Polyester Polyurethane Ionomers

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Synopsis

The urethane elastomers based on 4,4'-diphenylmethane diisocyanate (MDI), oligo (ethylene adipate) (OEA) with different chain extenders, and dibromohexane or ammonium salt were synthesized. Their mechanical and thermal properties were studied by stress-strain analysis, thermomechanical methods, and differential thermal analysis. It was demonstrated that the incorporation of ionic groups in the structure of urethane elastomers due to the reaction of dibromohexane with a tertiary amine or urea NH group improves their tensile strength and thermal resistance.

INTRODUCTION

In recent years there has been a great deal of interest in the synthesis and properties of conventional urethanes and their microphase structure, which is responsible for increasing material strength.[1-5] Relatively little has been done about urethanes containing electrical charges in the backbone or in the side chain.[6-14]

Ionic polyurethanes include urethane polyelectrolytes and urethane ionomers. The principal difference between ionomers and polyelectrolytes is that the latter consist essentially of ionic monomer units and ionomers contain only relatively small amounts of ionic groups. These ionomers are not only interesting scientifically because of their specific structure but are also important commercially because of their solventless application. Since polyurethane coatings were first developed by Bayer and his coworkers[15] significant progress in this area has been made due to the low cost and wide latitude in physical properties, ranging from very flexible to hard materials. It is known from the area of urethane polyelectrolytes that ion incorporation causes dramatic changes in the physical properties and solubility of polymers.[6,7] The tensile strength is increased, and with high concentration of charges the normally hydrophobic urethanes become highly hydrophilic and occasionally soluble in water.

Today, because of regulations concerning the environment, a great deal of effort is being made to reduce as much as possible the solvent content in polymers through the development of high-solid materials as well as water-based coatings.

Recent works involve the incorporation of ionic groups into polyurethane elastomers and the study of this effect on their physical properties and of a strong additional influence on their microstructure and domain morphology. The field is still in the early stages and has been explored by only a small group of investigators.[8-14] An essential stage in the preparation of urethane elastomers is the chain extension process.[16] In this study, attempts

are made to employ different chain extenders, some of them contain the tertiary nitrogen atom capable of forming ammonium salts. This ability can lead to the formation of a cross-linking of ionic type, if a dihalogene alkane is used. The aim of this work is to show the influence of ionic groups on the network and mechanical and thermal properties of cast urethane elastomers.

EXPERIMENTAL

Materials

Oligo (ethylene adipate) (OEA, Bydgoskie Zakady Chemiczne, Poland, average MW 2000) was dried before application under vacuum at 393 K for 3 h. 4,4'-Diphenylmethane diisocyanate (MDI, Farben Fabriken Bayer AG-FRG) was purified by filtration of the liquid at 343 K. N-methyldi-ethanoloamine (MDEA, Fluka AG, Chemische Fabrik, Switzerland), 3,3'-dichloro-4,4'-diaminediphenylmethane (MOCA, Gee Lawson Chemicals, Great Britain), and triethanoloamine (TEA, L. Light, Great Britain) were all used as received. Butanediol-1,4 (BD, BASF, West Germany) and dibro-mohexane (DBH, UCB, Belgium) were dried under vacuum.
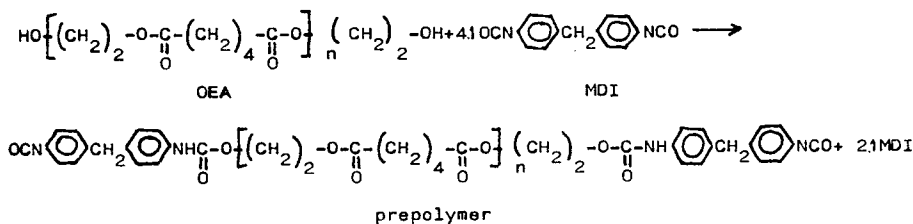
Synthesis of Urethane Elastomers

The urethane elastomers (PU) were prepared by a two-step condensation reaction.[16] The schematic representation of the synthesis procedure is shown in the Figure 1. The prepolymer was made as follows: OEA was placed in a typical reactor provided with a mixer and a thermometer. Then, determined quantities of MDI, resulting from a NCO-OH ratio of 4:1, were added at 393 K. The synthesis of urethane prepolymers was carried out at 393 K for 30 min. The final stage of the synthesis was carried out during the last 30 min at a vacuum of ∼ 150 Pa.

The prepolymer was characterized by determining the concentration of free isocyanate groups using the amine equilibrum method.[17] Then, chain extenders (glycols or diamine) with dibromohexane in an appropriate quantity to maintain a molar ratio NCO-OH of 1.1:1 (to be sure that the allophanate and biuret cross-links appear) was added to the prepolymer with intensive mixing at 363–383 K. After 15–90 s mixing, the reactor content was poured into a mold that had been heated to a temperature of 393 K. The mold was placed in an air-tight drier and heated at the same temperature for 24 h or more. The sample characterization is presented in Table I.
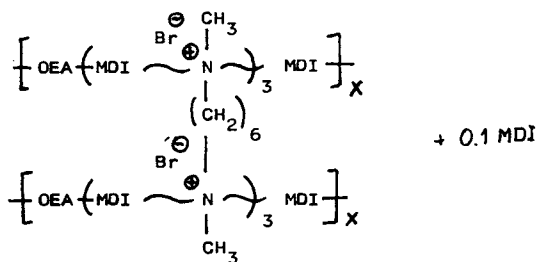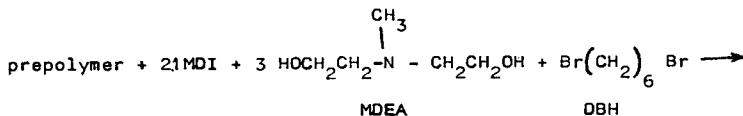
Methods of Measurements

