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Synthesis and characterization of film-forming poly(urethaneimide) cationomers containing quaternary ammonium groups

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Abstract

In a recent work, we have described an original family of poly(urethaneimides) containing tertiary amine groups from a polytetramethylene oxide diol (PTMO1000), *N*-methyldiethanolamine (MDEA), 4,4′-methylene-bis-phenylisocyanate (MDI) and 4,4′-hexafluoroisopropylidene-bis-phthalic anhydride (6FDA). This paper reports their quaternization with various alkylating agents to give the cationic quaternary ammonium groups. An optimization of the experimental conditions led to three new families of PUI cationomers with a good structural control and high quaternization degrees. These polymers differed in the number of their cationic groups ($0 < x \leq 0.7$ equiv.), the type of their counter-ions X^- (methyl sulfate, tosylate, triflate, chloride, bromide, iodide) and their steric hindrance by the length of their *n*-alkyl side chain (C_1–C_6). Complementary NMR techniques, including HSQC and COSY two-dimensional NMR, enabled to characterize the control of the polymer structure and to determine quantitatively the quaternization degree of the PUI cationomers. Properties in solution (solubility and viscosity) and in the solid state (film-forming ability and density) were then examined in relation with the membrane separation application targeted for these new PUI cationomers.

Keywords: Polymer chemistry; Polymer materials

1. Introduction

Poly(urethaneimide) block copolymers are film-forming materials with interesting features for membrane separation processes. Their really high withstanding to solvent exposure and the possibility to vary their permeability and selectivity make them particularly suitable for separating organic mixtures by pervaporation and vapor permeation [1,2]. Most often, their chemical structure can also be varied gradually with interesting prospects for fundamental studies to identify original structure–property relationships [3–5].

In a preceding work, we have obtained an original family of poly(urethaneimides) (PUI/*x*) containing tertiary amine groups in their polymer backbone from the *N*-methyldiethanolamine (MDEA) reactant [6]. The new synthesis method led to the PUI copolymers in high yields, with a good structural control and in particular that of their tertiary amine content *x*. The quaternization of the tertiary amine groups of these PUI copolymers with various alkylating agents can lead to different types of quaternary ammonium groups. These PUI copolymers are thus reactive polymers which can be considered as versatile precursors for the synthesis of a wide range of poly(urethaneimide) cationomers.

A few other works have already shown the excellent performances of ammonium-containing polymers for the purification of the methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether (ETBE) fuel octane enhancers [7–9]. However, the rather poor control of their macromolecular structure did not allow any detailed analysis of the role of the cationic groups on their selective permeability.

In this work, the quaternization of the PUI precursors leads to several families of PUI cationomers which differ in the number *x* of their cationic groups, the nature of their counter-ions

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X^- and their steric hindrance through the control of the length of their *n*-alkyl side chain R.

One of the great advantages of this new approach is that it is possible, from the same batch of PUI precursor, to obtain several PUI cationomers with the same macromolecular backbone, which thus only differ in the characteristics related to their ammonium groups. The properties of these cationomers can then be easily compared to those of the corresponding precursor, which gives the specific influence of the cationic sites in a straightforward way. Another advantage is the great structural variety allowed by this synthesis scheme which should open the way for the first systematic fundamental analysis of the influence of cationic groups on the selective permeability of cationomers towards purely organic mixtures of industrial interest.

This new approach to original PUI cationomers containing ammonium groups has been briefly explored in a short communication reporting preliminary results for a given family of polymers [10]. To the best of our knowledge, this short communication followed the single former paper in the literature on the synthesis of PUI cationomers containing ammonium groups reported by Al-Salah [11] and proposed a new synthesis scheme with both a gain of one step compared to the former route and great structure variability.

Nevertheless, a further investigation has since then shown that the quaternization step can be sometimes fairly difficult to handle. In particular, the main challenge is to operate in optimal conditions, i.e. soft enough to avoid deteriorating polymer chemical functions while still providing high quaternization degrees. Therefore, the synthesis of several families of new PUI cationomers with a strict structural control required another thorough investigation which is the subject for this paper.

In a first part, we describe the synthesis of three new families of PUI cationomers, the soft conditions required for the successful chemical modification of the corresponding PUI precursors and the solving of the particular problem of introducing long *n*-alkyl side chains which had not been properly identified at the early stage of our first preliminary study. Various spectroscopic techniques including two-dimensional NMR enabled to characterize the control over the polymer structure and the ammonium content for each polymer of the new families.

The second part focuses on some general features of the PUI cationomers. A few properties in solution (solubility and viscosity) and in the solid state (film-forming ability and density) are eventually discussed in relation to the membrane applications targeted for these new polymers.

2. Experimental section

2.1. Materials

1-Propanol (99.5+% Aldrich), 1-butanol (99.5% Merck), 1-pentanol (puriss. p.a. Fluka), 1-hexanol (99% Fluka), dichloromethane (99% Aldrich), chloroform (99% Carlo Erba) and petroleum ether ($T_{eb} = 35-60$ °C Carlo Erba) were stored for one week over molecular sieves 4 Å under argon before use.

The polytetramethylene oxide diol (PTMO1000, Merck) was used as received. 4,4′-Methylene-bis-phenylisocyanate (MDI, TCI) was distilled under vacuum and stored at −20 °C. *N*-Methyldiethanolamine (MDEA, Aldrich) was fractionally distilled under vacuum and stored over 4 Å molecular sieves. 4,4′-Hexafluoroisopropylidene-bis-phthalic anhydride (6FDA, Lancaster) was sublimed twice under reduced pressure. In order to prevent contamination by atmospheric moisture, all the former reagents were stored under dry argon.

Methyl *p*-toluenesulfonate (methyl tosylate MeOTs, 97% Acros), methyl trifluoromethanesulfonate (methyl triflate MeOTf, 99+% Aldrich), ethyl trifluoromethanesulfonate (ethyl triflate EtOTf, 99% Aldrich), trifluoromethanesulfonic anhydride (triflic anhydride, 98+% Acros), bromomethane (99.5+% Aldrich), 1-bromoethane (99% Fluka), 1-bromo-*n*-propane (98% Aldrich), 1-bromo-*n*-butane (97% Aldrich), 1-bromo-*n*-pentane (97% Aldrich), 1-bromo-*n*-hexane (98% Aldrich), chloromethane (99.5+% Aldrich) and iodomethane (99% Aldrich) were used without further purification.

Pyridine (99.5% Aldrich) was distilled over sodium hydroxide and stored over 4 Å molecular sieves under dry argon. Dimethyl sulfate (99% Aldrich) was distilled under reduced pressure (ca. 1 mm Hg) and stored at 6 °C under dry argon. *N*,*N*-Dimethylformamide (DMF, pure for synthesis, SDS) was distilled fractionally over calcium hydride under reduced pressure (ca. 5 mm Hg) and stored over 4 Å molecular sieves.

2.2. Synthesis

2.2.1. Alkyl trifluoromethanesulfonates (alkyl triflates ROTf)

n-Propyl, *n*-butyl, *n*-pentyl and *n*-hexyl triflate were prepared by adapting a literature procedure reported by Fife et al. [12]. A solution of the corresponding ROH primary alcohol (3 mmol) and pyridine (1 equiv., 0.25 mL) in 3 mL CH_2Cl_2 was added dropwise at 0 °C under vigorous stirring to a solution of triflic anhydride (1.1 equiv., 0.56 mL) in 3 mL CH_2Cl_2 under dry argon and left to react for an additional 45 min at the same temperature. The pyridinium salt by-product was eliminated by filtration-chromatography of the reaction mixture on a short column (diameter 6 mm, length 10 mm) of aluminium oxide (neutral aluminium oxide 90, activity 1, Merck) and dichloromethane was then removed under reduced pressure at room temperature. The crude product was extracted into dry petroleum ether and then filtered to eliminate the last traces of pyridinium triflate. The pure alkyl triflates were recovered by carefully removing the solvent in vacuum at room temperature and stored under argon at −20 °C. Yields: 65–70%. The ^1H NMR spectra ($CDCl_3$) confirmed the purity of the C_3 to C_6 triflates thus prepared and were in good agreement with the literature data [12–14].

