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# Ionomer-based polyurethanes: a comparative study of properties and applications

Olivier Jaudouin,<sup>a,b</sup> Jean-Jacques Robin,<sup>b\*</sup> José-Marie Lopez-Cuesta,<sup>a</sup> Didier Perrin<sup>a</sup> and Claire Imbert<sup>b</sup>

## Abstract

Polyurethanes cover a large range of materials exhibiting various physical and mechanical properties making them useful in different applications such as elastomers or biomaterials, for instance. The introduction of ionic groups in the polyurethane backbone opens the way to new applications where the ionic groups can act as physical crosslinkers that greatly modify the final mechanical and thermal properties of the materials. Furthermore, the hydrophilicity of the chains can be enhanced by the presence of the ionic species, and so the materials can be processed as conventional dispersions even in a polar solvent such as water. As a consequence the applications are numerous; the main commercial outlets are focused on coatings and textiles industries where they can be used as waterproof coatings or substitutes for leather. But these materials can also be used in high-tech industries for shape memory materials, biomedical devices and biocompatible materials. This review summarizes the latest developments of this class of promising materials and provides the reader with the potentialities of these polymers in various areas.

**Keywords:** polyurethanes; ionomers; waterborne materials; thermal stability; mechanical properties; physical properties

## INTRODUCTION

Segmented polyurethanes (PUs) are versatile polymers which have received widespread attention for many years because of their properties ranging from those of thermoplastics to thermosets and from those of soft to hard materials. The properties of these materials can be designed according to the requirements of end users. Hence, they are used for various applications. A number of handbooks present these special polymers, their synthesis, properties and applications.<sup>1–4</sup>

Polyelectrolytes are polymers possessing ionic groups on the polymer backbone and are used in a tremendous number of applications such as in membranes or batteries. Such functional polymers having less than 15 mol% of ionic groups are called ionomers. In recent years, many ionomers have been developed or even commercialized. The best example is Nafion<sup>®</sup>, a perfluorosulfonated ionomer mainly used for fuel cell membranes. Polyelectrolytes and ionomers have been greatly studied and various books deal with their synthesis and properties.<sup>5,6</sup>

Polyurethane ionomers (PUIs) combine the advantages of both PUs and ionomers. For example, conventional PUs are very often hydrophobic in nature; however, it is possible to incorporate ionic hydrophilic segments into PU chains opening the way to dispersion or emulsion of PUs. Various reviews have reported the synthesis and properties of ionomers and their applications,<sup>7</sup> especially in aqueous media.<sup>8,9</sup>

The aim of this article is to review the various classes of PUIs and recent developments. First, an overview of the different synthetic routes is presented. This part also describes one of the most important advantages of PUIs, i.e. emulsion polymerization of PUs in polar solvents such as water. Then the impact of the addition of ionic groups on thermal, mechanical and dilute solution properties

is discussed. Finally, a non-exhaustive coverage is given of the main applications such as waterborne PUs, shape memory PUs and biomedical materials.

## OVERVIEW OF IONOMERS AND OF THEIR SYNTHESSES

In the area of ionomer chemistry, ionic groups can be incorporated into the chains as reactants (ionic diols or ionic diisocyanates) or by post-polymerization of a PU with an ionic reactant. Three main classes of PUI exist and the various synthesis methods are described below.

### Polyurethane anionomers

#### *Polymerization with anionic monomers*

This class of PU can be achieved according to two main polymerization routes. PU anionomers can be prepared by combining diisocyanates containing ionic groups with conventional diols or by combining ionic diols with conventional diisocyanates. The

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introduction of diols containing ionic groups has been greatly studied<sup>10–19</sup> and is the common route for the preparation of ionomers. Sulfonic,<sup>20–26</sup> phosphoric<sup>27–29</sup> or carboxylic acids are the most used functions.<sup>30–42</sup>

Fragiadakis *et al.*<sup>11,43</sup> synthesized a PUI using a diol containing a sulfonate salt group. First, they reacted a dimethyl-5-sulfoisophthalate sodium salt with an excess of poly(ethylene glycol) in order to form a prepolymer. Then, the final polymer was

formed by chain extension of the prepolymer with isophorone diisocyanate (IPDI). The chemical structure of this polymer is presented in Fig. 1.

Jaisankar *et al.*<sup>12</sup> synthesized a semi-interpenetrating polymer network based on poly(vinyl chloride) and PU. To increase the miscibility and thus the degree of interpenetration, they created attractive interactions using PUIs. Poly(vinyl chloride) was dissolved in tetrahydrofuran and a PU prepolymer based on polycaprolactone diol and toluene diisocyanate was prepared in solution. 2,4-Dihydroxybenzoic acid was then added to the solution to extend the prepolymer. Finally, triethylamine was reacted with the COOH groups of 2,4-dihydroxybenzoic acid to give the corresponding ammonium salt.

Tsonos *et al.*<sup>15</sup> prepared a carboxylate-containing PU by mixing in solution (isopropanol or acetone) *para*-hydroxybenzoic acid with magnesium oxide at 60 °C. After washing the resulting product with acetone and filtering, they obtained a magnesium salt diol. Then, they condensed two equivalents of toluene diisocyanate with one equivalent of oligo(oxytetramethylene glycol) in order to prepare a PU prepolymer. The anion-containing PU was then prepared by mixing one equivalent of the prepolymer with one equivalent of the magnesium salt diol.

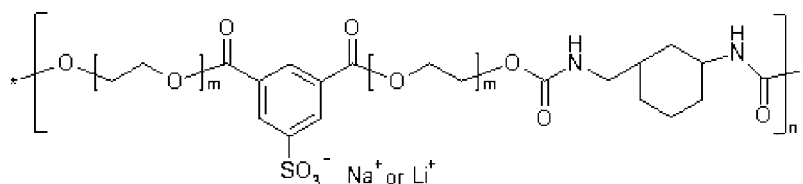
Recently, a diol has received widespread attention for the manufacture of hydrophilic PUs: dimethylolpropionic acid (DMPA; Fig. 2).<sup>44–65</sup> This reagent is interesting, since it contains a carboxylic acid playing the role of emulsifier for synthesizing PU dispersions and emulsions in water. Thus, Zhu *et al.*<sup>45</sup> synthesized ionomers using 4,4'-methylene-bis(phenyl isocyanate), polycaprolactone diols, 1,4-butanediol and DMPA. Zagar and Zigon<sup>48</sup> used hexamethylene diisocyanate, poly(tetramethylene oxide) and different chain extenders in varying proportions: neopentyl glycol for non-ionomeric groups and DMPA for ionomeric groups.

Wang *et al.*<sup>44,50</sup> synthesized ionomeric water-based PUs based on fluorescent dyes, where the hydrophilic properties of the PUs were due to the carboxylic group of DMPA. The synthesis is summarized in Fig. 3.

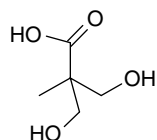
Mao *et al.*<sup>62</sup> tested blood-compatible PUI nanoparticles prepared by emulsion polymerization. A solution of 4,4'-methylenediphenyl diisocyanate (MDI), poly(tetramethylene ether) glycol, DMPA, isopropanol as end-capping agent and triethylamine was prepared and added to a solution of water and sodium dodecylsulfate, leading to the formation of micelles. The last step of the nanoparticle formation was the dispersion of the solution in a phosphate buffered solution under ultrasonic agitation; the phosphate groups were dispersed around the micelles. Dialysis purifications were then carried out. This synthesis process is shown Fig. 4.

#### *Post-functionalization of polyurethanes*

Another method for preparing anionomers is the post-functionalization of PUs using ionic groups. For example, the hydrogen belonging to the urethane group can be substituted.<sup>65,66</sup> Robila *et al.*<sup>66</sup> synthesized a linear poly(ester-urethane) by polyaddition of an  $\alpha,\omega$ -poly(ethylene glycol adipate) diol (number-average molecular weight,  $M_n = 2000 \text{ g mol}^{-1}$ ), MDI and 1,4-butanediol with a molar ratio of 1 : 6 : 5, respectively. Then, this PU was reacted with sodium hydride in dimethylformamide under inert atmosphere. Stoichiometric quantities of hydride were used to control the degree of substitution of urethane hydrogen. The sodate PU was then reacted with an equivalent amount of sodium chloroacetate to form an ionomer (Fig. 5).



