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The formation, structure, and properties of network polyurethanes

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ABSTRACT. Questions concerning the influence of the density and chemical nature of the cross-links on the properties of cross-linked polyurethanes are examined. The existing ideas about the mechanism of the formation of the network structure in polyurethanes are analysed and the causes of the inhomogeneity of the three-dimensional network in cross-linked polyurethanes are discussed. The principal advances in the study of the influence of the chemical microstructure of the macrochains of polyurethanes on the microphase separation process in thermoelastoplastics are described.
The bibliography includes 174 references.

Contents

I. Introduction 312
II. Network formation in polyurethanes and its influence on the properties of network polyurethanes 312
III. Urethane thermoelastoplastics 317

I. Introduction

Probably none of the classes of industrial polymers existing at the present time and produced on a large scale, with the exception of polyurethanes (PU), permits the variation of their properties, from those of elastomers, thermoelastoplastics, and foams to plastics and fibres by a slight alteration of the chemical structure of the macromolecules. A combination of increased hardness, a high modulus of elasticity, and a high elasticity is characteristic of polyurethane elastomers alone, while as regards resistance to wear they have no equal. It is not fortuitous that the industrial output of PU in the countries of Western Europe, the USA, and Japan has been doubling in each decade[1] and has reached about four million tonnes in 1986. In the USSR, the output of PU is approximately 100 000 tonnes per year and a growth of the manufacture of network polyurethanes (NPU) by a factor of four relative to 1985 is planned for 1990. The aim of the present review is to consider the principal results of research into the formation, structure, and properties of network polyurethanes.

II. Network formation in polyurethanes and its influence on the properties of network polyurethane

Processes involving the branching and subsequent cross-linking of linear macromolecules of a polymer have a decisive influence on its properties.[2] At the present time, one may claim that the formation of a network suppresses the microphase separation characteristic of certain polyesterurethanes to a greater extent the denser the network formed.[3,4] On the other hand, when a more flexible polydiene block has been introduced into the PU macromolecule instead of the ester block, then the microheterogeneity is retained regardless of the density of the network.[5]

Numerous studies have been devoted to the influence of the frequency of the cross-linking on the crystallisation and glass point (T_g) of network polyurethanes (NPU). Whereas the available data on the crystallisation of NPU are unambiguous,[6,7] namely the degree of crystallisation diminishes down to zero with increasing degree of cross-linking, the results for T_g differ greatly. It has been established for the NPU based on polyoxy(ethylene glycol) and 4,4′-diphenylmethane diisocyanate (MDI) [8] that T_g increases linearly with the density of cross-linking. On the other hand, when hexamethylene diisocyanate (HMDI) is used, the above relation passes through a maximum. On these grounds, it has been concluded that the aromatic nuclei and urethane groups in the macrochains exert a decisive influence and that T_g depends only slightly on the chemical cross-linking. A similar conclusion that the interaction of the polar groups in NPU has a strong influence has been reached in another study.[9] Nevertheless, some investigators believe that the T_g for NPU tends to increase with increasing degree of cross-linking.[10] Using the principle that individual structural elements influence independently the T_g for the polymer, Becker and Neumann[11] obtained formulae for the theoretical calculation of T_g taking into account the degree of cross-linking. An experimental test was performed on 59 linear and 27 cross-linked amorphous PU and demonstrated a satisfactory agreement between the calculated and experimental data.

The influence of the chemical nature of the cross-links on T_g is characteristic of NPU. It has been observed by broad band NMR [12] that T_g for PU based on poly(ethylene glycol adipates) (PEGA) and MDI with allophanate cross-links is −20 °C, while that for the PU with biuret cross-links is −15 °C. On the other hand, when ionic cross-links are introduced into the same PU, the mobility of the segment diminishes and T_g is in the range between −13° and −8° C. With increase in the concentration of interchain carbon–carbon bonds, T_g increases from −50 °C for a weight fraction of dicumenyl peroxide of 1.4 to 0 °C for a weight fraction of 2.5 relative to the non-cross-linked PU. Cross-linking by chemical bonds by employing trifunctional polyesters (PE) with a molecular weight (MW) in excess of 5000 g mol^{-1} does not alter the degree of self-association compared with linear PU.[13]

The nature of the cross-links influences not only T_g and the degree of self-association but also many other properties of the NPU. Thus the interaction of 2,4-tolylene diisocyanate (2,4-TDI) with the ions of 3*d* elements[14,15] in certain solvents can yield in the

final stage polynuclear complex forms of the diisocyanate whose functionality with respect to the NCO group is greater than two. Subsequent reaction with polyesters results in the formation of an NPU whose specific conductance is 5–6 orders of magnitude greater[16] than that of the usual NPU.[17] The strengths and thermal parameters of such NPU are close to those of the industrially manufactured PU, while their elasticity and resistance to wear are actually greater. The thermal stability of NPU can be significantly increased by using Mannich bases as catalysts of the urethane formation reaction.[18] This entails not only an increase in the length of the macromolecules as a result of the interaction of the macrodiisocyanate with polyesters but also the formation of a network as a result of the cyclotrimerisation of the terminal NCO groups.

The degree of homogeneity of the reactions occurring in the reaction system has become one of the first controversial problems as regards the formation of NPU. Two points of view have arisen in this connection. According to the studies by Lipatova and co-workers,[19–21] the formation reaction of the three-dimensional structure consists of two stages which differ sharply in their rates. The reaction is described by a second-order kinetic equation only up to 45–50% conversion owing to a change in the physical process conditions.[19] Beyond the gel point, the formation of the polyurethane network is described satisfactorily by the Avrami-Erofeev equation. It has been suggested that, after the attainment of a certain degree of conversion, the system undergoes microphase separation and the urethane formation kinetics begin to be determined by physical and no longer by chemical processes. Indeed, studies on the formation of NPU by the turbidity spectrum methods[20] have shown that, in the two-stage method of synthesis of NPU, particles of sizes of the order of 650 Å appear by the time of attainment of 70% conversion. Measurements of the angular dependence of the scattered light intensity indicate the presence of cross-linked microparticles and not aggregates of macromolecules. A single network is produced by the chemical cross-linking of network microblocks.[21] On the other hand, it is now difficult to regard the conclusion that physical factors have a decisive influence on the urethane formation kinetics beyond the gel point as rigorously demonstrated, because the power exponent in the Avrami-Erofeev equation is almost unity.

