

Synthesis of New Anionic HTPB-Based Polyurethane Elastomers: Aqueous Dispersion and Physical Properties

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ABSTRACT: New segmented polyurethane (PU) anionomers based on hydroxytelechelic polybutadiene (HTPB) were synthesized via an environment-friendly chemical route. Incorporation of carboxylated functions on the PU soft segment was carried out using a thiol-ene reaction on HTPB vinyl double bonds with thioglycolic acid. PU water dispersions were obtained by addition of a water dispersible polyisocyanate, i.e., Bayhydur® 3100, to the modified ionic HTPB water dispersions. The key factor of this formulation is the control of ionic concentration apart from the hard segment content, oppositely to all other PU anionomer formulations. The influence of ionic content was studied through all steps of the PU material synthesis, from aqueous

dispersions up to crosslinked materials' physical properties. For fully neutralized precursors, the stability of the ionic aqueous dispersions was higher than that was in six months. In all cases, particles were smaller than 200 nm. PU glass transition temperature, surface hydrophilicity and swelling increased with ionic content. But, however, PUs exhibit hydrophobic surface properties with a maximum surface tension of 45 mN m⁻¹ and a limited water uptake. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3312–3322, 2006

Key words: polyurethanes; elastomer; dispersions; particle size distribution; networks

INTRODUCTION

Because of environment requirements to reduce volatile organic compounds, strong interest was led to formulate waterborne systems for use as coatings or adhesive over the last decades.¹ Polyurethanes (PUs) based on various types of polyol (polyether, polyester, or polycarbonate) followed this trend and several reviews describe the preparation of aqueous polyurethane dispersions (PUD).^{2–4} Hydrophobic PUs were first dispersed in aqueous media by addition of external emulsifiers such as polyethylene oxide.^{5,6} These formulations were rapidly discarded because they were unstable along time. The covalent bound insertion of hydrophilic ionic functions within the PU chains by means of ionic chain extenders is nowadays the adopted strategy. The chain extenders can be cationic, in which case a tertiary amine is quaternarized by an alkyl agent.^{6–9} However, water cationic PU dispersions are less commercially developed because of a lack of stability compared to the anionic ones.⁶ Anionic PU dispersions can involve either sulfonated^{10–14}

or more often carboxylated chain extenders.^{15–21} Among these latter, dimethylolpropionic acid (DMPA) is by far the most used in commercial formulations.

Commonly, DMPA is neutralized with a tertiary amine to introduce anionic carboxylated function before water addition and evaporation of the organic solvent. These systems are usually prepared in two steps at least. First, an isocyanate-terminated ionic prepolymer is synthesized by mixing a polyol, a diisocyanate, and an ionic chain extender in appropriate proportions. All these reactants are mixed most of the time in an organic solvent, used as viscosity corrector in one^{17,22} or two steps.^{22,23} Then, it is dispersed in aqueous media in the presence—or not—of a diamine, allowing the chain extension and the crosslinking step.

All these waterborne systems lead to PUs bearing ionic groups in the hard segment region. This may have a twofold disadvantage: first, the number of urethane bonds rises with the ionic content, strongly modifying the mechanical properties of the final material^{24–26}; and secondly, interactions between the ionic group and the neighboring urethane bonds are likely to occur. The ionic group may be therefore trapped in the hard segment domain, affecting its availability at the surface.

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Kim et al.²² delocalized the ionic group using a step by step method. Briefly, the ionic chain extender (DMPA) was first reacted with a diisocyanate. Then, the polyol soft segment was added to the resulting product. Lastly, a further amount of isocyanate and a chain extender was reacted to this functionalized prepolymer. The resulting PU exhibited increased soft-hard segment phase mixing compared to that of the conventional formulated ionic PU. However, in this case, the resulting material properties are more likely driven by the hydrogen-bond formation between the homogeneously distributed urethane groups of soft and hard segments rather than by the presence of delocalized ionic groups. Others prepared PUs bearing the ionic moieties on the polyol soft segment. Lewandowski et al.²⁷ reacted dimethyl-5-sulfoisophthalate sodium salt with polycaprolactone and subsequently obtained a sulfonated PU via the acetone process. Rajan and coworkers²⁸ inserted chlorosulfonate groups on castor oil soft segment using chlorosulfonic acid. Propane sultone, which reacts with urethane groups of PUs, was also used to introduce sulfonate groups.^{14,29} In all these cases, hard segment content could be controlled apart from ionic content to produce PUs with a wide range of physical properties.

The aim of this study is to describe a new approach of water dispersible PU synthesis, by reacting a modified prepolymer bearing hydroxyl chain ends with a water soluble polyisocyanate. Such polyisocyanate can be obtained by reacting a fraction of the isocyanate groups of the selected polyisocyanate with monofunctionalized polyethylene oxide chains [30–32,5]. Wicks⁵ reported that a modified hexamethylene diisocyanate (HDI) isocyanurate had good water stability when short oligomers ($5 < X_n < 10$) were used.

Numerous hydroxyl-terminated polymers, such as polyesters or polyethers, were used to synthesize PUs. For specific applications, other polymer backbones, such as polyolefins, were tested. Hydroxytelechelic polybutadiene (HTPB) is a polyol that has been often used for the synthesis of PUs networks.^{14,19,33} HTPB-based water dispersions were thoroughly investigated with regard to the numerous patents.^{34–37} However, an ionic chain extender was always present in the described formulations. Here, HTPB water dispersions will be prepared without the use of a chain extender.

