Molecular Mobility and Hydration Properties of Segmented Polyurethanes with Varying Structure of Soft- and Hard-Chain Segments

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ABSTRACT: The molecular mobility and hydration properties of model segmented polyurethanes from either poly(propylene glycol) (PPG) or poly(butylene adipate) (PBAD), both of molecular weight 2000 (soft segments), and three different diisocyanates (all-*trans* 4,4′-dicyclohexylmethane diisocyanate, 100% t,t HMDI; HMDI with 20% of *trans* isomers, 20% t,t HMDI; and 4,4′-diphenylmethane diisocyanate, MDI) (hard segments) were investigated using differential scanning calorimetry (DSC), thermally stimulated depolarization currents (TSDC) measurements, ac dielectric relaxation spectroscopy (ac DRS), equilibrium water-sorption isotherms (ESI), and dynamic water-sorption isotherms (DSI). No effects of the structure and of the amount of the soft segments on the overall degree of microphase separation (DMS) into microphases rich in soft and hard segments, respectively, were observed. On the contrary, DMS depends on the composition of the diisocyanates used and systematically increases in the order MDI, 20% t,t HMDI, 100% t,t HMDI as indicated by DSC, TSDC, and ac DRS. The PPG-based polyurethanes are characterized by larger values of water content at saturation, h, and smaller values of the diffusion coefficient of water, D. h increases with temperature, indicating that the sorption process is endothermic. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1209–1221, 1999

Key words: segmented polyurethanes; incomplete microphase separation; glass transition; dielectric relaxation; hydration properties

INTRODUCTION

We report in this work on the structure–property relationships of linear thermoplastic polyurethane systems consisting of a macroglycol (either polyether or polyester), an aromatic or aliphatic diisocyanate, and a diol as a chain extender. Dielectric relaxation spectroscopy measurements, using thermally stimulated depolarization currents (TSDC), and ac methods were used, in addition to differential scanning calorimetry (DSC) and equilibrium and dynamic water-sorption isotherm (ESI and DSI, respectively) measurements to study the molecular mobility and the hydration properties of these systems.

The polyurethanes under investigation were block copolymers. The soft block was derived from polyether or polyester of a molecular weight 2000 and a glass transition temperature well below room temperature. The hard block, having a T_g above

room temperature, consists of a diisocyanate and a diol. The diisocyanate was aromatic MDI (4,4′-diphenylmethane diisocyanate) or aliphatic hydrogenated MDI (HMDI, 4,4′-dicyclohexyl methane diisocyanate) which has three geometric isomers. The elastomers produced from aromatic diisocyanate (such as MDI) are frequently opaque and then become yellow during storage due to the presence of the aromatic rings. For application where transparency and nonyellowing are important, aliphatic diisocyanates (such as HMDI) are the compounds of choice.[1] A major factor controlling the degree of microphase separation (DMS) in segmented polyurethanes (SPU) into a microphase rich in soft segments and a microphase rich in hard segments is the intrinsic flexibility of the hard segments: For example, fairly high DMS in SPU based on polycaprolactone and hexamethylene diisocyanate (HDI) could be reduced to nearly zero by a simple replacement of HDI with stiffer MDI.[2]

Most of the investigations on polyurethanes were concentrated on polymers based on aromatic diisocyanates[3,4] and only a relatively few studies have dealt with aliphatic diisocyanates.[1,5,6] Thermoplastic elastomers based on HMDI have been found to exhibit excellent UV stability,[7] superior retention of physical properties at elevated temperatures, and better mechanical properties.[1,8]

The first goal of this work was to study the effects of the relative isomer ratio in the hard segment, of the hard-segment content, and of the type of the soft segment (polyester or polyether) on the structure and properties of the resulting polyurethanes. In the literature, relatively little attention has been paid to the hydration properties of the polyurethanes.[9–11] However, investigations of the hydration properties of polymers can provide information on the significant importance for many applications of both fundamental and practical interest, such as morphology investigations,[12–14] investigations of hydrolysis stability, and preparation of biocompatible polyurethanes and polyurethane hydrogels.[15]

The second goal of this work was to study the hydration properties of the polyurethanes prepared. In particular, the hydration properties studied refer to the amount of water sorbed at equilibrium and the diffusion coefficient of water in the polyurethane under investigation, as well as to the effects of sorbed water on the molecular mobility.

