rate of separation, time of contact, molecular weight of polymer, etc. A test of this equation was satisfactory to a first approximation: graphs of the variation in strength of self-adhesion with time of contact and with molecular weight of the polymer were similar in shape to the corresponding experimental curves[4,6,7], although calculated absolute values of the adhesive strength were greater than the experimental values. The theory also provides a good explanation of the increase in self-adhesion strength with increase in the number of sufficiently long branches, with rise in the contact temperature, and with increase in the polydispersity of the polymer.

Vasenin's theory is still far from perfect. In particular, it is doubtful whether the molecules can diffuse only at their ends. As Vasenin himself points out, it is probable that under certain conditions the middle portions of the chains can diffuse. Further, it seems to us that the theory has not taken into account the effect on diffusion of entanglement of the chains, which has already been discussed above. It is perhaps for this reason that the calculated values of the self-adhesion strength were greater than the experimental values. Finally, the physical significance of some of the coefficients in Vasenin's equation is not entirely clear. Nevertheless, this work is undoubtedly of interest as the first quantitative treatment of self-adhesion, and hence of self-diffusion.

In conclusion it must be stated that the above molecular picture of self-diffusion and interdiffusion is only a crude approximation to the process which actually occurs. At the present time the concept of the bundle structure of polymers[13,14] is becoming more and more widespread. The presence of bundles and other structural elements of higher order (ribbons, lobes, globules) in real polymers must undoubtedly affect self-diffusion and interdiffusion, complicating the elementary act and giving to these processes their characteristic features. Obviously the quantitative theories of these phenomena, too, must be corrected for the presence of supermolecular structures in high polymers.

IV. INFLUENCE OF TIME, TEMPERATURE, AND CONCENTRATION ON SELF-DIFFUSION AND INTERDIFFUSION IN POLYMERS

As already mentioned, very little direct research has yet been done on diffusion and interdiffusion in polymer systems. In writing the present section and the next, therefore, we have made extensive use of the well-known relation between self-diffusion (interdiffusion) and self-adhesion (adhesion) of polymers. Furthermore, in considering the effect of various factors on diffusion phenomena in elastomers, we have been forced to turn, owing to the inadequacy of the experimental data, to analogies between the diffusion and interdiffusion of polymers, on the one hand, and the diffusion into polymers of substances of low molecular weight on the other.

Effect of Time

The variation of the self-diffusion of polymers with time can be assessed from results[6,7], obtained by the separation method, on the dependence of the self-adhesion of polyisobutylenes of different molecular weights on the period of contact. As a result of the interpenetration of molecular chains by diffusion, the self-adhesive strength increased in all cases with time, at first rapidly and then more and more slowly, tending to a definite limit. The increase in self-adhesion strength with time, and hence also the increase in the rate of diffusion, were greater the shorter the molecule. These results indicate that, in the case of polymers, diffusion takes place mainly at the ends of the molecular chains. Other investigators have expressed[34-38] a similar view, most of them considering that during diffusion a linear macromolecule is oriented parallel to the direction of diffusion.

Forbes and McLeod[4] determined the self-adhesion strength from the resistance to rupture of specimens of the same high polymer which had been brought into contact. They found that the period of contact necessary for the self-adhesion strength to become equal to the cohesive strength varied within very narrow limits for different polymers.

Thus this time was only 3–5 min for butyl rubber, while it was 4–5 h for natural rubber and 14–17 h for a butadiene–styrene copolymer. It is significant that in these experiments the limiting self-adhesion strength, equal to the cohesive strength, was reached with all the polymers investigated which had rubberlike elasticity at ordinary temperatures. The situation is different with rigid thermoplastics, which exhibit self-adhesion only at elevated temperatures, as we shall see below.

Insufficient experimental data are available to judge whether or not self-diffusion and interdiffusion of polymers obey Fick's law. In systems comprising a substance of low molecular weight and a polymer at temperatures below the glass point of the latter, the diffusion coefficient usually varies with time[39–41]. Such variation is due either to a change in the properties of the polymer during diffusion, to conformational changes in the polymer molecules with time, or to dissolution of the crystalline regions. However, these considerations do not apply to self-diffusion or interdiffusion, since both these phenomena occur only with polymers which are not in a state of rubberlike elasticity. Another possible cause of the variation with time of the coefficient of self-diffusion and interdiffusion is the stress arising in the diffusing chains owing to their getting entangled or caught up in one another. However, this question requires special investigation.

Effect of Temperature

The temperature dependence of the self-diffusion and interdiffusion of polymers is clear from work on the influence of the contact temperature on the self-adhesion and the adhesion of polymers[6,7,42]. The temperature dependence of the coefficient of self-diffusion has been studied directly[12]. Experiments showed that self-diffusion and interdiffusion increase exponentially with rise in temperature. A similar relation has been found for the diffusion of organic molecules into polymers[19,38,43,44].

The activation energy for the diffusion of organic compounds of comparatively low molecular weight into polymers has been found in several cases[19,38,43] to increase with rise in molecular weight. This is because transition of small molecules from one equilibrium position to another in the course of diffusion requires a greater consumption of energy the larger the molecule. However, study of the temperature dependence of the self-diffusion and interdiffusion of polymers of quite high molecular weight has shown that the activation energy is practically independent of the size of the macromolecule. This confirms that the kinetic unit in the diffusion of chain molecules is not the whole molecule but only a segment thereof.

The increase in the self-adhesion of high polymers with temperature[6,7,42] occurs, of course, only over a certain range of temperatures, between the glass point and the transition point for the state of viscous flow. Below the glass point self-diffusion is impossible, so that self-adhesion is also absent. At temperatures corresponding to viscous flow of the polymer, the self-adhesion strength for a given period of contact is practically independent of temperature, since under such conditions complete coalescence of the polymer surfaces takes place almost instantaneously, and the structure characteristic of the bulk of the polymer is very rapidly established in the zone of contact. A similar situation has been observed in the welding of rigid thermoplastics[45–47].

Similar arguments can be developed for the adhesion of two polymers.

Effect of Concentration

No experimental data are available on the effect of the concentration of polymers on their interdiffusion, and discussion of this question can be based only on general considerations and analogies with the effect of concentration on the diffusion of substances of low molecular weight[48].

