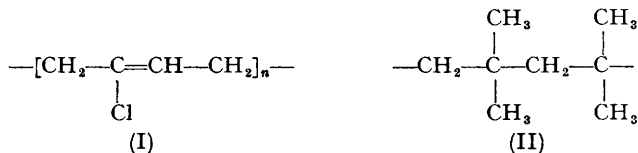


GENERAL DISCUSSION

Dr. P. J. Garner (*Birmingham*) said: Alexandrov and Lazurkin's treatment of high elasticity expounded by Eley and by Tuckett only applies to supercooled liquids. It must be emphasised that the equilibrium state of rubber at low temperatures is crystalline, the melting point being between $+40^{\circ}$ and 50° C. A high elasticity temperature of -70° C. for rubber is only obtained when it is supercooled, which is made possible by the avoidance of large deformations ($> 15\%$) which would induce crystallisation. The useful properties of rubber under normal conditions are largely due to crystallisation on stretching. The effect of vulcanisation in lowering the temperature range of usefulness is probably connected with the suppression of crystallisation. This fact is the basis of the T-50 test for vulcanisation.

Tuckett's theory relating elastic behaviour to molecular structure illustrates the dangers of over-simplification of the problem. The existence of gutta-percha is inconvenient to most theories and it is generally ignored. Any satisfactory theory must account not only for the properties of rubber, but also of both α and β gutta-percha, all of which are polyisoprenes. Furthermore, it is incorrect to assign a rubber-like nature to chlorinated rubber as of course it is very brittle at room temperature and has a high elasticity temperature of about 100° C.

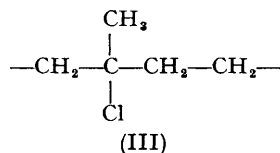
Then, again, the high elasticity of polychloroprene (I) is assigned to the



polar chlorine atoms being too far apart to affect each other and so to restrict rotation, and in polyisobutene (II) it is assumed that the non-polar character of the side groups permits rotation in spite of their proximity. Yet rubber hydrochloride (III) in which a non-polar methyl group is added to the polychloroprene structure in which the Cl atoms are supposed to be too far apart to interfere, is crystalline at room temperature and has a high elasticity temperature of $+95^{\circ}$ C.

Another example of the danger of these simple ideas of free rotation is provided by the homologous polymethacrylates; polyethyl methacrylate having a lower high elasticity temperature than methyl whereas one would expect the rotation to be further restricted.

Dr. R. M. Barrer (*Bingley*) said: The discussion on this and the previous paper has shown a vagueness concerning the way in which a coiled long chain may diffuse. Consider, in the two-dimensional analogue, a single chain (Fig. 1). In configuration A the centre of gravity of the chain is shown. The chain reorients itself to give configuration B, and the centre



of gravity is seen to have moved forward a distance x . In the two-dimensional case such a reorientation would require bond-deformation, but in the three-dimensional case the reorientation may easily occur by partial or free rotation round C—C bonds without deformation of bond angles.

It is also advisable at this point to summarise the main features which contribute to rubber-like elasticity. From the molecular viewpoint elasticity requires or is favoured by

- (1) Relative apolar chains ;
- (2) Very long chains ;
- (3) Relatively apolar side chains ($-\text{Cl}$, CH_3- , C_2H_5- , C_6H_5-) ;
- (4) Special kinks in chains introduced, for example, by double bonds ;
- (5) No cross-linking, or not too extensive cross-linking, by chemical bonds.

Referring to (1) and (2), the chains must be sufficiently long to become thoroughly entangled, and must not interact strongly enough to crystallise. The rubber is then a fluid in one sense, but the great chain length immobilises the chain as a whole, though intermeshing.

In shorter chains, onset of rotation is not enough to produce elasticity. Above certain temperatures long chain hydrocarbons rotate in their crystals but develop no rubber-like or even fluid properties.

At least two effects may be ascribed to (3) :

(a) There is the steric hindrance to rotation discussed by Tuckett, which decreases fluidity.

