

Fluorinated Segmented Polyurethane Anionomers for Water–Oil Repellent Surface Treatments of Cellulosic Substrates

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ABSTRACT: Three model structures of linear segmented anionomeric polyurethanes based on perfluoropolyether dimethylol-terminated oligomers, isophorone diisocyanate, and dimethylol propionic acid were synthesized and obtained in the form of aqueous dispersions. The structures differed from each other in the chemical nature of the chain extender (diol or diamine) and in the content of carboxylic acid. Dispersions and polymer films were characterized by dynamic light scattering, dynamic mechanical analysis, differential scanning calorimetry, and contact angle measurements. Diluted aqueous dispersions were also evaluated as

protective sizing agents in paper treatment, both as bulk modifiers and as surface treatments. Paper sheets characterized by high water and oil repellence were obtained. The results showed that performance is mainly related to the ionic group content of the polymer and to its molecular architecture. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1364–1372, 2005

Key words: perfluoropolyether; polyurethane; paper; oil repellence; water repellence

INTRODUCTION

The field of products used to impart water–oil repellence and soil release to substrates like paper, textiles, stones is dominated by both oligomeric (phosphates, carboxylates, quaternary ammonium salts) and polymeric (mainly copolyacrylates) fluorochemicals, which have in common the presence of linear and branched monofunctionalized fluoroalkyl chains.^{1,2} More recently, copolymers based on the presence of bifunctionalized perfluoropolyether (PFPE) chains are being used in industrial applications in the same sector.³ Among the various possible structures, ionomeric polyurethanes (PUs) are very suitable to obtain partially fluorinated copolymers in the form of stable aqueous dispersions or emulsions.

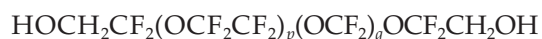
In this work model structures of anionic PUs based on the presence of PFPE chains are synthesized and physicochemically characterized. They were obtained by a two-step polymerization process, consisting of the formation of a prepolymer followed by chain extension and dispersion in water. When diols are used as chain extenders, linear polymers containing only urethane linkages are formed. Conversely, if chain

extension is carried out with diamines, the final polymer will contain both urethane and urea bonds. They were also evaluated as polymeric additives in paper sizing applications. It is recognized that paper used for food packaging must possess sufficient grease and oil resistance, which is usually conferred by sizing with fluorochemical oligomeric or polymeric additives.⁴ The simplest way to measure the oil repellence (OR) is the evaluation of the resistance of the paper sizing to the penetration of hydrocarbon mixture droplets, which have a progressively decreasing surface tension. Moreover, water repellence (WR) is important because water can cause excessive swelling of the cellulosic material, worsening the performance, even against fats and oils. The combination of physicochemical characterization along with performance testing is focused on the understanding of the key compositional or structural parameters affecting the water–oil repellent behavior of these new partially fluorinated polymers.

EXPERIMENTAL

Materials

The PFPE dimethylol-terminated sample (Fomblin ZDOL, Solvay–Solexis) used in this work has the following chemical structure:



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where $p/q = 2.1$, the number-average molecular weight is 1500, the viscosity is 150 mPa s, and the glass-transition temperature (T_g) is -94°C . The monomers isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), ethylenediamine (EDA), cyclohexane-1,4-dimethanol (CHDM) and the chemicals triethylamine (TEA), dibutyltin dilaurate (DBTDL), *N*-methyl pyrrolidone, and methylethyl ketone (MEK) were supplied by Aldrich.

Prepolymer synthesis

PU_s

The PFPEs ZDOL (1 mol) and IPDI (2 mol) were charged into a reactor. The reaction was catalyzed with 1 drop of DBTDL and kept at $+90^\circ\text{C}$ for 1 h, until no more $-\text{CF}_2\text{CH}_2\text{OH}$ free groups were detected in the NMR analysis.

PU-ureas

The details of the preparation procedure for PU-ureas are reported in another work.⁵ The main difference is that the NCO-terminated prepolymer is formed with a randomized reaction among ZDOL, IPDI, and DMPA, in such a way that $\text{NCO}/\text{OH} = 2$ mol, but including in the calculation both the OH equivalents of DMPA and those from ZDOL.