**Figure 1.** Sulfonic ionomer synthesized by Fragiadakis *et al.*<sup>11,43</sup>



**Figure 2.** Dimethylolpropionic acid.<sup>44–65</sup>

Starting from  $N^-$  urethane activated species, another method for the synthesis of ionomers involves the addition of sulfones (cyclic sulfonic esters). Thus, Zhu *et al.*<sup>45</sup> synthesized an ionomer by reacting a polydioxolane (PDXL) PU prepolymer with sodium hydride. Trimethylenesultone was then added to form a sulfonic ionomer (Fig. 6).

Ramesh and Radhakrishnan<sup>26</sup> and Sukhorukova *et al.*<sup>67</sup> developed an original method to create anionomers with maleic anhydride. For instance, polyester diols were synthesized starting from maleic anhydride and a short diol such as butanediol. These polyester diols were converted into PU by reacting with a diisocyanate. Finally, the ionomer was obtained by reaction of sodium

bisulfite with the unsaturations of the maleate esters inserted in the polymer chains to give an anionic PU containing sodium sulfonate groups.

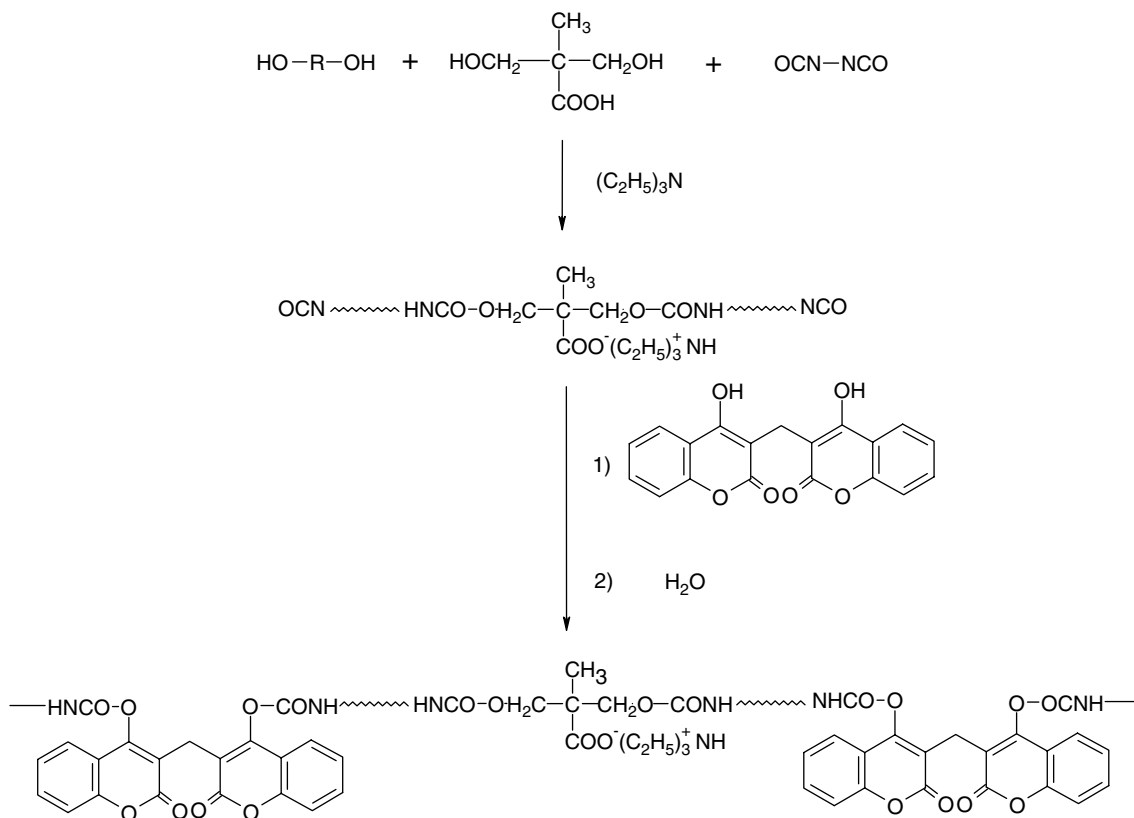
### Polyurethane cationomers

PU cationomers are mainly prepared by the reaction of diisocyanates with nitrogen-containing alkyl diols or with sulphur-containing diols. The ionic groups are produced by quaternization of nitrogen atoms or 'ternization' of sulfur atoms.<sup>68–80</sup>

Charnetskaya *et al.*<sup>77</sup> synthesized cationomers by polycondensation of oxytetramethylene glycol and 2,4- or 2,6-toluene diisocyanates with a stoichiometric quantity of *N*-methyl-diethanolamine (MDEA). The desired concentration of ionic centres was obtained by quaternization of MDEA segments with hydrochloric acid.

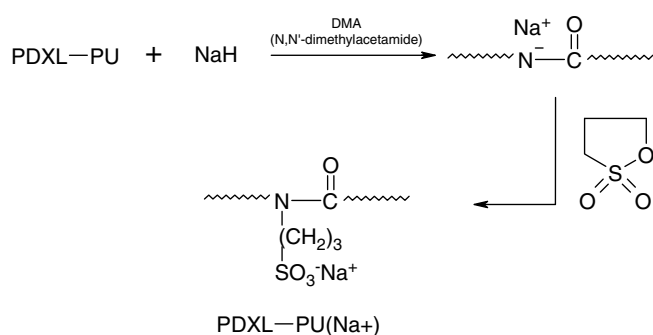
Buruiana *et al.*<sup>80</sup> synthesized short cationic diols bearing stilbene groups and quaternized amines. A PU was then synthesized by polycondensation of this diol with  $\alpha,\omega$ -poly(tetramethylene oxide) diol and MDI according to Fig. 7.

Zhu *et al.*<sup>78,79</sup> synthesized a shape memory segmented PU from a prepolymer based on an  $\alpha,\omega$ -poly(butylene adipate) diol and MDI



**Figure 3.** Synthesis of ionomeric PU based on a fluorescent dye and DMPA.<sup>44,50</sup>





**Figure 6.** Synthesis of a sulfonic ionomer.<sup>45</sup>

Quaternized salts of diamines can also be used directly when their solubility in solvents allows.<sup>21</sup>

### Polyurethane zwitterionomers

Zwitterionomers are polymers containing both positive and negative charges located on different atoms but with a neutral global charge.

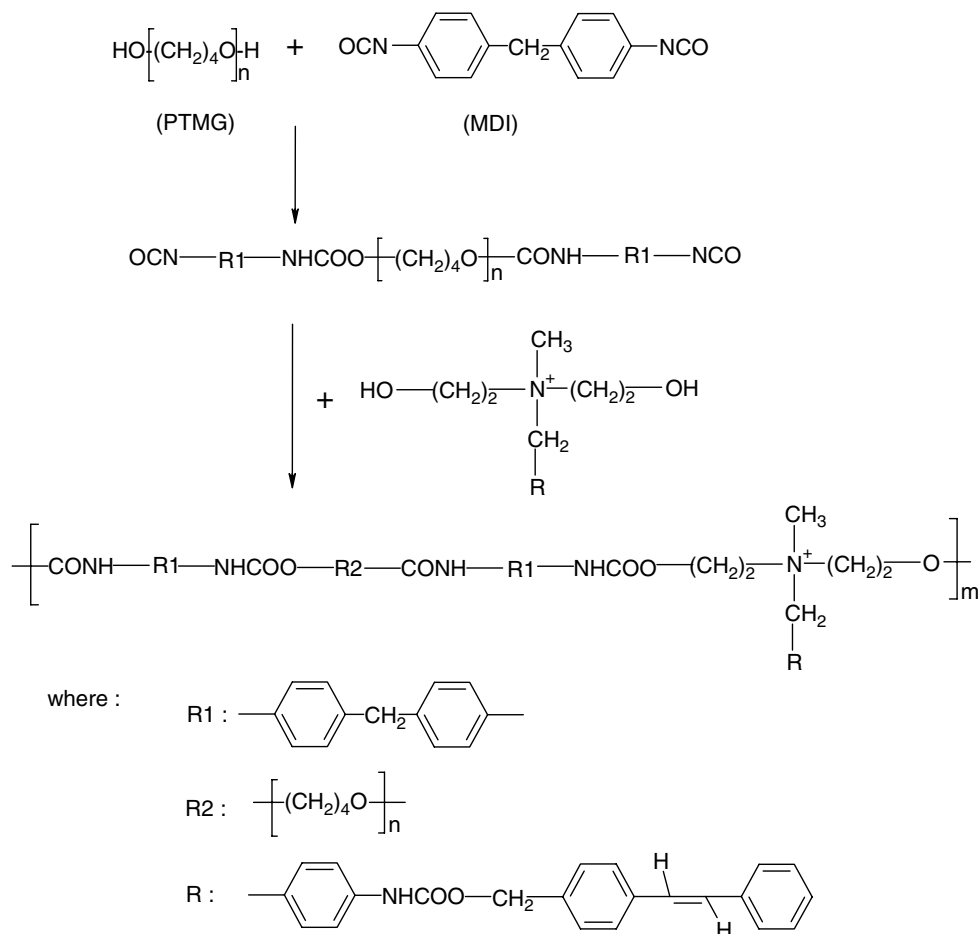
The synthesis of zwitterionomers is quite similar to that of cationomers. They are mainly synthesized by quaternization of *N*-alkyldiols using sultones, especially 1,3-propanesultone as shown in Fig.9. They are also prepared by the reaction of

urethane protons with sultones or lactones using NaOH or NaH as activator.<sup>82–86</sup>