The study of the urethane formation kinetics before the attainment of the gel point and beyond it revealed[22] that in the temperature range 20–60 °C the reaction rate constants are virtually identical and the activation energies are 40.8 and 45.6 kJ mol^{-1} respectively, from which it is concluded that the rate of reaction is not diffusion controlled after gel formation. This conflicts with the view expressed by Lipatova and Ivashchenko[23] and Rumyantsev et al.[24] Data obtained[25] by the repeatedly distorted total internal reflection method led to the analogous conclusion that the kinetics of the formation of PU both in the liquid phase and beyond the gel point are the same. These results conflict with the conclusions reached by Lipatova and co-workers. It is notable that experimental data similar to the observations by the Kiev group of investigators have been obtained in a number of foreign studies. Hager et al.[26] and Huang et al.[27] arrived at the conclusion that phase separation takes place during the urethane formation process. A dependence of the urethane formation rate constant on the degree of conversion starting from 30–40% conversion has also been reported.[28]

In our view, the conflict between the conclusions reached by these research groups is only apparent. As will be seen from further exposition, the chemical processes leading to gel formation are extremely sensitive to many factors: the chemical nature of the reaction system, the presence and nature of a solvent, the concentration and stoichiometry of the reactants, the temperature, etc. For this reason, in each case a specific situation can arise. Under certain conditions, microregions with an increased content of the cross-linking agent or an increased concentration of NCO groups can appear in the reaction system even at the beginning of the reaction. This can occur either as a result of self-association,[29] or as a result of the poor compatibility of the components,[30,31] or because of the physical influence of the urethane groups which have appeared in the reaction system.[32,33] Clearly cross-linking in these regions occurs already in the early stages, which results in the appearance of the microgel. Further consumption of the NCO groups can take place in regions with different ratios of the functional groups, which is the reason for the observed change in kinetics. On the other hand, when the gel formation conditions are such that the concentration of the reactants is constant throughout the reaction volume, the microgel is not formed up to the gel point. The kinetics of the consumption of the NCO group beyond the gel point remain the same as before, because their reactions occur mainly in the sol fraction. The results of the studies considered above and our own data[34,35] lead to these conclusions. Thus the study of the influence of the number of stages in the formation of NPU on their strength parameters revealed that the bimodality of the distribution on the probability curve for the appearance of a particular tensile strength is more pronounced for the single-stage NPU preparation conditions. On the other hand, when the network polyurethane was obtained via a stage involving the synthesis of the macrodiisocyanate, the bimodality was much less marked, which can be explained by the lower concentration inhomogeneity of the terminal NCO group and hence by the lower inhomogeneity of the three-dimensional network of the PU. When rolled PU was vulcanised, the distribution curve was unimodal.

The change in the urethane formation mechanism is frequently inferred from the deviation of the kinetics of the consumption of NCO group from a second-order irreversible reaction. Apparently this can be done legitimately only for non-catalytic urethane formation processes. In the case of catalysed reactions, the consumption of NCO groups is described by more complex relations. Indeed, in a study of the urethane formation reaction between the macrodiisocyanate based on PEGA and 2,4-TDI and butane-1,4-diol (BD) in the presence of iron acetylacetonate,[36] the order of the reaction varied from three at the beginning to two at the end. The analytical expression describing the rate of consumption of NCO groups assumes the following form:

$$R = (AX^3 + BX^2)/(CX + K_1^-),$$

where A, B, and C are algebraic combinations of the rate constants for the individual urethane formation stages and the catalyst concentration, X is the current concentration of NCO groups, and K_1^- the rate constant for the decomposition of the binary intermediate complex into the initial reactants. At the beginning of the reaction, $AX^2 < BX^3$ and $CX < K_1^-$, so that the order of the reaction is three. As the reaction proceeds, the term BX^3 diminishes faster than AX^2 and the order tends to two. For other reaction systems, where this mechanism operates, a situation may be encountered where $AX^2 > BX^3$ and $CX \gg K_1^-$. The order of the reaction should then be unity throughout the kinetic curve. Thus the observed change in the rate of urethane formation is presumably in many cases associated with purely kinetic factors and not with a change in mechanism.

A complex gel formation process depends on many factors. In a study of the formation of NPU from PE, 1,1,1-tri(hydroxymethyl)-propane (THMP) and 2,4-TDI, it was shown[37] that, depending on the type of medium and the degree of dilution, the relative reactivities of the reactant as well as the tendency of the system towards ineffective macrocyclisation or three-dimensional polycondensation change significantly. The changes in the relative reactivities of the hydroxylated components in the reaction with diisocyanate can be achieved also by introducing a catalyst. The addition of tin dibutyl dilaurate [bis(butyl laurate)tin?] to the reaction system described above leads to the formation of a NPU with good physicomechanical properties,[38] while in its absence gel formation does not occur at all. The presence of hydroxylated compounds with different reactivities can entail a non-equilibrium distribution of cross-links in the polymer network and can reduce the modulus of elasticity compared with the calculated value.[39] The self-association of THMP can actually result in the appearance of polyfunctional branching units.[29]

Network formation in PU is frequently complicated by cyclisation especially near the gel point.[40,41] The fraction of cyclised molecules in the synthesis of PU in bulk can attain 2–3% for a degree of conversion of 0.9 and an initial ratio of the NCO and OH groups of unity. In the 0.1% solution, the fraction of cyclised molecules for the same conversion in the synthesis of PU increases to 85%.[42] The study of the cyclisation process is also essential because the pre-gel formation of loops and not entanglement make the main contribution to the defects.[43] Furthermore, there is a close relation between the intramolecular reactions before the gel formation point and the network defects. Such reactions result in the formation of elastically ineffective rings whose influence on the physical parameters of the network is opposite to that exerted by molecular entanglement.[44] The elastically ineffective rings at a concentration of 3% diminish the concentration of elastically active chains and the equilibrium modulus by ~30%.[45] With increase in the degree of cyclisation, the molecular weight of the region between neighbouring nodes of the network increases.[46] The degree of cyclisation depends not only on the ratio of the NCO and OH groups in the system, the degree of its conversion, and its dilution, but also on the MW of the polyester[47] as well as on the presence or absence of the catalyst in the system.[48] The higher the MW of the polyester, the greater the tendency towards cyclisation.[47,49] The tendency towards cyclisation is greater in the case of a two-stage cross-linking process than for a single-stage process, which is associated, according to the authors, with the possibility of the formation of MDI–THMP clusters when the reactivities of the OH groups are not the same.

