Macromolecules

Volume 28, Number 21 October 9, 1995

Segmented Poly(tetramethylene oxide) Zwitterionomers and Their Homologous Ionenes. 1. Synthesis, Molecular Characterization, and Thermal Stability

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Received April 11, 1995; Revised Manuscript Received August 3, 1995[⊗]

ABSTRACT: The synthesis of segmented poly(tetramethylene oxide) (PTMO) zwitterionomers and their homologous ionenes was achieved through a multistep strategy involving (i) polyaddition of living bifunctional monodisperse PTMO chains (THF/$(CF_3SO_2)_2O$/20 °C, $M_n^O \sim (2-7) \times 10^3$) over diamines $(CH_3)_2N(CH_2)_xN(CH_3)_2$ ($x = 2, 3, 6$) or α,ω-dimethylamino-PTMO to yield segmented PTMO ionenes with fairly high degrees of chain extension ($N_w^i \sim 20-170$), (ii) quantitative exchange of the triflate anion on the ionene by propanesulfonate ($CH_3(CH_2)_2SO_3^-$) and ethoxydicyanoethenolate ($C_2H_5OCOC^-(CN)_2$) anions, (iii) quasi-quantitative and selective demethylation of the original ionene ($LiEt_3BH$ in THF at 50 °C, demethylation selectivity $s = 0.97 \pm 0.01$) to yield tertiary amino segmented PTMO with only weak chain degradation, and (iv) quantitative functionalization of the tertiary amino polymeric precursor into the zwitterionomers of the ammonioalkanesulfonate ($N^+(CH_2)_pSO_3^-$, $p = 3, 4$) or (ammonioalkoxy)dicyanoethenolate ($N^+(CH_2)_pOCOC^-(CN)_2$, $p = 2, 3$) type. For all the functionalized polymers, weight loss under nitrogen does not occur below 200 °C, and the thermal stability of the zwitterionic structure at 130 °C over long periods (24 h) is well ascertained. Because of the good control of their structural parameters, these tailor-made segmented PTMO should allow a comprehensive analysis of the typical microphase separation of the hard dipolar units within the soft PTMO matrix as a function of their structure (dipole moment, bulkiness, comparison between zwitterions and ion pairs) and of their density along the chain.

Introduction

Statistical amorphous zwitterionomers associating in their chain apolar or weakly polar A units with low to moderate amounts (molar fraction ~ 0.04−0.35) of highly dipolar zwitterionic B units show a very typical two-phase morphology characterized by the dispersion of zwitterion-rich and "hard" microdomains in a nearly pure A "soft" matrix. The statistical copolymers *n*-butyl acrylate/3-[dimethyl-(2-methacrylamidopropyl)ammonio]-propanesulfonate (functional side groups $N^+(CH_2)_3SO_3^-$, $\mu = 24$ D) studied in our laboratory probably display at the highest level all the most salient structural features and properties of biphasic zwitterionomers such as (i) the presence of two well-defined glass transitions identified by differential scanning calorimetry (DSC) and supported by the analysis of chain dynamics through ^1H broad-line nuclear magnetic resonance spectroscopy (NMR),[1] (ii) the presence of the so-called "ionic peak" in the small-angle X-ray scattering patterns (SAXS)[1] (corresponding Bragg spacings in the range 4−7 nm), (iii) the presence of very rigid and thermally stable aggregates where spin diffusion occurs over a distance of about 10−20 Å, as observed by ^{13}C dipolar-decoupled magic-angle spinning NMR spectroscopy (^{13}C CP/DD/MAS NMR),[2] (iv) the enhanced dynamic mechanical properties characterized by two dispersion regions and an intermediate strongly extended rubbery plateau of increased pseudoequilibrium modulus,[3] and (v) finally, the possibility of preferential plasticization of the soft matrix (*n*-butyl phthalate) and of selective plasticization of the hard domains (water, ethylammonium nitrate).[4]

More recent work on analogous statistical *n*-butyl acrylate/2,2-dicyano-1-[(dimethyl(2-(acryloyloxy)ethyl)-ammonio)ethoxy]ethenolate (functional side groups $N^+(CH_2)_2OCOC^-(CN)_2$, $\mu = 25.9$ D) essentially leads to similar conclusions.[5]

The close analogy with the well-known ionomers[6−9] is quite evident, and their recent structural model proposed by Eisenberg et al.[10] may be directly transposed to these zwitterionomers. Strong dipolar interactions between the zwitterionic units[11] within the very mobile and weakly polar $(A)_n$ matrix lead to their primary aggregation in "multiplets". The overlap of

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1995.

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regions of restricted mobility anchored to the multiplets, which occurs progressively as the zwitterion content of the material increases, results in the emergence of rigid "clusters" of sufficient size (~100 Å) to show their own glass transition. Structural features typical of ionomers were also derived in an elegant way from those observed in multiblock copolymers in the "superstrong segregation regime" and extrapolated to the limiting case of only one polar unit per polar block.[12]

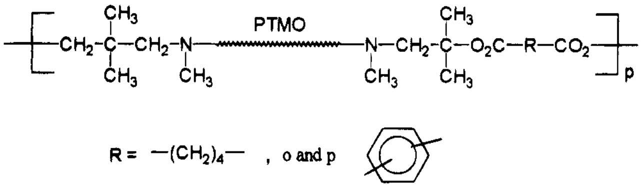
Up to now, long-range order has never been observed in these zwitterionomers (one single peak in the SAXS patterns), and the dipolar multiplets dispersed within the apolar matrix are usually assumed to display only liquid-like order.[1,5,13-15] Disconnecting the ionic sites from the chain backbone through a long enough spacer may induce some weak order in ionomers,[16] but the most noticeable exception however is that of statistical polysiloxane zwitterionomers bearing bis(ammoniopropanesulfonate) side groups,[17] where a lamellar morphology was well ascertained through SAXS measurements and transmission electron microscopy.[18] In most cases, the statistical distribution of the comonomers along the chain, which arises from the free-radical copolymerization process involved in their synthesis,[19,20] is very likely the major reason for the lack of a well-defined organization in these copolymers. A regular distribution of the strongly interacting units should result in their more quantitative segregation from the matrix and a possibly weaker aggregation number of the multiplets[12] and, most interestingly, in an increased order in the bulk material. This last trend is actually observed in some segmented poly(tetramethylene oxide)[21] or poly(propylene oxide) ionomers[22] (cubic or body-centered cubic lattice of spherical multiplets in the latter case) and in segmented poly(tetramethylene oxide) ionenes (cylindrical hexagonally packed array of multiplets[23] or lamellar arrangement of disklike multiplets[24]).

The purpose of this series of papers is the comprehensive study of microphase separation and of the development of a potential long-range order in linear segmented zwitterionomers. Poly(tetramethylene oxide) (PTMO) displays a number of advantages as a weakly polar soft segment ($T_g \sim -86$ °C) since its chemistry should allow the synthesis of tailor-made segmented polymers (see further) and since its low melting point ($T_m \sim 43$ °C) compensates the drawback of its crystallinity. Moreover, comparison with homologous PTMO ionomers[21] and ionenes[23,24] already described in the literature should be of interest. The influences of three main structural parameters of the segmented PTMO have to be considered: (i) for a given zwitterionic structure, the zwitterion density along the chain, (ii) for a given PTMO block length, the structure (dipole moment, bulkiness) of the zwitterionic moiety, and (iii) finally, the substitution of the zwitterions by the homologous ion-pair structures with identical chemical architecture of the charged sites (ionenes versus zwitterionomers).

The first part of this series of papers is thus devoted to the synthesis, the molecular characterization, and the thermal stability of tailor-made PTMO zwitterionomers and ionenes. They must not be confused with the much studied and more complex zwitterionic polyurethanes,[25-30] where phase separation occurs in many cases before zwitterionic functionalization of the hard segments.

