1918 (1959) [Russ.J.Phys.Chem., 220 (1959)].
118. S.S.Kirilyuk and S.P.Miskidzh'yan, Ukrain.Khim.Zhur., 25, 312 (1959).
119. S.P.Miskidzh'yan and T.N.Gladishevskaya, Zhur.Fiz. Khim., 36, 1045 (1962) [Russ.J.Phys.Chem., 548 (1962)].
120. S.S.Kirilyuk and S.P.Miskidzh'yan, Zhur.Fiz.Khim., 31, 1714 (1957); 33, 2786 (1959) [Russ.J.Phys.Chem., 629 (1959)].
121. A.N.Burmistrova, "Kharakter Dissotsiatsii Solei Chetyrekhzameschchennogo Ammoniya v Nevodnykh Rastvoritelyakh" (Nature of the Dissociation of Quaternary Ammonium Salts in Non-Aqueous Solvents), Candidate's Thesis (Ph.D.Equivalent), Dnepropetrovsk Institute of Metallurgy, 1953.
122. N.A.Izmailov, "Elektrokhimiya Rastvorov" (The Electrochemistry of Solutions), Kharkov, 1959.
123. A.I.Shatenshtein, "Izotopnyi Obmen i Zameshchenie Vodoroda v Organicheskikh Soedineniyakh" (Isotopic Exchange and Hydrogen Substitution in Organic Compounds), Moscow, 1960.
124. N.A.Izmailov, Zhur.Fiz.Khim., 30, 2164 (1956).

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MODERN VIEWS ON THE PLASTICISING OF POLYMERS

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CONTENTS

1. Introduction 151
2. Historical 152
(a) The plasticising of amorphous polymers 152
(b) The plasticising of crystalline polymers, graft and block copolymers 153
(c) The influence of the chemical structure of plasticisers on the plasticising of polymers 154
3. Plasticising in the light of new views on the structure of linear polymers 155

1. INTRODUCTION

There have been various fundamental changes in views on the structure of linear polymers and the nature of plasticising which have not found their way into the reviews on the subject (see *e.g.* Tager[1]). We thought it desirable to collect the main facts about the plasticising of polymers by low-molecular-weight plasticisers without considering the questions of chemical and mechanical plasticising and the plasticising of polymers by high-molecular substances.

Polymers without additives are comparatively rarely used in technology because of their considerable brittleness, their tendency to crack during storage and use, the difficulty of forming them into articles, and various other deficiencies; the polymers are therefore modified, *i.e.* their properties are changed (improved).

One of the most important methods of modifying the properties of linear polymers is to plasticise them with low-molecular-weight substances. This type of plasticising can be considered as the combination of the polymers with certain low-molecular-weight substances of a definite chemical structure to form, because of steric effects and the altered energy relationships, polymeric materials which are usually more plastic and more elastic. The substances producing this effect are known as plasticisers.

For a long period the problem of plasticising has been solved purely empirically. A theoretical founding of this effect became possible only after the basic kinetic features of the behaviour of polymers had become evident, and after the discovery of the relaxation mechanism of the deformation of polymeric materials and the introduction of the concepts of the macromolecular and then of the globular-packet structure of high-molecular-weight compounds.

It has been shown[2] that the extent of highly elastic deformation has a clearly expressed relaxation (retardation) character, *i.e.* it depends on the period over which deformational stresses act on the polymer. Brittleness appears in polymers when the increase in stress in specimens subjected to deforming forces is not accompanied by macromolecular rearrangements leading to stress-relaxation[3]. Hence it is concluded that the brittleness of polymers can be reduced by the introduction of plasticisers, since in their presence the rates of relaxation processes are increased and the growth of cracks is stopped or greatly reduced.

The mechanical properties of polymeric materials have been determined as a function of the period over which external forces act upon them[4]; the strength of polymers and similar materials depends greatly on the duration of deforming stresses on the specimen, and all polymeric materials have such a strength *vs.* time relationship[5-7].

X-Ray and electron diffraction of amorphous polymers[8-10] have clarified the structure of such substances and allowed the orientated state of the chains to be considered as an enforced and unstable state of the polymeric system. Similar conclusions were reached from an investigation of the differential heats of sorption of polymeric materials[11].

The change in views of the structure of polymers has enabled knowledge of their behaviour on deformation to be expanded. In linear polymers under certain conditions there is movement of the chains as a whole, causing the plastic properties (flow) of polymers, and movement of individual segments of the chains, producing flexibility and elasticity of the polymeric material[12]. The flexibility of the macromolecular chains is in its turn determined by the potential barrier, *i.e.* the energy required to pass from one conformation to another. The potential barrier depends on the chemical nature and structure of the chains producing the intramolecular and intermolecular interactions, and on the temperature and various other factors. Depending on the temperature, polymers can exist in three main physical states[13-15]: vitreous, highly elastic, and viscous liquid; the length and flexibility of the macromolecules play a significant part in these transformations. Further studies led[16] to a theory of the mechanical properties of amorphous linear polymers and to two mechanisms for

vitrification, based on (1) the increase of viscosity with fall in temperature, and (2) the sharp increase of the rigidity of chain molecules on cooling. Two different plasticising mechanisms must correspond to the two vitrification mechanisms.

Extensive electron microscopic studies led[17] to the globular-packet theory of the structure of linear polymers.

A consequence of the changes enumerated above in views on the structure and properties of linear polymers has been a more correct evaluation of the nature and laws of the plasticising of polymers by low-molecular-weight substances.

2. HISTORICAL

(a) The Plasticising of Amorphous Polymers

Plasticising has long been used technologically to improve certain properties of polymers. More than 100 years ago castor oil[18] and camphor[19] were employed to plasticise cellulose nitrate, and at the beginning of the 20th century tricresyl phosphate began to be used for the same purpose. Paraffin, tars, waxes, and bitumens have been used as plasticisers (softeners).

