

New Linear Polyurethaneureas Based on Polyoxytetramethylene, Aliphatic Diisocyanates, and Aromatic Diamines

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Synopsis

New polyurethaneureas have been synthesized with α - ω hydroxylated polyoxytetramethylene, aliphatic diisocyanates and nonhalogenated aromatic diamines. Four series of PUR have been studied by varying the PTMO molecular weight, the stoichiometry, the nature of the aliphatic diisocyanate, and the steric hindrance of the aromatic diamine. Quantitative evaluation of the degree of phase separation was obtained by DSC. An estimation of the dispersed soft segments outside the soft phase could thus be made. In addition to DSC, dynamic mechanical properties, were obtained for the four series of PUR over a wide temperature range. The hard segments in the PUR chains are amorphous and their high temperature behavior depends only on the strength of interactions in the amorphous state. Finally, stress-strain measurements were carried out on a few samples, and a wide range of tensile properties has been observed.

INTRODUCTION

The purpose of this study was to synthesize polyurethaneureas whose properties were in the range obtained when the methylene *bis*-chloroaniline (MOCA) chain extender was used.

Indeed, the use of the diamine is now very limited by its high toxicity. The formulations studied are based on aliphatic or cycloaliphatic diisocyanates (because of their low reactivity), low toxicity aromatic diamines, and polyoxytetramethylene as soft segment. On a molecular basis, linear polyurethaneureas elastomers may be described as block copolymers of the (AB)_n type. They also typically have a "domain" morphology that arises from the thermodynamic incompatibility between the two types of segments of the chain.¹⁻³ These materials consist of alternating hard rigid blocks and soft flexible units. In our case, the hard segments are composed of aliphatic (or cycloaliphatic) diisocyanates linked by aromatic diamines. The soft segment is poly(tetramethylene oxide) (PTMO) in the typical number average molecular weight range of 650–2900.

Several studies have been performed with regard to the various relationships of molecular structure and physical properties for thermoplastic polyurethaneureas.^{4,5}

In this study, the thermal and mechanical properties of four series of polyurethaneurea elastomers have been investigated. The first three series are synthesized with a 1 PTMO/3 diisocyanates/2 diamines molar ratio.

First the chain length of the soft segment was modified (by changing the PTMO molecular weight) whereas the hard segments were kept the same.

Second, we modified the hard segment composition by varying the nature of the diisocyanate group whereas the diamine and soft segment were unchanged.

Lastly, we modified the third component of the polyurethaneureas, in other words the diamine, while the diisocyanate and soft segment were kept the same.

In the fourth series we kept the same three components but the stoichiometry varied.

In the third series we also measured the degree of phase segregation by a new method developed in our laboratory.^{7,8}

EXPERIMENTAL

α - ω Hydroxylated Oligomers

We used poly(tetramethylene oxide) oligomers of molecular weights from 650 to 2900. Table I shows the main characteristics of these polyethers. \bar{M}_n was determined by cryometry, the glass transition temperature (T_g) by differential scanning calorimetry (DSC), the molecular dispersity by gel permeation chromatography (GPC), and the hydroxyl number \bar{X}_n (obtained by titration).

Aliphatic and Cycloaliphatic Diisocyanates

The components are listed in Table II.

Purity analyses were carried out by gel permeation chromatography (GPC) as shown in Figure 1. We see that there is only one sharp peak for each diisocyanate, indicating a good purity. This point is confirmed by DSC analyses (listed in Table II) which give a purity over 99% for the crystalline products.

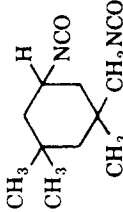
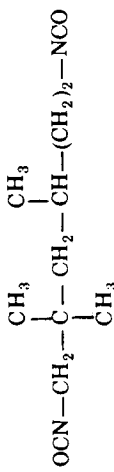
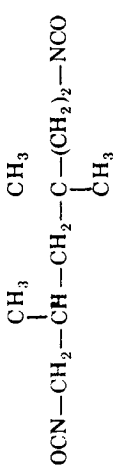
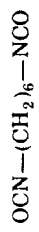

IPDI is a cycloaliphatic diisocyanate, liquid at room temperature; moreover it has been shown by Cunliffe and colleagues⁹ that this product consists of a mixture of two isomers (see Fig. 2) in which the NCO and CH₂NCO are in *cis* or *trans* position on the cyclohexane ring.

Measurement of the isomer ratio from ¹H and ¹³C nuclear magnetic resonance (NMR) and gas chromatography (GC) indicate similar values of about 72% for the *cis* isomer and 28% for the *trans* isomer. The reactivity of these

TABLE I
Characteristics of Poly(tetramethylene oxide) Oligomers

	\bar{M}_n	\bar{X}_n ($\pm 5\%$)	\bar{F}_n	T_g ($^{\circ}$ C)	Molecular dispersity
PTMO 650	710 \pm 50	175.3	2.22	-96.5 \pm 1	1.4
PTMO 1000	1020 \pm 50	116.6	2.12	-94 \pm 1	1.63
PTMO 2000	2150 \pm 100	58	2.23	-91.5 \pm 1	2.37
PTMO 2900	3300 \pm 300	39.2	2.3	-90.0 \pm 1	2.1

TABLE II
Characteristics of the Diisocyanates Used for the PUR

Chemical identification	Component structure	Mol. wt (g)	Glass trans. temp. (°C)	Melting temp. (°C)	Purity	
					Given by suppliers	Determined by DSC
3 Isocyanatomethyl-3,5,5-trimethyl cyclohexyl-diisocyanate (Isophorone diisocyanate) (IPDI)		222	-100	Amorphous	> 98%	> 98%
Trimethyl hexamethylene diisocyanate		210	-128	Amorphous	> 98%	> 98%
(TMDI)						
1-6 diisocyanato hexan (Hexamethylene diisocyanate) (HMDI)		168	-145	-70.5	98%	99.4%
<i>trans</i> cyclohexyl-1,4-diisocyanate (CHDI)		166	—	52	—	99.8%

