Synthesis and properties of polyurethanes based on polyolefine: 1. Rigid polyurethanes and amorphous segmented polyurethanes prepared in polar solvents under homogeneous conditions

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(Received 19 September 1989; accepted 12 February 1990)

Pure hard-block polyurethanes and amorphous segmented hydrogenated polybutadiene (H.PBD)-based polyurethanes have been synthesized under homogeneous conditions in solution. All amorphous semi-crystalline pure hard blocks show a glass transition temperature, T_g, detected by differential scanning calorimetry (d.s.c.), depending on the nature of the diisocyanate and of the chain extender. Segmented amorphous H.PBD polyurethane exhibits two glass transitions: a soft phase $T_g(S)$ and a hard phase $T_g(H)$. Thermal treatments show rearrangements in the two-phase materials. Quantitative evaluation of phase separation, as determined by the heat capacity change, $\Delta C_p(S)$, at the glass transition of the soft phase, $T_g(S)$, shows that the phase separation of the soft segments is in the range 85–95%. These particular non-polar soft segments force the polar hard segments in the hard phase to be well organized due to inter-urethane hydrogen bonding, which produces a higher $T_g(H)$ in the segmented polyurethanes than the T_g of the pure hard blocks. The morphology of such polyurethanes with non-polar soft segments can be well characterized by dielectric measurements. Dielectric spectroscopy is in good agreement with d.s.c. results. A third transition between the soft and hard phase transitions has been detected. This relaxation is attributed to the mixed interfacial region. Increasing the hard-segment content increases this interfacial region.

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

INTRODUCTION

Segmented polyurethanes are linear block copolymers which are obtained from the reaction of three monomers: a macroglycol, a diisocyanate and a low molecular weight diol. The macroglycols are hydroxy-terminated polyesters, polyethers, polyalkyls or polysiloxanes with molecular weight between 500 and 5000. The hard segments are essentially urethane oligomers of two monomers, diisocyanates and diols, which are connected to soft segments through urethane linkages. Diisocyanates such as 4,4′ methylene bis(*p*-phenyl isocyanate) (MDI) and isomeric blends of toluene diisocyanate (TDI) are frequently used. 1,4-butanediol (BDO) is the most commonly used chain extender and provides the optimum properties.

Most segmented polyurethanes are prepared from a two-step method where the macroglycols are end-capped with an excess of diisocyanates, followed by chain extension with stoichiometric amounts of diols. In the final polymer, the hard and soft segments tend to segregate, due to their immiscibility, and produce a phase-separated morphology of hard-segment-rich and soft-segment-rich phases[1]. This two-phase structure gives rise to the interesting and useful properties of these materials.

But, in fact, segmented polyurethanes can also be polymerized under a wide variety of conditions leading to different distributions of the molecular weight hard segment length and composition. The effect of changing these distributions on sample properties and morphology are not well understood because of the difficulties in obtaining accurate experimental characterization of the distributions[2–4]. Peebles[5,6] has shown that under ideal conditions, and with 100% conversion, the distribution of the hard segment lengths follows the most probable distribution.

Several investigations have indicated that compositional heterogeneity in segmented polyurethanes can be caused by premature phase separation. Macosko and

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0032-3861/91/0200343-10

co-workers[7–9] showed, by using viscosity and turbidity measurements on a one-step polyether polyurethane polymerization in bulk, that phase separation occurred when the average hard-segment block length was ≈ 1.3. In this system, phase separation probably occurs due to segregation of longer hard segments either because they become immiscible with the soft segments as their length increases or because of their propensity to crystallize. MacKnight and co-workers[10–12] have provided strong evidence for the occurrence of macroscopic phase separation during a two-step polymerization in bulk of polybutadiene-based polyurethanes. They observed that, when the chain extender, 1,4-butane diol (BDO), was added in the second step of the reaction, it formed a separated phase immediately. This behaviour was observed for both crystallizable and amorphous hard segments, indicating that the cause of phase separation was not crystallization but the initial immiscibility of the reactants. These materials exhibited two hard-segment glass transition temperatures, low molecular weights, broad molecular weight distributions, and poor mechanical properties. In fact, the samples could be thought of as blends of two polyurethanes with different stoichiometries.

The authors suggested a scheme for the polymerization where the diisocyanate TDI diffused into BDO droplets and reacted to produce regions of virtually pure hard-segment polymer. The isocyanate-capped macroglycols could not readily diffuse into the BDO droplets and thus reacted primarily at the boundary between the two phases or by diffusion of BDO into the soft-segment rich phase.

Cooper and co-workers[13–16] have developed a Monte-Carlo simulation utilizing several simplifying assumptions proposed previously by Peebles[5,6]. The model calculates the molecular weight and composition distribution of the final polymer and simulates fractionation of the polymer based on the composition. With this model, it was then possible to explore the potential effects of premature phase separation on these molecular weight and composition parameters. These effects are a limiting of the degree of polymerization in each phase, which is presumably due to the stoichiometric imbalance of reactants in the two phases, and also a broadening of the composition distribution and the molecular weight distribution.

Macroscopic phase separation during a two-step polymerization can be suppressed in solution by using a suitable solvent. Bengston *et al.*[12] have synthesized a series of polybutadiene-based polyurethanes in tetrahydrofuran (THF). The appearance of samples obtained from this solution polymerization differs from that of the bulk-polymerized samples. In the case of the solution, all of the samples were transparent to light and completely soluble in THF. Single hard- and soft-segment T_g values were observed, confirming the microphase nature of this system.

In conclusion, the morphological complexity of segmental polyurethanes can be interpreted by taking into account the domain formation due to the segregation phenomena on different levels, namely macrophase and microphase separation (molecular scale). The polyalkyl-based polyurethanes exhibit a high level of macrophase separation when they are prepared in bulk and a high level of microphase separation when they are prepared in solution under homogeneous conditions. These effects are attributed to a large difference in their segmental structure and polarity as well as the absence of intersegmental hydrogen bonding. For good properties (mechanical and dielectric behaviour, moisture sorption, etc.), the challenge is to obtain a high level of microphase separation for bulk prepared polyurethanes.

The various results in the literature point out the difficulty in obtaining morphological information with only one technique. Dielectric spectroscopy is a complementary technique to those mentioned in the literature such as differential scanning calorimetry (d.s.c.), dynamical mechanical analysis, small-angle X-ray scattering or electron microscopy, which can be used to study the nature of molecular motions in polymer systems. For instance, despite the non-polar nature of the 1,4-polybutadiene-1,2-polybutadiene (PBD) diblock copolymer, it was recently found[17] that both glass transitions and secondary transitions associated with the individual blocks and the effects of polymer–polymer mixing on these relaxations can be resolved by dielectric spectroscopy. Most of the studies on polyurethanes in this field have been done on polyether or polyester segmented polyurethanes[18,19]. In particular Delides *et al.*[18] discussed the dielectric data as two relaxation processes: the higher frequency process (low temperature) is attributed to motion of the ester chain forming the soft phase, while the low frequency process (high temperature) is associated with molecular motion of chains in the mixed interfacial region. From this point of view, polyalkyl-based polyurethanes would be a good model for the study of the interface by dielectric spectroscopy.

