Translated from *Uspekhi Khimii*, **46**, 320-344 (1977)

U.D.C. 547.922.2

Structural Peculiarities of Homo- and Co-polyurethanes

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Recent advances in the investigation of polyurethanes are surveyed. Considerable attention is paid to copolyurethanes based on multicomponent initial constituents, which may exhibit thermoplastic or thermoelastoplastic properties depending on the distribution of the components in the chain and the length of the glycol constituent. A list of 142 references is included.

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I. INTRODUCTION

Almost all technically valuable polymeric materials—rigid and elastic fibres and rubbers, film materials, coatings, adhesives, rigid and elastic foam plastics, etc.—can be based on polyurethanes. The possibility of obtaining such diverse materials is governed by peculiarities of the chemical structure of the polyurethanes, which in turn are determined by the structure of the initial components and the conditions of synthesis. Because of the variety exhibited by the chemical structure it is especially important to establish the fundamental relations between chain structure and properties, and to elucidate specific aspects of structure formation in polyurethanes. Information on structure and properties has been summarised previously [1], but new advances have been made during recent years, and a tendency has appeared to develop new lines of investigation, primarily in the field of random copolyurethanes and segmented polyurethanes (block copolyurethanes). Moreover, the literature reveals no uniform approach to the separation of polyurethanes into individual groups or types on the basis of their structure or properties. Depending on their chemical structure these polymers may acquire the properties either of thermoplasts or of elastomers and thermoelastoplasts, so that the segregation of polyurethanes as a single class of polymers is extremely arbitrary. In this connection it is very convenient to classify polyurethanes according to the molecular mass of the glycol component [2].

The present Review discusses mainly the principal papers that have appeared during the past five years on the structure and the physicochemical properties of polyurethanes and related compounds [polyurethanureylenes, poly(urethane semicarbazides), polyamidourethanes, etc.]. We shall base our survey on one of the main parameters of the chemical structure of a polyurethane—the molecular mass of the glycol component of the polyurethane chain.

At the present time polyurethanes comprise a very large class of polymers, often differing significantly in chemical nature and chain structure, but invariably containing a number of urethane groups $-NH.COO-$, [1-4] e.g. polyesterurethanes based on oligoesters, etc. The chemical structure of linear polyurethanes can be represented by the general formula

$$[-R_1-OCONH-R_2-NHCOO-]_x \quad (1)$$

where R_1 and R_2 are chain segments of the initial glycol and di-isocyanate components respectively. Hence, by varying the structure and the chemical nature of R_1 and R_2, we can obtain polyurethanes of diverse molecular structure, with different concentrations of urethane groups governed by the length of the glycol component. The latter factor largely determines the type of polymer properties acquired by the polyurethane materials. The use of mixtures of glycols differing in molecular mass, as well as trifunctional compounds to provide a three-dimensional structure, provides wide opportunities for controlling the properties of polyurethanes.

In view of the above considerations we have divided polyurethanes into two main classes, obtained respectively from lower glycols and from oligomeric glycols, for the discussion of their structure and properties.

II. POLYURETHANES BASEDON LOWER GLYCOLS

1. Linear Homopolyurethanes†

One of the chief representatives of this type is that obtained from tetramethylene glycol and hexamethylene di-isocyanate (4,6-polyurethane)

$$[-OC(OCH_2CH_2CH_2CH_2)_nOCONH(CH_2)_6NH-]_x \quad (2)$$

($n = 1$), which, because of its good fibre-forming properties, has long been the subject of comprehensive investigation [2]. This polymer crystallises well, with a lattice exhibiting sharply defined anisotropy [5,6], for it comprises "planar networks", between which van der Waals bonds operate; within a network the macromolecules are combined by regular hydrogen bonds. This is a necessary condition for the establishment of a fully crystalline structure within 4,6-polyurethane, and is responsible for the peculiarities of its formation and its breakdown. The crystal lattice contains both di-isocyanate and glycol units. Thermographic and calorimetric investigations have shown [7-9] that structural features of 4,6-polyurethane also effect the variation in its thermodynamic properties.

Calorimetric investigations were made [10] on a series of polyurethanes synthesised from carbon-chain glycols $HO.[CH_2]_n.OH$ ($n = 2-10$) and various di-isocyanates—hexamethylene, methane-*pp'*-diphenylene, and 4-methyl-1,3-phenylene di-isocyanates. The melting points of the polyurethanes investigated, like those of polyamides,

† We apply the term *homopolyurethanes* to polyurethanes formed from single initial components (glycol and di-isocyanate).

depend on whether n is odd or even. The maximum glass point is found with specimens obtained from the diphenylmethane derivative, for which it falls uniformly with increase in n. For the tolylene series the glass points vary irregularly with increase in n, and the glass points of the hexamethylene polymers are independent of n.

Structural changes[11] and structure[12] were investigated in oligourethanes of general formula $CH_3.CO.\{O.[CH_2]_5.NH.CO\}_nO.CH_3$ ($n = 2-5$, $8-10$) as well as in a specimen of high molecular weight. Crystals grown from solution were studied. In oligourethanes having $n = 2-8$ the size (height) of the crystallites was independent of the conditions of heat-treatment, but for the remaining oligourethanes it increased on annealing at high temperatures, which indicates structural rearrangement with transition of chains from a folded to an elongated conformation (for $n = 9$, 10). The heat of fusion and the crystallinity of the oligourethanes diminish with increase in n. The crystallites have a two-phase structure, consisting of a very dense crystalline phase and a less dense intercrystalline phase containing mobile free ends of macromolecules.

When the length of the glycol component is increased and an oxygen atom is introduced to give 5-oxanonane-1,9-diol, the resulting polyurethane [formula (2) with $n = 2$] has a lower melting point and exhibits a characteristic change in crystalline structure, becoming polymorphic[13,14]. Infrared spectroscopy reveals three modifications, denoted α, α', and β.[13] The transition $\alpha \rightarrow \beta$ is a polymorphic process accompanied by change in the conformation of the chain with rotation of the urethane group. The transition from the α to the α' structure does not fit into a simple scheme of fusion of the former and appearance of the latter at this temperature, but involves an "intermediate" structure, which subsequently melts[14]. The change from the α to the intermediate structure is a transition from one crystal lattice to another, accompanied by a change in the chain conformation, which in this case, however, does not involve urethane group. The transition from the intermediate to the α' structure is in turn also accompanied by changes in crystal lattice and chain conformation, which become the same for the α' as for the α structure.

It will be of interest to examine the structure and properties of polyurethanes based on ethylene glycols[8,15-26], whose general formula can be written

$$[-OCO(CH_2CH_2O)_nCONH(CH_2)_6NH-]_x \quad , \qquad (3)$$

where $n = 1-6$. The structure[15,21] and the thermodynamic properties[16] of the product having $n = 2$, i.e. polyurethane-2 based on diethylene glycol and hexamethylene di-isocyanate, have been investigated. Conditions were found for the appearance of two different crystallographic modifications, α and β, melting at 124 and 128°C respectively. The dimorphism of polyurethane-2 must explain the complicated fusion peak on the heating thermogram[8] and the temperature dependence of the heat capacity[16]. Furthermore, polyurethane-2 is able to form two types of supermolecular structure (annular and needle-shaped spherulites)[21]: the former correspond to only one of the two crystallographic modifications, but the latter spherulites contain crystals of both modifications.

