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# Preparation of aqueous anionic poly(urethane-urea) dispersions. Influence of the incorporation of acrylic, polycarbonate and perfluoro-oligoether diols on the dispersion and polymer properties

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Aqueous poly(urethane-urea) dispersions were prepared by the prepolymer mixing technique, without using any organic solvent. This work focused on the incorporation into the prepolymer chain of specific macrodiols bearing acrylic, polycarbonate and perfluoro-oligoether chains, in conjunction with a poly(propylene oxide) diol ( $M_n = 1000$ ). All the dispersions were synthesized with a fixed NCO/OH ratio, using  $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-xylylene diisocyanate, a fixed proportion of emulsifying agent (dimethylol propionic acid, neutralized with triethylamine) and the same chain extender (1,2-ethylene diamine). The properties of both the dispersions and the dried polymer films were characterized as a function of the nature of the specific incorporated diol and its proportion in the polymer chain, in order to establish criteria leading to an optimized performance in terms of particle size, viscosity, and polymer film properties.

**KEYWORDS:** aqueous poly(urethane-urea)s; dispersions; macrodiols; viscosity; films

## INTRODUCTION

Given the need for cost reductions and the progressive restrictions associated with the decrease in the level of organic solvent emissions, water-based polymer systems have recently received considerable attention, particularly in coating and adhesive applications.

Aqueous polyurethane dispersions (PUDs) are one of the major families of such materials because they combine these advantages with the unique properties of polyurethanes, particularly in terms of flexibility, adhesion and anti-abrasion resistance.<sup>1–4</sup> Since the behavior and properties of PUDs are significantly different from those of solvent-based counterparts, the development of competitive PUDs for industrial applications has called upon numerous studies which provided valuable information on both the synthetic aspects and the properties of the ensuing dispersions and polymers.<sup>5–9</sup>

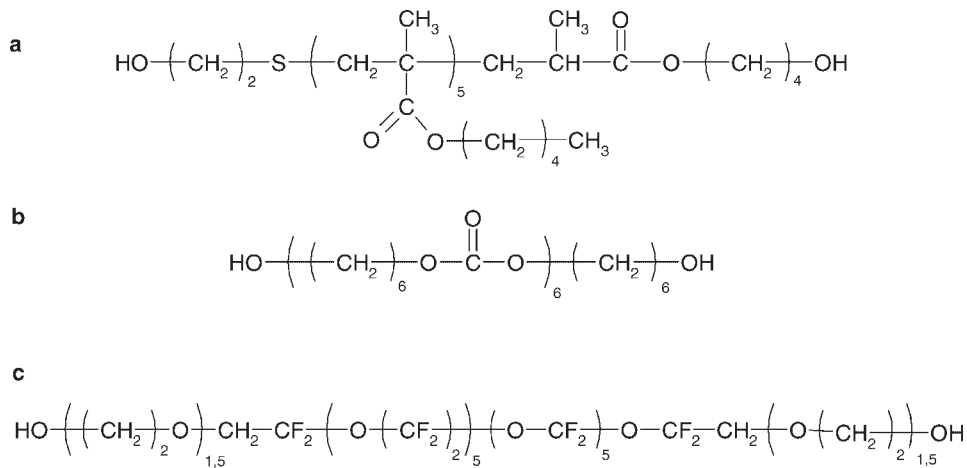
In pursuit of an ongoing investigation on PUDs, prepared without any organic solvent,<sup>10,11</sup> focus has been on the incorporation of three novel macrodiols in the prepolymer

chain, namely an acrylic, a polycarbonate and a perfluoro-oligoether diol.

As has been shown in a previous study,<sup>11</sup> the chemical nature of the macrodiol chain affects such properties as the dispersion stability, the particle size<sup>1</sup> and the polymer mechanical properties.<sup>3</sup> The addition of acrylic structures in polyurethane chains has been reported to improve the polymer mechanical properties, thermal stability and resistance to hydrolysis,<sup>12,13</sup> and to decrease the polymer hydrophilicity, resulting in a higher average particle size and a reduced viscosity.<sup>14</sup> Carbonate groups would favor interchain interactions by hydrogen bonds with urethane and urea moieties and consequently improve the polymer mechanical properties and resistance to hydrolysis and solvent.<sup>15–17</sup> Finally, the incorporation of perfluoro-oligoether diols was expected to improve more drastically the polymer resistance to hydrolysis and oils, particularly in coating applications, because these structures are known to reduce dramatically the surface energy of materials. Moreover, their highly hydrophobic character could also affect the average particle size of the dispersions.<sup>18</sup>