In the ideal case the diffusion coefficient is independent of the concentration of the substance which is diffusing. However, its value will be affected by any interaction between the diffusing molecules, an example being provided by the diffusion of water in polyethylene[49]. On reaching a definite concentration, the water molecules which have penetrated the polyethylene begin to form aggregates by hydrogen-bonding which, of course, tends to diminish their mobility and the diffusion coefficient.

On the other hand, simple molecules diffusing into a polymer can rupture the bonds between macromolecules[50,51], resulting in a change (loosening) of the structure of the system into which diffusion is taking place. It is clear that the higher the concentration of substance which has diffused, the greater will be this change, and the more sharply will the diffusion coefficient increase.

Both processes can obviously take place in the interdiffusion of polymers. The resultant effect should ultimately be determined by the relation between the energies of interaction of the diffusing molecules with one another and with the polymer molecules among which diffusion occurs. In this case, of course, the phenomenon may be complicated considerably by purely steric factors, which may be especially significant in the diffusion of polymer into polymer.

V. INFLUENCE OF MOLECULAR STRUCTURE AND PROPERTIES ON SELF-DIFFUSION AND INTERDIFFUSION IN POLYMERS

Effect of Size of Molecules

The relation between the diffusion coefficient of simple molecules moving in a polymer and their molecular weight has been studied by several investigators[19,38,45,52]. According to Auerbach *et al.*[19] the relation between diffusion coefficient D and molecular weight M can be represented by the power function

$$D = KM^{-\gamma}, \quad (1)$$

where K and γ are constants.

However, a far more definite relation was found to exist between the diffusion coefficient and the molecular volume v of the diffusing substance[43,53–55], the former decreasing with increase in the latter, not as a power function, as might be expected from the approximate proportionality of molecular volume to molecular weight, but exponentially:

$$D = Ae^{-\rho v}, \quad (2)$$

A and ρ also being constants. The exponential relation between D and v showed that the volume of a molecule has a greater influence on its rate of diffusion in polymers than has its weight.

In the case of the self-diffusion and interdiffusion of polymers, special interest attaches to the relation between diffusion coefficient and molecular length. This relation has been investigated experimentally in the case of the diffusion of alkanes into polymers by Prager *et al.*[56,57], Aitken and Barrer[37], and McCall *et al.*[58] As was to be expected, increase in the length of the molecule was found to be accompanied by a decrease in the diffusion coefficient, which was especially marked at the beginning of a homologous series.

Vasenin[59] gives the following explanation of the variation of the diffusion coefficient for alkanes into a polymer with the molecular size of the former, on the assumptions that the diffusing molecules are oriented in the direction of their motion and that the drag arising in this case can be calculated in a similar manner to that between two moving layers of a liquid[27]. If in an unbranched alkane molecule consisting of n identical CH_2 or CH_3 groups the mass of each group is m, the speed of the molecule being v, the momentum of an individual group will be mv. As a result of interaction with the relatively immobile macromolecules, each group causes an analogous group in a polymer macromolecule to move with velocity v'. From the law of the conservation of momentum, $mv = 2mv'$, whence $v' = \frac{1}{2}v$. Thus in unit time each group will transmit momentum $\frac{1}{2}mv\nu$, where ν is the frequency of collision between each group and surrounding groups of the macromolecules. The momentum transferred in unit time by all the groups is

$$F = \frac{mv}{2} \nu n. \qquad (3)$$

If this value of F, which represents the drag, is substituted in the well-known Einstein equation, with $\nu = 10^{13}$ s^{-1}, $T = 300$°K, and $m = 16$, the diffusion coefficient is found to be 3×10^{-4} cm^2 s^{-1}. This is an order of magnitude greater than the diffusion coefficient of ordinary liquids. Vasenin explains this discrepancy by the fact that the calculation took account only of the resistance due to friction at the "lateral" surface of the moving molecule, *i.e.* "lateral" or viscous resistance. In order that the molecule can move in the polymer, however, work must be done also in continually separating the macromolecular chains. The magnitude of such work will depend on the size of the gap, which will in turn be determined by the dimensions of the diffusing molecule. Thus according to Vasenin, account must be taken in diffusion not only of viscous drag but also of "frontal" resistance to movement of the molecule.

Vasenin assumes that to a first approximation the resistance to movement of a molecule in a polymer is

$$F = A\frac{mv}{2} \nu S^{\alpha} n, \qquad (4)$$

where S is the cross-sectional area of the leading group in the diffusing molecule, and A and α are constants. Substitution in the Einstein equation of the values found for F gives a relation between diffusion coefficient, S, and n

$$D = \frac{2kT}{Am\nu S^{\alpha} n}. \qquad (5)$$

In much of the work on the diffusion of simple molecules into polymers, the dependence of the diffusion coefficient on the molecular weight of the polymer has also been investigated[19,36,60-64]. The rate of diffusion of gases and substances of low molecular weight, and also the corresponding activation energy of the process, are found to be practically independent of the molecular weight of the polymer. This can be explained by the fact that the microvoids in the polymer, into which the diffusing molecules penetrate, are formed by thermal fluctuations of segments of the macromolecules, the size of which is the same over the range of molecular weights chosen.

The relation between the coefficient of self-diffusion of polymers and their molecular weights was first investigated by Bueche *et al.*[9], who used a radiometric method. In subsequent work Bueche provided a theoretical basis for the experimental relationship. Since Flory[65] had shown that the viscosity of a polymer should fall with decrease in molecular weight, it could be concluded from the experimental results that the rate of diffusion should be greater with polymers of lower molecular weight. As we have seen above, Bresler *et al.*[12] also reached similar conclusions in the case of the diffusion of synthetic polyisoprene into natural rubber at 100°. For this pair of polymers the relation between diffusion coefficient D and molecular weight M of the diffusing species can be expressed by the empirical equation $D = 6.6 \times 10^{-8} M^{-1.31}$.

The dependence of the rate of self-diffusion and interdiffusion on the dimensions of the macromolecules has been investigated indirectly also by Voyutskii *et al.*[7,66,67] in experiments on the self-adhesion and adhesion of polymers. Work with polyisobutylenes of different molecular weights showed[7] that the increase in the self-adhesion strength with time, due to the interpenetration of molecules as a result of diffusion, is greater the lower the molecular weight. In a similar manner it has been shown[66,67] that the rate and depth of diffusion of macromolecule segments of butadiene–acrylonitrile rubbers into a polyamide are greater the lower the molecular weight of the diffusing molecules. An analogous relation between self-diffusion and molecular weight has been observed by Forbes and McLeod in an investigation of the self-adhesion of polyisoprenes of different molecular weight[4].

