Influence of NCO:OH Relation and Chain Extender on Primary and Secondary Valence Crosslinks in Urethane Elastomers

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Synopsis

The subject of this study was urethane elastomers synthetized from oligo (ethylene adipate) and diphenyl-methane-4,4'-di-isocyanate extended by means of 3,3'-dichloro-4,4'-diamine-diphenyl-methane with 1,4-butylene glycol. It has been demonstrated, with the aid of the method used by Weisfeld and co-workers that the changes in the NCO:OH molar relation from 2.75 to 5 at the pre-polymer synthesis stage are the cause of an increase in the total crosslinking density as well as those derived from the primary and secondary valence crosslinks. The application of diamine as a chain extender, in comparison with glycol, causes an increase of the crosslinking densities under investigation. The observed changes in the crosslinking stage of the elastomers obtained have been explained on the basis of the segment structure of the normal chains. The apparent differences in the crosslinking density by primary valence crosslinks, as determined chemically and by the method of Weisfeld et al., have been explained on the basis of IR measurements of the changes in the hydrogen bonding contents as functions of temperature.

INTRODUCTION

The abundance of original substances used for obtaining urethane elastomers in conjunction with the wide variety of reactions taking place at their syntheses cause the highly complicated chemical structure of the space network of this group of polymers.[1-5]

In addition, the presence of functional groups with various chemical structures and polarity in the normal chains and in the primary (allophanate and biuret) valence crosslinks is the cause of the appearance of secondary valence crosslinks in the structure of the space network in urethane elastomers.

The problem of determining the contents of primary and secondary valence crosslinks in urethane elastomers is dealt with by Weisfeld, Little, and Wolstenholme.[6] On the basis of equilibrium modulus measurements at various temperatures, they proposed a method for determining the quantitative share of the primary and secondary valence crosslinks in the structure of the space network in urethane elastomers.

The method of Weisfeld et al. has been applied in this study to investigate the influence of the NCO:OH molar relation in polymers that were being changed at the stage of synthesis, within a 2.75–5 range, on the content of the primary and secondary valence crosslinks in the elastomers obtained.

With the use of this method, it has been demonstrated on the example of 3,3'-dichloro-4,4'-diamino-diphenyl-methane (MOCA) and 1,4-butylene glycol that the chain extenders applied also have an influence on the content of the

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crosslinking bonds in the elastomers obtained. In addition, the contents of chemical crosslinking bonds were being determined by a chemical method[7] in the elastomers obtained.

The differences that were found between the results in the quantitative determinations of the primary valence crosslinks by Weisfeld's method and by the chemical method have been explained on the basis of changes in the content of hydrogen bonds as a function of temperature, determined by IR spectroscopic measurements.

EXPERIMENTAL

Materials

The oligo(ethylene adipate) used had a hydroxyl value equal to $L_{OH} = 55$ and an acid number equal to $L_{COOH} = 1.2$.

The diphenyl-methane-4,4′di-isocyanate (MDI) was from Farben Fabriken Bayer AG.

The 1,4-butylene glycol, from BASF, was subjected before application to dehydration at a temperature of 393–403 K in a vacuum of ~150 Pa for 2–3 hr.

The 3,3′-dichloro-4,4′-diamine-diphenylmethane (MOCA), from Gee Lawson Chemicals, was used as obtained from the supplier.

Synthesis of Elastomers

First, 700 g oligo(ethylene adipate) were placed in a typical reactor, provided with a mixer and a thermometer, and subjected to dehydration at a temperature of 393–403 K for 2–3 hr at a vacuum of ~150 Pa.

Then, predetermined quantities of MDI, resulting from the changes in the NCO:OH relation at scheduled experiments of 2.75, 3.5, 4.25, and 5 respectively, were added at a temperature of 363 K.

The synthesis of urethane prepolymers was carried out at a temperature of 383 K for 30 min. The final stage of the synthesis, i.e., during the last 20 min, was being carried out at a vacuum of ~150 Pa.

The prepolymers that had been obtained at various NCO:OH relations were characterized by determining the concentration of free isocyanate groups using the amine equilibrium method.[8] Then, a chain extender (glycol or diamine) in an appropriate quantity to maintain a steady NCO:OH relation equal to 1.1 was added to the obtained prepolymers with intensive mixing at a temperature of 333–363 K.