Results and Discussion

Overview of the Synthetic Strategy. PTMO segmented polymers characterized by a regular alternation of monodisperse PTMO blocks and short tertiary amino segments and by *the lack of any bond able to self-associate through hydrogen bonding (amide, urethane, etc.) between these two chain constituents* clearly appear as very versatile precursors toward the target polymers: the selective and quantitative functionalization of the tertiary amino segments should afford a series of homologous zwitterionomers[15] showing broadly varying values of their local dipole moment.[31] To the best of our knowledge, chain extension of bifunctional living PTMO previously end-capped with azetidinium ions by sodium dicarboxylates is the only example of such a synthesis (see structural formula below), but the efficiency of this process remains unknown.[32]



Some exploratory experiments toward similar PTMO precursors were thus performed according to the following two lines:

(i) Polyesterification between α,ω-dihydroxy telechelic PTMO ($M_n^o = 2 \times 10^3$) and N-methyliminodiacetic acid or ethylenediaminetetraacetic dianhydride: only rather low degrees of polycondensation were obtained ($N_w^i <$ 8) and the optimization of the process did not appear straightforward.[33] Moreover, the necessary quantitative methylation (diazomethane) of the carboxylic acid groups resulting from the anhydride ring opening complicates the process.

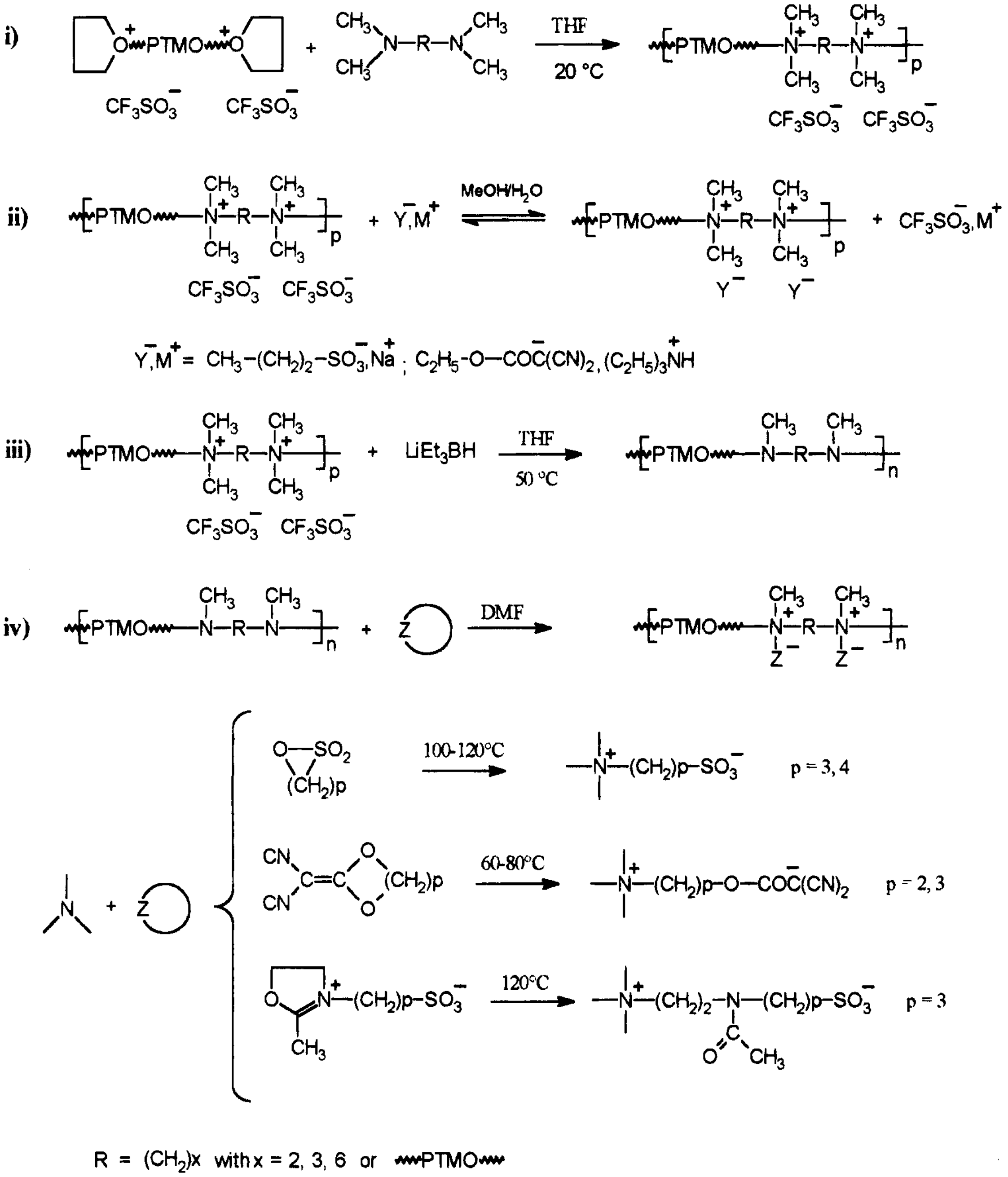
(ii) Polycondensation of bifunctional living PTMO (see further) on a secondary diamine such as piperazine, as suggested by the work of Richards et al.:[34] this also failed to yield well-defined linear segmented polymers because of competitive branching through quaternization of the new and more nucleophilic tertiary amino function in the short segment by living PTMO.[35]

The following strategy, outlined in Scheme 1, was thus adopted for the whole work: (i) synthesis of segmented PTMO ionenes through polyaddition of bifunctional living PTMO over α,ω-tertiary diamines or α,ω-diamino telechelic PTMO; (ii) quantitative exchange of the triflate anions on the initial ionenes to yield directly the target ionenes; (iii) selective and quantitative demethylation of the initial ionenes into the tertiary amino segmented PTMO; (iv) selective and quantitative functionalization of the tertiary amino PTMO into the target zwitterionomers.

These four different steps will be discussed successively. In all the following text, the upper indexes o, i, and a will refer to the initial PTMO segment, the ionene, and the amino segmented PTMO, respectively.

Synthesis of the Segmented PTMO Ionenes. The cationic bulk polymerization of tetrahydrofuran (THF) between −10 and +20 °C initiated by trifluoromethanesulfonic anhydride (TFA) essentially occurs according to a quasi-living process provided that the ratio [monomer]/[initiator] remains higher than 100 and the conversion lower than about 20%.[36-38] Moreover, chain extension of the bifunctional living PTMO chains by α,ω-tertiary diamines affords a very direct and efficient

Scheme 1



pathway toward segmented PTMO ionenes,[24,39,40] since quaternization of tertiary amines of high basicity and low steric hindrance by PTMO oxonium end groups is a very fast, selective, and quantitative process.[35] This already classical strategy was thus adopted because of its easiness (no byproduct in the initiation step) and its versatility (potential structural variations in the diamine short segment). All the polymerizations were carried out in bulk at 20 °C in the presence of a constant initiator concentration of 2.46×10^{-2} mol·L^{-1} ([THF]/[TFA] = 500). Conversion and molecular weights were directly monitored through the reaction times (see Experimental Section), and a series of samples of number-average molecular weight M_n^0 in the range $(2-7) \times 10^3$ (end group titration on the corresponding α,ω-dihydroxy chain) characterized by polydispersity indexes $M_w/M_n < 1.15$ was thus easily obtained. Polyaddition of living bifunctional PTMO chains over *N,N,N',N'*-tetramethyl-α,ω-diaminoalkanes ($(CH_3)_2N(CH_2)_xN(CH_3)_2$, $x = 2, 3, 6$) or α,ω-dimethylamino telechelic PTMO was performed at room temperature with a stoichiometric ratio [diamine]/[TFA] = 1 (see Experimental Section). The resulting ionenes were characterized by three complementary methods:

(i) ^{1}H-NMR spectroscopy: the dimethyammonium groups are identified as a well-defined singlet at 3.1 ppm in CDCl$_3$ solution, as shown in Figure 1.

