

Thermal Stability of Modified Telechelic Polystyrenes

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SYNOPSIS

The thermal stability of telechelic polystyrenes bearing quaternary ammonium iodide or ammonium sulfonate end groups is presented. It appears that the ammonium iodide functions are stable below 200°C. Above that temperature, the polystyrene irreversibly loses its functional end groups. The weight loss then observed leads to the conclusion that a Hofmann-type degradation mechanism is likely to take place. In contrast, the ammonium sulfonate-terminated polystyrene begins to degrade at 180°C and leads to a polymer which is no longer end-capped with sulfonic acid or sulfonate groups. This behavior is of importance, especially for the study of multiblock ionic copolymers which are prepared by blending two telechelic polymers, one of them bearing sulfonic acid end groups and the other one tertiary amine functional groups. © 1993 John Wiley & Sons, Inc.

Keywords: ionomers • telechelic polymers • quaternary ammonium sulfonate • thermal stability • degradation

INTRODUCTION

The incorporation of ionic groups into hydrophobic polymer backbones changes the ultimate physical properties of the materials, e.g., their solubility in organic solvents, glass transition temperature, melt and solution viscosities, and mechanical behaviors. This is a consequence of mutual interactions between the ionic moieties¹⁻⁶ which lead to the formation of thermoreversible crosslinks, allowing the materials to be repeatedly processed by conventional transformation techniques, such as extrusion and injection molding, provided that the ionic groups are thermally stable at the processing temperature.

This concept can be applied to any ion pair, and several different functional groups were grafted onto common macromolecular compounds—mainly metal carboxylates, sulfates, sulfonates or phosphonates, and quaternary ammonium salts. However, the literature does not provide much information

about the thermal stability of the ionic groups themselves (irreversible chemical degradation).

The thermal stability of quaternary ammonium salt ionomers is, especially, poorly documented. To our knowledge, there are only two articles by Eisenberg et al., who investigated the thermal stability of styrene-vinylpyridine copolymers by differential scanning calorimetry (DSC), quaternized with alkyl iodides.^{7,8} An endotherm was found between 160 and 190°C and assigned to the dequaternization of the ammonium functions. This reaction occurs at relatively low temperatures (135°C) with 2-vinylpyridinium units, but can be prevented up to 200°C with 4-vinylpyridinium and 2-methyl 5-vinylpyridinium groups, enabling the corresponding copolymers to be studied by mechanical measurements up to their respective critical temperatures. A recent article discussed the thermal properties of 4-vinylpyridinium trifluoromethanesulfonate monomers substituted at the nitrogen position with H, O, CH₃, C₂H₅, C₆H₁₃, or C₁₂H₂₅ groups.⁹ The authors reported that the corresponding polymers, poly(4-vinylpyridine *N*-oxide), decomposed at lower temperatures than the *N*-alkylated macromolecules (290°C vs. 420–430°C). They did not notice, however, an endotherm attributed to dequaternization.

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In this article, the thermogravimetric behavior of dimethylamino telechelic polystyrene, quaternized with a series of *n*-alkyl iodides, is presented. The thermal stability of α,ω -sulfonic acid polystyrene, previously neutralized with tertiary amines, is also discussed.

EXPERIMENTAL

Telechelic polystyrenes were prepared by anionic polymerization as reported elsewhere.¹⁰ The living macrodianions were deactivated by 1-chloro 3-dimethylamino propane¹¹ and 1,3-propanesultone¹² leading to α,ω -dimethylamine [PS(NMe₂)₂] and α,ω -sulfonic acid [PS(SO₃H)₂] polystyrenes, respectively. Molecular weights and polydispersity were determined by vapor pressure osmometry and size exclusion chromatography; functionality determination was achieved by potentiometric (acid-base) titration of the end groups¹² (Table I). Quaternization of the amino polystyrene was carried out in a THF/methanol solution, according to a previously reported quantitative method.¹³ PS(SO₃H)₂ was quantitatively neutralized with aliphatic tertiary amines, using potentiometric titration of the polymer in a toluene/methanol (90/10 v/v) mixture. The resulting neutralized and quaternized polystyrenes were carefully dried under vacuum at 80°C, for more than 1 month.

