Synthesis and properties of polyurethanes based on polyolefin: 2. Semicrystalline segmented polyurethanes prepared under heterogeneous or homogeneous synthesis conditions

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Semicrystalline segmented polyurethanes based on hydrogenated polybutadiene (H-PBD) soft segments and butanediol (BDO) or di-β-hydroxyethyl hydroquinone (HQEE) as chain extenders were synthesized under different homogeneous or heterogeneous conditions, in solution or in bulk. Segmented semicrystalline H-PBD polyurethanes exhibit two glass transitions: a soft-phase transition $T_g(S)$ and a hard-phase transition $T_g(H)$. Thermal treatments show rearrangements in the two-phase materials. The dielectric relaxations, α_S and α_H, confirm the thermal behaviour and also the presence of a mixed interfacial region (α'_H). Increasing the hard-segment content increases this mixed-phase relaxation. This effect is also observed in the polyurethanes prepared in bulk instead of in solution, because of the decrease in the segregation ratio of the soft segments. Bulk samples also contain short isolated or amorphous hard segments as shown by size exclusion chromatography results and the conduction process appearing in the dielectric measurements. Such different routes of preparation induce various characteristics and tensile properties of the corresponding polyurethanes attributed mainly to premature phase separation occurring during the polymerization and the competition between the phase separation rate and the polymerization rate.

(Keywords: semicrystalline; polyurethanes; microphase; morphology; transitions; relaxations; thermal properties; dielectric properties)

INTRODUCTION

Linear segmented polyurethanes that consist of alternating soft and hard segments offer unique possibilities for tailor-made polymers by varying block length and composition. The soft segments are typically polyether or polyester, which provide the flexible character of the polymer. These segments are connected by hard segments formed from the reaction of diisocyanates with diol chain extenders.

Thermodynamic immiscibility between hard and soft segments induces phase separation and generates a two-phase morphology in these segmented block copolymers[1]. It is widely accepted that the engineering properties of these $(A-B)_n$-type thermoplastic elastomers are determined to a large extent by phase separation.

More recently, polyurethanes based on hydrocarbon soft segments, primarily polybutadiene and polyisobutylene, have been investigated[2–6]. Compared to polyether or polyester polyurethanes, these polyalkyl polyurethanes demonstrate superior hydrolytic stability and lower moisture permeability, especially for adhesives and electrical potting applications, and do not present intersegmental hydrogen bonding because of a large difference in their segmental structures and polarities.

MacKnight and coworkers[4–6] have provided strong evidence for the occurrence of premature macroscopic phase separation during a two-step bulk polymerization of polybutadiene (PBD) polyurethanes. Cooper and coworkers[7–9] have developed a Monte Carlo simulation study of the bulk polymerization of polyurethanes. The models determine the molecular weights and composition distribution of the final polymers. It appears that the major effect of the phase separation is to limit the molecular weight of each phase, presumably due to the stoichiometric imbalance of the reactants in the two phases. The phase separation process also led to a broad molecular-weight distribution, which is probably due to different average degrees of polymerization in the two phases. Premature macroscopie phase separation can be

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suppressed if polyurethane synthesis is carried out in a suitable solvent[5,10].

So the morphological complexity of such materials can be interpreted by taking into account the domain formation due to the segregation phenomenon on different levels, namely macrophase and microphase separation.

In a previous paper[11] we presented results obtained with amorphous polyurethanes based on hydrogenated polybutadiene (H-PBD) and with amorphous hard segments, all synthesized under homogeneous conditions in a polar solvent to prevent any premature macroscopic phase separation.

The d.s.c. studies of the glass transition temperature, T_g, have shown one T_g in the case of the pure hard-block polyurethanes, depending on the nature of the diisocyanate and of the chain extender, and two glass transitions in the case of the amorphous segmented H-PBD polyurethanes: a soft-phase $T_g(S)$ and a hard-phase $T_g(H)$.

These two-phase materials have shown molecular rearrangements under thermal treatments. The phase separation was quantitatively determined to be in the range of 85–95%.

As the urethane linkages in the materials can play the role of a probe in an electric field and lead to the appearance of dielectric relaxations, dielectric measurements show two relaxations related to the two thermal transitions and have confirmed their high level of microphase separation. But there is also evidence of a third relaxation between the soft- and hard-phase transitions, which has been attributed to a mixed interfacial region. Increasing the hard-segment content increases this interfacial region.

The understanding of the properties and related behaviour of such amorphous segmented polyurethanes (PU), considered as model systems, will aid in further investigations on more complex morphologies. In the present study, the thermal, mechanical and dielectric properties of hydrogenated-polybutadiene-based polyurethanes with semicrystalline hard segments are presented. The hard segment is based on 4,4′-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) or di-β-hydroxyethylhydroquinone (HQEE). In the first part of this study, a series of solution-polymerized polyurethanes has been studied as a function of the hard-segment content varying from 20 to 50 wt%. In the second part, a comparison of the properties of a polyurethane produced using the same formulation but with a fixed hard-segment content and prepared by different processes is presented. These processes include preparation in a good solvent, in a non-suitable solvent, with or without catalyst and in bulk.

EXPERIMENTAL

Materials and synthesis

The hydrogenated polybutadiene oligomer (H-PBD, Nippon Soda; $\bar{M}_n = 2100$ g mol^{-1}, $\bar{F}_n = 1.8$; 18% ethylene, 82% butene) was degassed at 60°C for 24 h before use. Pure MDI (Bayer), BDO (Aldrich) and HQEE (Eastman Kodak) were used as received. The solvents used for solution polymerization, tetrahydrofuran (THF) (Solvants Documentation Syntheses) and toluene (Tol) (Solvants Documentation Syntheses), were dried over molecular sieves before use. All the syntheses were carried out using a conventional two-step method. The procedure was as follows:

(i) In stage 1, the H-PBD was mixed with an excess of MDI in bulk at 80°C for 4 h under vacuum.

(ii) The procedure used in the second stage depends on the solvent. For the polymers prepared in homogeneous solutions, 200 cm^3 of THF were added at room temperature. The chain extender and catalyst, dibutyltin dilaurate (DBTDL) (0.01% by weight of the reactants), were then added and the reaction continued for 3 h at 50°C with mechanical stirring. The total concentration of PU was 10% and the solution remained clear throughout the reaction except in the case of the MDI–HQEE hard segments where the solution became opaque due to the high crystallinity of the hard segments. The polymer was then precipitated in methanol and dried under vacuum at 60°C for 24 h. Samples were prepared by compression moulding at 150°C for 10 min.

For the polymers prepared in heterogeneous solution, 200 cm^3 of toluene were added at room temperature. The solution was heated to 80°C before adding the chain extender and the reaction was allowed to proceed for 48 h. Generally the solution became opaque immediately after the addition of the chain extender. In the case where a catalyst was used, the solution was brought to 60°C, and the solution stayed clear with the addition of the chain extender. The reaction was carried out for 3 h.

For the polymers prepared in bulk, at 80°C in case of BDO and at 110°C in case of HQEE, after the addition of the chain extender, the reaction mixture was vigorously stirred mechanically for 2 min, degassed and poured into a 1 mm thick mould. Curing was carried out at 110°C for 24 h.

All samples were kept at room temperature for 20 days before testing.

