Crosslinked polycarbonate polyurethanes: preparation and physical properties

N. Cao, M. Pegoraro, F. Severini, L. Di Landro, G. Zoia
Dipartimento di Chimica Industriale e Ingegneria Chimica 'G. Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

and A. Greco
Enichem Syntesis, S Donato Milanese, Milano, Italy
(Received 11 January 1991; accepted 2 April 1991)

Polyurethanes (PUs) were prepared by using diols containing polar groups such as carbonic groups –O–COO–, carbonic and ester –COO– groups, carbonic and ether –O– groups. Synthesis and film preparation conditions are given. The physical properties of the PUs such as density, glass transition temperature, T_g, melting point, T_m, are all presented. A correlation between T_g and the rotational energy barriers of the polydiol single units is discussed. The PUs were characterized by mechanical tests on dry samples. The crosslink density of the PU network was evaluated by mechanical equilibrium relaxation tests on samples swollen in toluene. The results are discussed according to the more recent Flory's theory of rubber elasticity. PUs containing a CO_3 group present an affine-like behaviour while PUs containing both CO_3 and ether or ester groups show a behaviour in between affine and phantom models.

(Keywords: crosslinking; polyurethanes; synthesis)

INTRODUCTION

Polyurethanes are very versatile polymers. In the last few years we have prepared different types of polyurethanes based on polyether diols, polyester diols and polysiloxanes polyethylenoxide terminated. The correlations between structure and gas transport properties of these polymers were investigated[1,2]. In this work polyurethanes (PUs) obtained from polycarbonate diols containing methylene, methylene and oxygen and ester groups, as well as carbonate groups, are discussed. As a comparison data obtained from polyester PUs will also be discussed.

Thermal properties, with reference to the rotational energy barriers of the polydiol single units present in the chain, mechanical properties and measurements of crosslinking density of the PU network carried out on swollen samples in accordance with the more recent Flory theory of rubber elasticity, are discussed.

MATERIALS

The polyurethanes employed in this work were based on the following diols:

Polycarbonate diols:
(a) Polycarbonate diols containing the –OC(O)O– group and the hexamethylene group (PEMCD), or the tetramethylene (PTMC) or both the pentamethylene and the hexamethylene group (PPMEMCD).
(b) Polycarbonate diols containing the –OC(O)O– group, the –O– ether group and the methylene only or the methyl-substituted methylene group:
—poly triethylene glycol carbonate diol (PTEGCD)
—poly dipropylene glycol carbonate diol (PDPGCD)
—poly dipropylene glycol polypropylene glycol carbonate diol (PDPGPPGCD)
(c) Polyestercarbonate diols containing the –OC(O)O– group and the –C(O)O– ester group (P(C-ES)D). These were obtained by reacting dimethylcarbonate with hexandiol and caprolactone.

$$HO(CH_2)_6[OCOO(CH_2)_6]_n[OOC(CH_2)_5]_nOH \qquad n = 7.29$$

Polyester diols:
—poly (tetramethylene adipate) diol (PTMAD)

Table 1 shows the formulae. *Table 2* reports the principal properties of the diols used: OH equivalents, average molecular weights calculated from the number of OH, glass transition temperature and melting point if any. The unsaturations present in the diols were of the order of 0.01 mequiv. g^{-1}. The diols were prepared by Enichem Synthesis[3].

TDI: Toluene diisocyanate CH_3–$C_6H_3(NCO)_2$, a Bayer product; the mixture of the toluene–diisocyanate 2,4 and 2,6 isomers was 80/20 by weight.

Crosslinking agent: TIPA–triisopropanolamine N–$(CH_2CH(CH_3)OH)_3$, a Fluka product.

Solvent: dry ethylacetate (EA), b.p. = 77°C, Carlo Erba R.P.

Crosslinking catalyst: stannous octoate $(C_7H_{15}$-$COO)_2Sn$, diluted to 20% by weight in EA (stored under N_2).

EXPERIMENTAL

Film preparation

The PU synthesis was carried out by the two-step process[4]. The films were formed during the second step (*Table 3*).

