

Synthesis methods of fluorinated polyurethanes. 1. Effects on thermal and dynamic-mechanical behaviours

Claudio Tonelli^{a,*}, Giuseppe Ajroldi^b, Antonio Turturro^c, Antonio Marigo^d

^aAUSIMONT S.p.A., Research and Development Center, V.le Lombardia 20, I-20021 Bollate, Italy

^bVia A. Campiglio, 9, I-20133 Milan, Italy

^cDipartimento di Chimica e Chimica Industriale dell'Università, via Dodecaneso 31, I-16146 Genova, Italy

^dDipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università, via Loredan, 4, I-35131 Padova, Italy

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Abstract

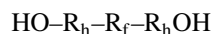
Fluorinated polyurethanes (FPU) were synthesised from 4,4'-methylenebis(phenylisocyanate) (MDI), 1,4-butanediol (BDO), as a chain-extender, and soft perfluoropolyetheric block (ZDOLTX), by a two-step polymerisation technique, following specific procedures to obtain chains with a regular-segmented structure or polymers characterised by having high hard (MDI–BDO) segment polydispersity.

Calorimetric and dynamic mechanical data, reported in this first part of our work, show that, independently of the synthesis method, the polymers are always characterised by a heterogeneous structure. This is true not only at molecular level but also at a macroscopic scale, in which the continuous soft phase contains different populations of crystalline hard domains. However, the crystallinity degree decreases on increasing the weight fraction of the soft phase. The so-called 'regular synthesis' seems to favour the MDI–BDO–MDI sequence, which is the largest constitutive part of the hard phase, but the macrostructure is less regular than that present in the other FPU. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated polyurethanes; Perfluoropolyethers; Thermal transitions

1. Introduction

Fluorinated polyurethanes (FPU) are a class of new materials which have outstanding properties in terms of mechanical and surface characteristic, and chemical resistance. They can be prepared from diisocyanates, like 4,4'-methylenebis(phenylisocyanate) MDI, chain-extenders, and macrodiols of general structure:



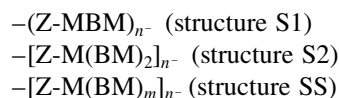
where $R_h = -\text{CH}_2-$, $-\text{CH}_2(\text{OCH}_2\text{CH}_2)_n$ ($n = 1, 2$), and $R_f = -\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_p(\text{CF}_2\text{O})_q\text{CF}_2-$. The central fluorinated block has the copolymeric structure of the perfluoropolyether class, which is obtained by photo-polymerisation of tetrafluoroethylene and oxygen at low temperature [1–3]. The perfluoropolyetheric segment (PFPE) is characterised by a very low glass transition temperature T_g (about -120°C for a polymer of infinite molecular weight and with a p/q ratio of 1). It has been shown that T_g is a function of the O/C ratio, decreasing with the increasing oxygen content [4].

The soft fluorinated and the hard segments are not compatible, so that phase segregation occurs, as we have observed in a previous paper about the FPU morphology [5].

It is well known from the literature that, apart from the phase separation behaviour, the structure of polyurethanes is dependent on the synthesis employed. The standard bulk two-step polymerisation yields a statistical distribution of the length of the hard segment, which arises from the reaction product of diisocyanate and chain-extender. More ordered structures of the hard segment, characterised by a practically monodisperse distribution of chain lengths, can be obtained only adopting specific synthesis techniques [6–12].

Our unpublished results suggest that the regularity of the hard segment affects both the morphology and the calorimetric behaviour of FPU; in the sense that calorimetric transitions were better defined, and the morphology was more regular.

It is thus clear that, if different methods of synthesis are used, polymers with different structure and properties can be obtained. In the present study the following structures were considered:



* Corresponding author. Tel.: +39-02-3835-6485; fax: +39-02-3835-2152.

E-mail address: claudio.tonelli@ausimont.com (C. Tonelli).

Table 1

Structural, molecular and some physical characteristics of ZDOL TX macromonomers. ($p/q = C2/C1$ ratio; $n =$ average number of the hydrogenated $-CH_2CH_2O-$ units; $F =$ functionality)

ZDOLTX sample	p/q	n	F	Equivalent weight	Molecular weight	Density (g/ml)	T_g (°C)
1000	1.11	1.6	1.99	724	1440	1.71	-99
2000a	0.94	1.3	1.95	1140	2222	1.75	-105/-91
2000b	1.02	2.3	1.96	1162	2279	1.71	-
3100	0.73	1.3	1.94	1596	3103	1.78	-116/-105
3800	0.65	1.4	1.93	1970	3799	1.80	-120/-102

where Z is the fluorinated soft segment, M is the diisocyanate and B is the chain-extender. While in the first two cases the length of the hard segment is well defined, within the synthesis limits, in the last case the hard segment length is statistically distributed.

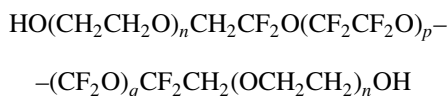
The aim of the present work is to study the influence of the synthesis and of the soft and hard segment length on the structure, as determined by calorimetry and dynamic mechanical analysis, small- and wide-angle X-ray diffraction and transmission electron microscopy.

In this first part of our work, the thermal and dynamic mechanical results obtained on FPU prepared following three procedures of synthesis are discussed.

2. Experimentals

2.1. Synthesis of materials

The macrodiols used to synthesise the FPU investigated in the present study are represented by the following structure:



According to the above structure, these fluorinated building-blocks (produced by Ausimont S.p.A., Italy under the trade name ZDOLTX[®]) are a mixture of oligomeric products, consisting of a random distribution of $-CF_2CF_2O-$ (C2 unit) and $-CF_2O-$ (C1 unit), end capped by ethoxylated units $-CH_2O(CH_2CH_2O)_nH$ (where $n = 1$ or 2).

