Chemical Modification of Polystyrene. VI. Thermal Stability Studies of Sulfonic Acid Resins from Anhydride Modified Polystyrene

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ABSTRACT

Thermal stabilities of the H form of sulfonic acid resins from polystyrene electrophilically substituted with phthalic anhydride, pyromellitic dianhydride, trimellitic anhydride, and cis-1,2,3,6-tetrahydrophthalic anhydride have been studied and compared by DTA and TGA. Isothermal degradation studies of these resins at 150 ± 10°C for 72 h in air and nitrogen reveal significant changes in IR, decreases in sulfur content, and increases in ion-exchange capacity values. The pH-metric titration characteristics of the pyromellitic-dianhydride-modified sulfonated polystyrene after isothermal heating under the above conditions indicate weak acid behavior, in contrast to the strong acid nature of the original resin.

The isothermal decomposition of the resins in water reveals a maximum capacity loss of ~15% in all the resins except for the polystyrene-pyromellitic dianhydride resin for which the corresponding loss is ~3.5%. The sodium salts of the resins exhibit, in general, better thermal stabilities. Attempts have been made to rationalize these observations on the basis of the structural characteristics of the resins.

INTRODUCTION

Part V [1] of this series described the syntheses and the results of the evaluation of the physicochemical properties of three cation exchange resins prepared by the sulfonation of polystyrene (PS) electrophilically substituted with phthalic anhydride (PA) [2], trimellitic anhydride (TMA) [3], and cis-1,2,3,6-tetrahydrophthalic anhydride (THPA) [4], respectively. It has already been shown that PS, thus modified with these anhydrides including pyromellitic dianhydride [2, 5], exhibits significantly better thermal stability relative to unmodified PS. It is expected that further modification of these anhydride-modified PS polymers through sulfonation will introduce additional cross-links in the polymer matrix, thereby imparting greater chain rigidity and resistance to hydrolytic and thermal degradations. This paper presents the results of comprehensive thermogravimetric analysis and hydrolytic stability studies of the sulfonated resins and their sodium salts and attempts to rationalize the observed features on the basis of the structural characteristics of the resins.

EXPERIMENTAL

Materials. The detailed syntheses of the modified PS polymers by electrophilic substitution with phthalic anhydride pyromellitic dianhydride [2], trimellitic anhydride [3], cis-1,2,3,6-tetrahydrophthalic anhydride [4], and the corresponding sulfonated resins [1, 4, 5] therefrom were described in earlier publications. The pertinent physicochemical properties of the resins used in this study are shown in Table 1.

IR Spectra. All IR spectra were recorded on a Perkin-Elmer 237B Grating IR spectrophotometer from KBr pellets.

Elemental Analyses. Estimation of sulfur in the polymers was done by a standard method [6].

Evaluation of Total Ion-Exchange Capacity. The total ion-exchange capacity was determined by a recommended procedure [7, 8].

Thermal Characteristics. The TGA of polystyrene-phthalic anhydride-sulfonated resin (PSPAS) and of polystyrene-tri-

TABLE 1. Physicochemical Characteristics of Anhydride-Modified Polystyrene Sulfonated Resin

Resin	Physicochemical characteristics		Sulfur content (%)
	Total ion-exchange capacity (meq/g)	Salt-splitting capacity (meq/g)	
Polystyrene-pyromellitic dianhydride-sulfonated (PSPMDAS)	5.75	4.58	16.42
Polystyrene-phthalic anhydride-sulfonated (PSPAS)	5.79	5.42	23.35
Polystyrene-trimellitic anhydride-sulfonated (PSTMAS)	5.49	4.98	15.58
Polystyrene-tetrahydro phthalic anhydride-sulfonated (PSTHPAS)	5.74	5.22	20.60

mellitic anhydride-sulfonated resin (PSTMAS) were studied both in
air and nitrogen with a Stanton Red-Croft TG-750 (U.K.) model up to
~1000°C. The DTA of these resins were studied with Shimadzu, Ther-
mal Analyzer, DT-30 (DTA = ±100 μV) over temperatures up to 800°C
·in nitrogen atmosphere.

The TGAs of polystyrene-tetrahydrophthalic anhydride-sulfonated
resin (PSTHPAS) and of polystyrene-pyromellitic dianhydride-sul-
fonated resin (PSPMDAS) have been reported elsewhere [4, 5], and
they will be referred to for comparative evaluation.

Both the TGA and DTA of the Na forms of the resins PSPAS, PSTMAS,
and PSTHPAS were studied with Shimadzu Thermal Analyzer specifica-
tion, as above, over temperatures up to 900°C in a nitrogen atmosphere.
In all cases the heating rate was 10°C/min.