(b) The side chains help to prevent easy crystallisation by making close packing more difficult. They therefore increase fluidity which, coupled with the intermeshing of coiled very long chains, renders the polymer elastic. The double bonds, by introducing unavoidable special kinks in the chains, also reduce the ease with which they may pack together and crystallise and so favour elasticity.

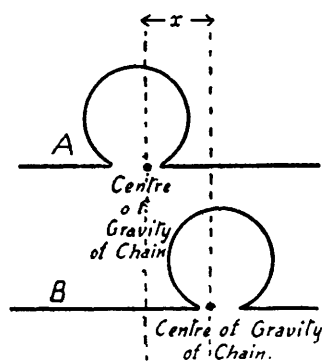
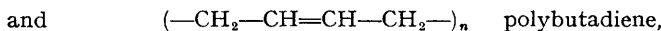


FIG. 1.

which they may pack together and crystallise and so favour elasticity. For example, of the polymers



the first is inelastic and wax-like at ordinary temperatures ; the two latter are elastic. Similarly, "Nylon" polymers without side chains are inelastic, but when suitable side chains are introduced a rubber-like polymer may be obtained.

Referring to (5), it will be clear that cross-linking serves to reduce plastic deformation, but if not present to a too great extent may not impair rubber-like elasticity. Excess cross-linking, as in ebonite or poly-*p*-divinyl benzene, destroys elasticity.

Mr. C. W. Bunn (Northwich) said : In considering the "freezing points" T_f of different high polymers and their relation to the flexibilities of the molecules, it does not appear to be sufficient to take into account only the interaction of the side chains on each other. This is shown by

the fact that polyethylene, which has no side chains, has a high freezing point ($115^{\circ}\text{C}.$) while polyisobutene, which has a pair of methyl groups on every other chain carbon atom, has a very low freezing point ($-65^{\circ}\text{C}.$). Evidently, there must be some other factor, and I suggest that this other factor is the potential barrier associated with the preferred (staggered) position of the bonds themselves.¹ At any rate, by assuming that both these factors play a part, it is possible to explain some otherwise puzzling phenomena, such as the low freezing point of polyisobutene—for the two factors may sometimes act in opposition and so cancel each other out. If a model of the polyisobutene molecule is made, it will be found that, if the configuration is such that the bonds of linked carbon atoms are staggered, then the methyl side groups are overcrowded, while if (by rotation round the chain bonds) the methyl side groups are given greater clearance, then the bonds of linked carbon atoms are no longer staggered; thus the bonds prefer one configuration while the methyl side groups prefer another, the net result being that all configurations have much the same energy, the barriers to rotation are small, and the freezing point low.

Dr. G. Gee (*Welwyn Garden City*) said: I am not clear whether Table V is intended to show the effect of chemical cross-linking, but I should prefer to regard the observed rise of the high elasticity limit of rubber as due to the combination of sulphur. I do not see how a relatively small number of cross-links could influence the rotation of the main part of the rubber chain. It would be interesting to compare the high elasticity limits of two rubbers of different combined sulphur content, vulcanised to the same state of cure.

Dr. G. D. Coumoulos (*Cambridge*) said: In a paper to be published shortly, jointly with the President, we give full account of electron-diffraction examination of polyacrylate and -methacrylate esters and polyvinyl acetate. The patterns of multilayers and thin lenses of these polymers reveal the fact that it is the side chains that give the major contribution to the diffraction features; the polymers are in the liquid state and no crystalline features appear even on stretching. The side chains tend to orientate their axes parallel to one another and take up the position of close-packing. A molecular configuration is suggested in which the chief long chain is a plane zig-zag form and the side chains hang alternately on either side of this plane in the 1, 3 positions (Fig. 2). This configuration for polymers with long side chains presents the following differences with respect to rubber:

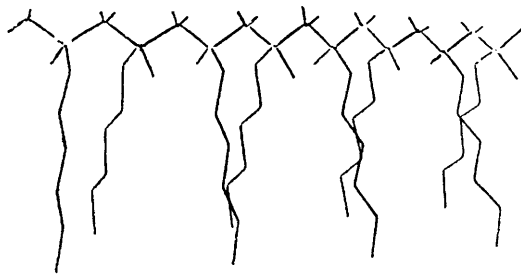


FIG. 2.