2.2.2. Poly(urethaneimide) precursors (PUI/*x*)

The synthesis of the precursors PUI/*x* (i.e. (PTMO1000 $(1-x$ equiv.$)$ + MDEA (x equiv.)/MDI (2 equiv.)/6FDA (1 equiv.))) containing x equiv. ($x = 0.2-0.7$) of MDEA tertiary amine groups was formerly reported [6]. In the present work, the former procedure – which had been initially reported for the synthesis of a few grams of polymers only – was successfully extended to the batch synthesis of 20 g of PUI/0.5 with identical results.

2.2.3. *Poly(urethaneimide)s containing quaternary ammonium groups from alkylating agents RX other than alkyl triflates (PUI/x/RX)*

PUI/*x* (0.6 g) was dissolved under dry atmosphere in 25 mL of the appropriate anhydrous solvent, i.e. DMF in the case of the alkyl halides, chloroform for dimethyl sulfate and methyl *p*-toluenesulfonate. A very large excess (0.2 mL) of the alkylating agent was then added and the mixture was left to react under stirring at 60 °C for 48 h in the case of the alkyl halides or at 20 °C for 48 h and then 60 °C for 4 h when using dimethyl sulfate or methyl *p*-toluenesulfonate. Bromo- and chloromethanes (gaseous at ambient temperature) were introduced as liquids from cooled gas cylinders in the cooled (by liquid nitrogen) PUI/*x* solution in a glass tube which was then inserted into a high-pressure stainless-steel bomb.

After quaternization and cooling to room temperature, the reaction mixture was poured into an excess of dry diethyl ether (250 mL) under vigorous stirring to precipitate the polymer which was filtered, washed twice in diethyl ether, and collected on a PTFE plate to be dried in vacuum at 70 °C for 8 h (chloroform used as solvent) or for 16 h (in the case of DMF).

^{1}H NMR characterization (DMSO-d_6): as expected from their closely related structures, the PUI cationomers PUI/*x*/RX gave close ^{1}H NMR patterns which usually differed by the resonance of the protons of their alkyl side chain or those of their counter-ion.

Typically for PUI/0.5/Me_2SO_4 (δ ppm, 300 MHz, for indexing refer to Fig. 2): 9.66 and 9.50 (f,f′, 2H), 8.15 (k, 2H), 7.94 (j, 2H), 7.74 (i, 2H), 7.5–7.0 (a,b,d,e, 16H), 4.54 (l, 2H), 4.06 (g, 2H), 3.92 (c, 2H), 3.76 (m, 2H), 3.1–3.4 (g′,p, z, 29H), 1.4–1.7 (h,h′, 28H).

In addition to the former peaks characteristic for the macromolecular chain, the following other peaks characterized the alkyl side chain or the counter-ion of the other quaternized PUIs. PUI/0.5/MeOTs: 7.5–7.0 (a,b,d,e, OTs, 18H), 2.28 (CH_3–Ph, 1.5H). PUI/0.5/EtBr: 3.30 (αCH_2, 1H), 1.29 (βCH_3, 1.5H). PUI/0.5/PrBr: 3.32 (αCH_2, 1H), 1.30 (βCH_2, 1H), 0.91 (γCH_3, 1.5H). PUI/0.5/BuBr: 3.35 (αCH_2, 1H), 1.5 (βCH_2, 1H), 1.3 (γCH_2, 1H), 0.91 (δCH_3, 1.5H). PUI/0.5/PentBr: 3.32 (αCH_2, 1H), 1.5 (βCH_2, 1H), 1.27 (γCH_2, 1H), 1.27 (δCH_2, 1H), 0.86 (εCH_3, 1.5H). PUI/0.5/HexBr: 3.30 (αCH_2, 1H), 1.5 (βCH_2, 1H), 1.26 ($\gamma,\delta,\varepsilon$ CH_2, 3H), 0.91 (ωCH_3, 1.5H). The number of protons was reported according to the corresponding polymer stoichiometry. Moreover, the ^{1}H NMR spectra of the PUI cationomers obtained from *n*-alkyl bromides other than methyl bromide also revealed the presence of a new peak at 4.42 ppm, characteristic for a competing elimination, which will be discussed in Section 3.

2.2.4. *Poly(urethaneimide)s containing quaternary ammonium groups from alkyl triflates (PUI/0.5/ROTf)*

PUI/0.5 (0.3 g, 0.21 mmol) was dissolved under dry atmosphere in 6 mL of anhydrous dichloromethane and the mixture was cooled at the temperature *T*. A solution of *q* mmol of alkyl triflate in 6 mL of anhydrous dichloromethane was then added dropwise and the mixture reacted at the same temperature for a time t_1. The reaction mixture was then allowed to slowly rise to room temperature during a time t_2 before the PUI cationomer was precipitated and treated by the same procedure as above. Table 1 gives the best operating conditions *T*, t_1 and t_2, found for each alkyl triflate (C_1–C_6) and the corresponding experimental results. The ^{1}H NMR (DMSO-d_6) spectra showed the same ^{1}H resonances as those observed for the PUI cationomers obtained with *n*-alkyl bromides with the exception of the peak at 4.42 ppm which was not observed (see Section 3).

2.2.5. *Poly(urethaneimide) cationomers containing ammonium ^{+}NH groups only*

A large excess (0.55 mL) of hydrobromic acid (48% Aldrich) was added to a solution of 0.6 g of PUI/0.5 in 25 mL of DMF. The reaction mixture was then stirred at 60 °C for 48 h and the resulting PUI/0.5/HBr recovered as above. ^{1}H NMR (DMSO-d_6): only one resonance (4.42 ppm) was observed in the chemical shift range 4.40–4.60 ppm characteristic for the presence of ammonium ^{+}NH groups.

2.2.6. *Deprotonation of poly(urethaneimide)s containing ammonium ^{+}NH groups*

A large excess of sodium hydrogenocarbonate was added to a solution of 0.6 g of polymer in 25 mL chloroform. After 30 min of stirring at room temperature, the mixture was filtered, cast on a PTFE plate and the solvent removed first at atmospheric pressure, then in vacuum at 60 °C to afford a thin film. ^{1}H NMR (DMSO-d_6) showed the disappearance of the peak at 4.42 ppm.

2.3. *Polymer characterization*

Infra-red spectra were recorded by transmission on a Bruker Tensor 27 FT-IR spectrometer using thin polymeric films cast on KBr disks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.15 MHz and 75.5 MHz, respectively. The chemical shifts were referenced

Table 1
Synthesis of PUI cationomers with different lengths of the alkyl side chain R

Alkyl triflate	q^{a}	T (°C)	$t_1{}^{b}$ (h)	$t_2{}^{c}$ (h)	Quaternization degree (%) (^{1}H NMR)
Methyl triflate	0.23	−20	2	3.5	100
Ethyl triflate	0.23	5	15	3.5	100
n-Propyl triflate	0.53	10	48	1	≈100
n-Butyl triflate	0.53	10	48	1	≈100
n-Pentyl triflate	0.53	10	48	1	95
n-Hexyl triflate	0.53	10	48	1	95

Quaternization with *n*-alkyl triflates CF_3SO_3R of the PUI precursor containing 0.5 equiv. of tertiary amine groups PUI/0.5: PTMO1000 (0.5 equiv.) + MDEA (0.5 equiv.)/MDI (2 equiv.)/6FDA (1 equiv.).
Solvent: dichloromethane.