Isothermal Degradation Studies. Known weights of the
resins in the H-form were heated in air and in a nitrogen atmosphere
in a Muffle furnace at 250 ± 10°C. At time intervals of 12, 24, and 72
h, the weight losses, sulfur contents, and the ion-exchange capacities
of the resins were determined. The IR spectra of the resin residue
left after 72 h of isothermal heating were recorded, and the pH titration
patterns of them were also obtained following the usual procedure [7-9].

Thermal Stability in Water. Known weights of the resins
were treated with 25 mL of deionized water in different glass ampules,
which were then sealed and heated at desired temperatures for a period
of 24 h. The contents were then removed, washed, and dried, and the
ion-exchange capacities were evaluated.

RESULTS AND DISCUSSION

Thermal Analysis Studies of the Resins (H forms)

Thermogravimetric Analyses. Figure 1 presents the
thermograms of PSPAS and PSTMAS in air and nitrogen, respectively.
Table 2 compares the thermal stabilities of PSPAS and PSTMAS with
the corresponding data for PSPMDAS and PSTHPAS. Figure 1 reveals
that PSTMAS is somewhat more stable than PSPAS, both in air and
nitrogen. Table 2 suggests the following order of thermal stability for
the resins: PSPMDAS > PSTHPAS > PSTMAS > PSPAS.

The highest thermal stability of PSPMDAS relative to others is
justified in terms of the polymer structure [5] suggested for PSPMDAS
(Fig. 2). There is apparently more interchain cross-linking in
PSPMDAS than in the others, and particularly in PSPAS, which con-
tributes to a major extent to the overall thermal stability of PSPMDAS.

DTA Characteristics. Figure 3 presents DTA traces for
PSPAS and PSTMAS, while Table 3 summarizes the DTA characteris-
tics of PSPAS, PSTMAS, PSTHPAS, and PSPMDAS resins in the H form.
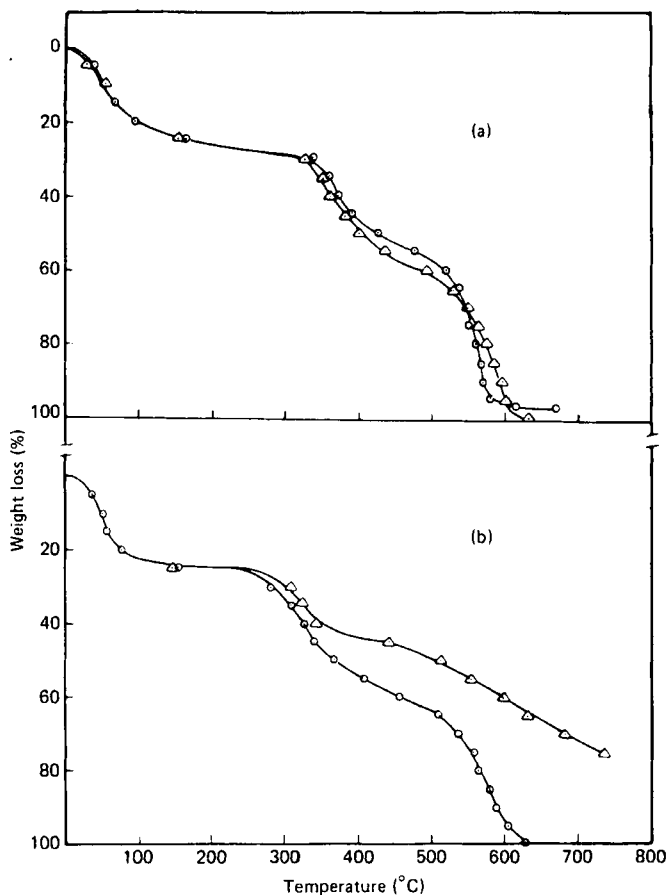The endothermic humps around 70-90°C for PSPAS and PSTMAS, ap-

FIG. 1. TGA curves of PSPAS (⊙) and PSTMAS (▲); in air (a) and in nitrogen (b).

parently corresponding to dehydration of the resin [10, 11] which oc- curs at higher temperatures, viz., 120-140°C for PSTHPAS and PSPMDAS. These data imply that the resins absorb moisture to vary- ing extents depending on the network structure. The exothermic ef- fects above 400°C are common in all the resins, irrespective of the atmosphere of heating. The maximum exothermic effects correspond to a weight loss of ∼62 and 53% for PSPAS and PSTMAS, respectively.