EXPERIMENTAL

Materials

The model polyurethanes used in this study were supplied by Miles Inc., Pittsburgh, PA, USA Poly-

mers Division, in the form of sheets of about 3-mm thickness. They are based on either a polyether soft segment [poly(propylene glycol) (PPG) Mutranol 3600] or a polyester soft segment [poly(butylene adipate) (PBAD), Desmophen 2502]. In both cases, the molecular weight of the soft-segment polyol was 2000. The idealized structures of those polyols are the following:

$$HO—[—CH_2CH(CH_3)O—]_n—H$$

poly(propylene glycol) (PPG), $n \cong 34$, and

$$HO—(CH_2)_4—O—[—CO—(CH_2)_4$$
$$—COO(CH_2)—O]_n—H$$

poly(butylene adipate) polyol (PBAD), $n \cong 10$, where n is the number of monomers.

The hard segment consisted of a diisocyanate and 1,4-butanediol (BDO). The diisocyanates were MDI or hydrogenated MDI (HMDI), which has three geometric isomers:

4,4′-diphenylmethane diisocyanate;

CIS - TRANS

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4,4′-dicyclohexylmethane diisocyanate.

Table I Materials Used, Details in the Text

Sample	Isocyanate	Polyol	Wt % Hard Block
1	20% t,t HMDI	2000 MW PPG	30
2	100% t,t HMDI	"	30
3	MDI	"	30
4	20% t,t HMDI	2000 MW PPG	50
5	100% t,t HMDI	"	50
6	MDI	"	50
7	20% t,t HMDI	2000 MW PBAD	30
8	100% t,t HMDI	"	30
9	MDI	"	30
10	20% t,t HMDI	2000 MW PBAD	50
11	100% t,t HMDI	"	50
12	MDI	"	50

PPG = poly(propylene glycol); PBAD = poly(butylene adipate).

The compositions of the three different diisocyanates used in this study are given below:

1. 20% t,t-HMDI, Desmodur W: 4,4′-Dicyclohexylmethane diisocyanate with an isomer distribution of $\sim$ 20% *trans,trans,* $\sim$ 55% *cis,trans,* and $\sim$ 25% *cis,cis,* which also contained $\sim$ 5% of 2,4′-structural isomers;
2. 100 % t,t-HMDI: 4,4′-Dicyclohexylmethane diisocyanate with an isomer content of 97% *trans,trans,* 2% *cis,trans,* and 1% *cis,cis;* and
3. MDI: 4,4′-Diphenylmethane diisocyanate, which also contained < 2% of the 2,4′-isomer.

The polyurethanes were prepared according to the prepolymer method.[1] All the samples used are listed in Table I.

Techniques

Dielectric Relaxation Spectroscopy (DRS) Measurements

Ac Dielectric Relaxation Spectroscopy (a.c. DRS) Measurements. For a.c. DRS measurements in the frequency range 10^2 to 10^7 Hz and in the temperature range −40 to +60°C, a Hewlett–Packard HP4192A impedance analyzer combined with an Ando type TO-19 thermostatic oven and an Ando SE-70 dielectric cell with nickel-coated stainless-steel electrodes was used. The samples were cylindrical sheets of 15-mm diameter and 3-mm thickness. We performed complex admittance measurements in a two-terminal electrode configuration.

Thermally Stimulated Depolarization Current (TSDC) Measurements. The TSDC method consists of recording the thermally activated release of frozen-in polarization and corresponds to measuring dielectric losses versus temperature at low frequencies in the range of 10^{-4} to 10^{-2} Hz.[16] A brief description of the method is given in the following: The sample is inserted between the plates of a capacitor, made of brass, and polarized by the application of an electric field E_p at a temperature T_p, for a time t_p, large compared with the relaxation time at T_p of the dispersion under consideration. With the electric field still applied, the sample is cooled down to a temperature T_0 sufficiently low to prevent depolarization by thermal agitation. Next, it is short-circuited and reheated at a constant heating rate. A discharge current is generated as a function of temperature which is measured with a sensitive electrometer (Keithley 610C). The TSDC spectrum thus obtained often consists of several peaks whose shape and location are characteristic of the relaxation mechanisms of the sample. The analysis of the shape of the TSDC curve makes it possible to obtain the activation energy E, the preexponential factor τ_0, and the contribution $\Delta\varepsilon$ of a peak to the static permittivity. We used a common experimental apparatus for TSDC measure-

ments in the temperature range of −170 to +20°C.[17,18] Similar to the ac DRS measurements, the samples cut from the compression-molded sheets were cylinders of 15-mm diameter and 3-mm thickness. Typical experimental conditions were 2 kV/cm for the polarizing field, 25°C for the polarization temperature, 5 min for the polarization time, 6 K/min for the cooling rate, and 3 K/min for the heating rate.