After 15–90 sec of mixing, the reactor content was poured into a mold which had been heated to a temperature of 383 K. The mold was placed in an air-tight drier and heated at the same temperature for 24 hr. Specimens, 100 mm in diameter and 10 mm high, were cut out of the disks obtained and used for taking measurements of the equilibrium modulus at compression.

Method of Measurement

The equilibrium modulus at compression of urethane elastomers was measured by means of a Höppler consistometer which had been additionally provided with equipment for compressing the test specimens at a temperature range of 293–400 K.

Determinations of allophanate and biuret crosslinks in the structure of the space network were carried out by such method as described by Foliforowa.[7] Changes in the content of hydrogen bonds in the elastomers obtained were investigated as a function of temperature by means of the Specord (GDR) IR spectrometer with a heating attachment.

Decreases in the quantitative share of hydrogen crosslinking bonds was determined on the basis of a change in the transmission of the maximum analytical band at a frequency of $\sim$3330 cm^{-1}. This is characteristic for the NH bonded group, when using as a standard an internal band at a frequency of $\sim$2970 cm^{-1} for valence vibration of the CH group. The specimens for the spectroscopic tests were in film form.

RESULTS AND DISCUSSION

The results of experiments, as shown in Figures 1 and 2, indicate clearly that an increase in the NCO:OH molar relation at the prepolymers synthesis stage
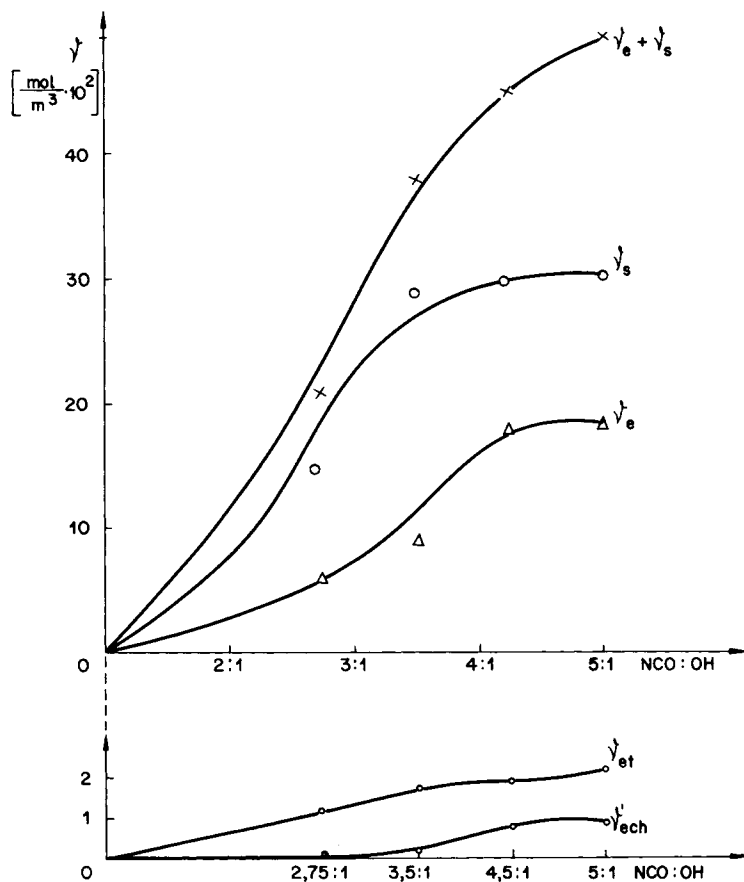