Attempts to explain the plasticising of specific polymers were made in the nineteen-twenties and -thirties by Obrist[21] who proposed the now discarded colloidal theory of plasticising, and by others[22-24].

Ueberreiter[11] introduced the term "internal plasticising of polymers" by which he meant the penetration of plasticiser molecules between the macromolecular chains of the polymer, causing them to separate and weakening the interaction between them.

The plasticising of polymers by low-molecular-weight substances can, as we have said[25], be called "physical plasticising", since the new plasticised polymeric system is produced solely as the result of various physical bonding forces.

Several workers have considered plasticising as the blending of liquids[30]. It has been said[26-31] that the plasticiser molecules diffusing into the polymer enter into a definite energetic interaction with certain groups of the macromolecular chains, forming with them molecular sorption compounds of a certain type. The particular action of plasticisers on polymers is determined, according to Kirkpatrick[32], by the presence in polymer and plasticiser of groups which can interact with each other, by their most favourable mutual disposition, by the shape of the plasticiser molecules, and by purely geometrical factors.

The phase equilibrium in colloidal systems of the polymer–plasticiser type, the equilibrium conditions in such systems, and the change of the mechanical properties of the products have been studied as functions of temperature and amount of plasticiser[33-35]. The equilibrium diagram has been used to indicate the range of compatibility of the plasticiser with the polymer[34]; the compatibility of plasticiser and polymer was shown to depend on the position of the curve depicting the separation of the system into two phases. The properties of the polymer–plasticiser system have been more fully described by using the temperature *vs.* composition diagram on which the isoviscous solution curves are plotted as well as the phase equilibrium curve of the components[35]. It was assumed that a given plasticiser can affect the plasticity and elasticity of the polymer, depending on the amount of plasticiser added to the polymer system.

In a polar polymer a typical plasticiser is not randomly distributed[36], since it interacts mainly with the polar groups of the polymer. Under such conditions the plasticiser can block the force field of these polar groups, weakening the interaction between neighbouring chains, *i.e.*, the polymer becomes, as it were, less polar as the result of the plasticising.

Plasticisers have been divided[37-39] into actual plasticisers, which only increase plasticity (*e.g.* dimethyl phthalate), and the so-called elasticisers (*e.g.* dibutyl phthalate) which at a definite content also increase the elasticity of the polymer.

The thermodynamic theory of polymer solutions[40] has been used to attempt a quantitative interpretation of the mutual solubility of polymers and plasticisers[41]. The interaction in the system depends very greatly on the vapour pressure of the plasticiser and the temperature and is independent of the type of plasticiser[42].

A mainly new and thorough quantitative investigation of the plasticising of polar and non-polar polymers was carried out in the early nineteen-forties by Zhurkov[43-45], who formulated the rule of "mole fractions", which states that with polar polymers the plasticising effect depends on the mole fractions of polar plasticisers introduced, but is independent of their size, chemical nature and structure. Similar conclusions were reached by Fuoss and coworkers[46] when studying the plasticising of poly(vinyl chloride) by various low-molecular-weight substances, but the rule was not obeyed in the case of poly(vinyl chloride) copolymers.

Later Zhurkov and Levin showed[47] that reaction between the polar groups of polymer and plasticiser is indicated by the appearance in the spectrum of poly(methyl methacrylate) plasticised with n-butanol of a band characteristic of hydrogen bonding. The concentration of hydroxyl groups of the n-butanol taking part in the blocking of the polar groups of the polymer could be found by measuring the intensity of the absorption band; the concentration of alcoholic hydroxyl groups combined with the polar groups of the polymer is less than the total concentration of alcohol added to the polymer. The reduction in the glass temperature remains proportional to the concentration of added plasticiser only with a low content of n-butanol; further increase in the alcohol content produces a relatively smaller reduction in the glass temperature, but it remains proportional to the alcohol concentration determined spectroscopically, which corresponds to the amount of alcohol reacted with the polar groups of the polymer. It is these alcohol molecules which take part in the plasticising; the other alcohol molecules, although present in the system, do not. This work enabled Zhurkov to confirm his earlier suggestion that plasticising consists in the screening of the functional groups of the polymer by polar plasticiser radicals and to confirm his rule of "mole fractions".

Kargin remarks[48] that the introduction of plasticisers into a polar polymer produces the same effect as if the number of stronger polymer–polymer bonds were reduced.

Sedlis[49] considers plasticised systems as solid solutions, and the plasticising of polymers as analogous to mechanical orientation and chemical modification by copolymerisation.

Some workers (*e.g.* Simril[50]) relate the main role in plasticising only to the structure of the polymers themselves, and ascribe no influence to the structure of properties of plasticising additives or to the mechanism of their interaction with the polymers.

Merz[51] divides plasticisers into three types: primary, having good compatibility with the polymers and exhibiting a good plasticising action; secondary, not showing good compatibility but imparting definite properties to the polymers; and diluents, which reduce the cost of compositions

Sokolov and Fel'dman[52] considered the effect produced by plasticisers to be comparable with the reduction of freezing point observed in dilute solutions, and called the effect colligative, *i.e.* depending in the main on the number of added plasticiser molecules, but independent of the composition, structure, and molecular weight of the plasticising materials.

Aiken and coworkers showed[53] that plasticising does not always produce the same effect, which for a given polymer depends to some extent on the structure of the plasticiser.

Fuoss and Mead[54] thought that plasticisers of about the same molecular size and shape exhibit similar plasticising actions on a given polymer. However, polar polymers can only react with a plasticiser if its molecule contains polar or readily polarised groups, the plasticising effect consisting of the separation of the polymer macromolecules by plasticiser molecules, which produces a sharp decrease in the macroscopic and micro-coefficient of friction.