0032-3861/92/071384-07

Table 1 Composition of polymeric diols

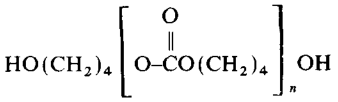
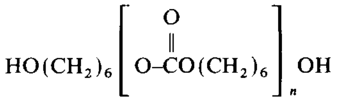
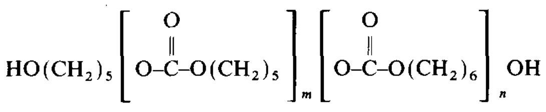
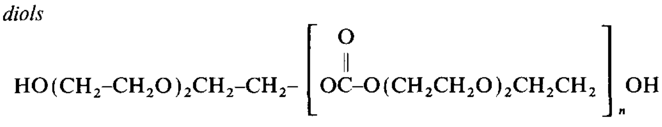
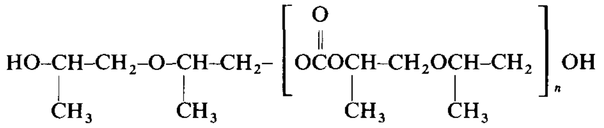
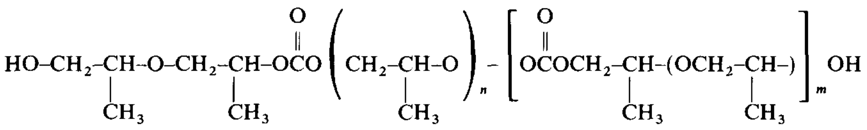
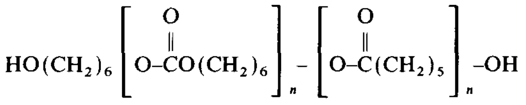
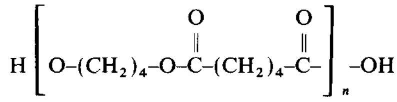
Abbreviation	Formula	Extended name
Polycarbonate diols		
PTMCD	 $HO(CH_2)_4\left[O\text{–}\overset{O}{\overset{\|}{C}}O(CH_2)_4\right]_n OH$	Polytetramethylene carbonate diol
PEMCD	 $HO(CH_2)_6\left[O\text{–}\overset{O}{\overset{\|}{C}}O(CH_2)_6\right]_n OH$	Polyhexamethylene carbonate diol
PPMEMCD	 $HO(CH_2)_5\left[O\text{–}\overset{O}{\overset{\|}{C}}\text{–}O(CH_2)_5\right]_m\left[O\text{–}\overset{O}{\overset{\|}{C}}\text{–}O(CH_2)_6\right]_n OH$	Polypentamethylenehexamethylene carbonate diols
Polyethercarbonate diols		
PTEGCD	 $HO(CH_2\text{–}CH_2O)_2CH_2\text{–}CH_2\text{–}\left[O\overset{O}{\overset{\|}{C}}\text{–}O(CH_2CH_2O)_2CH_2CH_2\right]_n OH$	Polytriethyleneglycol carbonate diol
PDPGCD	 $HO\text{–}\underset{CH_3}{CH}\text{–}CH_2\text{–}O\text{–}\underset{CH_3}{CH}\text{–}CH_2\text{–}\left[O\overset{O}{\overset{\|}{C}}O\underset{CH_3}{CH}\text{–}CH_2O\underset{CH_3}{CH}\text{–}CH_2\right]_n OH$	Polydipropyleneglycol carbonate diol
PDPGPPGCD	 $HO\text{–}CH_2\text{–}\underset{CH_3}{CH}\text{–}O\text{–}CH_2\text{–}\underset{CH_3}{CH}\text{–}O\overset{O}{\overset{\|}{C}}O\left(CH_2\text{–}\underset{CH_3}{CH}\text{–}O\right)_n\text{–}\left[O\overset{O}{\overset{\|}{C}}OCH_2\text{–}\underset{CH_3}{CH}\text{–}(OCH_2\text{–}\underset{CH_3}{CH}\text{–})\right]_m OH$	Poly(dipropyleneglycol polypropyleneglycol carbonate diol)
Polyestercarbonate diols		
P(C–ES)–D	 $HO(CH_2)_6\left[O\text{–}\overset{O}{\overset{\|}{C}}O(CH_2)_6\right]_n\text{–}\left[O\text{–}\overset{O}{\overset{\|}{C}}(CH_2)_5\right]_n\text{–}OH$	Polyhexamethylene carbonate pentamethylene ester diol
Polyester diols		
PTMAD	 $H\left[O\text{–}(CH_2)_4\text{–}O\text{–}\overset{O}{\overset{\|}{C}}\text{–}(CH_2)_4\text{–}\overset{O}{\overset{\|}{C}}\text{–}\right]_n\text{–}OH$	Polytetramethylene adipate diol

Table 2 Physico-chemical properties of polydiols

Polydiols	Molecular weight	Physical state[a]	OH equivalents[b]	T_g (°C)	T_m (°C)
PTMC-D-670	670	S	167.6	−50	49
PTMC-D-1093	1093	S	102.6	−57.5	55
PTMC-D-2600	2600	S	42.9	−46	62
PEMC-D-565	565	S	211.2	−50	29.2
PEMC-D-840	840	S	132	−56	39.1
PEMC-D-1025	1025	S	108.9	−56	39
PEMC-D-1900	1900	S	59.4	−58	36–45
PEMC-D-2370	2370	S	47.2	−60	46
PPMEMC-D-1700	1700	L. Viscous	66.3	−55	*
PDPGC-D-2100	2100	L. Viscous	52.8	−38	*
PTEGC-D-2537	2537	L. Viscous	44.2	−23	*
PDPGPPGC-D-1545	1545	L. Viscous	72.6	−46	*
P(C-ES)-D-2000	2000	L. Viscous	62	−62	*