Dielectric spectra were measured with a semiautomatic bridge of the BM 484 "Tesla" type for one standard frequency ($f = 1592$ Hz). The measurements were performed between 180 K and 400 K, and the sample chamber was filled with nitrogen gas. The automatic temperature regulation system secured a stabilization of temperature with an accuracy of ± 0.01 K and an indication of temperature with an accuracy of ± 0.05 K. The construction

I step of polycondesation:

HO$\left[(CH_2)_2-O-\underset{O}{\overset{\parallel}{C}}-(CH_2)_4-\underset{O}{\overset{\parallel}{C}}-O\right]$ $(CH_2)_2$ $-OH+4.1$ OCN⬡CH$_2$⬡NCO ⟶

OEA   MDI

OCN⬡CH$_2$⬡NH$\underset{O}{\overset{\parallel}{C}}$-O$\left[(CH_2)_2-O-\underset{O}{\overset{\parallel}{C}}-(CH_2)_4-\underset{O}{\overset{\parallel}{C}}-O\right]$ $(CH_2)_2$ $-O-\underset{O}{\overset{\parallel}{C}}-NH$⬡CH$_2$⬡NCO+ 2.1 MDI

prepolymer

II step of polycondesation $\left(\text{in case of MDEA}\right)$:

$$\text{prepolymer + 2.1 MDI + 3 HOCH}_2\text{CH}_2-\overset{\overset{\displaystyle CH_3}{|}}{N}-\text{CH}_2\text{CH}_2\text{OH} + Br(CH_2)_6 Br \longrightarrow$$

MDEA   DBH

+ 0.1 MDI

PU

$\left(\text{MDI} \frown \overset{\overset{\displaystyle CH_3}{|}}{N}\right)_n$ = $\left(\text{MDI} - \text{MDEA}\right)_n$ hard segment.
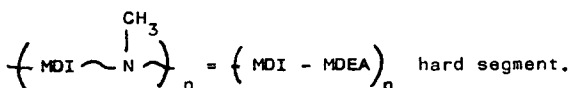
Fig. 1. Synthesis of polyurethanes.

of the sample chamber, the bridge used, and the position of electrodes on the samples assured a three-terminated measurement that eliminated the capacity of the leads. The cross-linking density of nonswollen samples (A, AI, C, CI, CAI, and CA) was determined by the stress method[18] from stress-strain equilibrium measurements of molded films. It was performed with a model VEB tensile tester (East Germany) at 273 K. The swollen samples in benzene or ethyl acetate were determined by the equilibrium swelling method[19] using the procedure described earlier.[20] For other nonswollen and swollen samples (with triethanoloamine), only the stress method was employed for the determination of the cross-linking density. In this case the equilibrium modulus at compression of urethane elastomers was measured by means of a Höppler consistometer that had been additionally provided with equipment for compressing the test specimens at 273 K.

Tensile strength modulus values (PN-65/C-04206) were determined from stress-strain measurements of films performed with a VEB testing machine employing an extention rate of 10 cm/min and using a sample length of 2.5 cm. Thermomechanical analysis was carried out with a testing instrument built by the Technical University of lódź using a sample length of 2.5

TABLE I
Characterization of MDI/OEA-Based Urethane Elastomers

Polymer designation	Extending and cross-linking systems (Molar Ratio)
A	MDEA
AI	MDEA + DBH (1:1)
C	MOCA
CI	MOCA + DBH (1:1)
CA	MOCA + MDEA (1:1)
CAI	MOCA + MDEA + DBH (1:1:1)
OT	BD
2T	TEA + BD (1:49)
2TI1	TEA + BD + DBH (1:49:1)
2TI2	TEA + BD + DBH (1:49:2)
2TI4	TEA + BD + DBH (1:49:4)
2TI6	TEA + BD + DBH (1:49:6)
5T	TEA + BD (1:19)
5TI1	TEA + BD + DBH (1:19:1)
5TI3	TEA + BD + DBH (1:19:3)
5TI4	TEA + BD + DBH (1:19:4)
5TI6	TEA + BD + DBH (1:19:6)
10T	TEA + BD (1:9)
10TI1	TEA + BD + DBH (1:9:1)
15T	TEA + BD (1:5.6)
15TI1	TEA + BD + DBH (1:5.6:1)
20T	TEA + BD (1:4)

cm with a heating rate of 2 K/min under the conditions of fixed loading of $200 \times g$, based on the measurements of the relative elongation changes $\Delta l / l$ of the sample in temperature function.

For thermal characterizations, a MOM derivatograph (Hungary) was used with a heating rate of 12 K/min, a temperature range of 298–673 K, and a sensitivity of DTA $= 1/3$ and $T_g = 100$. Decomposition temperature was accepted as a value at which a 2% loss of the sample mass was observed. Al_2O_3 was used as a model substance.

