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Urethanes and polyurethanes bearing furan moieties: 5. Thermoplastic elastomers based on sequenced structures

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Segmented furanic polyurethanes based on the three typical components – macrodiol, diisocyanate and diol chain extender – were prepared and characterized. The furan heterocycles were introduced through the diisocyanate, through the chain extender or through both, and took different configurations with respect to the main chains, i.e. as side groups or as an integral part of the backbone. Differential scanning calorimetry analyses of these materials provided information about glass transition and melting phenomena and about microphase separation between soft and hard domains. Dynamic mechanical properties and stress–strain behaviour completed this study and showed the specific temperature ranges within which each material could be used as an elastomer. The role and the interest of the presence of the furan moieties in these thermoplastic elastomers is discussed.

(Keywords: thermoplastic elastomers; furanic moieties; microphase separation)

INTRODUCTION

We previously synthesized and characterized a series of furanic diols and diisocyanates[1] and the corresponding polyurethanes[2], and showed that the presence of the heterocycle does not introduce any problem or anomaly in terms of structural irregularity or polymer degradation. On the contrary, the fact of having furan rings pendent to the polymer backbone or as an integral part of the latter, or both, gives rise to interesting properties which can be modulated according to these structural variables[2]. The polyurethanes studied to date were linear macromolecules prepared from a diol and a diisocyanate including completely furanic monomers, aromatic/furanic and aliphatic/furanic combinations[2]. In other words, only homopolymers made from standard small monomeric structures were prepared.

Our continuing interest in exploiting natural renewable resources[3] as alternative raw materials to petrochemicals prompted us to pursue the study of more elaborate materials based on furanic polyurethanes which would simulate the well-known aromatic–aliphatic structures usually called 'thermoplastic elastomers'. These linear polymers are normally prepared from a polyether or polyester macrodiol (with molecular masses ranging from a few hundred to a few thousand) coupled with an excess of a conventional diisocyanate, usually of the aromatic series, to give a diisocyanate polymeric precursor which is finally chain extended by a conventional diol or diamine[4,5]. The resulting materials are characterized by glass transition temperatures (T_gs) which are dominated by the flexible polyether or polyester segments and by physico-chemical crosslinking induced by hydrogen bonding among urethane moieties, coupled with local crystallization of the short rigid urea or urethane segments formed at the chain-extension stage. This mixed structure results in the formation of microdomains which ensure the elastic properties (soft segments) without appreciable flow at temperatures lower than the 'melting' temperature of the crystalline regions (hard crosslinking segments). The term 'thermoplastic elastomers' clearly evokes the fact that these polymers can be turned into viscous liquids above their critical flow temperature, i.e. they can be recycled.

It seemed interesting to explore similar structures, but introducing the furan ring as a novel moiety. This was done by using our previously prepared furanic diisocyanates and/or diols[1] and by calling upon commercial macrodiols. To our knowledge, only one previous paper has dealt with this topic[6]; moreover, that work employed a single macromolecular structure which limited the scope of the study and prevented the establishment of structure–property relationships.

EXPERIMENTAL

Scheme 1 shows the monomeric furanic, aromatic and aliphatic diols and diisocyanates used in this work. The commercial macrodiols and their basic chemical characteristics are summarized in *Table 1*.

The polycondensations were carried out in two steps following essentially the procedure described by Schneider and Matton[7]. This consisted of (i) reacting the macrodiol with an excess of diisocyanate in bulk without catalyst for 2 h at 50°C and then (ii) adding the diol chain extender in stoichiometric amounts with respect to the remaining

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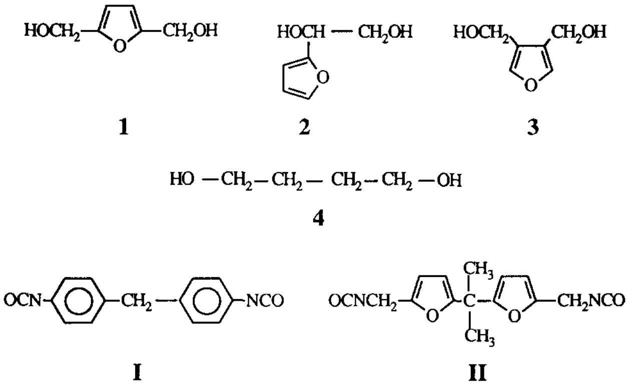


Scheme 1 Monomeric furanic, aromatic and aliphatic diols and diisocyanates used in this work

Table 1 Molecular weight (M_n), hydroxy index (I_{OH}) and average functionality (F) of commercial macrodiols

Macrodiol	M_n	I_{OH}	F
Poly(tetramethylene oxide) glycol, **PTMG**	2030	56.3	2.04
Poly(caprolactone) glycol, **PCL**	1985	56.0	1.98
Poly(butadiene) glycol, **PB**	2700	45.0	2.16

NCO terminal groups at 50–70°C (according to the viscosity of the medium) while stirring for several minutes to homogenize the mixture and evacuating the air trapped within it. The resulting viscous liquid was quickly poured into a Teflon mould and left for 24 h at 100°C before the 5–7 mm thick membrane was demoulded at room temperature. All the above operations were conducted in an inert dry atmosphere.