The appreciable weight loss accompanying the strongly exothermic reactions indicates that the polymer matrices undergo oxidative de- gradation in both air and nitrogen atmospheres. The formation of H_2SO_4 and the evolution of SO_2 during thermal decomposition of

TABLE 2. Comparative Evaluation of Thermal Stabilities[a] of Resins in H- and Na-forms

Polymer	Temperature (°C) for weight loss (%)				
	20	40	50	70	Constant weight loss
PSPAS (H form)	75	311	366	536	629 (100%)
PSPAS (Na form)	425	540	800	840	850 (57%)
PSTMAS (H form)	94	341	511	676	734 (75%)
PSTMAS (Na form)	300	530	785	795	810 (78%)
PSTHPAS (H form)	107	331	420	739	896 (75%)
PSTHPAS (Na form)	460	775	795	860	900 (75%)
PSPMDAS (H form)[b]	237	361	637	-	895 (58%)
PSPMDAS (Na form)[b]	-	545	755	-	800 (54.5%)

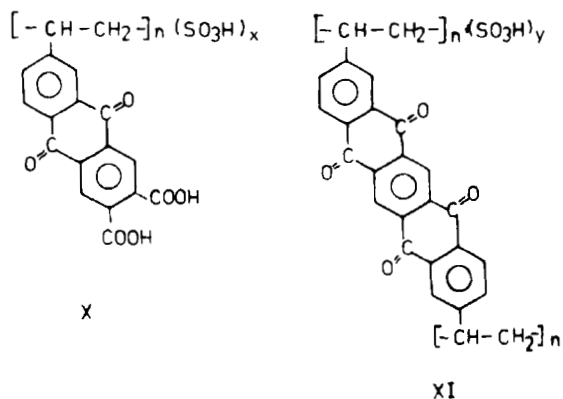[a]All measurements in nitrogen atmosphere.
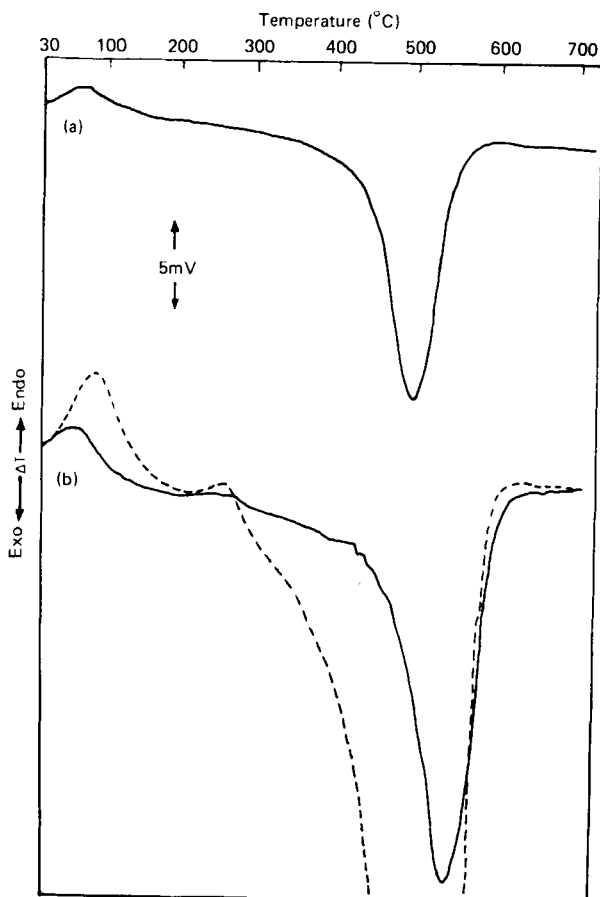[b]In air [4, 5].

FIG. 2. Quinonic structures of PSPMDAS.

FIG. 3. DTA curves of PSTMAS (a) and PSPAS (b); (—) 4.99 mg PSPAS and (--) 16.25 mg PSPAS.

S-DVB sulfonic acid resins have been demonstrated by several workers [10, 11, 14, 15]. Accordingly, the following mode of thermal decomposition for the anhydride-modified PS resins is offered under the present circumstances. After an initial moisture loss, the resins undergo such desulfonation reactions as [11, 14]
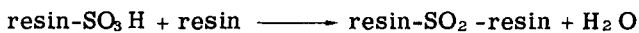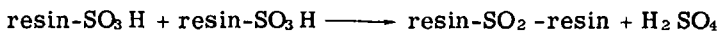
$$resin\text{-}SO_3 H + resin\text{-}SO_3 H \longrightarrow resin\text{-}SO_2\text{-}resin + H_2 SO_4$$

$$resin\text{-}SO_3 H + resin \longrightarrow resin\text{-}SO_2\text{-}resin + H_2 O$$