(ii) Determination of the nitrogen content from elemental analysis and comparison with the corresponding theoretical value calculated from the M_n^0 value of the PTMO segment assuming a high degree of polyaddition. The observed differences are always lower than 5%: see, for instance, for a short segment $x = 3$, % $N_{exp} = 1.32$ versus % $N_{calc} = 1.29$ for $M_n^0 = 1.75 \times 10^3$ and for a short segment $x = 6$, % $N_{exp} = 0.40$ versus % $N_{calc} = 0.39$ for $M_n^0 = 6.67 \times 10^3$. This good agreement confirms that the quaternization reaction is very fast with respect to the propagation step of the THF polymerization and that the chain growth within the very

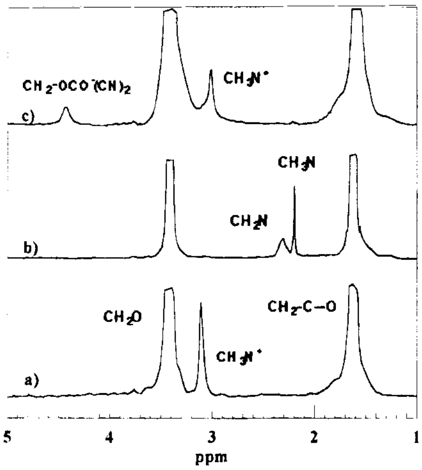


Figure 1. ^{1}H-NMR spectra at room temperature of three related segmented PTMO ($M_n^O = 2 \times 10^3$, $x = 6$): (a) initial ionene ($CF_3SO_3^-$ as counterion) in $CDCl_3$ solution; (b) tertiary amino chain in $CDCl_3$ solution; (c) zwitterionomer of the ethoxydicyanoethenolate type in $CDCl_3$–TFE (9:1 by volume) solution.

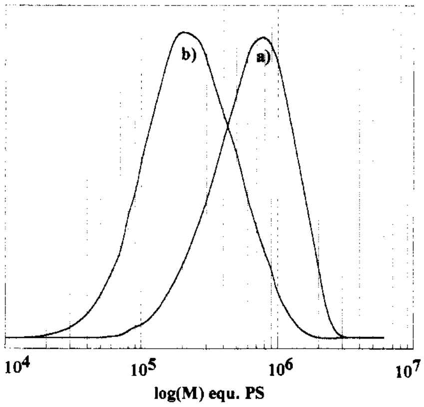


Figure 2. SEC chromatograms of segmented PTMO (DMAC–0.01 M $Bu_4N^+Br^-$ solution): (a) initial ionene ($M_n^O = 6.7 \times 10^3$, $x = 6$, $M_w^i = 1.3 \times 10^6$ from light scattering, $M_w/M_n = 1.7$); (b) PTMO zwitterionomer of the ethoxydicyanoethenolate type derived from the previous ionene ($M_w = 2.63 \times 10^5$ from $[\eta]$ measurements, $M_w/M_n = 2.0$).

short time between the PTHF withdrawal for M_n^O determination and the diamine addition is quite negligible (see Experimental Section).

(iii) Molecular weight measurements: Size exclusion chromatography (SEC) measurements in dimethylacetamide (DMAC)/0.1 M $Bu_4N^+Br^-$ solution at 25 °C essentially show unimodal distribution curves, without any residual peak corresponding to the PTMO precursor; see Figure 2. Apparent M_w^i values are in the range $(0.7–8) \times 10^5$ according to polystyrene calibration and polydispersity indexes N_w^i/M_n^i between 1.8 and 2.3, as compared with the theoretical value of 2 for infinite chain extension of monodisperse bifunctional prepolymers. Absolute molecular weight determination by light scattering implies a good solvent with high enough refractive index increment for these polyelectrolytes. To the best of our knowledge, the only measurements on analogous PTMO ionenes were performed in chloroform solution where ion aggregation may likely bias the M_w values, as recognized by the authors themselves.[42] Two protic mediums allowing a good solvation of the *whole* ionene chain were thus selected: methanol/0.05 M $Et_4N^+CF_3SO_3^-$ for ionenes with low molecular weight PTMO segment ($M_n^O < 5 \times 10^3$) and ethyl acetate–2-propanol (9:1 by volume)/same salt for the other ones (quasi-isorefractive solvent pair in the latter case: n_D^{20}(EtOAc) = 1.372, n_D^{20}(*i*PrOH) = 1.377). The Zimm plot of the sample derived from the PTMO precursor of the highest molecular weight ($M_n^O = 6.67 \times 10^3$, $x = 6$), given in Figure 3, is typical of an aggregate-free solution.

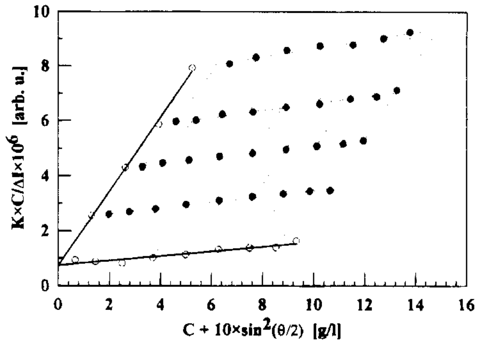


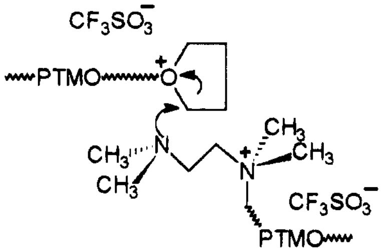
Figure 3. Zimm plot of the initial PTMO ionene (see GPC, Figure 2) in solution in EtOAc–*i*PrOH (9:1 by volume) ($M_w^i = 1.3 \times 10^6$, $(S_z^2)^{0.5} = 650$ Å, $A_2 = 6.8 \times 10^{-4}$ mol·g^{-2}·mL).

Table 1. Chain Extension of Bifunctional Living PTMO by *N,N,N′,N′*-Tetramethyl-α,ω-diaminoalkanes $(CH_3)_2N(CH_2)_xN(CH_3)_2$ in THF at 20 °C

PTMO precursor $M_n^O \times 10^{-3}$	x	N_w^i	M_w^i/M_n^i
2.20	6	27	2.4
1.92	6	30	
2.00	6	75[a]	
1.75	3	21	
2.10	2	10	
2.00	2	8	
1.91	*b*	23	
3.63	6	32	2.5
3.66	6	80[a]	
3.48	2	18	
5.19	6	54	2.0
6.70	6	169	1.7

[a] Reaction performed on 800 mL of THF (400 mL in all the other cases). [b] Chain extension of a bifunctional living PTMO ($M_n^O = 1.91 \times 10^3$) by a telechelic α,ω-dimethylamino PTMO ($M_n^O = 1.97 \times 10^3$, functionality $f > 1.90$).

The weight-average degrees of chain extension N_w^i, defined as M_w^i/M_w^O taking into account the molecular weight of the short segment, are given in Table 1. In all the systems under study, polyaddition occurs in solutions characterized by a constant concentration of reactive sites of 4.92 mol·L^{-1}, whatever the length of the PTMO precursor and the structure of the diamine. The N_w^i values should thus be identical provided that deviations from stoichiometry are negligible and that the extent of reaction is the same in all cases. Sometimes, but not systematically, scaling up the reaction device by a factor of 2 (800 instead of 400 mL of THF) results in higher N_w^i: this merely reflects that deviations from the reagent stoichiometry cannot be completely avoided (see the experimental procedure) and may be minimized on larger volumes. The observed variations of the N_w^i values should thus be considered very cautiously, but some apparent trends are worth discussing even if they are not definitely ascertained. For a given diamine such as *N,N,N′,N′*-tetramethyl-1,6-hexanediamine (TMHDA), N_w^i appears significantly higher for the PTMO precursors of the highest molecular weight. This trend cannot be unambiguously ascribed to physical factors such as the very sharp viscosity increase of the reaction medium arising from the strong association of the ammonium triflate ion pairs in the poorly solvating THF solvent (see Experimental Section). For a constant ion-pair concentration, gelification of the solution is actually observed for the longer PTMO segments ($M_n^O > 5 \times 10^3$): higher polymer concentration and longer ionene chains of lower charge density. For a PTMO segment of constant molecular weight, N_w^i significantly decreases in the case of the shortest diamine, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), suggesting lower extent of the reaction. This may be tentatively ascribed more likely to steric hindrance effects rather than to unfavorable electrostatic interactions between the oxonium end group of the PTMO chain and the ammonium group *β* to the reaction site: see scheme below.



Chain extension of bifunctional living PTMO by TMEDA has already been claimed in the literature, but without any mention of the corresponding N_w^i values.[35]

Finally, the synthesis of the segmented ionene with a single ammonium ion pair between the PTMO segments rests upon the polyaddition of a bifunctional living PTMO over a bifunctional α,ω-dimethylamino-PTMO precursor previously prepared by end-capping of the corresponding living PTMO by a large excess of dimethylamine[34,40,41] (see Experimental Section). Analogous coupling reaction of the corresponding monofunctional living PTMO has already been described.[34] In spite of a more tricky experimental procedure (the two reactant species are telechelic polymers), the degree of chain extension is fairly similar to that obtained with TMHDA.