Chain extension and dispersion in water

PU_s

Once the NCO-terminated prepolymers were formed, chain extenders were added along with the solvent (MEK, 70% final solid). In one case (PU1) only DMPA was added, whereas in another case (PU2) an equimolar mixture of DMPA and CHDM was used. For both structures the overall OH/NCO stoichiometric ratio was 1.05. TEA was also added dropwise in order to dissolve the solid DMPA in the reaction mixture. As discussed in the next section, different NET_3/COOH stoichiometric ratios were evaluated. Polymerization was continued under stirring at $+70^\circ\text{C}$ until no more free NCO signals were detected in the FTIR analysis. Once the polymerization was completed, the organic solution of the polymer (70% solid) was poured into a second water-containing vessel equipped with a turbine impeller rotating at 100 rpm. After polymer dispersion, the solvent was evaporated by vacuum distillation at $+50^\circ\text{C}/30$ mmHg and a 30% solid aqueous PU dispersion was obtained.

Polyurea-urethanes (PUUs)

The details of the PUU synthesis are reported in another study.⁵ The main difference with the above-

described process is that the NCO-terminated prepolymer (also containing COOH groups in this case) was chain extended in the aqueous phase with EDA in a slight stoichiometric defect ($\text{NH}_2/\text{NCO} = 0.98$).

Molecular characterization

^{19}F -NMR spectroscopy was carried out with a Varian 300-MHz instrument that was used to check the conversion of ZDOL in the prepolymerization step, as already reported for similar systems.⁶ FTIR spectroscopy was utilized to confirm the end of the polymerization process by monitoring the disappearance of the NCO band at 2260 cm^{-1} with a Perkin-Elmer model 1600 FT spectrometer. The molecular weights of the final polymers were estimated by intrinsic viscosity measurements in a solvent mixture made of 8/2 trifluorotoluene/trifluoroethanol or by gel permeation chromatography (GPC) using a Waters instrument and a set of Ultrastyrigel columns (porosity = $500\text{--}10^5$ Å) with THF as the eluent and polystyrene calibration standards.

Particle size measurements

The average particle dimensions and polydispersity of the final PU dispersions were measured by dynamic laser light scattering with a Brookhaven goniometer and correlator equipped with an argon ion laser operating at 514.5 nm. The radii (R) of the particles were estimated from the diffusion coefficients (D) by means of the Stokes-Einstein relationship, $D = k_B T / 6\pi\eta_0 R$.

Rheological measurements

Viscosity measurements were obtained at $+20^\circ\text{C}$ with a Rheometrics Scientifics DSR 200 rotational rheometer in cone-plate geometry.

Dynamic mechanical analysis (DMA)

DMA spectra were obtained in torsion mode with a Rheometric Scientifics ARES 3/A25 dynamic mechanical spectrometer on 0.8 mm thick samples obtained by casting and oven drying. A dynamic temperature ramp of about $2^\circ\text{C}/\text{min}$ (from -150 to $+150^\circ\text{C}$) and a frequency of 1 Hz were used.

Differential scanning calorimetry (DSC)

DSC thermal analyses were carried out with a Perkin-Elmer DSC 2 instrument calibrated with indium and *n*-hexane. The glass transitions and specific heat changes at the T_g were evaluated from heating runs from 20 to 200°C and cooling runs from 20 to -160°C at a rate of $20^\circ\text{C}/\text{min}$.

TABLE I
Characteristics of Fluorinated Polyurethanes

Polymer	Fluorine as PFPE (wt %)	COOH content (eq/kg)	Position of DMPA monomer	Intrinsic viscosity (mL/g)
PU1	71	0.50	Chain extender	12.0
PU2	70	0.21	Chain extender	13.0
PUU	65	0.25	Within prepolymer	15.0

Contact angle measurements

Static contact angles against bidistilled water and the highest purity *n*-alkane droplets (from *n*-hexadecane to *n*-octane) were measured at +23°C with a Kruss G10 DSA instrument according to the sessile drop method. Thin polymer films (5–10 μm) were bar applied on chromated aluminum panels and oven dried at +105°C for 5 min. Advancing and receding contact angles against water were also measured on dip-coated glass slides at 20°C by the Wilhelmy plate method, using a KSV Sigma 70 dynamic contact angle meter (1 mm/min speed). Samples were prepared by dipping in 10% PU dispersions to insure a completely coated surface. Results were expressed as the mean of 10 independent measurements.