All the materials obtained were characterized by thermal and mechanical tests. Differential scanning calorimetry (d.s.c.) measurements were made with a Setaram analyser in a stream of helium, scanning at 10°C min^{-1}. The dynamic mechanical properties were measured with a Metravib torsion viscoelasticimeter. Traction experiments were carried out at room temperature with a Zwick dynamometer using an extension rate of 20 mm min^{-1}. Shore hardnesses were determined with a standard penetrometer.

In order to simplify the notations, the following abbreviations will be used in the text: first the letters corresponding to the macrodiol (see *Table 1*), then the arabic numeral corresponding to the chain extender (see *Scheme 1*) and finally the roman numeral corresponding to the diisocyanate (see *Scheme 1*). These symbols describing the composition are followed by three digits indicating the molar ratio of the three components in the same order. Thus, for example, **PTMG/1/II 123** means that the polymer was made using one mole of poly(tetramethylene oxide) glycol plus two moles of 2,5-bis(hydroxymethyl)-furan and three moles of 5,5′-isopropylidenebis(2-furfuryl isocyanate).

RESULTS AND DISCUSSION

Given the ample evidence gathered in previous studies proving that the reactivity of furanic monomers used in the synthesis of polyurethanes and the structure of the corresponding polymers do not show any anomaly[1,2], it was deemed unnecessary to carry out any spectroscopic characterization of the present materials. It was, however, shown that the two phases of polymerization went to completion as indicated by the total disappearance of the NCO peak in the infra-red spectra of the second reaction mixtures.

Thermal characterization

The d.s.c. thermograms of all the segmented polyurethanes were carefully analysed to gather a maximum of information concerning their microstructure. The features sought were: (i) the glass transition temperature, (ii) the enthalpic contribution relative to the purely soft microdomains and (iii) the occurrence of melting. *Figure 1* shows an example of a series of thermograms for a particular series of polymers prepared with the same precursors, but mixed in different proportions. The glass transition and melting are clearly visible in all instances, whereas the crystallization exotherm is only observed neatly in one case. Different combinations resulted in different features according to the corresponding morphology obtained; i.e. following the relative importance of elastomeric *versus* crystalline domains.

Table 2 gives the salient data concerning most of the polyurethanes prepared with the furanic isocyanate **II** and the macrodiol **PTMG** with different chain extenders and with different molar ratios. The latter parameter was changed so as to vary the proportion of hard segments in the materials. Note that *Table 2* also gives the thermal properties of the reference structure before chain extension, i.e. of the 'end-capped' prepolymer. A discussion of the results in this table provides the essential elements related to the microstructures encountered in these polyurethanes.

The glass transition temperatures reported in *Table 2*

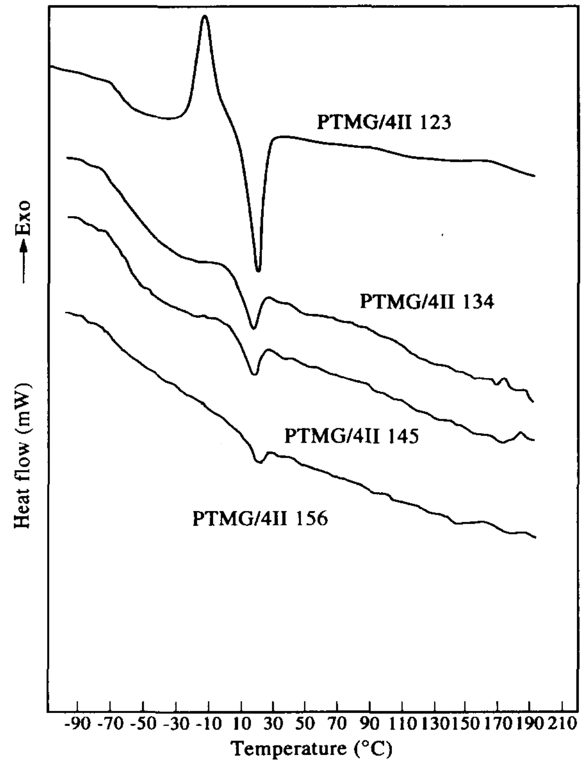


Figure 1 D.s.c. tracings of sequenced polyurethanes made from PTMG, chain extender **4** and diisocyanate **II** with different molar ratios

Table 2 Thermal data of elastomeric sequenced polyurethanes made from **PTMG** and diisocyanate **II**

Polyurethane	W_s (%)[a]	Hardness Shore A	T_{gs} (°C)[b]	T_g(Fox) (°C)[c]	ΔC_{p1} ($J\,°C^{-1}\,g^{-1}$)[d]	$\Delta C_{p1}/\Delta C_{p0}$ (%)[e]	T_m (°C)[f]
PTMG/II	0		−70		0.62		
PTMG/1/II							
123	33	60	−56	−49	0.49	80	
134	44	65	−62	−40	0.37	60	
145	55	72	−68	−32	0.45	75	
PTMG/3/II							
112	26	53	−60	−63	0.40	65	
123	36	60	−61	−55	0.33	54	
134	44	67	−65	−48	0.29	47	160
145	50	71	−67	−42	0.19	31	
PTMG/4/II							
112	24	40	−65	−72	0.46	75	
123	33	45	−61	−53	0.37	61	
134	40	59	−57	−46	0.36	58	
145	45	69	−62	−39	0.19	31	140
	50	72	−70	−33	0.18	30	
PTMG/2/II							
123	36	33	−50	−56			
134	44	40	−45	−49			