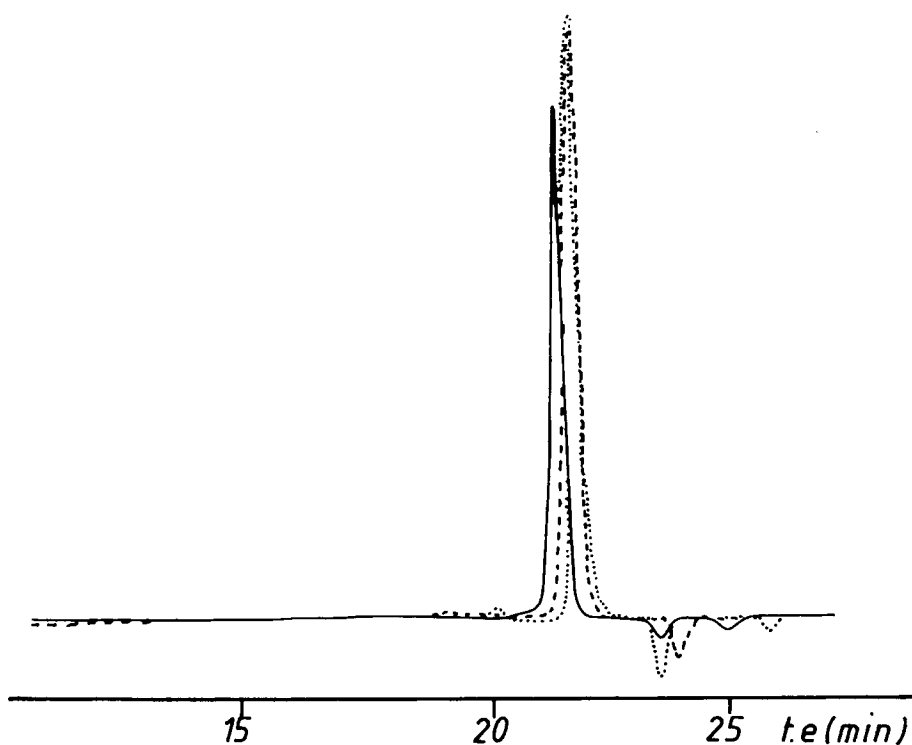


Fig. 1. GPC chromatograms of the aliphatic (and cycloaliphatic) diisocyanates. TMDI (.....); HMDI (-----); IPDI (—).

isocyanates has been reported in many publications.^{9,11-13} Cunliffe et al.⁹ found that differences between the various isocyanate groups are small (< 2.5 at 60°C) while other workers¹¹ found that the aliphatic isocyanate group is about ten times more reactive as the cycloaliphatic one.

CHDI is crystalline at room temperature. Due to the symmetrical structure of this molecule, a very cohesive structure of the hard segments is promoted in the PUR systems.^{10,14}

TMDI, is an aliphatic diisocyanate, chemically derived from isophorone, liquid at room temperature. The molecule is a mixture of two isomers 2,2,4 and 2,4,4 in nearly the same proportions.¹¹

HMDI is liquid at room temperature, a recent study¹² showed the higher reactivity of the two isocyanate groups, compared with other aliphatic ones.



Fig. 2. *cis* and *trans* isomers of isophorone diisocyanate.

TABLE III
Characteristics of the Diamines Used for the PUR

Designation	Chemical identification	Component structure	Mol. wt (g)	Glass trans. temp. (°C)	Melting temp. (°C)	Purity	
						Given by suppliers	Determined by DSC
MBMEA	Methylene-bis-(2-methyl-6-ethylanilin)		282	—	86	> 99.5	99.74
MDFA	Methylene-bis-(2,6-diethylanilin)		310	—	87.5	> 99	99.4
MMIPA	Methylene-bis-(2-methyl-6-isopropylanilin)		310	-10	Amorphous	95	—
MDIPA	Methylene-bis-(2,6-diisopropylanilin)		366	-4	Amorphous	87.5	—

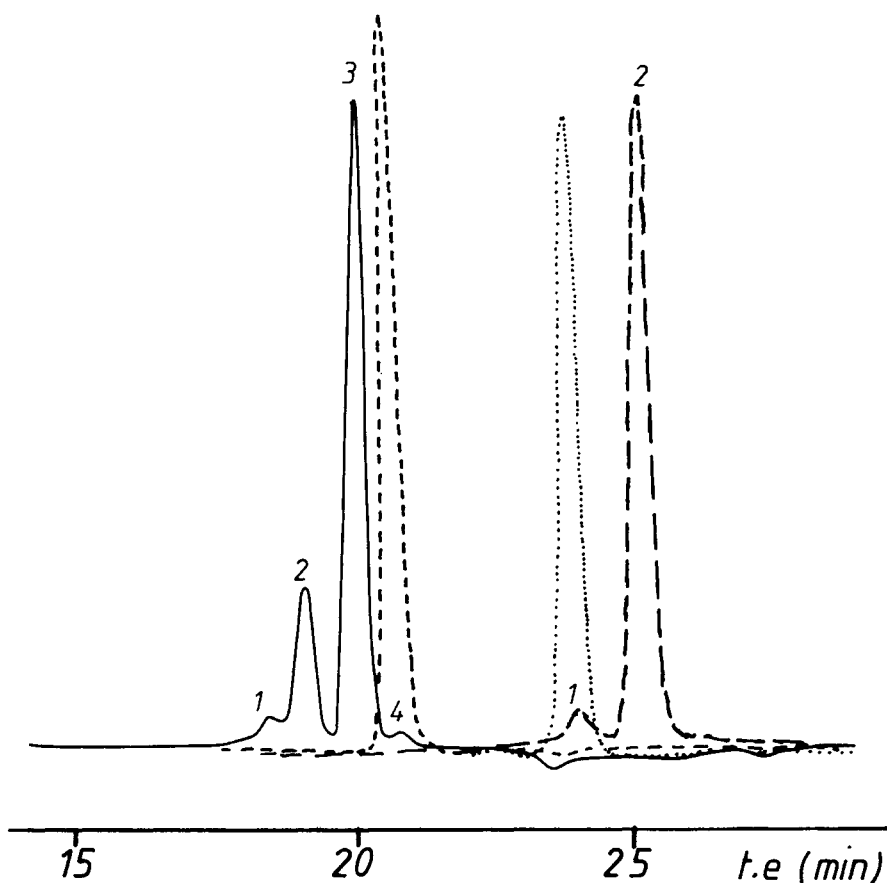


Fig. 3. GPC chromatograms of the aromatic diamines. MBMEA (-----); MDEA (.....); MMIPA (-·-·-·-); MDIPA (—).