The present investigation deals with numerous PUDs, prepared with the same diisocyanate, a fixed NCO/OH ratio, the same catalyst, emulsifying agent (in a fixed proportion), and chain extender, but with different mixtures of macrodiols, made up of varying proportions of a conventional poly(propylene oxide) diol and one of the three new

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**Figure 1.** Specific macrodiol structures (a, acrylic macrodiol; b, polycarbonate diol; c, perfluoro-oligoether diol), as assessed by spectroscopic techniques.

macrodiols. These aqueous dispersions and the ensuing dried polymer films were then characterized in order to establish criteria related to their structure-properties relationships.

## EXPERIMENTAL

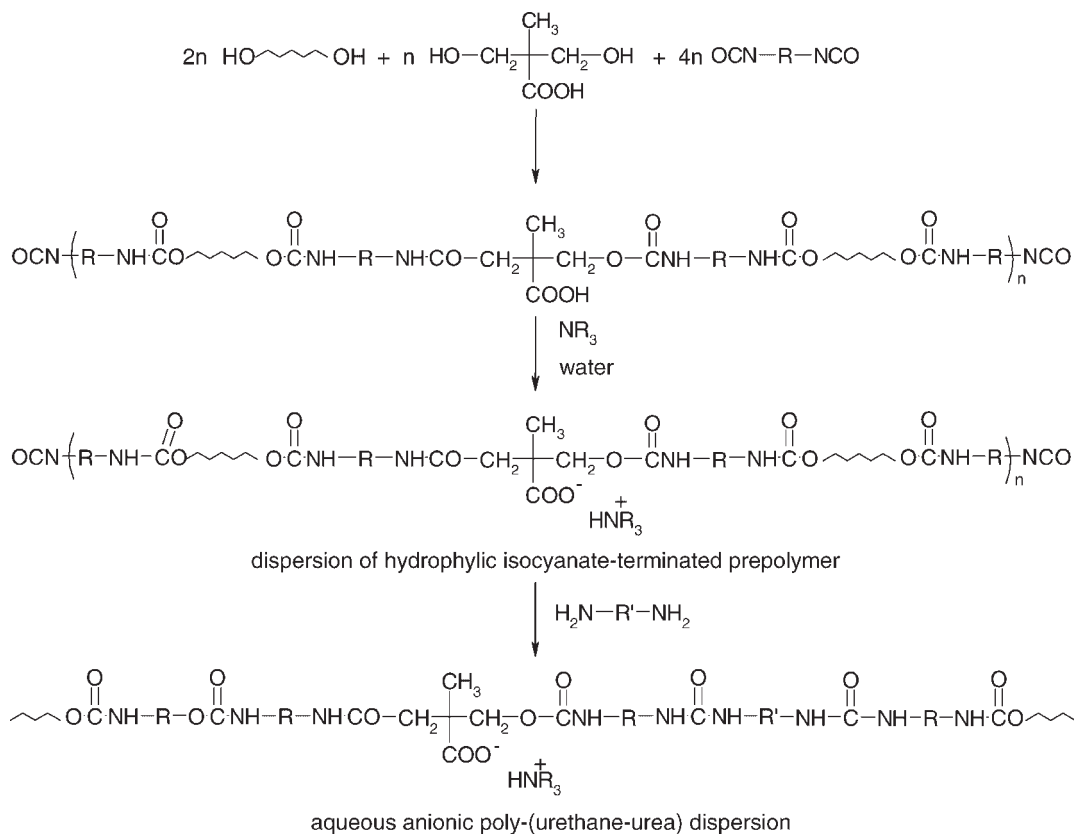
### Materials

The following commercial reagents were used without further purification:  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-xylylene diisocyanate (TMXDI, Cytec), poly(propylene oxide) glycol (PPG,  $M_n=1000$ , Shell), acrylic macrodiol (Tego,

$M_n=1000$ ), polycarbonate diol (UBE,  $M_n=1000$ ), perfluoro-oligoether diol (Fomblin,  $M_n=1200$ ), dimethylol propionic acid (DMPA, Perstorp), dibutyltin dilaurate (DBTL, Aldrich), triethylamine (TEA, Acros) and 1,2-ethylene diamine (EDA, Acros). The structure, functionality and molecular weight of the three new macrodiols (Fig. 1) were verified by FT-IR and  $^1\text{H-NMR}$  spectroscopy.