[a] Mass fraction of hard segments
[b] Glass transition temperature related to soft microdomains
[c] Glass transition temperature obtained from Fox's law
[d] Specific heat related to the glass transition of the soft segments
[e] Relative proportion of soft segment microdomains
[f] Melting temperature of rigid microdomains

refer to the softening of the polyether segments. With chain extenders **1**, **3** and **4**, the range of the T_g values remained within some 15°C whereas the calculated values span over 40°C and of course increase as a function of the relative content of hard segments. These values refer to the 'ideal' T_g based on a single-phase polymer and were obtained from Fox's law:

$$\frac{1}{T_g}=\frac{W_s}{T_{gs}}+\frac{W_h}{T_{gh}}$$

where T_{gs} is the glass transition temperature of the soft segments taken on their own (here **PTMG**) and T_{gh} refers to the hard segments alone, i.e. the polyurethanes obtained from the corresponding diisocyanate plus diol (chain extender) combination without macrodiol. The latter values were determined in our previous study[2]. W_s and W_h are the mass fractions of each type of segment in the various polyurethanes reported in *Table 2*.

The striking difference between the experimental and calculated T_g values is made obvious in *Figure 2*. It seems obvious that these materials prepared with chain extenders **1**, **3** and **4** are not homogeneous and one must consider phase segregation as an important feature for all of them. This behaviour is not new and has been discussed extensively in the context of thermoplastic elastomeric polyurethanes and polyamides[8–11] prepared from **PTMG** and aromatic reagents. The existence of distinct microphases allows the use of specific heat contributions as obtained from the d.s.c. tracings[12,13]. The ratio between the specific heat related to the glass transition of the soft segments in each polyurethane and the value related to the reference polymer **PTMG/II** prepared without chain extender, $\Delta C_{p1}/\Delta C_{p0}$, is a measure of the proportion of elastomeric domains made up of soft segments. As one would expect, this ratio decreases as the proportion of urethane moieties increases because the latter parameter is related to the presence of hard segments, as shown in the corresponding column of *Table 2*. *Figure 3* shows this trend for the materials based on the chain extenders **3** and **4**. The different shapes of the two curves suggest that,

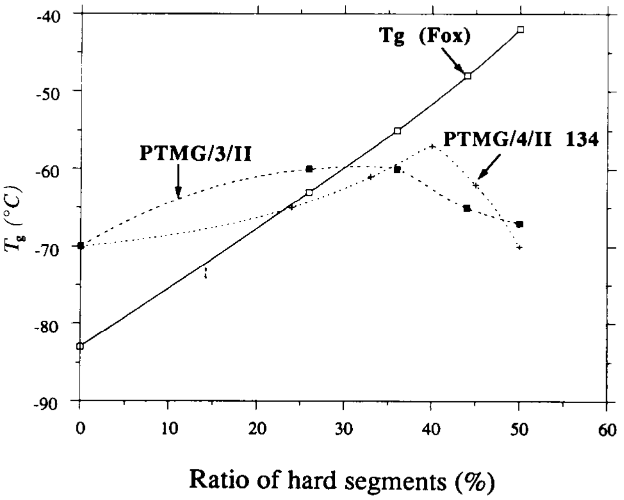


Figure 2 T_g values calculated from Fox's law and determined by d.s.c. as a function of the percentage of hard segments of sequenced polyurethanes made from **PTMG**, chain extenders **3** and **4** and diisocyanate **II**

Table 3 Thermal data of elastomeric sequenced polyurethanes made from **PTMG**, different chain extenders and diisocyanate **I** with the same molar ratio

Polyurethane	W_s (%)	Hardness Shore A	T_{gs} (°C)	T_{gh} (°C)[a]	T_m (°C)	ΔH_m ($J g^{-1}$)[b]	Crystallinity (%)[c]	$\Delta C_{p1}/\Delta C_{p0}$ (%)
PTMG/1/I 123	33	90	−65	58	195	24	16	88
PTMG/3/I 123	33	82	−61	43	180	13	8.5	68
PTMG/4/I 123	30	85	−65	54	175	17	11	62
PTMG/2/I 123	33	46	−38	–	–	0	0	–

[a] Glass transition temperature related to hard microdomains
[b] Heat of melting of hard microdomains
[c] Referred to crystallinity of polyurethane **PTMG/4/I 123**