Aromatic Diamines

The components are listed in Table III. All the diamines have the same backbone, diaminodiphenylmethane with different steric hindrances (methyl, ethyl, or isopropyl) of the amine groups. The volume of these hindrances can be calculated on the basis of Van Krevelen's work¹⁵ and are taken between 63.6 cm³/mol for the ethyl-methyl group, and 114.5 cm³/mol for the di-isopropyl ones.

Analyses were carried out by GPC and we note in Figure 3 that the two crystalline diamines MBMEA and MDEA have typically pure products sharp peaks.

The MDIPA diamine elutes in a larger region. We found four peaks: the peak number three (which area is 10.0 cm²) corresponds to the diamine; the peaks 1, 2, 4 have areas of, respectively, 0.58 cm², 2.83 cm², 0.23 cm² and correspond to impurities or additives.

The other amorphous diamine, MMIPA gives a chromatogram with two peaks, the peak number two (11.9 cm²) very sharp, corresponds to the diamine and the peak number one (which area is 0.64 cm²) corresponds to a product with higher molecular weight.

SYNTHESIS

For hard block, with low dispersity in length, the PUR were prepared in two steps: first taking into account the oligomer's true function, we carried out the reaction between one mole of oligomer and two, three, or four moles of diisocyanate at 80°C for 4 hours before adding, respectively, one, two, or three moles of chain extender (aromatic diamine) at 60°C. For all the systems studied we note a total compatibility of the three reactants. It augurs good mechanical properties of the final PUR without the macroscopic segregation observed with the classical RIM systems based on diol extenders.

The GPC study of the first step shows no peak evolution after four hours at 80°C. The crystalline diamines were melted at 90°C before adding. The pot-life at 60°C is quite short: between a few minutes and 20 seconds for the different formulations.

Then the mixture was cast in a mould at 100°C and cured three hours at this temperature.

CHARACTERIZATION METHODS

Gel Permeation Chromatography

Gel permeation chromatography was conducted with a WATERS HPLC instrument at 25°C with a μ -sterigel column set of 1000, 500, 100, and 100 Å and a type R401 Refractometric detector, using tetrahydrofuran (THF) as solvent. The product concentration was 1 mg/mL and the flow rate 1.5 mL/min. The calibration was carried out using polystyrene standard with narrow weights distributions.

Differential Scanning Calorimetry (DSC)

DSC thermograms were recorded using a Mettler TA 3000 instrument, with heating rates of 7.5 K/min in argon. DSC was used to determine quantitatively the segregation degree of the soft segments in polyurethanes by a method developed in our laboratory.⁷⁻⁸ The heat capacity change ΔC_p during the glass transition of the soft segment in polyurethaneureas was measured and compared with the ΔC_p of the pure soft segment. This determination was made possible by the fact that during the glass transition of hard blocks, the heat capacity changes are small and almost undetectable.¹⁶⁻¹⁸ Scanning from -170°C provides excellent base lines for ΔC_p determination. Five to ten runs were made for each product. The difference ΔC_p between each run was not more than $\pm 5\%$. Therefore, the average ΔC_p can be estimated within 2%. We will always mention after the mean values the standard deviation (with population parameter taken to be "n").

Dynamic Mechanical Measurements

Dynamic mechanical data were collected at 11 Hz using a Toyo-Baldwin Rheovibron DDVIIB viscoelasticimeter with a heating rate of 1°C/min.

Static Mechanical Measurements

Uniaxial stress-strain experiments were carried out on a JJ T5002 tensile testing apparatus at room temperature, with a crosshead speed of 5 mm/min for the elasticity modulus determination, and 25 mm/min for the ultimate properties determination.

The elongations of the samples were determined by a pulsed infrared noncontacting extensometer which provides a better accuracy. Samples were cut with an NFT 51-034 H2 die and had a gauge length of 25 mm.

RESULTS AND DISCUSSION

Sample designation code indicates whether the sample is IPDI (I), CHDI (C), TMDI (T), or HMDI (H) based, the PTMO molecular weight is 650, 1000, 2000, or 2900, the type of chain extender is MBMEA (ME), MDIPA (DI), MMIPA (MI), or MDEA (DE) and the stoichiometry polyether-diisocyanate-diamine is 1-2-1 (1), 1-3-2 (2), or 1-4-3 (3). For example T-1000-ME-2 indicates a PUR synthesized with 3 moles of TMDI, 1 mole of PTMO 1000 and 2 moles of MBMEA.

Study as a Function of the Polyether Molecular Weight

DSC Analyses. In this series, the composition of the PUR was: 1 PTMO-3 TMDI-2 MBMEA, but the molecular weight of the PTMO varied.

One can observe in Table I, that the T_g of the pure PTMO increases when the molecular weight of PTMO increases: this can be classically explained by the variation of free volume associated to the chain ends concentration.

On the other hand, the T_g of the soft phase in the PUR increase when the molecular weight of the PTMO decreases (see Fig. 4). In the block copolymer, the PTMO chains are end-linked by urethanes. So, when the chains become shorter, their mobility decreases and their glass transition temperature increases.

After the T_g of the soft phase, an exotherm peak is observed near -60°C corresponding to the crystallization of a part of the soft phase (about 10%). Then the correspondant melting endotherm occurs with range $0-10^\circ\text{C}$. At higher temperature, nothing else could be observed. As shown by many authors, the glass transition of the hard blocks is hardly detectable by DSC because of the low heat capacity changes and a wide temperature range.^{16,17} This transition is more easily detected by dynamic mechanical measurement. The absence of melting endotherm up to 280°C indicates a quasiamorphous structure of the hard segments.

