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Effect of Space Network Structure on Molecular Mobility of Urethane Elastomers

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SUMMARY

In this study the changes in the width of the derivative NMR absorption line and the second moment as the function of temperature were investigated for typical urethane elastomers. The polymers crosslinked only by allophanate and biuret bonds as well as modified by the presence of carbon-carbon and ionic bonds were used. It has been found that carbon-carbon and ionic crosslinking bonds cause considerable changes in the glass transition temperature.

INTRODUCTION

The broad line NMR analysis provides some information on the supermolecular structure in the polymer as well as on the mobility and flexibility of the macromolecules and their subunits(1) .Changes in the width of the NMR lines and the second moment as function of temperature are an evidence of the motion of macromolecules and subunits.(2).

Molecular mobility of polymers is also strictly connected with the nature of crosslinking bonds. This phenomenon seemed to be especially interesting in the case of urethane elastomers, the structure of which was modified by the presence of various crosslinking bonds such as allophanate, biuret, carbon -carbon and ionic ones (3-5).

EXPERIMENTAL

Urethane elastomers were synthesized by the prepolymer method at the temperature of 395 K from poly ethylene adipate glycol, diphenyl-methane-4,4'-diisocyanate at the molar ratio of

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NCO:OH = 4:1. Further, the prepolymer was extended and crosslinked at the temperature of 395 K. The various extending and crosslinking agents are listed in Table 1.

TABLE 1

Characteristics of the tested urethane elastomers

Synthesis	Chain extender	Crosslinking agent
1	Butanediol-1,4	
2	Butanediol-1,4	1,6 hexane-(N,N'-di/di-ethanol-methyl/amino) dibromide
3	3,3'-dichloro-4,4' diamino-diphenylmethane	
4	3,3'-dichloro-4,4' diamino-diphenylmethane	dibromohexane
5	α-allyl-glycerinether	dicumyl peroxide 1.5% by weight
6	α-allyl-glycerinether	dicumyl peroxide 2.5% by weight
7	butanediol-1,4	dicumyl peroxide 1.5% by weight

All the samples of the obtained elastomers were conditioned at the temperature of 395 K for 24 hours. The elastomers were additionally heated for 0.5 hour at 433 K. The urethane elastomers were tested by the broad line NMR within the temperature range from 130 K to 400 K. Measurements were carried out with a resonance spectrophotometer Varian WL-109 at the frequency of 35 MHz. The temperature range was stabilized by means of an E-257/WL 257 device and the measurements were registered with an accuracy of ± 1K by means of a Ni-Cr thermoelement.

RESULTS AND DISCUSSION

Figures 1 and 4 show the changes of the width of the derived NMR absorption line as the function of temperature and Figures 2 and 3 show the temperature dependences of the second moment. Polymers obtained by synthesis 1 and 4 are typical elastomers extended with butanediol-1,4 and crosslinked by allophanathe bonds as well as extended with 3,3'-dichloro-4,4'-diamino-diphenylmethane and crosslinked by biuret bonds. From the curve showing the changes both of the width of the derived NMR absorption line and of the second moment it may be found that a gradual decrease of those values takes place beginning from 220 K.

A high diversity of functional groups in the polyurethane chains makes them undergo activation at various temperatures. Thus, various decreases of the second moment are found as a function of temperature. This may also be an indication of inhomogenous polymer materials.

The glass temperature, T_g, as determined on the basis of the $\delta H = f(T)$ dependence for a butanediol extended elastomer (crosslinked by allophanate bonds only - synthesis 1) occurs at ~ 253 K, and for an elastomer extended with 3,3'-dichloro-4,4'-diamino-diphenylmethane (crosslinked by biuret bonds - synthesis 3) - at 258 K, respectively.

The application of diamine as a chain extender increases the share of rigid segments from those aromatic rings which are already present in the main chains from diisocyanate. This causes, in connection with polar groups of chlorine, a higher stiffening effect of the main chains and consequently a slight increase in the glass transition temperature.

Highly polar urea derivative groups as well as biuret crosslinking bonds are capable to form, at a higher degree than urethane and allophanate arrangements, hydrogen bonds influencing the formation of rigid domains. At the temperature of 273 K the δH amounts to $1 \cdot 10^{-4}$ T for synthesis 1, and $2 \cdot 10^{-4}$ T for synthesis 3. The value for the second moment, however, is $8 \cdot 10^{-8} T^2$ for both elastomers.