Fig. 1. Effect of NCO:OH molar proportion changed during synthesis of the network density of polyurethane elastomers extended with butandiol-1,4. $\nu_e + \nu_{sec}$ is the total network density. ν_e is the density of the network with I-type crosslinks. ν_s is the density of the network with II-type crosslinks. ν_{ef} is the theoretical network density calculated from stoichiometry of the process. ν_{ech} is the network density obtained by the chemical method (after synthesis).
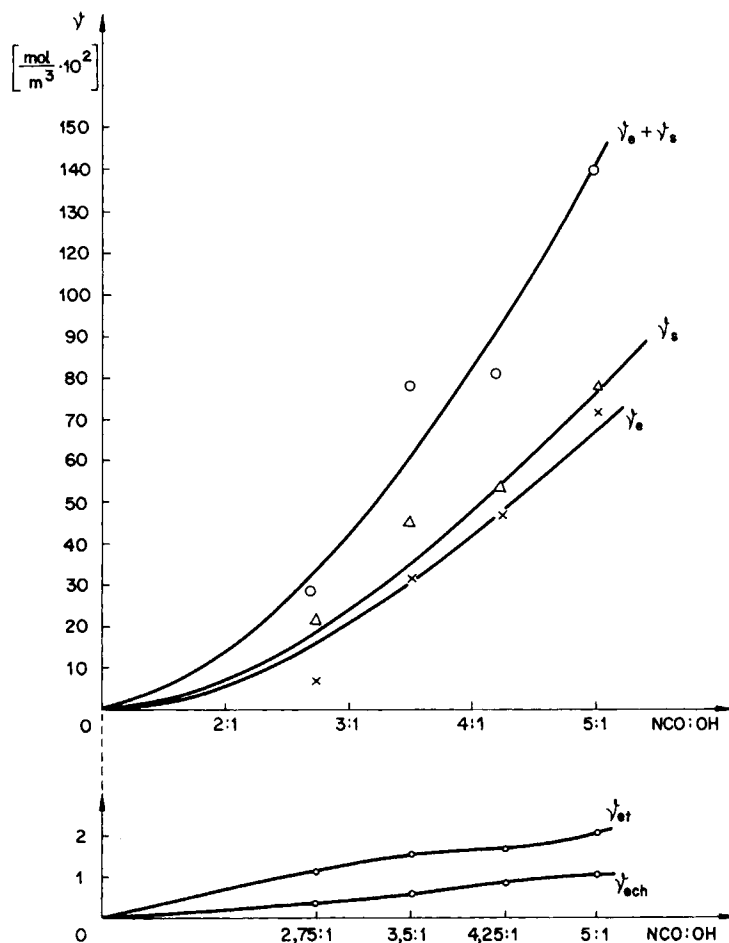
Fig. 2. Effect of the NCO:OH molar proportion changed during prepolymer synthesis on the network density of polyurethane elastomers extended with 3,3′-dichloro-4,4′diaminodiphenyl-methane. $\nu_e + \nu_s$ is the total network density. ν_e is the density of the network with I-type crosslinks. ν_s is the density of the network with II-type crosslinks. ν_{ef} is the theoretical network density calculated from stoichiometry of the process. ν_{ech} is the network density obtained by the chemical method (after synthesis).

is the cause of an increase in the quantitative share of primary and secondary valence crosslinks (ν_e and ν_s) in the space network structure in the elastomers obtained. In effect, the summary crosslinking density ($\nu_e + \nu_s$), as measured by the method Weisfeld et al., also increases.

The observed dependences appear both for elastomers synthetized by means of MOCA and of glycol. In addition, the application of MOCA as the chain extender makes the elastomers have a higher summary crosslinking density. This is also seen with the primary and secondary crosslinks compared with those synthetized with the use of glycol (data obtained using the method of Weisfeld et al.).

It is our opinion that the observed increase in the quantitative share of primary and secondary valence crosslinks in the space network of the elastomers obtained, which takes place together with an increase in the NCO:OH molar relation, re-

sults from a different structure of the normal chains and the sequent reproducible elements in the structure.

At an increase in the NCO:OH relation within the range of 2.75–5, the mean molar mass of the prepolymers obtained decreases and the content of free di-isocyanate increases. Subsequently, while subjecting the initial prepolymers to chain extension, the content increased in the elastomers obtained from rigid segments of this type. ∼Oligomer (di-isocyanate-chain extender-di-isocyanate)-oligomer ∼ appear as the result of the reaction of the free-urethane oligomer isocyanate groups with the MOCA and glycol extenders applied.

Increasing the NCO:OH molar relation at the prepolymers synthesis stage, the quantitative share of superrigid segments of the type ∼ (-di-isocyanate-extender-di-isocyanate)$_n$ ∼, where $n \geq 2$, also increases in the structure of the normal chains in the elastomers obtained.

The previously described segments appear because of a reaction of free di-isocyanate with the chain extenders used.

The appearance of rigid and super rigid segments makes the normal elastomer chains become rigid and leads to a decrease in their flexibility and molecular mobility.