Experimental methods

A Waters h.p.l.c. apparatus equipped with refractometric (r.i.) and ultra-violet (u.v. at 254 nm) detectors was used for size exclusion chromatography (s.e.c.) analyses. Microstyragel columns with 1000, 500 and 100 Å pore sizes were used. The solvent (THF) flow rate was 1.5 cm^3 min^{-1}. All molecular weights reported are based on a calibration curve from polystyrene standards.

A Mettler TA 3000 microcalorimeter was used for the d.s.c. measurements. The d.s.c. runs were performed under argon using a heating rate of 7.5 K min^{-1}.

Scanning from −170°C provided an excellent baseline for ΔC_p determinations. Five to ten runs were made for each sample type. The difference ΔC_p between each run was not more than $\pm 5\%$. Therefore, the average ΔC_p can be estimated to within 2%. The sample weights were 15–20 mg. The glass transition temperature was taken as the onset of the phenomenon.

The static mechanical properties were carried out on a 5002 type JJ Lloyd traction machine with a traction speed of 20 mm min^{-1}.

Dynamical mechanical properties were observed by means of Rheovibron RVIIB viscoelasticimeter (Toyo Baldwin) using a heating rate of 1°C min^{-1} and a frequency of 11 Hz.

Dielectric measurements were carried out with a Polymer Laboratories cell connected to Hewlett–Packard 4274A and 4275A multifrequency LCR meters. The measurements were performed in the temperature range −70 to +180°C and using frequencies of 100 Hz to

100 kHz with a heating rate of 1°C min^{-1} under dry nitrogen.

RESULTS AND DISCUSSION

Properties of homogeneous solution-polymerized polyurethanes as a function of hard-segment content

A series of semicrystalline segmented polyurethanes based on MDI–BDO hard blocks have been synthesized in THF at room temperature (homogeneous solution). The weight per cent, which is defined as the per cent by weight of the isocyanate and chain extender in the polymer, was varied from 11 to 53%. All the films were clear except the one with a hard-segment content of 53%. For this polymer the opacity was due to a higher amount of crystalline hard blocks. All the samples were completely soluble in THF. *Table 1* gives the s.e.c. and d.s.c. data. The number-average molecular weights, $\bar{M}_n$, were found to be in the range of 19 000–27 000 g mol^{-1}, as calculated from a conventional polystyrene standard calibration curve. The polydispersity index, $\bar{M}_w/\bar{M}_n$, was found to be in the range of 2.2 except for the polymer with a high hard-segment content. The theoretical value of the polydispersity index for a step-growth polymerization is equal to 2. Similar results have been obtained by Bengston *et al.*[6] on PBD-segmented polyurethanes with amorphous TDI–BDO hard blocks and also by Chen *et al.*[12] for solution-polymerized polyureas. The increase in the polydispersity to 4.3 for the hard-block-rich polyurethane is certainly due to partial crystallization and phase separation during the polymerization.

Several transitions can be observed using d.s.c.: the glass transition of the amorphous phases and the exothermic or endothermic behaviour due to the crystallization or melting of the semicrystalline hard phase.

Figure 1 shows the d.s.c. curves of two H-PBD polyurethanes heated at a rate of 7.5 K min^{-1} (a) on the compression-moulded film (150°C) and (b) on the same sample after quenching from 250 to −100°C. We clearly observe the appearance of the step change characteristic of a hard-segment glass transition in the quenched runs. Single hard- and soft-microdomain T_g values confirmed the two-phase nature of these polyurethanes even in the melt. An exothermic peak due to crystallization is observed just after T_g(H).

A summary of the d.s.c. transition temperatures for all samples is presented in *Table 1*. The soft-microphase glass transition, T_g(S), is independent of the thermal history and slightly dependent on the hard-segment content.

The sample without BDO is an amorphous one-phase system. The segmented polyurethane 1/2/1 with a hard-segment content of 20% is a two-phase system as will be confirmed by the analysis of the mechanical relaxations, although we observe only a small melting endotherm at 150°C during the first scan. The T_g(H) of the hard microdomains is not discernible during the second scan. The T_g(H) values of the hard microdomains are observed for all the other polyurethanes. As for amorphous segmented polyurethanes[11] the T_g(H) values of the semicrystalline segmented polyurethanes seem to be quite independent of the hard-segment content and are in the same range as the value determined for the pure MDI–BDO hard copolymer, which is T_g = 107°C[11].

Finally, moulded films of H-PBD polyurethanes show one or two broad endotherms in the first d.s.c. run. One occurs at $T > 200°C$ in the same temperature range as the melting temperature of the model hard blocks[13–19] and has been ascribed in the literature to a pure spherulite crystalline organization. The other endotherm, at $T < 200°C$, may correspond to a lower range ordered structure. These two endotherms have been described in the literature[15–17] for polyether-based polyurethanes and were assigned to different chain conformations of hard

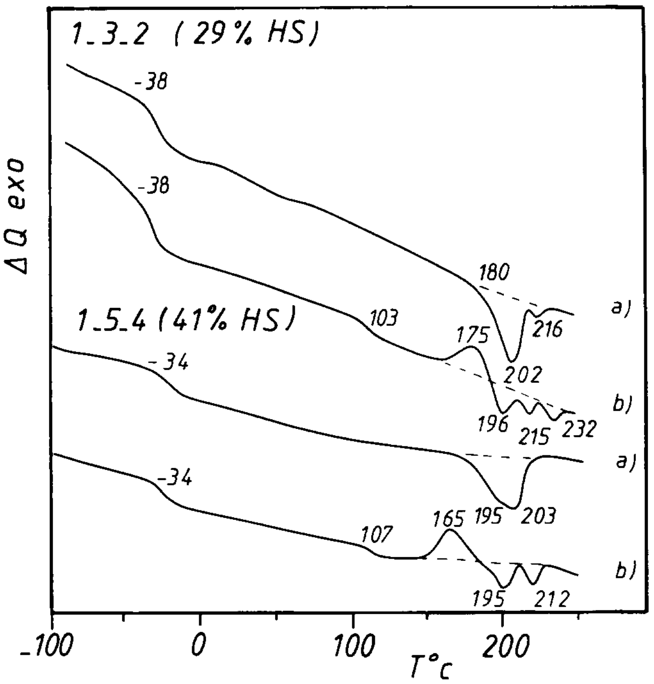

Figure 1 D.s.c. traces for semicrystalline segmented polyurethanes based on H-PBD–MDI–BDO: (a) first scan to 250°C; (b) second scan after the first one

Table 1 S.e.c. and d.s.c. data

Molar ratio	HS (wt%)	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	T_g (S) (°C)	T_g (H)[a] (°C)	T_c (°C)		T_m[a] (°C)	
1/1/0	11.1	19 200	54 000	2.8	−32	Amorphous one-phase system				
1/2/1	20.4	20 200	40 400	2.0	−36	(see text)				
1/3/2	28.8	24 900	54 800	2.2	−38	103	175	196	215	232
1/4/3	35.6	27 100	59 600	2.2	−37	106	155	195	212	
1/5/4	41.2	27 200	65 300	2.4	−34	107	165	195	212	
1/8/7	53.3	19 300	83 000	4.3	−32	106	152	195	215	

[a] Obtained during the second run after the first scan up to 250°C followed by a quench

segments (extended or contracted). The higher melting point is probably due to tighter packing. This melting peak becomes more defined after the first scan.