[a] *q*: Number of mmol of alkyl triflate for 0.21 mmol (0.3 g) of PUI/0.5.
[b] t_1: Reaction time at temperature *T*.
[c] t_2: Time of rise to room temperature.

to TMS and were calculated by using the residual isotopic impurities of the deuterated solvent.

Viscosities were measured at 25 °C for filtered polymer solutions (0.2 μm PTFE membranes, Alltech) using a Schott semi-automatic capillary viscometer.

The film-forming ability was assessed by the following test. Twenty-five milliliters of a polymer solution in chloroform ($C = 2.5\%$ w/v) was prepared, filtered on glass fibers and cast into a PTFE mould (diameter 130 mm). After evaporation of the solvent (2 h) at ambient temperature, the residual chloroform was removed in vacuum (2 h at 20 °C). This procedure was applied to polymers with quaternary ammonium contents up to 0.6 equiv. For higher contents, the polymer had to be dissolved in DMF at ambient temperature and the solution obtained was filtered and cast as above. Most of the DMF was then evaporated in a convection oven at 50 °C for 24 h. The residual DMF was eventually removed under vacuum at 70 °C for 24 h. The thicknesses of the polymer films were ca. 40 μm.

Density measurements were carried out with a helium Micromeritics AccuPyc 1330 gas pycnometer using ca. 300 mg of polymeric film pieces.

Solubility tests were performed with 0.125 g of polymer in 2.5 mL of solvent at ambient temperature and at a higher temperature which depended on the solvent tested.

3. Results and discussion

3.1. Synthesis and characterization of the PUI cationomers PUI/x/RX

A new family of PUI cationomers with great structure variability was obtained by alkylating polymer precursors which had been obtained in a former work [6]. In the present work, the functionalization took place at the tertiary amine groups which had been introduced during the synthesis of the PUI precursors by using *N*-methyldiethanolamine as a comonomer diol. It had been shown in the former work that the introduction of the tertiary amine groups was easily controlled over the whole composition range, leading to new polymer materials with predefined structures. Using the same standard as that commonly found in the polyurethane literature, the structure of the PUI precursors can be described from the name of the starting reagents and the corresponding number of equivalents used for the polymer synthesis: PTMO1000 ($1 - x$ equiv.) + MDEA (x equiv.)/MDI (2 equiv.)/6FDA (1 equiv.). For the sake of simplicity and also because x is the single variable parameter for the PUI precursors, they will be designated by PUI/x in the following.

The quaternization of the PUI precursors using various alkylating agents (RX) gave a wide range of new PUI cationomers (designated as PUI/x/RX) which differed in:

- the number of their cationic groups x,
- the nature of their counter-ions X^-,
- the size of their *n*-alkyl side chain R.

Fig. 1 describes the principle of their synthesis and summarizes the different possibilities which have been explored. Two of the most important issues during this work were to obtain quasi-quantitative alkylation degrees and to guarantee the structural purity of the resulting cationomers. The obtained results clearly depended upon the nature of the alkylating agent and the experimental conditions.

An alternative synthesis scheme which consisted of quaternizing the MDEA monomer before its incorporation in the PUI formulation was also tested but it readily appeared that it did not meet the former requirements. Although the same type of procedure had been already reported for the successful synthesis of simple polyurethane cationomers [15–17], it could not be easily transposed to the synthesis of poly(urethaneimide) cationomers. In the later case, a degradation of ca. 30% of the quaternary ammonium groups was indeed observed by ^{1}H NMR after the thermal curing at 130–140 °C during 15 h which was required to complete the formation of the imide rings [6].

Another advantage of the method described in this work is that it enables to synthesize a wide range of PUI cationomers from the same PUI precursor. Therefore, this method allows comparing the properties of closely related cationomers with those of the PUI precursor with exactly the same macromolecular backbone. This is an important point for the fundamental analysis of structure–permeability relationships as intended in the second part of this research work which will be reported shortly.

3.1.1. PUI cationomers differing in the number of their ammonium groups: PUI/x/$(CH_3)_2SO_4$

PUI cationomers which differed in the number of their ammonium groups were synthesized by quaternizing quantitatively PUI precursors with increasing contents in tertiary amine groups.

To obtain this first family of PUI cationomers, the PUI precursors were alkylated using dimethyl sulfate, known as a very reactive alkylating agent in mild conditions. Another advantage of dimethyl sulfate was that it contained methyl groups which cannot generate the side reactions occurring with several other alkylating agents as it will be discussed thoroughly in a later part of this work.

The reaction was followed by ^{1}H NMR on the final copolymers. Although it has been very scarcely reported for the characterization of polyurethane cationomers [18,19], ^{1}H NMR was highly powerful to characterize the quaternization as shown in Fig. 2 which displays the spectra for the PUI with 0.5 equiv. of MDEA (PUI/0.5) before and after quaternization with dimethyl sulfate.

The quaternization was mainly responsible for three strong shifts of the characteristic resonance bands of protons l, m and p. One of these shifts was particularly useful because it enabled a quantitative assessment of the quaternization degree. This strong shift was related to the methylene protons $O-CH_2-CH_2-N^+$ (protons l) which are both in β to the ammonium groups and in α to the oxygen of the corresponding urethane groups. The corresponding peak was shifted from

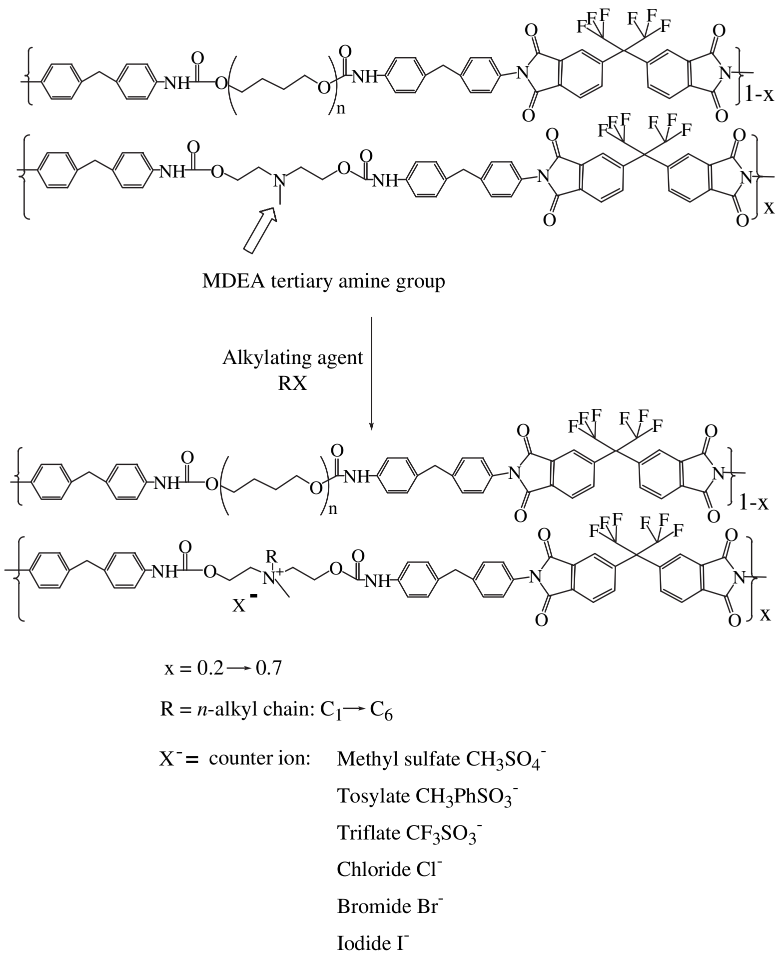

Fig. 1. Global synthesis scheme for the poly(urethaneimide) cationomers varying in the number of their cationic ammonium groups, the length of their alkyl side chain R or the nature of their counter-ions X^-.