It is of interest to note that macrocyclisation is observed even in those cases where the possibility of the formation of NPU is ruled out[50,51]—for example, the degree of cyclisation increases with increasing MW of the chain.

The influence of the flexibility of the polyester chain on the effective density of the three-dimensional network of the PU and on their structure has been traced in the study of Eremeeva et al.[52] It was then found that a denser and more stable effective three-dimensional network is formed in NPU based on flexible-chain oligoesters compared with PU having rigid macromolecules.

There exist interesting data concerning the influence of the nature of the PE on the gel formation process.[53] In the synthesis of linear oligoesters based on diethylene glycol and various dicarboxylic aliphatic and aromatic acids and the study of their reactions with the adduct 2,4-TDI–THMP in cyclohexanone, it was found that the rate of formation of MPU up to a degree of conversion of 60–70% is described by a second-order equation, while for higher conversions the process is complicated by gel formation and takes place under microheterogeneous conditions. The degree of reaction at the gel point and the critical degree of branching depend on the nature of the acid residue of the PE and particularly the greater the flexibility and the smaller the steric hindrance characterising the PE chain.

Complex PE [polyethylene(diethylene glycol adipates)], characterised by different degrees of molecular and topological inhomogeneity have been synthesised.[54] The degree of inhomogeneity of the chemical three-dimensional network of the NPU obtained on their basis depended directly on the degree of inhomogeneity of the initial PE. On the other hand, the inhomogeneity of the physical three-dimensional network, observed for small degrees of monoaxial equilibrium stretching deformation (<2%), was proportional to the concentration of the urethane groups in the macrochain. A transition from linear to viscoelastic behaviour, occurring in the region of low deformations of ~0.5–3.0%, has been reported.[55] The authors believe that the phenomenon is due to the thixotropic breakdown of the aggregate formed via intramolecular interaction.

The influence of a solid surface on the characteristics of gel formation in PU has been traced.[56,57] The data obtained have been interpreted from the standpoint of the heterogeneity in the reaction mixture, which is manifested at a specific stage of the PU formation process.[56] The nature of the PE does not alter the character of the influence of the filler (aerosil) on the structure formation in the hardening system. The filler prevented the formation of a gel in the system comprising a polyether, THMP, and MTI. On the other hand, when 2,4-TDI was used instead of MDI,[57] then the aerosil actually created more favourable conditions for gel formation. The strong influence of fillers on the structure of the three-dimensional network has been indicated.[58,59] A strong chemical interaction of the PU macromolecules based on a polyester with technical carbon particles has been observed.[60] The activation energy for the formation of the chemical bond was 123 kJ mol^{-1} and the limiting surface area of the technical carbon per bond of this kind was 11 $Å^2$. Under conditions where physical as well as chemical interaction between the technical carbon and PU is possible, this area is 7 $Å^2$, which indicates an appreciable fraction of physical cross-links.

The presence of a well developed physical network, whose appearance is due to a broad spectrum of intermolecular interactions, is characteristic of PU. This is no longer disputed at the present time but quite a few studies have been devoted to the determination of the quantitative relation between the densities of the chemical and physical networks in the NPU and also to the elucidation of factors influencing this relation. Such studies have been stimulated primarily by the strong influence of the nodes of the three-dimensional physical network on a series of physicochemical and operational characteristics of the PU. Thus sorption, thermo-mechanical, and spectroscopic studies have been carried out[61,62] on the network in the PU based on tri(hydroxymethyl)propane phthalate and aliphatic polyisocyanate. It has been shown that a fairly open chemical network is formed with M_n = 2500 g mol^{-1}. The physical nodes are extremely varied with respect to density (M_n of the order of 200 and 500 g mol^{-1}) and greatly increase the effective density of the network. The appearance of three-dimensional structures with network nodes, formed as a result of specific physical interactions, has been noted[63] already in the initial stages. Deformation tests on an NPU with a controllable network topology led Allen et al.[64] to the conclusion that the influence of physical entanglements in unswollen specimens on the modulus of the network is comparable

in magnitude to the influence of chemical cross-linking. Admittedly, the nature of the physical entanglement was not specified and one cannot therefore rule out the possibility that the increase in the modulus is associated with the occurrence of intermolecular interactions. Indeed, Dusek and Ilavsky[65] found in the determination of the equilibrium moduli of urethane networks that the structural front-factor A may be greater than unity, i.e. greater than the value expected for phantom networks, for which $A \leqslant 1$. This confirms the hypothesis that the interchain contacts may contribute to the equilibrium moduli. It has been stated[66] that the networks obtained are affine rather than phantom. This shows that polyurethane networks are more perfect than fully random networks.

As a rule, the dependence of the conventional strain in the NPU (σ) on the degree of its deformation (λ) is described satisfactorily by the Mooney–Rivlin equation.[67,68] However, it has been observed[69] that the classical relation $\sigma = f(\lambda - \lambda^{-2})$ for the PU investigated is represented by straight lines as far as $\lambda - \lambda^{-2} \simeq 0.1$, which subsequently become bent as the origin of coordinates is approached. In terms of the variables of the Mooney–Rivlin equation, the experimental data did not fit on the straight line and the constant C_2 did not really remain constant. It decreased with increasing degree of deformation and became a maximum at $\lambda = 1$; analogous data have been described elsewhere.[70]

Walsh et al.[71] concluded that polyurethane networks containing short polyol chains differ significantly in their deformation behaviour from ideal networks. They explain the results in terms of phase separation occurring in such PU. In a study of the deformation of diamine-hardened PU,[72] the constant C_2 of the Mooney–Rivlin equation actually proved to be negative.