Few studies have been reported on polyolefin-based polyurethanes[20]. As for those based on polybutadiene, hydrogenated polybutadiene-based polyurethanes offer the advantage of low moisture permeability, especially for adhesives and electrical coating applications, and they also offer a better resistance to oxidation. The aim of this work is to control the morphology of such bulk prepared polyurethanes. In this first paper in the series, we report on the synthesis and properties of rigid polyurethanes and of amorphous segmented polyurethanes based on hydrogenated polybutadiene. In the second paper[35], we will present a study on the same polyurethanes with semi-crystalline hard segments, prepared in solution and in bulk. Finally, in the third paper[36], we will present work on synthesized polyurethanes in bulk in the presence of different emulsifiers with the purpose of minimizing the effects of the premature macrophase phenomenon.

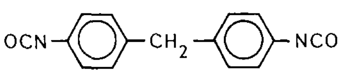
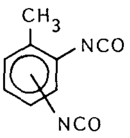
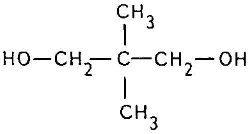
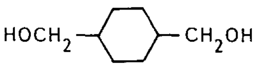
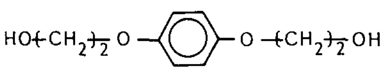
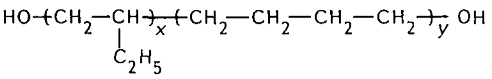
EXPERIMENTAL

Materials and synthesis

The formulae, suppliers and molecular weight of the materials are listed in *Table 1*. The various products were used as received. Hydrogenated polybutadiene (H.PBD) was degassed at 60°C for 24 h before use.

Pure hard-segment copolymers were prepared by solution polymerization. The pure 4,4′-methylene bis(*p*-phenyl isocyanate) (MDI), the 2,4- and 2,6-toluene diisocyanate (TDI) and the chain extender were dissolved in tetrahydrofuran (THF) at room temperature. A catalyst, dibutyl tin dilaurate (DBTDL) (0.01 wt% of the reactants), was then added and the solution was brought to 50°C for 3 h with mechanical stirring. The solution remained clear throughout the reaction, except for the semi-crystalline hard copolymers. The products were precipitated in methanol and dried under vacuum at 60°C for 24 h.

Table 1 Characteristics of products used for the polyurethane synthesis

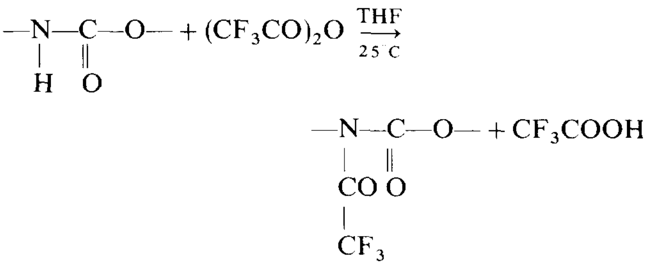
(a) Diisocyanates:		
4,4'-Methylene bis(*p*-phenyl isocyanate) (Bayer)		MDI $M = 250$ g mol^{-1}
2,4- and 2,6-Toluene diisocyanate (Fluka)		TDI $M = 174$ g mol^{-1}
(b) Chain extenders:		
1,4-Butanediol (Aldrich)	$HO{+}CH_2{+}_4 OH$	BDO $M = 90$ g mol^{-1}
2,2-Dimethyl-1,3 propanediol (or neo-pentyl glycol) (BASF)	 $HO-CH_2-C(CH_3)_2-CH_2-OH$	NPG $M = 104$ g mol^{-1}
1,4-*Cis–trans* cyclohexyl dimethanol (Aldrich)		CHDM $M = 144$ g mol^{-1}
Hydroquinone di(β-hydroxyethyl)		HQEE $M = 198$ g mol^{-1}
(c) α-ω Hydroxy terminated oligomer: Hydrogenated polybutadiene $x = 34$, $y = 4$ (Nippon Soda)	 $HO{+}CH_2-CH(C_2H_5){+}_x{+}CH_2-CH_2-CH_2-CH_2{+}_y OH$	HPBD $\bar{M}_n = 2100$ $\bar{M}_w/\bar{M}_n = 1.5$ $\bar{F}_n = 1.8$

Segmented polyurethanes were prepared via a two-step reaction. Taking into account the oligomer's true functionality, a reaction is carried out between one mole of the macroglycol and an excess of x moles of diisocyanate in bulk at 80°C for 4 h under vacuum. Then 200 ml of THF was added at room temperature. Then $x-1$ moles of chain extender and catalyst were added and the reaction continued for 3 h at 50°C. The total concentration of polymer in THF was $\approx 10\%$. All of the solutions remained clear throughout the reactions. The polymer was precipitated in methanol and dried under vacuum for 24 h at 60°C. Films were cast on glass dishes from a solution of the redissolved polymer in THF, at room temperature under a dry air purge at 60°C for one week under vacuum. Film thickness was varied, depending on the test requirement. All films were transparent to visible light.

Experimental method

Waters high performance liquid chromatography (h.p.l.c.) apparatus equipped with a refractometric (RI) and an ultraviolet (u.v. at 254 nm) detector was used for size exclusion chromatography analysis (s.e.c.). We used four microstyragel columns, 10^3 Å*, 500 Å, 100 Å and 100 Å. The solvent (THF) flow rate was 1.5 ml min^{-1}. All molecular weights reported are based on a calibration curve from polystyrene standards.

A chemical modification can be used to improve the solubility of semi-crystalline polymers such as polyamides[21,22] or polyurethanes[23] in common solvents. The reaction is carried out at room temperature in a 5 wt% THF solution with a large excess of trifluoroacetic anhydride:



$$-N(H)-C(=O)-O- + (CF_3CO)_2O \xrightarrow[25^\circ C]{THF} -N(COCF_3)-C(=O)-O- + CF_3COOH$$

Semi-crystalline hard copolymers were modified by trifluoroacetic anhydride at room temperature. The mixture is stirred until the solution becomes clear. We have shown[24] that the reaction kinetics and yield depend on the structure of the polyurethane and on the nature of the solvent. Contrary to polyamides, the modification is partial but the reaction products are stable under ambient conditions. However, all polyurethanes cannot be solubilized by this technique.

A Mettler Inc. (TA 3000) microcalorimeter was used for the d.s.c. Temperature and enthalpy calibrations were made by using indium or other organic compounds with known T_m and enthalpy. A heating rate of 7.5°C min^{-1} was used to assure thermal equilibrium of the d.s.c. cell.

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* 1 Å = 10^{-1} nm

Dry argon was used as the purge gas. The sample weights were 15–20 mg. Scanning from −170°C gave an excellent baseline for ΔC_p determination. The glass transition temperature was taken as the onset of the phenomena.

Dielectric measurements were made with a Polymer Laboratory cell connected to Hewlett–Packard 4274A and 4275A multifrequency Impedance Capacity Resistance (LCR) meters in the temperature range −70 to 180°C and frequencies of 100 Hz–100 kHz with a heating rate of 1°C min^{-1} under dry nitrogen.