Gal'perin and Moseev[55] found that in the plasticising of cellulose nitrate an energetically saturated solvate layer requires one mole of dibutyl phthalate or two moles of acetone for each two gramme-molar $-ONO_2$ groups, *i.e.* both ester groups of the dibutyl phthalate participate in the blocking of the polar groups of the cellulose nitrate, only the $-ONO_2$ groups reacting with the plasticiser.

Kargin and Malinskii showed[56,57] that equimolecular fractions of different plasticisers reduce the glass temperature T_g of polymers to different extents, the reduction of T_g for non-polar and weakly polar polymers obeying, to a satisfactory approximation, the rule of "volume fractions", *i.e.* it is proportional to the fraction by volume of plasticiser added. As far as its viscosity is concerned, the addition of plasticisers to a polymer is equivalent to the appearance of holes in it, since the viscosity of a plasticiser can be ignored in comparison with the viscosity of a polymer. These workers consider that the rule of "mole fractions" correctly represents the mechanism of plasticising only of polymers whose micro-viscosity changes on plasticising mainly because of decreased intermolecular interaction, *i.e.* polymers whose units possess considerable polarity. When the intermolecular interaction between the polymer units is small (with non-polar or weakly polar polymers) the reduction in micro-viscosity on plasticising would be expected to arise mainly because of a steric effect, and hence for non-polar polymers T_g will depend linearly on the concentration by volume of the added plasticisers. The rules of "molar concentrations" and "volume concentrations" are reflections of two different mechanisms of plasticising, and each is obeyed by only a few systems, in which the action of one or other of these mechanisms predominates; many real systems will show greater or lesser deviations from both of the rules, because both mechanisms of plasticising apply simultaneously with comparable strength.

Boyer and Spencer[58] consider that the extent to which plasticisers act on polymers depends on the plasticiser concentration, the plasticisers causing separation of the polymer chains and hence a reduced energy barrier in the polymer system.

According to Slonimskii's results[59,60] plasticisers affect a polymer in two ways: they cause a reduction in the intermolecular viscosity, and by reacting with individual chemical groups of the macromolecular chains they can produce either a decrease or an increase in the intramolecular viscosity.

Kargin and Slonimskii[61] have confirmed the applicability of the rules of "mole fractions" and "volume fractions" to various plasticised polymer systems; these rules represent extreme limiting cases of plasticising, and in real polymers they overlap.

(b) The Plasticising of Crystalline Polymers, Graft and Block Copolymers

It has been suggested[62] that the crystal structure of a polymer changes in the presence of plasticisers which cause it to swell. With plasticiser oils in the system an amorphous halo appears on the fibre diagram of the polymer. However, in the study of vinyl polymer–tricresyl phosphate systems[63] no changes in the initial structure of the polymer under the action of plasticisers could be detected on the X-ray diagrams.

The sorption of the vapour of low-molecular-weight plasticisers depends on the structure of the polymers; orientated crystalline polymers are more active in sorption than other types of polymer[64]. The addition of plasticisers (dimethyl phthalate, dibutyl sebacate, cetyl chloride) to crystalline polymers reduces their glass temperature in the same way as is observed with amorphous polymers[65], but with crystalline polymers the melting point is only very slightly reduced, *i.e.* the plasticising of crystalline polymers does not decrease but increases the difference between T_g and the melting point. The displacement of T_g with crystalline non-polar polymers obeys the same rule of "volume fractions" as with amorphous non-polar polymers and is independent of the nature of the plasticiser; however, with large plasticiser concentrations there is some deviation from this rule.

Study of the plasticising of systems in which the macromolecules contain both polar and non-polar sections[66] has shown that polar plasticisers (glycerol) and non-polar plasticisers (tetralin) act independently, the plasticising of the non-polar parts of the copolymer obeying the rule of "volume fractions", and the polar parts the rule of "mole fractions". Tetralin plasticises only the polystyrene units in accordance with the rule of "volume fractions", while glycerol under the same conditions acts primarily on the polar groups of polyvinyl alcohol and polyacrylic acid. When both plasticisers are present each supplements and strengthens the action of the other.

The plasticising of block copolymers in which the units are of greatly differing polarity using polar and non-polar plasticisers has been studied[67], using acrylic acid–styrene block copolymers, with glycerol and tetralin as plasticisers. With glycerol there is a sharp decrease in the glass temperature of the block copolymer, the first portions of glycerol reducing the glass temperature in proportion to the mole fraction of glycerol, but with a further considerable increase

in the glycerol content the reduction of T_g gradually tails off. An analogous effect was observed with the mixed type plasticiser dibutyl phthalate. When glycerol acts on the block copolymers it dissolves mainly in micro--regions enriched in acrylic acid, reducing T_g for the polyacrylic acid micro-regions and considerably lowering the softening point of the specimen as a whole, although regions enriched in polystyrene are practically unaffected. With the non-polar plasticiser (tetralin) which dissolves in the polystyrene micro-regions, there is no reduction in the softening point of the sample as a whole, since the hard polyacrylic acid micro-regions remain practically unaffected. Only when the polar and non-polar plasticisers act together are both types of micro-region plasticised, giving a general reduction [? of the softening point (Ed. of Translation)] of the block copolymer as a whole.

Although there have been few studies of the plasticising of crystalline polymers, graft and block copolymers, the data given above show that it involves the same processes and characteristics as the plasticising of amorphous polymers. The rules of mole fractions and volume fractions apply to this type of high-molecular-weight substance also, to a certain extent.

(c) The Influence of the Chemical Structure of Plasticisers on the Plasticising of Polymers

Of great significance for the further development of the study of plasticising is the investigation of the part played by the chemical structure of the plasticisers and particularly the relationship between the plasticising effect and the structure of the plasticisers (the plasticising effect can be measured by the change in T_g or in mechanical or other properties of the polymers under the action of a definite quantity of plasticiser).