The thermogravimetric analysis was made with a Perkin-Elmer thermobalance, controlled by a TADS computer system, with between 5 and 10 mg of sample. Weight losses were measured as a function of temperature at a heating rate of 5°C/min, under an inert nitrogen atmosphere. After testing, the furnace was heated up to 500°C for a few minutes under an oxygen stream, in order to remove any trace of residual material. The mass spectrum measurements were carried out at a pressure of 1 mPa, using a double focussing mass spectrometer (VGTS-250). The high pressure liquid chromatography

Table I. Main Characteristics of the Synthesized Polymers

Polymer	M_n (g/mol)	M_w/M_n	f^a
PS(NMe ₂) ₂ 6K	5700	1.4	1.97
PS(SO ₃ H) ₂ 9K	9100	1.3	1.82

^a f = functionality = average number of functionalized end groups per chain.

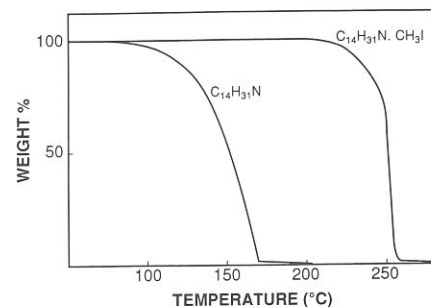


Figure 1. Weight loss as a function of temperature for *N,N*-dimethyldodecylamine, before and after quaternization with iodomethane.

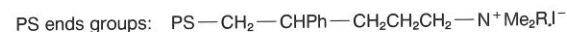
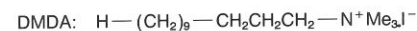
measurements were undertaken using a Waters HPLC integrated system, operating with a R401 differential refractometer and acetonitrile as eluent. The bromine index test is based on the high efficiency of Br₂ to react selectively and quantitatively with the double bond of olefinic compounds. The equivalent point is readily determined by potentiometric titration with a bromide/bromate solution of known concentration, in water.

RESULTS AND DISCUSSION

Quaternary Ammonium Telechelic Polystyrene

Dequaternization, unlike quaternization, can be achieved more easily if the corresponding amine is less basic, on the one hand, and sterically hindered, on the other hand.¹⁴ Since the pK_a 's of *N,N*-dimethyl *n*-butylamine and pyridine are, respectively, equal to 10 and 5,¹⁵ the quaternized dimethylamino end groups of the polystyrene under investigation are, therefore, expected to be more stable than the pyridinium functions of the quaternized poly(styrene-co-vinylpyridine) studied by Eisenberg et al.^{7,8}

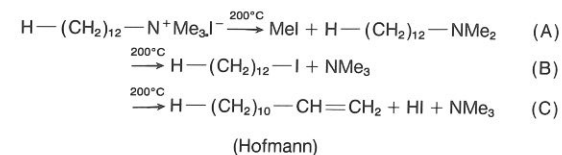
Before assessing the thermal stability of the telechelic polymer, we have studied a model molecule, *N,N*-dimethyldodecylamine (C₁₄H₃₁N), quaternized with MeI. Its structure is similar to that of the quaternized PS terminal functions:



where Me = CH₃, Ph = C₆H₅, and R = alkyl radical of quaternizing agent.

As shown in Figure 1, the pure amine, which is a liquid at room temperature, has totally volatilized at 170°C. Such behavior is expected inasmuch as the amine already evaporates at lower temperatures

under a reduced pressure (bp 111°C at 400 Pa). On the other hand, the model compound is a salt and is likely to volatilize at higher temperatures, provided that its ionic structure is kept unchanged. Surprisingly, it decomposes completely at 250°C (Fig. 1). It cannot be asserted that the process results from dequaternization but such an hypothesis is reasonable and compatible with the volatility, at 200°C and above, of the products formed according to the following equations:^{16,17}



In order to gain a better insight of the reactions occurring at those temperatures, the salt was annealed at 200°C for 5 min in a sealed tube, prior to be mixed with acetonitrile as eluent, allowing the resulting products to be analyzed by HPLC. Looking at Figure 2(c), and by comparison with the chro-