Differential Scanning Calorimetry Measurements (DSC)

DSC measurements were carried out on samples using a Perkin–Elmer DSC4 differential scanning calorimeter at heating scans from −80 to 0°C with a heating rate of 10°C/min. The samples of about 10 mg weight were dried in a vacuum at 120°C for 24 h, sealed in aluminum pans and cooled at 40°C/min until −80°C before the measuring scan. The thermograms were normalized to the weight of each sample.

Equilibrium Water-sorption Isotherm (ESI) Measurements

Equilibrium water-sorption/desorption isotherms were measured at 40°C. The samples were allowed to equilibrate to constant weight in various dessicators where the relative humidity (RH) was monitored between 6 and 97% using different saturated salt solutions.[19] The time required to reach equilibrium (sample weight change less than 10^{-4} g) was from several hours to a few days and it increases with increasing RH. The water content h, defined as grams of water per gram of dry sample, was determined by weighing. Drying in a vacuum (5×10^{-2} Torr) at 120°C for 24 h was adopted as the method for the determination of dry weights.

Dynamic Water-sorption Isotherms (DSI) Measurements

Dynamic water-sorption isotherm measurements, to study the kinetics of sorption, were carried out as follows: Samples were immersed in distilled water at a constant temperature. At defined time intervals, the samples were taken out of the water, carefully dried, and weighed. This procedure was followed to saturation (equilibrium). Measurements were carried out at three different temperatures of 20, 40, and 70°C. The diffusion coefficient D of water in the polyurethanes was determined from the time dependence of the water

Figure 1 TSDC thermograms of samples #1, 2, and 3.

uptake. The activation energy of D, W, was determined from the temperature dependence of D.

RESULTS AND DISCUSSION

TSDC Measurements

Figure 1 displays the TSDC thermograms measured on three different types of polyurethanes (samples #1, 2, and 3, Table I). The TSDC spectra from all the samples exhibit a structure similar to that shown in Figure 1. Three dispersions are distinguished, called the β, α, and MWS peaks in the order of increasing temperature. The weak secondary β peak, located at about −120°C, is attributed to the motion of the polar carbonyl groups of the polyurethane.[11] The α peak is dipolar and located close to the calorimetric glass transition temperature, whereas the MWS (Maxwell–Wagner–Sillars) peak is of the interfacial polarization type and related to morphology changes at the glass transition.[20] For the polyurethanes under investigation, the α-relaxation peak located at −60 to −30°C arises from the reorientation of the polar soft segments of the chain during the glass transition of the polyurethane amorphous microphase rich in soft segments. DSC measurements to be reported below confirm this result. The MWS peak located in the temperature range of −20 to 0°C is due to electric polarization at the interfaces of the sample between microphases rich in soft segments and microphases rich in hard segments of the sample.[20,21] It is interesting to note that in the SPUs studied here the shape of the α peak is complex (Fig. 1) compared to other polyurethane systems.[11,20,21] This result may reflect a broader dis-

Table II   Normalized Current Maximum I_n of the α-Peak and of the MWS Peak for the Polyurethanes Listed in Table I

Sample	I_n (au) α-Peak	I_n (au) MWS Peak
1	5	3
2	5	30
3	8	23
4	2	3
5	2	20
6	4	2
7	5	12
8	3	30
9	9	13
10	2	13
11	1	30
12	3	12

persion of microphase sizes in the SPUs studied here.

The normalized current maximum of the α-peak and of the MWS peak in Table II is the current maximum (current at peak temperature T_m) divided by the heating rate, surface area of the sample, and polarizing field. It is a measure of the contribution of a peak to the static dielectric constant $\Delta\varepsilon$, that is, a measure of the number of relaxing units contributing to the peak.[16]

We observe that the normalized magnitude I_n of the α-peak decreases with an increasing hard-component fraction in the polyurethanes (Table II), in agreement with our interpretation for the origin of this relaxation. No systematic changes were observed in the magnitude of the α-peak with the type of the soft segment (polyether or polyester). With respect to the composition of the three diisocyanates used, I_n is systematically larger for samples prepared with MDI (Table II and Fig. 1), whereas no systematic differences were observed between samples prepared with 20% t,t and with 100% t,t HMDI. We will come back to this point later in discussing the DSC results.