A multiplicity of thermal transitions[8,17,25-27] and a variety of supermolecular structures[19] are found also when $n = 3$. Optical microscopic investigation of the spherulitic crystallisation of polyurethane-3 (from triethylene glycol and hexamethylene di-isocyanate) has shown[19] that extremely diverse structures (annular and radial spherulites, lamellar spherulitic aggregates, etc.) may appear depending on the conditions of crystallisation (temperature, from solution or melt, thickness of crystallising film). X-Ray examination has in turn revealed[18] the presence of two crystalline modifications (α and β). However, calorimetry indicates[25,27,28] a more complicated pattern of structural changes when this polyurethane is heated. Indeed, more detailed investigations of the structure and structural transitions of polyurethane-3 shows[26] that it can crystallise in at least four crystallographic modifications $\alpha-\delta$, and many transitions appearing in particular on the heating thermograms and the temperature dependence of the heat capacity are a consequence of polymorphic transitions and the melting of individual modifications, in one case of melting followed by recrystallisation. These polymorphic transitions are realised only with relatively slow heating.

At least two crystalline modifications α and β may appear in polyurethane-4 [based on tetraethylene glycol and hexamethylene di-isocyanate—formula (3) with $n = 4$].[23] This polymer is also characterised by a variety of supermolecular structures (positive and negative annular spherulites of different degrees of perfection, sheathlike spherulites). A significant feature is the coexistence of two crystalline modifications—positive rings comprising α-crystallites, and negative rings of β-crystallites—in an annular spherulite of polyurethane-4. This provides further confirmation of the formation of annular spherulites by "rhythmic" crystallisation[29-31]. However, the opposite phenomenon has been observed with polyurethane-2[21] and polyurethane-3:[26] i.e. annular spherulites grew in the temperature range of one crystalline modification, and their optical patterns were consistent rather with a structural hypothesis suggested by other workers for annular spherulites[32,33].

Calorimetric investigations[34] on polyurethane-4 and polyurethane-6 (the latter from hexaethylene glycol and hexamethylene di-isocyanate) have yielded information on their thermodynamic properties. In particular, true values were obtained for the enthalpy and entropy of fusion of polyurethane-4: $\Delta H_f = 28.5$ cal g^{-1} and $\Delta S_f = 29.0$ cal $mole^{-1}$ deg^{-1}; the corresponding values for polyurethane-6 were 30 cal g^{-1} and 40.0 cal $mole^{-1}$ deg^{-1}. The contributions of urethane groups to the entropies of fusion of these polyurethanes were estimated. It is interesting that the contributions of methylene groups and of urethane groups differ not only in absolute magnitude but also in sign, respectively 2.4 and -4 cal $mole^{-1}$ deg^{-1}. The negative entropy indicates that the presence of urethane groups diminishes the number of conformations of the chain in the melt: i.e. it lowers the configurational entropy of the melt. Hence increasing the concentration of urethane groups in the chain should raise the melting point of the polyurethanes (with closely similar true heats of fusion). Such regular rise in the melting point is indeed observed on passing from polyurethane-6 to polyurethane-2.[8,9,16,17,34].

It is significant also that the glass points of this series of polyurethanes increase linearly[27] with the concentration of urethane groups. Extrapolation to zero concentration then gives $T_{gl} = -83$°C, which will yield the glass point of poly(ethylene oxide), the macromolecular polymer-homologue of the glycol chain segments of these polyurethanes. For polyurethane-4 and polyurethane-6 the excess entropy at the glass point has also been obtained, as well as the contributions thereto made by urethane groups. The energy of hydrogen bonds involving urethane groups in these polyurethanes was estimated as ~4 kcal $mole^{-1}$.

A new structural feature of this series of polyurethanes (formula 3) has been revealed by the X-ray examination of oriented fibres and films[24]: the observed identity periods were shorter than the theoretical values $C_{exp} < C_{theor}$. The difference was due to the divergence between the c axis of the inverse lattice and the texture axis of the polyurethanes, and was increased by any spatial position of the crystallite axes relative to the orientation drawing axis. The parameters of the unit cell of polyurethane-3 were found to be

$$\begin{aligned} a &= 9.24\ \text{Å}; & \alpha &= 77°; \\ b &= 8.01\ \text{Å}; & \beta &= 90°; \\ c &= 23.90\ \text{Å}; & \gamma &= 68°; \\ \rho_{exp} &= 1.23; & \rho_{X\text{-ray}} &= 1.31; \\ & N = 4. \end{aligned}$$

with the presence of sloping crystallites taken into account. Another peculiarity of the orientational behaviour of crystallites of polyurethane-3 in the β form was that on elastic deformation they underwent three-dimensional rotation until the axes of the molecules coincided with the texture axis. Furthermore, elastic deformation of a polyurethane-3 specimen containing the γ modification leads to breakdown of the γ form with transition to the β modification.

Replacement of the aliphatic di-isocyanate unit in polyurethane-3 by an aromatic unit, i.e. passing to a polyurethane based on triethylene glycol and methane-*pp'*-diphenylene di-isocyanate (polyurethane-F3), [35] results not only in loss of the ability to crystallise but also in a rise in the glass point and an anomalous process of vitrification. This is indicated by the occurrence of two successive jumps in heat capacity in the region of the glass point. Analysis of the process suggested that the first abrupt change in heat capacity corresponded to the development of mobility in microregions of the polyurethane in which were concentrated glycol chain segments, whereas the higher-temperature jump was due to disintegration of microregions with associated methanediphenylene di-isocyanate chain segments.

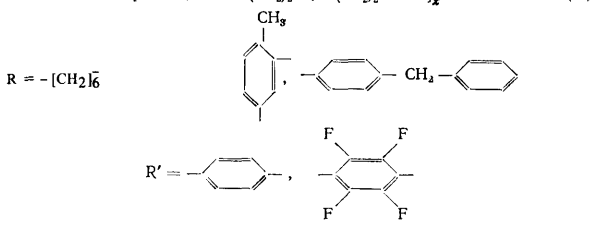
The diminished degree of hydrogen bonding on passing to *N*-substituted polyurethanes is responsible for several structural and thermal peculiarities. This was demonstrated in an investigation by infrared spectroscopy and thermography of *N*-methylated and *N*-benzylated polyurethanes based on ethylene glycol and 4-methyl-1,3-phenylene di-isocyanate[36].