RESULTS AND DISCUSSION

Size exclusion chromatography and differential scanning calorimetry

A series of hard block polyurethanes (rigid polyurethanes) of high molecular weight were synthesized in solution (THF). *Table 2* gives the s.e.c. and d.s.c. data.

Rigid polyurethanes based on MDI with BDO, HQEE or CHDM are semi-crystalline, but a glass transition of the amorphous phase could be observed during a second scan after an initial scan up to 250°C followed by a quench (*Figure 1*). The different melting temperatures will not be discussed here, but we note that the -(MDI–CHDM)- hard polyurethane stays amorphous after the first treatment. The other polyurethanes, -(MDI–NPG)- and -(TDI–BDO)-, are amorphous. For -(MDI–BDO)- and -(TDI–BDO)-, we have a good agreement between the glass transition temperatures obtained by us and those reported in the literature[12,25,26]. The lower T_g was obtained for -(TDI–BDO)- and the higher T_g for -(MDI–CHDM)-. Contrary to what we have suggested previously[20] for low molecular weight hard blocks, the ΔC_p's at T_g for high molecular weight hard-block polymers are different from zero.

Amorphous segmented polyurethanes based on hydrogenated polybutadiene (H.PBD), with different amorphous hard blocks were also synthesized (*Table 3*). The hard segment content was defined by using the common definition: mass of chain extender and diisocyanate divided by the total mass. With different hard blocks, molar composition has been chosen to have a hard

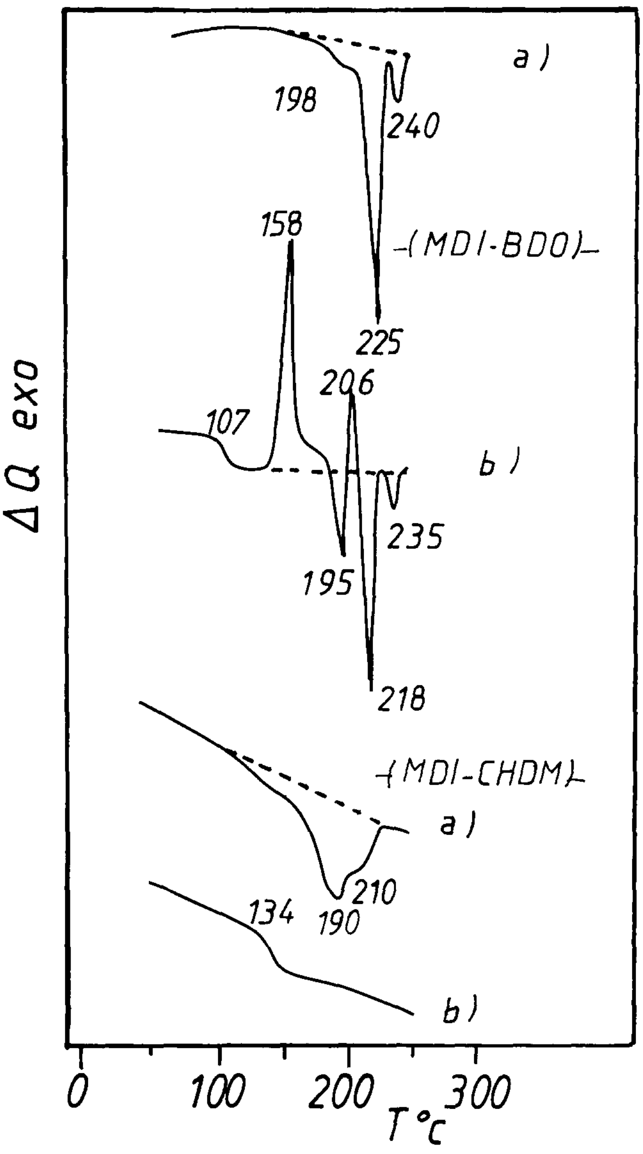

Figure 1 D.s.c. thermograms of two hard copolymers: (a) first scan, (b) second heating after quenching

Table 2 Molecular weight and transitions of different crystalline and amorphous hard copolymers

Hard copolymers	$\overline{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\overline{M}_w$ ($\mathrm{g\,mol^{-1}}$)	T_g (°C)	ΔC_p ($\mathrm{J\,g\,K^{-1}}$)	T_m (°C)
-(MDI–BDO)-$_n$	24300[a]	41300[a]	107[b]	0.39	198–225–240
-(MDI–HQEE)-$_n$	not soluble		98[b]	0.40	215–245
-(MDI–CHDM)-$_n$	48200	91600	134[b]	0.30	190–210
-(MDI–NPG)-$_n$	11600	22100	94	0.34	Amorphous
-(TDI–BDO)-$_n$	17800	41600	72	0.33	Amorphous

[a] Soluble in THF after chemical modification by trifluoroacetic anhydride
[b] Results from the second scan, after an initial scan up to 250°C followed by a quenching

Table 3 S.e.c. results of amorphous segmented polyurethanes based on hydrogenated polybutadiene with different hard segments

Polymer	Molar ratio	HS (wt%)	$\overline{M}_n$ (HS) (calc.)	$\overline{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\overline{M}_w$ ($\mathrm{g\,mol^{-1}}$)
HPBD–TDI–BDO	1–4–3	30	867	18000	42000
HPBD–MDI–NPG	1–3–2	30	843	32800	107300
	1–5–4	41	1540	26500	90400
	1–7–6	50	2248	25900	76600
HPBD–MDI–CHDM	1–3–2	32	940	22500	56300

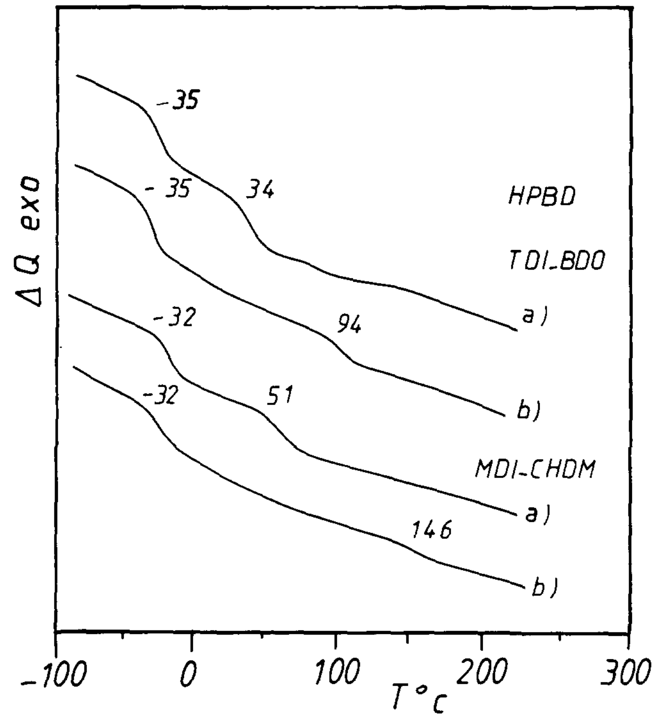

Figure 2 D.s.c. thermograms of two segmented polyurethanes (30% HS content): (a) first scan; (b) second heating after quenching

