New Film-Forming Polyurethaneimide Cationomers Containing Quaternary Ammonium Groups

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Introduction. Ion-containing polymers have been widely investigated for the selective transport of ions by membrane separation systems with a great range of industrial applications like electrodialysis[1] and, more recently, the highly challenging fuel cells.[2,3] However, so far, very little has been done to analyze in a systematic way the selective permeability of ion-containing polymers toward mixtures of organic solvents.

Two international patents[4,5] and also more recent results[6,7] obtained in our laboratory have shown that polymeric membranes containing quaternary ammonium groups are highly efficient to extract organic protic species (e.g., alcohols) from their mixtures with aprotic compounds (e.g., alkanes, ethers, and esters) with high potential applications for the petrochemical industry.[8] However, the rather poor control of the chemical structure of the former copolymers did not allow any detailed analysis about the influence of the cationic sites on their permeability.

To open the way for the first thorough analysis of the influence of cationic sites on the selective permeability of polymeric materials toward purely organic mixtures, we have recently undertaken a systematic investigation based on the synthesis of new polyurethaneimide block copolymers containing quaternary ammonium groups.

Certain of our previous works[9−11] have indeed shown that several polyurethaneimides combine an excellent filmogen character with a good compromise permeability/selectivity for the separation of protic/aprotic organic mixtures in general and the purification of ethyl *tert*-butyl ether (i.e., a fuel octane enhancer used instead of lead derivatives in the European Community) in particular. Incorporating quaternary ammonium groups into polyurethaneimide block copolymers should enable a further improvement in their selective permeability by reinforcing the specific interactions between the polymeric membranes and the protic species to be separated.

Moreover, the great structure versatility of PUI block copolymers[9−22] is another key advantage for a fundamental analysis of the cation influence. As already pointed out for nonionic block copolymers,[23] this characteristic feature should greatly facilitate the understanding of polymer permeability in terms of structure−property relationships.

Polyurethane cationomers have been investigated to a much less extent than polyurethane anionomers, and this trend gets even sharper for ion-containing polyurethaneimide block copolymers.

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To the best of our knowledge, there has been so far only one scientific paper dealing with the synthesis of polyurethaneimide block copolymers containing quaternary ammonium groups.[24] Unlike this single reference, which described their synthesis in four successive steps, we propose an original synthesis scheme of PUI cationomers in three steps only. Avoiding handling poly(amic acid) intermediates of the common route,[24] the new synthesis scheme takes advantage of the reaction of a diisocyanate with a dianhydride which gives the straightforward formation of imide rings after evolving of carbon dioxide.[25,26]

In addition to providing a great structure variability of the ion-containing block copolymers, the new synthesis scheme enabled to diminish the number of steps and to control the number and nature of their cationic sites as shown by the preliminary results described thereafter.

Experimental Section. a. Materials. The poly(tetramethylene oxide diol) (PTMO1000, Merck) was used as received. 4,4′-Methylenebis(phenyl isocyanate) (MDI, TCI) was distilled under vacuum and stored at −20 °C. *N*,*N*-Methyldiethanolamine (MDEA, Aldrich) was distilled fractionally under vacuum and stored over 4A molecular sieves. 4,4′-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA, Lancaster) was sublimed twice. *N*,*N*-Dimethylformamide (DMF, pure for synthesis, SDS) was distilled fractionally over CaH_2 under reduced pressure and stored over 4A molecular sieves. To prevent contamination by atmospheric moisture, all the former reagents and solvents were stored under dry argon. The alkylating agents (1-bromo-*n*-alkanes) were purchased from Aldrich and used as received.

b. Synthesis of the PUI Cationomer Precursors. The synthesis of the PUI cationomer precursors is described for a total number of moles of the diols MDEA (x equiv) and PTMO1000 ($1 - x$ equiv) of 2.5 mmol. By varying the proportion of both diols, one obtained a family of PUI block copolymers with different MDEA contents, MDEA being the precursor of the quaternary ammonium groups.

In a first step, 2.5 mmol (1 equiv) of the diols were dissolved in 5 mL of dry DMF with constant stirring at 20 °C under dry argon. After 30 min of reaction with 5 mmol (2 equiv) of MDI, the reaction mixture was diluted with 15 mL of dry DMF and kept under vigorous stirring for another period of 30 min at 20 °C. At this stage, the FTIR analysis showed the disappearance of the OH band at about 3500 cm^{-1}, which confirmed the completion of the first synthesis step.