Analogues of the polyurethanes

$$[-OCO(CH_2)_nOOCNH(CH_2)_6NH-]_x \qquad (4)$$

($n = 4-6$) in which 2–4 methylene groups have been replaced by difluoromethylene groups, in either or both di-isocyanate and glycol units, have been examined thermographically[37–41]. The introduction of fluorine atoms into one of the components results in anomalous melting, with two extrema on the fusion peak of the thermogram obtained when the polyurethane is heated. Such anomaly depends on the previous history of the specimen, and is due to the polymorphism of the crystalline phase, as with polyurethanes based on glycols containing oxygen in the chain. The ability to form a polymorphic crystalline structure diminishes as the number of difluoromethylene groups introduced into the chain decreases. When glycol and di-isocyanate components contain the same number of difluoromethylene groups, the resulting polyurethane exhibits no tendency to polymorphism. Conformational changes in the chain due to the sequence of difluoromethylene units are held responsible for the polymorphism of fluorinated aliphatic polyurethanes.

Fluorinated aromatic polyurethanes and their unfluorinated analogues of general formula



both crystallise poorly[42]. Those based on an aliphatic di-isocyanate exhibit the greatest tendency to crystallise. With an aromatic di-isocyanate the polyurethane has a higher melting point. Thus those obtained from hexamethylene, 4-methyl-1,3-phenylene, and methane-*pp'*-diphenylene di-isocyanates melt at 188, 190, and 222°C respectively, the corresponding glass points being 42, 47, and 49°C. It is significant that two glass points—as with the polyurethane from methane-*pp'*-diphenylene di-isocyanate and triethylene glycol[35]—are not observed here, which indicates that the introduction of a benzene ring into the glycol unit leads not only to an increase in the general rigidity of the polyurethane chain but also to a "levelling out" of the mobilities of di-isocyanate and glycol units. Probably this is responsible also for some tendency to crystallise shown by these polyurethanes based on aromatic di-isocyanates and glycols.

Formula (5) shows fluorine introduced into the benzene ring of the glycol unit, which should not affect the thermodynamic flexibility of the polyurethane chain. However, both the melting points and the crystallinity of all three types of fluorinated aromatic polyurethanes are lower than those of their unfluorinated analogues. The explanation is that the replacement of hydrogen by fluorine atoms leads to weakening of interchain interaction and of the tendency to associate at the fluorinated benzene rings. This is evidenced by the fall in the glass point of a polyurethane based on an aliphatic di-isocyanate when fluorine is introduced into the benzene ring of the glycol unit. However, the introduction of fluorine into polyurethanes based on an aromatic di-isocyanate, in which its benzene rings are also able to associate, does not affect the glass point of the polyurethane.

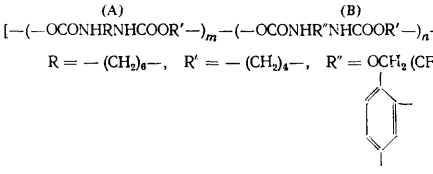
The above results indicate that, depending on the previous thermal, mechanical, etc. history of linear homopolyurethanes based on the lower glycols, their structure and physicochemical properties are predetermined by the chemical structure of the whole polymer chain. This implies that the main method of regulating the properties of polyurethanes of this type is, as before, to vary the chemical structure of the chains, not their physical structure.

2. Linear Copolyurethanes‡

Copolyurethanes of the simplest type are obtained from two di-isocyanates and one glycol or from two glycols and one di-isocyanate. They can be regarded as binary

‡ The term *copolyurethane* indicates that one of the initial constituents (di-isocyanate or glycol) comprises more than one component.

copolymers, in which units of two initial homopolyurethanes can be distinguished. Three types of random binary copolyurethanes have now been obtained, differing in their property–composition diagrams[41,43–47]. An example of the first type is based on tetramethylene glycol, hexamethylene di-isocyanate, and a fluorinated aromatic di-isocyanate having a structure resembling that of 4-methyl-1,3-phenylene di-isocyanate but with the methyl group replaced by a polyfluoroalkoxyl[45]. The chemical structure of this copolyurethane-I can be represented by the formula



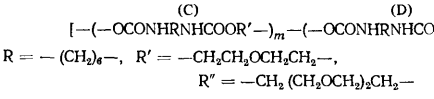
(6)

containing two kinds of units—4,6-polyurethane (A) and a polyurethane based on tetramethylene glycol and the fluorinated di-isocyanate (B)—corresponding to the initial homopolyurethanes. The latter, in contrast to 4,6-polyurethane, cannot crystallise. Thus copolyurethane-I contains units capable (A) and incapable (B) of crystallising. Thermographic examination has shown that the introduction of non-crystallising units causes the crytallisation and melting points of copolyurethane-I to fall and lowers the heats of crystallisation and fusion[45]. The reason is the diminished ability of the copolymer to crystallise with increase in the proportion of non-crystallising units, with a consequent lower degree of crystallinity and the formation of a less perfect crystal structure: copolyurethane-I containing >50 mole % of non-crystallising units is amorphous. This phenomenon leads to anomalous variation of the density of the copolymers, which increases linearly with the content of fluorinated units only for the amorphous copolymers. This is because the density is determined over the initial composition range (<50 mole % of non-crystallising units) by competition between two processes: the introduction of fluorinated units tends to increase the density by the substitution of fluorine atoms, but tends to diminish the density by disrupting the crystalline phase of the crystallising units (4,6-polyurethane).

Flory's equation for random binary copolymers comprising crystallising and non-crystallising units was applied to the depression of the melting point of copolyurethane-I. The calculated melting point was closely similar to the experimental value only for low contents of the non-crystallising units, but was above the latter at higher contents. Such anomaly is attributed to the presence in the non-crystallising units of long polyfluoroalkoxy-groups, which act as an internal plasticiser and intensify the general irregularity of the copolyurethane-I chains.

A copolyurethane of the same type is obtained from triethylene glycol with hexamethylene and methane-*pp*′-diphenylene di-isocyanates[47]. The initial homopolyurethanes are the crystallisable polyurethane-3 and the amorphous polyurethane-F3 (see Section I). In this case the melting point and the crystallinity of the copolyurethane also fall with increase in the proportion of non-crystallising units, but the copolymer becomes completely amorphous only when the content reaches 80 mole %. This provides further conformation that polyfluoroalkoxy-groups do indeed intensify the general irregularity of the copolyurethane-I chain.

An example of the second type of random binary copolymers is copolyurethane-II based on di- and triethylene glycols with hexamethylene di-isocyanate, whose chemical structure can be represented by the formula[43,44,46]

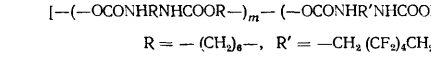


(7)

which shows that the initial homopolyurethanes are the above polyurethane-2 and polyurethane-3 (units C and D respectively). In contrast to copolyurethane-I, both kinds of units in copolyurethane-II are able to crystallise. Infrared spectroscopy and X-ray diffraction reveal a crystal structure identical with that of one of the initial homopolyurethanes. Transition from one type of structure to another is observed when the copolyurethane-II contains 60 mole % of C units. The composition dependence of the melting point contains a "eutectic minimum" at intermediate compositions, but no eutectic—mixture of crystals of the initial homopolyurethanes—is present. The occurrence of the eutectic minimum is due to the appearance of a less perfect crystal structure, owing to disruption of the regularity in the alternation of urethane groups that is necessary to produce a perfect crystal structure in polyurethanes of this type. The copolyurethanes, like the initial homopolyurethanes, are capable of a polymorphic crystal structure, but this ability diminishes with the transition to an equimolecular copolyurethane-II composition. Structural investigations have shown that the polymorphic transitions in the copolymer and in the initial homopolymers are a consequence of conformational changes in the chain, which may involve both the urethane group and the glycol unit. Thermographic and structural examination of mixtures of the initial homopolyurethanes crystallised together has shown that they are not isomorphous and cannot cocrystallise.