Preparation of water–oil repellent paper sheets by wet-end treatment of cellulose

A cellulose blend of 70/30 (w/w) bleached spruce kraft softwood/bleached eucalyptus kraft hardwood was refined to 32° Schopper–Riegler using a PFI beater. The pulp slurry pH was adjusted to 7.5 with 150 ppm NaHCO₃. It was then diluted to 0.4 wt % consistency and pretreated with 0.5 wt % cationic starch (Cato 235, National Starch; degree of substitution = 0.02, previously cooked to 10% solids at 90°C for 30 min in a jacketed heated vessel) to improve the dry-strength paper properties. The pulp slurry was then transferred into a laboratory sheet-forming machine, and 0.2 wt % (dry material on dry cellulose) of a high-charge density, crosslinked dimethylamine–epichlorohydrin copolymer (Nalkat 7607, Nalco Corporation; charge density = 6 mequiv/g) was added to the slurry before the addition of PU to improve the PU retention on the fibers. The different PU dispersions were added separately in amounts of 0.3–1.0% dry PU on dry cellulose.

The dosage of the dimethylamine–epichlorohydrin copolymer was selected in order to keep the total pulp charge close to neutrality. The total pulp charge (dissolved + adsorbed on cellulose) was measured using a Mutek particle charge detector coupled with an automated titrator. A 1 × 10⁻⁵ N poly-Diallyldimethyl ammonium chloride (DADMAC) standard solution was used to titrate the pulp slurry. After sheet forming, the wet paper sample was recovered and dried at

105°C in a rotary drier for 3 min. The amount of pulp slurry used was calculated in order to produce a paper specimen having a 65 g/m² basis weight.

The PU retention on cellulose fibers was 95–100% in each trial. It was controlled through the determination of the total fluorine content by total combustion of the paper specimen in an oxygen bomb and fluorine determination with a fluoride-specific electrode.

Preparation of water–oil repellent paper sheets by size-press treatment of cellulose

The paper base sheet (basis weight = 65 g/m²) used for the trials was made of 100% bleached kraft pulp (60/40 softwood/hardwood, w/w) without synthetic water sizing agents. The total ash content was approximately 0.3 wt % (TAPPI test method T-211). The Gurley porosity of this substrate was 40 s/100 mL (TAPPI test method T-460). This base sheet was treated with diluted (0.3–1%) aqueous solutions of the various fluorinated PUs in a laboratory size press at room temperature. The nip pressure was adjusted to 3 bar, and the linear speed was fixed at 15 m/min. The base-sheet wet pick-up in these machine conditions was in the range of 90–95%. After the size-press treatment, the wet paper sample was recovered and dried at 105°C in a rotary drier for 3 min.