All these facts definitely indicate that, with rare exceptions, the polyurethane networks are not ideal. This is apparently associated with the occurrence of strong intermolecular interactions in the NPU. These physical interactions are responsible for the large contribution by the energy component of the highly elastic deformation of NPU.[73,74]

The great influence of the chemical and topological structures of polyurethane networks on the properties of NPU has already been noted frequently above and in certain cases the effect of the network topology is comparable or even superior to the effects of the remaining factors. It is therefore extremely important to investigate the homogeneity of the polyurethane networks. The ideas of various authors on this question agree[75–79] and reduce to the fact that the network structure of the PU formed is inhomogeneous. The studies[80,81] in which it was concluded that the networks are highly homogeneous after investigating the mechanical, dielectric, rheopectic, and optical properties of model polyurethane networks constitute an exception. Admittedly, the same workers[82] reported the observation of an inhomogeneous network, but they explained its appearance by the microsyneresis occurring when the temperature of the synthesis is altered abruptly.

Lipatova et al.[77] also explained the increase in the heterogeneity of the NPU with increasing degree of cross-linking or the MW of the oligomer by the increase in the number of associated rigid chain fragments. The possibility of regulating the microheterogeneity of NPU by varying the intermolecular interactions in this system has been discussed.[74] It has been suggested in 1973 [32] that intermolecular interactions, leading to the fluctuation of the structural network in the oligomer even before the formation of a continuous chemical network, may play a major role in gel formation in oligomeric systems. Under such conditions, a preliminary order, leading to the microheterogeneity of the system, is established beforehand. X-Ray diffraction and other studies on swollen polyurethane networks[78,83] have also led to the development of an approach to the NPU as heterogeneous systems, their microregions being characterised by different parameters of interaction with the solvent.

It has likewise been demonstrated[84] that polyurethane networks are inhomogeneous, but the kinetic aspect of urethane formation, in particular the presence of monofunctional molecules in the system, is used as the mainstay of the explanation of the causes of this phenomenon. The observation of additional maxima in the thermostimulated depolarisation current is attributed to the accumulation of charge at the boundaries of regions with different degrees of cross linking.[85] The existence of a relation between the kinetics of the main chemical reaction (the formation of the urethane linkage), the gel formation process, and the structural characteristics of the hardened NPU has been reported also in another study by the same workers.[49]

The inhomogeneity of polyurethane networks as regards the cross-linking density results in a variable rather than a constant (as in an ideal network model) MW of the regions between the cross-linking nodes. In the treatment of the experimental data obtained, this must be taken into account, since a change in the conditions governing the synthesis of the polyurethane network can entail a significant alteration of the properties of the finished material.[86] An increase in the temperature of the synthesis led to an increase in the density of the three-dimensional chemical network as a result of a change in the ratio of the rate constants for the reactions of bi- and tri-functional alcohols with diisocyanate. Since the concentration of THMP was unaltered in all the experiments, the results obtained can be accounted for by a change in the distribution of M_n with respect to length.

Theoretical analysis of the MWD of the macrochain fragments between neighbouring cross-links carried out in a number of studies[87–89] makes it possible to approach the control of the molecular structure of network polymers with the aid of purely kinetic methods. Thus it has been shown theoretically[88] that, if the MWD in the initial oligomer is narrow, then the network chain distribution curve has a polymodal character. If the MWD becomes wider, the polymodality of the network chain distribution can ultimately vanish. An interesting outcome of the application of Zabrodin's theory[88,89] is the demonstration of the theoretical possibility of obtaining a narrower network chain distribution under certain kinetic conditions than the initial distribution. This conclusion has been criticised by Irzhak as erroneous.[2]

The kinetic approach to the study of the influence of the MWD and of the distribution with respect to different types of functionality (DTF) of the initial oligomers on the MWD and the DTF of linear molecules and network fragments has been developed.[90–92] It is notable that systems of differential equations are obtained with difficulty for the most realistic conditions in the synthesis of NPU, the equations often being simply insoluble, and the statistical approach to the solution of problems of this kind therefore appears more promising.[2]

When the mathematical theory of graphs was used in the study of the topology of a network polymer, it was demonstrated from the standpoint of conformational statistics[93] that the topological factors influencing the entropy of the system are responsible for the inhomogeneity of the networks, the inhomogeneity being greater the higher the network density.

Technological factors exert an enormous influence on the properties of the NPU and in the first place comes the number of stages in the urethane formation process.[94] In the single-stage

process, all the components of the reaction mixture are charged into the reactor simultaneously. In the two-stage version, the macrodiisocyanate pre-polymer is obtained initially by the reaction of the oligomer having terminal OH groups with an excess of the diisocyanate to which a chain lengthening cross-linking agent is added in the second stage. In the single-stage method of synthesis, the melting range of the PU crystallising is wider[95] than in the case where the pre-polymer with terminal NCO groups is formed in the preliminary step. According to the results of a number of workers, the set of physicomechanical properties is found to be best with the single-stage synthesis regime,[95,96] but the results of one study[97] permit the conclusion that the method of synthesis of PU based on polyethers is not appreciably reflected in the mechanical properties. For PU based on polyesters, the two-stage method has led to more effective mechanical parameters. The content of the sol fraction is reduced,[13,98] while the modulus of elasticity increases in the two-stage method of synthesis. Admittedly, Cherkasova et al.[99] arrived at the opposite conclusion that the less regular disposition of the units in the chain, observed in the single-stage method, ensures a higher value of the modulus.

A detailed comparison of the gel formation processes established[100] that the gel formation in NPU obtained in a single stage begins earlier. The networks formed in the single-stage process exhibit broader transitions at the glass point,[98] in agreement with data[95] indicating a broadening of the melting temperature range.

The facts presented show that the topological structure of the three-dimensional PU network depends greatly on the method by which it is produced and the results of different workers concerning the dependence of the mechanical properties on the regime used in the synthesis of the NPU do not agree. This is apparently due to the dependence of these properties on many factors and not only on the synthesis regime.