During the first scan, only the glass transition of the soft phase is observed by d.s.c., because the change in heat capacity of the amorphous hard blocks at T_g(H) is too small to be observed.

Through an analysis of the shift broadening and heights (ΔC_p) of the T_g of the soft blocks, qualitative and also quantitative information can be extracted concerning the composition of the phases and the interfacial area[11,20]. The heat capacity change, ΔC_p(S), per gram of soft segments in the polyurethane is compared with the ΔC_p°(S) of the pure soft phase measured for the oligomer or for the single phase H-PBD-MDI copolymer. ΔC_p° is equivalent to the ΔC_p per gram of the soft segments at the glass transition in totally phase-separated polyurethanes, and the ratio ΔC_p(S)/ΔC_p° corresponds to the per cent of segregation of the soft blocks.

We can see in *Table 2* that ΔC_p°(S) is lower than expected in the pure soft phase. This indicates clearly that a percentage of soft segment is derived from the soft phase and mixed with hard blocks in the hard microdomains or at the interface. The soft-segment segregation ratio was found to decrease with increasing hard-segment content. In *Figure 2* the glass transition of the soft phase, T_g(S), is plotted *versus* the quantitative d.s.c. evaluation of the degree of phase separation of the soft segments. The variation in T_g, with a minimum for formulation 1/3/2 and 1/4/3, clearly shows that the value of T_g(S) is dependent on two effects:

(i) A copolymer effect due to -(MDI)- groups introduced between two soft segments during the first step in the synthesis. This chain extension effect decreases when the excess of MDI in the first step increases.

(ii) An effect of the dissolution of hard blocks in the soft phase, increasing when the per cent of hard segments increases.

The stress–strain data as a function of hard-segment content are summarized in *Table 3*. The 11% of soft-segment sample without chain extender was too soft to be tested and is not included in this report. The segmented polyurethanes exhibit a wide range of behaviour, from that of a soft rubber for a low hard-segment content to a high-modulus hard plastic at a high hard-segment content. Compared to conventional polyurethanes, the samples of this study exhibit poorer mechanical properties. This point will be discussed later. From the molar ratio 1/3/2, as the hard-segment content increases, the tensile strength and Young's modulus increase while the ultimate elongation seems to decrease. These results can be explained in terms of a hard-segment filler effect and changes in the morphology and composition of the continuous phase of the material from predominantly soft-segment material to predominantly hard-segment material[21]. A sudden change in the properties of the 41% and the 53% hard-segment content samples is observed. Similar results were reported by Zdrahala *et al.*[22] for a polyurethane based on polycaprolactone. They argued that the change in properties was related to an inversion of the hard and soft phases in the polyurethane. A similar phase inversion was observed by Chen *et al.*[23] for a 50–60% hard-segment content in polyurea systems based on amine-terminated poly(propylene oxide). Such a phase inversion might have occurred at 45–50% hard-segment content in our system.

Table 2 Quantitative d.s.c. evaluation of the degree of phase separation of the soft segments: $\Delta C_p(S)/\Delta C_p^\circ$ is the ΔC_p of H-PBD or the ΔC_p of H-PBD-MDI and $\Delta C_p(S)$ in the ΔC_p of the segmented polyurethane

Samples	SS (wt%)	T_g (S) (°C)	ΔC_p(S) (J g^{-1} K^{-1})	$\Delta C_p(S)/\Delta C_p^\circ$ (%)
H-PBD	–	−45	0.43	–
H-PBD-MDI	–	−38	0.33	–
1/1/0	88.9	−32	0.42	–
1/2/1	79.6	−36	0.41	95–99
1/3/2	71.2	−38	0.39	90–94
1/4/3	64.4	−37	0.36	84–87
1/5/4	58.8	−34	0.32	75–78
1/8/7	46.7	−32	0.32	73–76

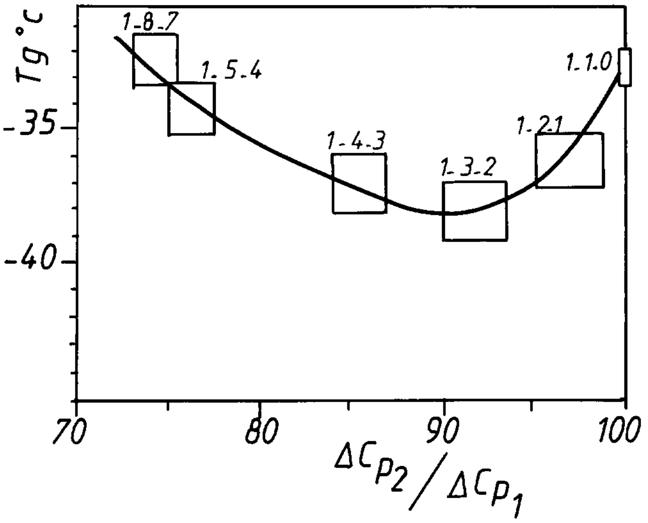

Figure 2 Variation of the glass transition temperature of the soft phase *versus* the segregation ratio $\Delta C_p(S)/\Delta C_p^\circ$

Table 3 Mechanical properties of solution polyurethanes as a function of hard-segment content

Sample molar ratio (HPBD/MDI/BDO)	Hard-segment content (wt%)	Young's modulus (MPa)	Tensile strength (MPa)	Ultimate elongation (%)
1/2/1	20.4	2.3	1.9	90
1/3/2	28.8	7.8	8.2	190
1/4/3	35.5	23.0	9.4	70
1/5/4	41.2	43.3	11.6	70
1/8/7	53.3	190	14.5	20

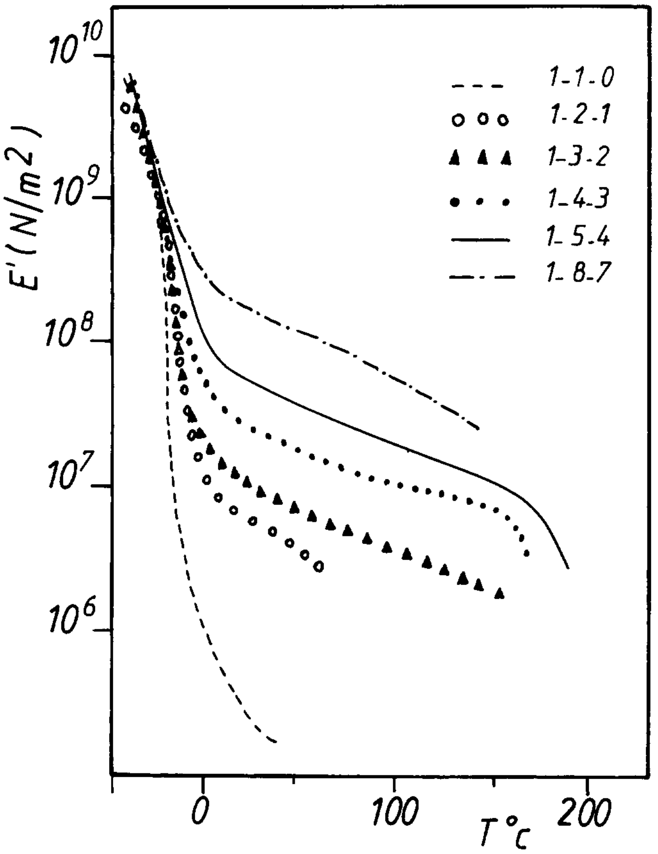

Figure 3 Storage modulus E' vs. temperature measured at 11 Hz for different polyurethanes based on H-PBD-MDI-BDO