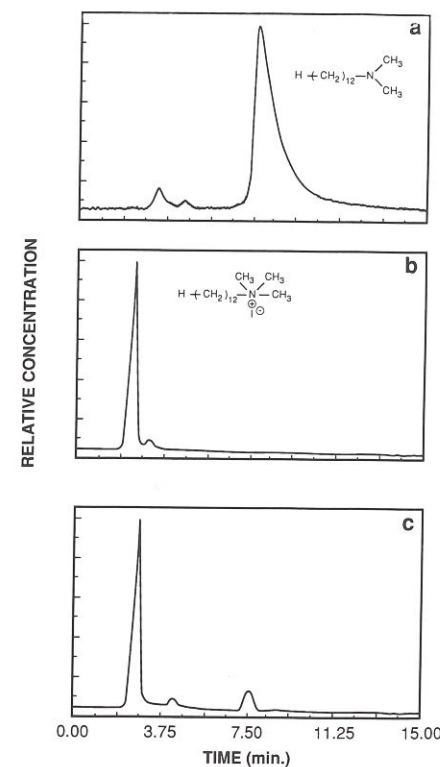


Figure 2. HPLC chromatograms for: (a) *N,N*-dimethyldodecylamine (b) *N,N*-dimethyldodecylamine after quaternization with iodomethane, (c) *N,N*-dimethyldodecylamine after quaternization with iodomethane and annealed at 200°C for 5 min.

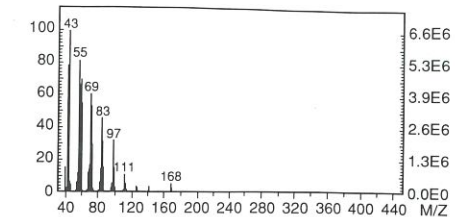
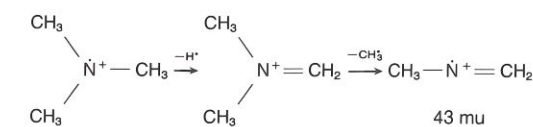


Figure 3. Mass spectrum of *N,N*-dimethyldodecylamine after quaternization with iodomethane and annealing at 200°C for 5 min.

matograms of the pure amine [Fig. 2(a)] and the undegraded salt [Fig. 2(b)], it is obvious that the ammonium iodide does not degrade to a large extent, as reflected by the major peak at 2.2 min. Nevertheless, some *N,N*-dimethyldodecylamine is released (peak at 7.55 min), indicating that reaction (A) actually occurs. It is not possible, however, to estimate the yield of the reaction since the method used in the investigation is only qualitative.

On the other hand, the bromide index test of the ammonium iodide products analyzed in Figure 2(c) indicates that a high concentration of olefinic molecules stems from degradation, which is confirmed by the mass spectrum shown in Figure 3, which reveals three interesting features. First, the constant difference of 14 mu between the major peaks (at 55, 69, 83, 97, and 111 mu) is a characteristic of olefinic compounds. Second, the small peak showing up at 168 mu merely corresponds to a molecular ion associated to 1-dodecene [reaction (C)]. Third, the major peak at 43 mu is likely to be attributed to a stable molecule resulting from rearrangement involving trimethylamine [reactions (B) and/or (C)]:

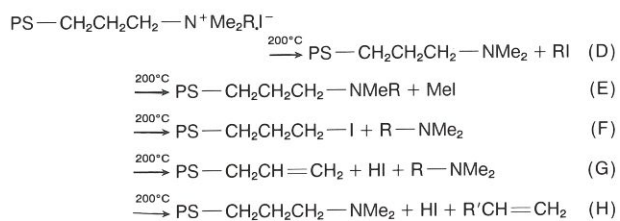


This observation, indicating that the Hofmann degradation occurs to some extent as well, is borne out by the results reported in a very recent article:¹⁸ Burch and Manring observed that the quaternary ammonium salts of aromatic polyamide polyanions experienced a Hoffman elimination at 200°C. Related model molecules containing Et₄N⁺ and (*n*-Bu)₄N⁺ cations were also found to lose ethylene and triethylamine, and 1-butene and tributylamine, respectively, at 155 and 179°C. Another interesting feature of Figure 3 is the very small peak located at 213 mu. As far as it is significant, it corresponds to a molecular ion associated to *N,N*-dimethyldodecylamine [mechanism (A)]. Therefore, it is con-

cluded that competitive reactions take place simultaneously during the thermal degradation of the ammonium iodide, most probably reactions (A) and (C).