In a second step, the macrodiisocyanates were chain-extended by reaction with 2.5 mmol of 6FDA (1 equiv) at 60 °C for 6 h. The reaction mixture was then heated to 80 °C for a polymerization time which depended upon the polymer MDEA content. During this stage, a rather strong evolving of CO_2 was observed, reflecting the formation of the imide rings.[25,26] The FTIR analysis confirmed the completion of the reaction with the disappearance of the very characteristic isocyanate band[27] at 2250 cm^{-1}.

The polymer was then precipitated in water, washed twice in cold water, and dried under vacuum at 70 °C. It was eventually cured thermally under vacuum to

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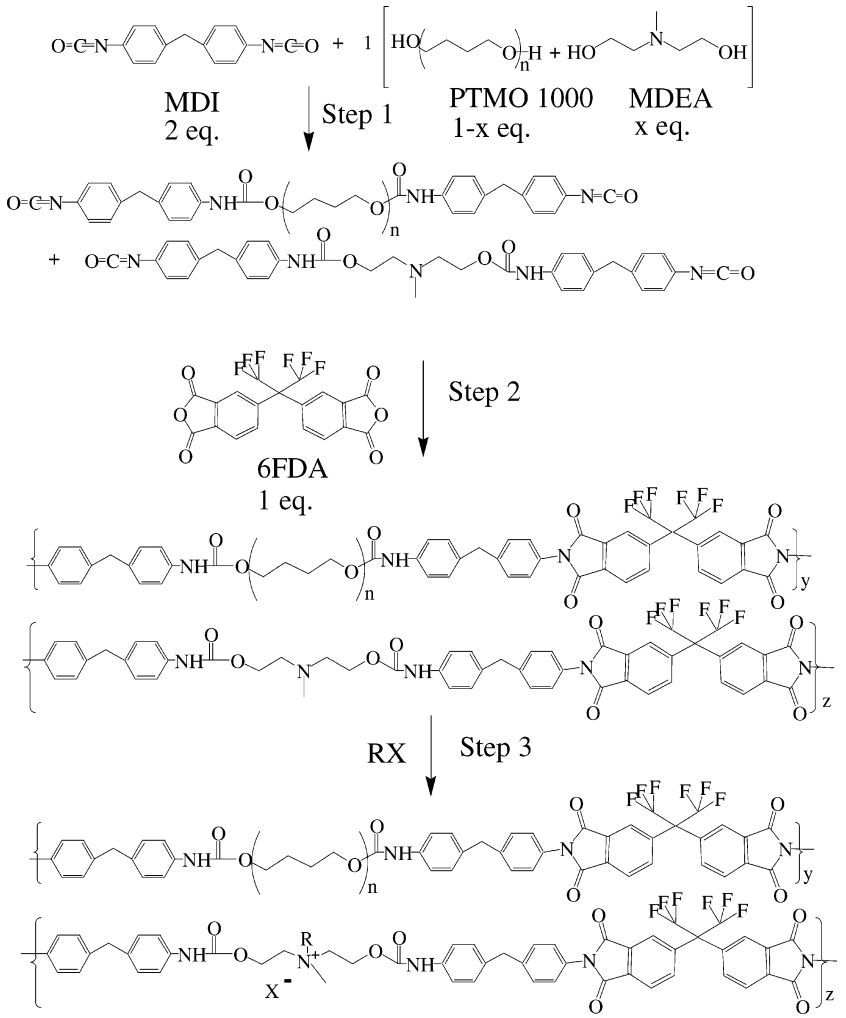

Figure 1. A new synthesis scheme for polyurethaneimide block copolymers containing quaternary ammonium groups.

ensure the complete cyclization of the imide rings, which could have been opened during the precipitation step (130−150 °C, depending on the polymer MDEA content, for 15 h). The PUI cationomer precursors were obtained as slightly yellow polymers in high yields (>90%). The polymer stoichiometry, and in particular the MDEA content, were determined by ^{1}H NMR.

c. Synthesis of the PUI Cationomers. The PUI cationomers were obtained by reacting the former block copolymers with 1-bromo-*n*-alkanes with different alkyl chain lengths ($C_1 \rightarrow C_5$). 0.6 g of the PUI cationomer precursor and ca. 0.2 mL (i.e., a very large excess) of quaternizing agent were dissolved in 25 mL of dry DMF in a glass tube inserted in a stainless steel bomb. The reaction was carried out at 60 °C for 48 h. The polymer films were recovered by solvent evaporation on a Teflon plate, dried under vacuum at 70 °C, and washed twice with diethyl ether before final vacuum-drying.

d. Polymer Characterization. Infrared spectra were recorded by transmission on a Brüker IFS 25 FTIR spectrometer using polymeric films obtained on KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Brüker Avance 300 spectrometer using polymer solutions in DMSO-d_6 and TMS as internal reference. Reduced viscosities were measured for filtered polymer solutions (C = 0.1% w/v) in anhydrous DMF at 25 °C using a Schott semiautomatic capillary viscometer.