The mechanical relaxation behaviour of the studied samples is illustrated in *Figure 3* with the variation of the modulus E' *versus* temperature. The temperature dependences of tan δ from mechanical measurements (at 11 Hz) and from dielectric measurements (at 1000 Hz) are compared in *Figure 4*. As can be seen in *Figure 3*, the curves show one main relaxation and one rubbery plateau corresponding to the two phases in the material. The maximum of the soft-segment relaxation at 11 Hz is at −10°C, which is consistent with the d.s.c. results. The soft-segment relaxation is also characterized by a step decrease of one or two orders of magnitude in the value of the storage modulus. The level of the storage modulus plateau above the soft-segment relaxation increases with increasing hard-segment content, which is consistent with the findings for other phase-segregated systems[12]. This effect can be attributed to an increase in the volume fraction of hard segments. The reinforcing nature of the hard microdomains is responsible for the increase in modulus.

The decrease in the modulus at high temperatures, characteristic of the plastic behaviour of the hard microdomains, occurs at a temperature lower than 150°C, just after the glass transition temperature of the amorphous hard microdomains and below the melting temperature observed by d.s.c. Though the crystallinity of the hard domains is too low, the temperature at which these hard domains become soft will depend mainly on the interaction strength in the amorphous state.

As the hard-segment content increases, the magnitude of the soft-segment damping peak observed in *Figure 4* decreases. Such changes in the damping behaviour of these materials clearly reflect changes in the relative amounts of the constituents in the soft phase.

In *Figure 5*, the variations in the Young's and storage modulus at 30°C and of the maximum of tan δ are plotted *versus* the per cent of hard segments. The behaviour of the single-phase sample is of course quite different from the others. A change is also perceptible between 40 and 50% of hard blocks, suggesting a change in sample morphology.

Figure 4 also shows the dielectric spectra of the different segmented polyurethanes:

(i) The single-phase system H-PBD-MDI (1/1/0) without chain extender has only one symmetrical and well defined relaxation peak with a maximum tan $\delta = 5 \times 10^{-2}$ at 23°C (frequency 1 kHz). This relaxation peak is associated with the transition observed at −32°C by d.s.c. and −10°C at 11 Hz in mechanical measurements, and indicates a cooperative motion of the non-polar and polar segments. In comparison with polyester-based polyurethanes[24,25], the intensity of the peak is 20 times lower (tan $\delta = 5 \times 10^{-2}$ as compared to 1). But due to the presence of dipoles of the urethane

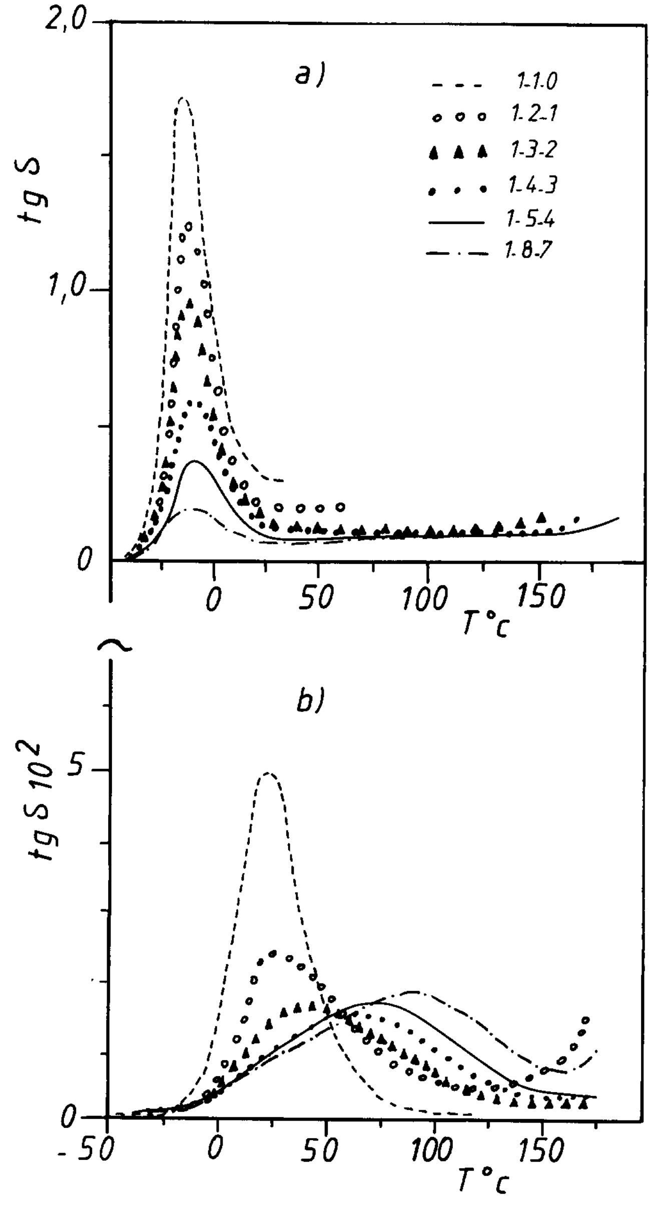

Figure 4 (a) Mechanical relaxation (at 11 Hz) and (b) dielectric relaxation (at 1000 Hz) for different segmented polyurethanes based on H-PBD-MDI-BDO

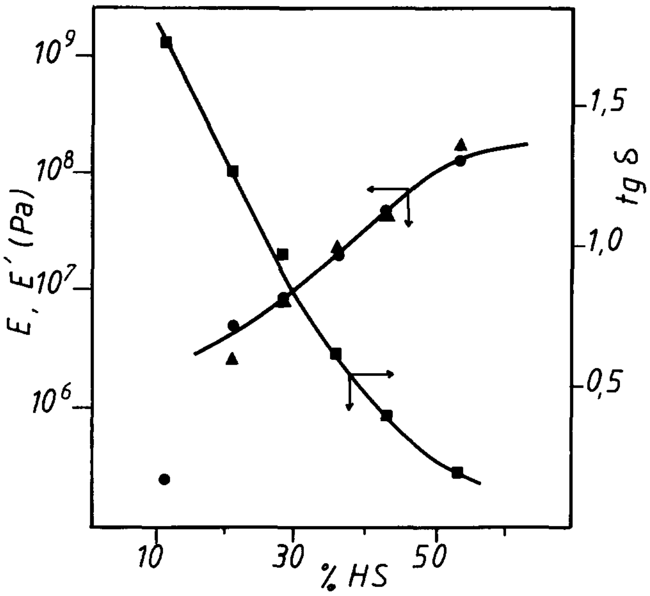

Figure 5 Modulus and tan δ vs. hard-segment content: (▲) Young's modulus E at 25°C; (●) storage modulus E' at 30°C

linkages in the non-polar H-PBD, the peak is four times higher than those observed for 1,4 and 1,2 PBD[26].

(ii) In contrast with H-PBD–MDI, the two-phase polyurethanes exhibit a broad peak α' with a peak or a shoulder α_S around 25°C and a maximum at 50–100°C, depending on the hard-segment content. The relaxation α_S can be related to the transition of the soft phase, T_g(S). The relaxation α', although no corresponding relaxation appears in the mechanical properties, is attributed to a mixed interfacial region shown in previous work[11,24,27].