4.1 ppm to 4.54 ppm in a spectral range free of other peaks. Another important shift was related to the methyl groups (protons p) on the nitrogen atom of the amine and ammonium groups. Varying from 2.25 ppm to 3.2 ppm, it was very characteristic for the disappearing of the tertiary amine groups provided the polymer solution in DMSO-d_6 be concentrated enough.

The quaternization of the PUI precursors with increasing tertiary amine contents was carried out in a solvent of medium polarity ($CHCl_3$) at a temperature less than 60 °C. The results (Table 2) show that, even in these mild conditions, the quaternization degrees ($\geq 95\%$) were in the very high range, given the uncertainty of the NMR technique for the quantitative analysis of polymeric materials, and they did not significantly depend upon the polymer tertiary amine content. This investigation was carried out for tertiary amine contents up to 0.7. For higher contents, the corresponding precursors PUI/*x* led to brittle films [6]. This drawback could only worsen after quaternization, which was incompatible with the intended use of the cationomers.

The full assignment of the ^1H NMR spectra of the PUI cationomers PUI/*x*/Me_2SO_4 was in good agreement with the expected macromolecular structures (Section 2 and Fig. 2). A detailed analysis by $^1H/^{13}C$ HSQC 2D NMR for PUI/0.5/Me_2SO_4 taken as way of example improved the identification of the different resonances. First, the two-dimensional spectrum confirmed the position of the different protons of the polymer backbone by simple comparison with that of the PUI precursor [6]. Moreover, it also enabled to identify precisely the protons of the counter-ion (proton z, $\delta = 3.4$ ppm) which could not be easily assigned with the simple ^1H NMR spectrum owing to an overlapping with the signal corresponding to the protons g′ of the PTMO soft block.

The ^{13}C NMR spectrum in the region of the carbonyl groups (Fig. 3) shows a broad splitting of the urethane carbonyls because one-half of these carbonyl groups is under the influence of the ammonium groups which is responsible for an upfield shift of 1 ppm. Moreover, the position of the doublet peak characteristic for the imide carbonyl groups (dissymmetric to the fluorinated junction) remains unchanged and there is no other peak appearing or disappearing in this spectral region which proves the integrity of the imide rings during the quaternization reaction. Moreover, a comparison of the ^{13}C NMR spectra of the PUI copolymers before and after quaternization confirms that the methylation occurs at the tertiary amine sites only, and that it does not affect the PUI chemical structure in any other way.

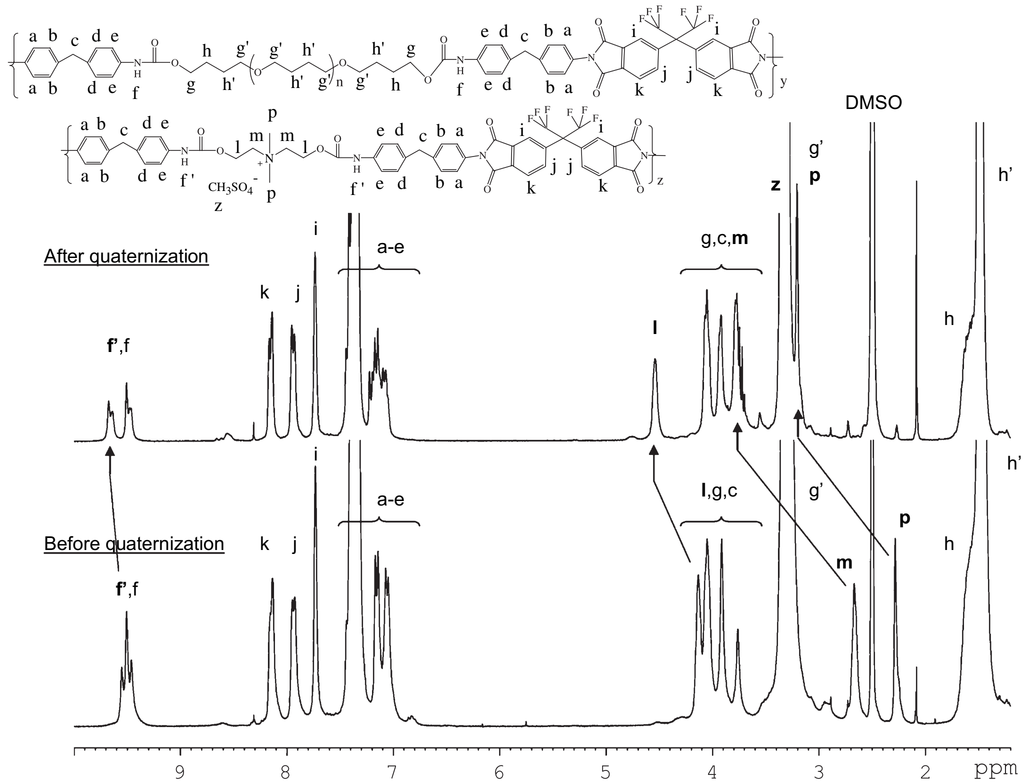

Fig. 2. ^{1}H NMR characterization of the PUI block copolymers. Example of the copolymer containing 0.5 equiv. of MDEA before and after quaternization with dimethyl sulfate (DMSO-d_6; 300 MHz).

3.1.2. PUI cationomers differing in their counter-ions: PUI/0.5/CH_3X

The main purpose was then to introduce counter-ions with different sizes and electronic densities of the negative charge, which would thus be more or less associated in the ion pairs with the ammonium cations.

An important consequence for the targeted application would be a change in polymer/solvent interactions, responsible for a difference in polymer swelling and permeability towards solvents, in the same way as what has been already reported for polymers containing carboxylate or sulfonate salts with different counter-cations [20–23].

The ease, as described above, with which the polymers PUI/*x* had been quaternized with dimethyl sulfate, offered interesting prospects for the quaternization of these polymers with other (in particular less reactive) methylating agents CH_3X, which would provide a very convenient way of introducing different types of counter-ions X^- on the PUI backbone.

Table 2
Synthesis of PUI cationomers with different contents in cationic ammonium groups

MDEA content *x*		Quaternization degree (%) (^{1}H NMR)
Theor.	Exptl. (^{1}H NMR)	
0	0	–
0.2	0.24	95
0.4	0.42	95
0.5	0.48	96
0.6	0.58	95
0.7	0.71	96

Quaternization with dimethyl sulfate of a series of PUI precursors with various contents *x* in tertiary amine groups PUI/*x*: PTMO1000 (1 − *x* equiv.) + MDEA (*x* equiv.)/MDI (2 equiv.)/6FDA (1 equiv.).

The investigation was carried out with a reference PUI precursor (i.e. PUI/0.5 corresponding to the middle of the PUI composition range) and a series of classical methylating agents (Table 3).

Although it is well known that the reactivity of methylating agents CH_3X towards the same nucleophile strongly depends upon the nature of the leaving group X^- [24], the quaternization degrees were very high in all cases. In particular, the quaternization was almost quantitative even in the mild operating conditions described in Section 2.

Nevertheless, unlike the other methylating agents which were used at moderate temperatures, methyl triflate had to be used at a much lower temperature (−20 °C) owing to its much stronger reactivity. The quaternization with this particularly powerful alkylating agent was quantitative.

A few complementary experiments (not reported in Table 3) also showed that the reaction solvent had a great importance on the reaction and enabled to better distinguish the differences in reactivity. Therefore, the methyl halides did not react or reacted incompletely in chloroform (solvent of medium polarity) and their reaction required a highly polar solvent like *N*,*N*-dimethylformamide to ensure the completion of the reaction within an acceptable period of time (ca. 48 h).

However, dimethyl sulfate reacted readily in chloroform in the same conditions but the conversion was limited to 80%.