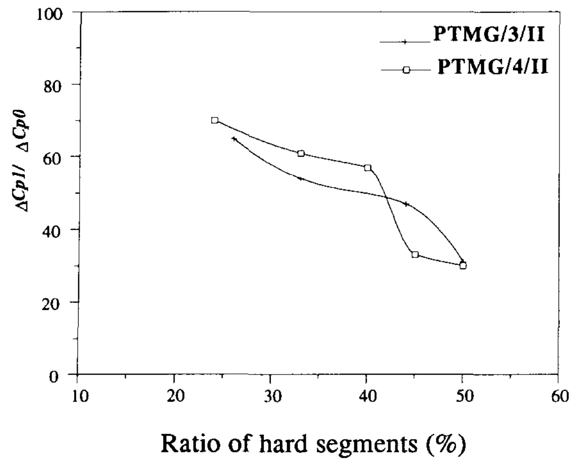


Figure 3 Relative proportion of soft segment microdomains *versus* ratio of hard segments of sequenced polyurethanes made from **PTMG**, chain extenders **3** and **4** and diisocyanate **II**

with **4**, a phase inversion occurs with about 40% of hard segments. The T_g values reported previously[6] on materials based on **4** are close to those found here.

The materials prepared with chain extender **2** behaved differently in that no apparent phase segregation was noticed. This exception must be related to the specific structure of **2** which is the only asymmetric diol among the chain extenders used in this work, i.e. its hindering effect against crystallization of the hard segments.

Table 3 gives similar data for materials prepared again with **PTMG**, but using aromatic diisocyanate **I** and the various chain extenders with constant values of the molar ratios among the three components. *Figure 4* shows the detailed features of the corresponding thermograms. Interestingly, one detects here not only the glass transition of the soft segments and the melting of the crystalline urethane domains, but also the glass transition of the amorphous portion of these hard segments. On the other hand, the melting of crystalline domains arising from the soft segments is much less systematically clear-cut than in the previous series (compare *Figures 1* and *4*). In this series of polymers the degree of microphase segregation is more pronounced than in the previous one, as additionally suggested by the high values of $\Delta C_{p1}/\Delta C_{p0}$. Again, chain extender **2** behaved differently in that the only clear-cut transition visible in the thermogram was a T_g considerably higher than those obtained for the soft segments of the homologous polyurethanes constructed using other extenders. This feature points once more to the minimization of phase separation when a strongly

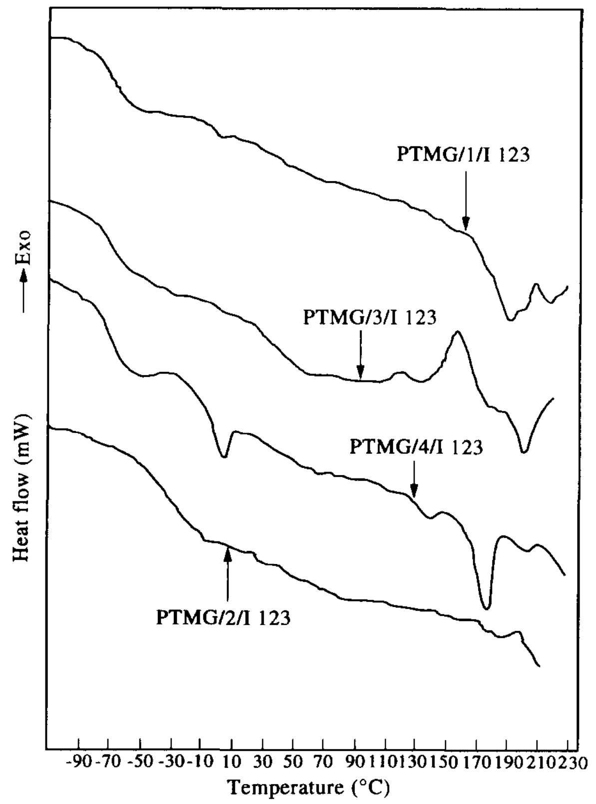


Figure 4 D.s.c. tracings of sequenced polyurethanes made from **PTMG**, different chain extenders and diisocyanate **I** with constant molar ratio

asymmetric element is introduced at the urethane sites, which inhibits crystallization and favours mixing to give essentially a single amorphous phase.

Table 4 collects the data provided by the d.s.c. thermograms of a third series of materials in which the macrodiol was now based on caprolactone units, the diisocyanate was the furanic homologue and the extenders were varied, but the molar ratios were kept constant. When these polyurethanes were scanned for the first time, their d.s.c. tracings displayed a melting feature attributed to the crystalline polycaprolactone chains. Quenching the hot samples in liquid nitrogen produced amorphous materials with T_g values indicating that good mixing among the different types of segments had occurred. *Figure 5* shows an example of this double scanning: the absence of a crystallization exotherm must be related to the proximity of the T_g of the overall structure and the T_m of the **PCL** chains. The melting of these segments on

Table 4 Thermal data of elastomeric sequenced polyurethanes made from **PCL**, different chain extenders and diisocyanate **II** with the same molar ratio

Polyurethane	W_s (%)	T_{gs} (°C)	T_g(Fox) (°C)	T_m (°C)	ΔH_m (J g^{-1})	Crystallinity (%)[a]	ΔC_p (J °C^{-1} g^{-1})
PCL	0	−55	–	58	57	100	–
PCL/1/II 134	44	−36	−17	40	27	47	0.16
PCL/2/II 134	44	−17	−28	40	23	40	0.26
PCL/3/II 134	40	−23	−26	40	21	37	0.22
PCL/4/II 134	44	−30	−25	40	22	38	0.23