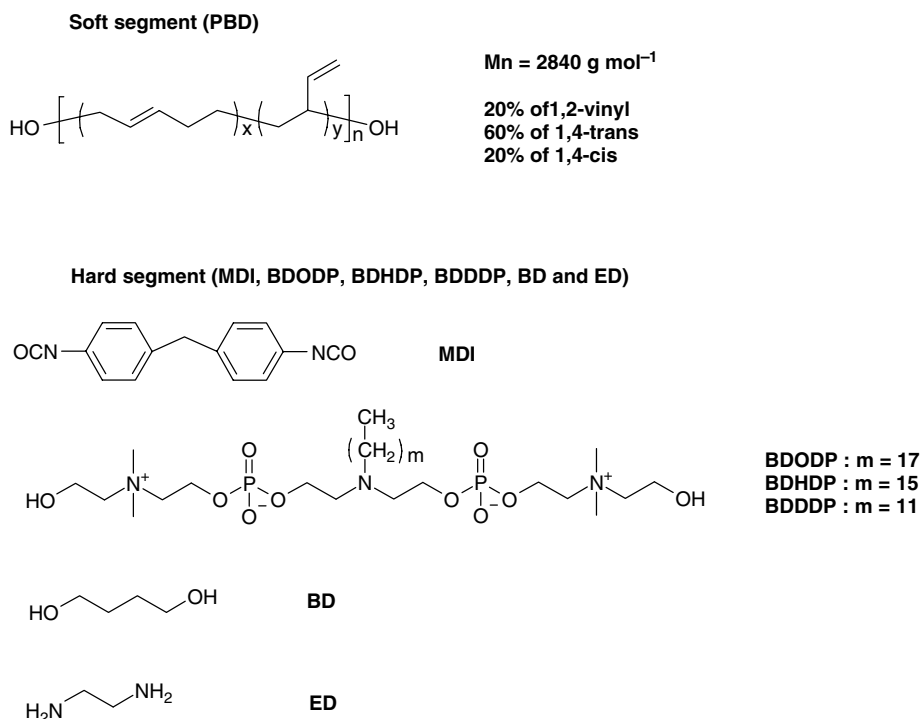
### Emulsion synthesis of polyurethane ionomers in polar solvents

PUIs can be synthesized in the bulk or in a solvent, and one of the main advantages of this class of polymers is their ease of being solubilized or dispersed in polar solvents, especially water. The formation of waterborne PUs was first reported by Schlack<sup>87–89</sup> in 1942, and most of the recent studies on PUIs in solution are still based on waterborne PUs. The main ionic diol used is DMPA since it is a cheap reagent. Moreover, its reactivity with various PU prepolymers bearing free isocyanate groups is excellent.

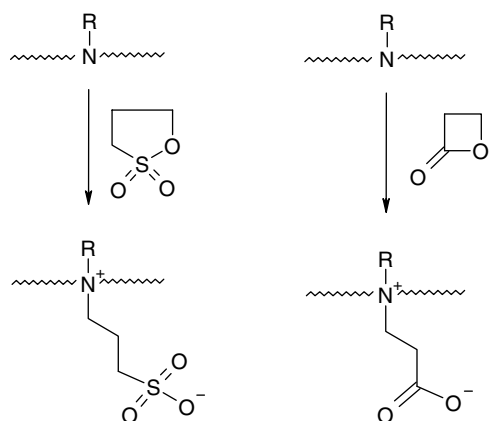
Cheong *et al.*<sup>53</sup> used water-soluble PUIs with DMPA as emulsifier in the emulsion polymerization of styrene and described the effect of the neutralization rate of the resin on the emulsion polymerization. Usually, emulsifiers are amphiphilic polymers such as grafted PUs. Here, hard segments with ionic groups played the role of hydrophilic segments and soft segments played the role of hydrophobic ones. The interest in the use of PUIs with DMPA as ionic group is that the rate of neutralization can be controlled as well as the critical micellar concentration, depending on the ionic strength. Cheong *et al.* noticed that the different parameters of the polymerization were influenced by the degree of neutralization of the ionomer resin. The degree of neutralization governs the formation of hydrophobic aggregates or micelles by electrostatic effects and the rate of polymerization or time of reaction was



**Figure 7.** Synthesis of a cationomer by quaternization of a tertiary amine.<sup>80</sup>



**Figure 8.** Synthesis of PUIs.<sup>81</sup>

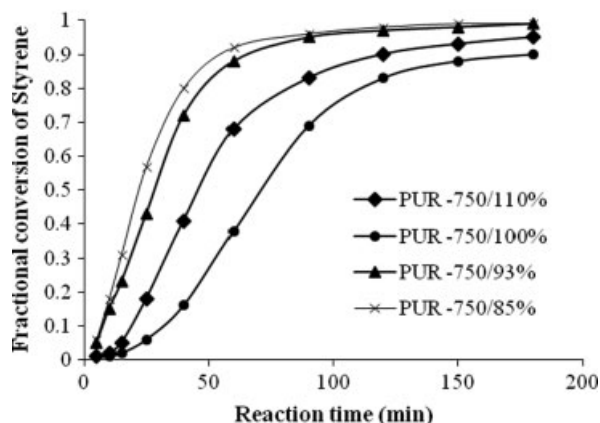
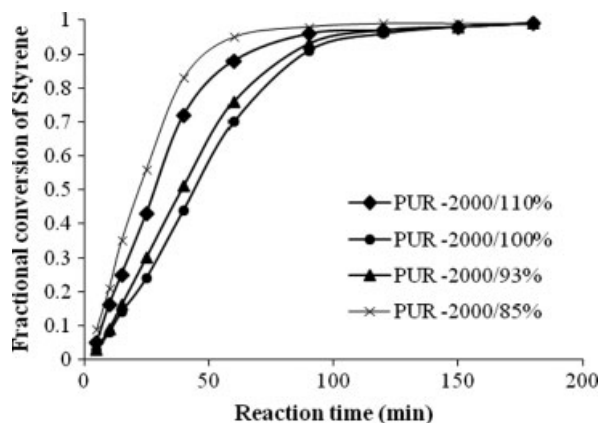


**Figure 9.** Synthesis of zwitterionomers by quaternization of *N*-alkyldiols using sultones or lactones.<sup>82</sup>

affected by the swelling ability of the aggregates for monomer (Fig. 10).

### Summary

PU anionomers, PU cationomers and PU zwitterionomers are very interesting materials since they can be processed in aqueous media. Anionomers are the most often studied materials and can be easily obtained by the condensation of non-ionic diisocyanates with conventional polyols and an anionic chain extender, frequently DMPA. This cheap reagent gives good results in terms of solubilization of PUs in polar solvents, especially in water, even with a small amount of this short anionic diol. This synthetic route avoids the use of polluting solvents leading to more eco-friendly materials and to biocompatible PUs.



**Figure 10.** Conversion of styrene in the emulsion polymerization of polystyrene as a function of reaction time for various neutralization rates of the ionomer resin.<sup>53</sup> (PUR-2000, PUR-750: PUs based on polyoxypropylene diol, IPDI and DMPA).



**Table 1.** TGA results for aromatic and aliphatic diisocyanates<sup>91</sup>

Formulation <sup>a</sup>	Weight loss (%) and decomposition temperature range (°C)		
	Step 1	Step 2	Step 3
PEG/EG/2MDI	10 (100–300)	60 (300–410)	28 (410–700)
PEG/EG/2HDI	7 (100–240)	77 (240–370)	15 (370–550)

<sup>a</sup> PEG, poly(ethylene glycol); EG, ethylene glycol.