The molecular weight range of the macromers used in this work was between 1400 and 3800. Their main compositional and physical characteristics are reported in Table 1. Macromers were dried before use under vacuum at 90°C for 2 h. MDI, (by ICI) was purified, from the dimer and urea impurities, by filtration at 40°C. Finally, the chain-extender 1,4 *n*-butandiol (BDO, from Aldrich) was dried before use under vacuum at 70°C for 2 h. FPU materials were prepared by a two-step polymerisation technique. The synthesis of the fluorinated prepolymer (first-step) was carried out in a solvent, while the subsequent chain extension was completed in bulk. Within this general reaction scheme,

specific procedures were used in order to obtain polymeric chains having a regular-segmented structure (S1 and S2 series), or polymers containing hard segments characterised by higher polydispersity (SS series).

2.2. S1 and S2 series

2.2.1. Prepolymer synthesis

The prepolymer synthesis was carried out using a six-fold excess of diisocyanate with respect to the fluorinated macrodiol. This large excess of diisocyanate strongly reduces the chain extension that occurs during the prepolymerisation. The diisocyanate solution was refluxed under nitrogen and the proper amount of the fluorinated diol was fed drop-wise over 3h. This procedure reduces the prepolymer growth, due to the poor solubility of the fluorinated macromer into the diisocyanate solution, giving a more regular polymeric structure after the chain extension. After the solvent removal, the prepolymer was washed several times with anhydrous hexane to eliminate the excess of free MDI. Finally, traces of solvent were completely removed in vacuum at 70°C.

The theoretical prepolymer composition is $M(ZM)_{s=1}$; however, longer oligourethanes could be present; they are mainly constituted by the dimer ($s = 2$). The average prepolymer composition was determined by chemical titration of NCO groups: an excess of *n*-butylamine was reacted with the sample in CFC 113, and back titrated with 1N hydrochloric acid in presence of isopropyl alcohol. These values are reported in Table 2, together with the corresponding theoretical values. The prepolymer composition reported in the last two columns of the Table 2 was calculated accordingly to the analysis results and under the hypothesis that no free MDI was present. As the prepolymers were prepared twice (for S1 and S2 series) these values are indicated separately.

Data show that the NCO content was generally slightly lower than the theoretical value. With the only exception of sample S1 2000 (which contains a small amount of free MDI), all samples resulted to be mainly constituted by the M-Z-M prepolymeric structure. In fact, the oligomeric chains of structure $M(ZM)_n$ (where $n > 1$) range from 7 up to 20% (on a molar base).

Table 2
NCO content of prepolymers and their structure

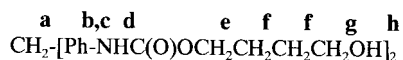
Sample	NCO _{theor.} (% w/w)	NCO _{exp.} (% w/w)	Molar fraction $s = 1$	Molar fraction $s = 2$
S1 2000	2.98	3.29	1.00	0
S1 3100	2.28	1.84	0.80	0.20
S1 3800	1.89	1.63	0.82	0.18
S2 2000	2.98	2.81	0.93	0.07
S2 3100	2.28	1.88	0.83	0.17

2.2.2. Chain extension

2.2.2.1. BDO as chain extender (S1 series). The prepolymer mass was degassed under vacuum and the calculated amount of BDO (NCO/OH ratio = 1.05) was added under vigorous stirring at 60°C. The final polymer was cast in a mould and put in a press to complete the polymerisation (2 min at 220°C followed by 7 h at 130°C).

2.2.2.2. BDO–MDI–BDO as chain extender (S2 series).

2.2.2.2.1. Chain extender synthesis. A MDI solution in DMF (50% w/w) was added drop-wise, at room temperature, to a large excess of BDO (OH/NCO ratio 9:1). The reaction was allowed to run to completion overnight. Adding a 9:1 solution of methanol and water precipitated the reaction product. The white solid was isolated by filtration and dried ‘in vacuum’ at 100°C (a slow evolution of BDO physically adsorbed on to the crystals was observed). The product was dissolved in hot butyl acetate (5% w/w), the insoluble oligourethanes of structure BDO–(MDI–BDO)_n–MDI–BDO (where $n > 0$) were eliminated by hot filtration. Finally, the BDO–MDI–BDO product was isolated by crystallisation. The ¹H NMR signals (relative to TMS as internal standard) are consistent with the expected structure and can be summarised as follows [standard symbols are used (s = singlet, t = triplet, dt = doublet of triplet, tt = triplet of triplet, m = multiplet) and a quantitative measure of the number of protons involved in the signal is given]: (D₆-DMSO); f 1.4–1.7 ppm (tt, 8H), g 3.4 ppm (dt, 4H), a 3.8 ppm (s, 2H), e 4.1 ppm (t, 4H), h 4.4 ppm (t, 2H), b 7.1 ppm (m, 4H), c 7.3 ppm (m, 4H), d 9.5 ppm (s broad, 2H).



The melting point, as determined by DSC, was 115°C and the melting enthalpy was 87 J/g.

2.2.2.2.2. Chain extension. The chain extension (NCO/OH ratio 1.05) was carried out in presence of benzoyl chloride as inhibitor (1% w/w). The high melting temperature of the BDO–MDI–BDO chain extender imposes severe conditions during the chain extension ($T > 120^\circ\text{C}$), as a consequence the pot-life of the system would be too short without the inhibitor, and the casting procedure would not be possible.

The proper amount of fluorinated prepolymer, containing the inhibitor, was heated at 95°C; then the chain-extender was added and the internal temperature was progressively increased up to 135°C. Finally, the viscous mass was cast in a mould and the polymerisation was completed accordingly to the established procedure (however, in the present case the heating at 220°C was extended to 5 min).