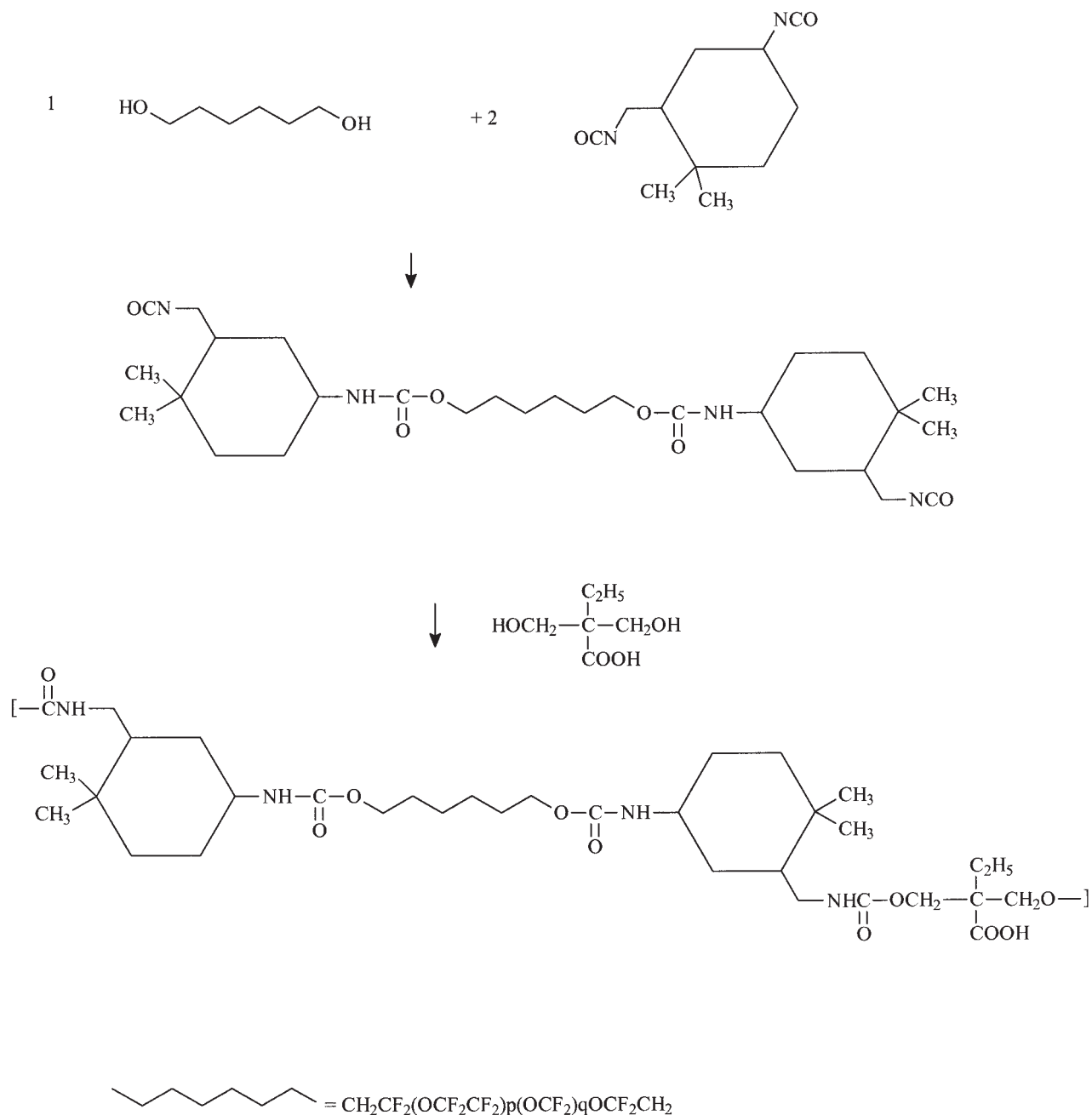
Evaluation of WR and OR

The OR of the treated cellulose was evaluated according to the Kit test method (TAPPI 557 test method) by measuring the resistance of paper to the penetration of progressively decreasing surface tension liquids. The results are expressed with a numerical scale ranging from 0 (pure castor oil) to 16 (pure *n*-heptane).

The WR was evaluated according to the Cobb test method (TAPPI T 441 test method), which is based on the determination of the weight increase of the paper specimen after exposure to water in standardized conditions. The results are expressed as grams per square meter of water absorbed.

RESULTS AND DISCUSSION

Some characteristics of the anionic PU structures selected for this study are shown in Table I. They differ



Scheme 1 The synthesis scheme of the PU1 polymer.

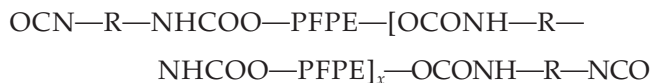
mainly in the content of COOH groups, the position of the ionic monomer (DMPA) within the macromolecular chain, and, to a lesser extent, the percentage of fluorine.

For PU structures PU1 and PU2, a polymerization scheme belonging to the so-called acetone process was followed.⁷ Scheme 1 shows the reaction scheme for the synthesis of the PU1 structure. PU2 was obtained in the same way, except for the chain extension step, where an equimolar mixture of DMPA and CHDM was used. The polymers were first synthesized as a 70% solid solution in a ketone-type solvent (MEK

instead of acetone because of its higher boiling point) and then dispersed in water through a physical dispersion process. The solvent was then removed by distillation to obtain the final polymer emulsion. In contrast, the PUU structure was obtained through a contemporaneous polymerization (chain extension) and dispersion process, according to the known prepolymer mixing method⁷ of PU dispersions. To this aim, introduction of the DMPA hydrophylic monomer already in the prepolymerization step is mandatory. A comparison of the two processes accounts for the structural difference in the molecular architecture of

the chain, in particular concerning the position of the ionic monomer DMPA, which is used as the chain extender in the PU1 and PU2 models but as the prepolymer comonomer in the PUU structure.

In all cases, the PFPE macromer was first derivatized with an excess of IPDI and then chain extended (multistep process). IPDI is often chosen as the diisocyanate in this kind of process. The commercial monomer is a mixture of different isomers. Concerning the reactivity, the secondary NCO function is less sterically hindered and more reactive with hydroxyls when metal catalysts are used, as in the case of DBTDL. The difference in the reactivity⁸ allows the minimization of chain growth during prepolymerization, which means a more regular segmented structure and a lower viscosity prepolymer. The degree of chain growth during prepolymerization of ZDOL (1 mol) and IPDI (2 mol) was evaluated in a series of separate experiments, in which the amount of free (unreacted) IPDI was measured by extraction with *n*-heptane and gas chromatography at the end of the prepolymerization step (conversion of $-\text{CF}_2\text{CH}_2\text{OH} \rightarrow -\text{CF}_2\text{CH}_2\text{OCONH}-$ reaction = 100% in the ¹⁹F-NMR analysis). According to these gas chromatography determinations, the chain growth of the prepolymer should be limited to 1.23–1.26; a more precise representation of the prepolymer is the following:



where $x = 0.23-0.26$. Although chain extension in water with EDA for the PUU structure is a quite fast process, the chain extensions in the solvent phase show a very slow overall kinetics. This is due mainly to the fact that diols are much less reactive than diamines, and the reaction must be carried out at moderate temperatures to avoid undesirable side reactions

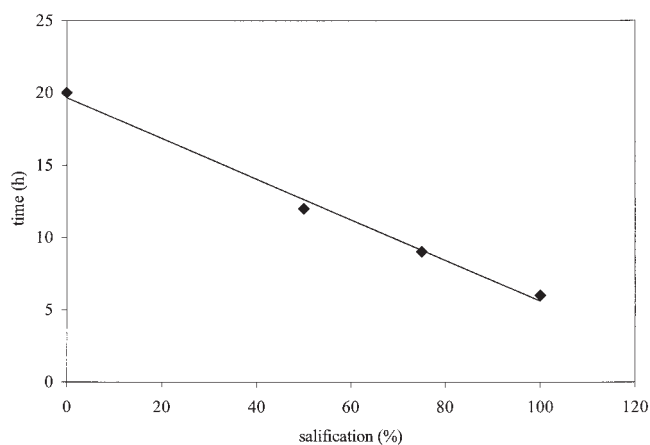


Figure 1 The reaction time versus the percent salification of DMPA in the synthesis of the PU1 structure ($T = 70^\circ\text{C}$).

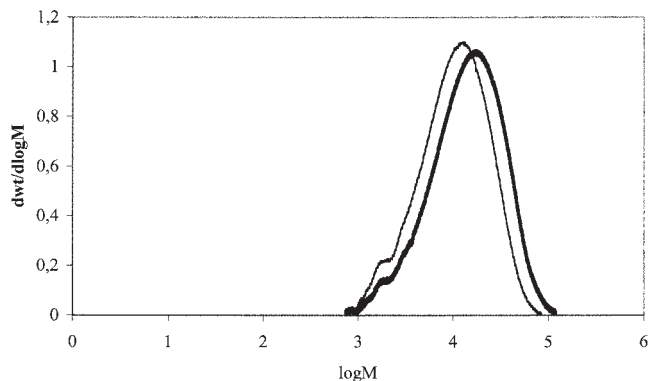


Figure 2 A comparison of GPC chromatograms of (thick line) PU1 and (thin line) PU2 polymers.

(such as the formation of isocyanurate rings). Moreover, other factors negatively affect the chain extension kinetics in the solvent phase: the strong increase in viscosity; the progressive lowering of the concentration of reacting groups; and the presence of COOH groups from DPMA, which may inhibit the urethane formation reaction. With regard to this last point, we found that the presalification of DMPA with TEA largely improves the overall polymerization kinetics. As an example, the behavior of the reaction time (time to reach 0 NCO in the IR analysis) versus the TEA/COOH ratio for the PU1 structure is shown in Figure 1. In the following, a TEA/COOH ratio of about 0.75–0.80 was used for the preparation of the dispersions as a compromise between the polymerization rate and the water dispersibility. The intrinsic viscosity values of the different synthesized polymers are very similar, even if the effect of different compositions on the polymer–solvent interaction parameters are unknown. Because the PU1 and PU2 structures are soluble in THF, their molecular weight distributions could also be estimated by GPC, as shown, for example, in Figure 2. The weight-average and number-average molecular weights relative to the polystyrene calibration curve confirm good reproducibility and similarity of the molecular weights of the two structures.

Some characteristics of aqueous dispersions are reported in Table II. The most significant differences concern the size of the polymer particles in the aqueous phase, which were estimated by dynamic light scattering. In fact, by using the same dispersion procedure, polymers PU1 and PU2 generate very different emulsions. In particular, PU1, which has a much higher hydrophilic character (high COOH content), is characterized by a nanoscopic particle size of about 20–30 nm (dispersion is translucent and more viscous) whereas the PU2 dispersion is a typical milky-white emulsion (150–180 nm). It is interesting to emphasize that the PUU dispersion, which has practically the same COOH content of PU2, is characterized by an

TABLE II
Characteristics of Fluorinated Aqueous Dispersions

Polymer	pH (25% solid)	Viscosity at 20°C (25% solid)	Particle size (nm)	Polydispersity
PU1	7.5	200	20–30	0.20
PU2	7.9	<50	150–180	0.15
PUU	8.5	<50	70–90	0.12

intermediate particle size value (70–90 nm). However, in this case, the polymerization process is very different, because it is based on contemporaneous dispersion and chain extension of an ionic, low molecular weight prepolymer.