The copolyurethane obtained from hexamethylene di-isocyanate and mixtures of ethylene and hexaethylene glycols is of the same type[48]. Both kinds of units are also capable of crystallising, and their melting point also falls as the equimolecular composition of the copolymer is approached. Yet several mechanical properties of the copolyurethane vary irregularly, which can be attributed to the absence of a random or nearly random distribution of glycol units and the presence of long sequences (blocks) of the same glycol units in the chain. This may be due to a difference in the conditions of preparation of the copolyurethane[49].

Binary copolyurethanes of the third type may have the chemical structure[41]



(8)

As with copolyurethane-II, the initial homopolyurethanes of copolyurethane-III can crystallise, but they are isomorphous and able to form a combined crystal structure. Further, the composition dependence of the melting point does not pass through a "eutectic minimum", but is linear, owing to isomorphism. Another difference is that the tendency to form a polymorphic crystal structure inherent in a fluorinated homopolyurethane is not suppressed by the introduction of units of the second homopolyurethane, and a polymorphic structure appears even when the copolyurethane-III contains 70 mole % of the unfluorinated homopolyurethane.

A series of copolyurethanes based on hexamethylene di-isocyanate and mixtures of glycols of general formula $HO[C_2H_4O]_nH$ ($n = 1-4$, 6) (copolyurethane-M) had a constant mean concentration of hydroxy-groups in the mixture equal to their concentration in triethylene glycol [27,49-51], so that the empirical formula of the copolymers corresponded to formula (3) with n adopting simultaneously all the above values. The properties of these copolyurethanes are compared with those of polyurethane-3, since they possess the same concentration of urethane groups, and differ only in the distribution of the latter in the chain. As in the case of copolyurethane-II, on passing from polyurethane-3 to copolyurethane-M not only the tendency to crystallise but also the ability to form a polymorphic crystal structure diminishes. The structure of copolyurethane-M containing 60% and 70% of triethylene glycol in the initial glycol mixture is identical with that of polyurethane based on triethylene glycol (polyurethane-3). Copolyurethanes having about the same contents of different glycols may have different types of structures depending on the conditions of crystallisation (from different solvents). The glass point of copolyurethane-M, in contrast to those of the initial homopolyurethanes, is determined not only by the concentration of urethane groups but also by their distribution in the chain. The temperature range of the glass transition also becomes wider, owing to the expansion of the spectrum of relaxation times resulting from differences in the mobility of individual chain segments caused by the irregular distribution of urethane groups in these copolyurethanes. Enthalpies and entropies of fusion as well as crystallinities have been determined for copolyurethanes-M. As in the cases of polyurethanes-4 and -6, the contribution of urethane groups to the entropy of fusion of the copolyurethanes identical in structure with polyurethane-3 has been estimated: they lower the entropy of fusion of the crystalline phase as in the other cases, the observed decrease being similar in magnitude to that of NHCOO groups in polyurethanes-4 and -6, and of NHCO groups in polyamides.

The data given on the structure and properties of linear polyurethanes obtained from the lower glycols indicate that their relation to the chemical structure of the chain is governed by the same laws as with other types of thermoplastic polymers capable of specific interactions (e.g. polyamides). Nevertheless, results for various random copolyurethanes obtained from multicomponent initial constituents suggest that the structure and properties of thermoplastic polyurethanes can be controlled extremely effectively by varying not only the chemical structure and nature of the initial constituents but also the distribution in the chain of polar—primarily urethane—groups, which determine the regularity of intermolecular hydrogen bonds in polyurethanes of this type.

III. POLYURETHANES BASED ON OLIGOMERIC GLYCOLS

1. Cross-linked Polyurethanes

Increasing the molecular weight of the glycol constituents of polyurethanes while chemically cross-linking their chains leads to a qualitatively new type of polymeric materials—elastomers (rubbers)—which have been the subject of many studies, mainly on their strength, elastic, and other operating properties. Since most of this information has been summarised in monographs, reviews, and symposia [1,3,4,52-54], we shall discuss here only some of the main conclusions that can now be reached concerning the relation between the chemical constitution of cross-linked elastomers and their structure and physicochemical properties.

Cross-linked polyurethane elastomers are characterised by the alternation in their macromolecules of oligomeric blocks differing in flexibility and nature, as well as rigid di-isocyanate units, and the presence of various polar functional groups capable of forming various types of physical cross-links and transverse chemical bonds, etc. All this combined determines the macroscopic properties of the polyurethanes (glass point, temperature and range of phase transitions in crystallisable polymers, mechanical and other properties). As a consequence, the three-dimensional network in cross-linked polyurethanes is formed by both chemical cross-links and physical (hydrogen) bonds [1,3,4], and the structure of the effective three-dimensional framework, together with other parameters, acquires especial importance [1]. The most convenient procedure in estimating the contributions of individual parameters to the variation in the properties of cross-linked polyurethanes is to study successively the initial components (oligoglycols), intermediate products in the synthesis (linear polyurethanes), and the final cross-linked polyurethanes, as has been done in several studies [2,55-58].

Blocks of oligomeric glycols have the predominant role in determining the structure and properties of polyurethanes derived from them. Thermodynamic analysis and structural investigations have shown [56-59] that the ability of these polymers to crystallise is determined by the corresponding ability of the oligomeric blocks, and increases with the molecular mass of the latter. The crystal structure appearing both in linear and in cross-linked polyurethanes is identical with that of the oligoglycol blocks and their high-polymer homologues, but is less perfect, since the di-isocyanate units—and in cross-linked polyurethanes also branch points of the chemical network with adjacent units—act as defects in the crystal lattice. Formation of a crystalline phase in cross-linked polyurethanes is responsible for the development of properties inherent in energy-elastic materials [2,60,61], but the action of temperature or mechanical stresses breaks down this phase and restores to the polyurethanes the properties characteristic of entropy-elastic materials.

An abrupt rise in the glass point is observed on passing to polyurethanes only from oligoglycols (oligoethers) comprising polar chains, as a consequence of the formation of a secondary physical network diminishing their kinetic flexibility [1,2]. In cross-linked polyetherurethanes the glass point (like that of linear polyurethanes, largely determined by the thermodynamic flexibility of the chain) depends mainly not on the frequency of chemical cross-linking but on the concentration of urethane groups forming branch points of the physical network. Indeed, calculation of effective and chemical densities of cross-linking for polyurethanes based on oligoethers showed that physical links constitute about 80% of the total three-dimensional network, whereas the corresponding proportion in cross-linked polyurethanes based on carbon-chain oligoglycols is 10–30% [63].