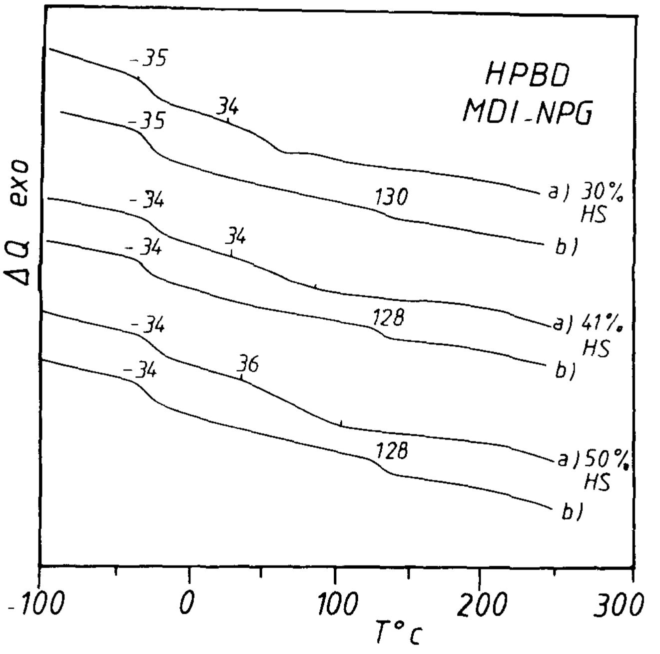

Figure 3 D.s.c. thermograms of three segmented polyurethanes based on MDI–NPG: (a) first scan; (b) second heating after quenching

segment content of ≈30 wt%. For MDI–NPG we modified the formulation to change the percentage and the length of hard segments. The two-step solution polymerization is a procedure for which Peebles[6] has devised a method to calculate the average hard block length and hence the average molecular weight. The reactivity ratio of the two isocyanate groups was taken to be $k_1/k_2 = 3$ for MDI and $k_1/k_2 = 12$ for TDI.

(1) *Figures 2* and *3* show d.s.c. scans for (a) the initial heating run and (b) the heating run after quenching from the melt. The results are given in *Table 4*.

The H–PBD–MDI polyurethane without chain extender and with 11% by weight of MDI hard blocks, exhibit only one glass transition temperature which is at −32°C. The two-phase behaviour of all of the other polymers is clearly shown in *Figures 2* and *3*, where two glass transitions are observed. Since the hard segments are amorphous, the driving force for phase separation must arise from the large degree of immiscibility between the polar hard segments and the non-polar soft segments. Furthermore, in these samples there is also no possibility of hydrogen bonding between hard and soft segments to enhance miscibility. However, chain extenders are necessary for phase segregation since they increase the chain length and the number of hydrogen bonds in the hard domains.

(2) The glass transitions at the lower temperature range, $T_g(S)$, are from the H.PBD rich phase. The closeness of these $T_g(S)$ to that of hydroxy-terminated H.PBD (−45°C) and to that of the phenylisocyanate end-capped H.PBD (−38°C) indicates that phase separation is nearly complete. A quantitative evaluation of the degree of phase segregation in segmented linear polyurethanes is possible by measuring the heat capacity change, ΔC_p, at the glass transition of the soft phase[20]. The heat capacity change, $\Delta C_p(S)$, per gram of soft segment in the polyurethane is compared with the $\Delta C_p^0(S)$ of the pure soft phase measured for the oligomer. $\Delta C_p^0(S)$ is equivalent to the ΔC_p per gram of the soft segments at the glass transition in totally phase separated polyurethanes, if restrictions resulting from the incorporation into the polymer are neglected. The ratio $\Delta C_p(S)/\Delta C_p^0(S)$ corresponds to the percentage segregation of the soft blocks; $\Delta C_p^0(S) - \Delta C_p(S)$ corresponds to the quantity of soft segments located out of the soft phase and, therefore, in the hard domain or at the interphase. These dispersed soft segments do not relax at the same temperature as in the continuous soft phase.

Since the amount of hard blocks in the soft phase is small, it is reasonable to determine $\Delta C_p(S)$ by neglecting the heat capacity change due to short hard block impurities that are within the soft phase. Regarding the $\Delta C_p(H)$ of the hard microdomains (*Table 4*), this assumption modifies $\Delta C_p(S)$ to <0.01 J g^{-1} K^{-1}. $\Delta C_p(S)$ is also assumed to be temperature independent; this second assumption is generally accepted in the case of polymer–polymer blends whose T_g shift is not important.

In previous work, we have taken $\Delta C_p^0(S)$ as the ΔC_p of the α,ω hydroxy terminated oligomer[20]. Koberstein *et al.*[27,28] have shown a good correlation between our d.s.c. results and small-angle X-ray scattering determination results. But, from *Table 4*, we can also take $\Delta C_p^0(S)$ as the ΔC_p of the single phase H.PBD–MDI copolymer; the difference would be $<4\%$. In contrast, the ΔC_p of the phenylisocyanate end-capped oligomer is different, lower than the previous one, and thus cannot be taken as $\Delta C_p^0(S)$.

We can observe in *Table 4* a small increase of $\Delta C_p(S)$ after the first run. Morphological rearrangements are possible. Taking account of the $\Delta C_p(S)$ values of the second run, we can determine the percentage segregation of the soft segments for the segmented polyurethanes. With polyurethanes based on MDI–NPG and on TDI–BDO, we obtain values of $\Delta C_p(S)/\Delta C_p^0(S) = 0.80$–$0.88$ in the same order as the values obtained previously[20] for semi-crystalline H.PBD polyurethanes with MDI–BDO as hard segment. The higher value obtained with

Table 4 Data of d.s.c. measurements ($q = 7.5°C\ min^{-1}$)

		Soft phase		Hard phase	
Polymer	HS (wt%)	T_g (°C) (±1)	ΔC_p ($J\ g\ K^{-1}$) (±0.01)	T_g (°C) (±1)	ΔC_p ($J\ g\ K^{-1}$) (±0.01)
HPBD		−45	0.43		
HPBD–PhI		−38	0.33		
HPBD–MDI	11	−32	0.42		
HPBD–TDI–BDO	30	−35[a]	0.22	34[a]	0.13
		−35[b]	0.26	94[b]	0.10
HPBD–MDI–NPG	30	−35[a]	0.22	36[a] (46)[c]	0.14
		−35[b]	0.24	130[b]	0.06
	41	−34[a]	0.20	34[a] (60)[c]	0.19
		−34[b]	0.22	128[b]	0.08
	50	−34[a]	0.17	36[a] (65)[c]	0.19
		−34[b]	0.19	128[b]	0.11
HPBD–MDI–CHDM	32	−32[a]	0.26	51[a]	0.10
		−32[b]	0.27	146[b]	0.06

[a] First run up to 250°C

[b] Second run after the first followed by a quench. T_g is taken to be the onset of the phenomena except where denoted by [c]

[c] Midpoint of the transition

MDI–CHDM hard segment, $\Delta C_p(S)/\Delta C_p^0(S) = 0.92$–$0.95$, is similar to those obtained for polyurethanes based on xylenediol or on diamines.