[a] S = Solid; L = Liquid

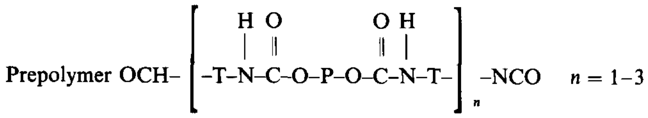
[b] mg of KOH equivalent for 1 g of polyol

*No melting point

Table 3 Preparation of the polyurethane films. Two-step process

HO-P-OH + OCN-T-NCO

Step 1: prepolymer preparation
$T = 80°C$
NCO/OH = 2, 1/1
Solvent = boiling ethyl acetate
Reaction time = 3-5 h

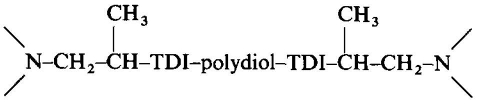


$$\text{Prepolymer OCH-}\left[\text{-T-}\overset{\text{H}}{\overset{|}{\text{N}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-P-O-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}\overset{\text{H}}{\overset{|}{\text{N}}}\text{-T-}\right]_n\text{-NCO} \quad n = 1\text{-}3$$

Step 2: Crosslinking
1. R—(OH)$_3$ crosslinking agent OH/NCO = 1, 1/1
2. Ethyl acetate (50% of solution, by weight)
3. Stannous octoate

Reaction temperature, 45-50°C

Crosslinked polyurethane



$$>\text{N-CH}_2\text{-}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{H-TDI-polydiol-TDI-}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{H-CH}_2\text{-N}< \qquad \text{(I)}$$

The polycarbonate diols were dried at 50°C under reduced pressure and then dissolved under nitrogen in anhydrous ethyl acetate in a reactor supplied with a condenser. The water content of the polyol was determined by the Fisher method[5] and was found to be less than 15×10^{-3} g H_2O/g polyol. In a few cases the polyol was found to contain traces of basic residues. In this case very small amounts of benzoyl chloride were added to inhibit the secondary reactions of the NCO groups which induce gel formation[4]. After adding TDI, the reaction conversion was followed from the NCO concentrations determined by the ASTM method[6]. In the second step a mixture of prepolymer and crosslinking agent, dissolved in EA, after adding the crosslinking catalyst (15–20 drops of a solution of 15% stannous octoate per cm^3 of solution) was spread on a glass sheet thermostatted at 45–50°C. To avoid the formation of bubbles of gas (air and solvent) after adding the TIPA, dissolved gases were eliminated by degassing under vacuum. The evaporation rate of the solvent from the film was kept sufficiently low to avoid the formation of bubbles in the film where the rheological properties change rapidly with crosslinking.

Mechanical tests on dry samples

Stress–strain tests were carried out on 'dogbone' samples using an Instron 1175 dynamometer. For high elongations an extensometer having a gauge length of 10 mm and amplification ratios ranging from 2 to 100 was employed. Samples were thermostatted at 23°C and 50% relative humidity before and during the tests. An elongation rate of 10 mm min^{-1} was used.

Mechanical tests on swollen samples

Equilibrium relaxation tests were performed on membranes swollen with toluene. Constant elongation was used for the samples immersed in the swelling solvent, and the load after equilibrium relaxation was recorded.

The presence of the swelling agent, in general, lowers the T_g so that polymers which exhibit a glass transition near room temperature may show an elastomeric behaviour in the swollen state. In this case their stress–strain behaviour can be treated by rubber elasticity theory. All the samples listed in *Table 6* have T_g below room temperature in the swollen state. The volume fraction v_{2c} of the dry network with respect to the volume of the network at the moment of its formation was estimated by evaluating the sample volume V_n after extraction of the uncrosslinked fraction and its corresponding volume V_0 of the starting solution in ethyl acetate. Furthermore the volume of the sample swollen in toluene was measured to estimate v_2 (see later).

Thermal analysis

A d.s.c. Mettler TA 3000 apparatus was employed in the −170 to 250°C temperature range at a heating rate of 10°C min^{-1}. The samples were dried under vacuum before the thermal analysis.

RESULTS AND DISCUSSION

Physical properties of polyurethanes

In *Table 4* internodal molecular weights, M_c, densities, glass transition temperatures, T_g, and melting points, T_m are reported. M_c was calculated on the basis of formula I (*Table 3*), considering that 2/3 of the molecular weight of crosslinking agent (TIPA) is part of each chain. As shown in *Table 4*, density ranges from a minimum of 1.16 g cm^{-3} (PDPGPPGC copolymer) to a maximum of 1.29 g cm^{-3} (PTMC670-PU). Polymethylene carbonate based polyurethanes (see Materials section) show a decreasing density on increasing the chain length. A smaller density is often observed for polyurethanes based on copolymeric diols (see Materials section). The decrease in density can be correlated to the increase in free volume. It is known that T_g[7] decreases on increasing the free volume. Accordingly T_g decreases on increasing chain length. PTMC-PU and PEMC-PU clearly show this behaviour (*Figure 1* and *Table 4*). T_g depends[8] either on intrinsic flexibility of the single macromolecules or on interaction between different chains. In general T_g increases on increasing the interchain forces and chain stiffness.