Results and Discussion. In the synthesis described formerly,[24] macrodiamine urethane oligomers were obtained in two steps and then reacted with an aromatic dianhydride following the most common route for polyimide synthesis. The resulting poly(amic acid)s were thermally cyclized to give PUI precursors containing tertiary amine groups to complete the third step. In a fourth step, the tertiary amine groups were quatermized using different quaternizing agents. The new synthesis scheme in three steps (Figure 1) proposes macrodiisocyanate urethane oligomers, obtained in a single step, be used for the synthesis of the PUI precursors. They were then reacted with an aromatic dianhydride to provide polyimide precursors in a straightforward way which avoided handling poly(amic acid) intermediates. The PUI cationomers were eventually obtained by quaternization with different alkylating agents.

Five original poly(ether urethaneimide) cationomers were obtained from this new synthesis scheme (Figure 1).

In the first step, 1 equiv of a mixture of a poly(ether macrodiol) (PTMO1000) and a shorter diol containing a tertiary amine (MDEA—the precursor of the cationic groups) was reacted with 2 equiv of an aromatic diisocyanate (MDI) to lead to a mixture of macrodiisocyanates.

The second step consisted of chain extending with 1 equiv of an aromatic fluorinated dianhydride (6FDA). Still rather uncommon for polyimide synthesis despite the first work of Meyers[25] in 1969, the reaction of isocyanates with anhydride groups gives imide rings