Thus it has been remarked[44,66-70] that the chemical structure of polymers and plasticisers actively affects only the compatibility of the components, and not the magnitude of the plasticising effect. There has been no observed influence of the chemical structure of the plasticisers on the plasticising of polymers when mixtures of plasticisers are used[71]. However, on systematic study of the process such an influence can be found in the most varied classes of organic substances[72].

The influence of the chemical nature and molecular size and shape of plasticisers on the plasticising of polymers has been studied[73-75] using trioctyl phosphate, tricresyl phosphate, and certain other plasticisers; different effects were observed, in particular polymeric materials containing different plasticisers had substantially different freeze--resistance properties.

Plasticisers of low- and of higher-molecular-weight behave differently in polymer compositions[76]. The part played by the chemical structure of plasticisers has been noted in various studies[77-78].

The plasticising of divinylbenzene-styrene rubber varies with different types of plasticisers (non-polar plasticisers are the best)[72]. With small concentrations of plasticiser in SKS-30A rubber the rule of volume fractions is obeyed fairly satisfactorily, the reduction in T_g not depending on the nature of the plasticiser[80]. With higher plasticiser concentrations there are deviations from this rule, and T_g for the rubber is lower with non-polar plasticisers than with polar. With not more than 20 vol. % of plasticiser in the vulcanisate the reduction in the tensile strength and the change in the relative extension are independent of the plasticiser structure; however, with a plasticiser content above 20 vol. %, and particularly above 50 vol. %, the plasticising effect does depend on the molecular structure of the plasticiser.

The effect of the chemical structure of the plasticisers on the plasticising of polymers has also been noted in a number of other studies[82-83] in which simple views of the mechanism of plasticising are also given.

The mechanical properties of certain polymers have been studied[84] as a function of the chemical structure of the plasticisers, in particular the influence of carbon chain length and number of polar groups using methyl, butyl, and ethylhexyl methacrylates as plasticisers. Changes in the structure of the plasticiser produce corresponding changes in the 100% modulus and tensile strength of the polymers, and the force *vs.* deformation curve varies in shape with compositions having different amounts of the different plasticisers.

Frissell[85] found a relationship between the minimum flow temperature of polymers and the structure of plasticisers having the same molecular weight, and showed that increased chain length of the esterifying groups in the plasticisers (esters of phthalic acid) increases the minimum flow temperature of the polymers.

The complex nature of the bonding in polymer–plasticiser systems has been pointed out[86,87]. Small amounts of different plasticisers are held strongly by the polymer, although to different extents, but with increasing plasticiser content a point is reached when additional plasticiser does not become bonded with the polymer chains; it is this part of the plasticiser which first migrates when the polymer is in storage or use. In the study of dielectric losses in plastics it was found that the plasticiser molecules associate with a definite number of polymer groups (depending on the chemical nature of the plasticiser)[88].

Würstlin and Klein[89] observed that T_g for amorphous polymers depends on the chemical structure of the plasticisers.

Thinius states[90] that the mechanism of plasticising is closely bound up with the structure of the polymers, and can be described by two theories: (1) the thermodynamic, which allows for physical and chemical interactions in the polymer–plasticiser system, and (2) the theory of action of plasticisers as lubricants, which does not. There are also theories which combine these two extremes, in which the role of the plasticisers is mainly to reduce the steric hindrance to rotation of the functional groups of the macromolecular chains. The dependence of the plasticising effect on the chemical nature of the plasticiser is particularly evidenced by the fact that different plasticisers affect the individual properties of polymers to different extents[90]. In their electron microscopic investigation of cellulose nitrate–dibutyl phthalate and cellulose nitrate–softener† systems, Ames and Sampson found[91] that the texture of the resulting films varied with the solvent power of the plasticisers, *i.e.* in the last analysis, with their structure.

In generalising data on plasticising, Voyutskii remarks[92] that the compatibility of polymers with plasticisers depends on the energy interaction between molecules of the two components and on the entropy of mixing. The plasticising

† Castor oil (Ed. of Translation).

effect also depends on the shape and size of the molecules of polar plasticisers, the polar group causing reaction with the polar group of the polymer (*i.e.* compatibility), and the non-polar part producing the actual plasticising effect by screening the interacting dipoles of the polymer macromolecules.

The influence of the chemical structure of plasticisers on the plasticising effect has also been quantitatively investigated in a number of other studies[93-98], which have demonstrated the dependence of the plasticising effect on the structure, polarity, size, and shape of the plasticiser molecules. The dependence of the plasticising effect on the position of functional groups in plasticiser molecules has been demonstrated[97], and in particular that α-naphthol is a more effective plasticiser for poly(vinyl chloride) than β-naphthol (although β-naphthol is more polar than α-naphthol); this is explained by the particular electronic structure of these molecules. A substantial influence on the plasticising effect is exerted by the structure of side chains (branching) in the molecules of certain plasticisers[100]; thus epoxidised tetrahydrophthalates with branched side chains are less effective than the corresponding plasticisers with linear chains.

Tager and coworkers used a thermomechanical method to study the influence of diphenic and naphthalic diesters and diphenic monoesters on T_g for polystyrene and polymethyl methacrylate containing 25 mole % of plasticiser[101,102], and showed a connection between the activity of a plasticiser and its compatibility with the polymers: the lower the critical mixing temperature, the lower is T_g. As the size of the alkyl radical of the ester increases, T_g decreases regularly to a certain alkyl chain length and then increases. The explanation of this is that the plasticiser molecules enter between and separate the macromolecules of the polymer, so decreasing the viscosity of the system. The vibratory motion of the units of the polymer chain is thereby facilitated and is retained down to lower temperatures, causing a reduction in T_g: the larger the alkyl radical, the greater is the separation of the macromolecules and the lower is T_g. However, very large alkyl radicals will increase T_g because of the unfavourable geometrical disposition of the longer plasticiser molecules in the polymer phase; to a considerable extent this depends on the particular structure of the plasticiser molecules. The high plasticising action of diphenic acid diesters is due to the great mobility of their molecules and their low rigidity, so that the molecules of the diphenic acid diesters can assume many different conformations and can be arranged in a large number of ways amongst the polymer molecules; this creates favourable conditions for improved compatibility of the components and a stronger plasticising action by the plasticiser on the polymer. With naphthalic acid esters, which contain the rigid planar dinuclear condensed ring system, the number of possible conformations is considerably less; hence they are less compatible with the polymers and their plasticising effect is less. In these studies[93,97-102] it is noted that the rule of mole fractions is not observed accurately in the systems investigated, since the plasticising effect depends substantially on the chemical structure and the size and shape of the molecules of plasticiser.