According to Bueche[11] the presence of free ends of polymer chains results in a loosening of the polymer, thus favouring the occurrence of diffusion processes therein.

The dependence of the diffusion coefficient of high polymers on their molecular weight is certainly also affected by the fact that movement of a macromolecular chain inside a polymer is retarded not only by friction with neighbouring macromolecules but also by segments of the latter getting caught on a diffusing macromolecule. The number of points at which this occurs will be greater the higher the molecular weight. Bueche has made a detailed examination[20] of the role of such attachments in the displacement of molecules in polymers.

Let us now consider briefly the data available on the dependence of the activation energy of diffusion E in polymers on the size of the diffusing molecules. Since E is proportional to the energy required to form a microvoid into which the diffusing molecule or a segment thereof can move, it should be greater the larger the kinetic unit. This has in fact been shown by Van Amerongen[68] and by Mears[69] for diffusion of gas molecules in polymers, the latter obtaining a linear relation between E and the square of the diameter of the molecules.

In the diffusion of alkane molecules into polymers, however, E does not increase indefinitely with increase in chain length, but approaches asymptotically a constant limit[55,70]. This led Kokes and Long to assume that, in the diffusion of alkanes in polymers of the same nature, each elementary act results in displacement of the molecule by the same amount, independently of its length.

The dependence of the apparent activation energy of the self-diffusion of polymers on their molecular weight was first investigated by Voyutskii *et al.*[6,7] in experiments on the temperature variation of the self-adhesion of polyisobutylenes differing in molecular weight. In this case the activation energy was found not to be a function of the molecular weight of the polymer. This was attributed to the uniform size, independent of the length of the molecular chain over the range of molecular weights selected, of the kinetic units taking part in self-diffusion. Later Bresler *et al.*[12] also concluded that the activation energy of diffusion is independent of the molecular weight of the polymer.

Effect of Shape of Molecule

The rate of movement of macromolecules in a polymer is very greatly influenced not only by the length of the diffusing molecules but also by their degree of branching. Aitken and Barrer[37] remark that the introduction of methyl side-groups into a molecule decreases the diffusion coefficient far more than does introduction of the same group into the main chain. According to these workers, the coefficient of diffusion into rubber for butanes and pentanes of different structures decreases in the sequence:

$$n\text{-}C_4H_{10} > n\text{-}C_5H_{12} > iso\text{-}C_4H_{10} > iso\text{-}C_5H_{12} > neo\text{-}C_5H_{12}.$$

Aitken and Barrer found a linear relation between the diffusion coefficient and the product of the minimum dimensions of the diffusing molecule. Park[54] reached similar conclusions from the relation between the diffusion coefficient and the size of the minimum orifice through which a molecule can move.

Vasenin[59] explains the diminished diffusion coefficient in the presence of side-groups by the work which must, of course, be done to increase the size of the microvoid into which the diffusing molecule moves. This work should obviously be proportional to the increase in cross-sectional area of the molecule resulting from the presence of the side-group. Using the above relations for the variation of the diffusion coefficient with the cross-sectional area of the molecule S and the number of group units n, Vasenin obtained the following equation linking the diffusion coefficient D of a given molecule with the diffusion coefficient D_1 of the first member of the homologous series

$$D = \frac{D_1}{\sigma^n}, \qquad (6)$$

where $\sigma = S/S_1$ is the relative increase in cross-sectional area of the molecule due to the presence of the side-group.

An approximate value can be obtained for the relative cross-sectional area of hydrocarbon molecules by determining the linear dimensions of normal and isomeric alkanes[37]. On multiplying the minimum dimensions of isoalkane molecules and of the methane molecule, and dividing the first product by the second, we readily find that for neopentane $\sigma = 2.1$, while for isoalkanes $\sigma = 1.75$. Vasenin compared experimental values obtained by other workers for diffusion coefficients into various polymers with values calculated from the above formula. Although in some cases the difference between calculated and experimental values reaches 30%, this test of the applicability of Vasenin's proposed equation must be regarded as satisfactory. The observed discrepancy between calculated and experimental diffusion coefficients is due to the fact that the latter were taken from different papers and had been determined by different methods. Furthermore, the error involved in determining diffusion coefficients is at best about 10–15%.

The diffusion coefficient is affected by the presence of side-groups not only in the diffusing molecules but also in the chains of the polymer into which these molecules diffuse. In this case, however, the effect of the side-groups on diffusion is usually precisely the opposite, since such groups tend to weaken interaction between molecular chains and result in a less dense packing of the macromolecules in the polymer. The presence of long branches in the macromolecule should have a similar effect on diffusion.

Papers on the dependence of self-adhesion and adhesion in polymers on their structure contain many data on the influence of side-groups and branches in the molecular chains on self-diffusion and interdiffusion.

Voyutskii and Vakula[71] have shown, on the basis of a large number of experimental results, that the adhesion of polymers, due to interdiffusion of the molecules, always falls with increase in the number of side-groups in the molecular chains. Furthermore, adhesion always decreases with increase in volume of the side-groups. Thus with the side-groups CH_3, C_2H_5, and C_6H_5 in the monomer units, adhesion is highest in a polymer containing methyl side-groups, and lowest in one containing phenyl side-groups.

It is interesting that not only do long branches not diminish adhesion but they tend to increase it[71,72]. This is because every sufficiently long branch of a linear macromolecule can act as a separate chain, capable of independent diffusion.

The diminished tendency of polymers to self-diffusion and interdiffusion with increase in the number and volume of sufficiently short side-groups in their molecules agrees well with the fact that the presence of such groups causes a decrease in intensity of micro-Brownian motion. This fact has been shown especially clearly in recent investigations of the segmentary motion of polymer chains in which use was made of nuclear magnetic resonance[73–78].