The interchain attractive forces certainly play an important role in determining the decreasing trend of T_g on increasing M_c. The chain contains both rigid urethane segments and flexible (polydiols) segments. The TDI rigid aromatic units are chemically joined to polar

Table 4 Polyurethane chemical–physical properties

Films	M_c	Density (g cm^{-3})	T_g (°C)	T_m (°C)
PEMC 565 PU	1040	1.29	38.5	*
PEMC 840 PU	1320	1.25	23.2	*
PEMC 1025 PU	1500	1.20	9	*
PEMC 1900 PU	2380	1.18	−14	*
PEMC 2370 PU	2860	1.18	−20	41
PTMC 670 PU	1150	1.29	29.5	*
PTMC 1093 PU	1570	1.27	8.2	*
PTMC 2600 PU	3070	1.21	−15.9	42.4
PPMEMC 1700 PU	2170	1.18	−13.5	*
PTEGC2100 PU	2580	1.20	−10	*
PDPGC2537 PU	3010	1.19	5.3	*
PDPGPPGC1545 PU	2020	1.16	− 3.7	*
PC-ES2000 PU	2470	1.17	−27	*

*No melting point

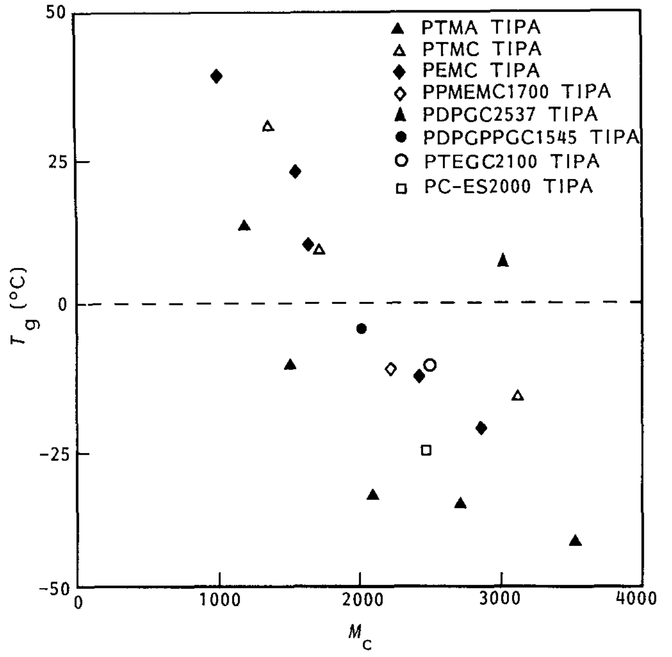


Figure 1 T_g values *versus* internodal molecular weight of polyurethanes obtained from the polydiols indicated in *Table 1*, crosslinked with TIPA

urethanic groups -NH-C(O)-O- which can form interchain hydrogen bonds with similar groups, and even with other electron donor groups present in the polydiol chain[9], as, for example, the -O-C(O)-O- groups, always present in the chain, or the -O- groups present in the ethylenoxide and propylene oxide units. Therefore, in general, on choosing polydiols of lower molecular weight, the amount of the reacted TDI, which acts directly and indirectly as a stiffening element, increases and the T_g of the corresponding polyurethanes increases. This is even though the T_g of the initial polydiols does not significantly depend on their molecular weight (*Tables 2* and *4*).

Influence of single chain rigidity. On increasing the diol weight fraction (and consequently M_c), the importance of the polydiol part in determining the global flexibility of the polyurethane chain increases.

At high M_c, when the density of hydrogen bonds is low, T_g depends in a relevant way on the rotational barriers of the polydiol repeating units. *Table 5* shows the rotational energy barrier *V*, found in the literature, for complete rotation or between two different conformations around the bonds, indicated in the table by a dash. The easiest rotations are around the C-C methylene bond and the O-C ether bond. Higher energies are required in the presence of an ester group (see *Table 5*, hexylacetate). A complete rotation around bond II requires a maximum energy of about 30 kcal mol^{-1} and about 10 kcal mol^{-1} around bond I. It was not possible to find data for the carbonate group. However, for symmetry reasons this group can be considered more stiffening than the ester. It should be necessary to evaluate not only the total energy required for complete rotation, but also the potential energy curve. For example, in the case of polyester (hexylacetate), the energy of formation of bond II presents a large minimum that indicates the possibility of partial rotations in a wide angle range and consequently good chain flexibility. In the case of bond I the very narrow minimum restricts the possibility of rotation around this bond even if the energy required for a complete rotation is lower than that required for bond II[11]. To give an exact correlation between T_g, flexibility and energy rotational barriers is a very complex problem.