In the case of T-2900 ME2, Figure 4 shows two thermograms of the same sample, the second corresponding to a run after quenching in liquid nitrogen. So, we note the polyether crystallization peak, and the heat capacity change of the whole soft phase in the amorphous state during the glass transition. So we can measure, as explained in the experimental part, the degree of soft phase segregation in this PUR. We also measured it for T-2000 ME2 but this was not possible for the two other samples because of the low soft segment molecular weight (< 2000).¹⁸ We logically observe an increase of the soft phase segregation degree (75% for T-2000 ME2 and 85% for T-2900 ME2)

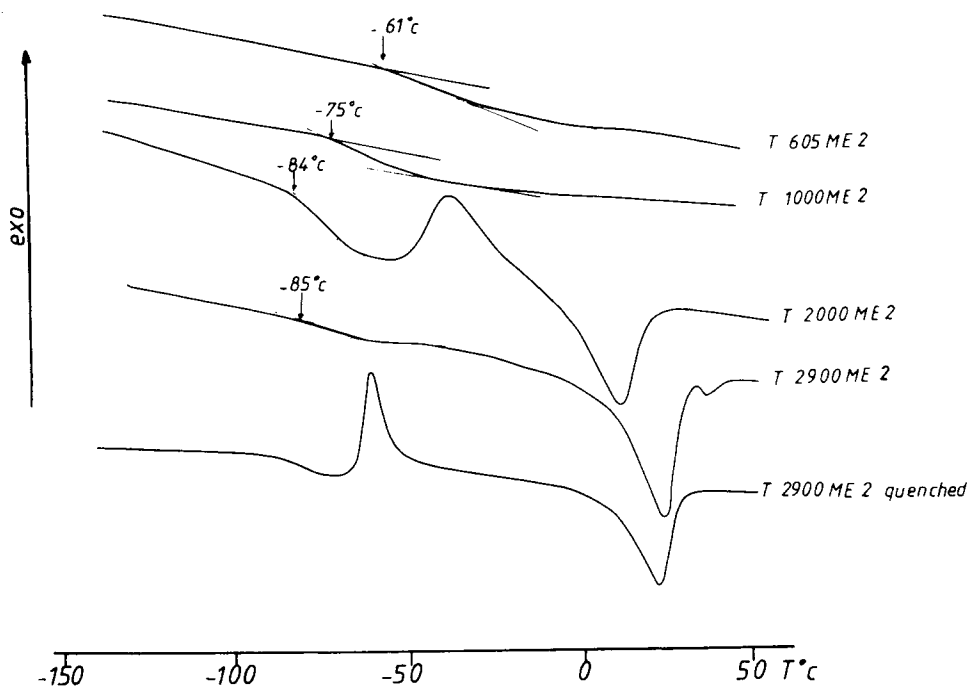


Fig. 4. DSC thermograms of the first series of PUR.

when the PTMO chain length increases.

This trend is confirmed by the works of Cooper et al.⁵ and Takahara et al.¹⁹

Dynamic Mechanical Properties. The storage modulus E' and the dissipation factor $\tan \delta$ of the first series of PUR are plotted as a function of temperature in Figure 5. One or two maxima in the $\tan \delta$ curves are observed. The first one occurs between -60°C and -50°C (for the four samples) and the second approximately at 40°C (for T-2000 ME2 and T-2900 ME2). The low temperature loss peak is attributed to the backbone motion of soft segment that accompanies its glass transition, whereas the high temperature loss peak is related to the melting of the crystalline part of the soft segment (only T-2000 and T-2900 as shown by DSC). E' curves indicate that three of the samples exhibit a rubbery plateau beyond 200°C . This indicates that the PUR are well phase separated. The plateau modulus increases logically upon increasing the hard segment content in the samples (this corresponds to a decrease of the molecular weight of PTMO for a constant stoichiometry). The high temperature behavior of the PUR can be explained by the presence of urea groups whose hydrogen-bonding networks enhance intradomain cohesion.⁵⁻²⁰ The low temperature behavior of the T-2900 ME2 sample is probably related to the important crystalline part of the soft segment (see also the DSC thermograms in Figure 4) which can be explained by the longer polyether chains between physical crosslinks. The beginning of the rubbery plateau corresponds to the melting of these soft segments; the end of the plateau also appears quite unusual (near 170°C), perhaps due to the lower hard segment content.

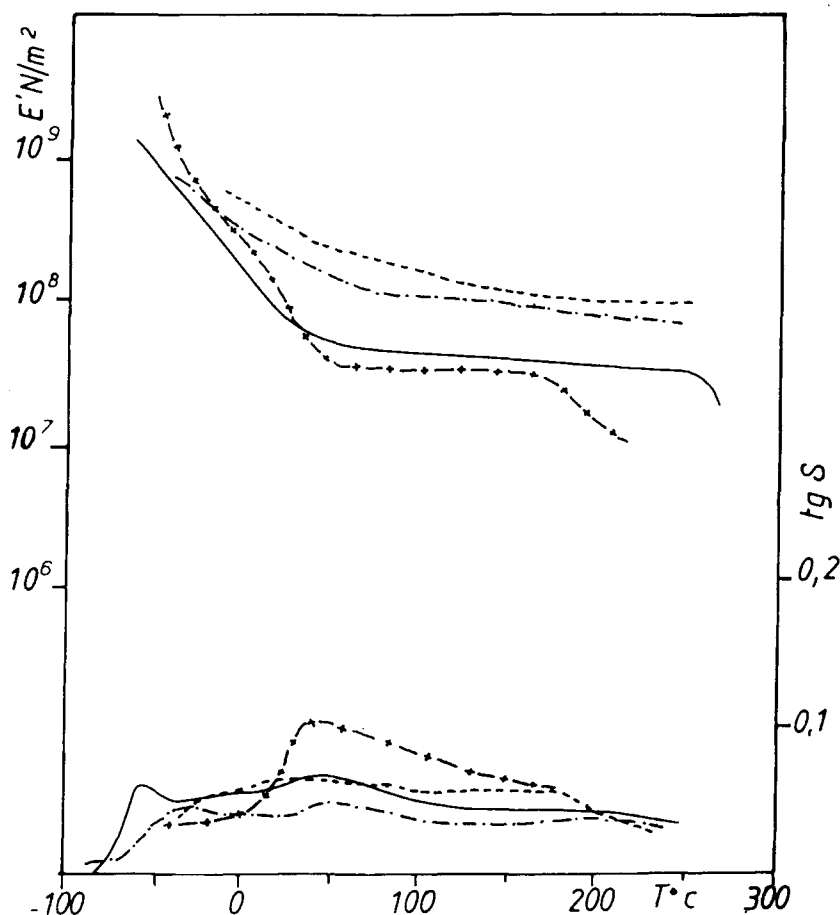


Fig. 5. Storage modulus and loss factor curves of the first series of PUR as a function of temperature. T650-ME2 (-----); T1000-ME2 (-.-.-.); T2000-ME2 (—); T2900-ME2 (+ - + - + -).