The thermal transitions by DSC of the three dried polymers are reported in Table III. Two T_g values were observed in all cases. The materials are therefore biphasic, which is typical of segmented copolymers containing PFPE blocks.⁹ The thermal transitions of PU1 and PU2 are quite similar, whereas significantly higher T_g values are measured for the PUU PU-urea. This high T_g is probably justified by the strong cohesive interactions related to hydrogen bonding of urea linkages —NHCONH—, which are absent in the other two model structures.

Different physical behaviors are also observed by examination of the dynamic mechanical spectra shown in Figure 3. Again, PU1 and PU2 appear to be very similar with a clear maximum of $\tan \delta$ at about -74 to -78°C , which is attributed to the segregated PFPE phase, followed by a poorly defined, broad relaxation that is better individuated by the marked softening of the material (sharp decrease of the storage modulus) at about $+40^\circ\text{C}$. In contrast, PUU shows two well-defined $\tan \delta$ maxima at -77 and $+108^\circ\text{C}$ and the storage modulus is always higher than PU1 and PU2 at $>0^\circ\text{C}$. The PU-urea is much more “solid” than fully PU structures, with a small intensity in the dissipation factor peaks.

The surface properties of the polymer films were estimated through evaluation of the critical surface tension of wetting (γ_c) by extrapolation at $\cos \theta = 1$ of the static contact angles of the *n*-alkanes series according to the classical Zisman method,¹⁰ $\cos \theta = a \times \gamma_{\text{liq-uid}} + b$. The main results are summarized in Table IV.

All the systems appear to be characterized by a quite low γ_c value of about 18 mN/m, which is the value reported in the literature for poly(tetrafluoroethylene),¹¹ which is a fully difluoromethylene surface. However, the γ_c value is significantly higher than the range reported for perfluoroalkyl copolyacrylates,¹² showing in many cases a critical surface tension of wetting as low as 10–12 mN/m. This is due to the fact that —CF₂— groups present in the PFPE macromer are less effective than trifluoromethyl groups in lowering the surface tension; in fact, the smallest γ_c value (as low as 6 mN/m) was calculated for a self-assembled monolayer of perfluorocarbon acid.¹³ In addition, PFPE-containing copolyacrylates based on monofunctional PFPEs (therefore, —OCF₃ terminated) were described in the recent literature.¹⁴ In that case, dependence of the dispersion force surface energy (γ_c^D) on the PFPE chain length and fluorine content was observed, leading in some cases to values comparable to fluoroalkyl-based copolyacrylates.

All the PU structures in the present work have quite similar surface behavior. However, the correlation coefficients calculated for the linear regression of $\cos \theta$ versus γ_{liquid} are quite poor ($R^2 = 0.85$ – 0.90) in spite of the large number of experimental determinations; they became acceptable only when excluding the data of contact angles versus water. This could happen because the Zisman plot specifically concerns interactions between dispersive London forces of the liquid and surface, which are involved in the oil repellent behavior, whereas interactions between water and the PU surface involve polar forces and hydrogen bonding. The contact angle against water was better studied by means of dynamic analysis, which allows both advancing and receding values to be measured. Actually, static contact angles versus water, which are routinely well above 100° , are not true equilibrium measurements, but instead refer to metastable states. All the tested PU structures show a very high advancing contact angle value (120°). However, a large thermodynamic hysteresis (i.e., the difference between advancing and receding contact angles vs. water) is generally shown, suggesting the formation of a strongly polyphasic fluorinated surface with “islands” of higher energy urethane moieties. The effect is partic-

TABLE III
Glass-Transition Temperatures and Heat Capacity Changes by DSC of Fluorinated Polyurethanes

Polymer	T_{g1} (°C)	ΔC_{p1} (J/g °C)	T_{g2} (°C)	ΔC_{p2} (J/g °C)
PU1	−86	0.103	+34	0.197
PU2	−87	0.061	+32	0.207
PUU	−90	0.075	>+50°C	ND