3. PLASTICISING IN THE LIGHT OF NEW VIEWS ON THE STRUCTURE OF LINEAR POLYMERS

The discovery of the globular packet structure of linear polymers[17] enables a number of facts on the nature and mechanism of the physical plasticising of polymers to be interpreted anew at a deeper level. Although there have been few studies in this field, the first positive results have already been obtained.

The plasticising of the rigid-chain polymer cellulose, which is poorly compatible with plasticisers, has been studied[103], using as plasticisers urea and guanidinium thiocyanate in quantities of 8 to 60%, in solution in ethanol. The thermomechanical properties of the system indicate that the plasticising effect does not correspond with the rules of mole fractions or volume fractions, and it was found in another work[104] that the plasticising of cellulose with triethylphenylammonium oxide can increase the elastic properties of the polymer. This demonstrates the existence of two greatly different mechanisms of the plasticising of cellulose. In the one case the introduction of the plasticiser leads to a regular decrease in T_g for cellulose, and the mechanism of plasticising can be explained by the rules of mole fractions and volume fractions. In the other case (with urea as plasticiser) the plasticising effect cannot be explained as the result of interaction between plasticiser molecules and polymer macromolecules (the plasticisers do not mix unrestrictedly with the polymer). The plasticising effect of this type of plasticiser is explained in terms of the packet theory of the structure of linear polymers, and two possible mechanisms of plasticising are suggested. According to one of these, plasticising occurs within the packets when the interaction between plasticiser molecules and the active groups of the polymer chains is greater than the intermolecular action in the polymer itself. The plasticising effect of such plasticisers which are fully miscible with the polymer is to destroy any secondary structural formations (including packets) in the polymer and form a solid solution of polymer and plasticiser. If the reaction of the plasticiser molecules with the active groups of the polymer chains is substantially weaker than the intermolecular interaction in the polymer itself, then the plasticiser is able to react only with molecules on the surface of the secondary structures (the packets of chains), and only plasticising between the packets occurs, without any significant change in the elastic properties of the system.

In plasticising between the packets a more important part is played by the packets themselves, these possessing elasticity of shape and being stable to temperature changes[105]. The polymeric materials obtained by plasticising between the packets should have high shock and freeze resistance. In the plasticising of cellulose triacetate with phenylethylphenols, which dissolve the polymer and lower its transformation points, the brittleness of the films is reduced less than in plasticising with dihexyl sebacate, which is only partially compatible with the polymer[106-108]; hence in the former case packet formation of macromolecules is limited, because the reaction of the plasticiser with the macromolecules of the polymer exceeds the intermolecular interaction of the polymer chains. The plasticiser is then distributed between the polymer chains, and by facilitating relaxation processes it provides for a relatively dense packing of the chains, so that the films show little shrinkage. In plasticising cellulose triacetate with the partially compatible dihexyl sebacate, whose reaction with the active groups of the polymer chains is less than the intermolecular interaction, there is no hindrance to the formation of packets. With a predominantly packet structure in the films relaxation processes become difficult, so that the plasticised material has a large shrinkage. Because of the looseness of the packing the elasticity of the

packets is substantially increased, which causes a reduction in the brittleness of the films and improved mechanical properties.

In general, when substances of limited compatibility are combined with cellulose triacetate, plasticising occurs between the packets[108], since the plasticisers cannot penetrate into the packets; with fully compatible plasticisers plasticising occurs within the packets, and the properties of the resulting polymer systems are different.

Study of the plasticising of polycarbonates, which are characterised by reduced relaxation and crystallisation processes and which tend to form definite secondary structures, has shown that plasticising can occur within and between the packets[109]; the action of different plasticisers usually involves a combination of these two extreme types of plasticising, with a greater or lesser approximation to one or the other. Thermomechanical investigations have established that the introduction of a plasticiser which gives mainly plasticising between the packets somewhat reduces the elasticity modulus of the polycarbonate films, which then remains constant over a wide range of plasticiser concentrations. The introduction of a plasticiser which more nearly corresponds to plasticising within the packets reduces the elasticity modulus of the films regularly, the reduction being strictly proprotional to the amount of plasticiser introduced.

The study of structure formation (the nature of the secondary structures) in plasticised crystalline polystyrene has shown[110] that the plasticising affects the characteristic conditions for the formation of secondary structures in the unplasticised polymer; dimethyl phthalate, dibutyl sebacate, and cetyl chloride were used as plasticisers, in amounts of 8–20% by volume. Plasticising of crystalline polystyrene, particularly at low temperatures and with a low plasticiser content, produces a sharp change in the structure of the secondary formations, considerably increasing the rate of growth of spherolites and preventing their aggregation into ribbons or plates (*i.e.* in the presence of plasticisers the crystallisation ceases with the formation of large spherically symmetrical particles). With plasticiser concentrations of less than 10% the strength of crystalline polystyrene is much reduced, because of changes occurring in the supermolecular structures of the polymer, with the formation mainly of spherolites separated by plasticiser molecules. The destruction of such spherolitic plasticised systems apparently proceeds along the boundaries of the spherolites.