(1) No crystalline features; (2) No double bonds; (3) No cross-linkings. This configuration further explains the different elastic properties of the polymers from the nature of their side chain: Me-acrylate, Me-methacrylate, and polyvinyl-acetate with side chains of the same length have different properties; our suggested configuration attributes these differences to the different packing of the polar groups in the side chains. It is also shown that by increasing the length of the side chains, these become more flexible. However, over a certain length they lose their flexibility and pack more regularly, because the distortion apparent in the 3 to 4 carbon atom side chains does not influence the longer chains.

¹ Kistiakowsky, Lacher and Ransom, *J. Chem. Physics*, 1938, **6**, 900; Bunn, *Proc. Roy. Soc., A*, 1942, **180**, 67.

Dr. A. Charlesby (*Imperial College, London*) said: In attempting to relate the elastic properties of a linear polymer to the structure of each individual molecule considered separately, one inevitably meets the following difficulty. If the freedom of rotation about the single C—C bond is simply restricted by the interaction of the side chains, the effect of increasing the length of these chains in any series of polymers should be to produce in a stiffer polymer. This is, however, not the case. In the methacrylate polymers, for example, the stiffness and elastic limit decreases rapidly with the length of the chain from methyl to butyl. This presumably corresponds to a decrease in T_E .

An alternative model provides an explanation of this decrease. If the main part of the resistance to strain arises from inter-molecular forces, these will in general be weaker in polymers with long side chains, since the main bulk of two adjacent chains then lies further apart. It is possible to consider the internal structure of a polymer as comprising mainly a large number of pseudo-crystalline regions formed by the packing together of small portions of polymer chains which lie in a suitable orientation. These regions can only be extensive with polymers such as polydichlorethylene, which have a symmetrical structure, and which are consequently crystalline. In other, "amorphous," polymers these crystalline regions may be estimated to comprise only about a hundred monomeric units or less. At low temperatures, the cohesion of these crystalline regions prevents high elastic deformation, but at higher temperatures the smaller groupings melt and considerable deformation is then possible.

The remaining few but larger crystalline regions do not however melt, and, bound together by portions of the polymer chains, serve to restore the initial shape when the external stresses are removed. Plasticity and viscosity can be related to the tendency to recrystallise in a new but less stable orientation. This outlook relates the high elasticity temperature directly to the melting point of crystallites rather than simply to the steric interference of side chains, and hence also serves to explain the elastic properties of polymers such as polyethylene and polydichlorethylene.

Physical evidence can be adduced for this hypothesis. Thin films of orientated polyethylene are crystalline at ordinary temperatures, but show an apparently amorphous structure (by electron diffraction) at temperatures in the neighbourhood of their melting point. If a film is raised to a temperature of up to 40° C. above its melting point, and re-cooled, its initial orientation reappears. This can only be due to the survival, in the liquid state, of some memory of its initial structure. This survival can best be explained by the retention within the liquid of some part of the crystal structure, if only on a statistical basis.

Mr. D. J. Crisp (*Cambridge*) said: It has been suggested that in rubbers and rubber-like substances the flexibility of the main chain is considerably influenced by the nature and position of side groups. I would like to mention some work on surface films of certain polymeric substances which support this view.

Polymers of the acrylate and polyvinyl series are found to spread uniformly on aqueous substrates giving monomolecular films at low pressures. The properties of these films depend upon (a) the interaction of the polar group with water, causing spreading and expansion. Substances with only weak polar groups such as polystyrene, rubber, chloroprene do not spread.

(b) The flexibility of the chains, which is evidenced by finite pressures, due to kinetic agitation, at relatively large areas of the order of 100-150 Å.² per residue.

(c) The interaction of chains with each other, due to non-polar forces, leading to condensation of the films. This can be reduced at an oil-water interface.

Thus polyvinyl acetate and acrylates give fluid expanded films whose

force-area relation follows a curve asymptotic to the area axis; while the presence of a methyl group opposite the side chain, as in methacrylates, reduces the flexibility and increases the cohesion. This makes spreading less perfect, and the resulting films are coherent and show a sharp rise in pressure at a fairly definite limiting area.