In the structure of elastomers the presence of ionic bonds

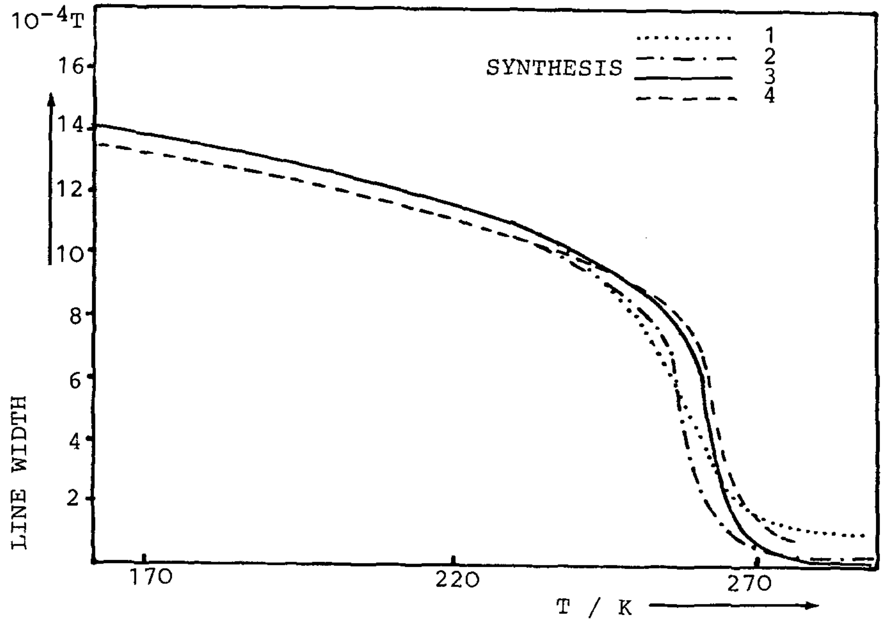

Fig.1 Line width as a function of temperature for urethane elastomers

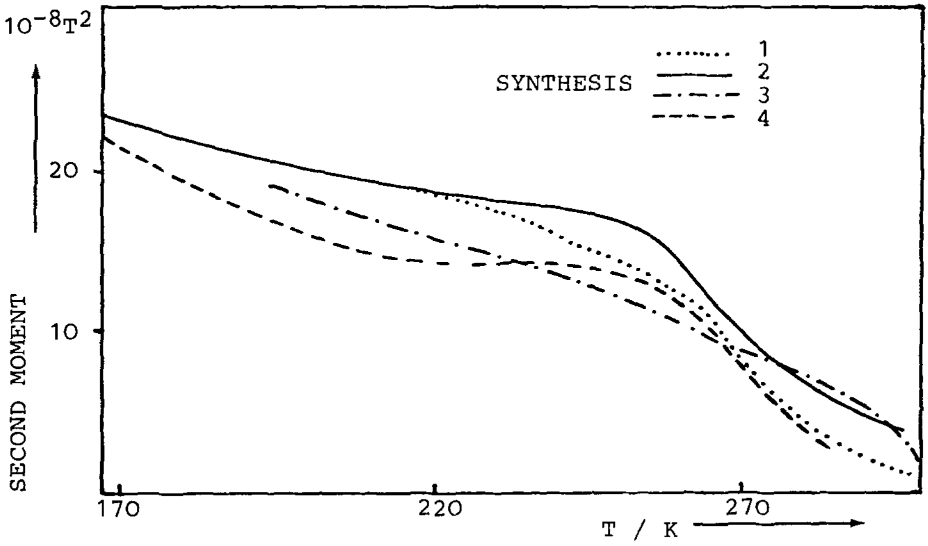

Fig.2 Second moment as a function of temperature in urethane elastomers

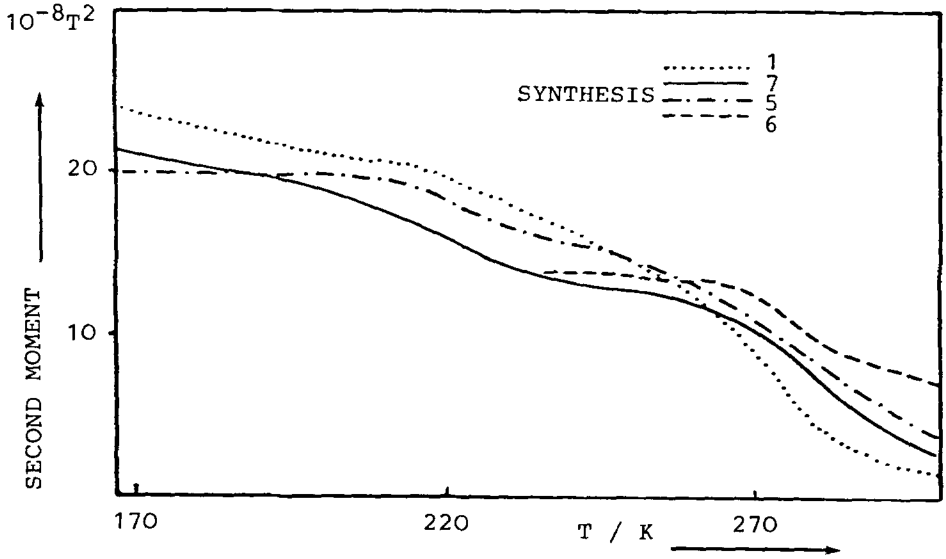

Fig.3 Second moment as a function of temperature in urethane

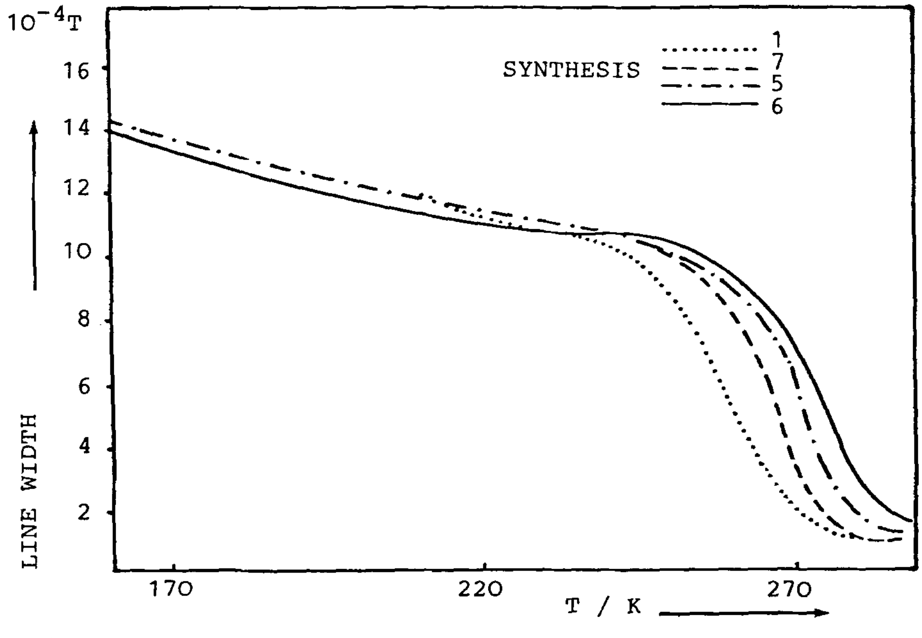

Fig.4 Line width as a function of temperature for urethane elastomers.

appearing as the result of a reaction of dibromohexane with tertiary nitrogen of N-methyl-diethanolamine (synthesis 2) or with an NH group of urethane or urea arrangement (synthesis 4) causes the value of the second moment to decrease distinctly not earlier than from the temperature of 250 K (synthesis 4) and 260 K (synthesis 2). This means that the mobility of segments is reduced by additional ionic crosslinking bonds of the ammonium salt type.

At the temperature of 273 K the value of the second moment amounts to $9 \cdot 10^{-8}\ T^2$ for the elastomer from synthesis 2 and $8 \cdot 10^{-8} T^2$ for the elastomer from synthesis 4. It is comparable with the value of the second moment of urethane elastomers crosslinked merely with allophanate and biuret bonds.

In the case of elastomers with ionic bonds a sharper transition is found at the temperature T_g (for the elastomer from synthesis 2 amounting to 260 K, and from synthesis 4 to $T_g =$ 265 K, respectively).

Introduction of transverse bonds C-C into the structure of the network (synthesis 5 to 7) as the result of radical reaction of double bonds in macrochains is the reason of the curves of the second moment changes and of the line width towards higher temperatures, the character of the decline being similar.