This is favorable for the creation of hydrogen bonding and increases the range of molecular interactions of the Waals' type. That is why an increase in the NCO:OH molar relation at the prepolymer synthesis stage is the cause of a very high increase in the quantitative share of secondary valence crosslinks in the space network structure of the elastomers obtained. Measurements of the crosslinking density in the elastomers obtained using the method of Weisfeld et al. also revealed the influence of a type of chain extender on the structure of the space network involved. The distinctly higher content of the secondary valence crosslinks in the elastomers obtained from MOCA, in comparison with that of their analogs synthesized from glycol, may also be explained on the basis of the segment structure of the normal chains.

The use of MOCA leads to additional rigidity of the natural chains in the appearing elastomers. This follows from the aromatic structure of the chain extender applied, as well as to the formation of a highly polar arrangement of carbamide derivatives and biuret crosslinking bonds. Capable of forming hydrogen bonds, this functional group increases the contents of secondary valence crosslinks.

The observed increase of the quantitative share of primary valence crosslinks, which follows from the increased NCO:OH molar relation, is also justified in view of theoretical calculation based on the stoichiometry of the process.

The calculation has shown that an increase in the NCO:OH relation at the polymers synthesis stage causes, in spite of maintaining a steady NCO:OH (NH_2) equal to 1.1 at the extension stage, an increase in the share of free isocyanate groups capable of forming crosslinking allophanate and biuret bonds (ν_{et} curves).

One result is the observed increase in the content of primary valence crosslinks in the urethane elastomers under investigation (ν_e curve). A comparative analysis of the data as shown in Figures 1 and 2 (ν_e and ν_{ech} curves) reveals the differences in the content of primary valence crosslinks measured by the method of Weisfeld and co-workers and determined chemically.

In addition, the results of determining the content of primary valence cross-

links as obtained by such method, as described by Foliforowa[7], are closely comparable with those calculated theoretically. This means that the chemically obtained contents of primary valence crosslinks in the elastomers involved in the study are close to reality. On the other hand, the results of determinations made by the method of Weisfeld et al. are overestimated. In order to find an explanation for the differences in the results of the determinations of crosslinking densities carried out by both the previously mentioned methods, IR spectroscopic measurements were taken of the elastomers involved at the temperature range 293–523 K. The results of the measurements, as given in Figure 3, indicate that in the spectra at a temperature of 293 K one absorption band appears with a frequency of 3330 cm^{-1}, which is characteristic for the NH group.

IR spectra, obtained at a temperature of 523 K, also have one absorption band each at a frequency of 3400 cm^{-1}; which, we think, comes from the free NH group.

The changes, as shown in Figure 4, in the transmission of the maximum absorption band at a frequency of 3330 cm^{-1}, determined in relation to the internal-band standard at a frequency of 2970 cm^{-1}, which is characteristic for the CH group, indicate that a distinct drop in hydrogen bonding takes place in the temperature range 293–423 K.

We think that the observed drop in the quantitative share of hydrogen bonds in the space network structure, at the described temperature range in the elastomers obtained, follows from the dissociation of those bonds in the elastic segments.

At a temperature range of 423–473 K, however, there is no change in relation to the absorption of the band under analysis. This indicates that no change of the hydrogen bonds takes place in the 423–473 K temperature range.

In the temperature range of 473–523 K, further changes take place in relation to the absorption of the band under investigation. We are of the opinion that they follow from the dissociation of the hydrogen bonds which appear in the rigid and superrigid segments of the elastomers involved. The results of measurements, as given in Figure 4, indicate a high thermal durability of the hydrogen bonds which appear in the elastomers obtained. The results are comparable with the reports given by Froix and Pochan,[9] who found that urethane–urethane hydrogen bonds appear to 473 K.
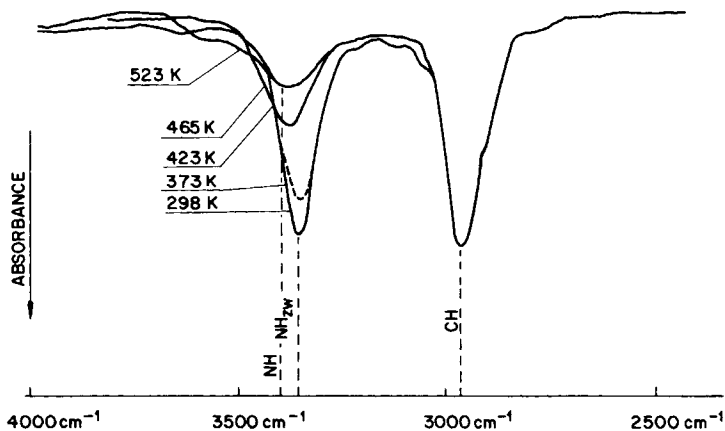