Ion Exchange on the PTMO Ionenes. The anion exchange on the original ionenes (triflate as counterion) proceeds through an equilibrium between the swollen but insoluble polymer (see Experimental Section) and the salt solution (8:1 (by volume) water–methanol) as outlined below:

$$\mathrm{P\overset{+}{N},CF_3SO_3^-} + \mathrm{\overset{-}{Y}\overset{+}{M}} \overset{K}{\rightleftharpoons} \mathrm{P\overset{+}{N},Y^-} + \mathrm{CF_3SO_3^-,M^+}$$

$$\text{with } \mathrm{\overset{-}{Y}\overset{+}{M}} = \mathrm{CH_3{-}(CH_2)_2{-}SO_3^-,Na^+};$$
$$\mathrm{C_2H_5{-}O{-}CO{-}\overset{-}{C}(CN)_2,(C_2H_5)_3\overset{+}{N}H}$$

The extent of ion exchange is directly measured on the recovered polymer by quantitative titration of the residual triflate anions through ^{19}F-NMR spectroscopy ($CDCl_3$ solution, singlet at −1.6 ppm with respect to 2,2,2-trifluoroethanol (TFE) taken as reference and internal standard), and it is further checked by UV spectroscopy in the case of dicyanoethenolate anions ($\epsilon = 16.1 \times 10^3$ L·mol^{-1}·cm^{-1} at $\lambda = 235$ nm for (triethylammonioethoxy)dicyanoethenolate in TFE solution). The apparent equilibrium constants of these ion exchanges (which do not occur in homogeneous solution) are easily derived from the fraction of exchanged ion α and from the ratio $[Y^-]/[CF_3SO_3^-] = r$, according to

Table 2. Ion Exchange on the Segmented PTMO Ionene: $M_n^O = 1.92 \times 10^3$, $x = 6$, $N_w^i = 30$

Y^-,M^+		*r*	α	*K*
$CH_3(CH_2)_2SO_3^-,Na^+$	first cycle	10	0.67	0.15
	second cycle[a]	25	0.76	0.10
$C_2H_5OCO\overset{-}{C}(CN)_2,(C_2H_5)_3\overset{+}{N}H$		0.9	0.65	4.8
	first cycle	1.5	0.80	4.6
		10	0.99	*b*

[a] Overall exchange of 0.92 after the two successive cycles. [b] The α value is too close to 1 to allow calculation of a reliable *K* value.

$$K = \alpha^2/(1 - \alpha)(r - \alpha) \qquad (1)$$

The typical *K* values (*K* = 1 when there is no preferential interaction between some of the various ionic species in the medium) given in Table 2 allow one to rank the various anions by increasing affinity toward the hydrophobic PTMO polycation according to

$$CH_3(CH_2)_2SO_3^- < CF_3SO_3^- < C_2H_5OCOC^-(CN)_2$$

This order is obviously that expected from their chemical structure, but the difference between the *K* values related to the most hydrophilic and the most hydrophobic anions measured by a factor of about 50 is worth stressing. In any case, quantitative exchange of the original triflate counterions may be easily performed through successive cycles.

Demethylation of the PTMO Segmented Ionenes. The synthesis of linear poly(tertiary amines) by demethylation of classical ionenes has already been performed using ethanolamine (150 °C, 4–5 h) or lithium propanethiolate in hexamethylphosphoric triamide (90 °C, 5–6 days) as reagents: quasi-quantitative demethylation was actually obtained, but rather strong main-chain scission (1–3 times per chain) could not be avoided in these drastic experimental conditions.[43] According to the literature,[44] lithium triethylborohydride ($LiEt_3BH$) in THF solution is a smooth and very selective demethylation reagent of quaternary ammonium salts, and it was thus selected as a potentially better reagent. The demethylation extent was controlled on the recovered polymers by (i) ^{1}H-NMR spectroscopy in $CDCl_3$ solution (progressive decrease of the dimethylammonium ($N^+(CH_3)_2$) singlet at 3.1 ppm and simultaneous increase of the NCH_3 singlet at 2.2 ppm and of the NCH_2 unresolved broad peak at 2.3 ppm (see Figure 1)), (ii) ^{19}F-NMR spectroscopy in $CDCl_3$ solution (titration of the residual triflate anion as previously described), and (iii) selective acid–base potentiometric titration of the free tertiary amino groups (see Experimental Section).

In the selected experimental conditions ($[LiEt_3BH]/[N^+] = 2$, $t = 50$ °C), preliminary kinetic experiments on a given ionene ($M_n^O = 5.2 \times 10^3$, $x = 6$, $N_w^i = 54$) have shown that the demethylation yield is about 90% in 1 h and higher than 95% for a reaction time of 4 h. All the reactions were thus performed for 5 h and quantitative demethylation was systematically obtained whatever the initial ionene. Molecular weights of the resulting polymers were derived from intrinsic viscosity measurements according to[45]

$$[\eta]\ (\mathrm{dL{\cdot}g^{-1}}) = 4.22 \times 10^{-4} M_w^{0.65} \quad \text{for PTMO in ethyl acetate at 30 °C} \qquad (2)$$

The assumption of identical hydrodynamic behavior of

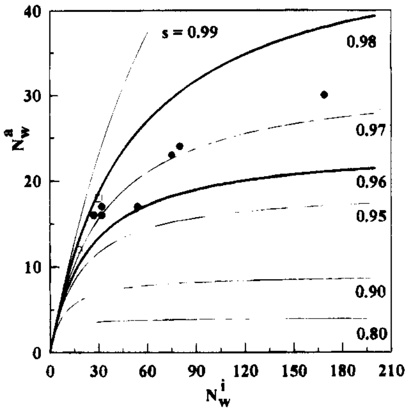


Figure 4. Variations of the weight-average degree of chain extension N^a_w of the amino PTMO versus the weight-average degree of chain extension N^i_w of the precursor PTMO ionene for a bifunctional short segment. Curves are calculated according to eq 3 for various demethylation selectivities *s*. Initial ionene: (●) $x = 6$; (□) $x = 3$; (○) $x = 2$.

the segmented PTMO and of pure PTMO in dilute solution is highly reasonable taking into account the chemical structure and the low amont (no more than 6%) of the diamino short segment. Comparison of the experimental values of the molecular weights of the tertiary amino polymer with the theoretical ones derived from the molecular weights of the ionene precursors shows that the reaction occurs with some chain degradation. In the kinetic experiment already considered, the intrinsic viscosity of the recovered polymer remains unchanged ($[\eta] = 0.76 \pm 0.01$ dL·g^{-1}) over 3 h after quantitative dealkylation is already reached within a 4 h reaction time. This feature shows that the excess $LiEt_3BH$ reagent is inert toward the tertiary amino PTMO and that chain scission arises from incomplete selectivity toward the methyl groups in the dealkylation process. For a given selectivity *s*, defined as the probability of $N^+{-}CH_3$ scission with respect to the four possible $N^+{-}C$ scissions around the ammonium cation, the weight-average degree of chain extension N^a_w of the resulting amino segmented PTMO and its polydispersity index may be calculated as a function of the weight-average degree of chain extension of the initial ionene N^i_w within the following assumptions:

(i) The molecular weight distribution of the ionene obeys the classical Flory–Schulz distribution.

(ii) Every ammonium cation is the site of a dealkylation step of selectivity *s*, and these successive reactions on a given chain are completely independent. More especially, the probability of survival of a bifunctional short segment is s^2.

(iii) The molecular weight of the ammonium short segment eliminated during the polymer recovery process is not taken into account.