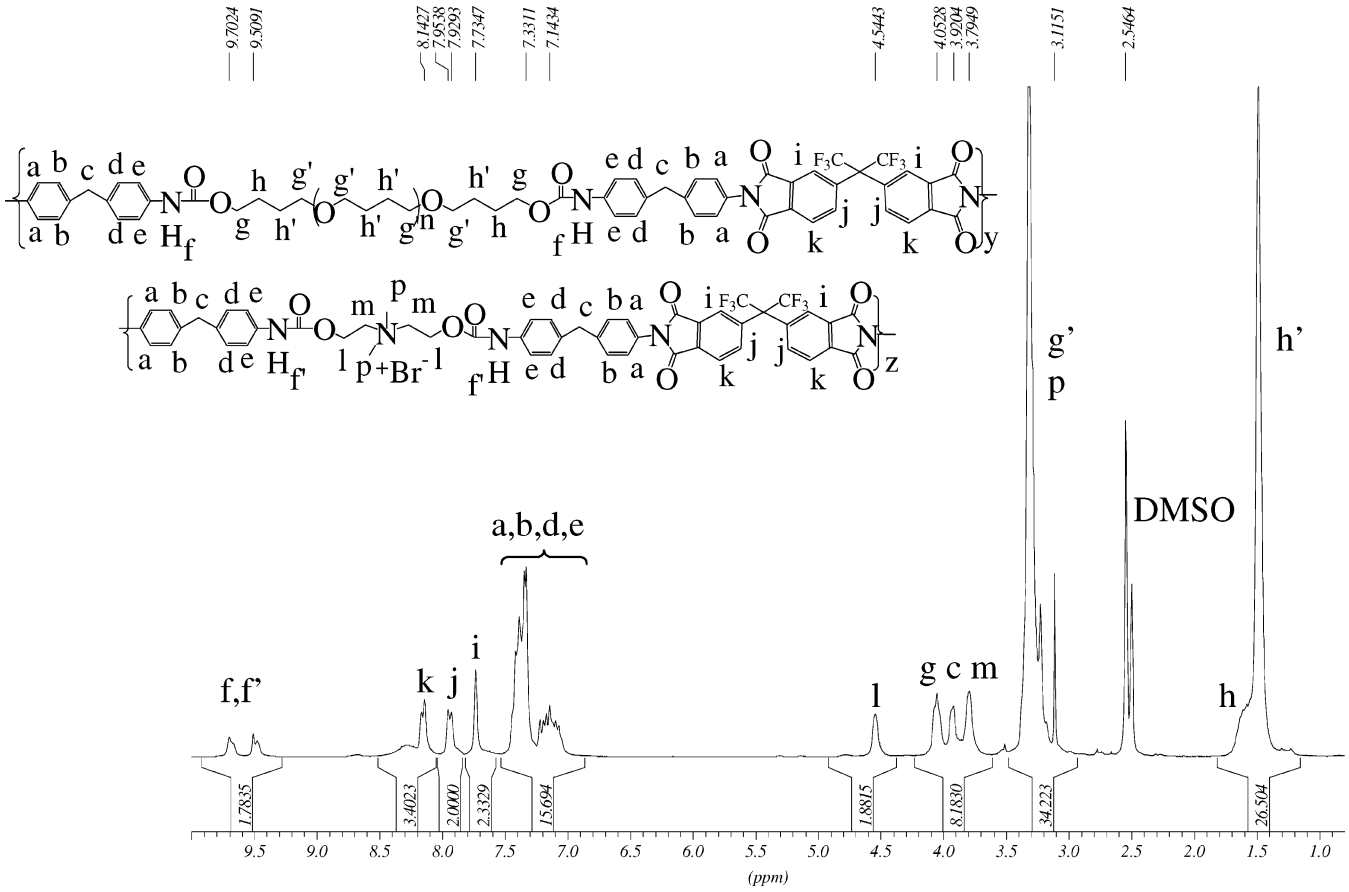

Figure 2. ^{1}H NMR characterization of the PUI cationomers. Example of an ion-containing polyurethanemide obtained by quaternizing a precursor containing 0.5 equiv of MDEA with bromomethane.

Table 1. Block Copolymer Precursors of PUI Cationomers: PTMO1000 (1 − *x* equiv) + MDEA (*x* equiv)/MDI (2 equiv)/6FDA (1 equiv)

MDEA content *x*		stoichiometry MDI/6FDA	yield	η^a
theor	exptl (^{1}H NMR)	exptl value (^{1}H NMR)	(wt %)	(dL/g)
0	0	2.06	96	0.91
0.2	0.24	2.04	93	1.08
0.4	0.42	2.06	94	1.13
0.5	0.48	2.06	94	0.95
0.6	0.58	2.06	93	0.86
0.7	0.71	2.06	92	0.83
0.8	0.81	2.10	92	0.46
1	0.96	2.12	96	0.36

[a] Reduced viscosity measured in anhydrous DMF ($C_{polymer}$ = 0.1% w/v) at 25 °C.

with evolving of carbon dioxide.[25,26] This reaction has the merit of enabling to combine easily the chemistry of polyurethanes with that of polyimides to lead to polyurethaneimides with a great structure variability.

Table 1 describes the results obtained for the synthesis of a family of poly(ether urethaneimide)s PTMO1000 (1 − *x* equiv) + MDEA (*x* equiv)/MDI/6FDA with different MDEA contents. The new polyurethaneimides were obtained in high yields (Y > 90%) and with high viscosities (η > 0.8 dL/g) for MDEA contents less than 0.8. Above this critical MDEA content, the much harder polyurethaneimides had much lower viscosities (−50%).

Moreover, proton nuclear magnetic resonance showed a very good control of the polymer stoichiometry with errors usually close to that of the NMR technique (Table 1). In particular, the polymer MDEA content was easily varied over the whole composition range (x: 0 → 1) (Table 1).

Table 2. New Polyurethaneimide Cationomers Containing Ammonium Groups: PTMO1000 (0.5 equiv) + MDEA (0.5 equiv)/MDI (2 equiv)/6FDA (1 equiv) Quaternized with Different 1-Bromo-*n*-alkanes

alkylating agent	quaternization degree (^{1}H NMR)	η^a (dL/g)
none	0	0.95
bromomethane	93	0.49
bromoethane	99	0.61
1-bromo-*n*-propane	94	0.68
1-bromo-*n*-butane	88	1.18
1-bromo-*n*-pentane	89	0.98

[a] Reduced viscosity measured in anhydrous DMF ($C_{polymer}$ = 0.1% w/v) at 25 °C.

Table 2 describes the results obtained for the quaternization (*third step*, Figure 1) of the PUI with a MDEA content of 0.5, polymer in the middle of the composition range chosen for these preliminary experiments. The alkylating agents were 1-bromo-*n*-alkanes which varied in the length of their alkyl chain ($C_1 \rightarrow C_5$). A systematic analysis by ^{1}H NMR confirmed the chemical structure of the polyurethaneimide cationomers (Figure 2). ^{1}H NMR also enabled to estimate the polymer quaternization degrees which were in the high range (typically about 90%). The viscosities obtained after the quaternization of the same polymer with different 1-bromo-*n*-alkanes were found to depend strongly upon the quaternizing agent, ranging from about 0.5 dL/g to about 1.2 dL/g.

Conclusion. A new synthesis scheme was proposed for the synthesis of original PUI block copolymer cationomers. In its principle, this synthesis scheme allows a great structure variability. Preliminary results con-

firmed a good control of the polymer structure and its content in the cationic site precursors over all the composition range. High quaternization degrees were obtained for different alkyl bromides with increasing alkyl chain length. All of these polyurethaneimide cationomers exhibited a very good film-forming character. This particular feature has recently opened the way for permeability investigations in progress.

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