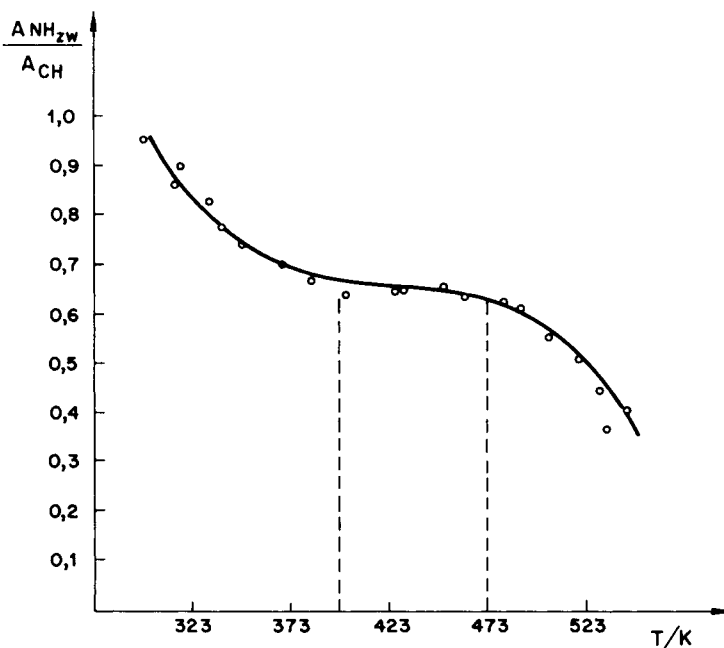Fig. 3. Effect of temperature on the IR absorption of NH groups.

Fig. 4. Effect of temperature on the amount of hydrogen bonding in the investigated urethane elastomers.

The results of our study, however, may be deemed to be controversial in light of the data pertaining to the value of hydrogen bonding energy which amounts to 9.62 kcal/mol in the extreme case for this group of polymers.[10] We think that the pseudo-high-thermal durability of the hydrogen bonds follows from the domain structure of the elastomers involved formed with the rigid and superrigid segments. Hydrogen bonds in domains remain in the so-called confined state, and their dissociation takes place parallel to melting of the domain areas at raised temperatures.

The results of measurement of the hydrogen bonding contents, as given, explain and justify the facts obtained using the method of Weisfeld et al. that there are higher density values of bonding by primary valence crosslinks in urethane polymers in comparison with those obtained by theoretical calculation and analytical determination. This also means that the density of primary valence crosslink bonding, as measured by the method of Weisfeld et al., partly includes hydrogen bonding.

On the basis of these tests, it may be concluded that the primary valence crosslink bonding measured by Weisfeld's method is inaccurate to some extent. However, it provides the possibility of forming a convincing explanation of the influence of the NCO:OH molar relation and of the kind of the chain extender on the crosslinking bonding in the elastomers obtained.

References

1. J. H. Saunders, J. A. Burronghs, and L. P. Williams, *J. Appl. Polym. Sci.*, **19**, 1387 (1975).
2. R. Bonart, *Morbitzer Kolloid. Z. Z. Polym.*, **241**, 909 (1970).
3. Ju. S. Lipatow, "Struktura i swojstwa poliuretanów," in *Naukowa Dumka,* Kijów, 1970, pp. 37–43.

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4. D. Wright and A. P. C. Cumming, *Solid Polyurethane Elastomers,* MacLaren, London, 1969.
5. E. Windemuth, *Kunststoffe,* **57,** 5, 337 (1967).
6. L. B. Weisfeld, J. R. Little, and W. E. Wolstenholme, *J. Polym. Sci.,* **56,** 455 (1962).
7. J. G. Foliforowa, *Zavod. Lab.,* **6,** 671 (1975).
8. H. Roth, *Mikrochim. Acta,* **6,** 766 (1958).
9. M. F. Froix and J. M. Pochan, *J. Polym. Sci., Polym. Phys. Ed.,* **14**(6), 1047 (1976).
10. D. S. Trifan and J. F. Ferenzi, *J. Polym. Sci.,* **28,** 443 (1958).