The calculations, detailed elsewhere,[46] lead to the equations

$$N^a_w = \frac{2N^i_w + p(1 - N^i_w)}{2 - p(1 - N^i_w)} \qquad (3)$$

$$\frac{N^a_w}{N^a_n} = \frac{2N^i_w + p(1 - N^i_w)}{1 + N^i_w} \qquad (4)$$

with $p = 1 - s$ for a monofunctional ammonium site between the PTMO segments and $p = 2(1 - s)$ for a bifunctional ammonium short segment. The calculated curves $N^a_w = f(N^i_w)$ related to a bifunctional short segment are plotted in Figure 4 for some selected *s* values. They show a characteristic asymptotic behavior ($N^a_w \rightarrow (2 - p)/p$ when $N^i_w \rightarrow \infty$) which is approached more rapidly for lower *s* values. For instance, for $s = 0.97$, an increase of the N^i_w value of the ionene precursor by a factor of 3, from 35 to 105, results in an increase of the corresponding N^a_w value by a factor of only 1.2, from 20 to 24. This typical trend may be intuitively understood since the quantitative dealkylation process of ionenes with higher initial N^i_w values requires a higher number of dealkylation steps on the same chain and a higher probability of multiple chain scissions. Moreover, it clearly shows that for demethylation selectivities lower than 0.98, there is not much point in optimizing the ionene synthesis in terms of very high degrees of chain extensions N^i_w, such as $N^i_w > 120$.

In spite of some scatter of the experimental points, the data related to all the ionenes under study, whatever the lengths of the PTMO precursor and of the short bifunctional segment, are fairly consistent with a selectivity of the demethylation reaction $s = 0.97 \pm 0.01$: see Figure 4. In the same way, the experimental data related to the unique sample of segmented ionene carrying only one ammonium site between the PTMO segments, $N^i_w = 23$ and $N^a_w = 20$, are compatible with a selectivity of 0.98, taking into account the experimental accuracy (calculated $N^a_w = 18.6$). The very good agreement of these selectivity values with that observed on low molecular weight dialkyldimethylammonium iodides,[44] $s = 0.96$, is worth stressing. For such a high *s* value, the amino polymers should only show a very slight trend toward a narrower molecular weight distribution with respect to that of the ionene precursor: see eq 4, which may be readily approximated by $N^a_w/N^a_n = 2 - p$ for N^i_w values higher than 30. Unfortunately, this prediction cannot be checked through SEC measurements because of strong irreversible adsorption of the amino segmented PTMO on the PS gel columns in THF solution. For instance, for a polymer of $M^a_w = 68 \times 10^3$ ($M^0_n = 3.6 \times 10^3$, $x = 6$), only a fraction of about 59% of the sample is actually eluted (calculated according to a polystyrene calibration, taking into account the respective refractive index increments of PS and PTMO), with apparent molecular weight and polydispersity index (PTMO calibration) of 2.1×10^4 and 4.6, respectively. This behavior is in sharp contrast with that of α,ω-ditertiary amino PTMO, which show only a weak trend toward slightly higher elution volumes with respect to their homologous α,ω-dihydroxy chains, without any significant peak broadening.[34] No definite and satisfactory explanation may be advanced at the present time (possible influence of residual ammonium ion pairs in too low amounts to be detected?).

Functionalization of the Tertiary Amino PTMO Segmented Polymers. The selective functionalization of the precursor amino polymers was performed in homogeneous aprotic solution using polymer concentrations in the range 9–17 g·dL^{-1}, corresponding to amine concentrations in the range 0.05–0.09 mol·L^{-1} (increasing polymer concentration when increasing the PTMO segment length). The reactions given in Scheme 1 systematically involve the nucleophilic ring opening of a variety of cyclic electrophiles by tertiary amino functions.[15] For the ammonioalkanesulfonate zwitteriono-

Table 3. Functionalization of Amino Segmented PTMO into Ammonioalkanesulfonates

reagent[a]	x	r[b]	solvent	T (°C)	time (h)	F (%)
PS	6	1.1	THF	60	20	58
		1.1	dioxane	100	20	80
		1.1	DMF	100	48	95
	3	1.1	DMF	100	48	94
	2	1.1	DMF	100	48	80
		2.0	DMF	120	48	100
BS	6	1.1	DMF	100	48	76
		1.1	DMF	120	48	84
		2.0	DMF	120	48	100
OXZ	6	1.1	DMF	120	24	61
		1.1	DMF	120	48	76

[a] PS, 1,3-propanesultone; BS, 1,4-butanesultone; OXZ, (2-methyl-1,3-oxazolino)-3-propanesulfonate. [b] r = stoichiometric ratio [quaternizing reagent]/[tertiary amine].

mers, the solution viscosity progressively increases as the reaction proceeds, because of the self-association of the dipolar units which are poorly solvated in aprotic solvents:[47] gelification is actually observed in THF or dioxane solution, but not in *N,N*-dimethylformamide (DMF) solution at 100 °C. For (ammonioalkyl)dicyanoethenolate zwitterionomers, self-association does not occur in DMF, which is a good solvent for this type of zwitterionic structure.[48] The reaction progress was monitored on the recovered polymers by ^{1}H-NMR spectroscopy (9:1 (by volume) $CDCl_3-CF_3CD_2OH$): quaternization results in a typical decrease of the original singlet NCH_3 at 2.2 ppm and of the broad unresolved multiplet NCH_2 at 2.3 ppm in the precursor polymer and in a simultaneous increase of the zwitterionomer N^+CH_3 singlet at 3.1 ppm (see Figure 1). The functionalization degree F (fraction of reacted amine × 100) was finally derived (i) from the comparison of the tertiary amine concentrations in the initial and reacted polymers measured by acid–base potentiometric titration (see Experimental Section) and (ii) from UV spectroscopy in the case of (ammonioalkoxy)dicyanoethenolate zwitterionomers, using the molar absorptivities of the model dizwitterions derived from TMHDA (see Experimental Section), $\epsilon = 3.80 \times 10^4$ and 3.47×10^4 $L{\cdot}mol^{-1}{\cdot}cm^{-1}$ at λ = 235 nm in TFE solution for the ethoxy- and propoxydicyanoethenolates, respectively. The agreement between the two methods is excellent as typified, for instance, by F = 89% as derived from both potentiometric and UV measurements for a zwitterionomer of the (ammoniopropoxy)dicyanoethenolate type. The results of the functionalization into ammonioalkanesulfonates performed under a variety of experimental conditions are given in Table 3. They suggest the following comments:

(i) The fairly smooth experimental conditions described in the literature for quantitative functionalization of polyurethanes bearing tertiary amino groups in their hard segment by 1,3-propanesultone[25-30] (stoichiometric ratio [PS]/[tertiary amine] = 1, t < 70 °C, 2–5 h) do not result, in our hands, in reaction yields over 80%. Quantitative functionalization requires much more drastic conditions, such as heating at 100 °C over 2 days.

(ii) For these experimental conditions, the reaction yield with PS is significantly lower for the bifunctional shortest segment (x = 2), probably because of steric hindrance effects, which are a major limiting factor in quaternization reactions.[49]

(iii) For identical experimental conditions, the reaction yield decreases when going from 1,3-propanesultone to 1,4-butanesultone, in good agreement with the respective reactivities of the five- and six-membered sultones.[50] Quantitative functionalization in ammoniobutanesulfonate remains however possible under more drastic conditions ([BS]/[amine] = 2, 48 h at 120 °C).

Table 4. Functionalization of Amino Segmented PTMO into (Ammonioalkoxy)dicyanoethenolates in DMF Solution Using a Stoichiometric Ratio r = 2

reagent[a]	x	T (°C)	time (h)	F (%)
DCKEA	6	60	2	98
	3	60	2	99
	2	60	2	82
		80	12	85
DCKPA	6	60	20	92

[a] DCKEA, dicyanoketene ethylene acetal; DCKPA, dicyanoketene propylene acetal.

(iv) Finally, (2-methyl-1,3-oxazolinio)-3-propanesulfonate[51] only affords partial functionalization. Moreover, the use of the reagent in a large excess is not practical since its elimination from the polymer is very cumbersome because of similar solubility properties for these two zwitterionic species (see Experimental Section).

Quantitative functionalization of the tertiary amino precursors into (ammonioalkoxy)dicyanoethenolates according to the reaction pioneered by Middleton et al.[52] is straightforward, but, here again, steric hindrance in the shortest segment (x = 2) results in a slightly lower yield; see Table 4.