2.3. SS series

First step: prepolymer synthesis

The stoichiometric amount of MDI (2:1 NCO/OH ratio) was dissolved in anhydrous ethyl acetate (100 ml of solvent for 100 g of fluorinated macromer). The solution was refluxed under nitrogen and the fluorinated diol was fed dropwise in 3 h, the reaction mass was kept for another 2 h at the reflux temperature, and the solvent was removed by vacuum distillation. The NCO content of the prepolymer was determined by titration with *n*-butylamine, according to the above-described procedure, the values were consistent with the theoretical ones within $\pm 5\%$.

Second step: chain extension

The prepolymer mass was degassed under vacuum and the calculated amount of chain extender (BDO) was added (NCO/OH ratio = 1.05). The reaction mass was vigorously stirred for 1–2 min under vacuum at 60°C. The mass was cast in a mould under the operating conditions described for the S1 series.

2.4. Density

The density was determined at 23°C following ASTM D 792.

2.5. Differential scanning calorimetry

The glass transition temperature, T_g , of ZDOLTX macrodiols was determined with a Perkin Elmer DSC 2C differential scanning calorimeter, equipped with a 3600 Data Station, according to ASTM D 3418, cooling down the samples at -150°C and heating to room temperature at 20 K/min. T_g was determined as the midpoint of the C_p step.

The melting behaviour (melting and crystallisation temperatures and the associated enthalpies) of FPUs was determined with a Mettler DSC 30, equipped with a control system Mettler TC 10 A. Specimens, about 10 mg by weight, were cut from compression moulded plaques. The

following thermal cycle was always used: heating at 20 K/min from room temperature to 270°C, holding at that temperature for 3 min, cooling down to room temperature at 20 K/min. Owing to the presence of multiple endotherms in the heating step, the peak temperatures were considered as melting temperatures.

2.6. Dynamic mechanical analysis

Dynamic mechanical properties were measured at a frequency of about 1 Hz with a free oscillation torsion pendulum (Torsionautomat by Brabender) according to ASTM D 2236B. The storage shear modulus G' and the mechanical loss factor Δ were measured as a function of temperature at 1°C intervals and at a scanning speed of 1 K/min.

3. Results and discussion

3.1. Density

Density data (ρ), together with the weight (w_h) and volume fraction (Φ_h) of the hard phase, calculated from stoichiometry, are reported in Table 3. The volume fraction of hard phase was calculated by assuming the volume additivity law, using the experimental density values of fluorinated macromers (ZDOLTX) and the MDI–BDO hard segment density ($=1.350$ g/ml) taken from Ref. [13]. Owing to the high degree of incompatibility between hard and fluorinated soft phases, the additivity law should be respected. By plotting copolymers' densities against the volume fraction of hard phase Φ_h , a straight line is obtained with a given scattering (Fig. 1). However, the main point is due to the fact that extrapolation to $\Phi_h = 0$ and $\Phi_h = 1$ gives $\rho = 1.852$ and 1.063 g/ml, respectively. The first value ($\rho = 1.852$ g/ml) should correspond to the fluorinated phase, but it has no physical meaning because it is obtained from copolymers containing fluorinated blocks with different lengths; $\rho = 1.063$ g/ml is too low with respect to one typical of hard phase. We believe that these discrepancies derive from different lengths of soft blocks in copolymers and synthetic methods used to prepare copolymers, which

Table 3
Weight, volume fraction and density of FPU samples

Sample	w_h	Φ_h	Density (g/ml)
S1-2000	0.203	0.243	1.634
S1-3100	0.137	0.174	1.711
S1-3800	0.119	0.153	1.732
S2-2000	0.276	0.326	1.583
S2-3100	0.200	0.248	1.685
SS-1000	0.286	0.337	1.594
SS-2000	0.205	0.251	1.657
SS-3100	0.156	0.197	1.700
SS-3800	0.130	0.166	1.721

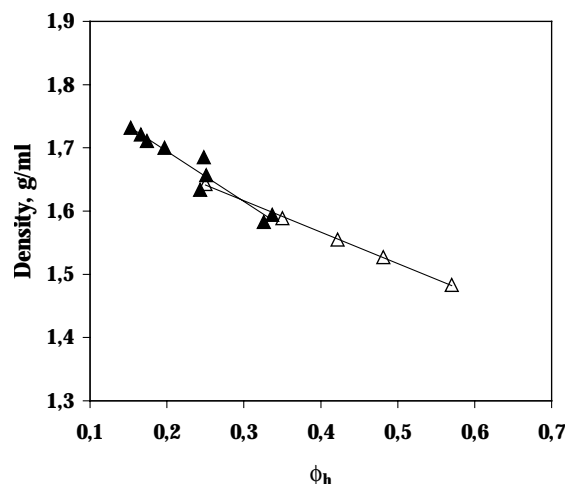


Fig. 1. Density of FPU copolymers as a function of the volume fraction of the hard phase; (▲) copolymers containing ZDOLTX 1000, 2000, 3100; (△) copolymers containing ZDOLTX 2000 as soft phase.

certainly give rise to several degrees of hard-soft separation, crystallinity and domain size-shape.

To better investigate the relation between composition and density, four copolymers have been specifically synthesized starting from the ZDOLTX 2000 macromer. Their hard phase content has been progressively increased by selecting different stoichiometry for polymerisation. Copolymer composition and the corresponding density values are collected in Table 4 and shown in Fig. 1. A very good linearity is observed and the following relation can be written:

$$\rho = -0.4816\Phi_h + 1.758$$

The limit value of the density for Φ_h approaching to zero gives $\rho = 1.758$ g/ml for the soft phase; this figure shows a good agreement with the density (1.740 g/ml) of the fluorinated building block used for the synthesis of this series. Moreover, the extrapolated density value for the pure hard phase is 1.276 g/ml, which lies between the corresponding aforementioned value available in Ref. [13] and the measured density ($=1.234$ g/ml) of MDI–BDO polymer specifically synthesized by us. Therefore, this evidence suggests that the density of segmented FPUs of the present study is mainly ruled by the volume fraction of hard phase taking the fluorinated chain length as being constant.