With oligomeric blocks of the same molecular mass, the same di-isocyanate structure, and the same degree of chemical cross-linking the fall in the glass point of the polyurethanes with decrease in the polarity of the oligomeric blocks is accompanied by extension of the temperature range of vitrification, owing to a change in the character of the intermolecular bonds in the polymers.

Application of the theory of the free volume to vitrification of the initial oligoethers and the resulting polyurethanes established[58,64] that the macromolecules of polyurethanes based on oligoesters are thermodynamically more flexible than those based on oligoethers, but kinetically less flexible. The high thermodynamic flexibility of oligoester blocks is due to the great mobility of the secondary physical network formed, so that the latter readily rearranges under the influence of temperature or mechanical stress[1]. The presence in polyetherurethanes of a dense physical network capable of structural reorganisation influences also the thermodynamics of their deformation: in contrast to ordinary rubbers, the deformation of polyetherurethane elastomers is accompanied not only by a decrease in entropy but also by a change in internal energy[61,65,66].

The dominant role of glycol blocks in determining structure and properties is indicated by the fact that the flexibility of the molecules in polyurethane networks is due not only to the formation of long sequences of relatively short oligomeric chains but also the intrinsic flexibility of the oligomeric blocks. The cleavage and redistribution of secondary physical bonds in amorphous polyesterurethane elastomers, which occur under the influence of temperature and mechanical stress, are then a consequence of the preservation of oligoester blocks of high thermodynamic flexibility (mobility) even after their introduction into the polyurethane[2]. The high mobility of the secondary network in polyesterurethanes suggests an analogy between these polymers and the thixotropic structures studied in colloid chemistry[1,67].

Polyurethanes based on oligoglycols and individual di-isocyanates can be regarded as block copolymers, but the individual properties of the di-isocyanate units do not develop in the polyurethane, owing to their small size and the small fraction of the volume of the polymer that they occupy.

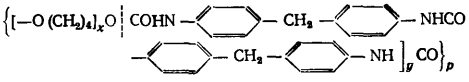
2. Segmented Polyurethanes

The introduction into the chain not only of oligomeric glycols but also of lower glycols or other bifunctional compounds (diamines, hydrazine, dihydrazides of dicarboxylic acids, etc.) leads to the formation of polyurethanes that, being linear or weakly cross-linked, develop under certain conditions the properties of elastomers, but at high temperatures or under the influence of solvents behave as ordinary thermoplastic polymers (polymeric materials).[1,68-73] Since the oligoglycol blocks are accompanied in the chain by relatively long sequences (segments, blocks) comprising di-isocyanate units and lower functional units, these polymers are usually termed *segmented polyurethanes*. The term "block copolyurethanes" is also fully applicable, but these compounds differ from traditional block copolymers (butadiene–styrene copolymers, etc.) in the relative smallness of the blocks, whose molecular mass reaches only a few thousands, so that the number of them in the chain is far larger. Since segmented polyurethanes have the properties both of thermoplasts and of elastomers, they have been termed *thermoplastic elastomers* (*thermoelastoplasts*).

During recent years quite a large number of studies have been published on segmented polyurethanes, concerned with their fine and supermolecular structure[71,74-93], their thermal and thermomechanical behaviour[94-110], and their physicochemical and physicomechanical properties[111-128]. The latter are related to the chemical constitution and to the supermolecular structure present in segmented polyurethanes.

(*a*) Structure

The chemical structure of segmented polyurethanes can be demonstrated by that based on an oligo-oxytetramethylene glycol, methane-*pp'*-diphenylene di-isocyanate, and tetramethylene glycol (chain lengthener)



(9)

one of the most thoroughly studied examples. Two types of blocks can be distinguished (separated by the broken line)—flexible (oligether) and rigid, comprising di-isocyanate and lower glycol (chain lengthener) units—the first of which exhibit relatively weak intermolecular interactions and are responsible for the elasticity of the system, whereas the second ensure strong intermolecular interactions in the chain, the total effect of which may be comparable with that of cross-linking of the chains by chemical bonds[129]. Investigation of intermolecular links, primarily hydrogen bonds, therefore becomes especially important in segmented polyurethanes. An additional reason is that both the concentration and the distribution of hydrogen bonds should depend significantly not only on the chemical structure of the blocks but also on the length of the rigid blocks—the values of y in formula (9)—as well as their proportion and distribution in the chain.

Information on chemical bonds, including hydrogen bonds, and physical interactions in polyurethanes has already been summarised[1]. Different types of hydrogen bonds may be formed in polyetherurethanes, involving either urethane or ether groups of the oligoether blocks. The type of hydrogen bond is largely determined by the concentration of urethane groups in the chain, increase in which results in hydrogen bonds formed predominantly between urethane groups. Fresh information on hydrogen bonds in polyurethanes has been obtained by the quantitative infrared spectroscopy of segmented polyetherurethane[77-81]. Examination of the efficiency of hydrogen-bonding in polymers based on methane-*pp'*-diphenylene di-isocyanate, tetramethylene glycol, and an oligo-oxytetramethylene glycol—formula (9)—or an oligo(tetramethylene adipate) of molecular mass 1000 has shown that almost all the NH groups in the urethane groups are hydrogen-bonded, with only about 60% bound to urethane carbonyls, and the remaining 40% to ethereal oxygen. Qualitatively similar results have been obtained for polyurethanes based on either oligoethers or oligoesters. A considerable number of hydrogen bonds between NH groups and ethereal oxygen in flexible chain segments are found in polyetherurethanes based on 2- and 4-methyl-1,3-phenylene di-isocyanates[81].

Whereas the presence of hydrogen bonds between urethane groups indicates the association of rigid blocks to form rigid domains[69], a high content of hydrogen bonds involving ethereal oxygen is evidence that segregation of rigid blocks in segmented polyurethanes does not (may not) go to completion. This may indicate that such bonds are formed at the boundary between the rigid domains and the flexible medium (matrix) formed by the oligoether blocks. Consequently, the spectral investigations of segmented polyurethanes are not inconsistent with

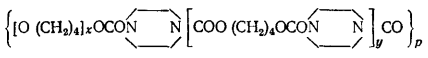
the conclusion that phase separation takes place in these polyurethanes, as in traditional block copolymers[68]. This is confirmed also by an investigation of the infrared dichroism of segmented polyurethanes[78], but in this case the regions of rigid urethane blocks and those of flexible oligoether blocks partly overlap.

X-Ray investigations have also been made[71,82-85,89] of the physical structure of the cross-links in segmented polyurethanes based on methane-*pp'*-diphenylene di-iso cyanate, an oligoether and an oligoester, and various chain lengtheners (tetramethylene glycol, ethylenediamine, hydrazine), both initially and after considerable deformation. The diffraction patterns of initial specimens containing hydrazine as lengthener show, besides a broad amorphous halo, a weak reflection with an interplanar spacing of 12 Å, which is a consequence of intermolecular packing of urethane segments[71]. Stretching the specimen by 200 to 300% results predominantly slanting orientation of rigid segments, while flexible segments are oriented in the direction of deformation. Further stretching leads to reorientation of rigid blocks. Heat-treatment in turn results in almost complete disorientation of flexible blocks, but does not affect the orientation of rigid blocks.