Molecular weight measurements on the segmented zwitterionomers by light scattering were unfortunately not possible because of the lack of any solvent (or isorefractive solvent pair) showing simultaneously high enough refractive index increment and good solvation power toward the PTMO chain *and* the zwitterionic short segment. However, in the case of the ethoxydicyanoethenolates, some GPC measurements carried out at 25 °C in DMAC/0.01 M $Bu_4N^+Br^-$ solution are instructive. Distribution curves are typically unimodal and show polydispersity indexes M_w/M_n in the range 1.8–2.3 (see Figure 2) and molecular weight M_w values in the range $(0.8-2.7) \times 10^5$ in polystyrene equivalents, compatible with the corresponding values of the amino precursors. In the smooth temperature conditions selected for the preparation of these zwitterionomers (only 60 °C), the lack of any significant chain degradation may be safely assumed. In our hands, the best solvent for all the zwitterionomers was the protic binary mixture chloroform–trifluoroethanol (9:1 by volume): chloroform is one of the best solvents for PTMO,[53] and trifluoroethanol is a good solvating agent of the zwitterion anionic site through hydrogen bonding.[47,48] Neglecting in a first approach the composition variations of the zwitterionomers (5–18% of dipolar segments) and the difference in the zwitterion structure itself, the intrinsic viscosities of the various zwitterionomers measured in this binary solvent were tentatively correlated with the calculated M_w values derived from those of their amino precursors (no chain scission). For the homologous series of the (ammonioethoxy)dicyanoethenolates with a short segment x = 6, the experimental data lead to eq 5:

$$[\eta]\ (dL{\cdot}g^{-1}) = 1.66 \times 10^{-4} M_w^{\ 0.79} \quad \text{at } 25\ ^\circ C,\ 0.3 < M_w \times 10^{-5} < 3 \qquad (5)$$

with a correlation coefficient of 0.975 over four data

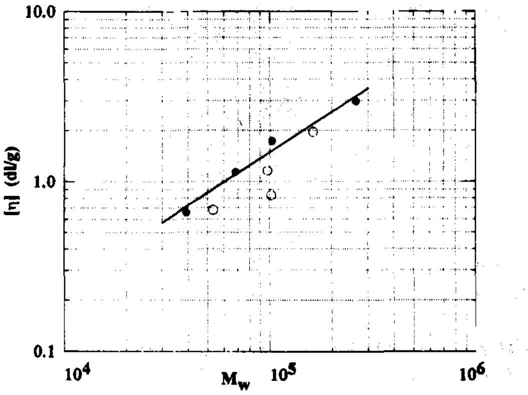


Figure 5. Mark–Houwink–Sakurada relationship for PTMO zwitterionomers ($x = 6$) in the binary solvent $CHCl_3$–TFE (9:1 by volume) at 25 °C: (●) (ammonioethoxy)dicyanoethenolates; (○) ammoniopropanesulfonates.

points (see Figure 5). Such a correlation may be considered as highly satisfactory, taking into account all the previous assumptions. The [η] values measured in the same conditions for the ammoniopropanesulfonate zwitterionomers are lower than the calculated ones by about 25%. This may merely reflect an overall lower chain expansion arising from weaker zwitterion–solvent interactions or a slight chain degradation (M_w decreased by a factor of about 0.7) during their synthesis: this contribution cannot be neglected because of the more drastic experimental conditions of the quaternization by sultones ($T \sim$ 100–120 °C).

Thermal Stability of the Segmented PTMO Zwitterionomers and Ionenes. Thermal stability was studied by thermogravimetric analysis (TGA) carried out under a nitrogen atmosphere (see Experimental Section) essentially to determine the temperature range of safe use of these polymers. Some representative TGA curves giving the variations of the ratio of the sample weight w at temperature T to its initial value $w°$ versus temperature are shown in Figure 6. The tertiary amino segmented PTMO, considered as the reference polymer, is degraded according to a single-step process (one single peak in the derivative trace d($w/w°$)/dt vs T), and the TGA curves are quasi-insensitive to the short segment length. Assuming first-order kinetics, an apparent overall activation energy E_a may be estimated within a temperature range where experimental data can be linearized according to eq 6:[54]

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left[\frac{AR}{\theta E_a}\left(1-\frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \qquad (6)$$

where α is the polymer fraction volatilized at temperature T ($\alpha = (w° - w)/w°$), θ is the heating rate, A is the Arrhenius frequency factor, and R is the gas constant. Some characteristic E_a values obtained along this line are given in Table 5. Comparison between the two telechelic PTMO emphasizes the major influence of the nature of the end groups in the initiation of the degradation. There is a translation of about 135 °C toward higher temperatures when going from the TGA curve of the α,ω-dihydroxy PTMO to that of the α,ω-diamino PTMO. However, no change in the corresponding activation energy may be observed, and its value is in fairly good agreement with that measured by TGA under vacuum on a high molecular weight PTMO, E_a = 188 kJ·mol^{-1}.[55] The segmented tertiary amino PTMO still appears more stable with a further shift of the TGA curve of about 25 °C toward higher temperatures but with a significant increase of the activation energy by a factor of about 1.5. Distribution of the tertiary amino function as chain ends in the low molecular weight telechelic polymer or in the chain of the high molecular weight segmented polymer is clearly a factor in the degradation mechanisms.

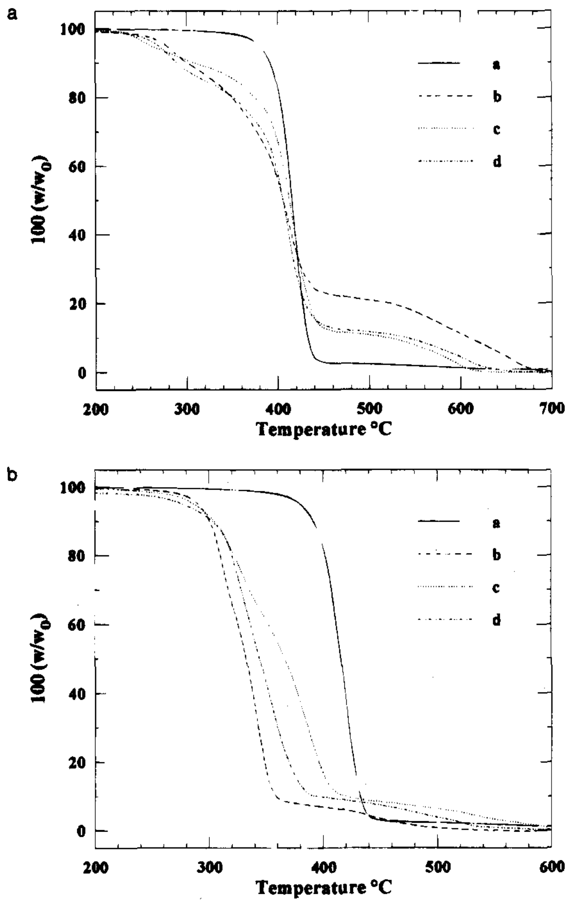


Figure 6. Thermogravimetric analysis of some representative segmented PTMO ($M_n^0 = 2 \times 10^3$, $x = 6$) in the dicyanoethenolate series (panel a) and in the sulfonate series (panel b): (a) reference amino PTMO; (b) PTMO ionene; (c) PTMO zwitterionomers, $p = 2$ for panel a and $p = 3$ for panel b; (d) PTMO zwitterionomers, $p = 3$ for panel a and $p = 4$ for panel b.

Table 5. Thermal Degradation under N_2 of Some Uncharged PTMO ($M_n^0 = 2 \times 10^3$ in All Cases)

polymer	T range (°C)	wt loss (%)	E_a (kJ/mol)
HO–PTMO–OH	160–230	91	160
$(H_3C)_2N$–PTMO–$N(CH_3)_2$	312–394	80	155
segmented tertiary amine PTMO[a]	386–432	80	249

[a] $M_w^a = 7 \times 10^4$, short segment $x = 6$.

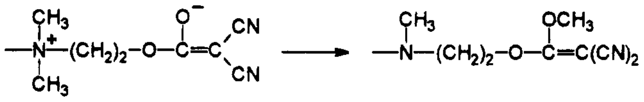
All the other functionalized segmented PTMO display a more complex multistep degradation. For a given polymer, the various values of the activation energy which could be calculated through eq 6 within successive narrow temperature ranges have likely no true physical meaning. At 460 °C, more than 95% of the PTMO should be volatilized and the residual weight in the zwitterionomers and ionenes may be ascribed to the presence of the functional structures. The TGA curves are nearly independent of the length of the short segment but not of its density along the chain. In the case of (ammonioethoxy)dicyanoethenolate zwitterionomers, for instance, the temperature of the maximum rate of the major weight loss (inflection point on the

TGA curve) increases from 378 to 416 °C when the molecular weight of the PTMO segment M_n^O decreases from 6.7×10^3 to 2.2×10^3.