The theory of plasticising between and within the packets has also been applied[111] to linear thermoplastic polar polymers of the poly(vinyl chloride) type. Small additions[5-10] of polar plasticisers have the effect of plasticising the polar polymer between the packets, or in general between the structures, while larger additions of the same plasticisers lead to plasticising within the packets (or structures). With this type of plasticising the strength of the polymer first increases to a definite limit, and then decreases as plasticising within the packets becomes more prominent.

Lipatov[112] has used the dilatometric method to investigate polystyrene or poly(methyl methacrylate) films filled with glass powder (50% of the total weight of the mixture) and containing various amounts of dimethyl phthalate as plasticiser. The filled polymers have higher values of T_g than the unfilled polymers, due to the reduced mobility of the chains and packets because of interaction with the surface of the filler. With both polymers, with more than a certain content of plasticiser T_g for the filled polymers becomes less than T_g for the unfilled polymers. It is suggested that the higher T_g for the filled polymers is due to the limited mobility of the packets near the surface of the filler caused by adsorption interaction and steric hindrance. During the formation of the polymer films in the presence of the filler, the packets or other secondary structures produced in the concentrated solutions become attached to the surface of the filler[113]. The presence of a plasticiser cannot prevent these effects of secondary structure formation in the solutions, and hence the plasticiser is not distributed evenly between all the macromolecules of the polymer. In the case of a filled polymer the interaction of the added plasticiser with the filler surface will to some extent prevent interaction of the packets with the surface, so that the packets of chains interacting with the surface in the presence of plasticiser will have a high mobility in comparison with that of the packets in the absence of plasticiser, or with that of the packets in the presence of the same amount of plasticiser but in the absence of filler. It can be assumed that with the filled polymer, where there is a sufficiently well-developed contact surface between the polymer molecules and the filler, the effects of breaking the bonding between the packets and the surface, like the effects of plasticising between the packets, will play the dominant role. Since it is this bonding which causes the sharp increase in T_g in the filled polymer, the breaking of this bonding should produce just such a sharp decrease in T_g for the plasticised filled polymer; therefore the effects of plasticising between the packets are more marked with filled polymers, which are characterised by looser packing on the filler surface. In this case, as the content of plasticiser in the polymer increases, the part played by plasticising on the boundary between the polymer and the filler surface is gradually reduced, and the more important part is played by the effects of the plasticising of the polymer itself, *i.e.* the breaking of intermolecular bonds in the polymer itself. Since the interaction of the polymer with the filler surface also takes place with a relatively large plasticiser content, further weakening of the bonding with the surface is superimposed on the actual plasticising of the polymer, and with an equimolecular content of plasticiser the over-all reduction of T_g becomes greater in the presence of the filler than in the case of the unfilled polymer. It is concluded from the above that the plasticising of filled polymers is determined by two effects: plasticising between the packets, caused by the breaking of filler surface–polymer bonding, and normal plasticising, caused by the breaking of polymer–polymer bonds.

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The study of the plasticising of polymers by low-molecular-weight substances has made considerable strides forward, so that the rules of mole fractions and volume fractions have been formulated, plasticising between and within packets has been discovered, and the effect of the chemical structure of plasticisers on the plasticising of polymers has been more clearly demonstrated.

1. A.A.Tager, Uspekhi Khim., 5, 557 (1949).
2. A.P.Aleksandrov and Yu.S.Lazurkin, Zhur.Tekh.Fiz., 9, 1249 (1939).
3. A.P.Aleksandrov, Vestnik Akad.Nauk SSSR, Nos.7–8, 51 (1944).