Effect of Polar Groups

The greater the dipole moment of the diffusing molecule and of the polar groups in the polymer, the smaller is the diffusion coefficient, since detachment of the moving molecule from the group in the polymer with which it is interacting is more difficult. This explains, for example, the well-known fact that the molecules CH_3CHCl_2 and CH_2ClCH_2Cl, which are identical in mass and composition, diffuse in polystyrene at different rates, the polar molecule moving more slowly than the non-polar molecule. Furthermore, increase in the dipole moments and in the number of polar groups in the polymer tends to increase the density of the latter, which also has an unfavourable effect on diffusion.

A decrease in diffusion coefficient with increasing polarity of the polymer in which diffusion is occurring has been observed many times. Van Amerongen[68] showed early that the diffusion of gases in butadiene–acrylonitrile polymers falls with increase in the number of nitrile groups in the copolymer molecules. He also established that the activation energy of diffusion is directly proportional to the cohesive forces acting between the polymer macromolecules. Pavlov and Lorant[79] confirmed a marked drop in the diffusion coefficient of water in poly(vinyl acetate) as

the latter was gradually hydrolysed to poly(vinyl alcohol). Experiments by Malinskii and his coworkers [80] on the diffusion of monatomic gases through polymer films of differing structure also showed that increase in the energy of interaction between macromolecules results in a continuous diminution in the diffusion coefficient.

Voyutskii *et al.*[66] also found, in an investigation of the adhesion of butadiene–acrylonitrile copolymers to a polyamide, that the interdiffusion of polymers diminished with increase in the content of polar groups.

The influence of polar groups on the activation energy of diffusion in polymers was studied by Voyutskii and Shtarkh[7], who determined the temperature dependence of the self-adhesion of butadiene–acrylonitrile copolymers containing different proportions of the nitrile. The apparent activation energy E was found to be higher the greater the nitrile content of the polymer (Table 1). An explanation is that the increase in polarity involves an increase in the energy necessary to ensure that the diffusing segment shall penetrate the microvoid between the molecules.

Effect of Molecular Unsaturation

There are indications[53,81] that molecules containing double bonds encounter less resistance than do molecules of the corresponding saturated compounds to movement through a polymer. Bent[81] attempts to explain this by the increased rigidity of the molecule accompanying increase in unsaturation; with increased rigidity the probability of the simultaneous translational motion of all parts of the molecule also increases. The latter should favour more rapid movement of the molecule. Vasenin[59], who made a detailed study of the relation between unsaturation and diffusibility of a molecule, considers that the smaller drag on an unsaturated molecule compared with a saturated molecule is due to a decrease in the number of individual kinetic units responsible for transferring momentum to the macromolecules of the medium. This can be seen, for example, from a consideration of the motion of the molecules CH_4 and C_2H_4. The latter contains two carbon atoms, but linked by a double bond and representing a single kinetic unit. The drag on methane and ethylene molecules can be written

$$F_{CH_4} = \frac{1}{2} mv\nu, \quad (7)$$

$$F_{C_2H_4} = \frac{Mm}{M+m} v\nu, \quad (8)$$

where M is the mass of the C_2H_4 molecule, and m that of a monomer unit in the polymer, in this case a CH_2 group, so that $M = 2m$. The ratio of the diffusion coefficient of ethylene $D_{C_2H_4}$ to that of methane D_1 gives

$$D_{C_2H_4} = \frac{3}{4} D_1. \quad (9)$$

Diffusion coefficients calculated by means of analogous equations agree with the experimental values to within 10%. Hence Vasenin considers the original hypothesis, that the number of kinetic units capable of transferring momentum diminishes when a single bond is replaced by a double bond, as quite reasonable.

Using the above ideas on the mechanism of the resistance offered by the medium to the movement of molecules containing n carbon atoms, Vasenin derived the following general relation between diffusion coefficient D and number of multiple bonds q

$$D = \frac{D_1 (2n-q)}{\sigma^q n (2n-2q)}. \quad (10)$$

This equation is more general than Eqn.(6), since it allows for the influence on the diffusion coefficient not only of the size and shape of the diffusing molecule but also of its degree of unsaturation.

Eqns.(6) and (10) are, of course, approximate both owing to the simplified scheme adopted in determining the drag on the moving molecule and also because their derivation is based on the assumption that the activation energy of diffusion is independent of the size and shape of the molecule, which is incorrect. Nevertheless, Eqn.(10) can be used to calculate approximate values of the diffusion coefficients of chain segments of different length in polymers of the same nature. Table 2 gives similar values calculated for diffusion in natural rubber. It is readily seen that the calculated values are comparable with values determined experimentally by Bresler and his coworkers for the diffusion coefficient of polyisoprene in natural rubber.

Experiment has shown that unsaturation in the polymer molecules in which diffusion occurs also tends to increase the diffusion coefficient. Auerbach *et al.*[19] showed, in a detailed study of this question, that the diffusion coefficient of octadecane had fallen by 47–61% after saturation of unsaturated polymers by hydrogenation. They found that the activation energy of diffusion in unsaturated polymers is 8–9 kcal mole^{-1}, compared with 10–11 kcal mole^{-1} in saturated polymers.

The presence of double bonds in a macromolecule substantially increases the probability of microvoids being formed in the bulk of the polymer, owing to local rigidity of the bonds and the resulting steric hindrance to the production of closer packing.

The comparatively slight changes in the density of unsaturated polymers resulting from their hydrogenation show, however, that the hindrance to diffusion is not confined to the creation of more favourable conditions for a

TABLE 1.

Nitrile content of copolymer, %	E, cal
19.6	4760
28.0	8670
36.9	16590

TABLE 2. Approximate diffusion coefficients of linear chains and segments of natural rubber.

M	D(40°), cm^2 s^{-1}	D(60°), cm^2 s^{-1}
68	$3.3 \cdot 10^{-7}$	$7.4 \cdot 10^{-7}$
138	$0.7 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$
1360	$0.7 \cdot 10^{-9}$	$1.6 \cdot 10^{-9}$
13600	$0.7 \cdot 10^{-11}$	$1.6 \cdot 10^{-11}$
136000	$0.7 \cdot 10^{-13}$	$1.6 \cdot 10^{-13}$

denser packing of the macromolecules. The fact that the diffusion coefficient of octadecane in completely hydrogenated polybutadiene, polyisoprene, and butadiene–styrene copolymer was still far greater than the diffusion coefficient in polyisobutylene indicates that peculiarities of the carbon skeleton of the macromolecule are of great significance for diffusion processes in polymers.