Polyester-based PTMA-PU (*Figure 1*) presents the lowest T_g at equal M_c while polycarbonates of similar structure have higher T_g. This agrees with the rotational energy trend indicated above and with the existence of interchain forces. Analogously the reduction of T_g in the case of P(C-ES) compared with PPMEMC-PU could be attributed to the higher flexibility of the chains containing the ester groups. Substitution of half of the carbonic groups with ester groups causes increased flexibility. *Table 4* shows the T_g of PPMEMC 1700 PU and P(C-ES) 2000 PU. In fact P(C-ES) 2000-polyurethane is a copolymer structurally similar to PPMEMC-polyurethane for the presence both of pentamethylene and hexamethylene groups, but it differs for the substitution of about half carbonic groups with ester groups. The substitution of methylenic groups with hydrogen in the ethylene oxide units causes a predictable rotational stiffening. The higher value of T_g in the case of PDPGC 2537 TIPA than in that of PTEGC 2100 polyurethanes is in qualitative accordance with this.

Crystallinity. Diols with only methylenic groups and CO_3 in the chain are usually crystalline solids at room temperature, while polyurethanes obtained with the same diols show a melting peak in the d.s.c. only in the case of high M_c. Crystallization is favoured by the packing of 'soft' segments which is easier the longer the diol chains. X-ray analysis on polyester polyurethanes has clearly supported this behaviour[12].

Diols containing ether, carbonate and methylene groups in the chain are viscous liquids at room temperature; the corresponding polyurethanes do not show melting points or any other evidence of crystallinity. The use of these copolymeric diols prevents the development of any crystallization.

Mechanical properties

Polyurethanes obtained from diols containing methylene and carbonic groups. The stress-strain plot of PEMC-PU series is shown in *Figure 2*. Different behaviour is observed as a function of the chain length. The network

Table 5 Rotational barriers for various molecules

Molecule	Barrier, V	Energy difference (kcal mol^{-1})	Method
CH_3-CH_3	V (Me)	3.06	I.r.[a]
CH_3-C_2H_5	V (Me)	3.4	μw[a]
C_2H_5-C_2H_5	V (t-g)	3.8	T[a]
CH_3-OCH_3	V (Me)	2.7	μw[a]
$(CH_3)_2CH$-OH	V (t-g)	1.6	μw[a]
$CH_3(CH_2)_5O$-$C(O)CH_3$ I	V (I)	10	MDNO[b]
$CH_3(CH_2)_5$-$OC(O)CH_3$ II	V (II)	30	MDNO[b]
$CH_3(CH_2)_5OC(O)$-CH_3	V (Me)	0.5	MDNO[b]

Me = methyl
I.r. = infrared
μw = microwave
T = thermodynamic
t = *trans*
g = *gauche*
[a] Ref. 10
[b] Quantum mechanic semi-empirical calculation MNDO[11]

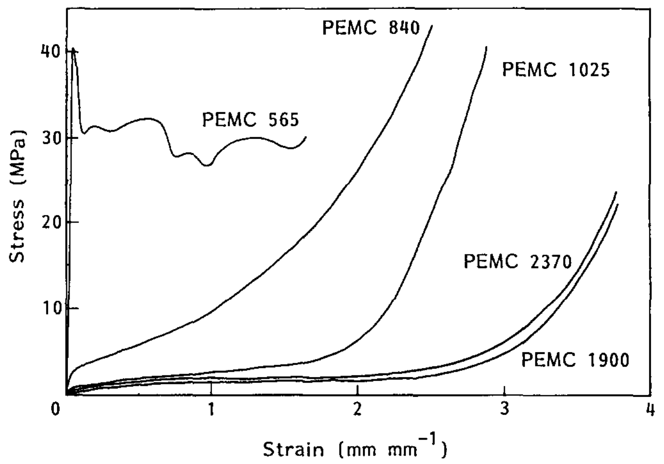


Figure 2 Stress–strain curves of polyurethanes of different molecular weight obtained from diols containing hexamethylene and carbonic groups (PEMC of different molecular weight)

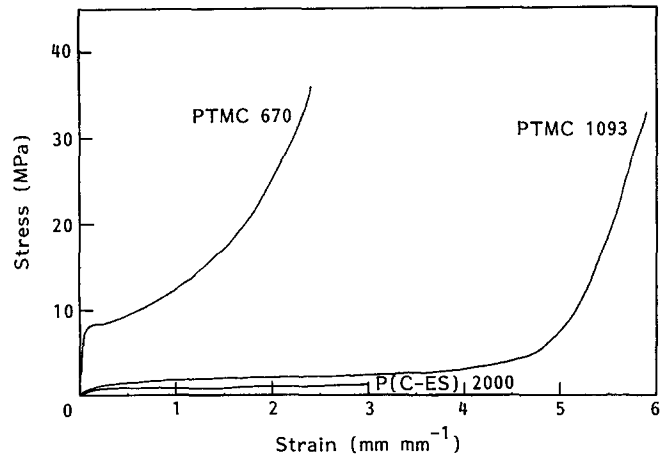


Figure 3 Stress–strain curves of polyurethanes obtained from diols containing tetramethylene and carbonic (PTMC); carbonic and ester (tetramethylene adipate) groups (P(C-ES))