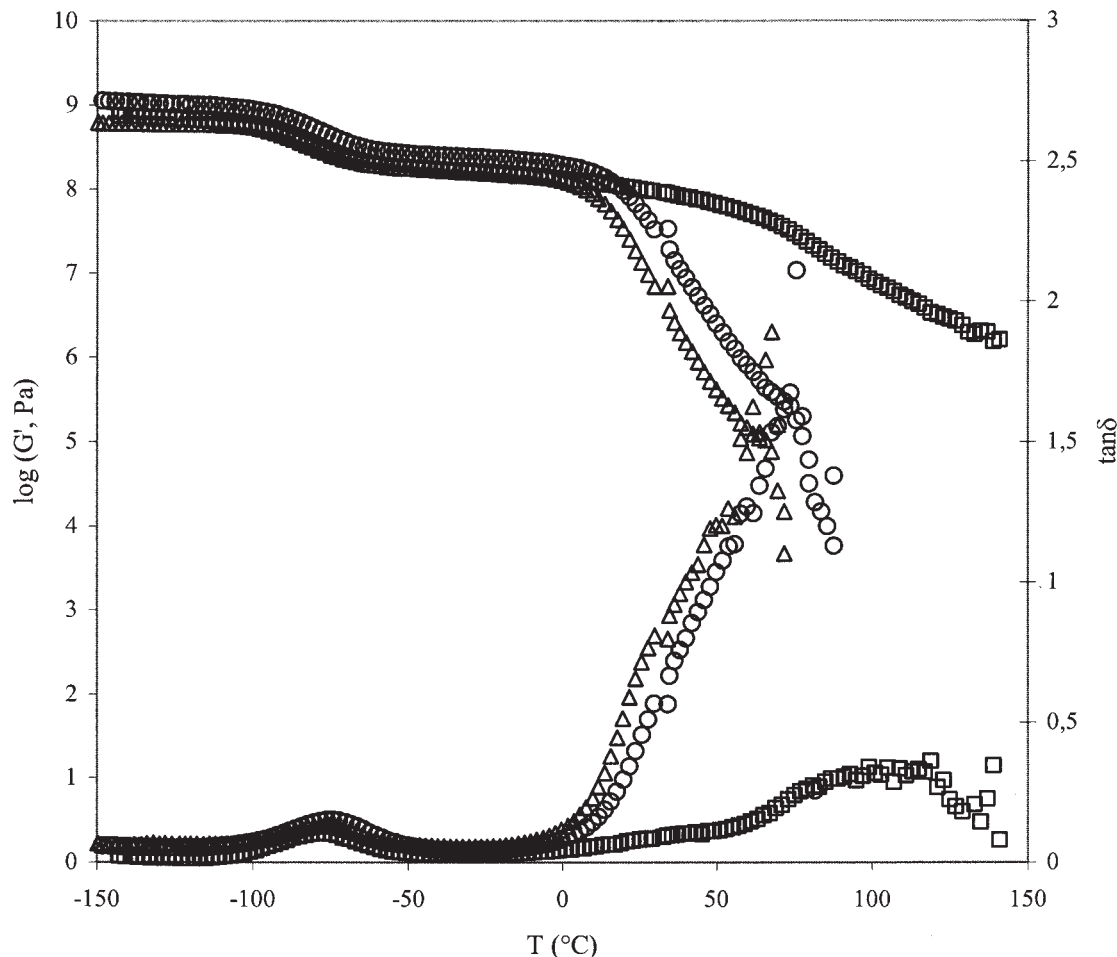


Figure 3 Dynamic mechanical spectra of (○) PU1, (△) PU2, and (□) PUU polymers.

ularly relevant for the PUU polymer, for which the hysteresis is as high as 75°.

From the results shown in Table IV, it appears that all three structures show a rather high water and oil repellency, as for the quite low γ_c values calculated for hydrocarbons and the high advancing contact angle against water. However, with respect to the latter point, the large hysteresis measured in all cases suggests the presence of polar interactions between water and the polymer surface.

Table V reports the results of performance testing carried out by using the three model structures in the manufacturing process of paper sheets by both wet-

end and size-press treatments. It should be mentioned that, for practical purposes, grease-proof paper should have an OR value of at least 6–7, with WR in between 25 and 18 g/m² in order to be hydrophobic, but still wettable and printable by inks. Moreover, an optimal sizing should be effective even at a very low bath concentration ($\leq 1\%$), mainly because of cost and paper recycling reasons.