The thermogravimetric curve of PS(NMe₂)₂ unquaternized and quaternized with *n*-iodopentane is given in Figure 4. For the sake of clarity, the curves for the other *n*-alkyl iodides investigated are not given since they all have the same shape. After a zone of stability, up to about 200°C, the sample loses weight, and then displays a characteristic plateau between roughly 200 and 380°C. This is followed by the main degradation step, between about 380 and 440°C, which is similar to that occurring with the unquaternized PS. This plateau is not seen with pure PS. The weight loss corresponding to the first degradation step was determined by taking the end of the degradation step corresponding to the point of lowest slope within the corresponding plateau (about 300–350°C). The experimental weight values thus determined for the series of *n*-alkyl iodide quaternized PS are reported in Figure 5, as a function of the length of the alkyl radical (methyl = 1, ethyl = 2, etc.). The longer the alkyl radical of the quaternized end groups, the higher the experimental weight loss.

Five principal mechanisms of end group degradation are likely to take place; their calculated weight losses are also reported in Figure 5:



where R = R'CH₂CH₂ in reaction (H).

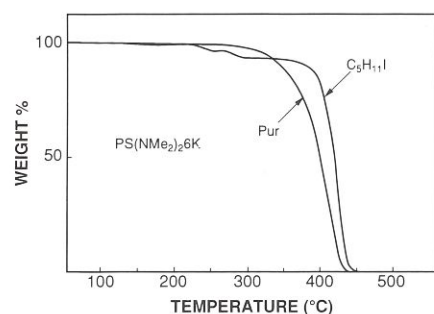


Figure 4. Weight loss as a function of temperature for PS(NMe₂)₂ 6K, unquaternized and quaternized with *n*-iodopentane. The quaternized sample was dried at 80°C under vacuum for 1 month and annealed at 160°C for 15 min in order to remove all traces of solvent.

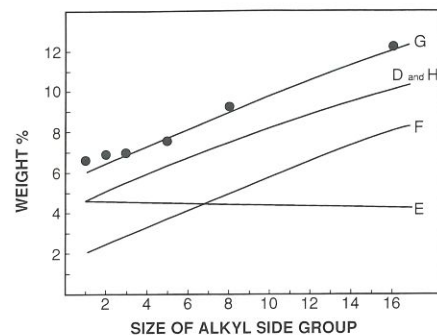


Figure 5. Calculated and experimental weight losses for PS(NMe₂)₂ 6K quaternized, with: iodomethane, iodoethane, 1-iodopropane, 1-iodopentane, 1-iodooctane, and 1-iodohexadecane.

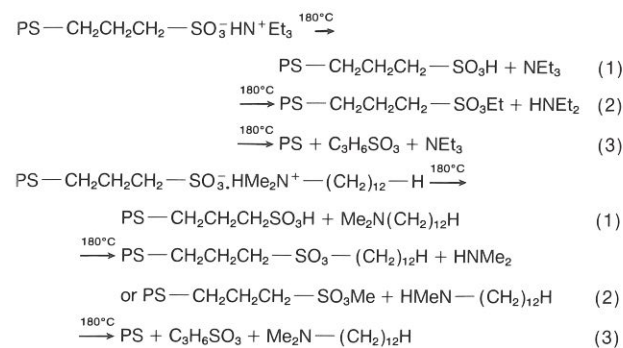
A comparison between the calculated and the experimental values indicates that some of the proposed mechanisms can be ruled out. First, the elimination of methyl iodide [reaction (E)] would lead to a decrease of the weight loss as the *n*-alkyl radical length increases. This is contrary to the experimental observation. Second, the elimination mechanisms (D), (E), and (F) would lead to insufficient weight losses as compared to the experimental data. The same observation can be made for reaction (H) which, moreover, does not apply to the sample quaternized with CH₃I. Mechanism (G) (Hofmann degradation) is then the most likely to occur, though several reactions can simultaneously contribute, to some extent, to the end group degradation.¹⁹