According to ¹H NMR analyses by Pham et al.,³⁸ the polyol used in this work (HTPB R20LM®) has a microstructure containing 22% 1,2-units and 78% 1,4-units. Having an average molecular weight of $\bar{M}_n = 1370$, the polyol therefore contains five 1,2-units per chain. According to literature, the latter can be preferentially modified by radical reaction of thiol derivatives,^{39–45} for which an anti-Markovnikov addition process is involved. Moreover, Bunel et al. have shown that at 70°C in MEK, for thiol contents lower or

equal to 1,2-units content, the reaction is selective.³⁹ Thus, authors incorporated carboxylic groups on HTPB chains using thioglycolic acid. Reaction kinetics was followed by thiol titration as described by Boutevin et al.⁴² and quantitative conversion was observed for all reactions. Thus, this chemical route gives the potential for having high densities of carboxylic function without changing the hard/soft segment ratio.

In this study, after neutralization of the incorporated acid functions using a slight excess of triethylamine, we first present the properties of modified HTPB-based aqueous dispersions. Influence of graft content was analyzed by conductivity studies. Stability of the water dispersions was studied by particle size and viscosity measurements to point out the optimum range of ionic functions that should be grafted on HTPB. Anionic PUD were synthesized by addition of a water dispersible polyisocyanate, i.e., Bayhydur® 3100. Stability of the PUDs was analyzed. Mechanical and surface properties of the resulting PU materials (after water evaporation) were studied and compared to those of the same materials prepared in 2-butanone (MEK).

EXPERIMENTAL

Materials

2-Butanone (MEK) and tetrahydrofuran (ACROS) were distilled and dried over 4 Å molecular sieves before use. Hydroxytelechelic polybutadiene (HTPB) R20LM® ($\bar{M}_n = 1370$, $f_{OH} = 2.7$) was kindly supplied by ARKEMA and degassed for 1 h at 70°C under vacuum (10^{-2} mmHg) before use. Triethylamine (TEA) and thioglycolic acid (TG) were purchased from Aldrich and were used without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) (ACROS) was used as received. Bayhydur® 3100 (17.4% NCO), a polyisocyanate based on hexamethylene diisocyanate (HDI) isocyanurate modified with a mono substituted polyethylene oxide chain,⁴⁶ was kindly provided by Bayer and used without further purification.

Bayhydur® 3100 analysis

NCO determination by titration

A classical back titration method was used to determine NCO content. Briefly, to a known amount of polyisocyanate was added an excess (5 mL) of dicyclohexylamine and 20 mL of MEK to react all NCO functions. After 1 h stirring at room temperature, the remaining amine was back titrated with a 0.1N HCl in isopropanol solution. The number of moles of NCO functions per gram is calculated according to eq. (1):

$$N_{NCO} = (V_0 - V_1)N/(1000P) \quad (1)$$

where V_0 is the HCl volume to titrate 5 mL of dicyclohexylamine, V_1 is the HCl volume to back titrate the excess of dicyclohexylamine after isocyanate neutralization, and P is the polyisocyanate amount (grams).

According to this procedure, NCO content was found to be 4.1 mmol g^{-1} corresponding to a NCO weight % of $0.0041 \times 42 \times 100 = 17.2\%$. This value is close to the supplier's one and will be the working one.

Electrospray ionization mass spectrometry

Mass spectra were recorded on an Esquire-LC ion-trap mass spectrometer equipped with an ESI source and the Esquire control 4.0 data system (Bruker Daltonics, Wissembourg, France). The ESI parameters were capillary voltage set at -4 kV , end plate at -3.5 kV , and skimmer voltage at 62 V . Nitrogen was used as drying (5 L min^{-1} , 300°C) and nebulizing (7 psi) gas.

The sample, diluted at a final concentration of $5 \text{ ng } \mu\text{L}^{-1}$ in $\text{CH}_3\text{OH}/30 \text{ mM}$ aqueous KI (1/1), was flow injected at $3 \text{ } \mu\text{L min}^{-1}$ by means of a syringe pump (Cole-Palmer, Vernon Hills, Illinois). KI was used to force the formation of MK^+ ionic species.

Positive ions were detected using the standard scan at normal resolution: the scan speed was $13,000 \text{ m/z}$ per second and the mass resolution was 0.6 U at half peak height (FWHM) over a mass to charge range 50 to 2200 m/z . Helium was the buffer gas and the pressure in the ion trap was $1.2 \times 10^{-5} \text{ mbar}$. The ion charge control was performed with a target set to 20,000 and a maximum accumulation time of 50 ms. Values of spectra averages and rolling average were 5 and 2 respectively.

Bayhydur® 3100 was neutralized by addition of an excess of methanol to avoid any possible side reactions inherent to the NCO group. The reactants were vigorously mixed to form a uniform solution and placed at 60°C for 72 h. The complete disappearance of

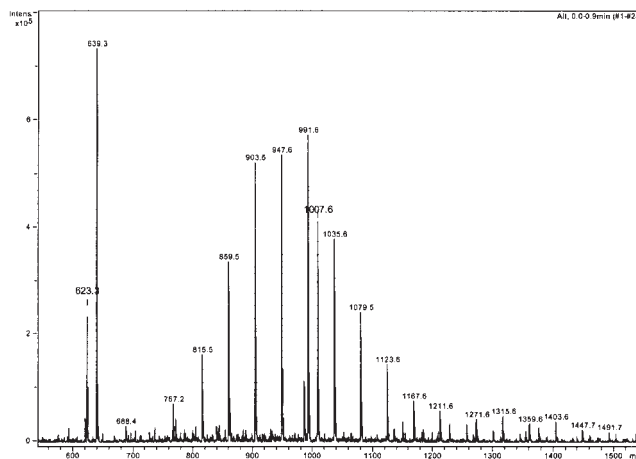


Figure 1 ESI-MS spectrum of Bayhydur® 3100.

the isocyanate band (2270 cm^{-1}) was observed by FTIR. The excess of methanol was then removed.