### Synthesis

All the dispersions were prepared by the "prepolymer mixing process" described in a previous studies.<sup>10,11</sup>



**Figure 2.** Mechanistic steps involved in the preparation of the dispersions.

### Prepolymer preparation

The synthesis of the polyurethane anionomers was carried out in bulk without the intervention of an organic solvent. This first step called upon the successive additions of DBTL, the diol mixture and DMPA to the diisocyanate in an inert atmosphere at 70–80°C under vigorous stirring. PPG and each new macrodiol were preliminarily mixed and placed in an oven at 80°C for 1 hr before the synthesis. Both the [NCO]/[OH] molar ratio ( $r = 1.8$ ) and the amount of DMPA (4.55% w/w, based on the prepolymer) were kept constant and only the nature of the specific diol and its relative proportion with respect to PPG were varied.

### Dispersion in water and chain extension

Once the prepolymer had reached the final expected NCO residual content (as assessed by FT-IR spectroscopy), it was slowly poured into an aqueous TEA solution kept at 25–30°C and stirred at 280 rpm. The amount of added TEA was calculated to ensure the complete neutralization of the carboxylic group of DMPA, namely a 20% molar excess. Immediately after the completion of this addition, the chain extender (EDA) was slowly added and thereafter stirring was pursued for 90 min. The quantity of EDA added was calculated in order to obtain a 1:1 [NCO]/[NH<sub>2</sub>] stoichiometry.

Figure 2 summarizes the different mechanistic steps involved in the overall preparation of these dispersions, which had a solid content of about 32% w/w.

### Characterization

The aqueous dispersions were spread on a Teflon mold and dried to constant weight in an oven at 60°C. FT-IR and <sup>1</sup>H-NMR spectra were taken with a Perkin-Elmer Paragon 1000 and a Bruker 300 instrument, respectively.

The thermal analyses [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)] were carried out using a Setaram DSC-TGA 92 calorimeter working under nitrogen, with a heating rate of 10°C/min. The values given as degradation temperatures in the text correspond to the temperature at which the sample lost 10% of its initial weight.

Static and dynamic contact angles on the polymer films were measured with a home-made goniometer equipped with a CDD camera working at up to 200 images/sec.<sup>19</sup> The results were collected on a video card and treated by image analysis software. Among the approaches enabling the determination of the different contributions to the surface energy of a solid from contact angle measurements,<sup>20</sup> those proposed by Owens and Wendt and by van Oss were chosen, as had been done in previous studies.<sup>10,11</sup> The first provided the polar,  $\gamma^p$ , and dispersive,  $\gamma^d$ , contributions and both methods gave the total surface energy  $\gamma^t$ .

The average particle size measurements of the aqueous dispersions were performed by light scattering, using a Malvern Autosizer 2c apparatus. The  $\zeta$  potential of these particles was measured by their electrophoretic mobility with a Malvern Zetasizer 2000 instrument.