NMR spectra of C and CI samples were obtained using Tesla 60 Model Instrument. Chemical shift δ referred to tetramethylsilane were expressed in ppm. The samples for analysis were made soluble into dimethylsulfoxide (DMSO) by degrading the allophanate and biuret linkages with n-butylamine[21] and because of a small amount of chemical cross-links due to DBH.

RESULTS AND DISCUSSION

Our studies of the existing literature[7] suggested that the action of di-halogenous compounds on tertiary nitrogen atoms of chain extenders would lead to the creation of ionic urethane elastomers.

In order to verify this theory, we have carried out dielectric studies of systems with triethanoloamine in the presence of dibromohexane as well as without it. Figure 2 shows variation of dielectric permitivity ϵ' and the loss tangent T_g δ with temperature for the elastomers under study.
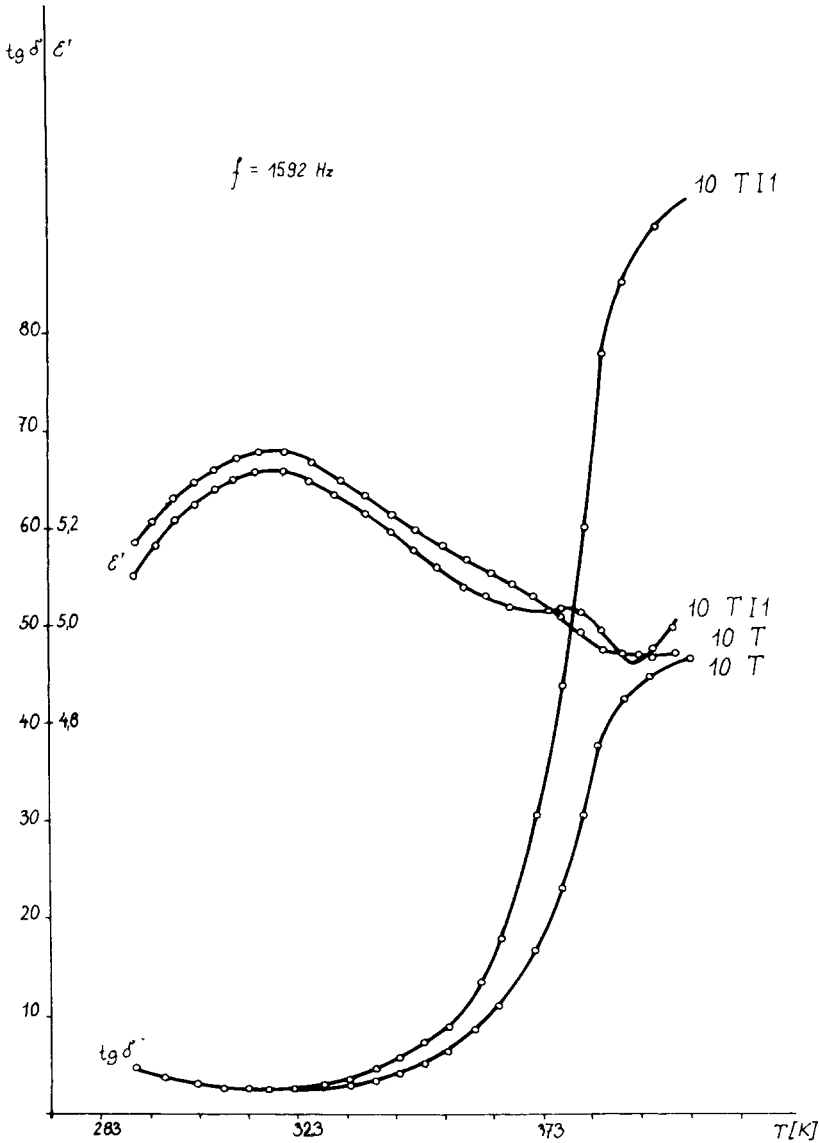
Fig. 2.   Variation of the dielectric permitivity ϵ' and the loss tangent $T_g\delta$ with temperature for the urethane elastomers 10T and 10TI1.

We have noted that the increase of the dielectric constant up to the temperature of 338 K is related to the glass transition temperature in the soft phase of elastomers and to the increase in the mobility of segments in the chain of elastomers. Above 338 K, and the T_g δ increases and reaches its maximum at the temperature of approximately 390 K. This maximum value is related to the softening of domains of hard segments. We have found that the observed increase in T_g δ is more rapid and of greater magnitude in systems containing dibromohexane.

In the region of elevated temperatures, we have observed a similar be-

havior of dielectric constant. This can be explained by the presence of ionic arrangements $(N,^+Br^-)$.

The positive charge is connected by nitrogen, which is included in the macrochain of the polymer. On the other hand, at lower temperatures, the bromine ion Br^- is closed in hard domains without any possibility of free dislocation. It is freed when the temperature reaches approximately 390 K, where the softening of hard domains occurs and acts as a free-charge carrier. In this condition, both the electric conductivity and the T_g δ increase.