It has been shown in relation to the preparation of the network structure in rolled and cast PU [101] that the macromolecules of the oligomer obtained in the first stage are highly branched even in the presence of a small excess of the diisocyanate relative to the polyester. Since the kinetic characteristics of the linear growth of the oligomer macromolecules and of their branching are various, the possibility arises of regulating the temperature of the first stage to alter specifically the degree of branching of the prepolymer and hence the topology of the network obtained in the second stage of the synthesis of the NPU. By carrying out the first stage of the synthesis in accordance with the temperature regime ensuring a low probability of the branching of the prepolymer macromolecules, a significant increase in the tensile strength and in the relative elongation of the NPU was achieved compared with specimens obtained in accordance with the traditional isothermal regime.[102] Furthermore, there was a sharp growth of the viability of the cast composition and the densities of the effective and chemical three-dimensional networks diminished somewhat. In view of the demonstration of the strong influence of the degree of branching of the macromolecules being cross-linked on the properties of the NPU, an accelerated method for its estimation, based on a combination of intrinsic and maximum Newtonian viscosity data, was developed.[103] It has already been mentioned earlier[86] that the density of the nodes of the three-dimensional network formed varies as a function of the urethane-formation temperature. Later the same workers[104] studied in detail the influence of the polycondensation temperature on the gel formation kinetics and the properties of cross-linked polyester urethanes based on the copolymer of tetrahydrofuran with epoxypropane, THMP, and 2,2-bis(4-isocyanatophenyl)hexafluoropropane. It was then found that the amount of the gel fraction and the effective concentration of the chains between the branching nodes are maximum at 27 °C, diminishing with increase in the hardening temperature. The glass point of the NPU obtained depends only slightly on the hardening temperature. The conventional tensile stress is a maximum for a hardening temperature of 50 °C and the relative tensile deformation at rupture increases with increasing gel formation temperature. Somewhat different results have been obtained for another reaction system using a copolymer of tetrahydrofuran with epoxypropane, THMP, BD, and 2,4-TDI. With increase in the synthesis temperature from 30° to 60 °C, the limiting content of the gel fraction rose and the gel point appeared for a lower degree of conversion of the isocyanate groups and tended to the theoretically calculated value. An increase in the density of cross linking, the conventional tensile stress, and the modulus of elasticity accompanied by a decrease in the tensile deformation were also observed. The authors see an explanation of these findings in a decrease in the fraction of the unreacted THMP cross-linking agent with increase in the temperature of the synthesis as a result of the equalisation of its reactivity to that of the tetrahydrofuran–epoxypropane copolymer.

At the same time, the changes in the growth of the macromolecules with increase in the reaction temperature from 70° to 125 °C have also been attributed[105] to the decrease under these conditions in the molecular interaction, which leads to a greater mobility of the macromolecules. There has been a tendency to explain the influence of the synthesis temperature on the structure and relaxation properties of elastic polyurethane networks in terms of purely physical factors.[96,106] The observed anomaly in the elastic properties and in the effective density of the network, consisting in a decrease in these characteristics with decrease in the hardening temperature when the latter is below 80 °C has been attributed to a corresponding increase in the amount of globular formations—the main type of supermolecular structures in the majority of NPU.[96] The size of the globules depends both on the MW of the PE and on the hardening temperature.

Globular formations in NPU have been observed also in other investigations.[12,107,108] The specimens synthesised by the single-stage method sometimes do not exhibit any signs of a globular structure and have better mechanical properties.

The possibility of regulating the dimensions and morphology of the supermolecular PU structures with the aid of the temperature regime has been reported.[109] A low-temperature regime ensured the formation of PU with a monodisperse granular structure.

The conditions in the synthesis of the NPU have a definite effect also on their resistance to thermal degradation.[110] Whereas the NPU synthesised at 40–90 °C decompose with an effective activation energy of 159–169 kJ mol^{-1}, the kinetic parameters of the thermal degradation of the specimens obtained at 30 °C depend on the rate of hardening of the polymer: the higher the rate of urethane formation, the lower the activation energy for thermal degradation. It has been suggested that the decrease in the activation energy for the cross-linked polyesterurethanes can be due to the formation of stressed chemical bonds.

The thermal stability of NPU is determined to a large extent by the chemical nature of the diisocyanate (DI). The NPU based on aromatic dinuclear DI exhibit the greatest thermal stability, while that of the NPU based on aliphatic DI is smallest.[111]

The hardening temperature can influence significantly the mechanical behaviour of NPU on extension. It has been observed[112] that a specimen of cast NPU, hardened at 80 °C, has a higher initial modulus and relative deformation on monoaxial extension compared with the specimen obtained at 140 °C (Fig. 1), which indicates the existence in it of a structure divided into separate regions.

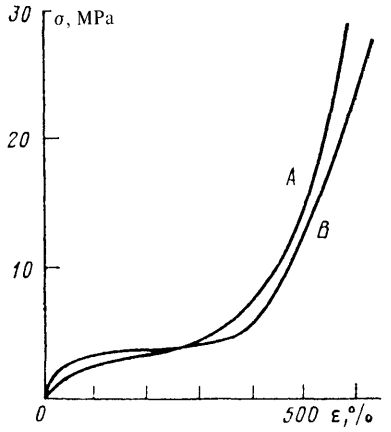


Figure 1. Dependence of the conventional stress σ on the relative elongation ε on monoaxial extension of the NPU: *A*, NPU specimen hardened at 140 °C; *B*, NPU specimen hardened at 80 °C.[112]

The influence of the ratio of the isocyanate and hydroxy-groups and also of the nature of the chain elongating agent on the chemical and physical nodes of the NPU network has been examined.[113] It was found that an increase in the NCO/OH molar ratio from 2.75 to 5.0 in the macrodiisocyanate formation stage leads to an increase in the densities of both the chemical and physical networks, the effective network density being much higher when the chain elongating agent is an aromatic diamine and not a low-molecular-weight diol. The study of the IR absorption spectra of the NPU obtained led the authors to the conclusion that hydrogen bonds exist up to 200 °C. The same view was arrived at also in other studies[114,115] where it was discovered that urethane–urethane hydrogen bonds exist even at 200 °C. On the other hand, Hagawa et al.[116] assume that hydrogen bonds begin to dissociate at ~70 °C. The differences between the results are apparently due to the presence in the NPU of hydrogen bonds of different nature and hence to their different thermal stabilities.