It is important to notice that the intensity of the peak α' (at 100°C) also increases with increasing hard-segment content. At higher temperatures, around 150°C, for some samples we observe an increase in tan δ, which can be attributed to the beginning of the relaxation of the amorphous hard microdomains, α_H. This relaxation is detected with the 1/2/1 polyurethane, possessing smallest average length, and also the 1/8/7 polyurethane, possessing the highest amount of hard segments.

(iii) *Figure 6* gives the dielectric loss peaks for semicrystalline segmented polyurethane of formulation 1/3/2, 30 wt% of hard segments (HS), for the initial heating run and second heating run after quenching from 170°C. For comparison, the behaviour of a blend prepared by mixing in THF of 80 wt% of single-phase H-PBD–MDI with 20 wt% of single-phase high-molecular-weight hard polyurethane MDI–BDO is also reported. This cast film obtained after the evaporation of the solvent was opaque, indicating macrophase separation and/or a high level of crystallinity. For all the materials, the main relaxation, α_S, is observed at 25°C. For the blend, no other dielectric loss after this relaxation is seen, indicating a high degree of crystallinity for the hard domains. For the segmented polyurethane 1/3/2, the spectrum shows a broad peak, α', attributed to the mixed phase. In the second scan, two peaks are observed, in addition to an increase in the relaxation, α_S, at 25°C of the soft phase, as described previously for amorphous segmented polyurethanes after a thermal treatment[11]. The amplitude of the α_S peak is higher than for the initial film because the annealing during the first measurement liberated the more flexible chains embedded in the mixed interfacial region. The relaxation peak associated with these flexible chains is narrower due perhaps to a decrease in the interphase area.

Finally we note that the dielectric losses are stable and low (tan $\delta < 1 \times 10^{-2}$) up to 175°C due to the fact that the dipoles of the hard segments are hindered by the crystallinity of the hard phase. Their dielectric properties are interesting to mention for possible electronic applications of these materials.

Influence of the synthesis process on properties of two polyurethanes based on BDO and on HQEE

Two types of polyurethanes with BDO or HQEE extenders (28.8 and 33.3 wt% HS respectively) were synthesized in a heterogeneous medium (toluene solution with or without a catalyst and in bulk) or in a homogeneous medium (in THF with a catalyst). Only the polyurethanes prepared in THF and the polyurethanes based on BDO prepared in toluene and with a catalyst were completely soluble in THF (s.e.c. eluant). This reflects a heterogeneity of the composition and the non-soluble part can be attributed to hard-segment-rich macromolecules.

Table 4 gives the s.e.c. data relative to polystyrene standards.

The polymers prepared in heterogeneous solution or in bulk have a broader molecular-weight distribution. The catalysed samples display a higher molecular weight and a narrower polydispersity than their uncatalysed counterparts. Camargo *et al.*[28] have obtained similar results in a study of catalysed and uncatalysed reaction injection-moulded polyurethanes. It was not reasonable to calculate molecular-weight values from the shape of the s.e.c. elution curves of the soluble fraction of the samples prepared in bulk. These s.e.c. curves are presented in *Figure 7*, which compares the s.e.c. traces of the solution- and bulk-prepared polyurethanes. Oligomer peaks are clearly evident on the bulk traces. Small-molecular-weight species are also evident. These species can be isolated short hard segments due to the stoichiometric imbalance in both phases. Willkomm *et al.*[12] obtained similar results on comparing polyureas prepared in solution or in bulk by reaction injection moulding (RIM). The bulk sample presents the broadest distribution curve with at the same time lower and higher molecular weights than in the solution-prepared materials. As reported by Cooper and coworkers[8–11], premature phase separation leads to a broadening of the composition and of the molecular-weight distributions. It also leads to a limiting of the degree of polymerization. In our case, only the synthesized THF catalysed polymers present the usual symmetric s.e.c. peaks.

The glass transitions of the soft and hard blocks and the transitions of the semicrystalline hard blocks were investigated by d.s.c. The thermograms are shown in *Figures 8* and *9*. The glass transition of the hard microphase in only detectable during a second heating scan after a quenching from the melting temperature of the hard microdomains.

The glass transition temperature of the soft phase, T_g(S), seems rather independent of the synthesis process. The measurements of the heat capacity change at T_g(S) allows the determination of the segregation ratio of the soft segments. The average values of ΔC_p are listed in

Table 4 S.e.c. data for solution-polymerized polyurethanes

Sample	HS (wt%)	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
H-PBD-MDI-BDO, THF, cat.	28.8	24 900	54 800	2.2
H-PBD-MDI-BDO, Tol, cat.	28.8	15 800	49 000	3.1
H-PBD-MDI-BDO, Tol	28.8	9900	33 700	3.4
H-PBD-MDI-HQEE, THF, cat.	33.3	18 700	60 000	3.2
H-PBD-MDI-HQEE, Tol, cat.	33.3	13 000	63 700	4.9
H-PBD-MDI-HQEE, Tol	33.3	14 000	29 500	2.1

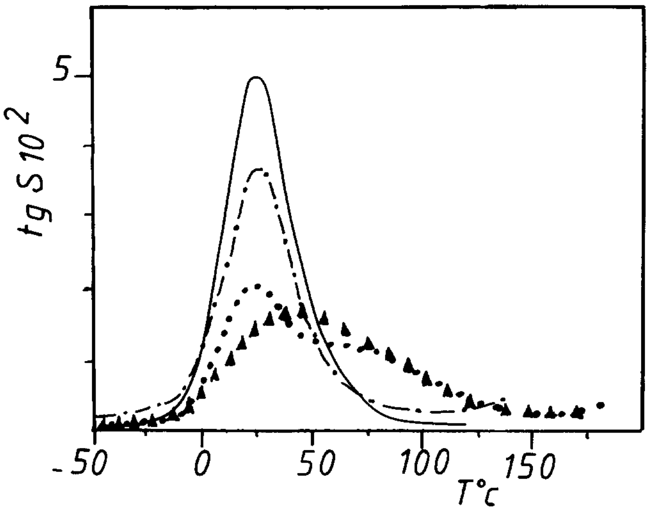

Figure 6 Dielectric relaxation (1000 Hz) for different polyurethanes and blends based on H-PBD, MDI and BDO: (——) H-PBD-MDI; (-·-·-) H-PBD-MDI + MDI-BDO (80/20); (▲) H-PBD-MDI-BDO 1/3/2 (first scan); (●) H-PBD-MDI-BDO 1/3/2 (second scan)

Table 5. The segregation ratio of the soft segments is found to decrease due to the premature phase separation that occurs when the synthesis is conducted in a heterogeneous medium. For both chain extenders, BDO and HQEE, the bulk samples present the lowest segregation ratio. The high value of the segregation ratio for the polyurethane based on HQEE is certainly due to the higher crystallinity of the hard microphase, obtained with the symmetric aromatic structure of HQEE.