Furthermore, structural differences may be observed in stretched polyurethanes depending on the structure of both flexible and rigid blocks. The differences in intensity of scattering of X-rays by various segmented polyurethanes are attributed to different degrees of aggregation of the rigid blocks[83]. Rigid urethane domains constructed from methane-*pp'*-diphenylene di-isocyanate and tetramethylene glycol units[85] possess a lamellar structure, with mean distances of 100–200 Å between their centres. Both X-ray and spectral studies indicate that the rigid segments of segmented polyurethanes form isolated domains within a rubberlike matrix of flexible blocks.

Electron microscopy of segmented polyurethanes also indicates a two-phase structure[88]. They are microheterogeneous two-phase systems with rigid domains of size 30–100 Å. The micrographs suggest that the domains are three-dimensional.

Structural investigation of the polyurethane[87,88]



(10)

from which hydrogen bonds should evidently be absent, also indicates the presence of domains. Furthermore, such segmented polyurethanes, with a narrow range of lengths of flexible blocks and a different (definite) length of rigid blocks, may contain structural formations ("superstructures" or "superdomain structures") substantially larger than the domains. These stable structural formations, which may extent to 1 μm, are revealed by the scattering of polarised light. Although they resemble spherulites, the pattern of scattering is somewhat different. The nature of these structures is related to the possible crystallisation of rigid chain segments, since flexible segments do not crystallise in the undeformed state. This indicates that the appearance of a domain structure in segmented polyurethanes is not a consequence solely of the presence in the rigid blocks of polar groups capable of forming hydrogen bonds. Phase separation in segmented polyurethanes, as in traditional block copolymers, is predetermined also by the limited compatibility of different blocks in the chain, differing in nature and flexibility.

(*b*) Thermal and thermomechanical behaviour

Both the chemical constitution and the structure of segmented polyurethanes govern also their thermal and thermomechanical behaviour. Calorimetric, differential thermal, dilatometric, thermomechanical, and other studies indicate that segmented polyurethanes undergo a multiplicity of temperature transitions, due to the occurrence of various processes. Thermal transitions have been investigated[95] in a segmented polyurethane based on an oligoethylene glycol adipate, tetramethylene glycol, and various di-isocyanates (methane-*pp'*-diphenylene, tolylene, etc.), in which several thermal transitions have been detected, three of which can usefully be distinguished. Thus a transition in the region of −40°C is due to the segmental mobility of units of the oligoether block, i.e. its vitrification, as in cross-linked polyurethanes based on the above adipate[1]. The temperature of this transition in the polyurethane is higher than the glass point of the initial oligoether. Yet the glass point varies little with the structure of the di-isocyanate units in polyurethanes, with the exception of tolylene di-isocyanate, which may raise the glass point of a segmented polyurethane.

The other two transitions, observed around 70–80° and 150–180°C, depend on the structure of the rigid blocks and represent processes occurring in the microregions formed by them. The higher glass point and somewhat lower temperatures of the high-temperature transitions in the polyurethane based on tolylene di-isocyanate are attributed to the diminished segregation of rigid blocks due to the large number of bonds formed between them and the oligoether blocks. Hence interaction between rigid and flexible blocks may lead to disordering of the rigid domains, resulting in depression of the transition temperatures characterising these domains. It was also concluded that rigid segments may achieve a high degree of order, but the high-temperature transition points in segmented polyurethanes are lower than those for the initial rigid blocks owing to their small proportion in the polyurethane or low percentage crystallinity resulting from their copolymerisation with flexible blocks or from branching. However, cases are possible in which the degree of order in the rigid domains is so great that the high-temperature transition point in the segmented polyurethane is almost identical with that in the initial rigid block.

The glass point in a segmented polyurethane can be lowered[96] by increasing the chain length of flexible blocks, shortening rigid blocks, replacing aromatic by aliphatic urethane units, and restricting the intermolecular interactions of flexible blocks. The introduction into a segmented polyurethane of oligoether blocks having a wide molecular-mass distribution leads in turn to widening of the temperature range of vitrification and crystallisation of the polyurethane (flexible blocks)[97].

Calorimetric investigations have been made on segmented polyurethanes obtained from various oligoethers—oligo-oxypropylene glycol, oligo-oxytetramethylene glycol, oligo(ethylene butylene glycol adipate)—varying in molecular mass, methane-*pp'*-diphenylene di-isocyanate, and tetramethylene glycol[101]. The concentration of urethane groups was controlled by varying the content of lower glycol units in the chain. As with cross-linked polyurethane elastomers[1], the glass points of these polymers depend on the total concentration of urethane groups in the chain, but this relation becomes less marked with increase in the molecular mass of the oligoether block.

In addition to the low-temperature vitrification, a high-temperature transition develops at 110–120°C, whose character depends on the length of the rigid block. It was suggested that this latter transition was due to the dissociation of hydrogen bonds between rigid blocks, caused by "thermal perturbation of adjacent polyether segments of the chain" [101].

Three thermal transitions have been revealed by thermographic and thermomechanical studies of segmented polyurethanes (polyurethane semicarbazides) [99,108] prepared from methane-*pp'*-diphenylene di-isocyanate, oligoethers (oligo-oxytetramethylene glycol, oligo-oxypropylene glycol), and chain lengtheners (hydrazine, adipo- and isophthalo-dihydrazines). The first transition occurs between −25 and −55°C depending on the chemical structure and the molecular mass of the oligoether block, as well as on the concentration of urethane groups, and is due to the segmental mobility of the oligoether blocks. The third transition, which begins around 70°C and is diffuse in character, represents the breakdown of association complexes formed from rigid blocks (devitrification of rigid blocks). The second transition occurs in the region of 25°C, and is probably due to dissociation of bonds between oligoether and rigid (di-isocyanate–lengthener–di-isocyanate) blocks. In a segmented polyurethane [100] having longer blocks capable of crystallisation the latter two transitions correspond to higher temperatures (50–100 and 140–200°C); in addition a new transition appears in the range 200–300°C, caused by the melting of paracrystalline ordered domains constructed from rigid blocks.

Thermal transitions and thermomechanical behaviour have been investigated also in segmented polyurethanes [103] obtained from 2- and 4-methyl-1,3-phenylene di-isocyanates, differing also in the proportions of the initial components and the previous history of the test specimens. Polyurethanes obtained from the symmetrical di-isocyanate crystallise; those containing the unsymmetrical 4-methyl-1,3-phenylene di-isocyanate unit are amorphous. Three temperature transitions are observed depending on the structure of the di-isocyanate unit, the composition of the segmented polyurethane, and the previous thermal history. The transition in the range 20–80°C is attributed to dissociation of bonds between loosely packed domains of rigid blocks, and that above 150°C to fusion of crystalline formations of rigid blocks.