The measured OR ratings ranged from 5 (mixture of 60% castor oil, 20% toluene, and 20% *n*-heptane) to 8 (mixture of 30% castor oil, 35% toluene, and 35% *n*-heptane) in most cases. In contrast, the WR behavior of the model fluorinated PUs shows some differences.

TABLE IV
Contact Angles Versus Water (Advancing and Hysteresis) and Versus *n*-Hexadecane (Static) and Critical Surface Tension (*n*-Alkanes) of Fluorinated Polyurethanes

Polymer	θ_{adv} vs. H ₂ O (°)	Hysteresis (°)	θ_{stat} vs. <i>n</i> -C ₁₆ (°)	γ_c (mN/m)
PU1	119 (±3)	64 (±2)	65.4 (±0.5)	18.2 (±1.8)
PU2	120 (±4)	60 (±3)	65.6 (±0.4)	18.5 (±2.0)
PUU	120 (±3)	75 (±3)	60.0 (±0.3)	18.0 (±1.8)

TABLE V
Water and Oil Repellence of Paper Treated with Fluorinated Polyurethane Dispersions

Polymer	Conc (%)	Application	Oil repellence (kit test, AU)	Kit solution surface tension (mN/m)	Water repellence (Cobb test, g/m ²)
None	—	—	0	—	>80
PU1	0.3	Size press	7	24.8	>70
	0.6	Size press	7	24.8	35
	0.6	Wet end	7	24.8	>80
	1.0	Size press	8	24.4	20
	1.0	Wet end	8	24.4	>80
PU2	0.3	Size press	5	26.3	21
	0.6	Size press	6	25.3	17
	0.6	Wet end	6	25.3	30
PUU	0.3	Size press	2	31.2	20
	0.6	Size press	6	25.3	17.5
	0.6	Wet end	5	26.3	36
	1.0	Size press	6	25.3	17.2
	1.0	Wet end	6	25.3	30

By an overall examination of the data, the following considerations can be made:

- The best OR performance is always obtained by PU1, which has relatively higher fluorine content and much higher COOH content. In particular, the best results were achieved both in wet-end and size-press treatments with the highest concentration (1%). However, WR is scarce in most cases and especially in the wet end.
- The lower COOH content PU2 structure shows quite high WR, even at very small concentrations, but the OR never reaches values as high as 7.
- The PUU structure again shows good WR but also the worst OR performance.

Therefore, the water and oil repellent behavior of polymers is well diversified, notwithstanding that the estimation of γ_c did not allow a clear preselection of structures. In particular, it seems that the COOH content is a fundamental parameter in decreasing WR, but it probably also contributes to the increased OR (see the comparison of PU1 and PU2 structures having roughly the same fluorine content). In fact, interactions between polar COOH groups and hydrocarbons are expected to be repulsive, as those between fluorine and paraffins. By tuning the carboxyl content with the partial substitution of DPMA with CHDM (from PU1 to PU2), a large increase in WR and probably some affinity between hydrocarbon droplets and hydrogenated segments of the PU is achieved. The presence of a regular segmented prepolymer, with the PFPE linked between the IPDI monomers, is allowed only in PU1 and PU2 structures obtained by a solvent process. In contrast, the prepolymer mixing process requires the formation of an ionomeric prepolymer with a subsequent less regular structure. This could explain the

poor OR performance of the polyurea model. Finally, the particle size of the polymer dispersion seems to be a parameter of minor importance. In any case, the polymer particles are significantly smaller than the porosity of paper (expected to be on the order of 10⁰ μm).

CONCLUSION

We showed that bifunctional PFPE macromers could be used for the synthesis of partially fluorinated anionic PUs. The new systems were characterized by good emulsion stability and good film-forming properties. Homogeneous and transparent thin films were obtained by coating and oven drying. The formed surfaces were predominantly fluorinated, as suggested by the quite low critical surface tension of wetting; but they are also characterized by large hysteresis phenomena, which is a low receding angle, which is likely indicative of the formation of a heterogeneous surface with zones of high energy phase.¹⁵ The aqueous PUs were used for low surface tension paper sizings. Interestingly, it resulted in the performance through WR and OR tests being much more diversified than the general surface behavior suggested by contact angle analysis. This could be explained by considering that the different structures did not form a continuous coating, but the few layers of PU absorbed on the cellulose substrate might assume largely different interfacial conformations. According to this view, the segmented model with the fluorinated prepolymer extended with a high content of carboxylic groups was the most promising candidate for the development of PFPE-based oil repellent sizings.

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