HDI isocyanurate characterization by Electrospray ionization mass spectrometry (ESI-MS) has been performed by Ni and coworkers.⁴⁷ It was found that HDI isocyanurate is a mixture of structural units in which main products are the trimer (80%) and pentamer (10%). Similar results were also observed by authors for an IPDI-based isocyanurate.⁴⁸

The reaction of a mono-functional PEG with a fraction of the isocyanate groups of HDI isocyanurate leads to a water dispersible polyisocyanate. The composition of the PEG used to produce Bayhydur® 3100 was determined from the ion abundances calculated from the electrospray mass spectrum (Fig. 1). It was found that the PEG average molecular weight is $\bar{M}_n = 380$ with a polydispersity of 1.04. According to Figure 1, the main product is the trimer modified by one PEG chain. However, it can be noticed that unmodified isocyanurate structures (trimer at m/z 639.3 and pentamer at m/z 1007.5) are present (Table I).

TABLE I
Main Structural Units and Observed Ions of the ESI-MS Spectrum for Methanol Neutralized Bayhydur® 3100

Peak (Da)	Structural units	Peak area	%
623.3	3HDI + 3CH ₃ OH + Na ⁺	31	5.2
639.3	3HDI + 3CH ₃ OH + K ⁺	100	16.3
767.2	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₃ CH ₃ + K ⁺	9.8	1.6
815.5	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₄ CH ₃ + K ⁺	22.3	3.6
859.5	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₅ CH ₃ + K ⁺	45.8	7.5
903.5	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₆ CH ₃ + K ⁺	71.3	11.7
947.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₇ CH ₃ + K ⁺	73.1	12.0
991.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₈ CH ₃ + K ⁺	78.1	12.8
1007.5	5HDI + 4CH ₃ OH + K ⁺	56.1	9.2
1035.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₉ CH ₃ + K ⁺	51.8	8.5
1079.5	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₁₀ CH ₃ + K ⁺	33.1	5.4
1124.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₁₁ CH ₃ + K ⁺	19.7	3.2
1167.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₁₂ CH ₃ + K ⁺	10.5	1.7
1211.6	3HDI + 2CH ₃ OH + HO(CH ₂ CH ₂ O) ₁₃ CH ₃ + K ⁺	8.0	1.3

¹H NMR analysis

¹H NMR analysis was performed on pure Bayhydur® 3100 in CDCl₃ at room temperature on a Bruker 300 MHz spectrometer (Fig. 2).

Signals were assigned according to literature.⁴⁷ First, according to signals p2 (O-CH₂CH₂) and p3 (OCH₃), the PEG molecular weight was estimated and found to be 340 whose value is corroborated by ESI-MS analysis. Secondly, according to the three different kinds of structures that can be present in the sample (Scheme 1), the NCO weight % could be estimated.

%NCO

$$= \frac{f \times 42 \times 100}{f \times M_{\text{HDI}} + f' \times \left(M_{\text{HDI}} + M_{\text{PEG}} \right) + \frac{a - (f + f')}{2} \times M_{\text{HDI}}} \quad (2)$$

where *a* is the integration of the methylene group near the isocyanurate structure, *f* the integration of the methylene group near the NCO group, *f'* the integration of the methylene group near the urethane structure, *M*_{HDI} the HDI molecular weight (168), and *M*_{PEG} is the PEG molecular weight (340).

According to ¹H NMR analysis, %NCO = 17.4% (18.0% when working with the PEG integration of the methylene group near the urethane structure). Thus, the representative structure of the main reaction product of HDI isocyanurate with a mono-functional PEG (ex: Bayhydur® 3100) can be considered as follows:

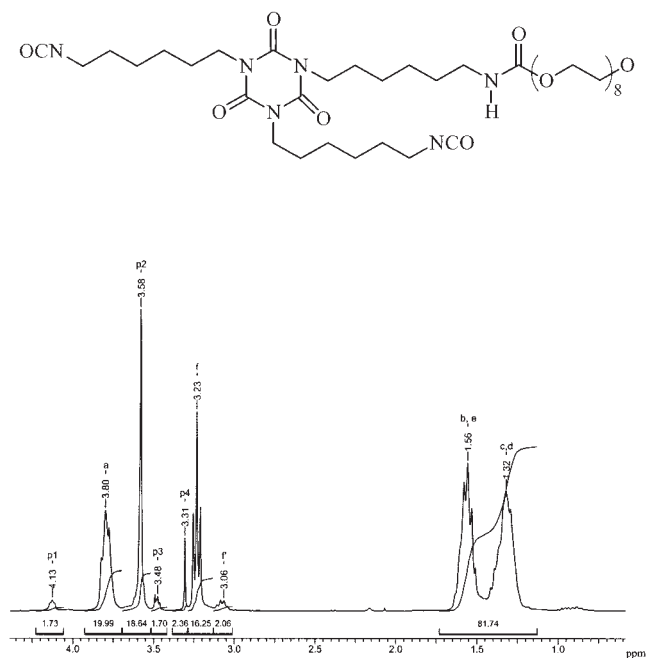
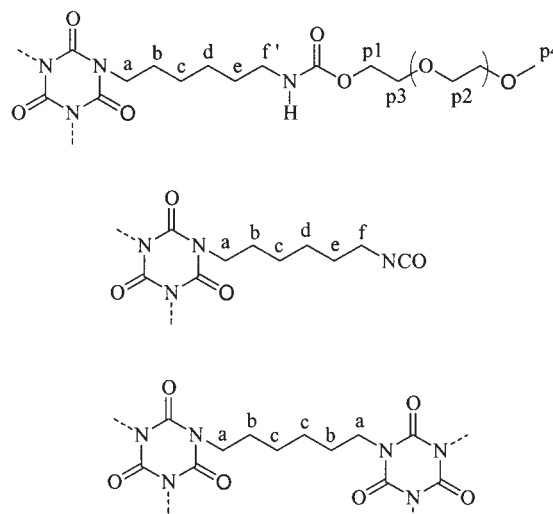


Figure 2 ¹H NMR spectrum in CDCl₃ at 298 K of Bayhydur® 3100.