The magnitude of the MWS peak was found to sensitively depend on the experimental conditions, in agreement with results obtained with other polyurethanes,[11,20] so that the I_n values for the MWS peak in Table II should be considered as rather indicative. It is striking, however, that systematically larger I_n values are obtained with the polyurethanes prepared with 100% t,t HMDI. These results suggests that the total surface area of the interface boundary region between hard-

and soft-segment phases is larger for the polyurethane prepared with 100 t,t HMDI. Combined TSDC and small-angle X-ray scattering (SAXS) measurements in model SPUs (work in progress) indicate that the I_n of the MWS peak increases with an increasing degree of microphase separation (DMS) into microphases rich in soft and hard segments, respectively. Thus, the results in Table II suggest that the DMS is higher in the samples prepared with 100% t,t HMDI. It is interesting in this respect to note that studies of the mechanical properties of polyurethane containing the same diisocyanate compositions as in the present work indicate that samples prepared with 100 t,t HMDI have smaller or more interconnected domains.[1,5]

We turn our attention to the temperature position of the α-peak. Ac dielectric measurements and DSC measurements of the dynamics of the glass transition in the glass-forming liquid salol (phenyl salicylate) have shown that the corresponding Arrhenius plots practically coincide in the common frequency range of the two techniques. These results suggest that, although the phenomena measured are physically different, both techniques probe at the glass transition the mobility of units of similar size.[22,23] This justifies best the use of dielectric techniques to measure glass transition temperatures. In addition, TSDC measurements are carried out at heating rates similar to those used in DSC (a few K/min), that is, TSDC and DSC are characterized by similar time scales. For these reasons, the temperature of the current maximum of the TSDC α-peak (peak temperature, T_α) is a good measure of the calorimetric glass transition T_g as confirmed by measurements on several systems.[11,20,21]

Our results show that T_α shifts to lower temperatures with an increasing fraction of t,t HMDI, that is, in the order MDI, 20%, 100% t,t HMDI. No systematic changes of T_α were observed by changing the hard-segment content and the type of the soft segment. We will comment on these points in discussing the DSC results.

Differential Scanning Calorimetry (DSC) Measurements

Figure 2 shows DSC measurements on samples #1–12. A specific heat jump at about −40 to −60°C was observed for all samples. It corresponds to the glass transition of the polyurethane amorphous soft-segment phase. The thermograms are normalized to the weight of each sample. Please note that the slope has no meaning at

Figure 2 DSC thermograms for all the samples under investigation.

all; it is just the result of the calculation procedure to subtract the baseline from the measured curve. Table III lists the results of the DSC measurements, $T_{g\text{onset}}$, $T_{g\text{midpoint}}$, and Δc_p.[24] We ob-

Table III   DSC Measurements Results

Sample	$T_{g\text{onset}}$ (°C)	$T_{g\text{midpoint}}$ (°C)	Δc_p ($T_{g\text{midpoint}}$) (J/gK)
1	−59	−53	0.37
2	−62	−58	0.35
3	−50	−42	0.39
4	−59	−52	0.21
5	−65	−58	0.22
6	−51	−35	0.28
7	−54	−47	0.28
8	−59	—	—
9	−48	−43	0.30
10	−54	−44	0.11
11	−62	−55	0.10
12	−52	−44	0.19

Figure 3 Calorimetric glass transition temperatures (○) T_g and (◇) T_α for all samples studied.

serve in Table III that the decrease of the soft-phase amount in the samples results in the decrease in the increment of specific heat capacity of glass transition Δc_p. With respect to the type of the soft phase, we observe that Δc_p is systematically larger for polyurethanes based on PPG (1–6) than for polyurethanes based on PBAD (#7–12). Please note that this systematic variation was not observed with the normalized current maximum I_n of the TSDC a-peak in Table II. Δc_p in Table III is larger for polyurethanes prepared with MDI, whereas practically no differences are observed between samples prepared with 20 and 100% t,t HMDI. Please note that similar results were obtained with the I_n of the TSDC a-peak in Table I.

We turn now our attention to the glass transition temperature T_g. We take $T_{g\text{midpoint}}$ as representative for that.[24] In Figure 3, we show T_g together with the peak temperature T_a of the TSDC a peak for all samples studied. As a general remark, we would like to note that T_a follows the changes of T_g with the sample, providing support that T_a is a good measure of T_g. Similar to other polyurethane systems,[11,20,21] T_g is higher than that of pure polyether or the polyester soft phase ($T_g = -76$°C for PPG and −68°C for PBAD) as a result of constraints imposed by bonding to hard blocks and by mixing with hard segments. No systematic changes of T_g and T_a are observed in Figure 3 by changing the hard-segment content and the type of the soft segment. With respect to the hard-segment content, similar results were obtained with DSC and TSDC

Figure 4 Isochronal plots, at fixed frequency $f = 30$ kHz, of ε' as a function of temperature T, for samples #1, 2, and 3.

measurements on thermoplastic polyurethanes based on polyethylene adipate, MDI and BDO.[20] T_g and T_a in Figure 3 shift to lower temperatures with an increasing fraction of t,t HMDI, that is, in the order MDI, 20%, 100% t,t HMDI.