Tensile Properties. The tensile behavior of segmented elastomers generally depends on the size, shape, and concentration of the hard domains. The stress-strain curves of this first series of PUR are shown in Figure 6. Table IV summarized the Young's moduli and elongations at break of the materials.

When the molecular weight of PTMO in the first series increases, two phenomena occur. On one hand, the block length of the soft segment increases and on the other hand, the hard segment decreases (but its length did not vary). So we logically observe a higher elastic modulus and a weaker elongation at failure when the polyether molecular weight decreases. These results are consistent with the dynamic mechanical data shown previously.

Study as a Function of the Diisocyanate Structure

In this series, the hard segment composition is changed by varying the nature of the isocyanate, the other components and the stoichiometry being the same. So this series is composed by: T2000 ME2, C2000 ME2, H2000 ME2, I2000 ME2.

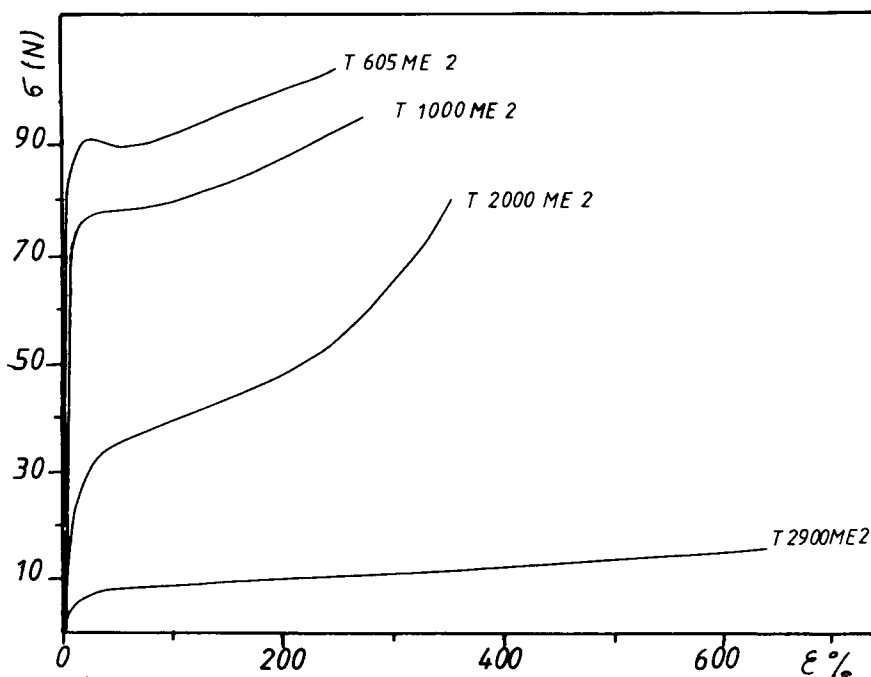


Fig. 6. Stress-strain curves of the first series of PUR.

TABLE IV
Tensile Properties of the First Series of PUR

Sample	T-650-ME-2	T-1000-ME-2	T-2000-ME-2	T-2900-ME-2
Young's Modulus (MPa)	180 ± 40	110 ± 30	45 ± 2	34 ± 4
Elongation at failure (%)	250 ± 50	280 ± 30	360 ± 50	500 ± 80

The data after the symbol ± is the standard deviation σ .

DSC Analysis. In this series, all the samples have a soft phase which crystallizes readily. Thus it was very difficult to quench the whole PTMO in an amorphous state and to measure the phase segregation degree. The glass transition of the soft phase did not vary in this family of PUR ($T_g = -84 \pm 1^\circ\text{C}$).

Dynamical Mechanical Properties. The data are plotted on Figure 7. The loss factor curves show two or three distinct peaks. The low (-60°C) and high temperature (over 200°C) ones are indicative of a two-phase microstructure and correspond to the glass transition of polyether and urethaneurea phases, respectively. The intermediate peak can be attributed to the fusion of the crystallized soft segments. The high temperature peak is hardly observable for three samples because of the weak motion of the hard segment chains, even over 250°C . The dynamic storage moduli data indicate that changing the nature of the isocyanate modifies the hardness of the final material. Therefore, we note that a PUR based on IPDI (I2000 ME2) has a rubbery plateau

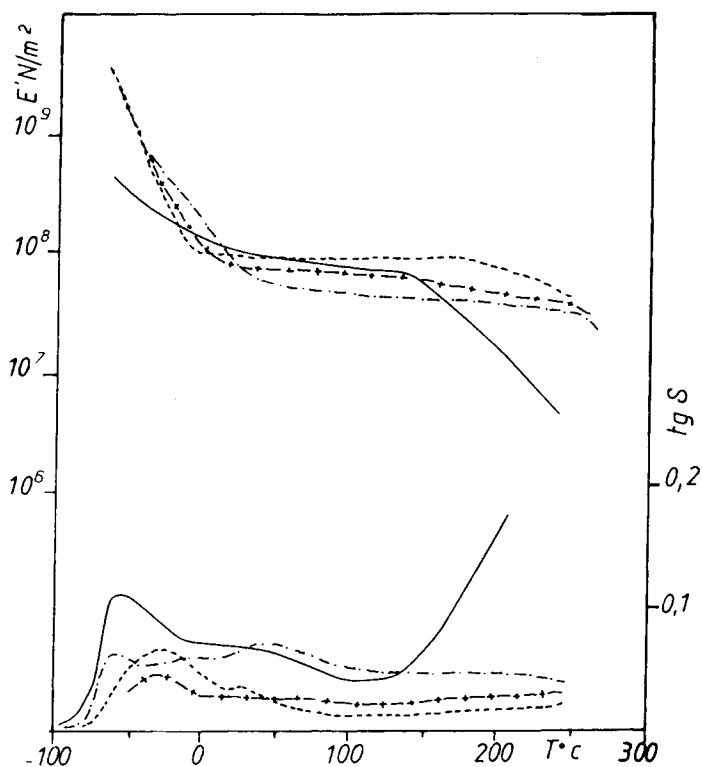


Fig. 7. Storage modulus and loss factor curves for the second series of PUR as a function of temperature. H2000-ME2 (-----); C2000-ME2 (+-+-+-+); T2000-ME2 (-.-.-.); I2000-ME2 (—).

between 70 and 80 MPa but that over 130°C the sample creeps and the modulus decreases readily. For the other three samples the temperature at the end of the rubbery plateau is in the range of 250°C. If a comparison is made with the Adiprene L-MBCA systems (DuPont de Nemours),^{21,22} we can see that these commercial products, for equivalent hardness have a rubbery plateau around 170°C; their hard segments are also urethaneureas, but from both aromatic diamine (MBCA) and diisocyanate (TDI). The discrepancies observed can be due to the asymmetric structure of the 2-4 toluene diisocyanate isomer.