TABLE 3. DTA Characteristics of the Resins (H forms)

| Resin | DTA peak at temperatures (°C) | |
	Endothermic	Exothermic
PSPAS	70	530 (sharp)
PSTMAS	70	490 (sharp)
PSTHPAS[a]	120	470 (sharp)
PSPMDAS[a]	140	240 (broad)
		405 } (sharp)
		520

[a]DTA recorded in a MOM Derivatograph under oxygen [4, 5].

beyond ~ 300°C. These reactions are endothermic, while the present decomposition reveals strongly exothermic peaks at higher temperatures (430-540°C). For PSPAS a feeble endo effect is shown around 260°C as revealed by the dotted curve of Fig. 3. This tendency is followed by the appearance of a strongly exothermic peak between 430 and 540°C. This suggests that endothermic desulfonation is dominated by some exothermic degradation processes. At temperatures > 430°C, the resins appear to undergo decomposition along with the carbonyl groups of quinonic structures [1, 5] (Fig. 2), which is subsequently followed by oxidation to aromatic carboxylic acids under the oxidizing action of the H_2SO_4 formed in the system. This reaction is apparently favored at this high temperature. Similar trends are exhibited in all four resins.

Isothermal Decomposition of the Resins

Additional support for the decomposition processes suggested above is available from the results of the decomposition studies of the resins in isothermal conditions for sustained periods. Table 4 summarizes the effect of heating the resins in air at 150 ± 10°C for different time intervals; 14, 24, 32, and 72 h. Changes in the total ion-exchange capacity and the sulfur content of the resins have also been recorded as a function of time (Table 5). The IR spectra of the resins left after 72 h of heat treatment were also recorded and compared with the IR spectra of the original resins (Fig. 4).

These data reveal that, in general, 60 to 70% degradation occurs for all the resins in 14 h; about 25% of PSPMDAS is retained even after 72 h as against 10% of the other three resins. The sulfur content of the resins consistently decreases with the time of isothermal heat-

TABLE 4. Temperature of Isothermal Heating and the Weight Loss of the Resins

Resin	% Weight loss at different time (h)			
	14	24	36	72
PSPAS	64.8	64.8	77.8	89.4
PSTMAS	72.2	73	74.9	89.1
PSTHPAS	62.8	63.2	73.8	85.8
PSPMDAS	70.9	71.3	71.9	73.9

TABLE 5. Sulfur Content and Total Ion-Exchange Capacity of the Resins after Isothermal Heating[a]

Resin	% Sulfur at different heating times (h)			Total ion-exchange capacity (meq/g) at different heating times (h)		
	Nil	24	72	Nil	24	72
PSPAS	23.35	8.51	3.14	5.80	4.12	6.54
PSTMAS	15.58	8.92	3.84	5.49	5.37	7.12
PSTHPAS	20.60	10.30	7.14	5.74	5.03	6.50
PSPMDAS	16.42	7.14	5.49	5.75	4.72	5.56

[a]$250 \pm 10°$C.

ing. PSPAS and PSTMAS undergo nearly 80% sulfur loss in 72 h as against 65% for PSPMDAS. Thus, all these features establish the higher stability of PSPMDAS in this series.

Remarkably, the total capacity of the resin during isothermal heating first shows a decrease at 24 h and then increases again to a value numerically greater than the ion-exchange capacity of the original resin.

The IR spectra of the resins left after 72 h of isothermal heating suggest: 1) the C=O stretching for the quinonic structure (1710 cm^{-1}) appreciably decreases; 2) the $-SO_3$H stretching bands at 1040 and 1200 cm^{-1} practically disappear; 3) the $-COOH$ stretching at 1700 cm^{-1} appears after isothermal heating in all cases; 4) isothermal heating of
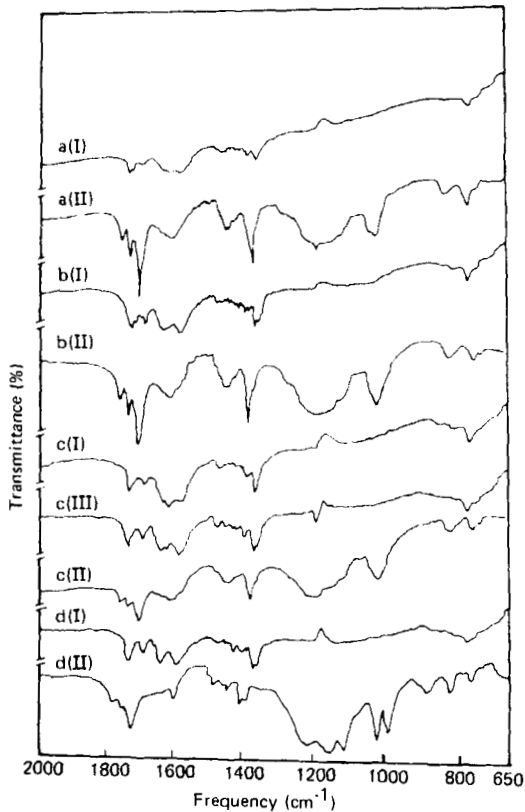
FIG. 4. IR spectra of initial (II) and degraded resins (I): PSPAS
(a), PSTMAS (b), PSTHPAS (c), PSPMDAS (d), PSTHPAS (nitrogen)
c(III).