[a] Referred to virgin polymer as seen in the first d.s.c. scan of *Figure 5*

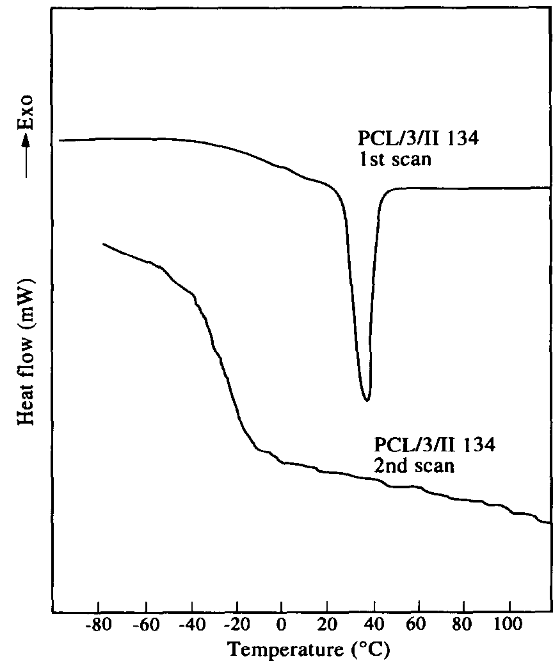


Figure 5 D.s.c. tracings of the sequenced polyurethane made from **PCL**, chain extender **3** and diisocyanate **II** with molar ratio **134**

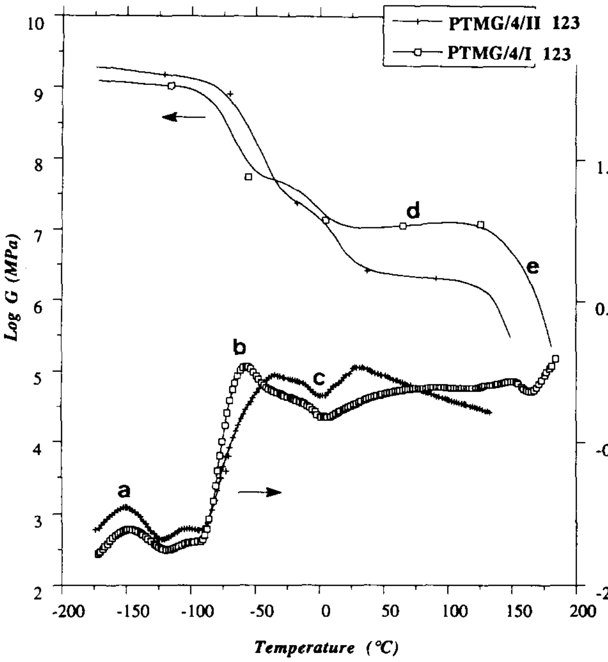


Figure 6 Dynamic mechanical behaviour of sequenced polyurethanes made from **PTMG**, chain extender **4** and two different diisocyanates (**I** and **II**) with molar ratio **123**. Symbols a–e explained in text

the first scan occurs at 40°C for all polyurethanes, i.e. some 20°C below the T_m of the corresponding **PCL** diol. This difference is mostly due to the role of the constant proportion of amorphous regions in the former materials in depressing T_m.

Dynamic mechanical properties

In this part of the study, efforts were concentrated on polyurethanes prepared with **PTMG** as macrodiol and comparisons were established as a function of the nature of the two other components.

Figure 6 shows the variations of the elastic modulus and tan δ with temperature for two products differing only in the type of diisocyanate used, i.e. furanic **II** or aromatic **I**. An analysis of the evolution of these curves with increasing temperature provides a clear phenomenology with both materials.

a. The first maximum in tan δ is assigned to the onset of individual rotational movements of the methylene groups in **PTMG** residues[14].
b. The next feature reflects the glass transition of the amorphous domains of soft segments which induces a drop in modulus of about two orders of magnitude.
c. The melting of the crystalline domains of these same segments occurs at somewhat higher temperatures and is accompanied by a further drop in modulus of about an order of magnitude.
d. The rubbery plateau follows and extends over 50 to 100°C, i.e. the temperature domain of practical interest for these materials.
e. Finally these polymers reach the melting of the hard segments and begin to flow as viscous liquids. Consequently, the modulus drops drastically.