III. Urethane thermoelastoplastics

One of the most interesting types of network polyurethanes is that of thermoelastoplastics (UTEP), sometimes referred to as segmented PU. Their distinctive feature compared with the usual NPU consists in the fact that the three-dimensional network of the UTEP is capable of reversible decomposition on heating. Depending on the nature of the three-dimensional network of the UTEP, it is possible to classify them in the following way. The first type of UTEP is characterised by a linear structure of the macromolecules and the presence of domains, whose appearance is due to microphase separation as a result of the presence in the macrochains of sections differing sharply in flexibility and in the strength of intermolecular interaction. The domains play the role of multifunctional physical cross-links between the macromolecules, which decompose reversibly at an elevated temperature. The presence of a chemical three-dimensional network with allophanate or biuret nodes is characteristic of the second variety of UTEP. The density of the chemical three-dimensional network is such that there is no microphase separation or it is extremely weak. At temperatures of the order of 110–150 °C the allophanate (or biuret) nodes decompose reversibly and the UTEP macromolecules acquire the ability to move relative to one another when a load is applied. The third variety of UTEP is intermediate between the first and second.

The greatest number of structural studies have been devoted to the microphase UTEP. The development of the ideas of Cooper and Tobolsky[117] about the morphology of PU using wide and small angle X-ray diffraction and light scattering methods as well as differential thermal analysis (DTA) has led to the demonstration that the rigid units of the macromolecules, formed when the diisocyanate interacts with a low-molecular-weight diol (and/or diamines), aggregate into individual microphases.[118–121] A microscope study of the segmented PU established[122,123] that the domains have a lamellar structure, whose extent can reach in certain cases 3000–8000 Å but is usually in the range 30–200 Å.[124–127] The rigid units in the domain are extented into a rod-like tactoid form,[128] the length of the rigid block being identical with the width of the domain.[129]

It has been recently observed[130] that flexible polyesterurethane segments of UTEP based on polyoxy(tetramethylene glycol) (POTMG) with a MW of 2000 g mol^{-1}, MDI, and BD are also capable of becoming ordered. They form lamellae ~300 Å high and 2000 Å wide.

Treatment of UTEP with polar solvents leads to the formation of domains with a more ordered structure, which affects the physicomechanical parameters.[131]

Two types of fine structure have been discovered by IR spectroscopy in UTEP based on di(hydroxyethyl)terephthalamide, MDI, and POTMG.[132] A difference in the orientational behaviour of different sections of the rigid segment in the more ordered structure has been established and its inhomogeneity has been postulated.

The conclusion that the structure of the domains is inhomogeneous has been reached also by Vatulev et al.[133] from calculations of the orientation factor for the probable conformation of the diphenylmethaneurethane fragment. The calculated data do not make it possible to reduce the difference in the dichroism of the corresponding bands solely to a difference in the mutual orientation of the urethane and amide carbonyls.

Interpretation of literature data showed[134] that the kinetics of phase separation in segmented PU based on polyethers and polyesters can be represented as the segregation of two types of rigid segments with relaxation times τ_1 and τ_2.

Various physical and chemical processes, influencing greatly the formation of domains, may occur in the reaction system where the complex urethane formation process takes place. The chemical cross-linking of macromolecules lowers their mobility, inhibiting the ordering processes,[132] and thereby prevents microphase separation. The physical three-dimensional network restricts the process involving the segregation of the flexible and rigid blocks in the

NPU to a greater extent than does the chemical network.[135] The cross-linking resulting from the introduction of low-molecular-weight agents diminishes the degree of self-association to a greater extent than the network with the same density formed by a trifunctional polyester with MW $\geqslant$ 5000 g mol^{-1}.[136] The degree of phase separation increases with increasing MW of the PE [137] and, in the case where oligodienediols are used in the reaction instead of PE,[138] is independent of the density of the network.

The question of the influence of hydrogen bonds on the microphase separation process in PU is extremely interesting. Bonart and Morbitger[139] believe that the degree of microphase separation depends on the affinity of the rigid segments for one another and also for the flexible segments. Owing to the affinity of the ester groups of the flexible segments for the urethane groups of the rigid segments, the degree of separation in UTEP of the ester type is systematically lower than in elastomers based on polyethers. Indeed, IR spectroscopic studies[140] have shown that mainly hydrogen bonds of the urethane–flexible segment type with inclusions of small self-associated species (dimers and trimers) exist at the beginning of the microphase separation. Subsequently the microphase separation is accompanied by the redistribution of the hydrogen bonds towards the occurrence of urethane–urethane interactions in the domains. As a consequence of kinetic and viscosity effects, this process is prolonged and it has been shown[141] that the time of attainment of equilibrium in the segregation process depends on the nature of the soft phase and is determined by molecular mobility and not thermodynamic parameters. Thus one must conclude that the greater the degree of hydrogen bonding in the system the less effective is the domain formation in it.[142,143] However, it has been shown[144,145] that the hydrogen bonds between the C=O group and the NH groups of the urea linkage intensify the phase separation effect in PU. All these facts show that the domain formation process is very complex and the ratio of the hydrogen bonds between rigid segments and also between rigid and flexible segments is not the least important factor on which it depends. The conclusion[146] that the flexible segments play the role of a diluent should be regarded not as a rule but rather as an exception to it. The hydrogen bonds between rigid and flexible units are responsible for the appearance of a transitional layer at the interface even in highly dilute systems.

Presumably the hydrogen bonds between rigid segments promote microphase separation, especially since the energy of the hydrogen bonds in polyesterurethaneureas can reach 50–100 kJ mol^{-1},[147] i. e. may be comparable to the energy of the covalent bonds and is the decisive factor in the free energy gain on microphase separation in PU.

In segmented PU with a rigid segment of the glycol diisocyanate type, the energy of the hydrogen bond is appreciably lower and microphase separation can also be caused by the thermodynamic incompatibility between the rigid and flexible segments and not only by the hydrogen bonds. This is supported by the occurrence of microphase separation on passing from PU with the –NHCOO– group to polymers without hydrogen bonds and containing >NCOO– or –COO-groups.[148]

The glass point T_g of UTEP is closely related to the question of microphase separation. A linear dependence of T_g on the concentration of urethane groups in the chain is characteristic of non-thermoplastic PU,[149] whereas for segmented PU containing an appreciable number of polar and primarily urethane or urea groups such a dependence becomes more complex. This is due to the dominant influence on T_g of the overall concentration of urethane groups and the character of their distribution along the macrochain. When all the rigid segments have been segregated into domains and there is no interaction between the rigid and flexible segments, two glass points should be observed theoretically: the glass point of the soft block in the low-temperature region, which is identical with the T_g of the initial polydiol, and the glass point of the rigid segment in the high-temperature region, equal to the T_g of the polymer obtained from the low-molecular-weight diol (and/or diamine) and the diisocyanate. However, the glass point in the low-temperature region is usually higher than for the initial PE, which indicates an increase in the rigidity of the PE macromolecules as a result of the interaction with the rigid segments.[150,151] A formula has been proposed[151] for the calculation of the mole fraction of the hydrogen bonds formed by the rigid and flexible blocks (X_b):

$$(T_{g,pe} - T_{g,pu})/T_{g,pu} = k \cdot X_b(1 - X_b),$$

where $T_{g,pe}$ and $T_{g,pu}$ are the glass points of PE and the soft PU segments and k = 1.2–1.5.