Table 4
Composition, weight, volume fraction and density of SS-2000 samples

Sample	Equivalent ratio ZDOLTX/MDI/BDO	w_h	Φ_h	Density (g/ml)
SS-2000-3	1:3:2	0.294	0.350	1.589
SS-2000-4	1:4:3	0.362	0.422	1.555
SS-2000-5	1:5:4	0.419	0.481	1.527
SS-2000-7	1:7:6	0.506	0.570	1.483

Finally, by considering literature data on PU, it seems that, independently of chemical nature of soft phase (hydrogenated or fluorinated), very similar hard phase density is always obtained, corresponding to that of MDI–BDO polymer.

3.2. Transitions

DSC scans of ZDOL TX-1000 and 3100 macromers are shown in Fig. 2; T_g values of all macromers examined are collected in Table 1.

The glass transition range of ZDOL TX-1000 is broader than all others; moreover, only one T_g at about -99°C is observed. The other three macromers always exhibit two T_g s; as a matter of fact ZDOLs TX of different ethoxylation degree are not mutually miscible at temperatures close to T_g [14]. Thus, the presence of two T_g s should indicate that two different populations are coexisting. Moreover, it is worthy to observe that the first T_g value is decreasing with increasing the molecular weight as found in the past for non ethoxylated diolic perfluoropolyethers by Danusso and co-workers [15]. Such an anomalous effect was attributed to the strong interactions among the polar chain ends. CF_3 -terminated PFPEs show, on the other side, a regular behaviour [16], i.e. T_g increases with the molecular weight. The trend of the second and higher T_g is not so well defined, but in any case it seems that the effect of chain ends is lowered by increasing the molecular weight.

It is well known that the thermal behaviour of hydrogenated polyurethanes (HPU) is rather complex and not yet completely understood, due to the different lengths of hard and soft segment sequences building up the macromolecules. Moreover, the morphological origin of the apparent multiple melting endotherms, observed in a large part of polyurethanes, seems to be still unresolved. Three endotherms are generally observed. A low temperature endotherm located from 20 – 40° degrees above the annealing temperature has been ascribed to short range reorganisation within the hard microdomains. The endotherm observed at temperatures ranging between 140 and 200°C is associated with the disruption of long-range structures. Finally, the endotherm observed above 200°C is assigned to the melting of microcrystalline regions of hard domains.

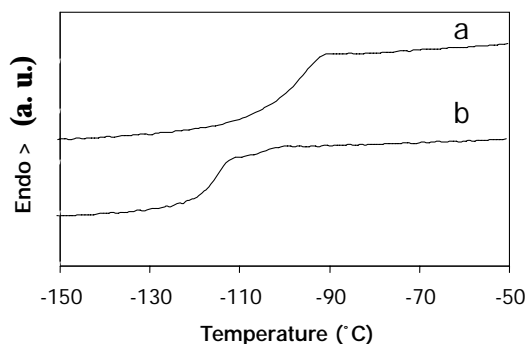


Fig. 2. DSC thermograms of ZDOL TX 1000 (a) and 3100 (b) macromers.

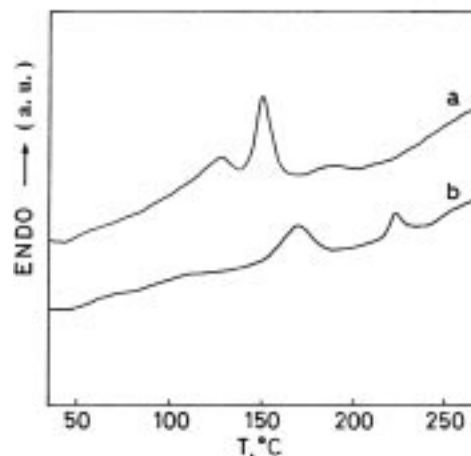


Fig. 3. DSC thermograms of S1-2000 (a) and SS-2000 (b) FPU.

Moreover, several studies have shown that the temperatures and enthalpies associated with these endotherms are functions of the thermal history and annealing conditions [17–24].

Our FPU are certainly characterised by a higher phase segregation than hydrogenated polyurethanes (HPU) because of the large difference in solubility parameters of hard and fluorinated segments which brings about a high thermodynamic incompatibility [25]. However, also in this case, block separation will not be complete, even allowing for the differences in the average length of hard segment sequences, so it will be possible that soft domains contain ‘dissolved’ hard blocks and viceversa.

All this gives rise to thermograms characterised by apparent multiple melting endotherms on heating from room temperature up to 270°C , as thermograms of S1-2000 and SS-2000 copolymers shown in Fig. 3. Copolymers of S1 and S2 series exhibit more or less similar endothermic effects in the range 100 – 200°C ; SS copolymers show these phenomena in a wider range of temperature from 70 up to 220°C . In this last case, the first endothermic phenomenon starts at about 70°C and ends at about 120°C . However, during cooling only one exotherm is present for all copolymers, probably due to kinetic reasons of segregation and organisation of different and several hard blocks. In any case it seems that the structure of the hard phase has only a second order effect on the crystallisation temperature; samples of SS series crystallise only few degrees higher than the other ones.