The shift of T_g (and T_a) to lower temperatures in the order MDI, 20%, 100% t,t HMDI, suggests that the DMS between the hard- and soft-segment phases increases in this order. In agreement with this interpretation, the glass transition becomes narrower in the 100% t,t HMDI (#2, 5, 8, and 11) as shown in Figure 2 and also indicated by the difference $T_{g\text{midpoint}} - T_{g\text{onset}}$ in Table III. Additional support for better phase separation in 100% t,t HMDI samples is provided by indications of cold-crystallization obtained with samples #8 and 11 in Figure 2. These indications consist of an exothermic peak followed by a deviation of the thermogram in the endothermic sense with respect to the baseline. Samples #7–12 are based on polyester soft segments (PBAD), which, in contrast, to PPG have a high tendency to crystallize.[25] We remind that the TSDC results for the MWS peak suggested a higher DMS in the 100% t,t HMDI, that is, in agreement with the DSC results.

Ac Dielectric Relaxation Spectroscopy (ac DRS) Measurements

Figures 4 and 5 show, in the form of isochronal plots, at a fixed frequency of 30 kHz, the real (ε') and imaginary (ε'') part of dielectric function

$\varepsilon^*(\omega, T) = \varepsilon' - i\varepsilon''$, respectively, as functions of temperature for polyurethane samples based on PPG and prepared with 20% t,t HMDI (#1), 100% t,t HMDI (#2), and MDI (#3) hard segments (Table I). The points are experimental data obtained from isothermal measurements while lines are to guide the eye. The gradual increase of ε' in the temperature range -5 to $+5°C$ clearly observed for sample #3 corresponds to the main relaxation (α-relaxation) at the glass transition of the amorphous soft-segment phase. The peak in Figure 5, which is in the same temperature range as the dispersion of ε' values in Figure 4, corresponds to the α peak at $T \cong -50°C$ that we studied by the TSDC technique (Fig. 1). We note that the equivalent frequency of the TSDC measurements is $f \cong 10^{-3}$ Hz,[16] so that the loss peak, which shifts to higher temperatures with increasing frequency, is located at higher temperatures in ac compared to TSDC measurements. The peak is more intense for samples with MDI (#3), in agreement with TSDC results (Table II). It shifts slightly to lower temperature in the order #3, #1, #2, in agreement with TSDC and DSC results (Fig. 3).

In Figure 6, we show $\varepsilon''(T)$ for samples with different types of the soft segment (PPG: #3 and 6, PBAD: #9 and 12) and different fractions of hard segments (30% wt hard block: #3 and 9; 50% wt: #6 and 12). The magnitude of the peak increases as the fraction of the hard segment decreases (#6 and 3 and #12 and 9), in agreement with our

Figure 5 Isochronal plots, at fixed frequency $f = 30$ kHz, of ε'' as a function of temperature T, for samples #1, 2, and 3.

Figure 6 Isochronal plots, at fixed frequency $f = 30$ kHz, of ε'' as a function of temperature T, for samples #3, 6, 9, and 12.

TSDC and DSC results (Tables II and III, respectively) and our interpretation of relating this dispersion to the soft-segment mobility. As the hard block content increases, from 30% wt in samples #3 and 9 to 50% in samples #6 and 12, the peak shifts to higher temperatures, in agreement with the TSDC results (Fig. 3). These results suggest that by increasing the hard-segment content the mobility of the soft segments is restricted, shifting the α-peak to higher temperatures.[20] In addition, the α-peak becomes broader, indicating a broader distribution of relaxation times, in agreement with our DSC results (Fig. 2). Replacing PPG (#3 and 6) by PBAD (#9 and 12) results in shift of the α-peak to lower temperatures (i.e., the mobility of the soft segments increases) and decrease of its magnitude. The ac results are here more clear and conclusive than the corresponding DSC (Table III) and TSDC results (Table II and Fig. 3). The decrease in peak magnitudes may be attributed, at least partly, to the higher tendency of PBAD to crystallize.