Figure 3 shows the change in T_g δ with the temperature for elastomers cross-linked by various amounts of triethanoloamine and dibromohexane. We have observed that the increase in the dielectric losses with temperature is faster and of greater magnitude in the presence of greater amounts of compounds creating ionic arrangement. This increase commences at the temperature of 345 K.

Figure 4 illustrates the influence of the content of ionogenic cross-linking mixture on the specific conductivity of investigated elastomers. The graph is based on tests carried out at the temperature of 333 K to show clearly the increase in the conductivity with increasing content of TEA + DBH. With the distance between ions of the order of 3-4 Å and the dielectric constant of the environment $\epsilon \sim 7$–9, we have estimated the energy of coulombic interaction of the order of 0.1–0.2 eV. It follows, therefore, that at temperatures of the order of 330–340 K, the thermal energy can be sufficient to free the bromine ions and to increase the conductivity of the elastomer. It follows, therefore, that the observed increase in the conductivity with increasing content of ionogenic mixture confirms the creation of ions in the structure of urethane elastomers.
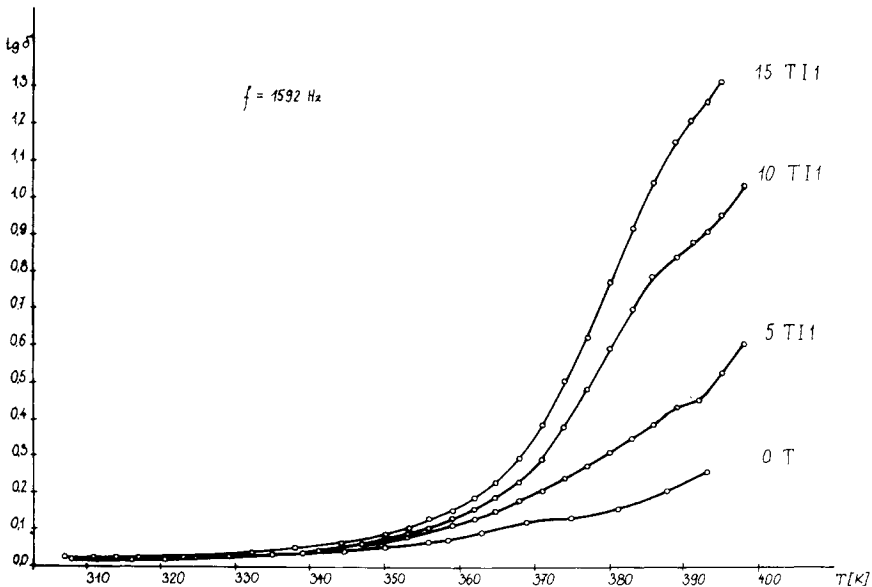

Fig. 3.   Variation of the loss tangent $T_g\delta$ with temperature for urethane elastomers cross-linked by various amounts of TEA and DBH.
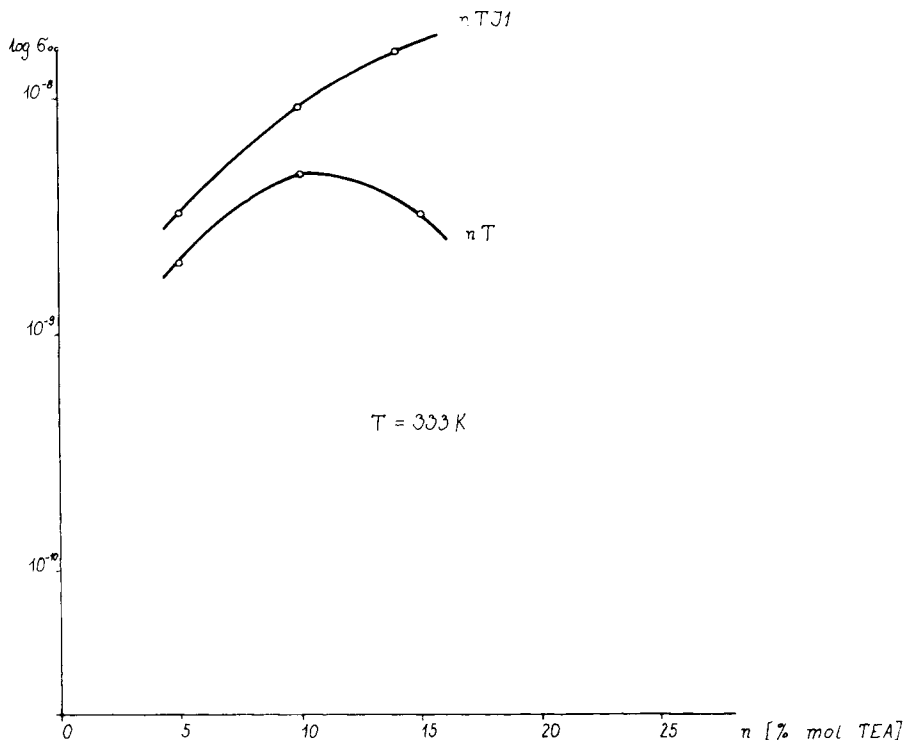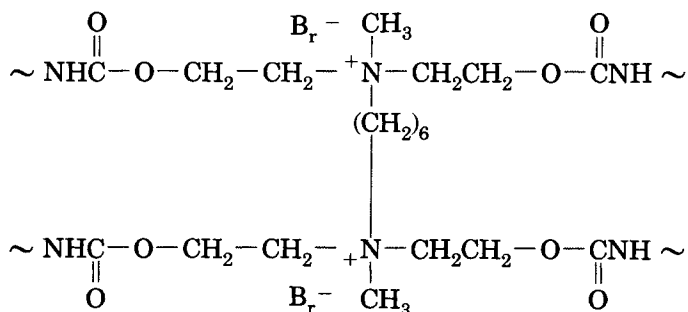
Fig. 4. The influence of the content of ionogenic cross-linking mixture on the specific conductivity of the urethane elastomers investigated.