## RESULTS AND DISCUSSION

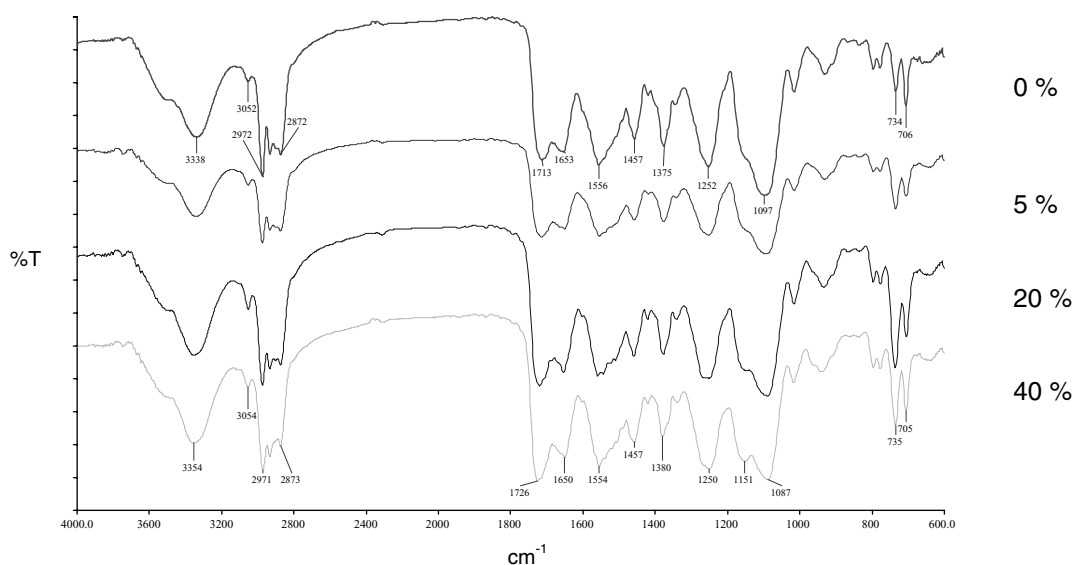
According to the results of a previous study<sup>10</sup>, TMXDI was chosen as the diisocyanate, because it proved particularly suitable for the preparation of PUDs, and a fixed [NCO]/[OH] ratio of 1.8, which gave low-viscosity easily dispersible prepolymers and stable polymer emulsions, characterized by low particle sizes. Moreover, a high ratio, synonymous of high urea moiety content, also gave polymers with higher glass transition temperatures and better thermal stability.

PPG was chosen as the standard macrodiol, because it has been previously found<sup>11</sup> to be one of the most suitable macrodiols for PUDs, in terms of dispersion stability and particle sizes, as well as polymer film properties.

For each specific macrodiol, several dispersions were prepared, varying the macrodiol proportion, namely 0, 5 or 10, 20 and 40% OH equivalents, relative to PPG.

### Effect of the incorporation of the acrylic macrodiol

The FT-IR spectra of the polymers prepared with the acrylic macrodiol and their characteristics are presented in Fig. 3 and



**Figure 3.** FT-IR spectra of polymers from PUDs prepared with different percentages of acrylic macrodiols.

**Table 1.** Effect of the acrylic macrodiol incorporation on the ensuing polymer properties

		Acrylic macrodiol (%)			
		0	5	20	40
Glass transition temperature,	$T_g$ (°C)	−26	−15	−12	1
Degradation temperature,	$T_d$ (°C)	305	—	310	—
Surface energy (Owens–Wendt method)	$\gamma^p$ (mN/m)	19.7	18.5	17.2	12.1
	$\gamma^d$ (mN/m)	17.7	19.2	19.4	19.0
	$\gamma^t$ (mN/m)	37.4	37.7	36.6	31.2
Surface energy (Van Oss method)	$\gamma^t$ (mN/m)	37.8	38.1	36.4	31.5

**Table 2.** Effect of the acrylic macrodiol incorporation on the ensuing dispersions properties

		Acrylic macrodiol (%)			
		0	5	20	40
pH		9.0	8.0	8.6	8.3
Surface tension	(mN/m)	38.6	38.4	39.0	41.3
Average particle size	(nm)	51.2	75.8	112.5	146.6
Zeta potential	(mV)	−39.5	−37.8	−35.8	−27.4

**Table 3.** Effect of the polycarbonate diol incorporation on the ensuing polymer properties

		Polycarbonate macrodiol (%)			
		0	5	20	40
Glass transition temperature	$T_g$ (°C)	−26	−37	−46	−52
Degradation temperature	$T_d$ (°C)	305	—	340	—
Surface energy (Owens–Wendt method)	$\gamma^p$ (mN/m)	19.7	19.0	17.1	15.2
	$\gamma^d$ (mN/m)	17.7	18.2	19.6	19.8
	$\gamma^t$ (mN/m)	37.4	37.2	36.7	35.0
Surface energy (Van Oss method)	$\gamma^t$ (mN/m)	37.8	37.3	36.9	35.8

Table 1. In addition to the peaks attributed to urea and urethane function, and the TMXDI structure, the presence and the intensity increase of peaks due to the acrylic ester function ( $1726$  and  $1151\text{ cm}^{-1}$ ) with increasing acrylic macrodiol, confirmed the efficient incorporation of this macrodiol into the polymer chain.