As to the range of lower temperatures, at which motion of side groups is found to take place only, the motion of chains is identical. Starting from 450 K the investigated elastomers have a gradual increase in their motion with rising temperature. A decline of the line width and of the second moment is found to occur. This gradual starting of the chain fragments means that the structure of the networks is diversified because there are both allophanate and carbon-carbon crosslinking bonds present in the system. Obviously, those fragments of the chain are started first which are most distant from the crosslinking bonds, and then gradually the closer (more rigid) ones.

In the case of elastomer from synthesis 5, the course of the line is broadened, which is an indication of a great diversity of the material. On the other hand, the shape of the line for the elastomer from synthesis 6 is complicated with a variety of arrangements (with different mobility). A distinct phase separation is observed.

The glass temperature for elastomers with 1.5% of dicumyl peroxide (synthesis 5) is 268 K, and for the elastomer with 2.5% of dicumyl peroxide (synthesis 6) it amounts to 273 K, respectively. Further, the elastomer from synthesis 6 has a higher value of the second moment at 273 K amounting to $11.5 \cdot 10^{-8} T^2$ in comparison with $10 \cdot 10^{-8} T^2$ for the elastomer from synthesis 5. This means that the arrangement is more rigid because of the higher quantity of the crosslinking C-C bonds. For the elastomer from synthesis 7, when the prepolymer is extended with butanediol, the temperature amounts to 263 K. Thus, the glass-temperature of the crosslinking arrangements additionally linked with C-C bonds are distinctly higher than in the case of elastomers crosslinked merely with allophanate and biuret bonds (synthesis 1 and 3).

Generally it may be stated that the results of investigation of the wide line NMR in respect to the tested urethane elastomers indicate a high heterogeneity of the material. A two-component character of the line in the vicinity of T_g suggests the presence of regions with various degrees of arrangements of various mobility, indicating a phase separation. The presence of crosslinking C-C and ionic bonds in the network stiffens their superstructure distinctly.

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