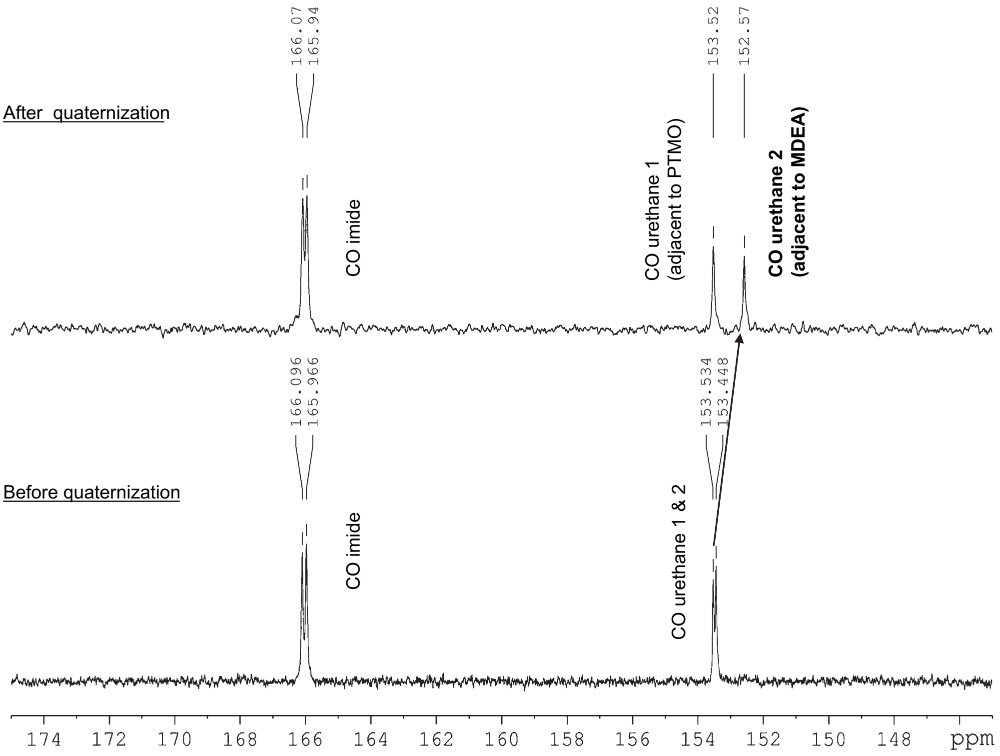

Fig. 3. ^{13}C NMR characterization of the PUI cationomers: analysis of the chemical structure of the hard blocks. Example of the copolymer containing 0.5 equiv. of MDEA quaternized with dimethyl sulfate (DMSO-d_6; 75.5 MHz).

To achieve the completion of the reaction with dimethyl sulfate, the temperature had eventually to be increased to 60 °C. The optimized operating conditions for each alkylating agent are described in Section 2.

The chemical structure of each polymer of this new family of PUI cationomers PUI/*x*/MeX was checked by ^1H NMR. As expected, their spectra were quasi-identical except for the resonances of the protons of the counter-anion if any. The full assignment of the different spectra is reported in Section 2.

3.1.3. PUI cationomers differing in the size of the n-alkyl side chain

The size of the *n*-alkyl side chain on the nitrogen atom of the quaternary ammonium groups is likely to have an influence on the morphology of the polymer materials and their properties: e.g. solubility, swelling, density, free volume, hard block polarity, permeability, etc. Therefore, by keeping in mind one of the key requirements to get a controlled and well-defined macromolecular structure, the synthesis of PUI cationomers PUI/*x*/RX with alkyl groups R of increasing size was also another interesting challenge.

Table 3
Synthesis of PUI cationomers with different counter-ions X^-

Counter-ion X^-		Quaternization degree (%) (^1H NMR)
Methyl sulfate	$CH_3SO_4^-$	96
Tosylate	$CH_3PhSO_3^-$	93
Triflate	$CF_3SO_3^-$	100
Chloride	Cl^-	99
Bromide	Br^-	93
Iodide	I^-	98

Quaternization with different methylating agents CH_3X of a PUI precursor containing 0.5 equiv. of tertiary amine groups PUI/0.5: PTMO1000 (0.5 equiv.) + MDEA (0.5 equiv.)/MDI (2 equiv.)/6FDA (1 equiv.).

Therefore, the reference PUI precursor PUI/0.5, chosen for the same reason as previously, was quaternized with alkylating agents with linear alkyl chains R of increasing length ($C_1 \rightarrow C_6$), with reactivity being known to depend upon the length of their alkyl chain [25].

Although very good results had been obtained with dimethyl sulfate, it was not possible to keep using dialkyl sulfates for this part of the work because the species with longer alkyl chains (except diethyl sulfate) are not commercially available and are difficult to synthesize and even more to purify.

In contrast, the 1-halogeno-*n*-alkanes are readily available with a good purity. The iodo derivatives were avoided despite their high reactivity because the anions I^- of the quaternary ammonium groups can be readily oxidized with release of iodine, which is detrimental to the intended use of these cationomers.

The first attempts were thus carried out with 1-bromo-*n*-alkanes in *N*,*N*-dimethylformamide to give the PUI cationomers PUI/0.5/RBr (Table 4). From the integration of the resonances in the spectral range 4.4–4.6 ppm which are characteristic for the protons $-O-CH_2-CH_2-N^+$, a very good global degree of modification was observed ($\geq$90%) [10].

However, a closer examination of the ^1H NMR spectra in this spectral range showed that these resonances were now constituted of two peaks (Fig. 4). The first peak 1 at 4.54 ppm corresponded to the formation of the expected quaternary

Table 4
Synthesis of PUI cationomers with different lengths of the alkyl side chain R

Alkylating agent	$^+$NR/$^+$NH Mol. ratio (^{1}H NMR)	Total degree of modification (%) (^{1}H NMR)	Quaternization degree (%) (^{1}H NMR)
Bromomethane	∞	93	93
Bromoethane	1.22	99	54
1-Bromo-*n*-propane	0.41	94	27
1-Bromo-*n*-butane	0.28	88	19
1-Bromo-*n*-pentane	0.25	89	18
1-Bromo-*n*-hexane	0.41	88	25

Quaternization with *n*-alkyl bromides RBr of a PUI precursor containing 0.5 equiv. of tertiary amine groups PUI/0.5: PTMO1000 (0.5 equiv.) + MDEA (0.5 equiv.)/MDI (2 equiv.)/6FDA (1 equiv.).

ammonium groups while the other one l′ at 4.42 ppm revealed the presence of another type of ammonium cation as clearly shown in Fig. 4c which was obtained for the PUI cationomer with the longest alkyl side chain (PUI/0.5/HexBr). This second peak appeared as soon as the alkyl chain had two carbon atoms and sharply increased in intensity for three and more carbon atoms.

It was fairly logical to ascribe the appearing of this new peak to the protonation of the tertiary amine sites of the precursor PUI/0.5, corresponding to the formation of non-quaternary ammonium groups with a slightly less shielded position for the corresponding protons in β. This protonation would be the consequence of an elimination competing with the expected nucleophilic substitution. Nevertheless, this competing reaction unexpectedly became particularly important for the mild experimental conditions used in this work.

To check the validity of this assumption, the precursor PUI/0.5 was fully protonated by reaction with HBr to give a ^{1}H NMR spectrum with a single peak at 4.42 ppm in the spectral range from 4.4 ppm to 4.6 ppm, therefore confirming its assignment to the protons in β to the protonated amine sites $^+$NH (Fig. 4d). A new peak which would be characteristic for the proton of the group $^+$NH was not observed in the ^{1}H NMR spectrum of this new cationomer. The corresponding region was already fairly complex and the new peak was most likely overlapped by the other proton signals. Nevertheless, the ^{1}H NMR spectrum of this PUI cationomer did not show any degradation of the macromolecular backbone after reaction with HBr and the appearing of two doublets for the protons of the urethane groups at 9.5 ppm and 9.67 ppm was another confirmation for the proper functionalization of the tertiary amine groups by HBr.