Effect of Relative Ordering of Molecules and of Phase Constitution of Polymer

All that has been said above about diffusion has applied mainly to typical unvulcanised rubbers, *i.e.* to polymers having the least clearly defined ordering of the chains. However, the view that a large number of elastomers contain, in addition to separate molecules, supermolecular structures — bundles, ribbons, lobes, and other formations — consisting of individual ordered molecular chains, is now finding increasing acceptance. It is clear that the above concepts must be suitably amended for such polymers.

Formation of such structures must result from orientation of the molecules, which can be achieved only by movement of molecular chains or segments thereof in the bulk of the polymer. In either case, of course, the process is none other than diffusion. The breakdown of supermolecular structures, which usually possess considerable lability, is also a diffusion process. It may be supposed that, under certain conditions, whole bundles and even more highly organised structural units may diffuse within the polymer. The possibility of such phenomena in the self-adhesion and the adhesion of polymers is mentioned in the literature [16,71]. Furthermore, since each bundle is a fluctuating structure with a long but nevertheless finite life, molecules may well be transferred, in part or in whole, from the surface of one bundle to another. Clearly, such molecular transfer must always be a diffusion process. Shtarkman *et al.* [82] were the first to point out the possibility of such a phenomenon in the formation of a self-adhesion bond between two portions of polymer containing supermolecular structures and brought into contact. It may also be suggested that a similar process should occur in adhesion, the sticking together of different polymers. One fundamental feature should be observed: apart from the main condition making adhesion possible, which is the capacity of the polymers for thermodynamic compatibility, in this case structural or conformational compatibility is also necessary.

Unfortunately, too few data are yet available to make possible a more detailed examination of diffusion processes in polymers containing supermolecular structures.

Far more experimental information is available on the way in which diffusion in polymers is influenced by the mutual ordering of the macromolecules, involving such factors as the compactness of their packing (density of the polymer), the degree of orientation of the molecular chains, the phase constitution of the polymer, etc.

The density of a polymer can be regarded as an indication of the volume of microvoids present. The diffusion of simple molecules or segment of macromolecules in a polymer must obviously be linked with the tendency for microvoids to be formed in the polymer, with the volume of such microvoids, and also with the passage of the diffusing kinetic units from one microvoid to another.

The relation between the diffusion coefficient of octadecane in various polymers and their density was investigated by Auerbach *et al.* [19], who showed that in general the rate of diffusion decreases with increase in density of the polymer, the decrease being more rapid with saturated than with unsaturated polymers.

Brandt [64] also found a decrease in diffusion coefficient with increase in polymer density for the diffusion of ethane into polyethylene. He assumed that such diffusion occurs only in the amorphous regions, the diffusion coefficient being about 3×10^{-6} cm^2 s^{-1}.

Tikhomirova *et al.* [80] showed that an increase in the packing factor, *i.e.* an increase in the proportion of the space occupied by the substance of the polymer, decreases the diffusion coefficient for a gas.

The effect of the proportion of crystalline phase in a polymer on the rate of diffusion of gases through it was studied in detail by Van Amerongen [68], who showed that crystallisation causes a decrease in the diffusion coefficient.

Auerbach *et al.* [19] found high activation energies for diffusion of organic substances in crystalline polyethylene and balata, 12.2 and 16.3 kcal mole^{-1} respectively. Klute [83] also found that the activation energy of diffusion increases with increasing content of crystalline phase in the polymer. The low diffusion coefficients and high activation energies of the process in crystalline polymers are obviously explained by the denser packing of the macromolecules in such polymers. On the other hand, Zhurkov and Ryskin [43], as well Jeschke and Stuart [84], observed an increase in activation energy when polymers passed, with rising temperature, from the crystalline and vitrified states into a condition of rubber-like elasticity. The first two workers explain such a relation, which does not fit our usual ideas on diffusion in polymers, by the temperature dependence of activation energy. Jeschke and Stuart are inclined to explain this phenomenon as due to the occurrence of diffusion mainly in regions of the crystalline phase having a distorted structure or at the interface between amorphous and crystalline phases.

Many workers have investigated molecular motion in crystalline and crystallising polymers by the method of nuclear magnetic resonance, determination of dielectric relaxation, etc.

Slichter [76,77] assumes that the motion of segments of macromolecules in polymers consists of a combination of different types of movement, the motion in crystalline regions of polymers differing in nature from that in amorphous regions. In the former, only vibrational motion of the carbon atoms about the C–C bonds is, obviously, possible. In amorphous regions, however, the segments can undergo rotation and translation, the extent of which is determined by the crystallinity of the polymer: Kline *et al.* [74] showed that increase in size of the crystalline regions produces additional stresses limiting the mobility of the polymer chains in the amorphous regions.

A rise in temperature results in fusion of the crystallites, with increased mobility of the molecular chains. Woodward *et al.* [75] investigated the motion of segments of polybut-1-ene macromolecules, and established that, within definite temperature ranges, large portions of the macromolecules undergo cooperative movement between the crystallites. Such movement is, of course, prevented by a high degree of ordering and denser packing of the macromolecules. For this reason the mobility of the segments in iso-

tactic polypropylene is lower than the corresponding mobility in the atactic polymer [73,76].

The movement of the segments is limited also by various interactions between neighbouring macromolecules. Thus in polyamides this will be represented by bonds between CONH groups in neighbouring chains; and in butadiene–acrylonitrile polymers by bonds between CN groups, etc.

Any weakening of intermolecular interaction in some way (by rise in temperature, introduction of non-polar groups into the molecule, etc.) results in more vigorous movement of the segments in these polymers [85].

Effect of Presence of Three-Dimensional Structures in the Polymer

The influence of the degree of cross-linking of polymers on their permeability to gases was studied in detail by Barrer and Skirrow [53], who showed that the diffusion coefficient falls with increase in the quantity of combined sulphur. Similar results were obtained by Aitken and Barrer [37] for specimens of rubbers which had been cross-linked with peroxides. It was found that the diffusion coefficient diminishes with increasing degree of cross-linking of the polymer, varying in direct proportion to the length of chain between two adjacent cross-links.