We realized that since most of the urethane elastomers exhibit phase separation, the strong intermolecular interactions in domains of hard segments and the presence of hydrogen bonds increase the number of effective elastic chains, that are capable of transferring stresses. Hard domains serve as a multifunctional cross-link between the flexible matrix chains and orient themselves under stresses. As elastic deformation progresses, the superstructure of urethane elastomers is destroyed.[22-26] However, the presence of chemical cross-links (and probably ionic crosslinks) makes the orientation of macrochains and formation of domains difficult, decreases the influence of viscoelastic effects on the modulus, and moves the deformational properties of cross-linking urethane elastomers toward higher elasticity resulting from theoretical dependence of stress-strain.[25,27] Moreover, as a consequence of swelling, just as in the case of temperature increase, the morphological changes take place in the network and lead to a decrease of phase separation in urethane elastomers. In this case, the deformational properties of urethane elastomers approach viscoelastic properties specified by the kinetic theory of rubber elasticity in the range of moderate elongations.[24,25,28]

Considering the above statements and trying to describe comparatively changes in the number of effective chains of the urethane elastomers investigated, we have applied the kinetic theory of rubber elasticity, which provides the only method of determination of the concentration of elastic effective chains in a network.

The results of measurements of the cross-linking density and tensile strength of urethane elastomers are presented in Table II. The cross-linking density of samples swollen in benzene is due to the presence of chemical bonds, ionic bonds, and probably partial hydrogen bonds. Samples swollen in ethyl acetate contain only chemical and ionic bonds, although the nonswollen samples show total cross-linking density, including a multifunctional cross-link due to the presence of hard domains. A comparison of these results shows a high content of secondary cross-linking bonds in the total network.

At the same time, it can be seen that, in the case of bifunctional chain extenders (MOCA and MDEA), the cross-linking density of the urethane elastomers obtained with dibromohexane is much higher than without it. The tertiary nitrogen atoms in MDEA can react with DBH, forming ammonium salt, which provides additional cross-linking bonds taking part in total cross-linking density and increasing mechanical properties (AI, CAI):

$$\sim NHC\overset{O}{\overset{\|}{}}-O-CH_2-CH_2-\overset{B_r^-\ CH_3}{{}^+N}-CH_2CH_2-O-CNH\overset{O}{\overset{\|}{}}\sim$$

$$(CH_2)_6$$

$$\sim NHC\overset{}{\underset{O}{\overset{\|}{}}}-O-CH_2-CH_2-\underset{+}{}N-CH_2CH_2-O-CNH\underset{O}{\overset{\|}{}}\sim$$

The urethane elastomer obtained only with MDEA was too weak to test the tensile strength and, consequently, the number of effective chains, but using DBH, which forms ionic cross-linking bonds with tertiary nitrogen

TABLE II
Urethane Elastomers Cross-linking Density and Tensile Strength (R_r) of the Investigated

| Urethane elastomers | Cross-linking density (mol/m^{-3}) | | | R_r (MPa) |
| | Nonswollen samples | Swollen samples | | |
		Benzene	Ethyl acetate	
A		1850	350	Too weak to test
AI	3300	1100	650	18.0
C	8000	4600	4400	38.3
CI	14500	4800	4700	42.0
CA	4850	2800	950	19.0
CAI	10000	5700	2000	32.6
5T	1200	690	460	37.0
5TI1	1150	630	410	32.7
5TI3	1400			
10T	1300	720	540	29.3
10TI1	1180	620	530	24.5

atoms, improved mechanical properties very distinctly. The increase in cross-linking density measured for samples swollen in ethyl acetate takes place because of the ionic bonds. The decrease in cross-linking density of samples swollen in benzene may be explained as due to a reduction of hydrogen bonds because of the presence of DBH. This explanation is in agreement with the work of Lorentz.[6]

The results of measurement of the cross-linking density of urethane elastomers extended by MOCA in presence of dibromohexane indicate that, also in this case, in spite of the initial high cross-linking density, its increase is found to take place along with the higher ultimate tensile strength (from 38 to 42 MPa). This means that not only the presence of the tertiary nitrogen atom in the structure of the elastomer chain extender but also urethane or urea arrangement favors the formation of cross-linking bonds with dibromohexane.[29,30]

It has been proved on the basis of model substances that difenyl urea forms a salt with n-propyl bromide (mp 538 K). Chemical shifts of characteristic groups in the investigated urethane elastomers are presented in Table III.

Figure 5 shows the high-resolution NMR spectra of the urethane elastomers C and CI. Comparing the signals of C with CI, we have noted that the peaks of protons of urea NH groups (d and f) disappeared in CI. The reaction of dibromohexane with urea NH groups has also been proved.