This phenomenology is common to both polyurethanes shown in *Figure 6*. Some important differences also appear when comparing the two sets of curves. In particular, the T_g is less sharp with the furanic structure and in the melting region this same structure displays a double feature with a considerably higher overall drop in modulus. This difference could be attributed to the fact that the urethane hard domains tend to crystallize less readily with the furanic structures and one sees therefore the softening of the resulting amorphous hard segments as the second drop in modulus at about 20°C (not detected by d.s.c.), which is absent in the case of the

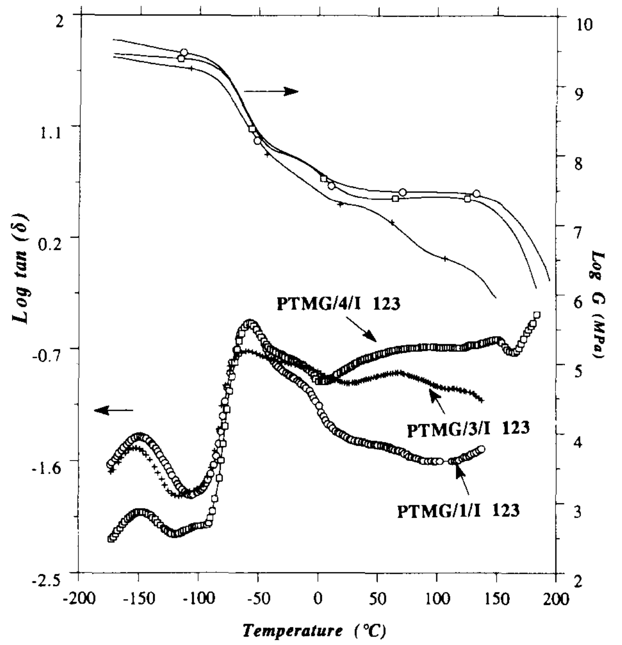


Figure 7 Dynamic mechanical behaviour of sequenced polyurethanes made from **PTMG**, different chain extenders and diisocyanate **I** with constant molar ratio

aromatic polymer. As a consequence, the two polyurethanes have different mechanical properties on the rubbery plateau, the furanic homologue giving a modulus some 12 times lower than that of the aromatic one. The dynamic mechanical behaviour reported previously[6] for structures **PTMG/4/II** is qualitatively similar to that obtained here (*Figure 6*), but the quantitative features are different. Although the relative compositions were not the same, the magnitude of the disagreement is hard to explain.

Figure 7 shows the influence of the chain extender, i.e. two types of furanic structure and an aliphatic one, on the dynamic mechanical behaviour of three otherwise identical polyurethanes. The essential features in the modulus and tan δ curves are very similar to those discussed in the previous context. Indeed, replacing 1,4-butandiol **4** by 2,5-bis(hydroxymethyl)furan **1** results in no change in the qualitative behaviour, but in a somewhat higher modulus, particularly at the rubbery plateau. This is understandable considering the increase in stiffness from the aliphatic to the furanic sites. The use of 3,4-bis(hydroxymethyl)furan **3**, on the other hand, produced a considerable change in the mechanical response of the corresponding polyurethane, particularly at the higher temperatures. After the melting of the crystalline polyether segments, the materials softened progressively leaving a very narrow rubbery plateau because the amorphous hard segments underwent their glass transition starting at about 50°C, this time also detected by d.s.c. at about 43°C (*Table 3*).

A brief investigation of the role of the frequency of mechanical excitation on the behaviour of a polyurethane gave the curves shown in *Figure 8*. From these data the activation parameters associated with the α and β transitions were calculated (E_α and E_β, respectively; *Table 5*). These results confirm that the extent of segmental involvement is very different for the two transitions: at lower temperature one deals with very localized movements (low value of E_β), whereas the α transition calls upon co-operative chain rotations.

Stress–strain behaviour

As with the dynamic mechanical properties, the stress–strain response of the polyurethanes was analysed as a function of a single structural variable. *Table 6* gives the data relevant to this part of the study.

Figure 9 shows the comparison between materials differing only by the nature of the diisocyanate used, i.e. aromatic **I** or furanic **II**. As already detected by viscoelasticimetry, the Young's modulus is more than 10 times lower with the furanic structure. Moreover, this polyurethane breaks without apparent crystallization under maximum extension.

Figure 10 compares four polymers in which only the nature of the chain extender was varied. The higher the structural symmetry of this moiety, the more readily stiffening by extension occurred. With diol **2** this phenomenon was particularly dramatic and was accompanied by a very low modulus. Indeed, this material was so soft that we could not analyse it properly by viscoelasticimetry.

Structure–property relationships

To rationalize the main trends encountered in this investigation, it seems useful to take a close look at the structure of the eight urethane moieties (hard segments)

Table 5 Activation energies for α and β relaxation related to soft segments

Frequency (Hz)	T_β (°C)	T_α (°C)	E_β (kJ mol^{-1})	E_α (kJ mol^{-1})
0.01	−160	−53		
0.1	−152	−50	36	317
1	−145	−47		