Concerning the hard phase, the samples possess a distinct hard-segment T_g(H) only on the second d.s.c. scan but one, two or three hard-segment melting peaks are visible. As mentioned before in the literature regarding polyurethanes based on BDO, the two endotherms observed at about 190–200°C and at 200–240°C are ascribed to two different degrees of organization: a paracrystalline structure with preferential orientation in the chain (small-scale ordering) and a pure spherulitic organization[13–15,18]. Moreover these two structures appeared to be dependent on each other: the first one can generate the second one according to the imposed thermal treatments[15,16,29–31]. A phenomenon of nucleation–growth can explain the observed peak of recrystallization in the melting zone of the paracrystalline structure of a second thermal treatment.

In addition to these morphological phenomena, chemical rearrangements occur depending on the

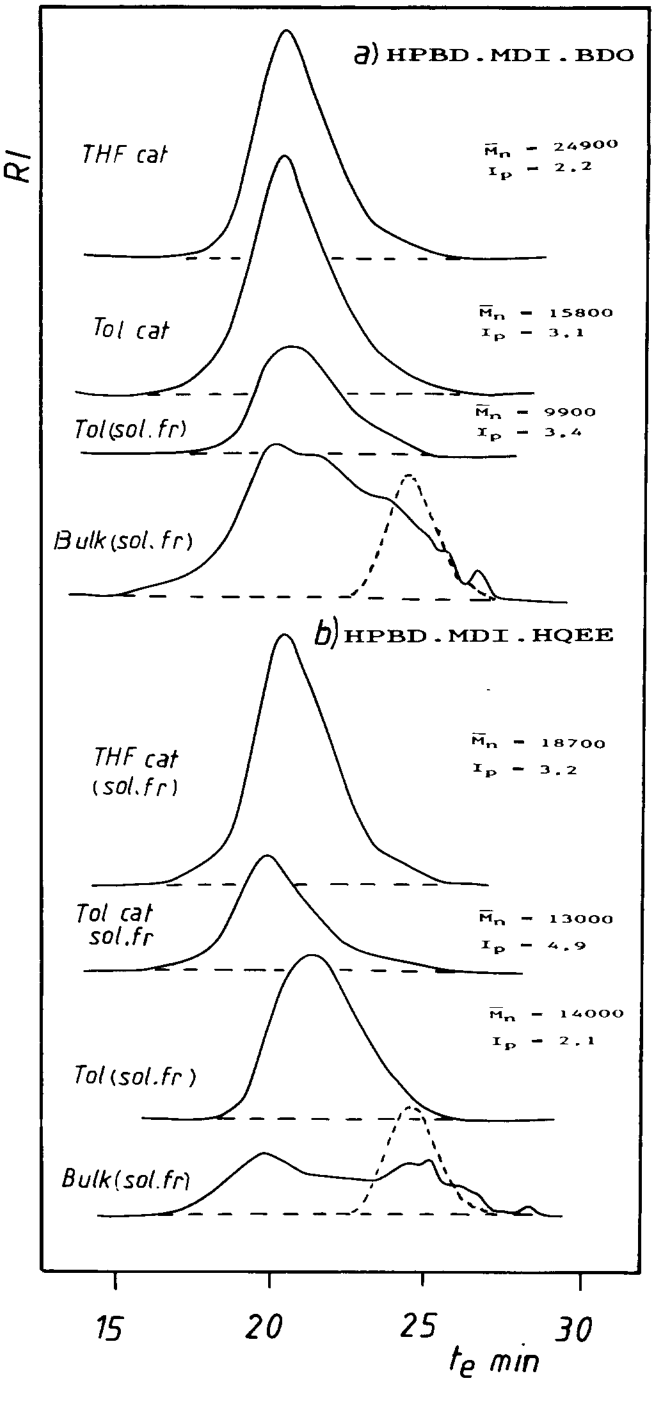

Figure 7 S.e.c. traces for solution and bulk polyurethanes at a hard-segment content of 29% (H-PBD-MDI-BDO) and at a hard-segment content of 33% (H-PBD-MDI-HQEE)

Table 5 Glass transition temperature and aggregation ratio of the soft segments for polyurethanes as a function of the synthesis route

Sample	T_g(S) (°C)	T_g(H) (°C)	ΔC_p(S) (J g^{-1} K^{-1})	$\Delta C_p(S)/\Delta C_p^\circ$ (%)
H-PBD-MDI-BDO, THF, cat.	−38	103	0.393	90
H-PBD-MDI-BDO, Tol, cat.	−37	103	0.375	86
H-PBD-MDI-BDO, Tol	−36	–	0.350	80
H-PBD-MDI-BDO, Bulk	−36	103	0.351	80
H-PBD-MDI-HQEE, THF, cat.	−37	99	0.412	95
H-PBD-MDI-HQEE, Tol, cat.	−37	–	0.404	93
H-PBD-MDI-HQEE, Tol	−38	95	0.397	91
H-PBD-MDI-HQEE, Bulk	−36	99	0.375	86

[a] Obtained during the second run after the first run up to 250°C followed by a quench

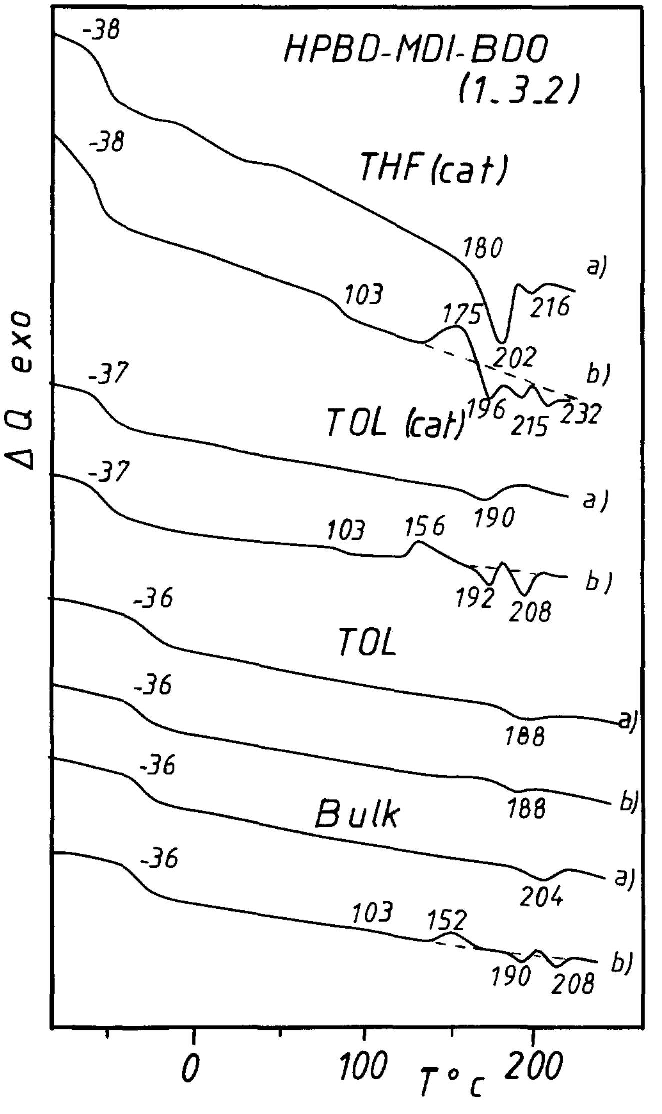

Figure 8 D.s.c. traces for solution and bulk polyurethanes for the formulation H-PBD-MDI-BDO 1/3/2 (29% HS)