The work of Benson et al.[31] on the subject of complexation of lithium bromide with copolyether urethane-ureas, which led to the formation of hydrogels, and of Ottenbrite[32] on the polymerization of N,N-dimethyl-3,4-dimethylene-pyrrolidinum bromide, confirm the possibility of this type of reaction.

TABLE III
Comparison of Proton Signals of Urea, Urethane, Biuret, Allophanate, and Amine Groups
with the Literature

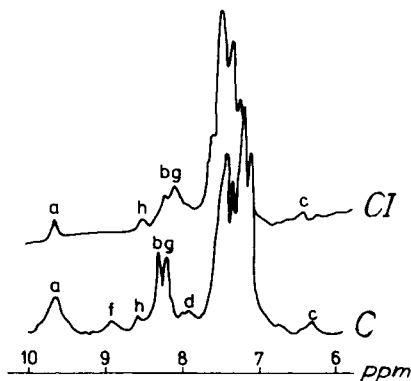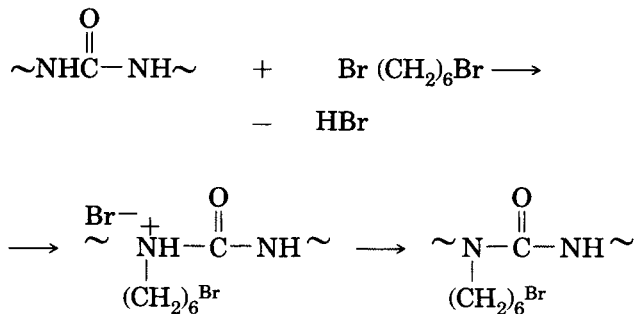| Elastomer	Signal	Chemical shifts (ppm)		Chemical structure
		Literature[21]	Determined	
	a	9.46	9.65	
C	b	8.32	8.3	$NHCOOC_2H_5$ a
	c	6.07	6.3	
	d	7.97	7.95	$NHCONHC_4H_9$ b c
	f	9.38	8.9	Cl
	g	8.28	8.2	$NHCONHC_4H_9$
	h	8.58	8.6	d
	a	9.46	9.65	Cl
	b	8.32	8.25	NHCONH
CI	c	6.07	6.4	f g
	g	8.28	8.1	
	h	8.58	8.55	NHCONH h h

Fig. 5.   The NMR spectra of the urethane elastomers C and CI.

Looking at the electronic structure of the resultant arrangement in the investigated elastomers, we must take under consideration the possibility of the elimination of hydrogen bromide and the formation of cross-linking chemical bonds with the simultaneous appearance of ionic centers:

$$\underset{\displaystyle \sim NHC-NH\sim}{\overset{\textstyle O \atop \textstyle \|}{}} \quad + \quad Br\,(CH_2)_6Br \longrightarrow$$

$$- \quad HBr$$

$$\longrightarrow \quad \underset{\displaystyle (CH_2)_6{}^{Br}}{\overset{\displaystyle Br^- \atop +}{\sim\;\underset{|}{NH}-\overset{O \atop \|}{C}-NH\sim}} \quad \longrightarrow \quad \underset{\displaystyle (CH_2)_6{}^{Br}}{\sim\,\underset{|}{N}-\overset{O \atop \|}{C}-NH\sim}$$

Yet, the number of chemical cross-links due to DBH is not sufficient to produce network behavior, as we see when preparing samples for NMR analysis.[21]

As can be seen from Table II, the increase in cross-linking density in the systems with dibromohexane when MDEA and MOCA are used as chain extenders is connected with higher tensile strength. Due to the reaction of dibromohexane with tertiary nitrogen of TEA, applied as a three-functional chain extender, only "binding" of chemical cross-linking nodes takes place and the presence of ionic centers (which has been proved by dielectric measurements[33,34]) does not bring about an additional effective cross-linking density in the system because the quantity of effective chains between the nodes, capable of transferring stresses, does not increase:

$$\overset{\displaystyle Br^- \qquad\qquad\qquad Br^-}{\sim\,{}^+\widetilde{N}-(CH_2)_6-\widetilde{N}{}^+\,\sim}$$
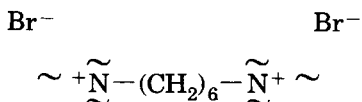
The length of chain $(CH_2)_6$ is too short in comparison to macrochains to transmit stresses.

The total cross-linking density is much lower in the systems with TEA, probably because of the lesser number of hydrogen bonds in such cross-link elastomers. The decrease in cross-linking density and tensile strength in the ionic systems (5TI, 10TI) can also be observed in comparison with the systems without dibromohexane. This is caused by the reaction that leads to the formation of branches, making the creation of cross-linking bonds difficult:

$$\sim\!\!\widetilde{N} + Br\!-\!(CH_2)_6\!-\!Br \longrightarrow -\widetilde{N}^+\!-\!(CH_2)_6\!-\!Br \quad \overset{\overline{\;Br\;}}{}$$
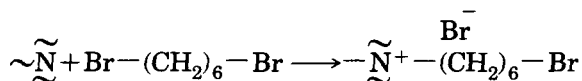
Figure 6 shows plots of tensile strength versus amount of TEA in the urethanes for two types of elastomers: nonionic and ionic. It is seen very distinctly that the incorporation of only a small amount of TEA (to mol 5%) into the system improves the strength of the elastomer. On the other hand, further increasing TEA decreases this property of the material. Due to the creation of too many cross-links makes the formation of hydrogen bonds difficult and consequently reduces the phase separation in the system responsible for the excellent mechanical properties of polyurethanes.