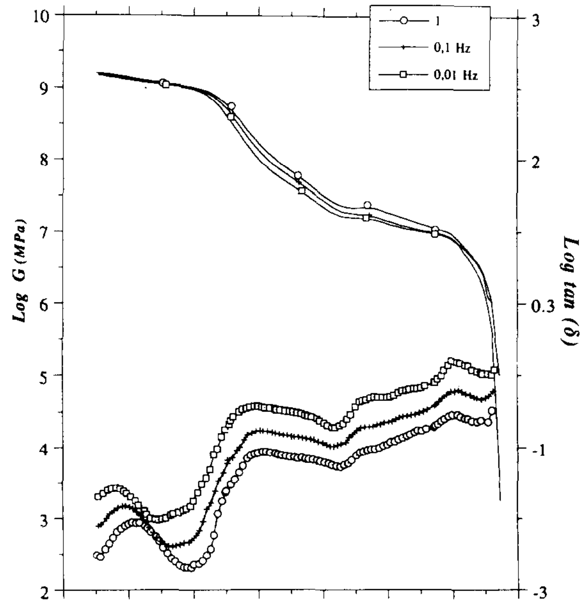


Figure 8 Dynamic mechanical behaviour of sequenced polyurethanes made from **PTMG**, chain extender **1** and diisocyanate **I** with molar ratio **123**

Table 6 Mechanical characteristics of some sequenced polyurethanes

Polyurethane	E (MPa)[a]	σ_r (MPa)[b]	ε_r (%)[c]	σ at 100% (MPa)	σ at 200% (MPa)	Resilience $(\mathrm{J\,m^{-2}}) \times 10^{-5}$
PTMG/1/I 123	35	39	335	5	10	11
PTMG/3/I 123	24	10	730	3.7	4.2	8.7
PTMG/4/I 123	29	27	445	5.5	8	12.5
PTMG/2/I 123	1.2	2	790	0.6	0.7	1.4
PTMG/4/II 123	1.5	3.5	680	0.7	0.9	1.8
PTMG/1/II 123	2.5	2.1	460	1.4	1.9	2.2
PCL/4/I 134	35	4.7	580	3.7	3.1	4.2

[a] Young's modulus
[b] Stress at break
[c] Elongation at break

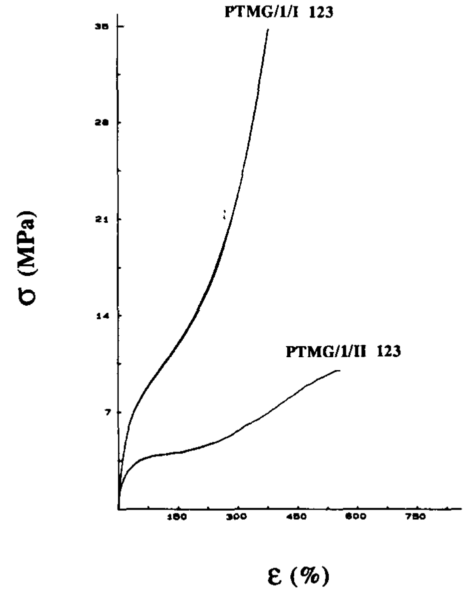


Figure 9 Stress–strain behaviour of sequenced polyurethanes made from PTMG, chain extender **3** and two different diisocyanates (**I** and **II**) with molar ratio **123**

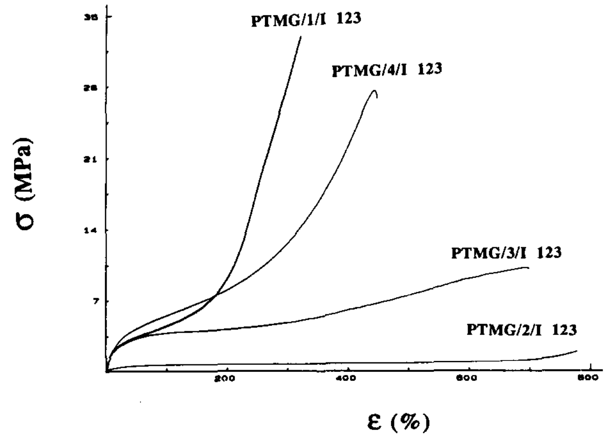
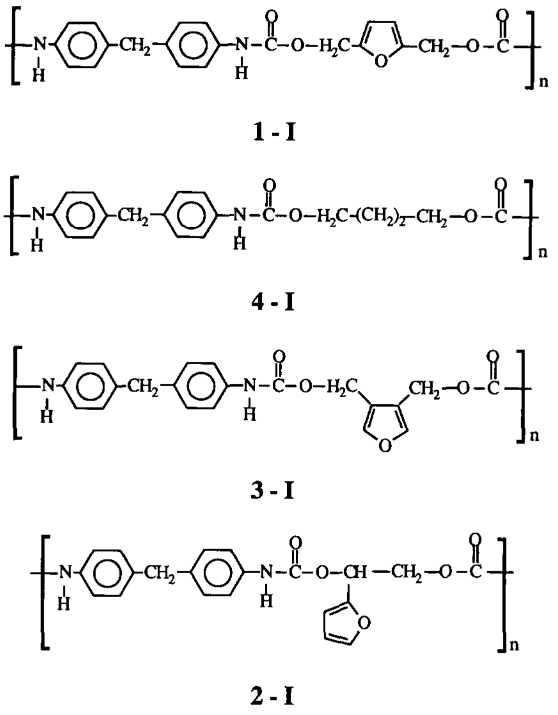


Figure 10 Stress–strain behaviour of sequenced polyurethanes made from PTMG, different chain extenders and diisocyanate **I** with molar ratio **123**