**Table 2.** TGA results for incorporation of ionic groups<sup>100</sup>

Ionic content (wt%)	First step of degradation, $T_{onset}$ (°C)	First step of degradation, $T_{max}$ (°C)	Second step of degradation, $T_{max}$ (°C)	Residue at 450 °C (%)
2.37	228	264	331	10.0
3.19	229	278	327	10.1
3.80	236	267	320	10.7
4.27	244	280	315	10.6

## PROPERTIES OF POLYURETHANE IONOMERS

### Thermal properties: thermal stability

PUs are usually stable materials but some differences can be observed as a function of the chemical structure of the various diols and diisocyanates used for their synthesis. At *ca* 230 °C, the scission of urethane groups is generally observed.

The nature of the diisocyanate of a PU is one of the main factors governing the thermal stability. PUs based on aromatic diisocyanates are more stable than those based on cycloaliphatic and aliphatic diisocyanates.<sup>90–92</sup> Aromatic diisocyanates produce fewer chain scissions; they are less sensitive to thermal oxidation and radiation. Oprea and Vlad<sup>91</sup> synthesized PUs with a polyether diol, ethylene glycol and two different diisocyanates: MDI and hexamethylene diisocyanate (HDI). They noted that the decomposition of PUs occurred in three steps. Degradation temperatures of MDI (aromatic)-based PUs were higher than those based on HDI (aliphatic). The results are presented in Table 1.

However, different results seem to be obtained with the use of thermoplastic elastomer PUs. With this type of PU, better thermal stability is reported with the use of aliphatic diisocyanates than with aromatic ones.<sup>4,93,94</sup> Xie *et al.*<sup>93</sup> synthesized PUs based on a polycaprolactone polyol, 1,4-butanediol and various cycloaliphatic diisocyanates. They obtained polymers with better thermal stability than those made with aromatic diisocyanates. Hepburn<sup>4,94</sup> showed that cycloaliphatic diisocyanates lead to more thermally stable PUs than linear ones.

Thermal degradation also depends on the ratio between hard and soft segments. Petrovic *et al.*<sup>95</sup> found that degradation of PUs in the initial stage is mainly dominated by the type and amount of hard segments.

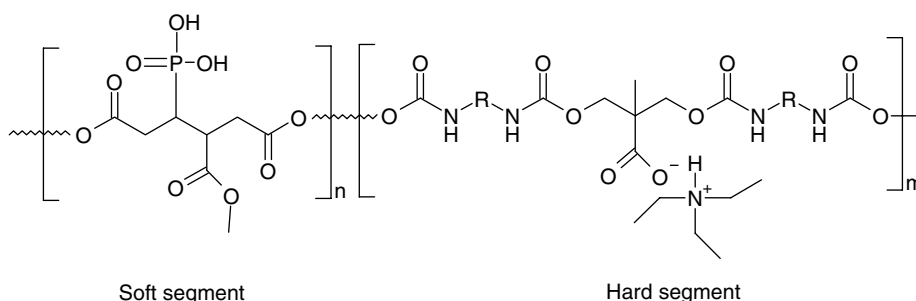
Polyols used in the synthesis of PUs are mainly based on esters and ethers. Ester-based polyols are thermally more stable than ether-based ones.<sup>96,97</sup> More specifically for this latter class of material, poly(tetramethylene glycol) (PTMG) is more stable than poly(propylene glycol) (PPG) or poly(ethylene glycol) (PEG). Hydroxytelechelic polybutadiene has also been used and the

resulting PUs are more stable than those formulated from ester- or ether-based polyols because of the absence of heteroatoms in their structure.

Although the thermal stability of PUs is mainly dominated by the nature of the diisocyanates, soft segments and hard segments, ionomer groups can influence the thermal stability of PUs. Usually the stability of PUIs is less at low temperatures than that of non-ionomer ones, and a weight loss is often observed at *ca* 100 °C probably because of the presence of water adsorbed by the ionic groups.<sup>20,26–28,98,99</sup> For instance, Mahesh *et al.*<sup>99</sup> compared PUs and PUIs synthesized from poly(tetramethylene oxide) glycol, toluene diisocyanate and 3,4-dihydroxycinnamic acid. They showed that the weight loss around 150 °C is low for usual PUs whereas it is not negligible in the case of anionomers because of free or bonded water molecules. As a consequence this weight loss at low temperature is not directly related to the PU structure.

An increase of thermal stability with an increase of ionic groups was reported by Yang *et al.*<sup>100</sup> They synthesized anionomer PUs based on PEG, DMPA, toluene diisocyanate or IPDI. Two steps of degradation were observed. An increase of the onset and of the maximum temperature of the first step was noticed as well as an increase of char residue at 450 °C with respect to the increase of ionic groups (Table 2). This increase of thermal stability with ionic group content was explained by the increase of thermally stable coulombic forces between the ionic centres.

A neutralizing base can also have an effect on the thermal stability of PUIs. For example, Mequanint *et al.*<sup>101</sup> studied the behaviour of carboxylate-based PUIs containing varying amounts of phosphate groups, and different neutralizing bases of the carboxylate groups (Fig. 11) using TGA. The phosphate-containing PUs showed an initial weight loss at *ca* 180 °C, but when the phosphorus content in the polymer increased, a residue was formed at 450 °C and they were thermally stable up to 700 °C. The initial weight loss temperature of these phosphate-containing PUs was lower than that of phosphate-free PUs, for which the initial weight loss was not observed below 245 °C.

**Figure 11.** Phosphonate PUIs studied by Mequanint *et al.*<sup>101</sup>



Such characteristic behaviour of phosphate-containing PUs was attributed to the relative ease of degradation of the phosphate-containing segments. The weight loss of these PUs prepared from dispersions was dependent on the neutralizing base used. TGA curves of PUs neutralized by triethylamine and used in dispersions showed no differences in comparison with the non-neutralized PU. However, a significant difference in weight loss was observed when the neutralizing bases were metal hydroxides, such as NaOH. This was attributed to the non-volatile products of degradation of the metal carboxylate. These formulations showed enhanced stability up to 220 °C.

### Thermal properties: glass transition temperature

The glass transition temperature ( $T_g$ ) of anionomers has been studied using DSC and dynamic mechanical thermal analysis. It is quite difficult to compare the results of the various studies because  $T_g$  values of PUs really depend on the nature of diols and diisocyanates, the nature of ionic groups and counter ions, and the concentration of ionic groups and their position in the PU backbone.

The morphology of PUs depends on the compatibility between soft and hard segments. Soft segments are composed of groups stemming from polyols and hard segments of groups stemming from chain extender and diisocyanates. If they are compatible, only one phase and one glass transition are observed. If these segments are incompatible, two different phases coexist and two glass transitions can be observed if hard segments are long enough to segregate and have polymer behaviour: the first one is attributed to the soft segments and the second to the hard segments. If the hard segments are small nodules, no hard-segment  $T_g$  is observed. As a consequence, most of time only one  $T_g$  can be seen; it corresponds either to the entire PU or only to the soft segments. This  $T_g$  decreases or increases with the introduction of ionic groups depending on the various interactions occurring in the PU chains. Both soft and hard segments exhibit partial crystallinity whatever the size of the hard segments. For soft segments, this crystallinity comes from the nature of the polyols used. Some of them are totally amorphous and no  $T_g$  is observed. In the case of hard segments, interactions of urethane groups lead to some order in the system giving some crystallinity.

### Decrease of glass transition temperature

The decrease of  $T_g$  resulting from the introduction of ionic groups in PUs has been explained in various studies.<sup>59,98,102</sup>

The ionomers that are most reported in the literature are polyether-based PUs. Among these, PTMG-based PUs have the lowest  $T_g$  values and PPG-based systems have higher  $T_g$  because of the axial methyl group on the secondary carbon. PEG-based systems have even higher  $T_g$  because of their compact morphologies.

Lee *et al.*<sup>103,104</sup> studied a model PU based on PTMG1000 and tolylene diisocyanate (TDI), where they replaced the urethane hydrogen with ionic groups. As the ionic groups are incorporated in the PU matrix,  $T_g$  of the polyol unit decreases. The shift of  $T_g$  to lower values was attributed to an aggregation of diisocyanate unit microphase, enriching the matrix in the lower  $T_g$  soft phase and thereby leading to a greater phase separation.