with the shortest chains (PEMC 565) has a definitely glassy behaviour exhibiting yielding ($T_g = 38.5°C$). With higher chain length the $\sigma(\varepsilon)$ curve is typical of elastomers and the modulus decreases remarkably in accordance with the fact that the glass transition of the samples is close to, or lower than, the room temperature at which the tensile tests were performed. This can be attributed to the increased distance between urethane groups which causes a decrease of the crosslink density. On the other hand crystallization of the hexamethylene units probably becomes easier: this is responsible for the appearance of a metastable or stable (for $M_c \geqslant 1900$) melting peak in the d.s.c. measurements and probably of the upturn of the $\sigma(\varepsilon)$ curve at high elongation. Behaviour similar to that of PEMC is observed for PTMC (*Figure 3*): the $\sigma(\varepsilon)$ curve upturn of the elastomeric samples obtained from diols of MW $\approx$ 1000 occurs at higher elongations than that for PEMC. The main structural difference is due to methylene groups present in shorter sequences and to a higher ratio CO_3/CH_2.

Polyurethanes obtained from diols containing both ether and carbonic groups. PTEGC-PU has a high elongation at break and an elastomeric behaviour without upturn of the $\sigma(\varepsilon)$ curve (*Figure 4*). The ethylene oxide repeat units interposed between the carbonic groups account for the higher chain flexibility. PDPGC-PU has a number of ether groups in each chain at equal M_c lower than PTEGC-PU; in addition the presence of $-CH_3$ side groups can influence chain stiffness. This is in agreement with a higher $\sigma(\varepsilon)$ curve, a lower elongation at break and a higher T_g.

PDPGPPGC-PU is structurally similar to PDPGC-PU: some dipropylene glycol units are randomly substituted by polypropylene glycol units having about six ether groups ($n \approx 6$, *Table 1*). The high internal flexibility of the chain segments related to the ether oxygens and the lower number of rigid groups (CO_3) in the copolymer can explain its elastomeric behaviour.

Polyurethanes obtained from diols containing carbonic and ester groups. The only polymer examined, P(C-ES)-PU was an elastomer due to its copolymeric composition; its modulus is comparable to that of PDPGC-PU (*Figure 4*). The mechanical behaviour of P(PMEMC)1700-PU which is homologous to P(C-ES) PU obtained by substitution of CO_3 groups for COO groups, is stiffer and exhibits strain hardening. This is in agreement with the rigidity induced by CO_3 groups and with the possibility of crystallization of the methylene group sequences.

Molecular weight evaluation according to rubber elasticity theories

The most recent Flory theory of crosslinked elastomer elasticity[13] relates their mechanical behaviour to the number of effective chains ν in the polymer network. The theory considers as limit cases both the 'phantom' model proposed by James and Guth[14] and the 'affine' model[15]. The general equation describing the elastic theory in case of a swollen network is[16]:

$$v_2^{1/3}\frac{\sigma}{\alpha-\alpha^{-2}} = \frac{FkT}{V_n}v_{2c}^{2/3} = \frac{\rho A}{M_c} \qquad (2)$$

where k is the Boltzmann constant; T the absolute temperature; V_n the volume of the dry sample; $v_{2c} = V_n/V_0$ the volume fraction of the dry network with respect to the reference volume V_0 of the network at the moment of its formation; $v_2 = V_n/V$ is the volume fraction of the

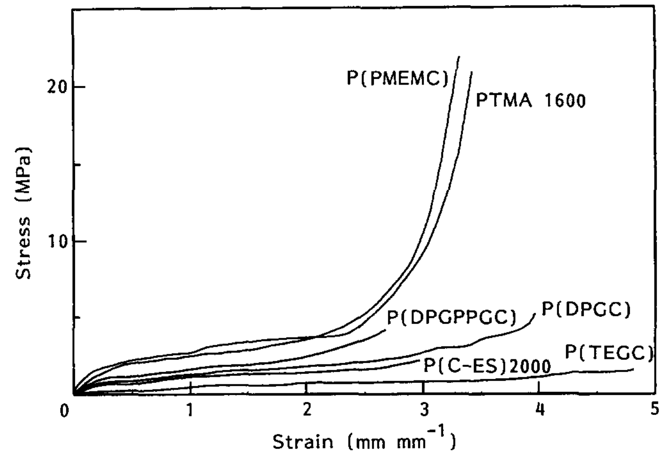


Figure 4 Stress–strain curves of polyurethanes obtained from diols containing ester (PTMA); carbonic and methylene P(PMEMC); carbonic and ether P(DPGPPGC), P(DPGC), P(TEGC); carbonic, ester and methylene groups (P(C-ES))