4. V.A.Kargin and G.L.Slonimskii, Dokl.Akad.Nauk SSSR, 62, 1239 (1948).
5. S.N.Zhurkov, Vestnik Akad.Nauk SSSR, No.11, 78 (1957).
6. S.N.Zhurkov and B.N.Narzulaev, Zhur.Tekh.Fiz., 23, 1677 (1953).
7. S.N.Zhurkov and E.E.Tomashevskii, Zhur.Tekh.Fiz., 25, 66 (1955).
8. V.A.Kargin, V.L.Karpov, and Z.G.Pinsker, Acta Physicochim.URSS, 7, 648 (1937).
9. V.A.Kargin and D.I.Leipunskaya, Zhur.Fiz.Khim., 14, 312 (1940); 15, 1011 (1941).
10. V.A.Kargin and N.V.Mikhailov, Zhur.Fiz.Khim., 14, 195 (1940).
11. K.Ueberreiter, Z.phys.Chem., 45, 361 (1940); 48, 197 (1941).
12. V.A.Kargin and G.L.Slonimskii, Zhur.Tekh.Fiz., 11, 341 (1941); 15, 1022 (1941).
13. P.P.Kobeko, "Amorfnoe Sostoyanie" (The Amorphous State), Gos.TTI, 1940.
14. P.P.Kobeko, E.V.Kuvshinskii, and G.I.Gurevich, Izv.Akad. Nauk SSSR, Ser.Fiz., 2, 329 (1937).
15. Yu.S.Lazurkin, Zhur.Tekh.Fiz., 9, 1261 (1939).
16. V.A.Kargin and G.L.Slonimskii, Dokl.Akad.Nauk SSSR, 62, 239 (1948).
17. V.A.Kargin, A.I.Kitaigorodskii, and G.L.Slonimskii, Kolloid.Zhur., 19, 132 (1957).
18. Paint.Oil.Chem.Rev., 97, No.9, 34 (1935).
19. Synt.Appl.Finish, 6, 62, 202 (1936).
20. I.I.Ostromyslenskii, U.S.P. 1721034 (1929); 1791009 (1930).
21. M.Obrist, Kolloid Z., 42, 174 (1927).
22. A.M.Nastyukov, "Vvedenie v Kurs Tekhnicheskoi Khimii Plastmass" (Introduction to a Course on the Technical Chemistry of Plastics), Moscow, ONTI, 1934.
23. I.Shaiber, "Khimiya i Tekhnologiya Iskusstvennykh Smol" (Chemistry and Technology of Synthetic Resins), Goskhimizdat, Moscow, 1949.
24. S.N.Ushakov, "Efiry Tsellyulozy i Plastmassy na ikh Osnove" (Cellulose Esters and Plastics Based on Them), Goskhimizdat, Moscow, 1941.
25. V.A.Voskresenskii, Nauch.Trudy Kazan.Inst.Inzh. Stroitelei Neftyanoi Prom., No.5, 101 (1957).
26. R.Pummerera and G.Susich, Kunststoffe, 7, 117 (1931).
27. C.Trogus, T.Tomonari, and K.Hess, Z.phys.Chem., 16, 35 (1932).
28. W.Raker, C.Fullera, and N.Pape, J.Amer.Chem.Soc., 64, 776 (1932).
29. W.Kargin and S.Papkov, Acta Physicochim.URSS, 3, 839 (1935).
30. A.A.Tager and V.A.Kargin, Zhur.Fiz.Khim., 15, 1036 (1941); 15, 1029 (1941).
31. A.G.Pasynskii, Zhur.Fiz.Khim., 20, 981 (1946).
32. A.Kirkpatrick, J.Appl.Phys., 11, 255 (1940).
33. S.P.Papkov, V.A.Kargin, and Z.A.Rogozin, Zhur.Fiz. Khim., 10, 157, 607 (1937).
34. S.P.Papkov, Zhur.Prom.Org.Khim., 6, 240 (1939).
35. S.P.Papkov, Kolloid.Zhur., 19, 333, 733 (1957).
36. T.Alfrey, "Mechanical Properties of High Polymers" (Translated into Russian), Inostr.Lit., Moscow, 1952.
37. P.V.Kozlov and E.F.Ruskova, Dokl.Akad.Nauk SSSR, 99, 105 (1954).
38. P.V.Kozlov and E.F.Ruskova, Dokl.Akad.Nauk SSSR, 35, 583 (1954).
39. P.V.Kozlov and E.F.Ruskova, Symposium, "Vysokomolekulyarnye Soedineniya" (High-Molecular-Weight Compounds), Goskhimizdat, 1952, pp.12, 44.
40. Ind.chem.Physics, 11, 512 (1945).
41. P.Doty and H.S.Zable, J.Polymer Sci., 1, 30 (1952).
42. M.L.Danius, J.Appl.Phys., 21, 505 (1950).
43. S.N.Zhurkov, Dokl.Akad.Nauk SSSR, 47, 493 (1945).
44. S.N.Zhurkov, "Trudy Vtoroi Konferentsii po Vysokomolekulyarnym Soedineniyam" (Proceedings of the Second Conference on High-Molecular-Weight Compounds), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1945.
45. S.N.Zhurkov and R.I.Lerman, Dokl.Akad.Nauk SSSR, 47, 109 (1945).
46. D.J.Mead, R.L.Tichenov, and R.M.Fuoss, J.Amer.Chem. Soc., 64, 283 (1942).
47. S.N.Zhurkov and B.Ya.Levin, Symposium, "Stroenie Veshchestva i Spektroskopiya" (Structure of Matter and Spectroscopy), Izd.Akad.Nauk SSSR, Moscow, 1960.
48. V.A.Kargin, "Trudy Vtoroi Konferentsii po Vysokomolekulyarnym Soedineniyam (Diskussiya)" [Proceedings of the Second Conference on High-Molecular-Weight Compounds (Discussion)], Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1945, p.66.
49. V.I.Sedlis, *ibid.*, p.70.
50. T.Simril, J.Polymer Sci., 2, 42 (1947).
51. A.Merz, Kunststoffe-Plastics, 5, 157 (1958).
52. S.I.Sokolov and R.I.Fel'dman, Symposium, "Issledovaniya v Oblasti Vysokomolekulyarnykh Soedinenii" (Studies on High-Molecular-Weight Compounds), Izd.Akad.Nauk SSSR, Moscow, 1949.
53. W.Aiken, T.Alfrey, A.Janssen, and H.Mark, J.Polymer Sci., 2, 178 (1947).
54. R.M.Fuoss and D.J.Mead, J.Phys.Chem., 47, 59 (1943).
55. D.I.Gal'perin and L.I.Moseev, Kolloid.Zhur., 19, 167 (1957).
56. V.A.Kargin and Yu.M.Malinskii, Dokl.Akad.Nauk SSSR, 73, 967 (1950).
57. V.A.Kargin and Yu.M.Malinskii, "Khimiya i Fiziko-Khimiya Vysokomolekulyarnykh Soedinenii" (Chemistry and Physical Chemistry of High-Molecular-Weight Compounds), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1952.
58. R.F.Boyer and R.S.Spencer, "Chemistry of Large Molecules" (Translated into Russian), No.2, Inostr.Lit., Moscow, 1948.
59. G.L.Slonimskii, Doctoral Thesis (D.Sc. Equivalent), Karpov Physicochemical Institute, Moscow, 1947.
60. G.L.Slonimskii, "Mekhanicheskie Svoistva Polimerov i Svoistva ikh Rastvorov" (Mechanical Properties of Polymers and Properties of Their Solutions), Gosizdatlegprom, Moscow, 1951.
61. V.A.Kargin and G.L.Slonimskii, "Kratkie Ocherki po Fiziko-Khimii Polimerov" (Brief Outline of the Physical Chemistry of Polymers), Izd.Moskov.Gos.Univ., Moscow, 1960.
62. W.Baker, Ind.Eng.Chem., 37, 246 (1945).
63. T.Alfrey, Ind.Eng.Chem., 41, 701 (1949).
64. V.A.Kargin and T.V.Gatovskaya, Dokl.Akad.Nauk SSSR, 100, 105 (1955).
65. V.A.Kargin, T.I.Sogolova, and G.L.Talipov, Vysokomol. Soed., 1, 1670 (1959).
66. V.A.Kargin, N.A.Plate, and V.P.Shibaev, Vysokomol. Soed., 2, 166 (1960).
67. V.A.Kargin, V.A.Kabanov, N.A.Plate, and N.P.Pavlichenko, Vysokomol.Soed., 2, 433 (1960).
68. V.A.Kargin and G.L.Slonimskii, Uspekhi Khim., 24, 785 (1955).
69. A.A.Tager, "Rastvory Vysokomolekulyarnykh Soedinenii" (Solutions of High-Molecular-Weight Compounds), Goskhimizdat, Moscow, 1951.
70. A.A.Tager, Doctoral Thesis (D.Sc. Equivalent), Gorky State University, Sverdlovsk, 1956.
71. R.I.Fel'dman and A.K.Mironova, Kolloid.Zhur., 17, 465 (1955).
72. B.A.Arbuzov, "Trudy Vtoroi Konferentsii po Vysokomolekulyarnym Soedineniyam (Diskussiya)" [Proceedings of the