In the sulfonate series and for a common short segment ($x = 6$), the structures leading to increasing stability (higher temperature for the initial degradation step) may be ordered as ion pair < zwitterion $p = 4$ < zwitterion $p = 3$ < uncharged diamine (reference polymer). In the dicyanoethenolate series however, all the polymers are much less differentiated and the ionene appears more stable than the zwitterionomer in the lower temperature range: this is the opposite behavior of that observed in the previous case.

The mechanistic analysis of the degradation process, which may be rather complex as already observed in other quaternary ammonium polymers[42,56-58] (dequaternization, Hofmann degradation, etc.) is beyond the scope of the present work.

Finally, because of irreversible slight discoloration of some samples at about 100-150 °C before any significant weight loss, the possible structural changes of a zwitterionomer of the (ammonioethoxy)dicyanoethenolate type was monitored by IR and UV spectroscopy during an isothermal treatment of the sample at 130 °C under nitrogen (this temperature proved to be well adjusted for sample molding). The two strong characteristic IR absorption bands of the zwitterionic structure,[52] ν(C≡N) at 2170-2195 cm^{-1} (sharp doublet) and ν(C=C) at 1655 cm^{-1}, normalized to the vibration of the C-O-C ether function of the PTMO segment at 1110 cm^{-1} chosen as internal reference, do not show any significant variations for treatments over 24 h. In the same way, the UV spectrum of the polymer (TFE solution) remains unchanged. The zwitterionic structure thus appears stable at this temperature. The potential intramolecular alkylation of the dicyanoethenolate anion, previously considered at a higher temperature of 160 °C in analogous n-butyl acrylate zwitterionomers,[20] may be ruled out:



$$-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-(CH_2)_2-O-\overset{O^-}{\overset{|}{C}}=C(CN)_2 \longrightarrow -\overset{CH_3}{\overset{|}{N}}-(CH_2)_2-O-\overset{OCH_3}{\overset{|}{C}}=C(CN)_2$$

The resulting dicyano enol methyl ether would display fairly similar IR characteristics,[59] but the UV absorption at 238 nm typical of the strongly delocalized anionic site would completely vanish.

Conclusion

In spite of some drawbacks such as an unavoidable weak chain degradation during the demethylation step, the adopted strategy readily allows the preparation of a series of homologous linear segmented PTMO zwitterionomers and ionenes with a very good control of the major structural parameters: length of the monodisperse PTMO segments ($M_n^O \sim (2-7) \times 10^3$) and length and structure of the zwitterionic or ionene short segment. Their weight-average degrees of chain extension are high enough (>15), their rather broad molecular weight distributions ($M_w/M_n \sim 2$) do not appear as a serious failure, and their thermal stability provides a sufficiently wide temperature range of safe use. The study of the bulk phase morphology of these model polymers should allow a comprehensive analysis of the microphase separation between the PTMO soft matrix and the dipolar hard segments as a function of their chemical structure (zwitterions of various dipole moments and bulkiness versus the homologous ion pairs) and their density along the chain. Structural studies by DSC, SAXS, or SANS, ^{1}H broad-line NMR, and spin diffusion measurement will be reported in following papers. Finally, the intermediate tertiary amine segmented PTMO may also be considered as a versatile precursor for macromolecular engineering: synthesis of new functionalized polyethers (N-oxides, ammonium ylides, etc.) and of comb-type branched PTMO ionenes (grafting of living monofunctional PTMO), for instance.

Experimental Section

Solvents and Reagents. Tetrahydrofuran was purified by a double distillation over the disodium benzophenone complex and stored under argon in a Schlenk vessel. Dimethylformamide (DMF) was distilled under vacuum over CaH_2 and stored over 4 Å molecular sieves. All the other solvents of the best reagent grade available were used without further purification. Trifluoromethanesulfonic anhydride (TFA) was purified by distillation over P_2O_5 under argon just before use. N,N,N',N'-Tetramethyl-1,2-ethanediamine, -1,3-propanediamine, and -1,6-hexanediamine were distilled over CaH_2. 1,3-Propanesultone and 1,4-butanesultone were purified by vacuum distillation. Dicyanoketene ethylene or propylene acetals[52] (DCKEA and DCKPA) and (2-methyl-1,3-oxazolinio)-3-propanesulfonate[51] were prepared according to the literature. Tetraethylammonium trifluoromethanesulfonate was obtained by neutralization of an aqueous solution of tetraethylammonium hydroxide (40% by weight) by the calculated amount of trifluoromethanesulfonic acid; the crystalline salt was recovered in quantitative yield by freeze-drying. Anal. Calcd for $C_9F_3H_{20}NO_3S$: C, 38.70; H, 7.22; N, 5.01. Found: C, 38.67; H, 7.39; N, 4.95.

(Triethylammonioethoxy)dicyanoethenolate. This compound was prepared by transposition of a literature method developed for the synthesis of the triethylammonium enolates of acylmalononitriles.[59] Ethyl chloroformate (9.6 mL (0.1 mol)) and 6.6 g (0.1 mol) of malonodinitrile were dissolved in 90 mL of toluene. A solution of 24 g of triethylamine (0.24 mol) in 200 mL of toluene was added dropwise under efficient stirring and in such a way that the temperature never exceeded 40 °C: yellow crystals of triethylammonium hydrochloride first appeared, followed by the progressive development of a reddish oil. The reaction medium was then left overnight at room temperature. After filtration of $Et_3NH^+Cl^-$, the oil separated from the toluene solution by decantation was dried at 30 °C under vacuum and redissolved in 80 mL of $CHCl_3$. After standing overnight, the solution was filtered from residual $Et_3NH^+Cl^-$ crystals and then rotary evaporated to yield 14.9 g of the salt as a reddish oil: yield 62%. ^{1}H NMR ($CDCl_3$) δ (ppm) 3.9 (q, 2H, CH_2O), 3.1 (q, 6H, CH_2N^+), 1.25 (t, 9H, $CH_3CH_2N^+$), 1.1 (t, 3H, CH_3CH_2O). Anal. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.85; N, 17.56; O, 13.37. Found: C, 59.58; H, 9.14; N, 17.53; O, 13.73.

Hexane-1,6-diylbis[(dimethylammonioethoxy)dicyanoethenolate]. A solution of 1.64 g (9.52 mmol) of TMHDA and 2.86 g (21.0 mmol) of DCKEA in 25 mL of DMF was stirred overnight at room temperature. The heterogeneous solution was precipitated into a large excess of acetone, and the zwitterion separated by filtration was thoroughly washed with acetone and finally dried under vacuum at 50 °C: 3.8 g (yield of 90%) of yellowish crystals were recovered. ^{1}H NMR (DMSO-d_6) δ (ppm) 4.3 (4H, OCH_2), 3.5 (4H, $OCH_2CH_2N^+$), 3.2 (4H, N^+CH_2), 3.1 (12H, N^+CH_3), 1.7 (4H, $N^+CH_2CH_2$), 1.3 (4H, central $(CH_2)_2$). Anal. Calcd for $C_{22}H_{32}N_6O_4$: C, 59.44; H, 7.25; N, 18.90; O, 14.40. Found: C, 59.26; H, 7.28; N, 18.85; O, 14.84.

Hexane-1,6-diylbis[(dimethylammoniopropoxy)dicyanoethenolate]. Quaternization of TMHDA by DCKPA was carried out in a similar way, but with a longer reaction time of 48 h: yield 36%. ^{1}H NMR (DMSO-d_6) δ (ppm) 3.9 (4H, OCH_2), 3.2 (8H, N^+CH_2), 3.0 (12H, N^+CH_3), 2.0 (4H, OCH_2CH_2), 1.7 (4H, $N^+CH_2CH_2$), 1.3 (4H, central $(CH_2)_2$). Anal. Calcd for $C_{24}H_{36}N_6O_4$: C, 61.00; H, 7.68; N, 17.78; O, 13.54. Found: C, 60.53; H, 7.69; N, 17.67; O, 13.55.