It is also seen very clearly (Fig. 6) that the application of DBH in equal molar ratio to TEA reduces tensile strength. This is the consequence of lower cross-linking density for reasons explained earlier.

As we can see from Table II, multiplying the amount of DBH in synthesis (5TI3) increases the cross-linking density (from 1150 to 1400 mol/m^2). Similar observation can be made for Figure 7, which is a plot of tensile strength of urethane elastomers containing 2% mol TEA versus the amount of DBH.

The application of molar excess of DBH in the DBH-TEA mixture results in improved mechanical properties because of the greater probability of cross-linking reactions of urethane NH groups or tertiary nitrogen atom in TEA with dibromohexane. These advantageous changes take place in sys-
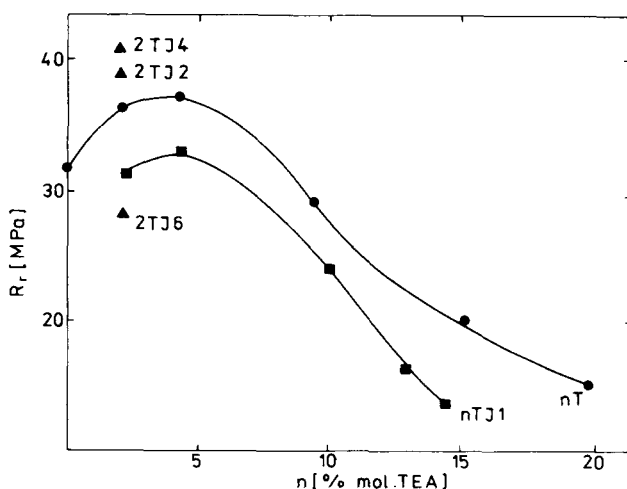

Fig. 6.   Variation of tensile strength with TEA content in the extending-cross-linking system for nonionic and ionic urethane elastomers.
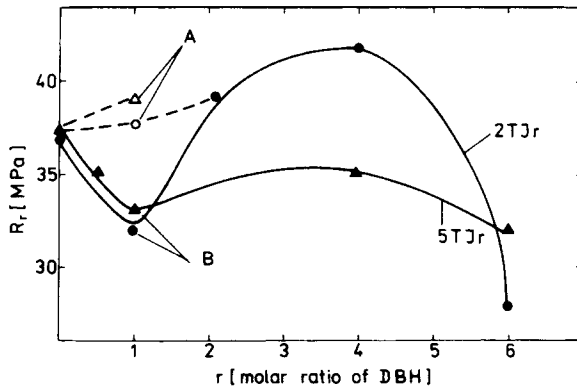
Fig. 7.   Variation of tensile strength with molar excess of DBH for urethane elastomers containing 2% mol TEA and 5% mol TEA.

tems with a low molar excess of DBH in the DBH-TEA mixture (up to 4:1). Using too high a molar excess of DBH in synthesis leaves some unreacted, and this serves as a plasticizer of the microstructure, reducing physical cross-links. As a result elastomers exhibit poor mechanical properties (2TI6).

In Figure 7, point A corresponds to the mixing of an exact molar equivalent of DBH and the chain extender mixture prior to adding the prepolymer, whereas point B corresponds to the direct addition of DBH to the prepolymer. The mixing of DBH and the extender mixture probably facilitates the formation of ionic cross-links and consequently improves the strength due to the increased hard domain cohesiveness caused by the aggregation of ionic groups.

The results of thermal and thermomechanical analyses are shown in Table IV. It follows from those data that the loss of elastic properties temperature T_f of elastomers based on MOCA is high (451 K) and increases for ionic systems (470 K). The chemical cross-link in systems with TEA has an effect on T_f that is much higher (416–425 K) than in the case of typical urethane elastomers (OT) ($T_f = 396$ K). The presence of ionic groups increases T_f by about 10–20 K. In systems with a small amount of TEA and DBH in the cross-linking mixture, the temperature at which the loss of elastic properties occurs ranges from 421 to 429 K, that is, 30 K higher

TABLE IV
Flow Temperature T_f and Decomposition Temperature T_d of the Urethane Elastomers Investigated

Elastomer	T_f (K)	T_d (K)	Ionic elastomer	T_f (K)	T_d (K)
C	451	530	CI	470	530
			2TI1	425	
			5TI1	421	563
5T	416	553			
			5TI3	427	
10T	418	548	10TI	429	573
15T	425	538	15TI	429	543
OT	396	548			

than in the case of typical urethane elastomers without ionic centers (OT). The decomposition temperatures T_d of ionic urethane elastomers with TEA are very high and range from 543 to 573 K and in same extreme case exceed the decomposition temperature of typical urethane elastomer by about 25 K.