Malinskii *et al.* [80] have investigated the influence of the cross-linking action of radiation (^{60}Co γ-rays) on the diffusion of gases in various polymers. They showed that the rate of diffusion of gases in irradiated polyethylene, polyamides, and SKS-30 rubber is lowered, probably because of the formation of cross-links between the macromolecules.

Auerbach *et al.* [19] investigated the diffusion of octadecane into natural rubber which had been vulcanised with dicumenyl peroxide. Instead of the expected fall in diffusion coefficient with increasing degree of cross-linking, diffusion was found to be improved at low degrees of cross-linking. It is probable that under these conditions lattice defects (free ends and interlocking loops) play an especially large role, destroying the compactness of the polymer structure and favouring the formation during vulcanisation of larger microvoids than in the crude rubber.

It is interesting that a similar relation had been found earlier by Voyutskii and Shtarkh [7] in an investigation of the self-adhesion of natural rubbers with different degrees of cross-linking. These workers explained the increase in self-adhesion at the start of vulcanisation by the increased extent of diffusion resulting from breakdown of the intermolecular bonds or even of the macromolecules themselves owing to oxidative degradation. Further vulcanisation produces a three-dimensional structure with a marked decrease in diffusibility of the cross-linked polymers.

Raevskii and Voyutskii [86] have studied the decrease in adhesion produced by the cross-linking of polymer molecules.

Bresler *et al.* [12] have used the radiometric technique described above to study directly the effect of the cross-linking due to vulcanisation on the interdiffusion of polymers. With polyisoprene of molecular weight 11 000 the diffusion coefficient was considerably lower in vulcanised than in unvulcanised natural rubber. Bresler explains this by the cross-linking of macromolecules into a three-dimensional network during the vulcanisation of rubber, the cells of this structure offering further resistance to diffusion.

The sharp fall in diffusibility accompanying vulcanisation of a polymer is associated with immobility of comparatively large sections of the molecular chain. This is indicated by the very slight influence of vulcanisation on the ability of short chains and individual groups to take part in the ordinary molecular motion, as revealed by nuclear magnetic resonance [77].

VI. IMPORTANCE OF SELF-DIFFUSION AND INTERDIFFUSION IN THE PROCESSING AND APPLICATION OF POLYMERS

Significance of Self-Diffusion for the Viscoelastic Properties of Polymers

Since diffusion phenomena underlie viscosity [22-30], the role of self-diffusion in the flow of polymers is obvious. This problem which has been studied in detail by both Soviet [87-89] and foreign [29,90,91] investigators, is thoroughly discussed in many present-day monographs and textbooks [92-95], and need not be considered here. However, the self-diffusion of segments is of great significance also for the elastic properties of polymers, as follows from the entropy character of rubberlike elasticity.

The diffusion character of rubberlike elasticity follows from the work of Frenkel' and also of Kargin and Slonimskii published during 1938–1949. The diffusion theory of the viscoelasticity of polymers was developed abroad by Kirkwood [96], Rouse [97], and Zimm [98]. Quite recently Mooney [99] has given a detailed analysis of this theory and suggested the appropriate mathematical treatment.

The diffusion theory of viscoelasticity predicts a distribution of relaxation times which agrees quite well with experiment. According to the suggested mechanism, when the statistical distribution of conformations of chain molecules is disturbed under the influence of an external load, the new conformations are not initially in the statistical equilibrium corresponding to this load. As a result, they gradually change towards the establishment of a new equilibrium. These changes in conformation are a consequence of the thermal kinetic motion of individual segments of chain molecules, *i.e.* of constrained diffusion. After removal of the applied load, the polymer specimen contracts owing to the reverse diffusion of the segments, due to their thermal motion and the tendency of the molecule to adopt the most probable conformation.

The theory ignores purely viscous resistance to deformation, which is typical of a liquid and which arises from simultaneous relative motion of chain segments. However, this resistance is usually extremely small compared with viscoelastic forces resulting from changes in entropy. Where it cannot be neglected, it can readily be allowed for in the modern theory.

Significance of Self-Diffusion for the Self-Adhesion of Polymers and for Their Processing

The phenomenon of self-adhesion, which underlies several technically important processes in the treatment and application of polymers, consists essentially in self-diffusion. Zhukov and Talmud [100] were the first to pay attention to self-adhesion. Later it was studied by several Soviet and foreign scientists [1,2,4-7]. A detailed description

of the phenomenon and a comprehensive bibliography will be found in a monograph on the subject[3].

The correctness of the view that self-adhesion results from the self-diffusion of macromolecules or their segments is supported by the dependence of self-adhesion on the time and temperature of the contact[2-7], by the closeness of its activation energy to those of diffusion processes, and by the characteristic influence of the size, shape, and structure of the polymer molecules on self-adhesion, as discussed above.

Of course, the concept of self-adhesion as caused by the interlacing of separate chain molecules by diffusion is to some extent simplified. It is more or less applicable only to those high polymers whose structure corresponds to a "felt" model. When bundles or structures of higher order are present in the polymer, the phenomenon of self-adhesion is considerably more complicated, although its primary cause remains self-diffusion. It may be supposed[82] that in this case self-adhesion will consist, in effect, mainly in the partial transfer by diffusion of macromolecules from bundle structures in one polymer layer to similar structures in the other layer.

Self-adhesion, and hence self-diffusion, form the basis of such important processes in polymer technology as milling, mastication, and the processing on mixing equipment in general. First of all, the flow of a polymer between the rollers of a mill or the rotors of a mixer is ultimately due, like any flow of polymers, to the diffusion of both molecular segments and entire molecules. Furthermore, if self-diffusion did not exist, processing of a polymer on mixing machinery, for example the milling of raw rubber or of vulcanised stock, would yield crumbs or sheets of loosely attached layers of the mixture, instead of a coherent and durable mass. It is only as a result of the self-diffusion of macromolecules that the thin layers of raw rubber leaving the gap between the rollers adhere firmly to one another and form a thick, solid sheet. Unfortunately, as far as we are aware, no one has studied the role of self-adhesion in the processing of mixtures using mixing equipment.

Self-diffusion phenomena are also of great importance in calendering. In particular, the diffusion of macromolecules and segments thereof while the mixture is between the rollers of the calender is explained by the anisotropy of the mechanical properties of the mixture, the so-called calender effect. Diffusion also explains the diminution in the calender effect when the mixture is stored, and its complete disappearance when the calender mixture is heated[101].