Inversely, when the cationomer PUI/0.5/HexBr (70% of protonated sites) was treated by a base like sodium hydrogenocarbonate, the peak at 4.42 ppm disappeared while the peaks m and p characteristic for the tertiary amine sites reappeared at the same locations as those before quaternization (Fig. 4e).

Therefore, for all the 1-bromo-*n*-alkanes except methyl bromide, the quaternization was limited by a competing elimination responsible for the appearance of protonated amine sites and a partial loss of control on the final polymer structure. This competing elimination even became preponderant for alkylating agents with more than two carbon atoms (Fig. 5).

At that stage of investigation, complementary experiments also showed that other solvents than *N*,*N*-dimethylformamide

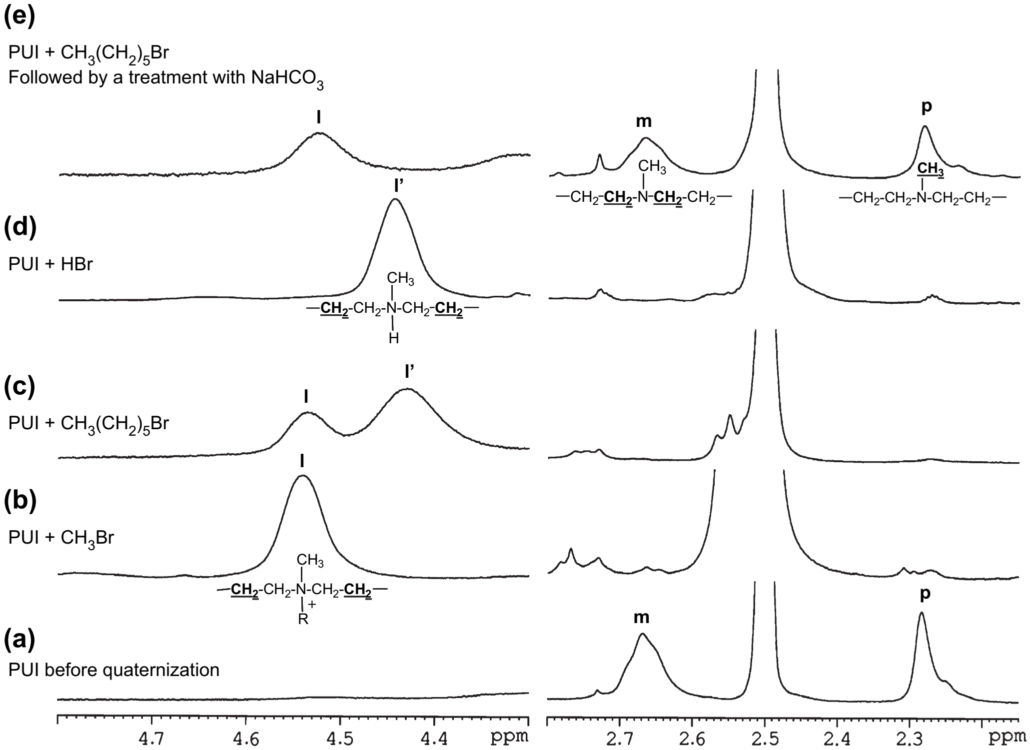

Fig. 4. ^{1}H NMR characterization of the PUI cationomers obtained by quaternization of the copolymer containing 0.5 equiv. of MDEA with *n*-alkyl bromides RBr (DMSO-d_6; 300 MHz).

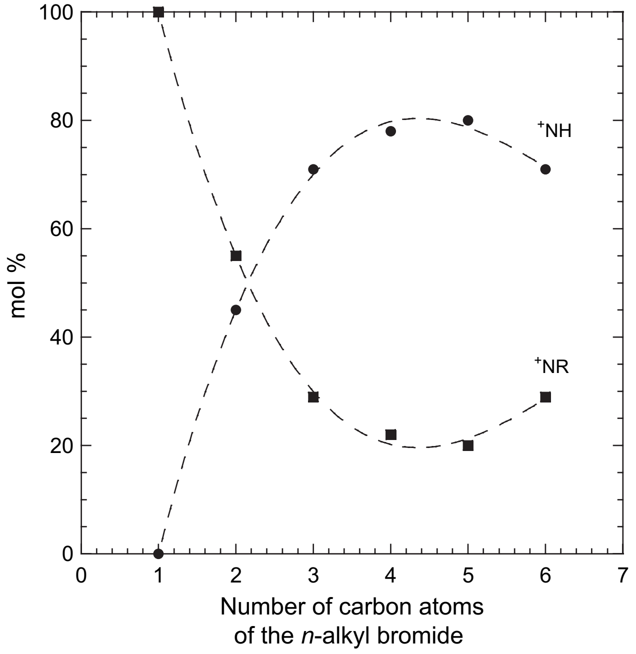

Fig. 5. Influence of the length of the alkyl group R on the repartition of the two cationic species observed during the quaternization of the copolymer containing 0.5 equiv. of MDEA with *n*-alkyl bromides RBr.

either did not give any reaction (for less polar solvents like chloroform) or accentuated the competing elimination (e.g. dimethyl sulfoxide).

In order to control the macromolecular structure of the targeted cationomers, the use of much more powerful alkylating agents was thus indispensable. Indeed, the very high reactivity of esters like alkyl trifluoromethanesulfonates (alkyl triflates ROTf) [26,27] usually enables to operate at much lower temperatures in slightly polar solvents, i.e. in conditions which should strongly limit the competing elimination.

Except for the first two terms of the series (i.e. methyl and ethyl triflates), alkyl triflates are not commercially available. Therefore, we carried out the synthesis of alkyl triflates with linear alkyl chains in C_3–C_6 from the reaction of the corresponding primary alcohols with triflic anhydride (Fig. 6). By adapting the procedure of Fife and co-workers [12], pure products were isolated in moderate yields (ca. 70%) and could be stored at −20 °C without degradation.

The reaction of the six different alkyl triflates thus available was then carried out with the reference precursor PUI/0.5 in particularly mild conditions (cf. Section 2) and gave very high degrees of modification. The quaternization degrees were quasi-quantitative, without any presence of protonated amine sites $^+$NH (Table 1).

Moreover, a detailed analysis by ^{1}H NMR (spectral range corresponding to the terminal CH_3 groups of the alkyl side chains) and by two-dimensional ^{1}H/^{1}H COSY 2D NMR also showed the absence of any isomerization of the side alkyl chains (Fig. 7).

Therefore, using *n*-alkyl triflates gave the new family of PUI cationomers PUI/0.5/ROTf with alkyl side chains of increasing size ($C_1 \rightarrow C_6$) and a particularly good control of the polymer structure.

3.2. Properties of the PUI cationomers PUI/x/RX

3.2.1. Properties in solution

All the PUI cationomers were readily soluble in strong dipolar aprotic solvents (e.g. DMF, NMP, etc.). Similarly as what had been observed for their PUI precursors [6], they were also generally well soluble in common organic solvents (e.g. $CHCl_3$, THF, etc.) in which most aromatic rigid polyimides are insoluble. This good solubility in a wide range of organic solvents was observed up to a critical content in cationic groups of 0.6 equiv. For higher contents in cationic groups, the hard blocks represented more than 76 wt% and the solubility decreased significantly.

However, the PUI cationomers were systematically less soluble than the corresponding PUI precursors. This observation is in very good agreement with those formerly reported by Dieterich et al. for polyurethane cationomers [28,29] and is usually ascribed to the increased physical cross-linking in presence of the cationic groups.