The different values of modulus at the rubbery plateau are consequent from the strength of interactions between the urethaneureas groups in the hard domains. HMDI which is a linear molecule, with no steric hindrance provides a very strong cohesion when reacted with MBMEA, up to 200°C. TMDI is also a linear molecule, but with three methyl substituents on the backbone. This more hindered structure reduces the packing regularity of the urea groups and can explain the lower value of the rubbery plateau. CHDI is a transsymmetrical cycloaliphatic diisocyanate, which produces hard domains with a very good thermal stability (over 240°C).

IPDI is also a cycloaliphatic diisocyanate, but with two isomers, three methyl substitutions, and a very asymmetrical structure. This can explain the

low phase separation characterized by the almost absence of a rubbery plateau. The presence of a large interface explains the relative hardness of I-2000 ME2 at room temperature and the rapid decrease of modulus at higher temperature.

Study as a Function of the Diamine Chain Extender Structure

In this third series, the hard segment composition is changed by varying the diamine nature. The different diamines are tested with two diisocyanates IPDI and TMDI. So we obtain two groups of products:

- I2000 ME2, I2000 DE2, I2000 MI2, I2000 DI2
- T2000 ME2, T2000 DE2, T2000 MI2, T2000 DI2

Differential Scanning Calorimetry. Analyses were carried out on the two groups of PUR. The temperature of the glass transition of the soft phase was for all the samples. $-85 \pm 1^\circ\text{C}$; the polyether phase was amorphous over room temperature. We measured segregation degree of the soft phase for the samples based on IPDI. The results are summarized in Table V. We note that for MBMEA-, MDIPA-, and MMIPA-based PUR the segregation is quite small by comparison with values previously found in our laboratory for such kind of products, based on aromatic diisocyanates and diamines.²³

I2000 DE2 shows a better phase segregation. As mentioned above, MDEA is a symmetrical diamine (the amine groups are sterically hindered by two ethyl groups); its melting temperature is higher than MBMEA's, indicating a greater cohesion, while MMIPA and MDIPA are amorphous. So it seems logical to obtain the best phase segregation when MDEA chain extender is used.

Dynamic Mechanical Properties. The curves corresponding to the IPDI and TMDI families are plotted in Figures 8(A) and 8(B), respectively. In the case of IPDI-based polyurethaneureas, we observed different behaviors for each sample. MDIPA-based PUR gives the weaker sample; the thermal stability of hard domain does not go beyond 110°C . In order of hardness and thermal stability increasing, we find I2000 DI2, I2000 MI2, I2000 ME2, and I2000 DE2. If we observe the chemical structure of the diamines, we note that the more sterically hindered one is M-DIPA (with two isopropyl groups for one amine groups); the PUR based on this diamine shows the lower properties. Then comes M-MIPA, which is also an amorphous diamine but with a lower hindrance; then the two crystallines: MBMEA which possesses the

TABLE V
Segregation Degree of the Soft Phase of IPDI-Based PUR of the Third Series

Sample	I2000 DE-2	I2000 ME-2	I2000 MI-2	I2000 DI-2
Percentage of soft phase	63.3%	64.5%	63.3%	61.1%
ΔC_p (J/g _{PTMO} .K)	0.49	0.44	0.45	0.43
Segregation of the soft phase (%)	72 ± 3	65 ± 1.6	66 ± 2	63 ± 2

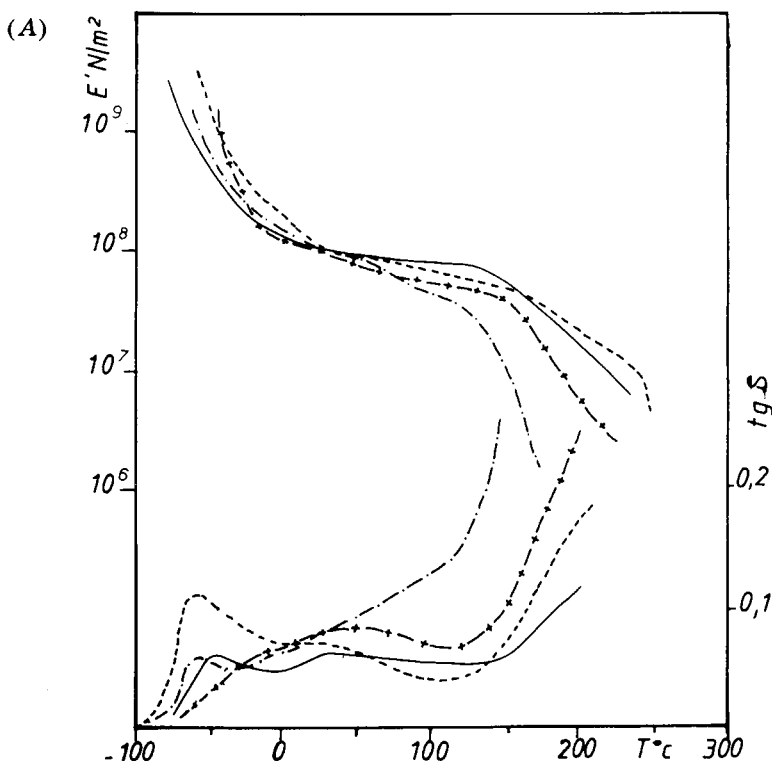


Fig. 8(A) and (B). Storage modulus and loss factor curves for the third series of PUR. (A) PUR based on IPDI. I2000-ME2 (-----); I2000-DE2 (—); I2000-MI2 (+-+-+-+); I2000-DI2 (x-x-x-x-x) and 8(B); PUR based on TMDI. T2000-DE2 (—); T2000-ME2 (-----); T2000-MI2 (+-+-+-+); T2000-DI2 (x-x-x-x-x).

lowest hindrance of all four diamines with a methyl and an ethyl group around each amine and M-DEA. This can be explained by the higher symmetry of this molecule and is confirmed by a higher melting temperature of pure M-DEA which indicates stronger interactions between M-DEA molecules than between MBMEA ones.