The manufacture of rubber goods and the covulcanisation of rubber stock are also based on self-adhesion and hence on diffusion. In the latter case, diffusion of macromolecules takes place during the first period of vulcanisation, when the temperature is still quite high but cross-linking by the formation of sulphur bridges between the molecules has not yet occurred[102]. Sometimes, special substances are added to polymers to increase self-adhesion[103,104].

Diffusion of macromolecules is responsible also for the firm bonding of the layers in multilayer rubber and rubber-fabric goods made both with and without the use of rubber adhesives. In both cases the article is vulcanised after assembly, which further strengthens the self-adhesion bond.

Diffusion is equally important in the welding of thermoplastics[105]. The welding of transparent poly(methyl methacrylate) and some other thermoplastics exhibits all the characteristics of self-adhesion[45-47]. At temperatures corresponding to a state of rubberlike elasticity, when only chain segments can diffuse, the strength of a welded seam in poly(methyl methacrylate) hardly ever reaches the cohesive strength of the material. At temperatures above that for transition to a state of viscous flow where complete macromolecules can diffuse, the strength of a weld is usually equal to that of the massive material.

For this transparent plastic, when the polymer chains were initially oriented with the macromolecules in the plane of the weld, far greater strength was obtained, on welding at temperatures corresponding to a state of rubberlike elasticity, than with the molecules oriented perpendicular to the plane of the weld. This is because in the former case interdiffusion and interlacing of the macromolecule segments take place readily, whereas in the latter case the diffusion of segments parallel to the direction of orientation is extremely difficult.

Diffusion also underlies the moulding of articles from powders or granulated thermoplastics[106,107]. It has been established that the sintering properties of moulding powders deteriorated with increased content of polar groups in the polymer, with increase in the molecular weight of the latter, and with decrease in the plasticiser content. This is completely consistent with the effect of these factors on self-adhesion. It has also been shown that powdered "cross-linked" polymers are incapable of complete irreversible sintering. The explanation given[108,107] for this fact is that the presence of cross-links raises the flow point of the polymer, ultimately to above the decomposition temperature. In our view this is due to the presence of bonds between the molecules, which prevent interdiffusion of the latter.

In the production of goods from moulding powders the interesting fact has been observed that increasing the pressure above a certain high value impairs the solidity of the specimen and lowers its strength. This has been explained by the increase in rigidity of the thermoplastic macromolecules with increase in pressure, which, of course, impairs their capacity for self-diffusion.

In conclusion we may note that self-diffusion and self-adhesion explain the formation of films from dispersions of elastomers, natural and synthetic latices. All attempts to explain film formation in such systems by simple coalescence of particles[108-110] have proved unsuccessful, as one of us has shown[111]. The production of continuous, stable, and water-resistant films by the simple drying of aqueous dispersion of elastomers is possible only as a result of the interdiffusion of macromolecules belonging to adjacent particles in the film. Dispersions whose polymer phase is in a vitreous state form a powder, not a continuous film, on being dried. However, such dispersions can yield continuous films at a high temperature, when the polymer passes into a state of rubberlike elasticity or of viscous flow and when interdiffusion becomes possible.

The mechanism by which a continuous film is formed from a dispersed elastomer differs from ordinary self-adhesion only in the fact that a layer of stabiliser is usually present on the surfaces of the dispersed particles, which complicates diffusion. Such stabiliser either remains in the film as discrete inclusions or a network, conferring heterogeneity on the film, or else it dissolves in the polymer. In the latter case the stabiliser may even favour diffusion and the formation of a homogeneous film,

owing to its effect in swelling and softening the surface layers of the polymer globules. It is the presence of stabilisers on the surface of the particles in a dispersion and their differing behaviour in film formation which explain the multiplicity of microstructures possessed by dispersion films. The mechanism of the formation of films from polymer dispersions has been discussed in several papers [112-115] and also in a special monograph [116].

Self-diffusion plays an important part, of course, not only in the preparation of films by drying but also in their production from latices by gelatinisation [117].

Significance of Interdiffusion of Polymer for Adhesion, the Reinforcing Action of Fillers, and the Compatibility of Polymers

According to the diffusion theory of the mutual adhesion of polymers developed by Voyutskii and his coworkers [42,66,71,118-121], the difference between adhesion and self-adhesion consists solely in the fact that the latter involves self-diffusion — *i.e.* identical molecules diffuse — whereas adhesion involves the interdiffusion of macromolecules of two different types. When one of the polymers is an elastomer, while the other is a rigid-chain polymer, diffusion is usually restricted, of course, to the penetration of macromolecules of the first polymer into the second However, interlacing of the chains occurs in this case, too. It is clear that such an explanation of adhesion is applicable only when these two polymers are to some extent compatible, since it is only under such conditions that interdiffusion is possible. On the other hand, it is well known that incongruous polymers possess poor adhesion to one another, and this case is of comparatively slight practical interest. The importance of the mutual solubility of high polymers for their adhesion was pointed out by Voyutskii [122], who proposed using the adhesion of high polymers to one another as a measure of their compatibility. Later Deryagin [123], who also emphasised the link between compatibility and adhesion, suggested assessing the latter from the former.

The importance for adhesion of the mutual solubility of the components, which is determined mainly by the relative polarities of the high polymers [124], is fully consistent with de Bruyne's well-known empirical rule, according to which strong adhesion is possible only when both high polymers are either polar or non-polar, but is difficult when one polymer is polar while the other is non-polar.

The fundamental difference between the diffusion theory and other theories of adhesion is that the former regards the formation of an adhesive joint as a bulk rather than a surface phenomenon. As a result of diffusion the boundary between adhesive and substrate disappears, and a peculiar kind of junction is formed, representing a gradual transition from one polymer to the other.

Evidence for the diffusion theory of adhesion is provided by the dependence of the strength of an adhesive joint between two polymers on time and temperature. Thus, for example, as in self-adhesion, the strength of the bond increases with duration of contact, tending to a definite limit. However, this increase is far slower in a normally vitrified or even crystalline substrate, probably because diffusion occurs with great difficulty. The diffusion theory finds very good support in the variation of adhesion with the size, shape, and polarity of the high polymer molecules [68,71,119,125-127].