To investigate water effects in the polyurethanes under investigation, ac measurements were carried out at several water contents h. As an example, we show in Figure 7 the dielectric losses (ε'') against temperature on sample #6 (with 50% hard blocks) at different values of h. The α-relaxation becomes faster (peak temperature shifts to lower values) with increasing water content while its magnitude increases, that is, it

is plasticized by water.[11,26] In addition, the width of the loss peak decreases with increasing water content, reflecting a narrowing of the distribution of relaxation times.[27] Despite the relatively low water contents (when expressed in terms of wt %), the plasticizing action is significant due to the low molecular weight of water. Similar results were obtained with thermoplastic polyurethanes based on poly(ethylene adipate) (PEA), MDI, and butanodiol (BDO).[11]

Equilibrium Water-Sorption Isotherm (ESI) Measurements

In Figure 8, we show equilibrium water-sorption isotherms measured on samples #1 and 7 during sorption and, in addition, on sample #7 during desorption at $T = 40°C$. They are representative of isotherms obtained with the polyurethanes under investigation. The plots are approximately linear for relative humidity values, RH $\leq 60\%$ ($h \leq 1\%$), where they start their upward swing. Linear water-sorption isotherms in polymers have been interpreted in terms of the molecular distribution of the sorbed water molecules.[28] Positive deviations from linear behavior at higher RHs have been explained, both qualitatively and quantitatively, in terms of the clustering of water molecules.[29–31] Thus, the results in Figure 8 suggest that the sorbed water molecules are molecularly distributed at RH $\geq 60\%$, while they form clusters at higher RH and h values.

Figure 7 Dielectric losses $\varepsilon''(T)$, at fixed frequency $f = 30$ kHz, for sample #6 at several water contents h, given in the plot.

Figure 8 Equilibrium (solid symbols) water-sorption and (hollow symbols) -desorption isotherms on samples (●) #1 and (■, □) #7. Lines are fittings of eq. (1) to the experimental data.

Table IV lists values of water content h at maximum relative humidity, RH = 96.4%, at T = 40°C for samples #1, 2, 3, 7, 8, and 9. In the same table are also listed the values of the average number N_c of water molecules in the clusters and of the Flory–Huggins interaction parameter χ, calculated following the analysis proposed by Brown.[29] This analysis combines conventional solution theory (Flory–Huggins) and cluster theory (Zimm and Lundberg). For further details on the application of the corresponding procedure, we refer the reader to our previous work on water effects in polyurethane block copolymers.[11]

We observe in Table IV that the samples based on PPG (#1, 2, and 3) absorb more water than those based on PBAD (#7, 8, and 9). Dynamic sorption isotherm measurements at 20, 40, and 70°C, to be reported in the next section (Table V), will provide further support for this result. One possible explanation for this behavior is that it is due to the higher tendence of PBAD to crystallize, compared to PPG, since it is generally accepted that water is sorbed only in the amorphous regions of the polyurethane soft phase.[11] However, crystallization within the series of samples #7, 8, and 9 was observed using DSC only for sample #8, as reported in the DSC Measurements section. Thus, the results in Table IV (and those of dynamic sorption isotherm measurements) suggest that the higher tendency of polyurethanes based on PPG to take up water compared to polyurethanes based on PBAD reflects the higher hydrophilicity of PPG compared to PBAD.

With respect to the composition of the diisocyanates, the results in Table IV show that within the first series of samples (#1, 2, and 3) h is lowest for sample #2. This result will be confirmed by those of dynamic sorption isotherm measurements (Table V). The results in Table IV are less conclusive regarding the second series of samples (#7, 8, and 9). However, the DSI results may suggest that h is lowest for sample #8 (Table V). It follows that, clearly for the first series of polyurethanes, and probably for the second also, the amount of water sorbed is lowest for the samples with 100% t,t HMDI, that is, for the samples with the highest DMS.

No systematic changes of the calculated values of the average number of water molecules in the clusters, N_c, and of the Florry–Higgins interaction parameter, χ, were observed, neither with the type of the polyol (PPG or PBAD) nor with the composition of the diisocyanates used. For comparison, values of N_c = 3.7–7.1 and of χ = 3.8–3.9 were determined for a polyurethane block copolymer system based on PEA, MDI, and BDO.[11]

The data plotted in Figure 8 were analyzed according to the so-called Guggenheim–Anderson–DeBoer (GAB) equation, which is an amended form of the classical Brunauer–Emmet–Teller (BET) equation.[32] Contrary to the BET equation, the GAB equation allows one to take into account the experimental data over the whole range of water activity (a = RH) up to a ≤98% (i.e., RH ≤ 98%):

$$h = h_m \frac{k\, f\, a}{(1 - fa)\,[1 + (k - 1)fa]} \qquad (1)$$

In this equation, h_m is the amount of water directly bound to the sorption sites (first monolayer sorption capacity), and k is the ratio of the binding constant of water molecules directly bound to the sorption sites in the first layer and of that of water molecules bound indirectly in the succeeding "liquidlike" layers; f, in similar way, is the ratio of the standard chemical potential of the indirectly bound water molecule and of that of the

Table IV Results of the Analysis Following Brown[29] of Water-Sorption Data at 40°C

	# Sample					
	1	2	3	7	8	9
h (%)	2.6	2.2	2.5	2.0	1.8	1.7
N_c	1.9	1.9	1.5	3.4	1.1	1.5
χ	7.9	8.9	7.9	8.4	7.9	8.1

h is the water content at RH = 96.4%; N_c, the average number of water molecules in the clusters; and χ, the Flory–Huggins interaction parameter.