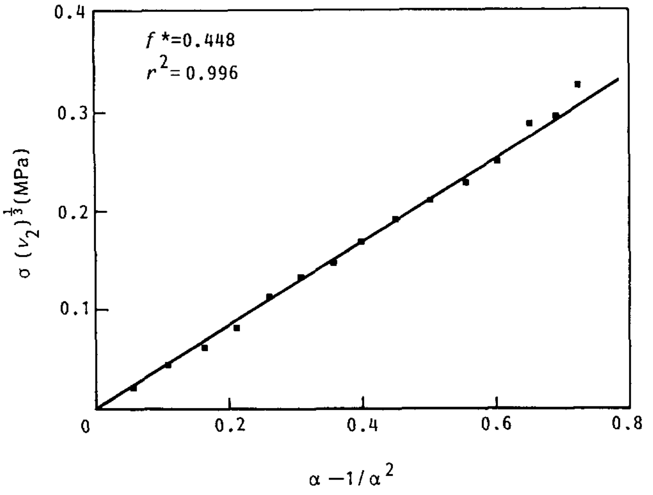


Figure 5 Experimental curve $\sigma(v_2)^{1/3}$ *versus* $(\alpha - 1/\alpha^2)$ of PEMC 1900 polyurethane. Modulus $|f^*|$, calculated from the slope, and correlation factor (r^2) of the fitting line are indicated

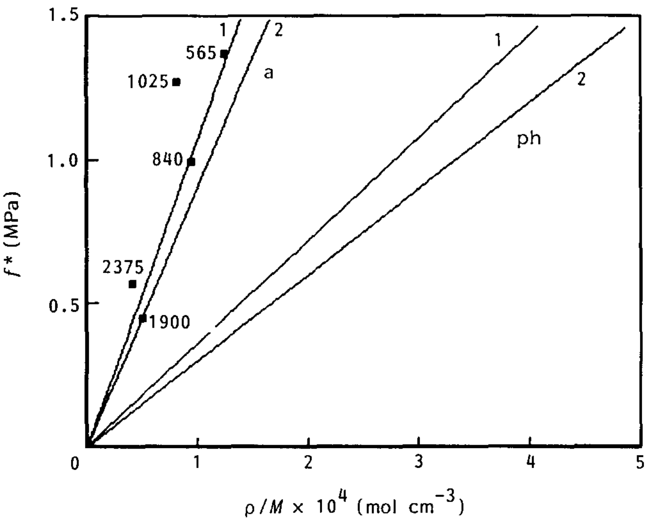


Figure 6 Modulus $|f^*|$ *versus* ρ/M of polyurethanes obtained from PEMC-D of different molecular weight. Theoretical lines correspond to the affine (a) and phantom (ph) models for different v_{2c} values: (1) $v_{2c} = 0.29$; (2) $v_{2c} = 0.22$

polymer in the swollen system, V being the volume of the swollen sample during the tensile test; σ is the stress referred to the dry sample section; F is a structural parameter whose value is given by[13]

$$F = \nu(1 - 2/\phi)(1 + f_c/f_{ph}) = \frac{\nu A}{(RTv_{2c}^{2/3})} \tag{3}$$

where ϕ is the crosslink functionality (3 in our case); f_c is the contribution to the force from the constraints on fluctuations of junctions and f_{ph} is the force that would be exerted by the equivalent phantom network (consisting of pure junction points).

The first term of equation (2) is often termed reduced stress or modulus $|f^*|$ of the rubber. It results from equations (2) and (3) that, in the case of $f_c = 0$ (phantom model), $F = \nu(1 - 2/\phi)$. If $f_c \neq 0$, F may assume the maximum value given by the affine model $(F = \nu)$. We showed[16] that experimental elastic measurements on the polymer network can only give limit values within which the molecular weight M_c of the chains joining the crosslinks should be included.

Figure 5 shows the experimental $\sigma v_2^{1/3}$ *versus* $\alpha - 1/\alpha^2$ data of PEMC 1900 PU as an example of the elastomeric PUs studied in this work. These data can be confidently fitted by straight lines whose slope $(=|f^*|)$, calculated by a least-squares analysis, allows the evaluation of the structural parameter, F. The slope of curves $|f^*|$ *versus* ρ/M is in fact $A_a = v_{2c}^{2/3}RT$ for the affine model and $A_{ph} = A_a(1 - 2/\phi)$ for the phantom model. The minimum (M_{ph}) and the maximum (M_a) limits can be therefore easily obtained (*Figures 6* and *7*) by intercepting the parallel to the abscissa axis, passing through f^*, with the two straight lines of slope A_a and slope A_{ph}. The uncertainty of M can be reduced as the chain molecular weight cannot be lower than M_c. *Table 6* gives all the experimental data on elastomeric samples necessary to calculate M_a and M_{ph}. M_c is presented as a comparison. The position of the points $(f^*, \rho/M_c)$ is shown on the graphs (*Figures 6* and *7*). Polycarbonates PU containing methylene and CO_3 groups are located near the affine line; all the copolymers (*Figure 7*) show a behaviour which is between the affine line and the phantom line. One polymer (PTEGC 2100 PU) appears to be positioned below the phantom line, having slope characteristic of $\phi = 3$. This could be attributed to an imperfect network formation.