Pérez-Limiñana *et al.*<sup>59</sup> characterized waterborne PUs containing varying amounts of ionic groups. The PUs were based on diethylene glycol, DMPA, tetramethylxylene diisocyanate and butanediol as chain extender. The DMPA content was varied from 5

**Table 3.**  $T_g$  from dynamic mechanical thermal analysis curves of waterborne PUs containing DMPA<sup>59</sup>

Sample	DMPA (wt%)	$T_g$ (°C)
1	5	-5
2	6	-10
3	8	-25

to 8 wt%. Dynamic mechanical thermal analysis showed that  $T_g$  of the PUs decreased on increasing the DMPA content as shown in Table 3. The decrease in  $T_g$  of PUs observed on increasing their hard segment content has also been reported by Garrett *et al.*<sup>105</sup> They showed that an increase in crystallinity of PUs resulted in an increase in  $T_g$  due to the restriction in the mobility of the amorphous domains in the polymer. This phenomenon was ascribed to the anchoring of neighbouring segments inside the crystallites. An increase of DMPA content produced a decrease in the crystallinity because of steric effects, consequently explaining the decrease of  $T_g$  with increasing DMPA content. Other investigations<sup>45,65,106</sup> of polydioxolane PUs led to similar conclusions.

Table 4 gathers results for the effect of the incorporation of ionic groups on soft-segment  $T_g$ . These data show a decrease of  $T_g$  with an increase of ionic group content.

### Increase of glass transition temperature

Nierzwicki and Rutkowska<sup>74</sup> studied the effect of ionic groups on microphase separation and on  $T_g$ . They compared a model compound based on PTMG ( $M_n = 2000 \text{ g mol}^{-1}$ ; PTMG2000), TDI and butanediol with a compound based on PTMG2000, TDI, butanediol, triethanolamine and dibromohexane.  $T_g$  of the soft segments shifted to higher temperatures with the introduction of ionic groups. Those authors supposed that the increase in the ionic group content, the groups being solubilized in the soft phase, could have a drastic effect on the chain mobility in this phase, due to the physical crosslinking of ionic groups.

Mondal and Hu<sup>63</sup> studied the thermal properties of polyether-based PUs. They condensed different amounts of PPG ( $M_n = 1000 \text{ g mol}^{-1}$ ), PEG ( $M_n = 3400 \text{ g mol}^{-1}$ ), butanediol and DMPA with MDI. The various compositions studied are listed in Table 5. The materials were studied using DSC. S14 showed endothermic and exothermic peaks during heating and cooling, whereas S15, S16 and S17 exhibited a glass transition in heating steps but no transitions in cooling steps. Hence, it could be stated that S14 had a semi-crystalline structure unlike the others. DSC could not highlight any trends for  $T_g$  for all segmented PUs. However, further investigations of these transitions have been performed using dynamical mechanical thermal analysis and the results are given Table 6.  $T_g$  of sample S15 was found to be much higher than that of the other samples because of the strong interactions between the polymer chains due to the presence of ionic groups. The storage modulus of S16 with both PEG3400 and DMPA was higher than those of PUs without carboxylic groups (S17 and S14). PPG1000 was used as soft segment and DMPA acted as hard segment. It was suggested that various strong interactions could take place because of the ionic groups:

- hydrogen bonding between carbamoyl group (NH-CO) of urethane and carbonyl group of carboxylic acid;
- dipole-dipole interaction between carbonyl groups; and
- induced dipole-dipole interaction between aromatic rings.<sup>107</sup>

**Table 4.** Increase of  $T_g$  with incorporation of ionic groups

Ionomer composition	Ionic content (wt%)	$T_g$ ( $^{\circ}$ C)	Ref.
Tetramethylene diisocyanate; 1,4-butanediolpolyadipate; diethylene glycol; DMPA	5	-5	59
	6	-10	
	8	-25	
MDI; butanediol; polydioxolane; trimethylsulfone	0	-43	65
	8.7	-46	
	13.5	-56	
	18.4	-51	
	0.050	-60	
MDI; poly(tetramethylene oxide) glycol ( $M_n = 1040$ g mol $^{-1}$ ); pyromellitic anhydride	0.059	-60	106
	0.067	-50	
	0.074	-52	
	0.084	-61	
	0.095	-74	
	0	-33	
MDI; poly(tetramethylene oxide) glycol ( $M_n = 700$ g mol $^{-1}$ ); propanesulfone	1.15	-38	103, 104
	1.74	-41	
	2.96	-52	
	0	-55	
MDI; poly(tetramethylene oxide) glycol ( $M_n = 1000$ g mol $^{-1}$ ); propanesulfone	1.24	-61	103, 104
	1.64	-64	
	2.55	-71	
	0	-68	
MDI; poly(tetramethylene oxide) glycol ( $M_n = 2000$ g mol $^{-1}$ ); propanesulfone	0.67	-72	103, 104
	1.3	-75	
	1.77	-78	
	0	-72	
MDI; poly(tetramethylene oxide) glycol ( $M_n = 3000$ g mol $^{-1}$ ); propanesulfone	1.29	-78	103, 104

**Table 5.** Compositions of the various samples studied by Mondal and Hu<sup>63</sup>

Sample	Feed ( $\times 10^3$ mol)				
	PPG1000	PEG3400	DMPA	Butanediol	MDI
S14	32.5	1.471	0	11.76	45.72
S15	22	0	30	4	56
S16	24	0.6	15	8.4	48
S17	26	0	0	22	48

**Table 6.**  $T_g$  values of samples S14 to S17<sup>63</sup> of Table 5

Sample	$T_g$ ( $T_g$ from $\tan \delta$ spectra) ( $^{\circ}$ C)
S14	-42
S15	38
S16	-1.5
S17	-25

All these interactions are able to increase physical crosslinks in the polymer matrix, hinder chain mobility and hence lead to higher  $T_g$ . Kim *et al.*<sup>55</sup> inserted ionic groups in soft segments and reported similar results.

In the case of PU cationomers and zwitterionomers based on pyridinium units, Mahesh *et al.*<sup>98,99</sup> noticed a decrease in the

**Table 7.** Increase of  $T_g$  with incorporation of ionic groups

Composition	Ionic content (wt%)	$T_g$ ( $^{\circ}$ C)	Ref.
MDI; poly(propylene glycol); DMPA; butanediol	0	-25	63
	15	-1.5	
	30	38	
Toluene diisocyanate; poly(tetramethylene glycol); 3,4-dihydroxycinnamic acid	12	-59.5	98
	19	-45	

$T_g$  value with an increase of quaternization of the pyridinium sites.

From these studies, it can be inferred that the size and the nature of ionic systems significantly influence the phase separation, this effect being dependent on the composition of the PU.

Table 7 compares the effect of the incorporation of ionic groups on  $T_g$  of the soft segment phase. It is evident that there is an increase of this parameter with an increase of ionic group content.

#### Influence of counter ions

Counter ions also have a significant influence on the properties of PUIs. Al-Salah *et al.*<sup>34</sup> noticed a change in  $T_g$  with the nature of the metal counter ions. Another study by Chui *et al.*<sup>108</sup> showed a decrease of  $T_g$  with the use of ionic chain extender. However, it was noted that the magnitude of the shift is lower when the counter

**Table 8.** Effects of counter ion on  $T_g$  values<sup>98</sup>

Sample	Composition <sup>a</sup>	$T_g$ (°C)
1	PTMG1000/2TDI/DCA	-59.5
	PTMG1000/2TDI/DCA; counter ion: Na <sup>+</sup>	-68
	PTMG1000/2TDI/DCA; counter ion: Zn <sup>2+</sup>	-63
2	PTMG1000/3TDI/2DCA	-45
	PTMG1000/3TDI/2DCA; counter ion: Na <sup>+</sup>	-69
	PTMG1000/3TDI/2DCA; counter ion: Zn <sup>2+</sup>	-62.5
3	PCL1250/2TDI/DCA	-28
	PCL1250/2TDI/DCA; counter ion: Na <sup>+</sup>	-45.5
	PCL1250/2TDI/DCA; counter ion: Zn <sup>2+</sup>	-40
4	PCL2000/2TDI/DCA	-25
	PCL2000/2TDI/DCA; counter ion: Na <sup>+</sup>	-26
	PCL2000/2TDI/DCA; counter ion: Zn <sup>2+</sup>	-25.5

<sup>a</sup> PCL, polycaprolactone; DCA, 3,4-dihydroxycinnamic acid.

ions are divalent metal ions in comparison with monovalent ones. For example, Mahesh *et al.*<sup>98</sup> studied PUs containing TDI, PTMG (1000 g mol<sup>-1</sup>) or polycaprolactone and 3,4-dihydroxycinnamic acid anionomers. They observed a shift in  $T_g$  of the materials as a function of counter ion. Table 8 shows these effects of monovalent or divalent counter ions.