Table V   Water Contents at Saturation *(h%)*, Water-sorption Diffusion Coefficients *D*, at Different Temperatures, and Diffusion Activation Energies *W* for the Samples Under Investigation

Samples	$T = 20°C$		$T = 40°C$		$T = 70°C$		W (eV)
	$h\%$ (g/g)	D (cm²/s)	$h\%$ (g/g)	D (cm²/s)	$h\%$ (g/g)	D (cm²/s)	
1	2.7	1.8×10^{-7}	2.9	6.4×10^{-7}	3.2	8.9×10^{-7}	0.26
2	2.3	1.8×10^{-7}	2.5	8.3×10^{-7}	2.6	7.9×10^{-7}	0.23
3	3.0	1.0×10^{-7}	3.3	4.2×10^{-7}	3.9	7.1×10^{-7}	0.33
7	1.9	2.7×10^{-7}	2.3	5.9×10^{-7}	2.9	8.4×10^{-7}	0.22
8	1.7	2.4×10^{-7}	1.9	4.3×10^{-7}	2.3	7.9×10^{-7}	0.21
9	1.7	2.4×10^{-7}	2.0	4.0×10^{-7}	2.8	7.3×10^{-7}	0.19

molecules in the bulk liquid state. For *k* values higher than 1, site-bound water molecules may be considered as "strongly bound," while indirectly bound water molecules may be considered as "loosely bound." When *f* = 1, the GAB equation reduces to the BET one and *f* values smaller than 1 reflect that indirectly bound water molecules are in a still more stable state than are water molecules in the bulk liquid state.

The GAB eq. (1) could be satisfactorily fitted to the experimental data (solid lines in Fig. 8). The values of the fitting parameters are listed in Table VI. As expected,[33] the BET equation was found to be valid only in a narrow range of RH up to about 50%. The *k* and *f* values for the polyurethanes under study remain respectively higher and lower than unity. This suggests different binding energies for the sorbed water, which decreases in the order site-binding > indirect binding > water–water in the bulk. The lack of any significant clustering of water molecules in the polyurethanes of the present study (low values of N_c in Table IV) is quite consistent with the fact that *f* < 1 (Table VI), which reflects that the indirectly bound water molecules are still in a more stable state than are the water molecules in the bulk liquid state.[32]

We observe in Table VI that the h_m values are lower for the PBAD-based polyurethanes compared to the PPG-based ones, following the correspondingly lower values of *h* for the former system in Table IV and V. Within the first series of samples (#1, 2, and 3), h_m is lowest for sample #2, that is, for the sample with the lowest *h* value in Table IV. Finally, all polyurethanes under investigation showed hysteresis (i.e., higher values of *h* in desorption following sorption) similar to sample #7 in Figure 8.

Dynamic Water-sorption Isotherm (DSI) Measurements

Assuming Fickian behavior with a constant (i.e., independent of *h*) diffusion coefficient *D*, the following equation holds for dynamic water-sorption and -desorption isotherms at relatively small values of time *t*, corresponding to $(\Delta m)_t/(\Delta m)_\infty$ < 0.6 (refs. 34 and 35):

$$\frac{(\Delta m)_t}{(\Delta m)_\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{tD}{l^2}} \tag{2}$$

where $(\Delta m)_t$ is the water uptake or loss at time *t* (sorption or desorption, respectively); $(\Delta m)_\infty$, the corresponding limited value at equilibrium; and *l*, the thickness of the sample, presumed constant over the whole sorption (desorption) process.

Figure 9 shows data from the water-sorption experiments on sample #2, at $T = 20°C$. The observed linearity extending to $(\Delta m)_t/(\Delta m)_\infty = 0.6$ and the curvature concave to the abscissa axis following the initial linear increase suggest that the sorption process is controlled by a simple Fickian diffusion.[34] The average diffusion coefficient *D* of

Table VI   Sorption Isotherm Analysis According to GAB eq. (1)

# Sample	h_m	k	f
1	0.0089	3.2	0.72
2	0.0075	3.6	0.72
3	0.0140	1.4	0.65
7	0.0076	2.6	0.70
8	0.0062	3.3	0.71
9	0.0060	3.0	0.68

Figure 9 Normalized dynamic water-sorption curve of sample #2 at $T = 20°C$.