The other relevant properties of these polymers are given in Table 1. The glass transition temperature increased with the proportion of acrylic macrodiol, which is due to the relative stiffness of its structure (Fig. 1a). Indeed, the glass transition temperature of this macrodiol was significantly higher than that of PPG (respectively  $-40$  and  $-65^\circ\text{C}$ ). However, the degradation temperature did not seem to be affected by the incorporation of the new macrodiol.

The ether group sequence of PPG gives rise to a higher polarity than the side alkyl groups of the acrylic macrodiol (Fig. 1a). The polymer surface energies were therefore logically affected by the increase of acrylic macrodiol content in the polyurethane chain, as shown by the progressive decrease in the polar contribution, which gave a corresponding decrease in the value of the total surface energy values (Table 1), obtained in good agreement using both approaches.

The polymer decrease in polarity involved a decrease of the polymer hydrophilicity, as indicated by the progressive

increase in the average particle size with increasing incorporation of the acrylic macrodiol. Also a significant decrease in zeta potential was observed with the addition of this diol, which was attributed to the fact that its alkyl side chains would migrate preferentially to the particle surface at the expense of the carboxylic moieties.

The dispersion properties are given in Table 2. The small increase in surface tension was probably due to the presence of polar additives in the commercial acrylic macrodiol. Finally, since the DMPA neutralization degree had been kept constant, the pH of these dispersions did not show any appreciable variation.

### Effect of the incorporation of the polycarbonate diol

The FT-IR spectra of these polymers showed unequivocally the presence and the intensity increase of peaks relative to the carbonate moieties ( $1740$  and  $1250\text{ cm}^{-1}$ ) which confirmed the efficient polycarbonate diol incorporation in the polyurethane chain. The other polymer properties are given in Table 3. Because of the enhanced segmental mobility introduced by the  $(\text{CH}_2)_6$  sequences of the polycarbonate diol (Fig. 1b), which confers a low glass transition temperature to this macrodiol ( $T_g = -63^\circ\text{C}$ ), a progressive decrease in the polyurethane glass transition

**Table 4.** Effect of the polycarbonate diol incorporation on the ensuing dispersions properties

		Polycarbonate macrodiol (%)			
		0	5	20	40
pH		9.0	8.3	8.8	8.7
Surface tension	(mN/m)	38.6	38.1	38.6	40.3
Average particle size	(nm)	51.2	94.6	97.9	102.4
Zeta potential	(mV)	-39.5	-38.5	-35.5	-28.7

**Table 5.** Effect of the perfluoro-oligoether macrodiol incorporation on the ensuing polymer properties

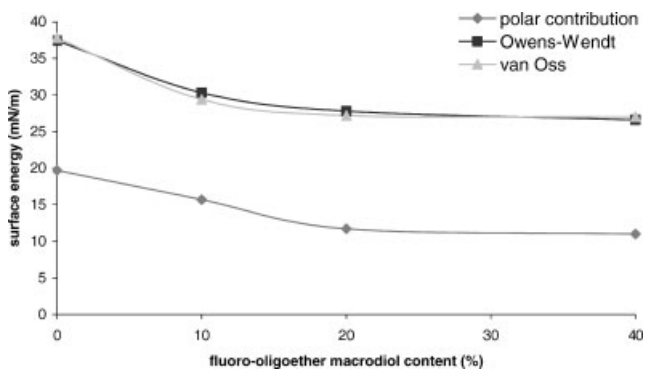
		Fluoro-oligoether macrodiol (%)			
		0	10	20	40
Glass transition temperature	$T_g$ (°C)	-26	-29	-33	-35
Degradation temperature	$T_d$ (°C)	305	—	300	—
Surface energy (Owens-Wendt method)	$\gamma^p$ (mN/m)	19.7	15.7	11.7	11.0
	$\gamma^d$ (mN/m)	17.7	14.6	16.1	15.6
	$\gamma^t$ (mN/m)	37.4	30.3	27.8	26.6
Surface energy (Van Oss method)	$\gamma^t$ (mN/m)	37.8	29.4	27.2	27.0

temperature was recorded with increasing polycarbonate diol content in the polymer chain. As expected from the fact that polycarbonates are among the most heat-resistant polymers, the polyurethane degradation temperature increased significantly with the incorporation of this macrodiol, namely from 305°C without polycarbonate diol to 340°C with only 20% (OH equivalent) of polycarbonate diol, which represented only 11% of the total prepolymer weight.