### Summary

The introduction of ionic groups influences the glass transition of soft segments.  $T_g$  decreases with an increase of ionic group content due to the lowering of crystallinity and increase of microphase separation of hard and soft segments.  $T_g$  can also increase with the amount of ionic groups creating strong interactions between polymer chains and increasing crosslinking of the polymer matrix. These two phenomena can occur simultaneously; as such, predictions about the effects of the incorporation of ionic groups on the glass transition are uncertain.

### Mechanical properties

All mechanical properties are influenced by the introduction of ionic groups in PUs, but the most important changes are observed for tensile strength of the materials. As for thermal properties, the nature of ionic groups, their location in the polymer chain and the nature of counter ions have a significant influence on this behaviour.

In most PUI systems, the introduction of ionic groups increases the tensile strength of the PUs. The addition of ionic charges creates physical crosslinking between the polymer chains.

Mondal and Hu<sup>63</sup> studied the mechanical properties of polyether-based PUs and showed that tensile strength and elongation at break are dependent on the hard and soft segments and more precisely on the overall morphology of the copolymer. Strain at maximum load increased whereas modulus decreased when PEG3400 (S14) was introduced in the polymer backbone as compared with the sample without any hydrophilic or carboxylic groups (S17). The effect was explained by the flexibility of PEG3400 which increases the chain mobility and ensures partial dissolution of hard segments in the soft phase, increasing the mobility of the hard segments. These results are presented in Table 9, where it can be seen that ionic groups have a strong influence on the mechanical properties of the PU. Modulus increased significantly

**Table 9.** Mechanical properties of samples S14 to S17<sup>63</sup> of Table 5

Sample	Elongation at break (%)	Modulus (MPa)
S14	1000	1.9
S15	188	90.2
S16	234	2.1
S17	237	10.1

when DMPA was used (S15) and a decrease of the maximum strain in elongation was observed. This was ascribed to the presence of carboxylic groups, which cause strong interactions between the polymer chains that form an entangled and interconnected network structure and prevent chain slippage during loading. The value of the modulus of the sample with PEG3400 and DMPA (S16) was between those of S14 and of S15, due to the presence of DMPA, on the one hand, which increases the modulus because of strong interactions, and to the presence of PEG3400, on the other hand, which increases the chain flexibility. There is a dual effect and, in this case, the role of PEG 3400 is predominant since the modulus of S16 is closer to that of S14 than to that of S15. Moreover the modulus of S16 is slightly lower than that of S17 which contains neither DMPA nor PEG3400. Wang *et al.*<sup>44,51</sup> and Chen *et al.*<sup>109</sup> drew to similar conclusions for the dependence of morphology on mechanical properties.

These observations are compatible with those concerning thermomechanical properties, which showed that strong interactions lead simultaneously to an increase in  $T_g$  and modulus and a decrease in elongation at break. We showed previously that an increase of ionic groups could result in a decrease in crystallinity and a better phase separation between soft and hard segments and could lead to a decrease in  $T_g$  of PUIs.<sup>59,105</sup> It can be suggested that an increase in phase separation and in chain mobility would bring about a decrease in tensile modulus and an increase in elongation at break for these PUIs. Most of the publications that report thermal properties do not detail the mechanical properties of the PUIs. However, Chwang *et al.*<sup>46,110</sup> reported an increase in tensile strength and modulus and a decrease in elongation at break with ionic group content (Fig. 12). These materials were synthesized from 1,3-propanesultone polyester ( $M_w = 2800$  g mol<sup>-1</sup>), PPG ( $M_w = 700$  g mol<sup>-1</sup>), butanediol and neopentyl glycol condensed with toluene diisocyanate. The ionic diols used were DMPA or 1,1-diaminopentanesulfonic acid sodium salt. The behaviour reported was explained by strong intramolecular interactions, entailing an increased phase separation and chain mobility.

In the specific case of anionomers, an increase of both tensile strength and elongation at break has been observed. For example, Ramesh<sup>111</sup> studied the effect of sodium and zinc carboxyl anionomers on systems of PTMG1000, TDI and phenolphthalein or thymolphthalein (Table 10). It was noticed that the ionic forces enhanced the cohesion of the polyol units during stress. The consequence was an increase in modulus and elongation at break.

Table 11 compares the effect of the incorporation of ionic groups on the mechanical properties of PUIs. It shows that the mechanical properties are not only dependent on the nature and the amount of ionic groups but also on the overall morphology of the ionomers.

### Dilute solution properties

The roles of solvent polarity, dielectric constant, size and nature of counter ion and location of ionic groups in the polymer

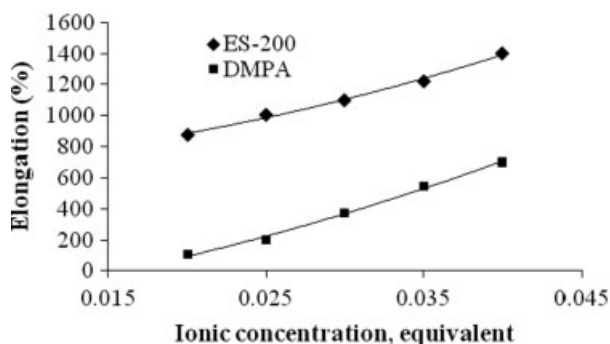
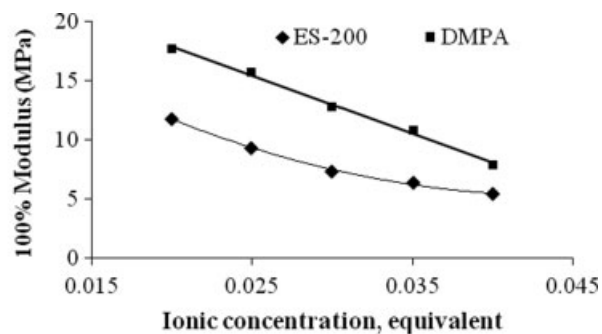
**Table 10.** Formulations of anionomers studied by Ramesh<sup>111</sup>

Composition	Tensile strength at break (MPa)	Elongation at break (%)
PTMG1000/TDI/phenolphthalein	2.50	1293
Sodium anionomer	4.70	2869
Zinc anionomer	12.1	2004
PTMG1000/TDI/thymolphthalein	0.39	2020
Sodium anionomer	0.62	2505
Zinc anionomer	1.33	1208

chain are significant in the properties of dilute solutions of PUIs. Polystyrene sulfonates have been studied by Lundberg and co-workers.<sup>112–114</sup> In polar solvents and for high dilution, ionomers behave as polyelectrolytes and polymer expansion takes place. Other studies<sup>115–117</sup> of the effect of counter ions were carried out for alkali metal salts and for anionomer systems. For sulfonate systems the order of counter ion–sulfonate bond force was reported as  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Ca}^{2+}$ .

Many studies have focused on the characterization of the properties of solutions of PUIs based on the measurement of conductivity and dielectric behaviour.<sup>10,14,15,17,18,43,45,65,118–121</sup>

Hsaing *et al.*<sup>58</sup> studied PUIs as dispersants in water-soluble acrylic paints with titanium dioxide pigments. In aqueous solution, the surface tension for PUI molecules with different ionic groups (DMPA, 4,4-hydroxybutane sulfonate and 2,5-diaminopentanoic acid hydrochloride) was found to increase with increasing concentration of the ionic groups. This results in an even better organization of the hydrophobic segment of ionomer molecules adsorbed at the air–water interface and at the titanium dioxide pigment–water interface. Consequently, a better distribution of the ionomers at the interfaces was observed and the dispersion was improved. Those authors showed that PU

**Figure 12.** Modulus and elongation at break as a function of ionic group content for the ionomers studied by Chwang *et al.*<sup>46,110</sup> (ES-200, 1,1-diaminopentanesulfonic acid sodium salt).

anionomers can be considered as good dispersants because the particles of titanium dioxide pigments were found to become finer as the stirring time and the ionic concentration of PU anionomers were increased.