While simple polyurethanes usually display a linear decrease in viscosity when the polymer concentration decreases, which corresponds to the usual Huggins viscosity law, cationomer polyurethanes show a different behavior in polar organic solvents [30–32]. Their viscosity usually sharply increases when the polymer concentration decreases in dilute solutions. This particular behavior is typical for polyelectrolytes and corresponds to an expansion due to the repulsion of the cationic groups in this concentration range [33]. This repulsion effect can be strongly reduced or even suppressed by adding an electrolyte like LiBr which is capable of screening the cationic charges. If the electrolyte concentration is high enough, a normal viscometry behavior can even be obtained for polyurethane cationomers in polar organic solvents [15,30].

Fig. 8 compares the reduced viscosity of the PUI copolymer containing 0.5 equiv. of MDEA before and after quaternization

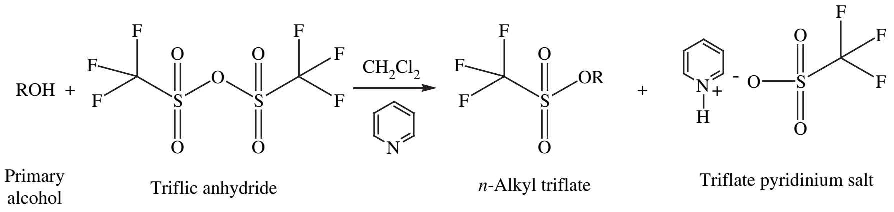

Fig. 6. Synthesis scheme for *n*-alkyl triflates.

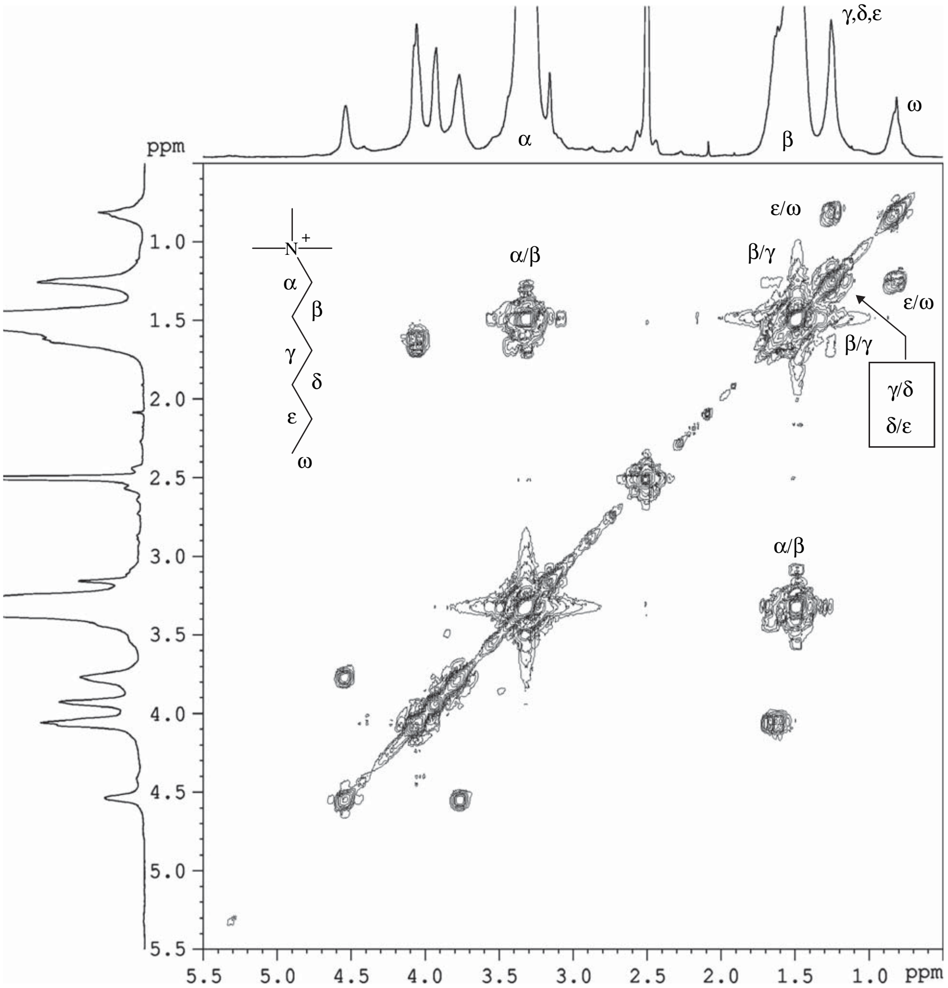

Fig. 7. Two-dimensional $^1H/^1H$ COSY NMR characterization of the PUI cationomer obtained by quaternization of the copolymer containing 0.5 equiv. of MDEA with *n*-hexyl triflate (DMSO-d_6; 300 MHz). Zoom showing the absence of isomerization of the C_6-alkyl side chain.

with methyl tosylate. The viscosity measurements were carried at different polymer concentrations in pure DMF, in DMF containing 2% w/v of LiCl and in chloroform.

While the PUI precursor shows a very low linear variation of the reduced viscosity as a function of polymer concentration in pure DMF, the corresponding PUI cationomer displays a behavior close to that formerly reported for polyurethane cationomers. Its reduced viscosity increases when the polymer concentration, and thus the ionic force, decreases in the dilute domain. This particular effect characterizes a polyelectrolyte behavior which, nevertheless, remains fairly mild in these conditions as shown by the corresponding almost straight line of Fig. 8.

Fig. 8 also shows that this polyelectrolyte effect can be simply suppressed by adding 2% w/v of LiCl in DMF, which enables an efficient screening of the cationic charges, leading to reduced viscosity values very close to those obtained for the PUI copolymer before quaternization.

In chloroform, which is far less polar than DMF and thus far less solvating, the reduced viscosity values are much lower than those found in DMF and there is almost no difference between the PUI copolymers before and after quaternization with methyl tosylate.

3.2.2. Properties in the solid state

Although polyurethane cationomers contain a very small amount of cationic charges, it is well known that their properties in the solid state are strongly influenced by their presence. The cationic groups usually form ionic aggregates through coulombic interactions and also strongly reinforce hydrogen bonding. Both effects increase the phase separation and the cohesion of the polyurethane rigid blocks, leading to a strong improvement in the material properties.

In this work, the focus was made on investigating key properties for the targeted membrane applications of the PUI cationomers, i.e. film-forming ability and material density.

The films were prepared from polymer solutions in chloroform, except for the cationomer PUI/0.7/$(CH_3)_2SO_4$ – insoluble in this solvent – which had thus to be dissolved in DMF. All the PUI cationomers displayed an excellent film-forming ability and the resulting films were strong enough to withstand the operating conditions required by the targeted membrane separation applications.

An attempt was also made to characterize tiniest morphological changes by analyzing the density of the different PUI

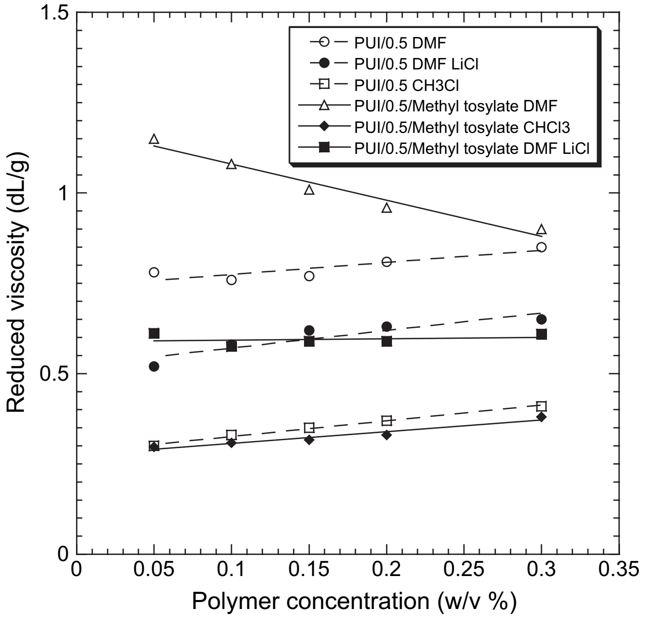

Fig. 8. Influence of concentration on the reduced viscosity for the copolymer containing 0.5 equiv. of MDEA before and after quaternization with methyl tosylate. Viscosity measured in pure DMF, in DMF containing 2% w/v of LiCl and in chloroform.