Thermomechanical and structural investigations of segmented polyurethanes based on oligoethers and oligoesters, methane-*pp'*-diphenylene di-isocyanate, and aliphatic diamines $NH_2[CH_2]_xNH_2$ (x = 0, 2–6) have established [106] that preliminary softening takes place at 60–70°C in specimens from diamines having x = 3, 5, which is attributed to interaction between phases formed by flexible and rigid blocks, leading to some mutual dissolution. The softening temperature of the polyurethanes varies from 130 to 190°C with change in x from 0 to 6. Softening temperatures are in all cases lower for polyurethanes containing oligomeric ester blocks than for segmented polyurethanes based on oligoethers. Small-angle scattering of X-rays shows that the softening temperature rises with increasing degree of isolation of rigid blocks. Varying the number of methylene groups in a segmented polyurethane alters the degree of aggregation of rigid blocks, although the content of urethane and urea groups remains the same. The aggregation of rigid blocks involves the formation of hydrogen bonds between functional groups in the blocks, which is governed by the number of methylene groups in the diamine unit. Aggregates of rigid segments act as an active filler or as branch points in the three-dimensional network of the segmented polyurethane.

The temperature of annealing has a complicated influence on transitions in and the structure of a segmented polyurethane [98]. It is concluded that annealing results in two types of microstructural changes: homogenisation of the system of hydrogen bonds includes the observed increase in order; and conversion into an ordered structure (perhaps microcrystalline) may involve reorientation of the domain structure. The effect of quenching (amorphisation) on thermal behaviour has been demonstrated in a thermographic investigation of a segmented polyurethane based on an oligo-oxytetramethylene glycol, hexamethylene di-isocyanate, and diethylene glycol [108]. Six temperature transitions were observed, associated with vitrification, crystallisation, and fusion of microregions formed by blocks of differing rigidity. The polar nature of the blocks leads to interaction between microregions differing in rigidity, which affects the transition temperatures. Nevertheless, the melting point of a rigid block remains almost unchanged after introduction into a polyurethane. This agrees well with an earlier conclusion [95] that a high degree of order may be possible in rigid domains.

Investigation of a polyurethane based on an oligobutylene glycol adipate, hexamethylene di-isocyanate, and an aliphatic (tetramethylene glycol) and an arylated chain lengthener has revealed [109] that the previous thermal history has a significant influence on the thermomechanical behaviour and other properties of segmented polyurethanes. The structure and the properties of these polymers depend on their state of phase aggregation, which depends both on the structure of the rigid blocks (governed by that of the chain lengtheners) and on the previous thermal history of the copolyurethane. The polyurethane based on the aliphatic lengthener exhibits considerable residual elongations, which are attributed to orientation crystallisation on stretching. The rather lower values found with aromatic lengtheners are consistent with the smaller tendency to crystallise shown by the resulting blocks than by those based on tetramethylene glycol.

Investigations on segmented polyurethanes [110] in which the chain lengtheners contain either non-polar or polar substituents have shown that increase in the polarity of a rigid block is accompanied not only by the regular rise in the flow point owing to the breakdown of rigid domains but also by a fall in the glass point of the flexible oligoether blocks. This phenomenon is attributed to an increase in the degree of segregation of rigid blocks with increase in their polarity.

Study of the thermal behaviour of the above segmented polyurethane devoid of hydrogen bonds (based on piperazine—formula 10) revealed [94] the properties of cross-linked elastomers over a wide temperature range, but at high temperatures this polymer melts, and can be processed by the methods used for plastics and fibres. Their three-dimensional network is formed by the association (crystallisation) of rigid blocks bound by intermolecular bonds. It is concluded that the flexible blocks act as a diluent and do not mix with the rigid blocks.

A multiplicity of transitions in segmented polyurethanes has been detected in an investigation of their relaxation properties by dynamic, mechanical [111,116,117], and dielectric [125–127] methods. Thus two principal transitions have been observed [111], corresponding to the glass points of

oligoether and rigid blocks (containing urethane groups). Several transitions corresponding to the movement of various groups in the blocks have also been found. All relaxation transitions depend on the molecular mass and the content of rigid blocks, as well as on the previous thermal history. Increasing the molecular mass of the rigid block leads to the formation of a semicrystalline material. Relaxation mechanisms in segmented polyurethanes depend not only on the crystallinity but also on the nature of the domain structure. The properties of segmented polyurethanes from oligoethers are determined by both the size and the structure of the rigid blocks [112,117]. In the case of a polyurethane having a non-polar flexible block the glass point of the latter is in turn independent of the nature and the concentration of the rigid urethane blocks [116].

Investigation of the influence of block dimensions and molecular-mass distribution on the properties of a segmented polyurethane shows [123] that a narrower distribution of rigid blocks gives a higher elastic modulus in the region of the plateau. The reason is that the domains formed in such a polyurethane are more perfect that those in a polyurethane having a wider molecular-mass distribution.

(*c*) Orientation and deformation behaviour

Application of infrared dichroism to orientation processes in segmented polyurethanes containing [90,91] and devoid of [92,93] hydrogen bonds reveals two different mechanisms of orientation for crystalline and amorphous segments formed by rigid blocks. In amorphous segments such blocks are oriented in the direction of stretching at small deformations. The orientation of crystalline segments takes place in two stages, the first of which consists in positive orientation of crystalline regions as a whole, leading to negative orientation of the blocks. In the second stage the primary crystalline segments break down, and the blocks are packed in microregions parallel to the stretching force. Segmented polyurethanes containing no hydrogen bonds exhibit enhanced deformability of rigid blocks and hysteresis in comparison with the hydrogen-bonded segmented polyurethanes. This difference applies to the decrease in energy of intersegmental bonds and the increase in crystallinity of the rigid blocks. Calorimetric examination of the stretching of segmented polyurethanes from crystallisable and non-crystallisable oligoethers indicates [119] in turn that mainly the flexible blocks are deformed when the polyurethane is stretched. Comparison of the energy of the probable hydrogen bonds with the quantity of heat evolved on stretching shows that these bonds are completely realised in the undeformed state. Crystallisation occurs in some polyurethanes even at small deformations, as is confirmed by X-ray diffraction. If the chain structure permits crystallisation, large residual deformations may be observed, which become reversible on subsequent heating.

Investigation of the structure of initial and stretched fibres of a segmented polyurethane showed [74] that orientation drawing is accompanied by a transition of flexible blocks from an unordered (amorphous) state to an ordered (crystalline) state. During drawing the chains slide over one another until the strong dipole–dipole interaction between rigid blocks inhibits such slippage. It was concluded that the deformed polyurethane contained an oriented supermolecular structure, whose character depended on the chemical structure and on the conditions of fibre formation. The influence of temperature and the previous history of stretching on molecular orientation in various blocks in a segmented polyurethane has also been examined [130]. A two-phase model is suggested for interpreting the morphology of polyurethane. It envisages two regions—one containing urethane blocks, and the other flexible oligoether blocks—which are semi-continuous and mutually overlapping. Those having a high elastic modulus, containing aromatic urethane units, reinforce the flexible phase. Since these phases are interpenetrating, both are deformed when stress is applied. On removal of the load, the flexible regions relax, whereas the rigid regions remain plastically deformed. Other investigations on the orientation of rigid and flexible blocks [131] are consistent with a model in which a segmented polyurethane consists of hydrogen-bonded crystallites formed by rigid blocks, which are distributed in a matrix of flexible blocks.