(3) The glass transitions at higher temperatures, T_g(H), are from the hard-block rich phase. For each polyurethane only one T_g(H) can be observed: at 34°C for TDI–BDO and MDI–NPG hard segments and at 51°C for MDI–CHDM hard segments. These values are lower than that measured for corresponding high molecular weight hard polymer (*Table 2*). For MDI–NPG-based polyurethanes, the onset of the change in the baseline height does not depend on the hard-segment content but on its breadth, noted by the midpoint of the transition increases (*Table 4*). Fu *et al.*[4] have observed an increase in T_g(H) as the hard segment length increases but only for monodisperse hard blocks. Polydisperse blocks or blends of monodisperse blocks exhibit a broader transition between the two transitions of the pure blocks. Our results can be explained by this observation.

After the initial run, ΔC_p(H) at T_g(H) decreases, which is in good agreement with the fact that, at the same time, ΔC_p(S) at T_g(S) increases. But most important is the fact that after the initial scan there is a large increase in the glass transition temperature of the hard microphase, T_g(H), of ΔT = 60–90°C, depending on the nature of hard segments. For all segmented amorphous polyurethanes, T_g(H) becomes higher than the T_g of the corresponding high molecular weight hard polyurethane. The comparison is given in *Table 5*.

To be sure that it is not an artefact, different isothermal treatments have been done at T_a on the H.PBD segmented polyurethane based on TDI–BDO. S.e.c. and d.s.c. results are given in *Table 6*. All treatments result in the same value of T_g(H), 94°C. A single thermal treatment on MDI–NPG-based polyurethanes give a similar result: T_g(H) = 130°C.

These results have not been observed previously. On the contrary, Bengston *et al.*[12] noted during their studies that the mechanical properties of similar polyurethanes based on polybutadiene were unaffected by their thermal history. They suggested that no thermally activated phase mixing, which can alter the sample, could occur. And they attributed the absence of thermal history effects to the lack of urethane bonding to the PBD soft segments by the hard-segment N–H groups. In our work, we conclude that, from d.s.c. and also by dielectric spectroscopy (next section), we observe a different behaviour.

Table 5 Comparison between the glass transition temperatures of high molecular weight hard polyurethanes and of the hard phase in segmented polyurethanes

Hard blocks	T_g (high $\overline{M_n}$) (°C)	T_g(H) (in segmented PU) (°C)	$T_g(H)/T_g$
TDI–BDO	72	94	1.06
MDI–NPG	94	130	1.10
MDI–CHDM	134	146	1.03

We have to keep in mind that the initial isothermal treatment of our samples is done at a low temperature T_a = 60°C and it is not surprising to observe morphological rearrangements at higher temperature. These rearrangements are thermally actived. At a lower $\Delta T = T_a - T_g(H)$, the rate of rearrangements is low but it increases when ΔT increases (*Table 6*). This behaviour has not been observed in the one-phase high molecular weight hard polyurethanes but is typical of two-phase systems. So, the initial low value of T_g(H) for different segmented polyurethanes on the first run could imply that a substantial fraction of soft-segment units and short hard segments, such as MDI, are mixed within the hard microdomains. This fraction can be evaluated with the increase of ΔC_p(S) at T_g(S) after the first scan. For every case the fraction is ≈10–15%.

For polypropylene oxide-based polyurethane, the microphase mixing transition (or upper critical solubility temperature, u.c.s.t.) between hard and soft microdomains has been estimated to be ≈150–190°C (References 27–29). We are sure that this transition is at a higher temperature for H.PBD-segmented polyurethanes. So, all the thermal and/or mechanical treatments done on our polyurethanes are in the two-phase region. In *Figure 4*, we try to model the coexistence curve

Table 6 Structural effects of thermal treatments on amorphous segmented polyurethanes, HPBD–TDI–BDO, 30% of hard blocks

Annealing					
T_a (°C)	t_a (h)	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w$ (g mol^{-1})	T_g(S) (°C)	T_g(H) (°C)
	Initial film	18 000	42 000	−35	34
(60)	(24)				
140	24	22 600	53 800	−35	75
	48	18 000	42 200	−35	94
150	2			−35	36
	12	22 800	48 200	−35	94
	24	16 400	38 300	−35	94
170	1	19 200	45 000	−35	74
	2	20 600	47 200	−35	94

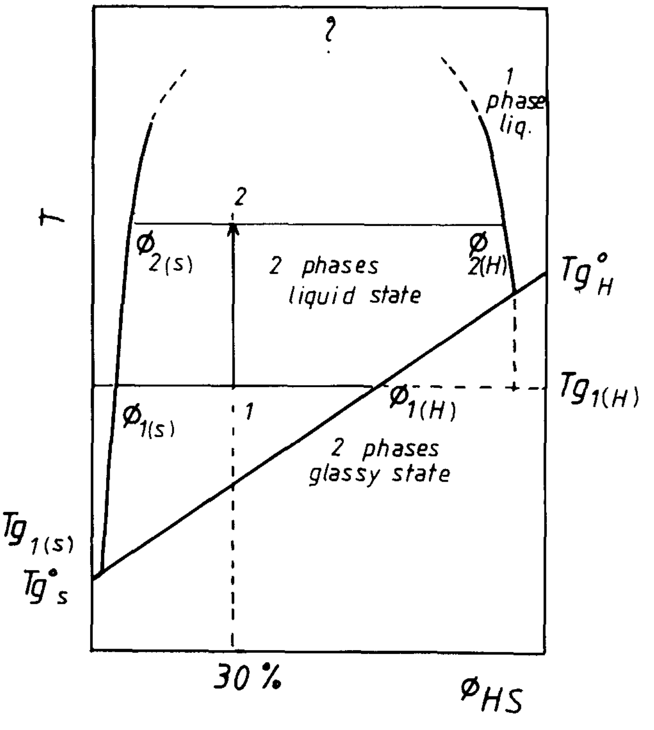

Figure 4 Phase separation and glass transition *versus* composition for an amorphous segmented hydrogenated polybutadiene polyurethane (considered as a binary mixture with covalent bond between components)

of the phase diagram between soft and hard segments. Since we have a complete immiscible system, the coexistence curve looks like two vertical straight lines near the axis with an hypothetical u.c.s.t. at a high temperature. We also plot a straight line between the two glass transition temperatures to model the glass transition diagram of a single-phase system. It is clear in this figure that for our samples, when we remove the solvent at 20°C and again at 60°C, phase separation is stopped by vitrification ϕ_1(H) and we have a two-phase system which is not in equilibrium. The phase separation phenomena is truncated by the glass transition process. This phenomenon is common in segmented polyurethanes and it can explain the discrepancies observed in the literature in transitions and morphologies.

At $T_a > T_g^0$(H), equilibrium phase separation becomes possible, ϕ_1(H) tends to ϕ_2(H) and T_g(H) increases from T_{g_1} to T_{g_2}. On the other hand, since we have an immiscible system (two vertical lines for the coexistence curve), the phase composition of the soft phase does not depend on the annealing temperature $\phi_1(S) = \phi_2(S)$.

But if all these effects explain well an increase of T_g(H) with annealing, they cannot explain a higher value than the T_g of the high molecular weight hard polyurethane.