Many facts supporting the diffusion theory of the adhesion of polymers to one another are given in a review [128] and in a monograph [3].

It has recently been argued against the diffusion theory that the diffusion of elastomer molecules into dense polymer substrates, for example regenerated cellulose film, is impossible [129]. To this it must be retorted that, as we have already mentioned, the adhesion of polymers is in effect their mutual dissolution. It is clear that in this case the ends or intermediate segments of an elastomer molecule bearing polar groups can penetrate the regenerated cellulose film in exactly the same way as water penetrates it when the film swells. It must be remembered that very shallow penetration (of the order of 10 Å) is sufficient to increase the adhesive strength many times [130]. Moreover, even if the elastomer as a whole is incompatible with the substrate, certain groups or chain segments in its molecules, which have a similar nature to some portion of the substrate surface, may penetrate the latter (diffuse to a limited depth), *i.e.* a process which can be termed "local diffusion" may take place.

The diffusion theory was put forward in the first instance to explain the adhesion of polymer to polymer. However, it is very likely that diffusion plays an important part also in the adhesion of high polymers to glass, metals, and other surfaces. Experiment has shown [131], for example, that the adhesion of elastomers to glass depends on time and temperature of contact, as well as on the molecular structure of the elastomer, in just the same way as does self-adhesion or the adhesion of elastomers to one another. A possible explanation is that the elastomer molecules diffuse either into the surface layer of the glass or into a thin, comparatively loose film of weathering products. The probability that segments of polymer chain molecules diffuse into the surface layer of glass was first pointed out by Korolev [132]. If, of course, the surface layer contains very fine cracks and pores, several molecules can penetrate simultaneously into these submicroscopic spaces, and then we ought to speak not of diffusion but of polymer flow.

Similar results have been obtained in our laboratory for the adhesion of elastomers to various metal surfaces. The elastomer molecules can diffuse into, for example, a comparatively loose layer of the oxide film which is practically always present on a metal surface. It has been reported [133] that the adhesion of polymers to aluminium sheet is considerably increased by the formation of a thick oxide film on the surface of the latter.

It would be wrong to conclude from this that the sole cause of adhesion is always the penetration of adhesive molecules into the surface layer of the substrate, *i.e.* their diffusion through the interface. This is not always so even in the adhesion of polymer to polymer. Voyutskii [120] and also Morozova and Krotova [134] considered in detail the systems and conditions to which a diffusion mechanism of adhesion is applicable and where adhesion must be explained by other causes, for example, adsorption or formation of an electrical double layer. Even with an adsorption mechanism of adhesion, however, diffusion phenomena may play a large part in the formation of a strong adhesive bond. It has been suggested [135,136], for example, that maximum adhesion occurs when the maximum number of active (polar) groups in adhesive and in substrate come together in the interface. Such coincidence, of course, is not achieved immediately, especially if adhesive and substrate are brought into contact in the absence of solvent, but is accom-

plished by the diffusion of flexible adhesive molecules along the substrate surface, which takes time. Similar arguments can be worked out when adhesion is due to electrical forces. In this case correspondence between electron--donor and electron-acceptor groups is necessary, and is also obtained by the diffusion of adhesive macromolecules along the substrate surface.

In addition to "surface" diffusion, the diffusion, from the bulk of the adhesive to the substrate surface, of macromolecular segments containing active groups can also play an important part in the adsorption or the electrical mechanism of adhesion. Such diffusion, followed by interaction between the groups which have diffused and active groups in the substrate, can also produce a considerable strengthening of the adhesive bond with increasing contact time.

The phenomena accompanying addition of a filler to a polymer are very closely related to adhesion. The mechanical properties of a filled mixture must in some measure resemble those of an adhesive joint, the polymer in the filled mixture obviously representing the adhesive, and the filler acting as substrate. In other words, a filled mixture is essentially an extremely complicated adhesive joint, consisting of a multiplicity of alternating layers of solid substrate (filler) and layers (films) of polymer. If this view is correct, diffusion phenomena at the polymer–filler interface, resulting in increased interaction between the two components of the mixture, should be of as great importance for the reinforcing action, as for ensuring good adhesion. In our view research on these lines might make a very valuable contribution to an understanding of the mechanism of strengthening.

In conclusion we may mention that diffusion is of great significance in the preparation of mixtures of two or more polymers, such as are extensively used in industry[101,137-139]. It is difficult by simple mixing on rollers or other mixing devices to achieve molecular distribution of one polymer in another, even if these polymers are thermodynamically compatible. There is every reason to suppose that, in the case of mutually soluble polymeric components, a homogeneous system can be formed only as a result of diffusion, with mechanical mixing in machines merely contributing to this. The most rapid formation of a homogeneous system is favoured, of course, by all the factors which accelerate diffusion — rise in temperature, decrease in viscosity by addition of solvent to the system, etc.

Diffusion is responsible not only for the formation of homogeneous systems in the case of compatible polymers but also for the production of microheterogeneities in artificially produced mixtures of thermodynamically incompatible polymers. Such diffusion does not usually terminate in the complete separation of the mixture into two macroscopic phases, but, owing to the great viscosity of the system, results in separation of the mixture only within microvolumes, in which are grouped monomer units of similar properties. Such a microheterogeneous system generally remains a single whole, since individual microregions remain linked to one another by long molecular chains[140].

Unfortunately, only the most general ideas can be discussed concerning the role of diffusion in the mixing of polymers and the separation of their mixtures. As far as we are aware, no one has yet undertaken quantitative investigations on this problem.

Value of Self-Diffusion and Interdiffusion for Studying the Properties of Polymers

In conclusion we may mention that investigation of the self-adhesion and the adhesion of polymers, together with the related phenomena of self-diffusion and interdiffusion, can be used to obtain new information on the structure and properties of macromolecules and on the structure of high polymers, since a close and direct link exists between the structure and properties of macromolecules on the one hand, and the self-diffusion or interdiffusion of polymers on the other. Therefore the study of self-diffusion or interdiffusion by any of the methods discussed in the early part of this review can yield valuable information on some problem associated with the properties of macromolecules or of a polymer.

In addition, methods of determining self-diffusion can be employed to investigate internal friction in polymers. The advantage of these methods compared with the usual methods of determining viscosity is that during diffusion no external force is acting on the macromolecules and the latter are not in a stressed condition.

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