Scheme 1

Ionic PUs synthesis

Synthesis of modified HTPB precursors

80 g of HTPB were introduced into a 250 mL reactor equipped with a mechanical stirrer (500 rpm), a switchable inlet for nitrogen and a vacuum connector. HTPB was first degassed for 1 h under vacuum (10⁻² mmHg) at 72°C and then kept under nitrogen atmosphere. MEK was added to HTPB to perform a 50% w/w solution. Then, α TG were grafted per HTPB chain to obtain the wanted G-α precursor (0.5 < α < 5). AIBN initiator (0.2% of HTPB total units), which does not induce the reaction of HTPB insaturations,³⁹ was dissolved into the smallest amount of MEK and added to the mixture to initiate the thiol-ene reaction. The reaction, under nitrogen flush at 72°C, was followed by volumetric 0.05M iodine titration by using a self-acting apparatus (Titroline Schott). When the reaction was completed, a viscous yellow liquid was obtained and kept for several months, at low temperature (4°C), prior to further use. Neutralization of acid functions was then carried out with a slight excess of TEA (10%) just before water addition.

Preparation of organic solutions and aqueous dispersions of PU

PUs were obtained via either organic solutions or aqueous dispersions with a constant NCO/OH ratio of 1.1 (Table II).

In the first case, the polyisocyanate was directly added to the organic solution containing the ionic modified precursors (G-α). The reaction was followed by FTIR (Perkin-Elmer Spectrum 2000), and the conversion *C_t* calculated according to eq. (3) using the methylene band of HTPB as reference:

TABLE II
Polyurethane Materials Chemical Composition Based on the Proportion of the Reactants

Material	Components	Molar ratio	NCO/OH	[COO ⁻] wt (%)
G-0	HTPB/Bayhydur® 3100	1/0.9	1.1	0
G-0.5	HTPB/TGA/Bayhydur® 3100	1/0.5/0.9	1.1	1.0
G-1	HTPB/TGA/Bayhydur® 3100	1/1/0.9	1.1	1.9
G-2	HTPB/TGA/Bayhydur® 3100	1/2/0.9	1.1	3.6
G-3	HTPB/TGA/Bayhydur® 3100	1/3/0.9	1.1	4.9
G-5	HTPB/TGA/Bayhydur® 3100	1/5/0.9	1.1	7.2

$$C_t = 100 \times \left(1 - \frac{[\text{NCO}]_t}{[\text{NCO}]_0} \times \frac{[\text{CH}_2]_0}{[\text{CH}_2]_t} \right) = 100 \times \left(1 - \frac{(h_{2270})_t}{(h_{2270})_0} \times \frac{(h_{2920})_0}{(h_{2920})_t} \right) \quad (3)$$

where $(h_{2270})_t$, $(h_{2270})_0$, $(h_{2920})_t$, and $(h_{2920})_0$ are the heights of the NCO and methylene (of HTPB) bands, respectively, at time t and initial time.

In the second case, after neutralization, distilled water was added to the mixture and MEK was then evaporated to obtain the ionic precursor aqueous dispersion. A constant 15% solid content was used along all study. PU aqueous dispersions were obtained by adding Bayhydur® 3100 to the precursor aqueous dispersions (Fig. 3). Reaction conversion was followed by determining the isocyanate content using a standard dicyclohexylamine back titration.

Preparation of the PU samples

Films for mechanical and surface properties characterization were obtained by casting the PU organic solu-

tions or aqueous dispersions into PTFE molds and dried at room temperature for at least 48 h to remove any residual solvent. Prior to any assay, the samples were analyzed by ATR-FTIR to detect any residual isocyanate function at the surface; no NCO bands at 2280 cm^{-1} were detected, the isocyanate excess being either hydrolyzed to amine functions, leading to urea groups, or reacting classically on urethanes to give allophanate functions during the process. PU Soxhlet extraction for 15 h in MEK did not show the presence of TEA. This last acts as counter ion, and the slight excess is removed during MEK evaporation under vacuum.

Dispersion characterizations

Conductimetry

Conductimetric studies (Tacussel CD60 DL) were achieved at room temperature to characterize the aqueous dispersions.

Light-scattering

Light-scattering studies were performed at $(25 \pm 0.1)^\circ\text{C}$ to measure particle sizes using a SEMATech Macrotron correlator equipped with a 25-mW argon-ion laser (vertically polarized incident radiation of wavelength 488 nm), a digital correlator (SEMATech Mach-2), and a computer-controlled, stepper-motor-driven variable angle detection system. The PCS measurements were conducted using the 12-channel Log-Log correlator, and the data were analyzed by cumulates analysis and singular system analysis.

Rheometry

Viscosity of the precursor dispersions was measured at $(25 \pm 0.1)^\circ\text{C}$ on an AR200 rheometer (TA Instruments) equipped with a two-cylinder adapter. Shear rate was determined at a shear stress range between 0.01 and 100 Pa. Reduced viscosity was calculated according to the following eq. (4), where η_0 was the apparent viscosity of water (1.02 mPa s at 25°C) and η_{app} the apparent viscosity of the modified HTPB-based dispersion at concentration c (g dL⁻¹).

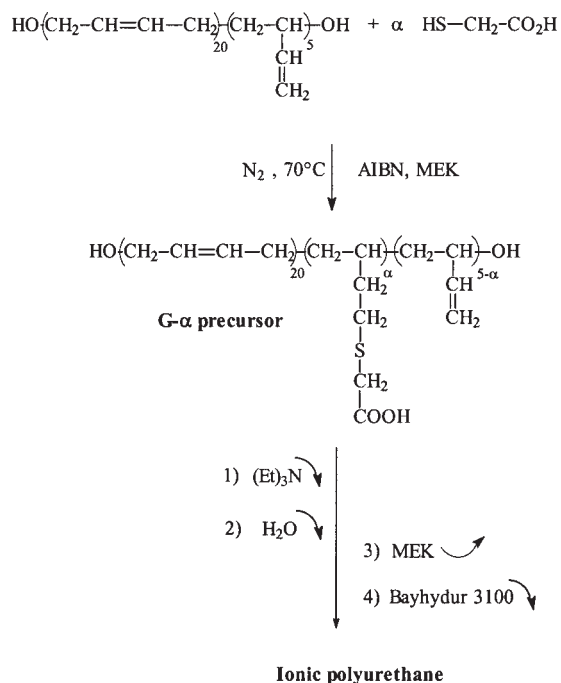


Figure 3 Synthesis scheme of the anionic G- α polyurethane family.