Living THF Polymerization and In Situ Polyaddition on *N,N,N',N'*-Tetramethyl-α,ω-diaminoalkanes. The polymerizations were carried out in a Pyrex double-wall reactor fitted with a mechanical stirrer and connected with an external Lauda cryothermostat allowing the temperature to be monitored within ±0.1 °C. The reactor was degassed and dried at 80 °C by successive vacuum–argon sweeping cycles and then cooled to 20 °C. Purified THF (400 mL (4.91 mol)) was then directly transferred from Schlenk vessel into the reactor, and 1.65 mL (9.83×10^{-3} mol) of purified TFA was then added all at once through a self-sealing rubber cap using a syringe technique (the accurate amounts of THF and TFA were further checked by weighing). Polymerization occurs in a quasi-isothermal way and after a given reaction time (5–20 min), selected with respect to the desired molecular weight, 10 mL of the solution was withdrawn using a syringe and immediately precipitated in slightly basic water for M_n^0 measurement on the PTMO segment. The calculated amount of the purified tertiary diamine (in stoichiometric amounts with respect to the initial TFA and taking into account the withdrawal amount) was then rapidly injected through a syringe into the reactor. There was no more than 20 s between the solution withdrawal and the diamine addition, which is immediately followed by a temperature increase of about 5 °C and a drastic enhancement of the solution viscosity: for PTMO molecular weights higher than about 5×10^3, the reaction medium is actually gellified. The reaction was carried out for 30 min and the ionene was then recovered by precipitation of its THF solution (eventually after a small addition of methanol to disrupt the gel) into an 8-fold excess of ice-cooled water maintained at pH 8. The polymer was separated by filtration or centrifugation, washed thoroughly with water, and dried under vacuum at 40 °C for at least 2 days.

α,ω-Dimethylamino Telechelic PTMO. The anhydrous gaseous dimethylamine liberated from the mixture of its crystalline hydrochloride with 2 equiv of solid potassium hydroxide (yield over 90%) was directly condensed in purified THF to lead to a concentration of about 15% by weight. End-capping of living PTMO chains were carried out by rapid injection in the polymerization medium of a large excess of the amine solution, [dimethylamine]/[oxonium end group] = 10. The excess amine was eliminated by rotary evaporation and the telechelic PTMO was recovered as previously described.

Demethylation of the Segmented PTMO Ionenes. All the reactions were carried out under an argon atmosphere at 50 °C using a stoichiometric ratio [$LiEt_3BH$]/[tertiary amine] = 2. To the very viscous solution of the ionene in THF (8% w/v), the calculated volume of a THF–0.1M $LiEt_3BH$ solution (Aldrich) was added dropwise under efficient stirring using a syringe–self-sealing rubber cap technique. The viscosity of the reaction medium immediately drops (disruption of the physical ionic network), and stirring was maintained at 50 °C for reaction times between 1 and 7 h. After careful neutralization of excess reagent by dropwise addition of 2 mL of water, the polymer was recovered by precipitation into water, thoroughly washed with water, filtered, and dried at 40 °C under vacuum.

Functionalization of Segmented Tertiary Amino PTMO. All the reactions were performed under an argon atmosphere on solutions of about 10–15% w/v of the precursor polymer using the experimental conditions (solvent, time and temperature, stoichiometric ratio r = [quaternizing reagent]/[tertiary amine]) given in Tables 3 and 4. The dicyanoethenolate polyzwitterions were recovered by precipitation of their solution into an 8-fold excess of water (the residual reagent is soluble in this binary DMF/H_2O mixture), thoroughly washed with water, filtered, and dried at 40 °C under vacuum. Precipitation of the solution of sulfonate zwitterionomers in identical conditions results in milky colloidal suspensions, which were exhaustively dialyzed against water using Spectrapor membrane (molecular weight cutoff 3×10^3); the polymers were finally recovered by freeze-drying and dried as previously described.

Physical Measurements. (i) Spectroscopy. IR (films from $CHCl_3$ solution) and UV spectra (TFE solution) were recorded on a FTIR Bomem-Michelson MB-155 spectrometer and on a Shimadzu UV-2101 PC spectrometer, respectively. ^1H (200 MHz) and ^{19}F (188 MHz) NMR measurements were performed at room temperature on a Bruker AC 200 spectrometer. In the case of ^1H NMR spectra, the chemical shifts δ are given in ppm with respect to the solvent resonances fixed at 7.27 ppm for $CHCl_3$ and at 2.49 ppm for DMSO.

(ii) Acid–Base Titration. Potentiometric titration of tertiary amine functions was performed on an automatic Mettler DK 11 device fitted with a Metrohm 6.0.203 joint calomel–glass electrode using a mixture of acetic acid–acetic anhydride (1:9 by volume) as solvent and perchloric acid (0.01–0.1 N) in acetic acid as titrating reagent. In such experimental conditions, the anionic sites of the zwitterionic chain have a basicity too low to be titrated.[31]

(iii) End Group Titration in α,ω-Dihydroxy-PTMO. It was performed by ^{19}F-NMR spectroscopy after quantitative derivatization into hexafluoroacetone hemiacetal according to the literature.[59,60] The reagent stock solutions in ethyl acetate, prepared by weighing and stored under argon, were about 0.3 M in hexafluoroacetone (HFA) and about 0.04 M in ethyl trifluoroacetate, chosen as internal standard; their precise concentrations were further checked by titration with a known amount of 2-propanol. A known weight of the PTMO sample was dissolved in a given volume (1–2 mL) of the reagent solution and after addition of 1 mL of $CDCl_3$ (lock) and annealing of the solution for at least 30 min, the ^{19}F-NMR spectrum was run and quantitatively analyzed for the sharp and well-separated resonance singlets of the PTMO hemiacetal $OC(CF_3)_2OH$ at 2.65 ppm and of the internal reference $CF_3CO_2C_2H_5$ at 7.05 ppm (downfield shifts with respect to the CF_3 singlet to the HFA hydrate resulting from addition of the excess reagent—CF_3 singlet at 7.48 ppm— to residual water). A statistical analysis of 24 runs on a given PTMO sample carried out by two operators using different reagent solutions led to a mean value of 2.375×10^3 with a root mean square standard deviation of 93 ($M_n = 2.375 \times 10^3 \pm 40$ for a 95% confidence level).

(iv) Molecular Weight Measurements. Viscosity measurements were carried out on a home-built automatic device (Ubbelohde type) and the intrinsic viscosity ($[\eta]$ dL·g^{-1}) was derived from the experimental data according to the classical Huggins equation. Specific index increments (dn/dc (mL·g^{-1})) were measured at room temperature on a Brice-Phoenix BP 1000V differential refractometer fitted with a neon laser beam (λ = 632 nm). Light scattering measurements were performed at room temperature on a Sematech 633 apparatus at the same wavelength. Size exclusion chromatography (SEC) measurements were performed in two different ways. For the PTMO precursors, measurements were performed at room temperature on a home-built device fitted with five columns in series packed with PL gels with upper permeability limits of 10^6, 10^5, 10^4, 10^3, and 5×10^2 Å. The mobile phase was THF at room temperature. Molecular weights were calculated after calibration with PTMO (Polymer Laboratories) or polystyrene standards. In the latter case, conversion of the initial molecular weight values in PS equivalents into actual PTMO values was performed according to the universal calibration using the Mark–Houwink–Sakurada equations for polystyrene and PTMO in THF solution at 25 °C taken from the literature:[56] it results in $M_n(PTMO) = 0.53 M_n(PS)$ over the molecular weight range of interest ($(1.7–7) \times 10^3$), in good agreement with the factor 0.55 previously reported for the same conversion.[62] For ionenes and segmented zwitterionomers, the SEC measurements were performed at room temperature on a Waters gel permeation chromatograph fitted with a set of PL gel mixed columns (10^5–500 Å), using DMAC–0.01 M $Bu_4N^+Br^-$ as the mobile phase. Molecular weights were calculated after calibration with polystyrene standards.

(v) Thermogravimetric Analysis (TGA). Dynamic TGA measurements were performed on 10–70 mg samples under a constant nitrogen flow (200 mL·min^{-1}) and at a heating rate of 5 K·min^{-1} using a Mettler TA 3000 TGA apparatus. The samples were previously dried in situ at 80 °C for 10 min before starting the heating cycle.

Acknowledgment. The authors gratefully acknowledge Mrs. H. Bellissent and Mrs. S. Jousset for their efficient contribution to the synthetic work and Mr. Y. Guilbert for thermogravimetric analysis. They are greatly indebted to Mr. J. Dubois (Rhône-Poulenc CRIT-Carrières) for GPC measurements in DMAC solution.

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MA9504983