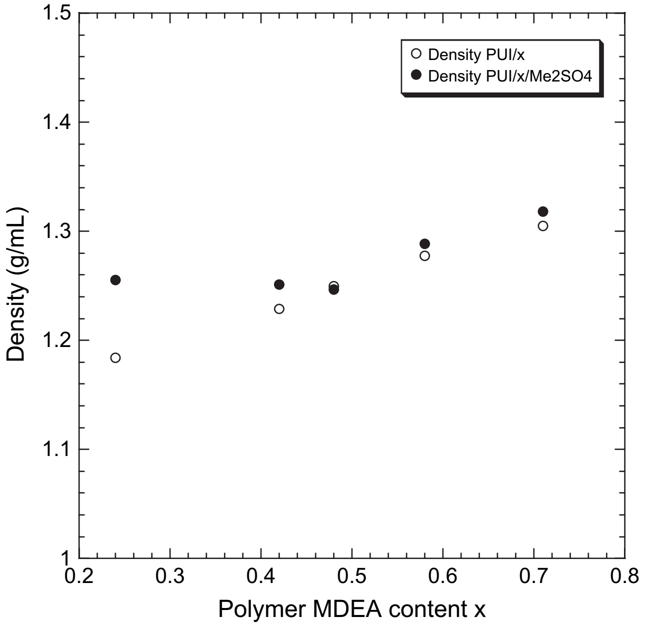

Fig. 9. Comparison of the density of PUI copolymers with different tertiary amine contents x before (○) and after quaternization (●) with dimethyl sulfate.

cationomers, which has an influence on the polymer free volume and permeability.

Whatever the structural parameter investigated (i.e. number of the cationic groups x, the nature of the counter-ions X^- or the length of the alkyl side chain R), the density of the PUI cationomers was systematically slightly higher than that of their PUI precursors, which can be related to the reinforced physical cross-linking of these new materials.

For the PUI cationomers which differed in the number of their cationic groups (First Family: PUI/0.5/$(CH_3)_2SO_4$), the density increased linearly with the cationic group content for contents of at least 0.5 equiv., following a trend fairly similar to that observed for the corresponding PUI precursors (Fig. 9). However, for lower cationic group contents ($x < 0.5$ equiv.), the variation of the cationomer density was more complex. In particular, a sharp increase in the density was observed for the cationomer containing 0.2 equiv. of cationic sites compared to that of the corresponding precursor. This result was easily reproduced with polymers obtained from several batches but the explanation for its origin is not known yet.

Another interesting trend was found for the PUI cationomers with different halide counter-ions X^-, which were obtained by quaternizing the same PUI precursor (PUI/0.5) with different methyl halides CH_3X. Fig. 10 indeed shows that the density of these cationomers varied almost linearly with the molecular weight of the counter-ion X^-. Therefore, it seems that, for these particular cationomers, the density was much more controlled by the counter-ion molecular weight rather than by its molecular volume or cross-linking power which both vary in opposite ways: Cl^-, Br^-, and I^-. Nevertheless, the trend appeared more complex for the molecular counter-ions (i.e. sulfate, tosylate and triflate) and no particular relationship could be found between the density (varying between 1.24 g/mL and 1.28 g/mL) and the molecular weight of these counter-ions (Table 5).

For the last family of PUI cationomers which differ in the length of their n-alkyl side chains, the cationomer density was systematically slightly higher than that of the corresponding precursor but it was almost constant irrespective of the alkyl side chain length (Table 5). This result was quite unexpected because it showed that the cationomer density did not significantly depend on the steric hindrance of the cationic groups.

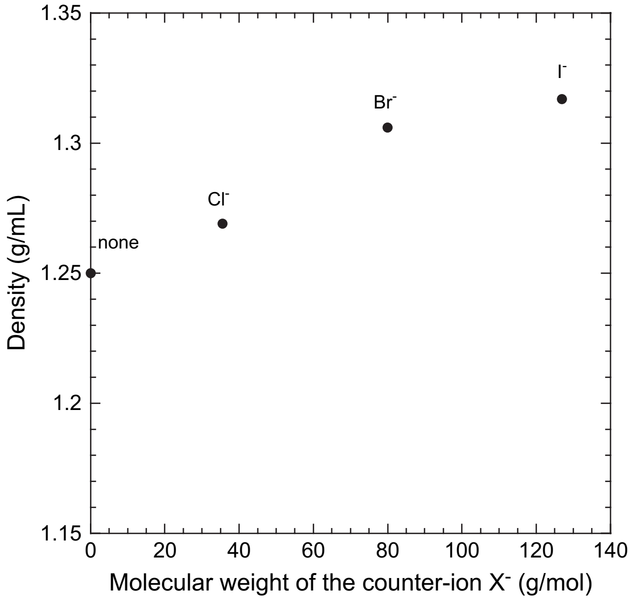

Fig. 10. Influence of the halide counter-ion X^- on the density of the PUI cationomers PUI/0.5/CH_3X.

Table 5
Density of the PUI cationomers varying in the nature of their counter-ion X^- or in the length of their alkyl side chain R

	Density (g/mL)
PUI cationomers with different counter-ions X^- and a methyl alkyl side chain	
None[a]	1.250
Methyl sulfate	1.247
Tosylate	1.260
Triflate	1.279
Chloride	1.269
Bromide	1.306
Iodide	1.317
PUI with different lengths of the alkyl side chain R and a triflate counter-ion	
None[a]	1.250
Methyl	1.279
Ethyl	1.272
n-Propyl	1.263
n-Butyl	1.272
n-Pentyl	1.269
n-Hexyl	1.267

[a] PUI before quaternization: PUI/0.5: PTMO1000 (0.5 equiv.) + MDEA (0.5 equiv.)/MDI (2 equiv.)/6FDA (1 equiv.).

4. Conclusion

Three new families of PUI cationomers were obtained by quaternizing PUI precursors containing controlled amounts of tertiary amine groups. Different alkylating agents were used in relatively soft conditions which avoided degrading the initial macromolecular backbone while still leading to particularly high quaternization degrees. The resulting copolymers differed in the number of their cationic groups ($0 < x \leq 0.7$ equiv.), the type of their counter-ions (methyl sulfate, tosylate, triflate, chloride, bromide, iodide) and the length of their *n*-alkyl side chain (C_1–C_6). A detailed analysis showed that particularly powerful alkylating agents (*n*-alkyl triflates) were required for the synthesis of the copolymers of the latter family to avoid a competing elimination reaction which occurred with less reactive ones (*n*-alkyl bromides).

The influence of the number of the cationic groups, the type of the counter-ions or the length of the *n*-alkyl side chain was then investigated for properties relevant to the intended use of these cationomers as separation membranes. In particular, the density of the PUI cationomers was systematically slightly higher than that of the corresponding precursors. The density increased with the number of the cationic groups for $x \geq 0.5$ equiv. and also with the molecular weight of the counter-ion for halide counter-ions. Nevertheless, the length of the *n*-alkyl side chain had no influence on the PUI cationomer density for *n*-alkyl chains in C_1–C_6. Last but not least, all the PUI cationomers were very good film-forming materials capable of withstanding the operating conditions of the targeted pervaporation membrane separation process.

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