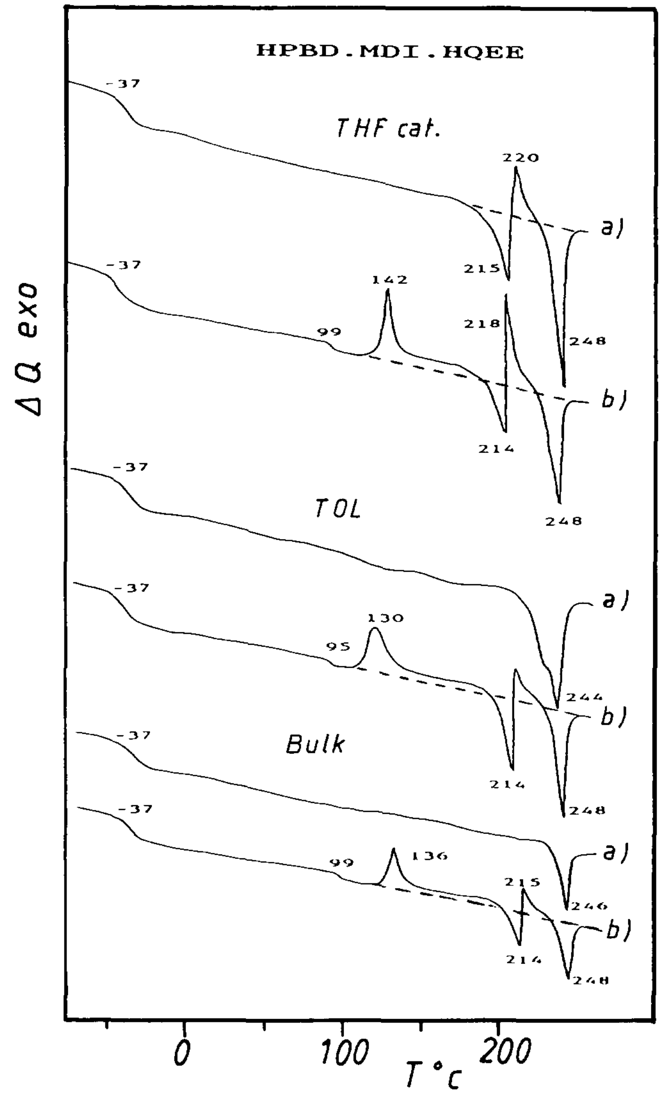

Figure 9 D.s.c. traces for solution and bulk polyurethanes for the formulation H-PBD-MDI-HQEE 1/3/2 (33% HS)

instability of the urethane bonds when the temperature exceeds 180°C. These rearrangements induce segment redistributions and chain scissions. The formation of long isolated hard segments that would favour a better hard-segment organization is not included.

The degree of crystallinity and the spherulitic organization is favoured in the case of HQEE as compared to BDO and in the case of homogeneous polymerizations and catalysed reactions as compared to the heterogeneous and uncatalysed conditions (bulk process included).

The stress–strain data are reported in *Table 6*. As mentioned before, polyurethanes based on non-polar soft segments show lower mechanical properties than conventional polyurethanes[32,33]. Cooper and coworkers[3]

Table 6 Mechanical properties of solution and bulk polyurethanes as a function of the synthesis route

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Ultimate elongation (%)
H-PBD–MDI–BDO, THF, cat.	7.8	8.2	190
H-PBD–MDI–BDO, Tol, cat.	8.4	9.5	300
H-PBD–MDI–BDO, Tol	10	10.3	130
H-PBD–MDI–BDO, Bulk	8	8.9	500
H-PBD–MDI–HQEE, THF, cat.	10	8.9	120
H-PBD–MDI–HQEE, Tol, cat.	20.1	12.5	200
H-PBD–MDI–HQEE, Tol	22.3	6.8	60
H-PBD–MDI–HQEE, Bulk	11.1	10	320

studied factors leading to reduced properties for such polyurethanes. It was pointed out that one major factor was the inaptitude of the soft segments to crystallize under strain. The low molecular weights and compositional heterogeneity also led to low tensile properties. The sharp interfaces in non-polar-based polyurethanes might also be an inherent factor leading to lower strength. Considering these assumptions, it is important to compare our results to molecular-weight and crystallinity data previously presented.

The results on the dependence on the synthesis route and concerning BDO and HQEE are in good agreement except in the case of the HQEE–Tol polymer whose very low molecular weight reduces the tensile strength value. The modulus and tensile strength are higher and the elongation at break is lower for the PU based on HQEE. But depending on the synthesis process, the main feature is the higher elongation at break for samples prepared in bulk.

In the case of the bulk samples, it is obvious that the sample morphology depends on the quality of the mixing of the reactants, as observed by Kolodzoek *et al.*[15] for RIM polyurethanes based on poly(propylene oxide). This factor is very significant for our system, whose reactants are quite immiscible. So these bulk samples are examples of the numerous morphologies that could be obtained with different levels of mixing. Their Young's moduli are close to that of the homogeneous polymer despite a lower segregation ratio. In fact, the samples have different post-reaction treatments: (i) the solution polymers were precipitated in methanol and the crystallization of the hard domains occurred during this precipitation; (ii) the bulk samples were moulded at 110°C and the hard-segment crystallization was hindered. The elongation at break is 2.5 times greater for the bulk samples than that of the homogeneous solution polymer. Two major reasons can explain this result: the higher-molecular-weight macromolecules in the bulk sample and a larger interfacial region (discussed in the next section).

The temperature dependences of tan δ as seen from mechanical measurements (at 11 Hz) and from dielectric measurements (at 1000 Hz) are compared in *Figures 10* and *11* for BDO- and HQEE-based PU, respectively. In the case of the solution-prepared samples, the results are in good agreement with the tensile properties. The storage modulus below the glass transition of the soft phase is the highest for samples prepared in a heterogeneous solution (toluene).

Polymers prepared in homogeneous solution (THF) present the lowest rubbery modulus and the smallest temperature dependence of the modulus. Considering the amplitude of tan δ at the glass transition of the soft phase, there is a good agreement with the d.s.c. results concerning the segregation ratio. The amplitude of the least segregated material is the lowest. This can be related to the fact that only a few soft segments relax in the soft phase or that their mobility is restrained by some hard segments dissolved in this soft phase.