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} = \frac{\eta_{\text{app}} - \eta_0}{\eta_0 \times c} \quad (4)$$

PU properties

Mechanical properties

Mechanical properties of the G- α PUs were assessed by Dynamic Mechanical Analysis (DMA 7 Perkin-Elmer) in compression mode with a 1-mm diameter stainless steel parallel plate probe at 1 Hz on 3×3 mm² samples. Static and dynamic forces were fixed at 110 mN and 100 mN, respectively, to reach 1 μ m amplitude deformation in the glassy state. Measurements were carried out under N₂ atmosphere between -120 and 200°C with a heating rate of 10°C min⁻¹. Standard calibration was performed with *n*-decane ($T_m = -50^\circ\text{C}$) and indium ($T_m = 156.6^\circ\text{C}$).

Water uptake

Swelling measurements were performed, for different times, on $10 \times 10 \times 1$ mm³ PU samples in water at $(20 \pm 1)^\circ\text{C}$. After weighing, m_s , swelled samples were dried at 60°C until a constant mass was reached, m_d . Swelling (Q) was calculated in eq. (5)

$$Q = \frac{m_s - m_d}{m_d} \times 100 \quad (5)$$

Surface properties

Surface tensions (γ) of the PU films were evaluated using a goniometer (DGD-ASE goniometer, GBX, Romans sur Isère, France). The static contact angle (θ) measurements on the air-facing surfaces were assessed using four liquids: water, formamide, diiodomethane, and ethylene glycol. Measurements on nine different spots were performed to calculate the mean static contact angle and its standard deviation. According to Owens-Wendt relationship, eq. (6), the dispersive γ_s^d and polar γ_s^p components of the PU films were determined as follows:

$$\frac{(1 + \cos\theta_1) \times \gamma_1}{2\sqrt{\gamma_1^d}} = \sqrt{\gamma_s^d} + \frac{\sqrt{\gamma_1^p} \times \sqrt{\gamma_s^p}}{\sqrt{\gamma_1^d}} \quad (6)$$

where γ_1 , γ_1^d and γ_1^p are the solvent (total, polar, and dispersive) superficial tension parameters.

RESULTS AND DISCUSSION

HTPB-modified precursors

Ionic-modified precursors were obtained by radical grafting of TG onto HTPB lateral double bonds ac-

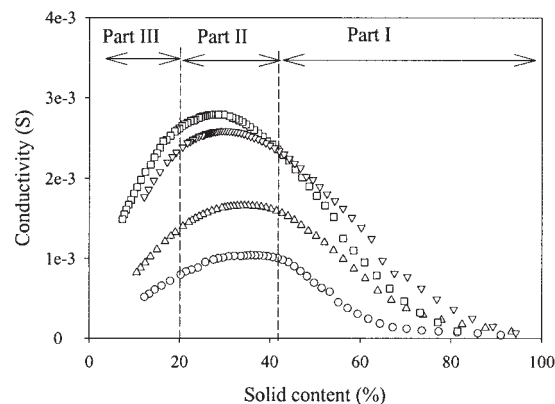


Figure 4 Conductivity analysis. Influence of the degree of neutralization for G-2 precursor dispersions. \circ : $\rho = 0.25$, \triangle : $\rho = 0.5$, \square : $\rho = 1.1$, ∇ : $\rho = 2$

ording to a modified method of Schapman.³⁹ α TG were grafted per HTPB chain to obtain the wanted G- α precursor ($0.5 < \alpha < 5$). Modified HTPB, G- α , were then neutralized with TEA. Conductivity was first used to characterize the anionic G- α dispersions, as described in previous work.³³ The dispersion process can be divided into three steps (Fig. 4), as described by Dieterich² and Chen.^{8,21}

In step I, conductivity increases slowly with water addition. The solution can be considered as an organic medium with aggregation of non solvated ionic segments stabilized by columbic forces.

In step II, when more water is added, the solution becomes turbid. This result indicates that ionic groups are completely solvated while hydrophobic segments contract progressively to the core. Ionic microspheres are formed and phase inversion occurs.

In step III, conductivity decreases linearly with water addition by dilution effect. The phase inversion is completed and most of the carboxylate groups are located at the particle surface. Then, the dispersion consists in a continuous aqueous phase with dispersed particles composed of hydrophobic core swelled by MEK and hydrophilic shell. Stabilization of such particles is enabled by the double shell of diffusion phenomenon.³

The maximum solid content for which stable dispersion over time are obtained is determined using the maximum conductivity, i.e., at phase inversion.

Influence of the degree of neutralization was first studied. The ratio of TEA over acid functions, ρ , varied between 0.25 and 2. For aqueous dispersion, it is generally demonstrated that particles' size decreases while dispersion viscosity and conductivity increase when ρ increases.^{49,50} Similar results are obtained here with all G- α ionic dispersions. In Table III, selected results obtained for G-2 are presented. The particles size decreases significantly with increasing neutralization of carboxylic acid groups, the increasing number

TABLE III
Aqueous Dispersion Stability of Ionic Precursors
(15 % Solid Content)

Dispersion at 15% solid content	ρ	Particle size (nm) after		
		1 day	1 month	6 months
G-0.5	1.1	190 ± 50	170 ± 30	140 ± 30
G-1	1.1	150 ± 60	100 ± 50	150 ± 60
G-2	0.25	1700 ± 350	demixion	—
G-2	0.5	260 ± 40	260 ± 60	—
G-2	1.1	100 ± 10	90 ± 10	120 ± 10
G-2	2	110 ± 10	100 ± 10	—
G-3	1.1	100 ± 10	80 ± 10	80 ± 20
G-5	1.1	<30	<30	<30

of anions having the ability to stabilize a greater total particle surface area. Adding a double excess of TEA had no significant effect on particle size, whereas neutralization lower than 50% ($\rho < 0.50$) led to unstable aqueous dispersions after one month. Thus, thereafter, the carboxylic functions were arbitrarily neutralized with an excess of 10% of TEA, i.e., $\rho = 1.1$, for all G- α polymers.