The mobility in the transitional regions formed by the flexible and rigid blocks as a consequence of their limited compatibility can be sometimes observed by the calorimetric method[152] from the heat change in the intermediate temperature range. This intermediate phase is observed especially clearly on the thermomechanical curves.[153] With increase in the MW of the PE, the individual sections of the flexible block emerge from the sphere of action of the domains, which lowers the T_g of the UTEP matrix.[154] An analogous picture is also observed when poly(isobutylene glycol) is used as the flexible block instead of the PE,[155,156] although the influence of the MW of the flexible block on the T_g is not so great.

The theoretical prediction of the temperature T_d of the reversible decomposition of the domain structure is extremely important for the practical utilisation of the UTEP of the first kind. A thermodynamic theory of UTEP with a domain structure has been proposed.[157] The equation for the calculation of the temperature T_d has the following form:

$$1/T_d = -(R/\Delta H_A) \ln [e^{\nu/Z}(\nu - 1)/N_A], \quad (1)$$

where ΔH_A is the enthalpy of the ordering of 1 mol of rigid units (the enthalpy of the phase transition), N_A the mole fraction of the rigid units (the enthalpy of the phase transition), N_A the mole fraction of the rigid units, ν the coordination number of the lattice, and Z the number of rigid and soft units of the macrochain forming the $A-B$ block.

The change in the disordering temperature on passing from the PU whose macrochains consist solely of rigid units (T_d^0) to the PU containing flexible segments is described by the formula

$$1/T_d - 1/T_d^0 = (R/\Delta H_A) \ln N_A. \quad (2)$$

Eqn. (2) is analogous in form to Flory's formula for the equilibrium crystallisation of polymers.

Analysis of Eqn. (1) shows that the decomposition temperature of the domain structure depends to a considerable extent on the chemical microstructure of the UTEP. Thermodynamic theory makes it possible to calculate the minimum number of rigid units Z_A^{min} in the block for which microphase separation is observed. It was found that Z_A^{min} should increase with increase in the MW of the flexible block (Fig. 2).

For the same MW of the flexible block, the increase in the continuous sequence of rigid units should lead to an increase in T_d.

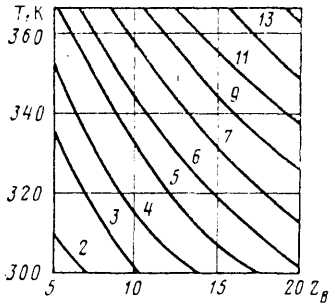


Figure 2. Dependence of Z_A^{min} on the number of units Z_B forming the flexible block and on the ambient temperature; ΔH_A = -9.8 kJ mol^{-1}; ν = 12.[157]

The conclusions of the theory have been confirmed by a series of experimental data. Thus UTEP with a specified chemical microstructure have been synthesised, the number of rigid units in the block varying from unity to three.[158] X-Ray diffraction study of the specimens showed that microphase separation is manifested following the attainment of a definite length of the rigid block. This conclusion agrees with other data,[159,160] which also reveal a 'critical' length of the rigid block, beyond which microphase separation is observed. The study of the dependence of T_d on the MW of POTMG of a urethane thermoelastoplastic based on MDI and BD showed[154] that the decomposition temperature of the domain structure shifts towards higher values with increase in the MW of the polyester. Analogous data have been obtained also in another investigation.[161] An increase in the length of the rigid block for the same MW of the PE entailed an increase in T_d.[162]

The marked dependence of the T_d for UTEP of the first kind on the chemical microstructure of the macrochains requires the development of quantitative methods for its calculation. We have suggested[163] that the theory of Markov chains be used for this purpose. It has been found that the chemical microstructure of the UTEP of both the first and second kinds can be defined fully with the aid of simple expressions involving the mole fractions of units of different types. It was found that the chemical microstructure of the UTEP of the first kind for a degree of conversion close to unity is almost independent of the relative reactivity of the hydroxylated monomers in the reaction with the diisocyanate and is determined by their initial molar ratio (Fig. 3). The microstructure of UTEP with allophanate or biuret branching and network nodes depends to a large extent on the rate constants for the branching process K_b. For a low value of K_b, the UTEP obtained contain virtually no cross-linking nodes and belong to the first type. On the other hand, for K_b comparable to the urethane formation rate constants the PU microstructure belongs to the UTEP of the second kind.

The chemical nature of the diisocyanates has a considerable influence on the properties of the UTEP. The asymmetry of the disposition of the isocyanate groups in 2,4-TDI leads to an amorphous structure of the domains, while symmetrical 2,6-TDI produces a crystalline rigid block.[7] It has been noted that the UTEP with the highest moduli of elasticity and tensile strengths are formed from symmetrical aromatic diisocyanates (MDI, 2,6-TDI, etc.). The symmetry of the structure of the diisocyanate influences also the degree of microphase separation. Koberstein[164] established by the small angle X-ray diffraction and small angle polarised light scattering methods that the PU specimens based on 2,4-TDI exhibit a smaller phase separation than the specimens obtained from MDI. However, the interface itself is more diffuse in the PU based on MDI.