Zhang *et al.*<sup>57</sup> studied the stability of emulsions of water-borne PUs. They prepared waterborne PUs based on IPDI,

**Table 11.** Modification of mechanical properties on incorporation of ionic groups

Composition	Ionic content (wt%)	Elongation at break (%)	Modulus (MPa)	Ref.
MDI; poly(propylene glycol); DMPA; butanediol	0	188	90	63
	15	234	2	
	30	237	10	
Toluene diisocyanate; dye polyol	0.0004	–	4	109
	0.0005	–	5	
	0.0006	–	6	
	0.0007	–	7	
	0.0008	–	8	
	0.0008	–	8	
Toluene diisocyanate; 1,3-propane polyester; poly(propylene glycol); butanediol; neopentyl glycol; 1,1-diaminopentanesulfonic acid sodium salt	0.02	820	12	46, 110
	0.025	970	8	
	0.03	1050	7	
	0.035	1210	6	
	0.04	1410	5	
	0.04	1410	5	
Toluene diisocyanate; 1,3-propane polyester; poly(propylene glycol); butanediol; neopentyl glycol; DMPA	0.02	90	18	46, 110
	0.025	200	15	
	0.03	370	12	
	0.035	790	10	
	0.04	660	8	

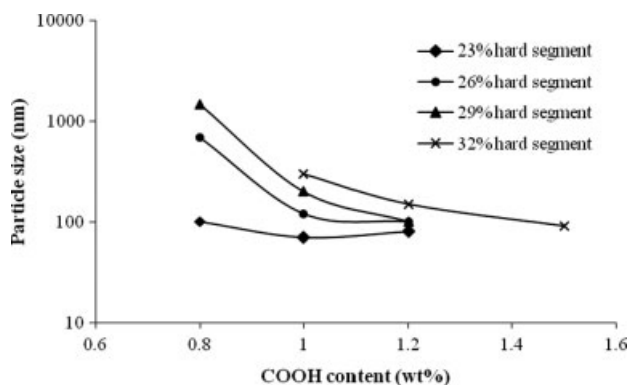


Figure 13. Influence of COOH content on particle size.<sup>57</sup>

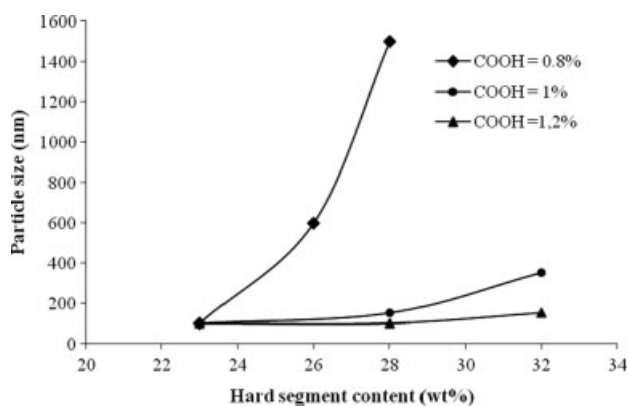


Figure 14. Influence of hard segment content on particle size.<sup>57</sup>

DMPA, poly(hexaneneopentyl adipate) glycol and poly(ethylene-butylene adipate) glycol (PE-BA). The stability of the emulsions was studied on the basis of the shelf life and particle size distribution of the emulsions.

Many factors can affect the stability of emulsions: solvents, COOH content, hard segment content, extenders and feeding process. Some results are presented in Figs 13 and 14.

An important factor for the stability of an emulsion is the size of the emulsion particles; the smaller the particles, the more stable is the emulsion. Zhang *et al.*<sup>57</sup> showed that the particle size of the emulsions decreased with increasing carboxylic group content (Fig. 13). Indeed, when the content of hard segments was fixed lower than 29% in a system containing IPDI, DMPA and PE-BA, an emulsion was created for a carboxylic group content from 0.8 to 1.2 wt%, and the particle size reached a minimum value when the content of carboxylic groups was 1.2 wt%. Above 1.2 wt%, the hydrophilicity of the PU molecules is so important that the PU was totally soluble in water. At the critical value of 1.2 wt% of carboxylic groups an emulsion was created and the particles were very small. Compared to larger particles, small particles have larger relative surface areas, and many carboxylic groups are needed to stabilize the emulsion. As the content of carboxylic groups decreased to 0.8 wt%, larger particles were formed to lower the surface energy. If the content of carboxylic groups reached the critical content (0.8 wt%), a PU emulsion was not created, and the two phases were completely separated.

The hard segment content also has a great influence on PU emulsion stability. Here the hard segments play the role of hydrophobic groups in opposition to the ionic groups located

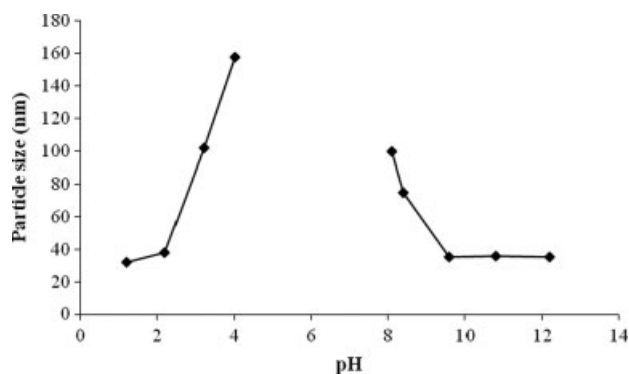


Figure 15. Influence of pH on particle size.<sup>125</sup>

on the soft segments. The particle size of the PU emulsions increases with the content of hard segments. With an increasing content of hard segments, PU molecules gather to form micelles as a result of hydrophobic interactions. For a high content of hard segments, the molecules are more hydrophobic and the chain interactions are stronger. Thus, particles create aggregates as a result of the interaction energies and consequently of the hard segment content. The role of hard segments is different from that of carboxylic groups in their contribution to particle size because carboxylic groups are located on the surface of particles whereas carbamate groups are inside.

In contrast to the effect of both carboxylic groups and hard segment content, the nature of extenders and the feeding process have few effects on the stability of emulsions.

Many other studies<sup>122-125</sup> have focused on waterborne PUs. For example Dong *et al.*<sup>125</sup> studied the influence of pH on the particle size of a PUI dispersion. They synthesized a PU by condensing poly(oxypropylene glycol), DMPA with carboxylate groups ( $-\text{COO}^-$ ), dimethylamino-1,2-propanediol (DPA) with dimethylammonium groups ( $-\text{N}^+(\text{CH}_3)_2$ ) and butanediol with IPDI. Various amounts of DMPA and DPA were used to control the amount of carboxylic and amine groups. They noted that the particle size was dependent on the pH of the solution. Figure 15 shows the evolution of the particle size of a PUI as a function of pH (with a molar ratio of 1 : 1 between carboxylic and amino groups).

PUs can be dispersed in acidic or basic solutions. The stability of the PU dispersions is maintained by the static repulsive interactions between the charged groups. As a consequence the degree of ionization of these groups controls the particle size of the dispersion. When the pH value is lower than 2.5 or higher than 9, the particle sizes are smaller than 40 nm and change markedly with pH. These PUs can be handled as powders which can be easily dissolved in HCl or NaOH aqueous solutions where the amine or carboxylic groups of the chain will form salt groups with positive or negative charges that can weaken the ionic or hydrogen bonds between the macromolecules. These compact powders are progressively expanded. The charged chain segments migrate towards the water-particle interphase whereas the hydrophobic segments such as soft segments gather to form a hydrophobic phase inside the particles coated by charged segments. This leads to a dispersion of the PU as nanoparticles. The charged acidic or basic groups can produce enough repulsive forces to stabilize the dispersion.

Around the isoelectric point (here  $\text{pH} = 6-7$ ) positive and negative charged groups are nearly equal. The interactions of acidic and basic groups create ionic bonds between the



macromolecular chains and hinder the dispersion of the PU. Particles of PU become insoluble, and therefore no curve can be established between pH values of 4 and 8 (Fig. 15).

When the pH of the solution is lower than 4 or higher than 8, enough free charged groups on the PU chains can create repulsive forces to allow dispersion and the formation of microspheres or nanospheres. The size of the microspheres decreases with increasing free charged groups to reach a size of 40 nm when all the charged groups are positive or negative.

## APPLICATIONS

### Waterborne polyurethanes

Basically, conventional PUs are hydrophobic materials. Owing to increasingly strict environmental regulations, solvent-based systems are now abandoned and waterborne systems are warranted.