Conductivity measurements of G- α ionic dispersions are shown in Figure 5. As expected, the increase of conductivity is α -dependent. However, solid content decreased from 50 to 20% when α increased from 0.5 up to 5 ionic functions per HTPB chain. This behavior was attributed to the increasing presence of initial ionic aggregates with carboxylate content, which are difficult to solvate during the dispersion process.

With the aim of an industrial application, these results demonstrate that too many anions at the particle surface could be a disadvantage for high solid content dispersions.

Particle size analysis and reduced viscosity were checked on the aqueous dispersions after MEK elimination under vacuum. A 15% w/w was kept constant

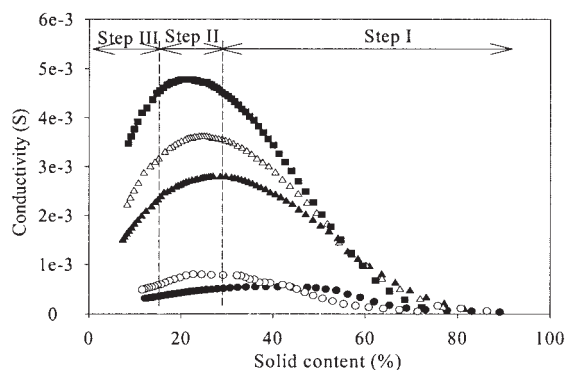


Figure 5 G- α precursors: Influence of ionic content on the conductivity of G- α precursors at $\rho = 1.1$. ●: G-0.5, ○: G-1, ▲: G-2, △: G-3, ■: G-5.

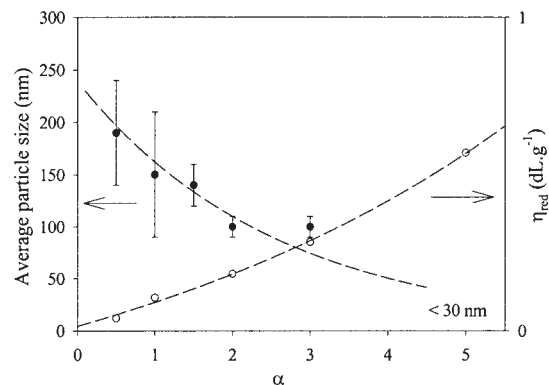


Figure 6 G- α precursors: Influence of ionic content on average particle sizes measured after one day and the reduced viscosities of dispersions at 15% solid content.

for all G- α dispersions (Fig. 6). As expected, the particle size decreased significantly with increasing α , i.e. from 200 nm for G-0.5 to less than 30 nm for G-5. For the latter, the particle size was unknown because it is lower than the limit of detection, i.e., 30 nm. This was also observed visually as a transition from a white dispersion to a transparent one for G-5. The viscosity increased with decreasing particle size as it is common for colloidal dispersions.

Dispersion stability was followed along time. Neither sedimentation nor significant particle size variation was observed after six months (Table III).

Polyurethanes

PUs were obtained by addition of the polyisocyanate ($r = [\text{NCO}]/[\text{OH}] = 1.1$) to the precursor aqueous dispersions and compared to PUs synthesized in organic media, i.e., addition of the polyisocyanate to a solution of the precursor in MEK. The reaction kinetic was followed using a common dicyclohexylamine back titration method.

Bayhydur® 3100 reaction with water was followed in the presence and in the absence of precursor. Figure 7 clearly shows that Bayhydur® 3100 is stable in water (less than 10% NCO reaction after 4 h) and that the reaction occurs preferentially on the hydroxyl functions of the polyol when present, regardless of thioacid content. For all G- α PUs, a similar rate of conversion was observed. Selected results are presented Figure 7.

In organic media, the reaction conversion was followed by FTIR. It is observed that the reaction is faster than in aqueous medium (Fig. 7). However, the reaction kinetic depends on ionic content, i.e., α . The triethylammonium counter ions present in the media are involved in the catalysis of the alcohol-isocyanate reaction, as described by Chen.²³

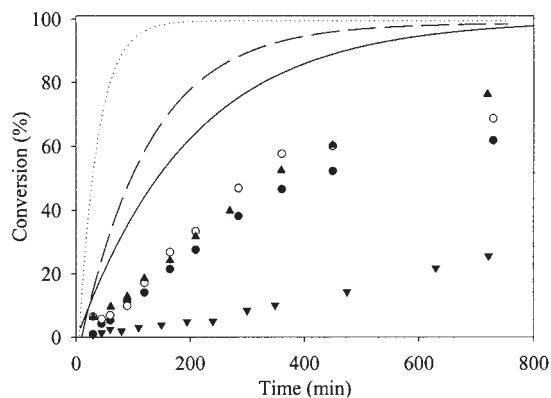


Figure 7 Bayhydur® 3100 and G- α reaction at room temperature. In water, ●: G-0.5, ○: G-1, ▲: G-2 and in the absence of polyol ▼: H₂O. In MEK, —: G-0.5, - - : G-1, · · · : G-2.

In water, the reaction occurs in a heterogeneous system. Small precursor droplets are suspended in water. Stabilization of the precursor particles is done by the grafted ionic groups. The alcohol-isocyanate reaction is diffusion controlled and thus, slower than in organic media. The reaction occurs in the core of the particles, where only few ionic charges are located, since most of them are on the shell. Thus, with the aqueous system no catalytic effect induced by the counter ions is observed, and the viscosity of the media remains almost constant.