Like the methyl substituent in the ring of the aromatic diisocyanate, the methyl side group in the diol also produces steric hindrance to the aggregation of the rigid segments into domains, which increases the T_g of the polymer.[165] On the other hand, apart from the increase in the fluidity temperature as a consequence of the decomposition of microregions with rigid blocks, the introduction of a polar substituent into the rigid blocks of polyurethanoureylenes

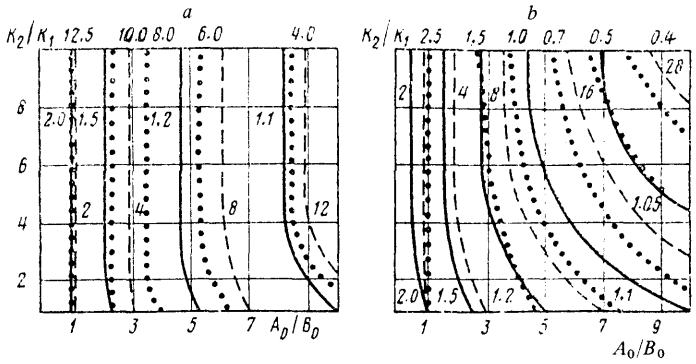


Figure 3. Dependence of the chemical microstructure of the UTEP macromolecules of the first kind $(A_mB_n)_c$ on the degree of conversion of the reaction system [*a*, α = 0.98; *b*, α = 0.90], on the initial molar ratio of the diol (A_0) and the polyester (B_0), and on the ratio of the rate constants for the interaction of the diol (K_2) and the polyester (K_1) with the diisocyanate; dashed line—*m*; continuous line—*n*; circles—*c*.

leads to an anomalous decrease in T_g owing to the manifestation of segmental mobility by the flexible oligoester blocks.[166]

During the past 10–15 years, many relations established previously as regards the influence of the molecular and chemical structures of the urethane formation process components and of the domain formation conditions on various properties of the UTEP have hardly changed significantly. They have all been described superbly in Kercha's monograph[7] and will not be considered in this review.

A series of novel investigations[30,31] devoted to the elucidation of the influence of the incompatibility of certain urethane formation process components with one another and of the rigid segments of different lengths on the structure and morphology of segmented polyurethanes have been published recently.

An interesting idea has been put forward by Teitel'baum et al.[167] According to their view, based on X-ray diffraction and thermomechanical investigations, the "kinetic limitation of the structure formation processes" can occur at a certain stage in the urethane formation process. The degree of perfection of the domain structure depends on the temperature of its formation. It has been shown that the ordering of the domain structure of amorphous polyesterurethanourea may be prolonged when it is heated above the hardening temperature. Analogous results have been obtained in the annealing or limited swelling of segmented polyesterurethanoureas in a series of low-molecular-rate solvents, which leads to further improvement of the microheterogeneous structure,[168] caused, according to the authors, by the orientational ordering of the rigid blocks.

A novel study of the influence of kinetic factors on the formation of the domain structure has been carried out.[169] By keeping PU based on POTMG, MDI, and PD at 190 °C, a specimen with microphase separation was obtained. This was followed by annealing at 120°, 90°, 80°, 60°, and 22 °C. With increase in annealing time, the glass point of the domain structure produced fell linearly with time in terms of semilogarithmic variables to a constant value and to a greater extent the lower the annealing temperature. The authors suggest that at low temperatures short and long sequences of rigid segments are rapidly segregated from the elastic phase, while at high annealing temperatures only the long sequences are segregated.

The significant influence of the number of stages in the synthesis of NPU on their parameters was already noted above. The two-stage synthesis of UTEP from POTMG, MDI, and ethylenediamine in solution with the reactants added in markedly different orders leads to the formation of sharply differing morphological structures.[170] UTEP with 50–80 Å crystalline domains has been obtained by adding ethylenediamine to the POTMG prepolymer and MDI. On the other hand, if ethylenediamine was added initially and then the product of its interaction with MDI was treated with POTMG, then the segmented PU formed had amorphous domains whose size reached 1000–2000 Å. The degree of phase separation was greater when POTMG was added gradually to MDI than for the converse addition.[171]

Studies by small angle X-ray scattering have shown[172] that the two-stage method of synthesis of UTEP from poly(tetramethylene glycol adipate) (PTMGA), MDI, and BD leads to a greater scattering intensity and width of the transition zone in the specimen than under conditions where it is synthesised by the single-stage method. When PTMGA is replaced by POTMG, the differences in the scattering intensity as a function of the methods of synthesis are significantly smaller. The observed behaviour can be explained by the greater degree of interaction of the flexible and rigid segments in the case of the polyester and the broadening of the distribution of the lengths of the rigid segments for the two-stage methods of synthesis of UTEP.

It has been suggested[173] that the UTEP based on POTMG, MDI, and BD, obtained in several stages, contains rigid blocks consisting predominantly of a single rigid diolurethane unit. In the segmented PU synthesised in one stage, the number of units forming the rigid block is greater than unity, which is the reason for the observed differences on deformation.

The physicomechanical properties of UTEP are greatly influenced by the MW and the MWD of the polyesters.[70] Segmented PU have been obtained by the reaction of poly(ethylene butylene glycol adipate) and BD with MDI. Two oligoesters with $\overline{M}_p$ = 1200 and 3000 were chosen for the investigation, a set of oligoesters with degrees of polydispersity ranging from 1.8 to 3.2 corresponding to each number-average molecular weight. The conventional tensile strength σ_t of PU-3000 proved to be greater and its relative elongation smaller than for PU-1200. In a series of PU-1200 specimens, σ_t fell with increase in polydispersity from 49.3 to 33.5 MPa. In contrast to PU-1200, σ_t for PU-3000 remained almost constant when the polydispersity was raised from 1.94 to 2.99. Deformation test calculations for the UTEP obtained using the model proposed by Kazama et al.[174] have led to the conclusion that the effective number of domains diminishes with increase in the polydispersity of the oligoester, which can be explained by the incompatibility of the rigid segment with the low-molecular-weight part of the polyester whose fraction is greater in specimens with a greater dispersity. With increase in dispersity, the boundary layer becomes more diffuse. It has been observed that phase separation takes place most effectively in PU-3000 specimens and improves as the polydispersity of the PU is reduced. Evidently this is the reason why the residual elongation and hysteresis losses are smaller by a factor of 2–3 for PU-3000 compared with PU-1200.

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The present review has shown that in most cases it is possible to obtain network polyurethanes with the required set of properties by the specific regulation of the chemical, physical, and technological factors. The greatest advances in the control of the properties of network polyurethanes have been made as regards thermoelastoplastics, which makes this type of polyurethanes most promising in view of the relative ease of their synthesis and their capacity for being worked repeatedly.

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