At an annealing temperature of $T_a > T_g^0$(H) for the hard polyurethanes, the H.PBD blocks attached to ends of each hard segment are highly mobile and the viscosity of the two-phase system is low. So we can imagine a structured amorphous liquid state. The driving forces for phase segregation, i.e. the large degree of immiscibility between the soft and the hard blocks and the tendency to form hydrogen bonds only between hard segments, force the hard segments to engage in a liquid-like contact with other hard segments in the same or neighbouring chains. This process will give rise to a well defined three-dimensional physical network which would 'melt-out' at higher temperatures. Some studies proposed that there should be an amorphous phase transition at $T > T_g$ which Boyer[30] denotes T_{11}; it is a molecular level transition-relaxation associated with the thermal disruption of segment–segment contacts, called 'segmental melting' by Boyer. He proposed the following relationship between T_g and T_{11}: $T_{11}/T_g = 1.20 \pm 0.05$, but for molecular weights above the oligomeric range and preferably above $\bar{M}_c$. T_{11} is supposed to involve motion of the entire molecule.

This transition T_{11} and the structure of the amorphous state are very controversial. Many criticisms have been formulated against T_{11} (see Reference 30 and references cited therein). But this transition has also evolved to explain the existence of thermally reversible gels from atactic polystyrene in relatively non-polar solvents such as toluene[31]. Boyer[30] also proposed that a $T > T_g$ relaxation for amorphous ionomers is indeed typical of T_{11}. The results we observed for amorphous polyurethanes can belong to this general category of $T > T_g$ phenomena. Strong hydrogen bonding only between hard segments should promote thermally reversible segment–segment contacts above T_g; and the great immiscibility of the two phases forces the existence of a well defined order inside the hard microdomains.

Dielectric measurements

Figure 5 shows different loss peaks for the initial cast films (low temperature treatment $T_a = 60°C$) of different amorphous segmented polyurethanes.

The single-phase system H.PBD–MDI, without chain extenders, has only one symmetrical and well defined relaxation peak with a maximum $\tan\delta = 5 \times 10^{-2}$ at 23°C (frequency = 1000 Hz). This relaxation peak is associated with the transition observed at −32°C by d.s.c. with a heating rate of 7.5°C min^{-1} and indicates a cooperative motion of the non-polar and polar segments. In comparison with polyester-based polyurethanes[18,19], the intensity of the peak is twenty times lower ($\tan\delta = 5\times10^{-2}$ compared to 1). But due to the presence of dipoles of the urethane linkages in the non-polar H.PBD, the peak is four times those observed for 1,4 and 1,2 PBD[17].

In contrast with H.PBD–MDI, the two-phase polyurethanes exhibit a broad peak with a shoulder around 20°C and a maximum at 70–120°C, depending on the nature of the hard segments and on the hard segment content. Since the shoulder, α_S, can be related to the transition of the soft phase T_g(S), we do not believe that the main relaxation can be only associated with the transition of the hard-segment T_g(H). The different transitions and relaxation temperatures are given in *Table 7* with their apparent activation energies.

Figures 6 and *7* give the loss peaks before and after an annealing at $T_a > T_g$(H) for amorphous polyurethanes based on TDI–BDO and MDI–NPG with different hard segment contents. We also give for comparison, the behaviour of a blend prepared by mixing in solution (THF) 80 wt% of the single-phase soft H.PBD–MDI polyurethane with 20% of the single-phase hard polyurethane TDI–BDO. The total amount of hard blocks, defined previously, is around 30 wt%. After evaporation of the solvent the film obtained is opaque, indicating macrophase separation. The blend exhibits three dielectric features: two relaxation processes and a strong increase of the dielectric losses at higher temperatures. The two relaxation peaks are separated and well defined.

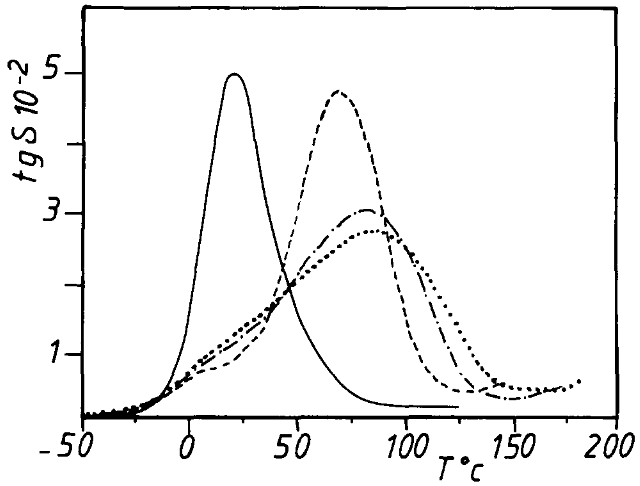

Figure 5 Comparison of dielectric loss spectra of amorphous segmented polyurethanes: ———, (H.PBD–MDI)$_n$; – – –, H.–PBD–TDI–BDO; ····, H.PBD–MDI–CHDM; —·—, HPBD–MDI–NPG, initial films

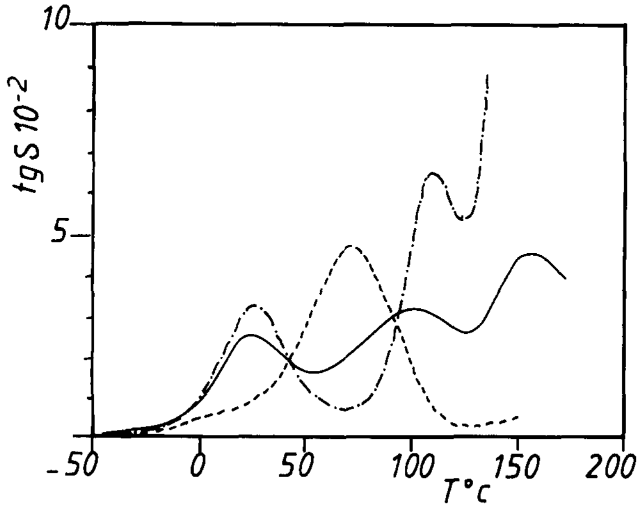

Figure 6 Comparison of dielectric loss spectra between (—·—) a blend (H.PBD–MDI)$_n$ plus (TDI–BDO)$_n$ and – – –, H.PBD–TDI–BDO initial film; ———, H.PBD–TDI–BDO after thermal treatment

Table 7 Characteristics of the dielectric relaxation of different amorphous segmented polyurethanes and copolymer blends