PU properties

Influence of ionic content on PU mechanical properties was analyzed by DMA (Fig. 8). $\tan \delta$ was used to follow the glass transition temperature of the PUs. $\tan \delta$ curves exhibit a distinct mechanical transition temperature, T_{α} , at which maximum can be assimilated to the soft segment glass transition temperature, T_g . Highly segregated soft materials are obtained. These properties are commonly observed for HTPB-based PU. HTPB has a very low glass transition (-75°C) and hydrocarbon-based PUs exhibit highly segregated structures, which are first linked to the large difference in surface energy between their hard and soft segments and second, to the absence of hydrogen-bonding between hard and soft segments. For the studied PUs, H-bonding may only occur within the hard segment region between urethane groups and possibly with the PEG chain present in Bayhydur® 3100. Overall, if present, H-bonding will have a similar effect on all PUs, since hard content is kept constant. Thus, the observed variations in $\tan \delta$ will be linked only to ionic content. For all studied PUs, $\tan \delta$ peaks exhibit similar amplitudes attesting no interference of the ionic groups in the chemical crosslinking process. Thus, relaxation time distribution is little affected with increasing α . Increase of T_{α} , from -50°C for G-0 to 0°C

for G-5 is attributed to the increasing presence of ionic aggregates within the soft segments region. When ionic content reaches 3 or 5 groups per chain ($\alpha = 3$ or 5), ionic interactions slightly affect the damping effect, i.e., $\tan \delta$ amplitude decreases. Storage modulus curves, E' , also highlight the presence of these ionic aggregates by the rise of the rubbery plateau with increasing α .

When prepared via organic media, ionic PUs exhibit similar properties, i.e., T_{α} increases with increasing ionic content (Table IV). This confirms that via aqueous dispersion very few isocyanate functions are likely to react with water when ionic HTPB is present. Thus, the crosslinking process occurs similar way, regardless of the chosen chemical route. Overall, synthesized ionic PUs are soft materials. This is the consequence of the presence of ionic groups in the soft segment region.

Up to now, ionic chain extenders were incorporated to prepare water dispersible PUs. Their presence in the hard segment region often induced perturbations of the usual physical crosslinking process between urethane groups. Aggregated ionic microdomains within the hard segments may take place,^{10,51} as well as interactions between the N—H urethane groups and the ionic groups. Moreover, when an ionic chain extender is used, changing ionic content affects the NCO/OH ratio. Thus, large differences in the mechanical properties of the PU are observed, with an evolution from soft to brittle behavior as ionic content increases.

Water absorption was followed at room temperature for up to 30 days (Fig. 9). Solvent uptake of thermosets is affected by the incorporation of ionic groups in soft segments, for example from 2% for G-0 to 18% for G-5. In comparison to other ionic PUs, water uptake is very low (1000%^{52–54}). This is to be related to the very hydrophobic properties of HTPB.

However, comparing the two PU chemical routes, different trends are observed. PUs prepared via or-

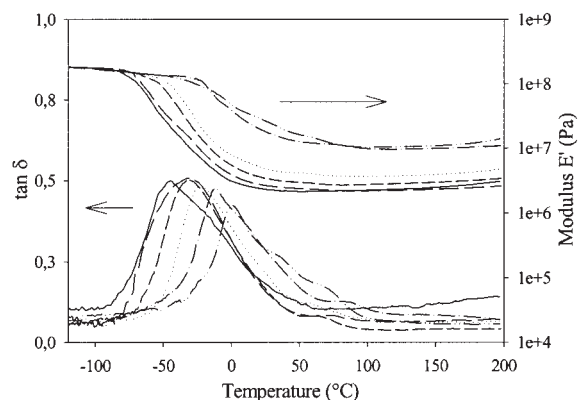


Figure 8 G- α PU prepared via aqueous dispersion. Influence of ionic content on the dynamical mechanical properties. —: G-0, — — : G-0.5, - - - : G-1, · · · : G-2, - · - : G-3, - · - · : G-5.

TABLE IV
Polyurethane Thermomechanical and Surface Properties

PU	$T\alpha$ (°C)	Water contact angle		$T\alpha$ (°C)	Water contact angle
		25°C	60°C		
G-0	—	—	—	-78	84 ± 1
Aqueous dispersion					
G-0.5	-77	76 ± 1	77 ± 1		
G-1	-59	71 ± 2	71 ± 2		
G-2	-52	67 ± 3	65 ± 1		
G-3	-28	56 ± 3	57 ± 2		
G-5	-25	49 ± 2	50 ± 2		
MEK solution					
G-0.5				-77	82 ± 2
G-1				-63	77 ± 3
G-2				-56	73 ± 3
G-3				-24	68 ± 2
G-5				—	—

ganic phase exhibit typical curves, i.e., increasing water uptake with time, up to a plateau (Fig. 9).

On the opposite, PUs prepared via aqueous phase exhibit atypical results after a drying step at room

temperature. Water uptake of G- α PU materials increased with ionic content. However, maximum water uptake is observed at short times followed by a decrease of swelling along time to tend to a similar plateau as mentioned above [Fig. 9(a)]. Two assumptions can be made to explain this result:

1. Uptake:
The existence of ionic preferential pathways formed during the slow water evaporation and the presence of remaining water molecules bound to the ionic regions, which promote water uptake.
2. Deswell:
a progressive conformational reorganization of the PU chains coming from water plasticization, leading to a more thermodynamically stable material.