Peak temperatures and enthalpies values are collected in Table 5 for all copolymers. Enthalpy values were normalised with respect to the hard phase weight fraction. As for HPU, it is difficult to carry out a detailed description and interpretation of each endothermic effect. However, some peculiar phenomena of each copolymer can be deduced. S1 copolymers show the main endothermic effect at $T_1 = 120$ – 130°C and $T_2 = 145$ – 150°C and, in the cooling scan, a well defined exothermic peak in the range 88 – 94°C . We deem that T_2 and T_c are melting and crystallisation

Table 5
Transition temperatures and enthalpies of the FPU samples

Sample	w_h	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	ΔH_1 (J/g _h)	ΔH_2 (J/g _h)	ΔH_3 (J/g _h)	ΔH_4 (J/g _h)	T_c (°C)	ΔH_c (J/g _h)
S1-2000	0.203	130	151	186	–	–37.6	–37.6	1.5	–	89	26.4
S1-3100	0.137	132	145	173	–	–45.0	–45.0	3.0	–	94	29.7
S1-3800	0.119	120	–	180	–	–26.0	–26.0	4.6	–	88	13.5
S2-2000	0.276	91	–	179	–	4.0	–	52.9	–	98	15.0
S2-3100	0.200	–	–	175	–	–	–	25.5	–	85	8.8
SS-1000	0.286	70–100	156	175	215	2.8	–38.1	–38.1	2.4	108	29.8
SS-2000	0.205	70–110	–166	–166	215	7.2	–14.8	–14.8	4.7	95	15.5
SS-3100	0.156	70–120	–171	–171	218	21.8	–12.2	–12.2	3.6	98	19.2
SS-3800	0.130	70–140	–	–	215	22.3	–	–	33.1	96	11.5

temperatures, respectively, of microcrystalline regions essentially build up of M–B–M hard segments.

In the literature it was reported that a Et–M–B–M–Et (Et = CH₃CH₂–) model compound melts at 193°C with a corresponding enthalpy of 95 J/g [21,22]. The corresponding lower values measured for the hard segment sequences of S1 copolymers could be attributed to the weaker interactions among hard segments due to the presence of soft blocks at both ends of hard M–B–M segment. This interpretation agrees with the findings about the negative influence of long end groups (like aliphatic hydrocarbons) on the thermodynamic stability of hard segment microcrystalline domains [26].

Copolymers of S2 series show the main transition in the range 175–179°C and always only one sharp crystallisation peak in the range 85–98°C. This suggests that, according to the synthesis method, S2 copolymer chain contain hard segments like –M–B–M–B–M–, longer than those of S1 copolymers. In other words, in S2 copolymers structured microdomains of hard segments, more stable than those of S1 series, would be present; these microdomains should be mainly constituted by hard segments containing three MDI units. All this agrees with literature data on hard phase models; it is shown indeed that the melting point increases with the polymerisation degree of hard segment up to a limiting value for infinite molecular weight [27].

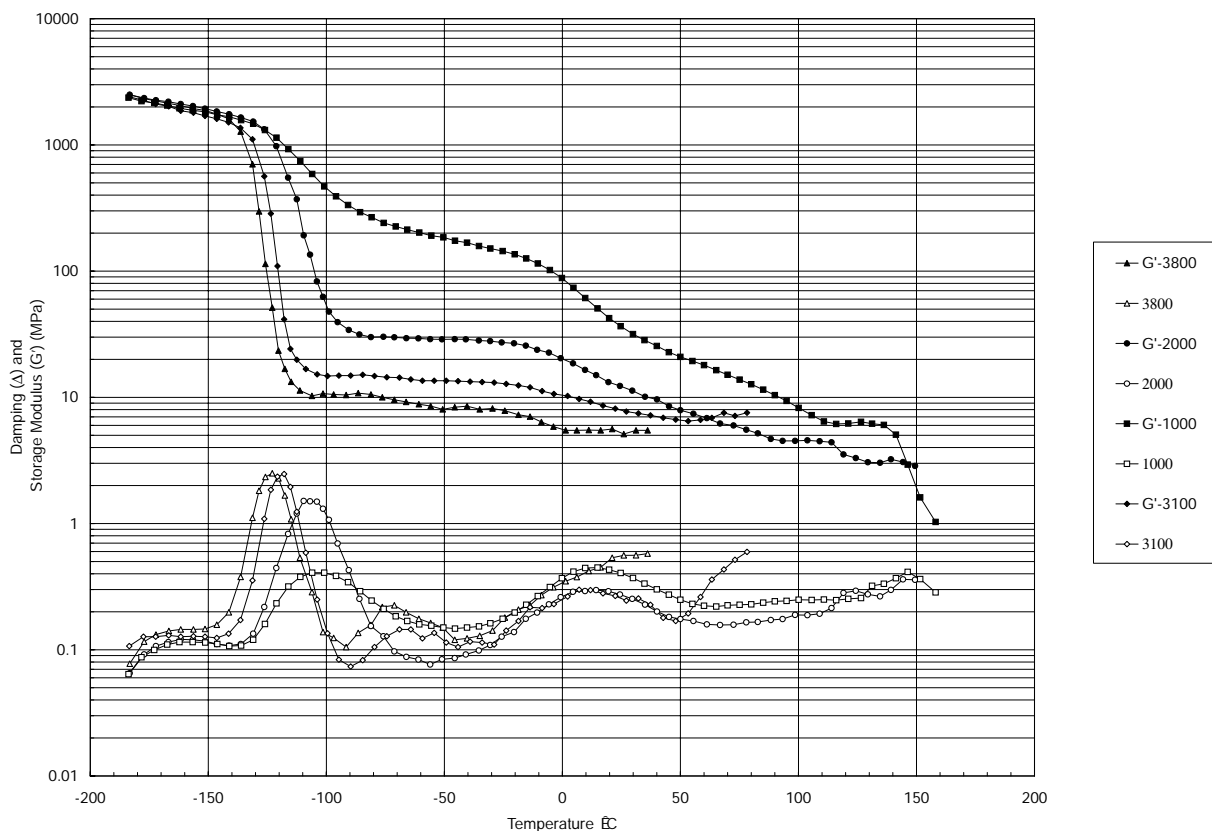


Fig. 4. Dynamic-mechanical spectra (G' and Δ vs. T) for samples of S1 series.