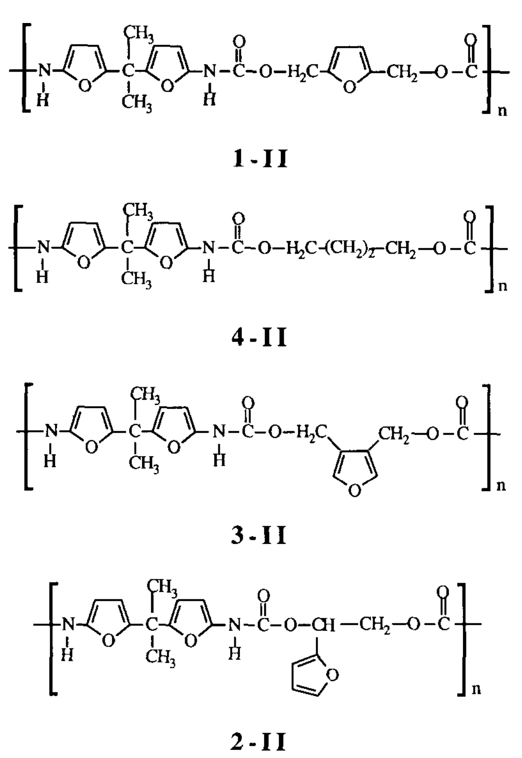
resulting from the various combinations adopted for the synthesis of these materials. In this approach the structure of the macrodiols (soft segments) will be considered as secondary and temporarily put aside.



Scheme 2 Polyurethanes based on the aromatic diisocyanate **I**

If one compares the thermal and mechanical properties of the polyurethanes based on the aromatic diisocyanate **I**, i.e. structures **1-I** to **4-I** (*Scheme 2*), the following points can be raised.

1. Between **1-I** and **4-I**, the replacement of a methylene sequence by a 2,5-dimethylene substituted furan ring results in an overall increase in the thermal transition, hardness, Young's modulus and extent of crystallinity of the hard segments. This is obviously due to the planarity and consequent stiffness of the heterocycle with respect to the flexible oligomethylene sequence. However, these changes are modest because on the one hand they correspond to a relatively minor change in the overall polymeric structure (the polyether portion coming from the macrodiol remains an important fraction), and on the other hand the furan ring is accompanied by lateral methylene groups which attenuate its rigidification effect. In our previous work on furanic polyurethanes[2], these types of substitution



Scheme 3 Polyurethanes based on the furanic diisocyanate **II**

produced more pronounced consequences because they were more important in terms of mass ratio. Nonetheless, from a practical point of view, this furanic polyurethane presents a wider temperature domain in which it could be used advantageously as a (tougher) elastomer, and therefore the introduction of the heterocycle is interesting.

2. Between **1-I** and **3-I**, one remains within aromatic–furanic combinations for the hard segments, but the heterocycle is now less well introduced into the backbone. This situation is analogous to replacing a *para*-substituted benzene ring by an *ortho*-substituted homologue, e.g. in polyesters, as already pointed out in our previous study on more straightforward furanic polyurethanes[2]. The consequences of this modification of the furan positional enchainment on the properties are mostly reflected by a worse crystallization and on a narrower rubbery plateau, which, of course, limits the potential applications.
3. Between **1-I** and **2-I**, the changes in properties are more drastic. In fact the ring has now moved completely outside the backbone and has become a side group. The resulting materials are homogeneous, amorphous (the chains cannot approach correctly because of the bulkiness of the ring and its asymmetric position, and hydrogen bonding becomes unfeasible) and therefore very soft and stretchable. Their possible uses are more in the realm of tightness. A similar evolution had already been observed with simple furanic polyurethanes[2].

If the comparison is now made between equivalent structures in terms of chain extenders, but with aromatic or furanic diisocyanates, namely between structures **1-I** to **4-I** and **1-II** to **4-II** (*Scheme 3*) one observes a systematic weakening of the materials. This is understandable in the first place because the presence of methylene groups at the end of each furan ring of the isocyanate precursor introduces a considerable degree of rotational freedom. The difference in the stiffening effect between a benzene ring and a furanic heterocycle is a second source of softening, but to a minor degree.

The materials prepared using furanic diisocyanate **II**, poly(butadiene)-α,ω-diol **PB** and chain extender **4** showed properties which changed with time, producing an increase in hardness and bulk modulus. This behaviour was attributed to cycloaddition Diels–Alder reactions between the furan rings (dienophiles) and the unsaturations (dienes) in the **PB** diol precursor producing crosslinks. These polyurethanes were therefore not studied in detail.

CONCLUSIONS

The study of thermoplastic elastomers based on furanic segmented polyurethanes has provided a new family of materials in which one or two of the three components contain the heterocycle and can be prepared from renewable resources. With respect to commercial materials based on aromatic/aliphatic precursors, these furanic homologues tend to display lower moduli and thermal transitions, but can be thought to fulfil important applications specific to their properties. In particular, the combination of an aromatic diisocyanate with 2,5-bis(hydroxymethyl)furan, which is an industrial commodity, and appropriate macrodiols gives materials with good mechanical and thermal performances.

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