Second Conference on High-Molecular-Weight Compounds (Discussion)], Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1945.
73. P.B.Stickney and L.E.Cheyney, J.Polymer Sci., 3, 237 (1948).
74. A.K.Doolittle, J.Polymer Sci., 2, 124 (1947).
75. Cash, Mod.Plastics, 21, 119 (1944).
76. D.J.Mead, J.Amer.Chem.Soc., 64, 283 (1942).
77. E.I.Barg and N.N.Mel'tova, Dokl.Akad.Nauk SSSR, 2, 92 (1953).
78. I.I.Losev and O.Ya.Fedotova, Khim.Prom., 10, 295 (1952).
79. P.I.Zubov and M.P.Zverev, Kolloid.Zhur., 18, 679 (1956).
80. M.P.Zverev and P.I.Zubov, Kolloid.Zhur., 19, 201 (1957).
81. R.R.Lawrence and E.B.Intyre, Ind.Eng.Chem., 41, 689 (1949).
82. H.Passedouet, Ind.Plast.Med., 10, 3 (1958).
83. R.E.Burk and O.Grummit, Interscience Publishers, 9, 300 (1943).
84. G.Lutzu, No.22, 8 (1960).
85. W.I.Frissell, Mod.Plastics, 38 (5), 232 (1961).
86. M.S.Welling, The Rubber Plastics Age, 38, 610 (1957).
87. R.Kadasch, Mod.Plastics, 36 (5), 69 (1959).
88. A.Hartman, Kolloid Z., 142, 123 (1955); 148, 30 (1956).
89. F.Würstlin and H.Klein, Makromol.Chem., 16, 1 (1955).
90. K.Thinius, "Chemie, Physik und Technologic der Weichmacher", Berlin, 1960.
91. J.Ames and R.Sampson, J.Appl.Chem., 1, 337 (1951).
92. S.S.Voyutskii, "Rastvory Vysokomolekulyarnykh Soedinenii" (Solutions of High-Molecular-Weight Compounds), Goskhimizdat, Moscow, 1960.
93. Sh.L.Lel'chuk and V.I.Sedlis, Zhur.Prikl.Khim., 30, 412 (1957).
94. Sh.L.Lel'chuk and V.I.Sedlis, Zhur.Prikl.Khim., 31, 887 (1958).
95. Sh.L.Lel'chuk and V.I.Sedlis, Zhur.Prikl.Khim., 31, 1397 (1958).
96. V.A.Voskresenskii and V.A.Byl'ev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., No.6, 1016 (1961).
97. V.A.Voskresenskii and L.M.Kozlov, Zhur.Prikl.Khim., 33, 191 (1960).
98. V.A.Voskresenskii, V.A.Byl'ev, and E.M.Orlova, Zhur.Prikl.Khim., 34, 225 (1961).
99. V.A.Voskresenskii and S.S.Shakirzyanova, Zhur.Prikl.Khim., 35, 217 (1962).
100. V.A.Voskresenskii, S.S.Shakirzyanova, and V.A.Byl'ev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., No.2, 322 (1962).
101. A.A.Tager, A.I.Suvorova, L.N.Goldyrev, V.I.Esafov, and V.L.Berestova, Vysokomol.Soed., 4, 803 (1962).
102. A.A.Tager, A.I.Suvorova, L.N.Goldyrev, V.I.Esafov, and L.P.Topina, Vysokomol.Soed., 4, 807 (1962).
103. V.A.Kargin, P.V.Kozlov, R.M.Asimova, and L.I.Anan'eva, Dokl.Akad.Nauk SSSR, 135, 357 (1960).
104. V.A.Kargin, P.V.Kozlov, and Wang Nai-ch'ang, Dokl.Akad.Nauk SSSR, 130, 356 (1960).
105. P.V.Kozlov, Plast.Massy, No.10, 4 (1961).
106. L.V.Rozental' and E.T.Belyanina, Plast.Massy, No.11, 6 (1961).
107. L.V.Rozental', Vysokomol.Soed., 3, 1406 (1961).
108. L.V.Rozental' and F.G.Zhurina, Zhur.Prikl.Khim., 35, 2512 (1961).
109. P.V.Kozlov, R.M.Asimova, and A.N.Perepelkin, Vysokomol.Soed., 4, 124 (1962).
110. V.A.Kargin, T.I.Sogolova, and G.Sh.Talipov, Dokl.Akad.Nauk SSSR, 142, 844 (1962).
111. V.A.Voskresenskii and S.S.Shakirzyanova, Zhur.Prikl.Khim., 35, 1145 (1962).
112. Yu.S.Lipatov, Dokl.Akad.Nauk SSSR, 143, 1142 (1962).
113. Yu.S.Lipatov, L.M.Sergeeva, and V.P.Maksimova, Vysokomol.Soed., 2, 1969 (1960).

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