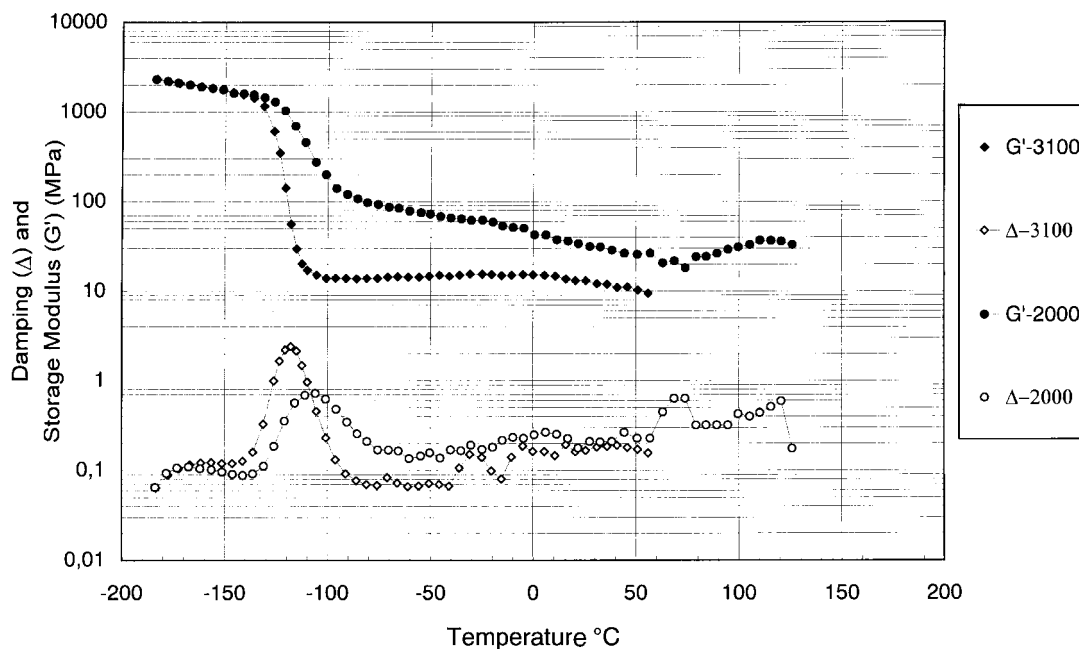


Fig. 5. Dynamic-mechanical spectra (G' and Δ vs. T) for samples of S2 series.

SS copolymers exhibit a more complex thermal behaviour, showing several transition temperatures, starting from 70 up to around 218°C. On increasing the ZDOL TX molecular weight, the enthalpy associated to the transition in the range 70–140°C increases of about one order of magnitude from SS-1000 to SS-3800. This trend, even more pronounced, is shown by the transition T_4 at about 215°C.

SS copolymers have the molecular architecture $-[Z-M(BM)_m]_n-$ where $-M-B-M-$ and M hard segments would be present. In fact, owing to the high incompatibility between M and Z , increasing with the molecular weight of Z , it is possible that, during the prepolymerisation stage, microsegregation occurs, thus modifying the product distribution as expected considering the selected stoichiometry. As a consequence, when the chain-extender (B) is added, longer hard blocks, like $-M-B-M-B-M-B-M$ would be formed.

We underline that the extent of the hard block organisation, as evidenced by ΔH_c values, decreases with increasing molecular weight of ZDOL TX soft block, in all copolymer series. This indicates that the viscosity and/or high mobility of fluorinated blocks have a significant influence on the kinetics of phase segregation and then on the formation of stable hard blocks microcrystals. Even if the reduced volume fraction of the hard phase (as the ZDOLTX MW increases), which inhibits the hard phase self-organisation during cooling, must also be taken into consideration.

3.3. Molecular relaxation processes

Several relaxation processes are evident in the spectra reported in Figs. 4–6 for S1, S2 and SS series, respectively;

numerical data about relaxation processes are reported in Table 6. The first relaxation process, of small intensity, is located at a very low temperature ($-165/-155^\circ\text{C}$) and it will be called γ ; the second one, which is well resolved, is related to the glass transition of the soft segment and it will be indicated as α_s ; on increasing the temperature ill defined maxima are observed which are related to the glass transition of the hard phase and they will be indicated as α_h . Finally a cold crystallisation process can be sometimes observed at higher temperatures by a contemporaneous increase of both storage shear modulus (G') and mechanical loss factor (Δ).

The γ maximum was observed years ago by one of the authors on PFPE of different structure and with OCF_3 end groups [28]. It was attributed to crankshaft-type motions of short chain segments (five to six chain atoms). As previously found this maximum is independent of the molecular weight and obviously from the polyurethane structure in the present case.

Temperature and amplitude of the α_s maximum are both a function of the molecular weight and, in a less defined way, of the PU structure. As the molecular weight increases T_{α_s} is shifted toward lower temperatures and the maximum becomes sharper. T_{α_s} data are shown in Fig. 7 as a function of M_n together with T_g data for ZDOL TX macromonomer used for the synthesis and for PFPE with the $-\text{CF}_3$ apolar chain ends [16].