In the case of TMDI based PUR [Fig. 8(B)], the same trend is observed, but the discrepancies are limited by the greater hard domains cohesion. Figure 8(B) shows a rubbery plateau up to 250°C for the better sample.

Tensile Properties. The stress-strain results for the IPDI-based PUR are collected in Table VI. We note that there are only a few differences at room temperature between the four products. These results are in agreement with the viscoelastic analyses. We can indeed observe on Figure 8(A) that the storage modulus values at room temperature are in the same range (the differences obtained are lower than the apparatus precision).²⁴ The behaviors differ only when the temperature is raised. The discrepancies observed between Young's modulus measured by the tensile testing machine and the storage modulus measured by viscoelastometry can be explained by the different kinds of sollicitation. The low sollicitation level of a viscoelastometer ($\Delta l/l < 10^{-3}$) logically provides a higher value of the modulus than the tensile measurements.

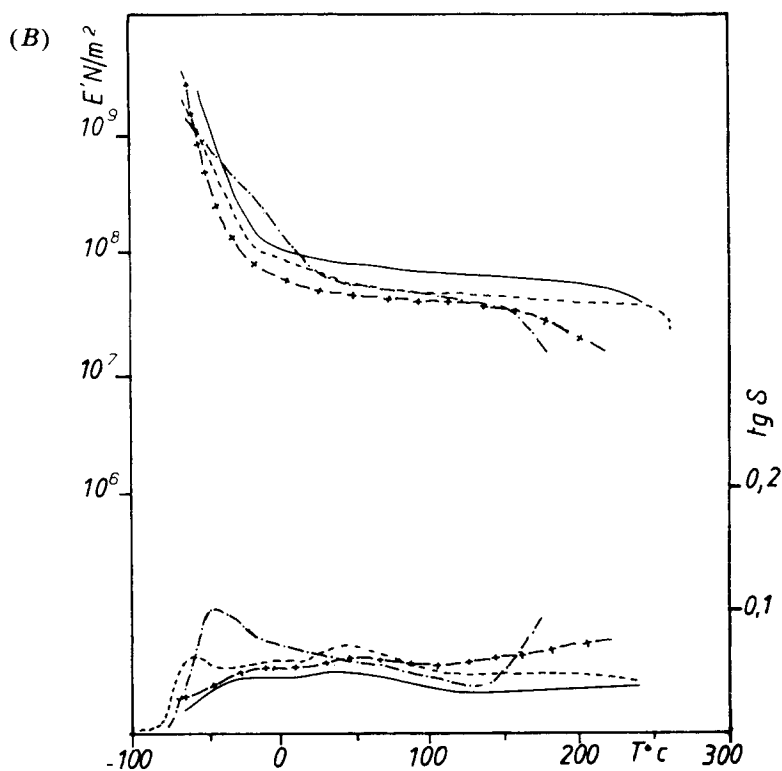


Fig. 8. (Continued from the previous page.)

TABLE VI
Tensile Properties of the IPDI-Based PUR of the Third Series

Sample	I2000 DE-2	I2000 ME-2	I2000 MI-2	I2000 DI-2
Young's modulus (MPa)	55 ± 10	64 ± 5	43 ± 6	54 ± 10
Elongation at failure (%)	510 ± 30	430 ± 20	415 ± 40	445 ± 20

The data after the symbol ± is the standard deviation σ .

Study as a Function of Stoichiometry

In the fourth series, the components are the same PTMO 2000, TMDI, and MBMEA, but the stoichiometry varies. We studied the three samples: T2000 ME1, T2000 ME2, T2000 ME3, corresponding to the stoichiometry ratio 1-2-1, 1-3-2, and 1-4-3.

DSC Measurements. The soft phase in these samples is semicrystalline, so quenching the samples in liquid nitrogen is necessary to measure the ΔC_p of the whole soft phase in our amorphous state. Thus, the degrees of soft phase segregation have been calculated for the three samples and summarized in Table VII.

TABLE VII
Soft-Phase Segregation Degree of the Fourth Series

Sample	T2000 ME-1	T2000 ME-2	T2000 ME-3
Percentage of hard segment	26.6	38.2	46.6
ΔC_p (J/g _{PTMO} ·K)	0.544	0.513	0.476
Segregation of the soft phase	80 ± 1	75.5 ± 2	70 ± 1.5
Percentage of soft segment in the hard phase and in the interphase (wt%)	35.5%	28.4%	25.6%

The data of the table's last line are calculated from the percentage of hard-segment and degree of soft-phase segregation with the hypothesis that the separated soft phase is nearly pure. This assumption seems reasonable considering that the T_g of pure and linked PTMO 2000 would be about -87°C .⁷

The measured values of T_g in the fourth series are $-85 \pm 1^\circ\text{C}$, which indicate a relatively low concentration of hard segment in this separated soft phase.²⁵

Results of Table VII indicate that the degree of the soft-phase segregation logically decreases when the hard-segment concentration increases. However, the mechanical behavior of segmented PUR strongly depends on the hard domains purity. Thus, an interesting parameter is the percentage of soft segment in the hard phase (and interphase), calculated as mentioned before. Thus we note on Table VII that the purity of the hard phase and interphase increases with hard-segment concentration, when the soft-phase segregation decreases. An interesting extension of this work, would be the use of small-angle X-ray scattering to measure the purity of the hard phase on the basis of work by Cooper^{26,27} and Koberstein.^{28,29}

Dynamic Mechanical Properties. The curves are plotted on Figure 9, where $\text{tg } \delta$ data indicate two maxima occurring at approximately -60°C and 20°C for the T2000 ME1 and T2000 ME2 samples, respectively, and only one at -55°C for T2000 ME3. The low temperature loss peak is attributed to the backbone motion of soft segment that accompanies its glass transition whereas the high temperature loss peak is related to the fusion of the crystalline part of the soft phase. These results are in good agreement with those obtained by DSC. The storage modulus (E') curves indicate a rubbery plateau with a high value when the stoichiometry in hard segment increases. The temperature at the end of the plateau is approximately:

195°C for T2000 ME1

250°C for T2000 ME2

255°C for T2000 ME3

These results are to be related to the higher hard domain purity measured by DSC when the hard segments' length increases.