Diisocyanates are sensitive to water and consequently the direct use of water as a solvent in the manufacture of PUs is not possible. However, it is possible to incorporate hydrophilic segments into a hydrophobic PU, so that the resulting PU can be easily dispersed. An aqueous PU dispersion is a binary colloidal system in which hydrophobic PU segments are dispersed in a continuous water phase. An appropriate combination of hydrophilic segments acts as an emulsifier and no additional emulsifier is needed. Various reviews address this particular subject of aqueous PU dispersions.<sup>8,9</sup>

This method also allows one to obtain high solid contents and high molecular weights since the viscosity of the dispersion is generally independent of the molecular weight of the dispersed polymer. Because of these factors, the mechanical properties of the materials based on this method after extraction of water are very interesting.

The price of waterborne PUs is often lower than that of other solvent-borne PUs. Because of this, aqueous PU dispersions are used in various industrial fields, such as coatings, especially in the textile industry,<sup>126–129</sup> and adhesives. Many patents have been registered on this subject since the 1960s and, more recently, they have been focused on novel coating processing and applications<sup>130–140</sup> and on the dispersion of modified waterborne PUs. Modification can be achieved by the grafting of other polymers on the PUs, crosslinking using internal or external agents, blending with other polymers or the formation of interpenetrating polymer networks. The global aim is to solubilize or disperse these agents or other polymers in water.

Recent studies have focused on the use of waterborne PUs as surfactants.<sup>52,53,55,59</sup> The advantages of PUs compared to internal emulsifiers are that they give a finer particle size and that this size can be controlled. Indeed, the solution behaviour of PUs can be easily influenced by ionic strength and pH in the case of weak acids or bases.<sup>52</sup> They are also often less toxic and less expensive than other waterborne PUs. A review is available of PU aqueous dispersions and their applications.<sup>141</sup>

Meng *et al.*<sup>126</sup> prepared waterproof textile coatings using a waterborne PU. These polymers were synthesized starting from three diols, i.e. PTMG, a poly[(ethylene oxide)-co-(propylene oxide)] (PPG2050) and an ionomeric diol such as DMBA, and IPDI. These polymers were coated on textiles and water vapour permeability and waterproofing were measured. Table 12 summarizes the results of these measurements. These materials show good water vapour permeability and waterproofing. For example, for PU-0, 1000 g m<sup>-2</sup> of water vapour can go through the textile in 24 h

**Table 12.** Water vapour permeability and waterproofing values of textile coatings prepared using waterborne PUs<sup>126</sup>

Sample <sup>a</sup>	Water vapour permeability (g m <sup>-2</sup> (24 h) <sup>-1</sup> )	Waterproofing (mm H <sub>2</sub> O)
PU-0	1000	> 8 500
PU-7	910	> 10 000
PU-14	960	> 10 000
PU-21	990	> 10 000

<sup>a</sup> Where x in PU-x represents the amount (wt%) of PTMG in a mixture of PTMG and PPG2050.

and the textile is almost impermeable to water drops, a pressure equivalent to 8500 mm of water being needed before the textile leaks.

Pérez-Limiñana *et al.*<sup>59</sup> synthesized waterborne PUs as adhesives. The materials used were tetramethylxylene diisocyanate, diethylene glycol and DMPA in water. The DMPA content varied from 5 to 8 wt%. In order to characterize the material, PU films were prepared by filling a polytetrafluoroethylene mould with 100 mL of an aqueous PU dispersion and allowing it to dry at room temperature for one week then heating at 80 °C in an oven for one week. Adhesive joints of these dried waterborne PU films were produced between two sheets of poly(vinyl chloride) and tested with T-peel tests. The joints produced between poly(vinyl chloride) and the waterborne PUs showed a high immediate adhesion.

### Shape memory effect

Shape memory polyurethanes (SMPUs)<sup>54,78,79,142–145</sup> are thermo-plastic block copolymers having unique mechanical properties, which are due to the thermo-responsive shape memory effect (SME). Owing to the presence of soft and hard segments, of which the former form a reversible phase while the latter form a frozen phase, the material can memorize the permanent shape and recover it from the temporary shape upon heating above a switch temperature after being strained. Theoretically, the reversible phase made of soft segments has a melting or glass transition temperature which governs the switch temperature and is used to hold the temporary deformation. The frozen phase made of hard segments inhibits the slip of the molecular chains by physical or chemical crosslinkage points and is responsible for memorizing the permanent shape. Due to this unique feature, this type of material has attracted research interest from both academe and industry in the last two decades.

For linear segmented PU systems, the presence of high polarity and hydrogen bonding effects due to the urethane and urea units in the hard segments lead to strong intermolecular forces and so create the frozen phase. The SME of PUs is therefore influenced by the content of hard segments and their molecular structure. In addition, it is reported that the content of soft segments, their molecular weights and morphological structures also play significant roles in the SME.

The introduction of ionomers in SMPUs has a very significant effect, and it was shown that ionic groups can slightly increase or decrease  $T_g$  of soft segments. Because of this effect, different switch temperatures can be set with the same PU system. Moreover, it was noticed that ionic groups enhanced the crystallization of hard segments and a better SME was consequently observed.<sup>78,79,145</sup> Zhu *et al.*<sup>79</sup> studied the effect of cationic groups in hard segments of shape memory fibres composed of 1,4-butanediol, MDEA,

**Table 13.** Activated partial thromboplastin time (APTT) and prothrombin time (PT) of citrated normal human plasma samples after treatment with various concentrations of PUI nanoparticles<sup>62</sup>

Concentration of PUI nanoparticles (mg/mL)	APTT (s)	PT (s)
0	37.0 ± 2.5	13.6 ± 0.9
10	43.8 ± 2.5	14.0 ± 1.4
15	49.4 ± 3.1	14.2 ± 1.3
20	51.4 ± 2.9	14.3 ± 1.2
25	61.4 ± 3.7	14.5 ± 1.3

MDI and poly(butylene adipate) diol. They showed that the incorporation of ionic groups can significantly change  $T_g$  of the material (from 63 to 71 °C) and that the ionic groups can facilitate the crystallization of hard segments in SMPU ionomer fibres.

### Biomedical applications

Urethane elastomers are biocompatible<sup>146–150</sup> since polyether-based PUs are resistant to hydrolysis by biological fluids. PU elastomers are used without surface treatment for devices such as artificial hearts, connector tubing for heart pacemakers, haemodialysis tubes, etc. Recently, PUs with and without ionic groups have been studied in detail for their potential biomedical applications.<sup>62,151–160</sup> PUs are also non-toxic and crosslinking offers a better resistance to biological fluids so that mechanical properties are maintained for a long time. PUIs containing sulfonate groups and phosphatidylcholine groups have been used for the development of polymers that are compatible with blood.<sup>81,161,162</sup>

Li *et al.*<sup>81</sup> synthesized PUs and poly(urethane-urea)s with polybutadiene and phosphatidylcholine analogues in the main chains and long alkyl segments in the side chains. Those authors evaluated the haemocompatibility of the segmented PUs and poly(urethane-urea)s and they noticed that the haemocompatibility of these new PUs was better than that of a medical-grade PU.

Mao *et al.*<sup>62</sup> tested blood-compatible PUI nanoparticles prepared by emulsion polymerization of MDI, poly(tetramethylene ether) glycol, DMPA, isopropanol as end-capping agent and triethylamine. The haemocompatibility of these nanoparticles was assessed using *in vitro* coagulation time tests: the activated partial thromboplastin time (APTT) and prothrombin time (PT) were measured. If a nanoparticle is haemocompatible, the coagulation times are longer. Table 13 shows APTT and PT of citrated normal human plasma samples after treatment with various concentrations of PUI nanoparticles.

### CONCLUSIONS

PUIs are a special type of PU containing less than 15 mol% of ionic groups in their backbones. These ionic groups can be anions (PU anionomers), cations (PU cationomers) or even zwitterions (PU zwitterionomers). These PUIs can be synthesized in various ways such as condensation of ionic diols with diisocyanates or post-ionization of PUs.

PUIs exhibit various properties, the most important one being their ability to be solubilized in water, opening the way to waterborne PUs. Their thermal and mechanical properties are also interesting since ionic groups can be used to tune the thermal

stability of PUs and their  $T_g$ . In addition, these groups can enhance mechanical properties such as modulus or elongation at break.

Various industrial applications of PUIs have been developed, particularly regarding their specific thermal and mechanical properties, leading to the production of new materials. Their dilute solution properties allow the use of PU water dispersions in paints, coatings and adhesives. Moreover, some waterborne PUs are biocompatible and are of interest in the field of biomedicine. Numerous publications and patents have described PUIs since their discovery. These materials are very promising and have a high potential for development. These relatively cheap materials combine interesting applications, low toxicity and low eco-toxicity with promise for expansion in a world where economic and ecological issues are decisive.

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