As discussed in a previous paper [29] the trend of the glass transition with molecular weight of the soft segment can be attributed to several kinds of constraints to the molecular motions, caused by glassy and/or crystalline hard phase of PU and by hydrogen bonding of polar chain ends of ZDOL TX. When constrains are not present T_g or T_{α_s} increases

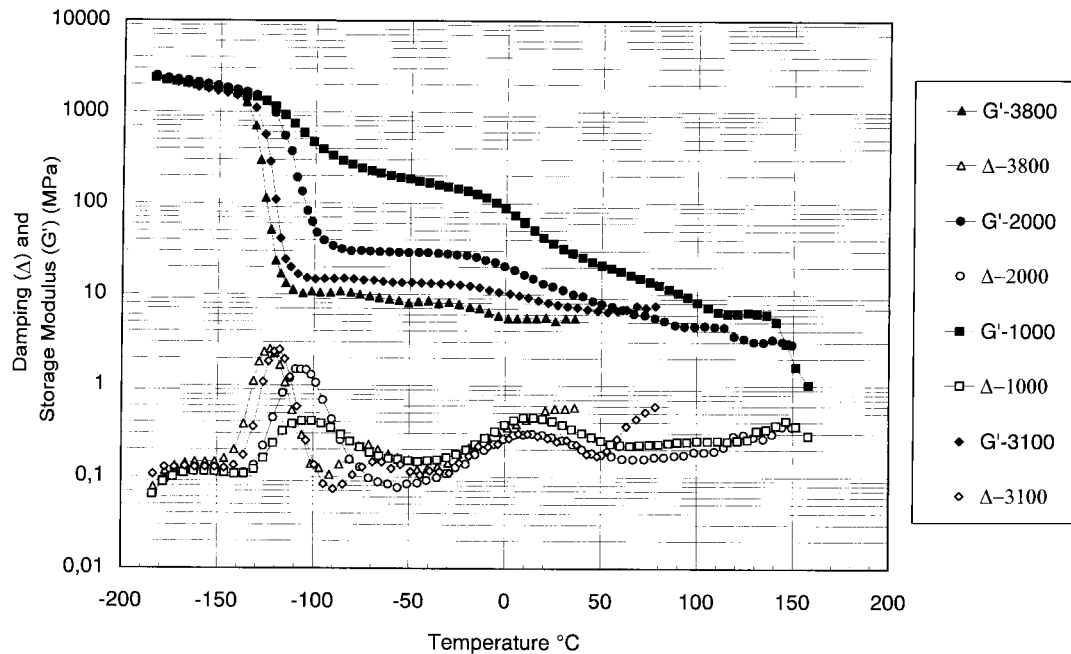


Fig. 6. Dynamic-mechanical spectra (G' and Δ vs. T) for samples of SS series.

regularly with the molecular weight as shown by unfunctionalized PFPEs. It is worthy of note that the nature of constraints is irrelevant in determining the dependence on the \bar{M}_n .

The peak intensity ($\Delta_{\alpha,s}$)_{max} and the half-width of α_s peak $\Delta\Delta(1/2)$ on the other hand are related to the volume fraction of the soft phase, as shown in Figs. 8 and 9. Peaks become sharper and increase in intensity with increasing the volume fraction, or the molecular weight, of the soft phase. Here some effects of the structure can be observed in the sense that samples of the S2 series exhibit higher peaks. Both the increase of the intensity and sharpening of the α peak depend on the volume fraction of the soft phase, due to the decrease of constraints with increasing \bar{M}_n .

Another variable to be considered is the plateau modulus in the temperature range between $T_{\alpha,s}$ and $T_{\alpha,h}$, where the material shows a rubberlike behaviour. Since $T_{\alpha,s}$ and $T_{\alpha,h}$ are both a function of the composition a criterion should be stated to define the temperature at which the modulus must be measured; the criterion chosen here was that of measuring G' at a reduced temperature $T = T_{\alpha,s} + 50^\circ\text{C}$. G' data so obtained are plotted in Fig. 10 as a function of the volume fraction of the soft phase. G' increases, as expected on the basis of the theory of two phase materials [30], with the volume fraction of the hard phase; some differences between the three series could be attributed to the structure. For example at the same volume fraction G' seems to increase in the order S2, SS, S1. On that basis it is possible

Table 6
Hard phase fraction, density and relaxation phenomena of the FPU samples

	S1			S2		SS			
	2000	3100	3800	2000	3100	1000	2000	3100	3800
T_γ (°C)	-160	-162	-160	-165	-158	-155	-160	-165	-160
$T_{\alpha,s}$ (°C)	-106	-116	-121	-106	-116	-103	-107	-118	-122
$\Delta(\alpha,s)_{\text{max}}$	1.15	2.4	2.62	0.75	2.6	0.42	1.50	2.50	2.50
$\Delta\Delta(1/2)^a$ (°C)	24	15	15	30	14	45	28	13	15
G' ($T_{\alpha,s} + 50^\circ\text{C}$) (MPa)	44	15.2	6.5	77	14.5	182	28	14.4	9.30
$T_{\alpha,h}$ (°C)	25	25	-65	13	-30	14	13	-70	-74
$\Delta(\alpha,h)_{\text{max}}$	0.19	0.18	0.1	0.30	0.20	0.55	0.30	0.15	0.24
			0.3					0.30	0.60
T_c^b (°C)	-	-	-	-	-	110	100	50	-

^a $\Delta\Delta(1/2)$ = half-width of α_s peak.

^b T_c = crystallisation temperature from G' trend.

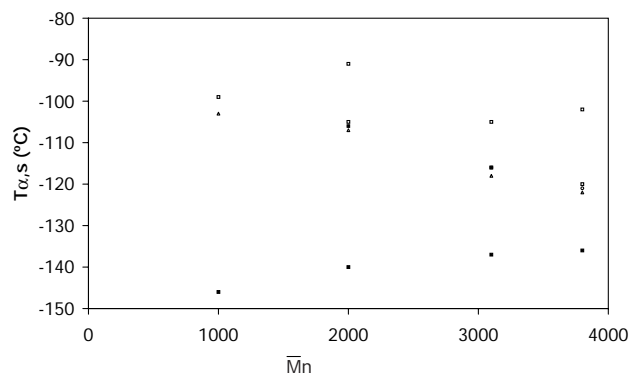


Fig. 7. $T_{\alpha,s}$ as a function of the molecular weight for FPU S1 series (O), PU S2 (x), PU SS series (Δ), ZDOL TX (\square), and PFPE Fomblin Z (\blacksquare).

to hypothesise that some fraction of the hard phase is dispersed in the matrix, acting as reinforcing agent. G' data seem to show that the incorporated amount of hard segment is the largest for the S1 series and the lowest for the S2 series.