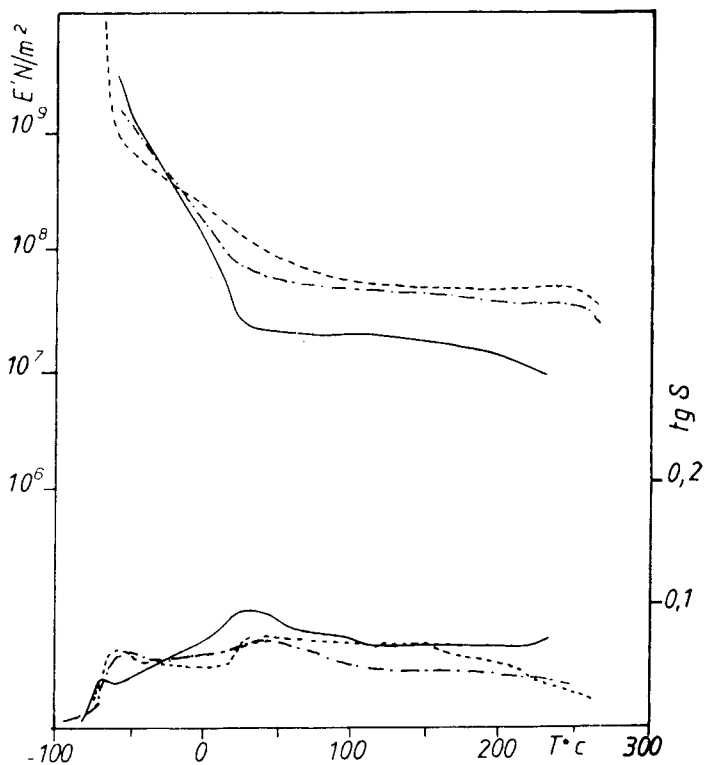


Fig. 9. Storage modulus and loss factor curves for the fourth series of PUR as a function of temperature. T2000-ME3 (.....); T2000-ME2 (-.-.-.-); T2000-ME1 (—).

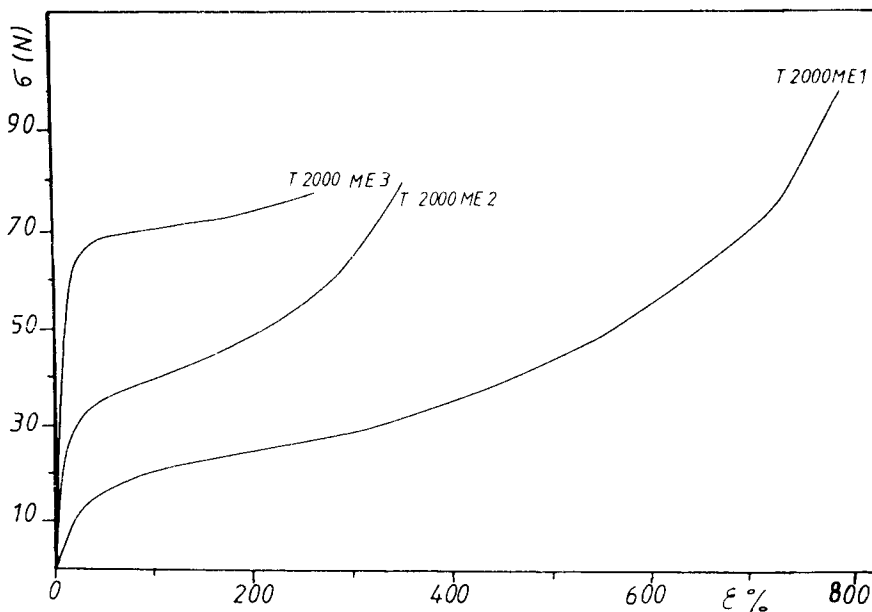


Fig. 10. Stress-strain curves for the fourth series of PUR.

TABLE VIII
Tensile Properties of the Fourth Series PUR

Sample	T2000 ME-1	T2000 ME-2	T2000 ME-3
Young's modulus E (MPa)	14 ± 4	45 ± 2	55 ± 5
Elongation at failure ϵ_r (%)	800 ± 100	360 ± 50	300 ± 80

The data after the symbol \pm are the standard deviations σ .

Tensile Properties. Stress-strain curves for these series are plotted in Figure 10 while tensile properties (Young's moduli and elongation at break) are listed in Table VIII. These results are in agreement with the E' data obtained by viscoelastometry and indicate a logical trend: the Young's modulus increases and the elongation at failure decreases, when the hard segments' concentration is raised.

CONCLUSION

This study showed how it was possible to synthesize new block copolymer polyurethaneureas, with equal or better mechanical and thermal behaviors than classical polyurethaneureas formulation and lower toxicity of the synthesis components. The gel time of these systems can be highly modified by changing the temperature; this makes them compatible with both casting and reaction injection molding (RIM). We have tested the systems studied in this work on an industrial casting machine with good results because of the total compatibility of the three initial reactants (it is not the case with classical RIM products based on diol extenders where a macroscopic segregation is observed, as shown by Macosko et al.^{30,31}). Another interesting aspect is the high stability of the prepolymers (because of the lower reactivity of the aliphatic isocyanate groups) both to aging and moisture effects. Also pointed out, is the large influence of the structure of hard segments (especially the steric hindrance and the symmetry of both diamines and diisocyanates) on the final properties of the polyurethaneureas.

Acknowledgment is made to the ALLRIM Society (Z.I. des Arbletters, rue de la Jalesie, 25400 Audincourt, France) for financial support.

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Received December 4, 1985

Accepted February 14, 1986