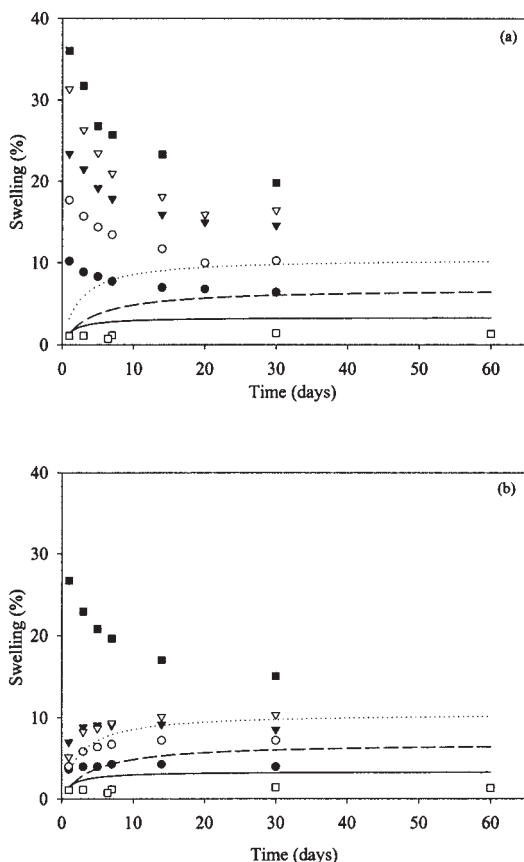


Figure 9 Influence of ionic content and drying temperature on water uptake. G- α PU prepared in organic medium, —: G-0.5, - - : G-1, · · · : G-2. G- α PU prepared in aqueous dispersion, ●: G-0.5, ○: G-1, ▲: G-2, △: G-3, ■: G-5. (a) After initial drying at 25°C, (b) after drying at 60°C compared to nonionic □: G-0.

When a second drying step is achieved at 60°C, classical swelling curves are observed again [Fig. 9(b)]. These are similar to water uptake curves obtained for PUs prepared in MEK, except for G-5. This observation was attributed to bounded water evaporation and chain reorganization, although no significant weight loss was observed during this second drying step. In these conditions, linked water molecule elimination is possible up to a limited concentration, since for $\alpha = 5$, preservation of the ionic preferential pathways is still observed.

Static contact angle measurements using water, ethylene glycol, diiodomethane, and formamide were achieved on the air-facing surfaces. Incorporation of ionic groups induces a significant decrease in water contact angle, indicating that surfaces become more hydrophilic. But, surface behaviors depend on the chosen chemical route. PUs obtained from aqueous dispersions and dried at room temperature exhibit smaller water contact angles than those obtained via

organic media (Fig. 10). These results corroborate water uptake observations and confirm that PUs obtained via aqueous dispersion have a different molecular organization.

Since the drying temperature affected the swelling behavior of the synthesized PU, we analyzed its effect on the surface properties. Results reported in Table IV show that a drying step at 60°C does not markedly affect water contact angle measurements. This observation implies that the ionic surface concentration remains similar whatever be the drying step conditions and that temperature mainly affects the bulk organization and reorganization.

The use of Owens-Wendt relationship enabled us to determine the polar and dispersive components of the surface tension, γ , for the different PUs. Accordingly, the influence of the carboxylic group on the surface properties could be quantified (Fig. 11).

Broadly, ionic PU surfaces remain hydrophobic, with surface tensions close to G-0, $\gamma = 40 \text{ mJ m}^{-2}$. As expected, increasing ionic content induces an increase of the polar parameter γ^p whatever be the chemical route.

CONCLUSIONS

The development of this new family of water dispersible PUs has been motivated by environmental considerations, i.e., no organic solvent emissions in the atmosphere and no use of free isocyanate during application. Compared to all ionic PUs in the literature, the prepared PUs differ from those materials in terms of the potential for having high densities of ionic functions within the chain at constant NCO/OH ratio and the specific chemistry of the aqueous dispersible polyisocyanate. Very stable HTPB-based aqueous dispersions with various TG contents were prepared. Particle sizes were dependent on ionic content and found smaller than 200 nm. Addition of a water solu-

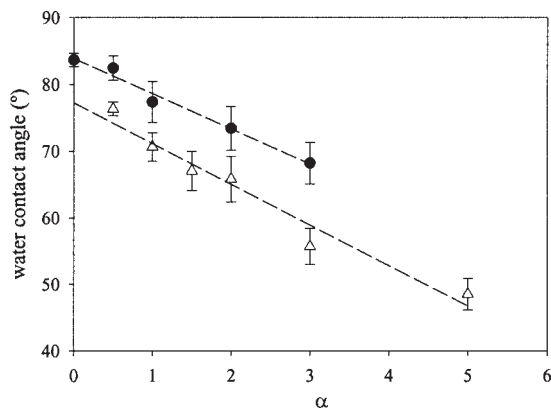


Figure 10 Water contact angle on G- α surfaces prepared in aqueous media: Δ or in organic medium: \bullet (mean \pm SEM, $n = 9$).

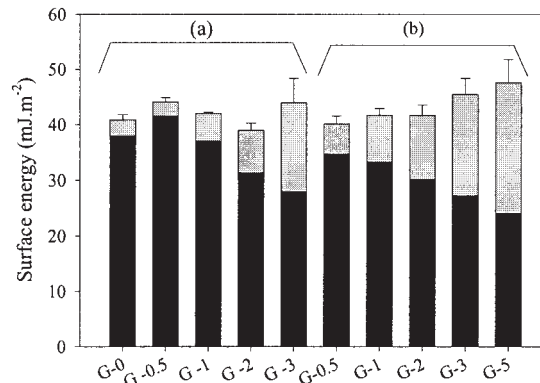


Figure 11 Surface energy of ionic PU. Influence of the synthesis route and ionic content. \blacksquare : dispersive component, \blacksquare : polar component. (a) via organic solution, (b) via aqueous dispersion.

ble polyisocyanate led to the final thermosets. Physical and surface properties of the resulting films were compared to identical PUs obtained via organic media. Although it exhibits similar mechanical properties according to DMA, a different organization of the ionic aggregates was assumed according to water uptake and water contact angle measurements.

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