Table 6 Polyurethane network, physical properties

Films	ρ (g cm^{-3})	v_2	v_{2c}	f^* (MPa)	M_c (g mol^{-1})	M_a[a] (g mol^{-1})	M_{ph}[b] (g mol^{-1})
PEMC 565	1.29	0.61	0.22	1.370	1040	846	282
PEMC 840	1.25	0.55	0.23	0.990	1320	1170	389
PEMC 1025	1.20	0.49	0.22	1.270	1500	850	284
PEMC 1900	1.18	0.22	0.29	0.448	2380	2860	953
PEMC 2370	1.18	0.25	0.26	0.571	2860	2087	695
PTMC 1093	1.27	0.59	0.21	0.118	1570	7620	2541
PPMEMC 1700	1.18	0.39	0.43	0.946	2170	1180	587
PDPGC 2537	1.19	0.24	0.43	0.218	3010	7710	2570
PDPGPPGC 1545	1.16	0.38	0.44	0.510	2020	3260	1900
PTEGC 2100	1.20	0.62	0.43	0.078	2580	21700	7240
P(C-ES) 2000	1.17	0.27	0.43	0.419	2470	3940	1310

[a] $M_a = (\rho/f^*)RTv_{2c}^{2/3}$
[b] $M_{ph} = (\rho/f^*)RTv_{2c}^{2/3}(1 - 2/\phi)$

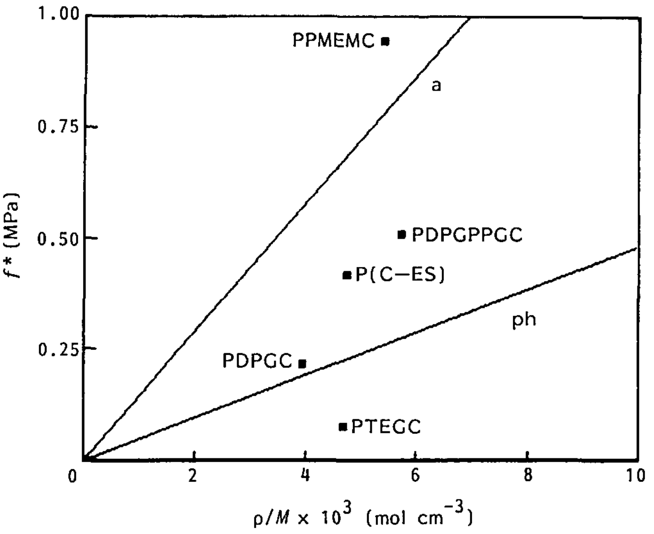


Figure 7 Modulus $|f^*|$ *versus* ρ/M of polyurethanes based on the copolymeric diols indicated in *Table 1*. Theoretical lines correspond to the affine (a) and phantom (ph) models for $v_{2c} = 0.43$

ACKNOWLEDGEMENT

The authors gratefully acknowledge the research funding given by CNR 'Progetto Finalizzato Chimica Fine II' and by MURST (40% and 60%) and the contributions of M. Del Zoppo for the discussions on the rotational barrier energies and F. Bianchi and A. Colosio for the tensile tests on swollen samples.

REFERENCES

1 Pegoraro, M., Penati, A. and Zanderighi, L. *J. Member Sci.* 1986, **27**, 203
2 Pegoraro, M., Penati, A. and Zanderighi, L. XVIII Fatipec Congress, Venezia, 1986, Vol. 3, p. 203
3 'Enichem Synthesis', US-Patent 4757116, Brev. It. 21080 A188
4 Buist, J. M. and Gudgeon, H. 'Advances in Polyurethane Technology', McLaren and Sons, London, 1968
5 Sounders, J. and Frisch, K. 'High Polymers: Polyurethanes Chemistry and Technology', Interscience, NY, 1962, Vol, 15, parts 1, 2
6 'ASTM Book of standards', D 2572-70
7 Williams, M. L., Landel, R. F. and Ferry, J. D. *J.A.C.S.* 1955, **77**, 3701
8 Elias, H. G. 'Makromoleküle', Hütig Verlag, Basel, 1975, p. 344
9 Coleman, M. M., Skrovanek, D. J., Hu, J. and Painter, P. C. *Macromolecules* 1988, **21**, 59
10 Sackwild, V. and Richards, W. G. *J. Mol. Structure* 1982, **89**, 269
11 Del Zoppo, M. (Politecnico di Milano), personal communication
12 Montani, A. (Eniricerche), personal communication
13 Flory, P. J. *Macromolecules* 1979, **12**, 199
14 James, H. M. and Guth, E. J. *J. Chem. Phys.* 1953, **21**, 1039
15 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
16 Pegoraro, M., Di Landro, L. and Cao, N. *Macromolecules* 1990, **23**, 3308