The polar contribution of the surface energy decreased with increasing polycarbonate diol content, because of the preferential migration of its polymethylene sequences to the film surface, compared with PPG moieties.

Table 4 gives the properties of the corresponding dispersions. As expected, there were no appreciable variations in either pH or surface tension with the incorporation of the polycarbonate diol.

The average particle size of the PUDs increased and the zeta potential decreased as the polycarbonate diol content in the polymers was increased. Because of its chemical structure,

**Figure 4.** Effect of the fluoro-oligoether diol content on the ensuing polymer surface energies.

and particularly the  $(CH_2)_6$  groups, this diol was clearly more hydrophobic than PPG, whose ether groups give a modestly hydrophilic character to the polymer. The increased hydrophobicity would again prevent a high proportion of carboxylic groups to be located at the surface of the particles, thus favoring higher particle sizes and lower zeta potentials. However, the average particle sizes of these dispersions were still sufficiently small (around 100 nm) for numerous applications and particularly for coatings.

### Effect of the incorporation of the perfluoro-oligoether diol

The FT-IR spectra of these polymers showed mainly the widening and the intensity increase of the 1300–1100  $cm^{-1}$  band arising from the C–F stretching contribution, which indicated the incorporation of the fluoro-oligoether macrodiol in the polyurethane chains.

Table 5 gives the properties of these fluorinated polymers. The perfluoro-oligoether diol (Fig. 1c) had a significantly lower glass transition temperature than PPG (–99 versus –69°C). Thus, the incorporation of this macrodiol in the polymer chains logically enhanced the softness consistency of the polymers, which resulted in a progressive glass transition temperature decrease with the increasing macrodiol content. Since this macrodiol was a polyether, like PPG, its incorporation into the polyurethane chains did not have any significant effect on their degradation temperature. Conversely, an important decrease in the surface energy values was observed as the fluoro macrodiol content increased (Fig. 4). The two determination approaches gave concordant results and the Owens–Wendt method highlighted that this decrease came mainly from the polar contribution. This feature was clearly attributed to the perfluoroalkyl moieties of the incorporated diol.

The hydrophobicity induced by the fluoro-oligoether segments had also an influence on the dispersion properties

**Table 6.** Effect of the perfluoro-oligoether diol incorporation on the ensuing dispersions properties

	Fluoro-oligoether macrodiol (%)			
	0	10	20	40
pH	9.0	8.7	9.3	8.8
Surface tension (mN/m)	38.6	36.1	36.9	35.8
Average particle size (nm)	51.2	59.7	68.0	71.8
Zeta potential (mV)	-39.5	-37.6	-36.5	-34.4

shown in Table 6, with the double effect of increasing the average particle size and decreasing their zeta potential. As in the other systems studied here, the presence of the perfluoro-oligoether diol in the polymer chains did not affect the pH and the surface tension of the dispersions.

## CONCLUSIONS

It was possible to add up to 40% of new macrodiols into the prepolymer chains and to obtain stable aqueous PUDs, with improved properties, without any modification of the straightforward synthetic procedure.

In particular, the addition of an acrylic macrodiol induced a higher glass transition temperature and a reduced surface energy to the ensuing polymers, which is very interesting in terms of coating applications. With the incorporation of a polycarbonate diol, the heat resistance of the polymers was particularly improved, even with relatively modest contents. Finally, the incorporation of perfluoro-oligoether moieties led to an important decrease in the polymer surface energy. This is a notable advantage for materials used in applications such as packaging or anti-graffiti coatings, where swelling must be reduced. All these improvements were obtained without any significant deterioration of the previously optimized properties associated with the use of the TMXDI/PPG monomer combination.

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