CONCLUSIONS

The urethane elastomers based on 2000 MW oligo (ethylene adipate), 4,4'-diphenylmethane diisocyanate with different chain extenders, and dibromohexane or ammonium salt were prepared and their cross-linking density and mechanical and thermal properties were determined. The ionic groups were incorporated into the structure or urethane elastomers, not only because of the reaction of dibromohexane with a tertiary amine, but also because the NH groups in the urea (or urethane) moieties are capable of forming cross-links in the presence of dibromohexane. It is likely that a reaction leading to the formation of a chemical cross-link with simultaneous appearance of ionic centers takes place in these systems. In general, material strength was found to increase because of increased hard domain cohesiveness caused by the aggregation of ionic groups in the case of difunctional extenders.

When triethanoloamine was applied as a three-functional chain extender, causing damage to phase separation, the appearance of ionic groups changed only the functionality of cross-links and did not improve their strength, as dibromohexane was used in equimolar ratio. The improvement in tensile strength was noticed for elastomers with a small molar excess of dibromohexane to triethanoloamine because of a probability of cross-linking reactions with urethane groups. Thermal analysis showed that the presence of ionic centers in the network of urethane elastomers improved their thermal properties.

References

1. S. L. Aggarwal, Ed., *Block Polymers*, Plenum Press, New York, 1970.
2. G. M. Estes, S. L. Cooper, and A. V. Tobolsky, *J. Macromol. Sci. Rev., Macromol. Chem.*, **4**, 313 (1970).
3. S. L. Cooper and G. M. Estes, Eds., *Multiphase Polymers*, Adv. Chem. Ser. 176, American Chemical Society, Washington, D.C., 1979.
4. P. E. Gibson, M. A. Vallance, and S. L. Cooper, in *Developments in Block Copolymers*, I. Goodman, Ed., Appl. Sci. Ser., Elsevier, London, 1982.
5. A. Noshay and J. E. McGrath, Eds., *Block Copolymers*, Wiley, New York, 1973.
6. A. Rembaum, *Advan. Urethane Sci. Technol.*, **2**, 109 (1973).
7. D. Dietrich, W. Keberle, and H. Witt, *Angew. Chem., Int. Ed. Engl.*, **9**, 40 (1970).
8. K. K. S. Hwang, Chang-Zheng Yang, and S. L. Cooper, *Polym. Eng. Sci.*, **21**, 1027 (1981).
9. J. A. Miller, K. K. S. Hwang, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B22**(2), 321 (1983).
10. Chang-Zheng Yang, K. K. S. Hwang, and S. L. Cooper, *Macromol. Chem.*, **184**, 651 (1983).
11. D. Lorenz and G. Rose, *Colloid Polym. Sci.*, **260**, 1079 (1982).
12. K. K. S. Hwang, T. A. Speckhard, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B23**(2), 153 (1984).
13. T. A. Speckhard, K. K. S. Hwang, C. Z. Yang, W. R. Laupan, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **B23**(2), 175 (1984).
14. K. Adibi, M. H. George, and J. A. Barrie, *Polymer*, **20**(4), 483 (1979).
15. D. Dietrich, O. Bayer, and J. Peter, Ger. Pat. 1184946, Farben fabriken Bayer (1962); *C.A.* **62**, 7984h (1965).

16. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology*, Part I, Chemistry, Interscience, New York, 1962.

17. S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley, New York, 1963.

18. G. Kraus, *Rubber Chem. Technol.*, **30**, 928 (1957).

19. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **2**, 512 (1943).

20. M. Rutkowska, M. Pilch, and A. Kwiatkowski, *Polimery*, **1**, 10 (1975).

21. H. Okuto, *Macromol. Chem.*, **98**, 148 (1966).

22. R. Bonart, *J. Macromol. Sci. Phys.*, **B2**, 115 (1968).

23. C. E. Wilkes and C. S. Yusek, *J. Macromol. Sci. Phys.*, **B7**, 187 (1973).

24. W. Dzierża, *J. Appl. Polym. Sci.*, **27**, 1487 (1982).

25. W. Dzierża, The influence of chemical structure of segmented polyurethane elastomers on their deformational properties, University of Toruń, Toruń, 1980.

26. G. L. Wilkes and J. A. Emerson, *J. Appl. Phys.*, **47**, 4261 (1976).

27. H. Goering, G. Pohl, and D. Joel, *Plaste Kautschuk*, **32**, 14 (1985).

28. W. Dzierża, *Makromol. Chem.*, **184**, 1519 (1983).

29. M. Rutkowska, Proceedings of Macromolecular Conference, Strasbourg, 1981, p. 86.

30. A. Balas and M. Rutkowska, Polish Pat. P 239027 (1985).

31. R. Benson, S. Yoshikawa, K. Knutson, and D. J. Lyman, in Advances in Chemistry Series No. 199, B10, Materials, S. L. Cooper and N. A. Peppas, Eds., A.C.S., 1982, p. 133.

32. R. M. Ottenbrite, *Polym. Bull.*, **6**, 225 (1981).

33. M. Rutkowska and R. Zieliński, Proceedings of the Symposium on Macromolecular Mobility in Polymer Systems, Leipzig, 1981, p. 233.

34. M. Rutkowska and R. Zieliński, Proceedings of International Rubber Conference 82, Paris, 1982, pp. 1–13.