It is interesting to recall that Adam, using films of cellulose ethers and esters, obtained a similar result, the presence of benzene rings in the side groupings precluded freedom of movement from the cellulose units.

Experiments show also that the length of the alkyl radical in the side chain of a polyester reduces cohesion to a minimum at 3 or 4 carbon atoms. Thus propyl acrylate gives a more expanded film than either ethyl or butyl acrylates, and in the methacrylate series expansion occurs progressively up to the butyl member, while octadecyl methacrylate gives films more closely resembling ethyl and methyl methacrylates. Presumably the alkyl radical first reduces cohesion by separating the main chains from each other, but long aliphatic chains will introduce strong attractive forces which counteract the initial effect.

Both in physical properties and in their effects on phase boundary potential the films closely parallel those of long chain ester compounds.

Dr. R. F. Tuckett (*Cambridge*), in reply, said: The multiplicity of points raised in the previous discussion makes it impossible for me to reply individually to each one and I shall content myself with a general discussion. The paper, as originally presented, put forward two main suggestions. The fundamental hypothesis was that there existed a close connection between the onset of high elasticity in a polymer and the extent of free rotation in the chain molecule, the latter being determined by steric and inter-chain effects; this was deduced from a variety of other physical data and the discussion has not diminished my faith in its essential validity.² The second point, namely, the connection between molecular structure and free rotation, was admittedly a bit more speculative and here it may be that the picture is not so simple as was first suggested. I would be the first to admit that simple concepts based on steric considerations are not in themselves sufficient to explain the various high elasticity temperatures encountered but they do correlate a number of diverse facts, *e.g.* the acrylate-methacrylate differences and the low T_E value of a 2 : 1 styrene butadiene co-polymer.

On the other hand, some molecules do not fit very well into the scheme. Polyethylene is difficult to explain on any general theory though the ease with which it crystallises makes the assessment of its elastic properties difficult—polyisobutene also seems to be an awkward case to some people. Rubber hydrochloride, about which my information was not as accurate as it might have been, definitely does not come into line with the theory, though it is difficult to see how it differs essentially from chloroprene in this respect.

The case of the various acrylates and methacrylates shows that a simple steric theory may not be adequate and that here the determining factor is the interaction between different chains. From the discussion, several points arise; the first is that softening temperatures which fall progressively as the methacrylate series is ascended, must not be confused with high elasticity (T_E) values—it will be shown elsewhere that softening points essentially represent iso-viscous states and hence will be dependent on molecular size; T_E values above a minimum chain length are independent of it; for the range of molecular weight over which this is true, Ueberreiter gives 33,000 to 484,000 for polystyrenes.

The effect of changing the side chain length in the acrylates and methacrylates is certainly not a simple steric one, and in this connection the complementary lines of investigation initiated by Coumoulos and

² Incidentally, Mark has recently come forward with a very similar suggestion. *Ind. Eng. Chem.*, April, 1942.

Crisp seem to be extremely promising. Mr. Crisp's work clearly indicates the importance of the interaction between different chains in determining elastic properties, a point which was emphasised in my original paper in the plasticiser section—a large side chain such as butyl may, in this respect, almost function as an internal plasticiser. It would be extremely interesting to study the effect of temperature on the shape of Crisp's unimolecular films—a transition from the coherent methacrylate to the expanded acrylate type as the temperature is raised would be good evidence for the original hypothesis.

In reply to a question by Whitby, Ueberreiter's T_g values show a spread of $\pm 5^\circ \text{C.}$ but a discrepancy of 15°C. would seem to require another explanation. Two suggestions can be made; one is that a small amount of residual monomer will depress T_g considerably (Ueberreiter's specimens were carefully purified from low molecular products by reprecipitation)—the second is that it might be due to the almost complete suppression of branching—this effect has not been considered in the treatment but would be expected to have the same general result as cross-linking though on a much smaller scale.

In reply to Gee, I think that the sulphur in vulcanised rubber, if not acting as a cross-linking agent but rather as a strongly polar addendum to the isoprene unit, would increase T_g by cutting down free rotation; my own knowledge of modern theories of vulcanisation does not, however, permit a differentiation between the two possibilities.