water within the polymer matrix was calculated from the initial slope following eq. (2). It is a mean value of the diffusion coefficient, which is, in general, a function of water concentration,[34] averaged over the range of concentration appropriate to the experiment. For sample #2 at 20°C (Fig. 9), D was found to be 1.8×10^{-7} cm^2/s for the sorption experiment. The experimental error for D is estimated to about 15%. Table V lists D values determined for samples #1, 2, 3, 7, 8, and 9 at 20, 40, and 70°C. D values in the similar range were reported for block polyurethanes based on PEA, MDI, and BDO.[11] For the lowest temperature of the measurements, 20°C, D is systematically larger for polyurethanes based on PBAD (#7, 8, and 9) compared to polyurethanes based on PPG (#1, 2, and 3), in good correlation with the higher hydrophilicity of PPG compared to PBAD (higher values of h in Tables IV and V for PPG-based compared to PBAD-based samples). This systematic variation of D is not observed at higher temperatures (40 and 70°C), despite the systematic variation of h (Table V).

Figure 10 shows the Arrhenius plot of D for sample #9. The data follow the Arrhenius relationship:

$$D = D_0 \exp\left[-\frac{W}{kT}\right] \qquad (3)$$

where D_0 is a constant (equal to extrapolated value of D for $T \to \infty$); W, the activation energy for the diffusion process; k, Boltzmann's constant; and T, the absolute temperature. Using a regression analysis, we obtained $W = 0.19$ eV for sample #9. The diffusion activation energies, for all the samples under investigation, are listed in Table V. Despite the large ambiguities in the de-

termination of W from Arrhenius plots with only three points, it seems that, in general, the activation energies for the polyurethanes based on PPG are higher than those for PBAD-based polyurethanes. This is consistent with the higher hydrophilicity of the PPG-based polyurethanes reflected in the higher h values (Tables IV and V).

For all samples studied, the amount of water at saturation (h in Table V) was found to systematically increase with increasing temperature, suggesting that the sorption of water is an endothermic process. The same has been observed also with polyurethanes based on PEA, MDI, and BDO.[11]

CONCLUSIONS

The main conclusions refer to the changes in morphology and molecular mobility induced by replacing the polyether PPG by the polyester PBAD, by increasing the amount of hard block from 30 to 50% wt, and by varying the composition of the diisocyanates used (20% t,t-HMDI, 100% t,t-HMDI, and MDI). Finally, some general conclusions for the hydration properties of the polyurethanes studied are drawn.

No systematic change of the glass transition temperature T_g of the soft-segment phase was observed by replacing PPG by PBAD, suggesting that the overall DMS into microphases rich in soft and hard segments, respectively, is not measurably affected by this change. It is interesting, however, to note that the α-relaxation, as measured by ac DRS, shifts to lower temperatures and its strength $\Delta\varepsilon$ decreases by replacing PPG by PBAD. Cold crystallization is observed with samples prepared from PBAD. With respect to the hydration properties, the water uptake at satura-

Figure 10 Arrhenius plot of diffusion coefficient D for sample #9.

tion h and the amount of water bound to the sorption sites h_m is larger for PPG-based compared to PBAD-based samples, reflecting the higher hydrophilicity of PPG. Consistently with that, the diffusion coefficient for water D (at 20°C) and its activation energy W are smaller and larger, respectively, for PPG-based samples.

By increasing the amount of the hard block from 30 to 50 wt %, Δc_p measured by DSC and the strength of the α-relaxation measured by both TSDC and ac DRS increase as expected. T_g and, thus, the overall DMS is not affected by this change. Interestingly, however, the α-relaxation is shifted to higher temperatures and is broader for the samples with 50% wt hard block. Hydration effects were not studied with the 50% hard-block samples.

DMS into microphases rich in soft and hard segments, respectively, was found to systematically change with the composition of the diisocyanates used and to increase in the order MDI, 20% t,t HMDI, 100% t,t HMDI. Evidence for that is provided by the systematic shift of T_g (DSC), T_α (TSDC), and T_m (ac DRS) to lower temperatures in the order given above and by the narrowing of the DSC signal. Additional support for the samples with 100% t,t HMDI showing the highest DMS is provided by the systematically larger values of the magnitude I_n of the TSDC MWS peak for these samples and by the observation of cold crystallization for these samples if the soft phase is PBAD. Surprisingly, the samples with 100% t,t HMDI show the lowest values of h and h_m, whereas the samples with MDI the highest values of Δc_p and of dielectric strength of the α-relaxation (both in TSDC and in ac DRS).

Sorption of water was found to plasticize the α-relaxation (shift to lower temperatures, increase of dielectric strength) and to reduce its width. Finally, the amount of water sorbed increases with increasing temperature, indicating that the sorption process is endothermic.

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