The nature of the end groups of dequaternized polystyrene certainly influences its thermal stability since most polymer degradations are initiated at the chain ends. This is particularly true for polystyrene.^{20–22} According to mechanisms (D)–(H), the polymer should be end-capped after dequaternization with either tertiary amines [(D), (E), (H)], alkyl iodides (F), or insaturations (G). With mechanisms (D), (E), and (H), and amino end groups, the polymer should behave as unmodified PS(NMe₂)₂, which does not occur, according to Figure 4. The expected lower thermal stability of amino terminated PS is supported by the fact that nitrogen atoms favor the appearance of radicals, which can afterwards initiate polystyrene unzipping.^{23,24}

Mechanism (G) (Hofmann degradation) is therefore the most likely to contribute to end group degradation, leading to polystyrene end-capped with olefinic insaturations. Although this conclusion cannot be proven unambiguously, it is very well supported by Figure 5.

Ammoniumsulfonate Telechelic Polystyrene

PS(SO₃H)₂ 9K was neutralized with triethylamine (TEA) and *N,N*-dimethyldodecylamine (C₁₄H₃₁N). The corresponding thermograms are plotted on Figure 6 with that of PS(NMe₂)₂ 6K which is used as a reference. The thermograms of the neutralized polymers both exhibit a small plateau above 180°C. The corresponding weight losses, calculated in the same way as those of Figure 4, are given in Table II. Indeed, three principal mechanisms of end group degradation are possible:



where mechanism (1) corresponds to deneutralization, mechanism (2) to an esterification, and mechanism (3) to a loss of the end groups. The calculated weight losses according to the proposed mechanisms are also reported in Table II.

A comparison between the calculated data and the experimental values clearly shows that mechanisms (1) and (2) do not contribute to a large extent to the end group degradation. Mechanism (1), though it might happen as an intermediate step, does not lead to a stable system inasmuch as aliphatic sulfonic acids are known to be unstable in dry conditions, even at low temperatures.²⁵ If aliphatic acid end groups were produced, they would systematically lose the sulfonic functions. Mechanism (3) is

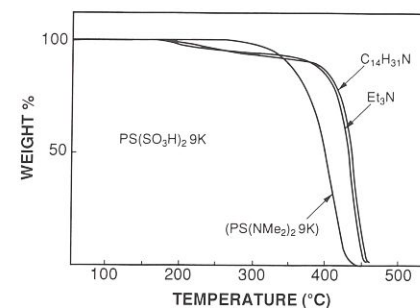


Figure 6. Weight loss as a function of temperature for PS(SO₃H)₂ 9K unneutralized and neutralized with triethylamine and *N,N*-dimethyldodecylamine.

Table II. Calculated and Experimental Weight Losses (wt %) of Sulfonated Terminated Polystyrenes

Sample	Mechanism			Measured
	(1)	(2)	(3)	
Et ₃ N	2.16	1.56	4.63	4.75
C ₁₄ H ₃₁ N	4.44	4.15	6.86	6.87
		0.92		

therefore the most likely. We do not propose, however, that the polymer loses propanesulfone and the corresponding amine. It can only be said that, in terms of weight, these two molecules are missing on each polymer chain. Only a detailed analysis of the products released during degradation could confirm the actual mechanism(s) of degradation. Nevertheless, the polymer loses its sulfonic functions in an irreversible way.

CONCLUSIONS

No dequaternization of the ammonium end groups of PS occurs provided that the temperature does not exceed 200°C. At higher temperatures, a Hofmann-type degradation is likely to occur, producing an olefinic insaturation at both chain extremities, and releasing nitrogen-containing molecules. The telechelic polymer is irreversibly degraded since it loses its amine functions.

Once neutralized with aliphatic tertiary amines, α,ω -sulfonic acid polymers are stable below 180°C. Higher temperatures lead to the removal of the sulfonic/sulfonate end groups of polystyrene. This observation is of great importance, especially for the study of multiblock ionic copolymers, which are obtained by blending two immiscible telechelic polymers one of them bearing sulfonic acid end groups and the other one tertiary amine functional groups.^{26,27}

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