	α(S) relaxation			α(H) relaxation		
Samples	T_g (d.s.c) (°C)	$T_{\alpha,\max}$ (1 kHz) (°C)	E_a (kJ mol^{-1})	T_g (d.s.c.) (°C)	$T_{\alpha,\max}$ (1 kHz) (°C)	E_a (kJ mol^{-1})
(H.PBD–MDI)$_n$	−32	23	120	–	–	–
Blends						
80 (HPBD–MDI)$_n$ and 20 (TDI–BDO)	−32	27	120	72	110	250
20 (MDI–NPG)$_n$	−32	26	125	62	114	265
Segmented PU, before treatment						
H.PBD–TDI–BDO	−35	≈20	–	34	70	170
H.PBD–MDI–CHDM	−32	≈20	–	51	87	190
H.PBD–MDI–NPG.30%	−35	≈20	–	34	83	170
H.PBD–MDI–NPG.40%	−34	≈20	–	34	102	200
H.PBD–MDI–NPG.50%	−34	≈20	–	36	117	200
Segmented PU, after treatment[a]						
HPBD–TDI–BDO	−35	25	120	94	155	140
					(α′) 100	190
H.PBD–MDI–NPG.30%	−35	26	120	130	–	–
					(α′) 157	260
H.PBD–MDI–NPG.40%	−34	26	120	128	–	–
					(α′) 155	260
H.PBD–MDI–NPG.50%	−34	27	120	128	–	–
					(α′) 156	260

[a] Thermal treatment for 24 h at 150°C

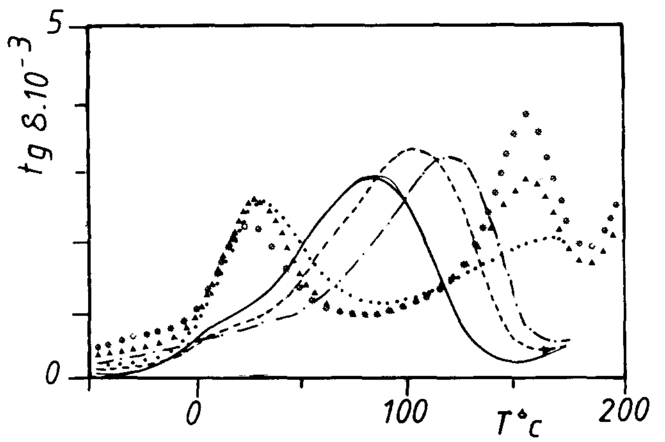

Figure 7 Comparison of dielectric loss spectra of polyurethanes based on MDI–NPG before and after a thermal treatment. 30% HS: ——, initial; ☆, after; 40% HS: ---, initial; ▲, after; 50% HS: —·—, initial; ●, after

It is clear that the first relaxation process is related to the relaxation α_S of the single-phase soft polyurethane from the observation that its amplitude is lowered from 5×10^{-2} to 3×10^{-2}. The mobility of the chains seems hindered by the presence of hard polyurethane. It can be concluded that some interactions between the high molecular weight, hard segments and the polar isolated groups of MDI along the polyalkyl chain are responsible for this phenomenon. The hard polyurethanes contribute to the α_H relaxation, the second relaxation of the blend. Finally, high dielectric losses can be due to Maxwell–Wagner–Sillars polarization in this macro-heterogeneous system.

For TDI–BDO-based polyurethanes, the broad peak and the shoulder observed earlier are decomposed into three relaxation peaks after annealing. The first, α_S, at 25°C is associated with the T_g(S) of the soft-segment microphase. The amplitude of this peak is higher than for the initial film. It could be due to the fact that annealing has liberated the more flexible chains embedded in the mixed interfacial region which contributed to the broad peak of the initial film, or it could be due to a modification of the morphology with a decrease of the interphase area. Cooper *et al.*[32] have found that for polybutadiene-based polyurethane at 30 wt% hard segment content, the hard segment phase is dispersed in a matrix of soft segments. During annealing, in a low viscous medium a coalescence of particles is possible, increasing their mean diameters and decreasing the surface area of the disperse phase.

The second relaxation, α_H, at 155°C can be associated with the T_g(H) of the well organized hard microphase. The shift in temperature of the dielectric peak, compared with its position in the blend, reflects the difference in the value of T_g obtained by d.s.c.

The third relaxation, α'_H, with a maximum around 100°C, which is not present in the blend, can be attributed to a mixed interfacial region. The amplitude of this process is comparable to that observed for the relaxation of the soft microphase and, therefore, it is reasonable to suppose that the process is a dipole relaxation rather than an interfacial polarization phenomenon. The latter will usually give rise to amplitudes which are several orders of magnitude larger than those observed for dipolar relaxation processes. This relaxation was in fact superimposed on the broad α_H relaxation observed on the initial film. During annealing, the hard segments have rearranged themselves to form organized hard domains which relax at high temperatures and others formed a mixed interfacial region. This mixed region gives a dielectric response at quite a high temperature, $T =$ 100°C, compared with $T = 70$°C before annealing. Therefore, this intermediate phase between the soft phase and hard domains has better defined arrangements in the final material.

It is important to mention that there is no interfacial region in the blend because there are no chemical linkages between the two phases. A similar relaxation process of a mixed interfacial region has been previously proposed by Pethrick *et al.*[18,33] for polyester-based polyurethanes, but the relaxation was not as well defined because of the polarity of both phases.

For MDI–NPG-based polyurethanes (*Figure 7*), annealing effects ($T_a > T_g$(H)) seem to be similar, but the higher T_g(H) (T_g(H) = 130°C) does not allow the appearance of the third relaxation α_H, attributed to the motion of dipoles in the well organized hard phase.

Before annealing, the breadth of α_H at the base becomes larger by increasing the hard segment content. This is in good correlation with the d.s.c. results: the start of the α_H relaxation is at the same temperature, but the top of the peak is shifted to a higher temperature. Thus, increasing the hard-segment content involves a weaker concentration of soft segments in the hard phase, indicating a higher degree of organization.

After annealing, only two out of three relaxations are visible in the range of temperature for our measurements. These two relaxations have the same position, indicating that the thermodynamical equilibrium has been reached by annealing. The amplitude of α_S in the three polyurethanes with different hard-segment contents has nearly the same value. Considering that the contribution of the polyalkyl chains is very weak compared with the dielectric loss of the urethane groups, we can conclude that the urethane concentration in the soft phase increases when the hard segment content increases. Concerning the relaxation α'_H, the peak maximum becomes higher by increasing the hard segment content. Assuming that the composition of the mixed interfacial region corresponding to this relaxation is the same for the three polyurethanes (same position of the peak), increasing the hard segment content increases this interfacial region.

A rodlike or lamellar structure was observed by Cooper *et al.*[32] in the polybutadiene–polyurethanes when the hard segment weight fraction was varied from 42 to 67%. The three-dimensional rod-like or lamellar morphology is bicontinuous with both phases interwoven, possessing high interconnectivity and explaining the increase of the mixed interfacial region.

It is difficult to compare the mobility of the dipoles via the apparent activation energies since the relaxations appear at very different temperatures. But for TDI–BDO-based polyurethanes, the relaxation associated with the mixed interfacial region has a lower apparent activation energy than the relaxation associated with the high molecular weight hard segments in the blend (*Table 7*), these two relaxations having their maximum in the same range of temperature. The difference in their molecular weights can explain this difference.

It is also difficult to compare the amplitude of the relaxation peaks, but the intensity of the relaxation α'_H attributed to a mixed interfacial region seems to be in the same range as that of the relaxation of the soft phase, α_S, or that of the hard phase, α_H. For comparison we can estimate the interfacial region from d.s.c. measurements:

(1) We have previously calculated the fraction of soft segments out of the soft phase, in the mixed interfacial region and in the hard phase, finding

$$\Delta C_p^0(S)W_S - \Delta C_p(S) \approx 8\% \qquad (1)$$

From equation (1) the contribution of the interface is underestimated because we have not taken into account the hard segments.