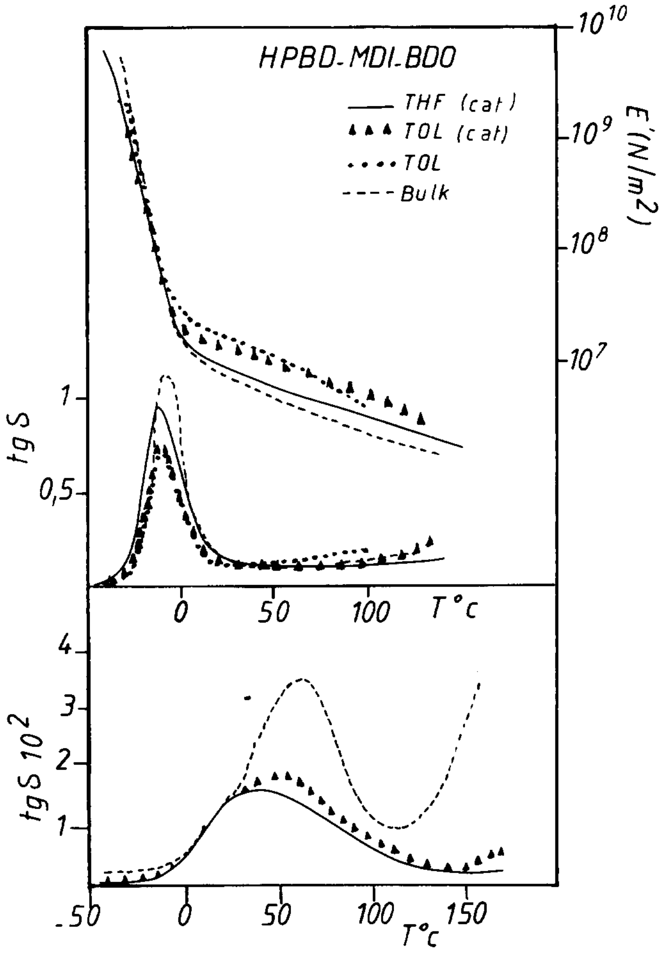

Figure 10 (a) Storage modulus vs. temperature, (b) mechanical relaxations (11 Hz) and (c) dielectric relaxations (1000 Hz) for solution and bulk polyurethanes for the formulation H-PBD–MDI–BDO 1/3/2

Regarding the bulk samples, the rubbery modulus is lower than that of the homogeneous solution-prepared polymers, but tan δ at the glass transition of the soft

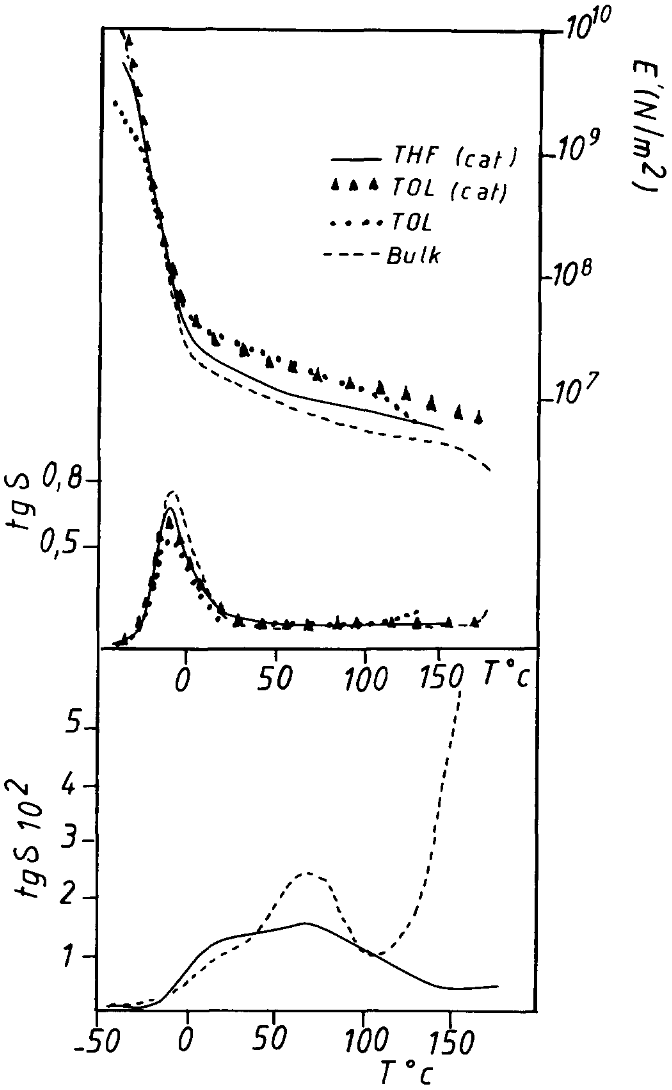

Figure 11 (a) Storage modulus vs. temperature, (b) mechanical relaxations (11 Hz) and (c) dielectric relaxations (1000 Hz) for solution and bulk polyurethanes for the formulation H-PBD-MDI-HQEE 1/3/2

phase is higher. The stoichiometric imbalance of reactants in each phase, due to premature phase separation, produces low-molecular-weight products with higher mobility.

As mentioned before, the broad relaxation peak observed in dielectric spectroscopy is a superposition of two well defined relaxations: a relaxation associated with the soft-phase glass transition and a second one associated with dipoles in the mixed interfacial region. In the case of solution polymers, the difference between a microseparated sample (THF) and a macroseparated sample (toluene, catalyst) is an increase in the part of the relaxation associated with the mixed interfacial region.

Regarding the bulk sample, the peak α' associated with the relaxation of the mixed interfacial region is about two times higher than the corresponding peak of the sample prepared in THF. In addition, a conduction process appears at about 120°C and is attributed to the motion of short isolated amorphous hard segements. In fact, for the samples prepared in bulk, the premature macrophase separation yields more amorphous hard-segment domains than for the samples prepared in solution. If the driving force for phase separation is the immiscibility of the two segment types, the factors influencing the microphase separation of PU must also include segment polarity, segment length, hard-segment crystallizability, overall sample composition, sample preparation (polymerization and moulding) and mechanical and thermal history. So the lower degree of crystallinity of the samples prepared in bulk must involve a broader interfacial region, and the variation in the interfacial-region parameters can also explain the differences obtained in stress–strain data.

Therefore this demonstrates that dielectric measurements are very useful for characterizing the degree of macrophase heterogeneity of materials and for explaining their properties.

CONCLUSIONS

Microphase-separated linear polyurethanes of different hard-segment contents were obtained via two-step polymerization in a polar solvent, THF. The influence of hard-segment content on mechanical, dynamic-mechanical, thermal and dielectric properties has been studied. All materials exhibit a two-phase morphology. The extent of phase separation as determined by the heat capacity change, $\Delta C_p(S)$, at the glass transition temperature of the soft phase decreases with increasing hard-segment content.

The modulus of the rubbery plateau and the elastic modulus increase with hard-segment concentration due to the reinforcing effect of the hard-segment domains. Inversion of the continuous and dispersed phase may have occurred at a hard-segment content of about 45–50 wt%.

Dielectric spectroscopy is a complementary technique, which can detect the interfacial region in polyurethanes based on non-polar soft segments. The relaxation attributed to the interfacial region increases with increasing hard-segment content.

The influence of phase separation on different levels has been investigated by evaluating the properties of two formulations based on semicrystalline hard phases:

(i) Premature macrophase separation during a low reaction rate limits the molecular weight of macromolecules. Long hard segments are produced and crystallized in a poorly organized structure, which tend to toughen the material.

(ii) Rapid polymerization limits the amplitude of the macrophase phenomenon. Intermediate properties are obtained in this case.

(iii) Bulk polymerization produces low-molecular-weight species, but also some high-molecular-weight polymers. The distribution and composition in this case are the broadest. Premature macrophase separation during the reaction limits phase segregation on the molecular level as determined by the heat capacity change at $T_g(S)$.

Dielectric spectroscopy also shows that macrophase separation involves a broader interfacial region, as well as a conduction phenomenon at low temperatures. The large increase in the dielectric losses for these two dielectric processes show quite well the differences in morphologies and properties introduced by different synthesis processes.

A third publication will relate how the use of emulsifiers can control the synthesis in bulk and how dielectric spectroscopy can be used to monitor such phase separations.

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