The analysis of the dependence of the α,h maximum on the molecular and structural variables is not easy because it is generally ill defined. In any case it can be deduced from data reported in Table 6 that $T_{\alpha,h}$ is decreasing with increasing molecular weight and that generally samples of series S1 have a higher $T_{\alpha,h}$ than samples of series SS. It is clear that for the systems considered herein T_g of the hard phase is not a function of the length of the hard segment (as a matter of fact a higher T_g should be expected for the SS and S2 series in comparison with the S1 series) but is a function of the size of the clusters of the hard phase. With decreasing the size of the clusters the surface increases, so that T_g is lowered. In the case of PU polymerised with 3,100 and 3,800 ZDOL TX sometimes two peaks are observed. One can hypothesize that two families of hard phase aggregates with different size are present [31].

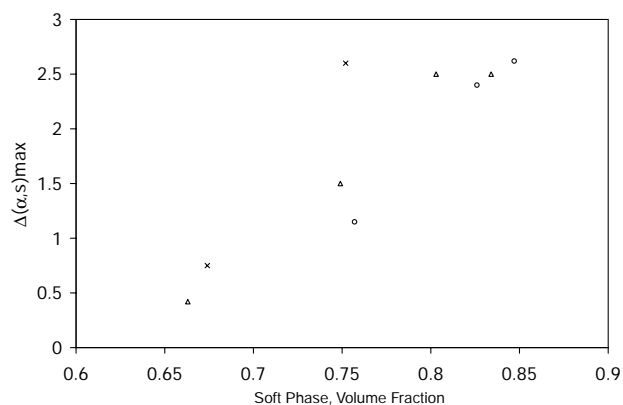


Fig. 8. Intensity of the α,s maximum as a function of the volume fraction of the soft phase for PU S1 series (O), PU S2 series (x), PU SS series (Δ).

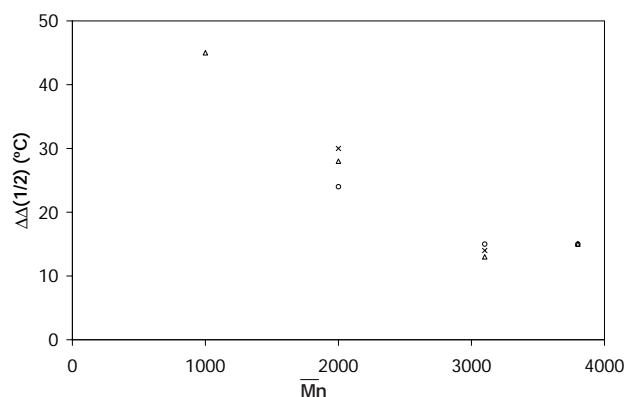


Fig. 9. Half-width of the α,s maximum as a function of the molecular weight of the soft phase for PU S1 series (O), PU S2 series (x), PU SS series (Δ).

4. Concluding remarks

The different characterisation techniques give, as expected, an insight about the structure of these materials.

The first important result is that two phases are always found (DSC and DMA data) even when both the soft and the hard segments are very short; this means that the two kinds of segments are incompatible, because of the large difference in the solubility parameters.

All these data suggest that these polymers are characterised by a heterogeneous structure not only at the molecular level but also at a macroscopic scale, in which a continuous soft phase is present containing different populations of hard domains. The macrostructure is more regular, as expected, for polymers prepared by S1 and S2 syntheses. In the case of SS series, three characteristic structured regions can be envisaged. Thermal transitions, located at 145–150, 170–185 and $\geq 215^\circ\text{C}$, can be tentatively related to the melting of domains mainly formed by hard chain containing 2, 3 and >3 MDI repeating units, respectively.

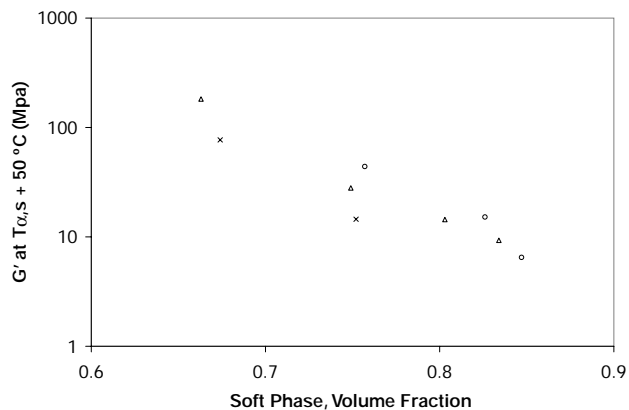


Fig. 10. Plateau modulus at $T_{\alpha,s} + 50^\circ\text{C}$ as a function of the volume fraction of the soft phase for PU S1 series (O), PU S2 series (x), PU SS series (Δ).

It is interesting to observe that the presence of such different micro- and macro-structures influences the value of the G' in the plateau zone between the transition of the soft and the hard segments. In fact, at constant volume fraction of one of the phases, the larger is the fraction of the hard phase dispersed in the soft matrix the higher is the modulus.

DSC analysis reveals that these materials are semi-crystalline; however, data of crystallisation enthalpy, normalised to the weight fractions of the hard phase, show that the ability to crystallise decreases with increasing the weight fraction of the soft phase. Wide-angle X-ray scattering doesn't evidence sharp peaks in the patterns; this could be related to the smallness of semi-crystalline regions in the hard phase [31].

In general it is possible to confirm that the so-called 'regular synthesis' brings to better defined structures, in which M–B–M segments seem to be the larger constitutive part of the hard phase. However, the complexity degree remains high, characteristic of the polyurethanes materials.

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