(2) MacKnight *et al.*[34] proposed the 'parameter *F*' to estimate the interfacial region:

$$F = \frac{W_S \Delta C_p(S) + W_H \Delta C_p(H)}{W_S \Delta C_p^0(S) + W_H \Delta C_p(H)} \qquad (2)$$

where $\Delta C_p^0(i)$ is the heat capacity change at T_g of the constituents before mixing, and $\Delta C_p(i)$ is the heat capacity change in the amorphous segmented polyurethane.

An infinitely sharp interface is therefore represented by an *F* value of 1. With the results from *Tables 2* and *4* we found *F* (or 1–*F*) in the range of 0.45–0.55 for all the products.

From the parameter *F*, the contribution of the interface is overestimated due to the use of two approximations: the use of the total weight fraction *W* in the numerator of equation (2) and the use of the value $\Delta C_p^0(H)$ of the high molecular weight hard polyurethane instead of the value for short, hard segments incorporated in the polymer.

However, these estimations from equations (1) and (2) indicate that the interfacial fraction can be important and can explain the relaxation $\alpha'(H)$ in dielectric measurements.

CONCLUSION

Amorphous segmented hydrogenated polybutadiene-based polyurethanes have been synthesized under homogeneous conditions in a polar solvent to prevent premature macroscopic phase separation. These segmented polyurethanes exhibit a high level of microphase separation even though a mixed interfacial region is seen with d.s.c. or dielectric measurements.

Amorphous segmented polyurethanes are used as model systems and are very useful for characterizing the effects of thermal history and annealing on the glass transition temperature of the hard phase. All of the thermal and mechanical treatments performed on these polymers are done in a two-phase system. At low temperatures, $T_a < T_g^0(H)$, phase separation can be stopped by vitrification. To obtain a system at equilibrium, it is necessary to anneal at $T_a > T_g^0(H)$.

Due to the large degree of immiscibility between the soft and hard segments, well defined three-dimensional physical networks can be obtained with a higher glass transition temperature $T_g(H)$ for the hard phase than the $T_g^0(H)$ of the single-phase system (rigid polyurethane).

We are now able to study segmented polyurethanes with more complex morphologies, with semi-crystalline hard segments[35], which are prepared in solution but also in bulk.

ACKNOWLEDGEMENTS

We thank the Société Industrielle d'Applications Nouvelles de Procédés de Moulage Industriels (SAMI) for supporting this work.

REFERENCES

1 Cooper, S. L. and Tobolsky, A. V. *J. Appl. Polym. Sci.* 1966, **10**, 1837

2 Harrel Jr, L. L. *Macromolecules* 1969, **2**, 607

3 Miller, J. A., Lin, S. B., Hwang, K. K., Wu, K. S., Gilson, P. E. and Cooper, S. L. *Macromolecules* 1985, **18**, 32

4 Fu, B., MacKnight, W. J. and Schneider, N. S. *Rubber Chem. Technol.* 1987, **59**, 896

5 Peebles, L. H. *Macromolecules* 1974, **7**, 872

6 Peebles, L. H. *Macromolecules* 1976, **9**, 58

7 Castro, J. M., Lopez-Serrano, F., Camargo, R. E., Macosko, C. W. and Tirrell, M. V. *J. Appl. Polym. Sci.* 1981, **26**, 2067

8 Castro, J. M., Macosko, C. W. and Perry, S. J. *J. Polym. Commun.* 1984, **25**, 83

9 Camargo, R. E., Macosko, C. W., Tirrell, M. V. and Wellinghoff, S. T. *Polym. Eng. Sci.* 1982, **22**, 719

10 Xu, M., MacKnight, W. J., Chen, C. H. Y. and Thomas, E. L. *Polymer* 1983, **24**, 1327

11 Chen, C. H. Y., Briber, R. M., Thomas, E. L., Xu, M. and MacKnight, W. J. *Polymer* 1983, **24**, 1323

12 Bengston, B., Feger, C. and MacKnight, W. J. *Polymer* 1985, **26**, 895

13 Speckard, T. A., Miller, J. A. and Cooper, S. L. *Macromolecules* 1986, **19**, 1558

14 Miller, J. A., Speckard, T. A. and Cooper, S. L. *Macromolecules* 1986, **19**, 1568

15 Miller, J. A., Speckard, T. A., Homan, J. G. and Cooper, S. L. *Polymer* 1987, **28**, 7589

16 Speckard, T. A., Homan, J. G., Miller, J. A. and Cooper, S. L. *Polymer* 1987, **28**, 768

17 Quan, X., Johnson, G. E., Anderson, E. W. and Bates, F. S. *Macromolecules* 1989, **22**, 2451

18 Delides, C. and Pethrick, R. A. *Eur. Polym. J.* 1981, **17**, 675

19 Vallance, M. A., Yeung, A. S. and Cooper, S. L. *Coll. Polym. Sci.* 1983, **26**, 541

20 Camberlin, Y. and Pascault, J. P. *J. Polym. Sci. Chem.* 1983, **21**, 415

21 Jacobi, E., Schuttenberg, H. and Schulz, R. C. *Makromol. Chem. Commun.* 1980, **1**, 397

22 Biagini, E., Gattiglia, E., Pedemonte, E. and Russo, S. *Makromol. Chem.* 1983, **184**, 1213

23 Merril, E. W. and Mahmud, N. A. *Polym. Commun.* 1985, **26**, 105

24 Darud, V. *Thesis*, IDI 18801, Institut National des Sciences Appliquées de Lyon, 1988

25 MacKnight, W. J., Yang, M. and Kajiyama, T. *Prep. Am. Chem. Soc. Div. Polym. Chem.* 1968, **9**, 860

26 Kolodziej, P., Yang, W. P., Macosko, C. W. and Wellinghoff, S. T. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 2359

27 Leung, L. M. and Koberstein, J. T. *Macromolecules* 1986, **19**, 706

28 Koberstein, J. T. and Russel, T. P. *Macromolecules* 1986, **19**, 714

29 Leung, L. M. and Koberstein, J. T. *J. Polym. Sci. Phys.* 1985, **23**, 1883

30 Boyer, R. F. 'T_{11} and related liquid state transition relaxations: a review', in *Polymer Yearbook 2* (Ed. R. A. Pethrick), Harwood Academic, London, 1985, pp. 234–343

31 Boyer, R. F., Baer, E. and Hiltner, A. *Macromolecules* 1985, **18**, 427

32 Chi Li, C., Goodman, S. L., Albrecht, R. M. and Cooper, S. L. *Macromolecules* 1988, **21**, 2367

33 Mahloubian Jones, M. G., Hayward, D. and Pethrick, R. A. *Eur. Polym. J.* 1987, **11**, 855

34 Beckman, E. J., Karasz, F. E., Porter, R. S., MacKnight, W. J., Van Hunsel, J. and Koningsveld, R. *Macromolecules* 1988, **21**, 1193

35 Cuvé, L., Pascault, J. P. and Boiteux, G., in preparation