Several studies have been made of the optical [114,118] and mechanical [118,120–122] properties of various segmented polyurethanes. The optical behaviour on deformation [114] indicates a segregated spherical structure comparable with that observed by electron microscopy in hydrocarbon block copolymers. Investigation of the optical and mechanical properties of various segmented polyurethanes containing optically anisotropic regions of size 50–200 μm, as well as spherulitic structures, has shown that both the anisotropy of their distribution and the mechanical properties of these polyurethanes are functions of composition. Some specimens are deformed with formation of a neck and the appearance of small hump on the stretching curve, and others have a curve characteristic of elastomers; the moduli of elasticity also differ. Such variation in mechanical properties is attributed to the formation of different domain structures, which explain also the low-temperature deformability of the segmented polyurethane obtained from an oligo-oxytetramethylene glycol, methane-*pp'*-diphenylene di-isocyanate, and isophthalodihydrazide [121]. The mechanism is assumed to resemble that of the large low-temperature deformations developed for crystalline polypropylene [132]. However, the deformation is due in this case to the slippage not of units of the supermolecular (spherulitic) structure but of domains or their units formed by rigid blocks. Hence the structural features of segmented polyurethanes govern also their typical orientation and deformation behaviour.

Thus, in spite of some ambiguity and occasionally contradictions in the results of individual investigations, there are nevertheless grounds for reaching definite conclusions on the structure and properties of segmented polyurethanes. Like hydrocarbon block copolymers, these materials possess a two-phase structure. Rigid domains, made up of rigid blocks, are distributed in a medium (matrix) of flexible oligomeric (oligoethereal) blocks and act as branch points of a physical network or as an active thinner. In the present case, however, the rigid domains are usually hydrogen-bonded and may possess a crystalline (semicrystalline) structure, depending on the chemical structure, the molecular mass and its distribution, and other properties of the rigid blocks determining their degree of segregation. The polar nature of blocks differing in rigidity and the presence in them of functional groups capable of specific interaction prevent the segregation of rigid blocks and favour the appearance of "transition" (mutually overlapping) regions. However, the presence in rigid blocks of polar groups capable of forming hydrogen bonds and other physical interactions is not the only factor responsible for the domain structure in segmented polyurethanes. As in hydrocarbon block copolymers, separation into phases is

due also to the limited compatibility of blocks differing in structure and rigidity. Segmented polyurethanes can be regarded as microheterogeneous systems.

3. Segmented Polyetherurethanes

The term "segmented polyetherurethanes" can also be applied in most cases to the polyurethanes discussed above (Section III, 2), but we have decided to use it for copolyurethanes whose chains contain two kinds of oligoether blocks, usually differing either in ability to crystallise or in flexibility, and linked by a di-isocyanate (lengthener). The general formula of such a polymer can be written

$$(-A-OCONHRNHCOO-)_{1-n}-(-B-OCONHRNHCOO-)_n \qquad (11)$$

in which A and B are segments (blocks) of different oligoethers, and R is part of the di-isocyanate unit. Several studies of these products [124,133-142] have examined such aspects as the influence on structure and properties of the chemical constitution, molecular mass, molecular-mass distribution, mole fraction, etc. of various oligoether blocks. Several properties of these polyetherurethanes have already been surveyed [1].

Study of the properties of segmented polyetherurethanes [134] prepared from an oligoethylene glycol adipate, an oligo-*p*-phenylenebisethylene glycol adipate, and hexamethylene di-isocyanate with different molar proportions of the blocks and different molecular masses of the acrylated oligoether established that each block could crystallise as a separate phase. The ability to form a crystalline phase decreases as the oligoether block becomes smaller. Polyetherurethanes with roughly the same number of blocks of each kind exhibit the smallest tendency to crystallise, which is responsible for their highest elastic properties. The increase in the content of urethane groups resulting from decrease in the length of the block raises the glass and melting points of homopolyurethanes of comparable molecular mass. The crystallinity of a segmented polyetherurethane is usually due to crystallisation of the oligoether block present in excess [133]. The glass and melting points of segmented polyetherurethanes are largely determined by the structure and the molar content of the oligoether blocks.

Investigation of segmented polyetherurethanes with crystallising blocks of oligo-*o*-phenylenebisethylene glycol adipate and amorphous blocks of oligo(diethylene glycol adipate) suggested [135] that the primary units of the spherulitic structures were formed only by crystallising blocks. Blocks of the amorphous component chemically combined with them, also present in the spherulite, were arranged on the periphery of the primary crystalline structures, acting as an interstructural plasticiser. Crystallisation processes taking place with time then result not in a rise but in a fall in the glass point, since crystallisation is accompanied by accumulation of the interstructural component in the spherulites. An analogous fall in glass point has been observed in other investigations of segmented polyetherurethanes containing crystallising and non-crystallising oligoether blocks [136-138], which indicates that during crystallisation the non-crystallising block forms a separate phase with its own inherent properties.

Thermographic investigations of a segmented polyetherurethane obtained from oligo-oxytetramethylene glycols of various molecular masses and an oligoethylene glycol sebacate have shown [140,142] that crystallisation occurs predominantly in the latter, but when the first block is sufficiently long both may crystallise. These polyetherurethanes exhibit two separate melting ranges, that at lower temperatures due merely to weakening of the "physical network" (fusion of the crystalline phase comprising oligo-oxytetramethylene glycol blocks) with a corresponding change in elastic properties, whereas the higher-temperature range (melting of the crystalline phase of oligoethylene glycol sebacate blocks) represents transition of the polyurethane to a state of viscous flow. The flow point of segmented polyetherurethanes can be raised by introducing tetramethylene glycol units into their chain, so that the concentration of urethane groups is increased, with an increase in branch points of the physical network. Strictly speaking, such modification of properties leads to the formation of a kind of "hybrid" segmented polyurethane, between the above segmented polyurethanes and segmented polyetherurethanes, since sequences of di-isocyanate and tetramethylene glycol units are produced (formation of a rigid block). Investigation of the structure of an analogous segmented polyetherurethane but with oligo-oxytetramethylene glycol blocks differing in polydispersity indicates [124] that the properties of these polymers are determined mainly by the structure and the properties of the crystalline phase, and to a less extent by the structure of the more flexible block. However, the most labile, easily reorganised crystal structure should be more readily achieved in copolymers with mobile fragments of the more flexible block. This should apply also to segmented polyetherurethanes with greater polydispersity of the oligo-oxytetramethylene glycol blocks, in which the network of physical bonds formed by the urethane group is most imperfect and labile.

Thus the above results for segmented polyetherurethanes indicate that they also can be included among thermoelastoplasts, but the crystalline structure produced in them, acting as branch points of the physical network, cannot provide adequate thermal and physicomechanical constants. This makes it necessary to introduce also lower glycols, which increase the concentration of urethane groups in the chain and localise them in separate microregions (domains). Strictly speaking, we return to the above segmented polyurethanes with two kinds of flexible oligoether blocks in their chains.

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