PSTHPAS in nitrogen and air for 72 h does not reveal any change in
the IR spectra (Fig. 4, C(I) and C(II)).

To identify the nature of the resin left after isothermal degradation
studies, pH-metric titration was performed (Fig. 5). The weak acid
nature of the material is quite apparent from the titration curve,
which is characteristically different from the original pH-metric titra-
tion curve obtained for PSPMDAS as a typical case.

The initial loss in the total ion-exchange capacity is ascribed to
the loss of sulfonic acid groups from the resin. The subsequent in-
crease is due to the formation of aromatic COOH groups in the de-
graded product as envisaged above. Biswas and Packirisamy [12] re-
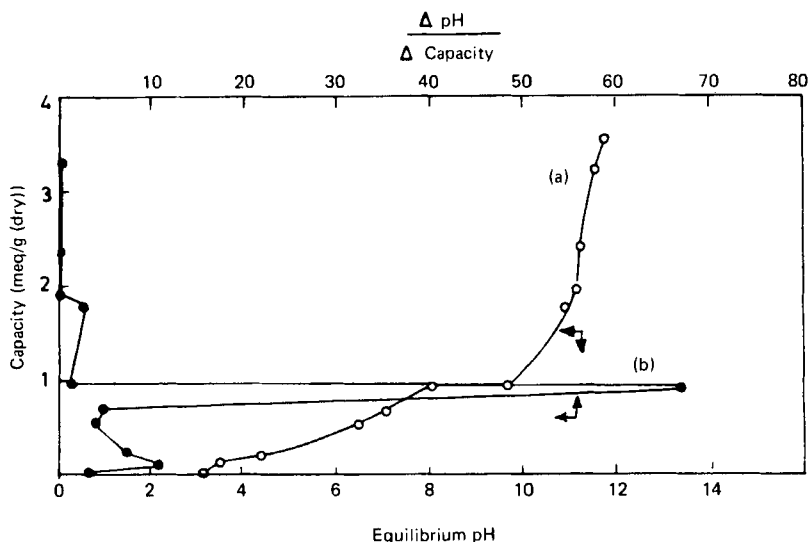ported a similar increase in the ion-exchange capacity of poly(N-

FIG. 5. pH-metric titration of PSPMDAS after isothermal heating for 72 h at $150 \pm 10°C$; pH capacity curve ($\circ$), differential curve ($\bullet$).

vinylcarbazole-furfural-phosphorylated) resin due to $-COOH$ group formation [12, 13].

Thermogravimetric and DTA Analysis of the Sodium Salts of the Resins

Table 2 compares the thermal stability of the H forms and the Na forms of the sulfonated resins. The resin salts consistently exhibit significantly higher thermal stability than H forms of the resins. This observation endorses the conclusions of Bothe et al. [11] and Korshak et al. [10] in their studies on S-DVB sulfonated copolymers.

On the other hand, the DTA curves of Na forms of the anhydride-modified sulfonic acid resins (Fig. 6) reveal strong exothermic peaks (Table 6) above 400°C, in striking contrast to the sharp exothermic peaks reported for S-DVB sulfonated resins. Compared to the H forms of the resins (Table 3), the sharp exothermic peaks of the Na forms appear at significantly higher temperatures, $\sim 700°C$, in all four resins, although the decomposition processes appear to start at 450°C. The maximum weight loss occurs between ~ 750 to 850°C in all cases.

Karpov et al., [14] pointed out that in PS-DVB sulfonated resins, probable reactions such as

$$resin\text{-}SO_3 \ Na + resin\text{-}SO_3 \ Na \longrightarrow resin\text{-}SO_2 \text{-}resin + Na_2 \ SO_4$$
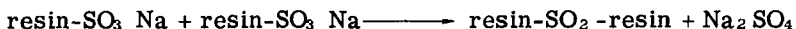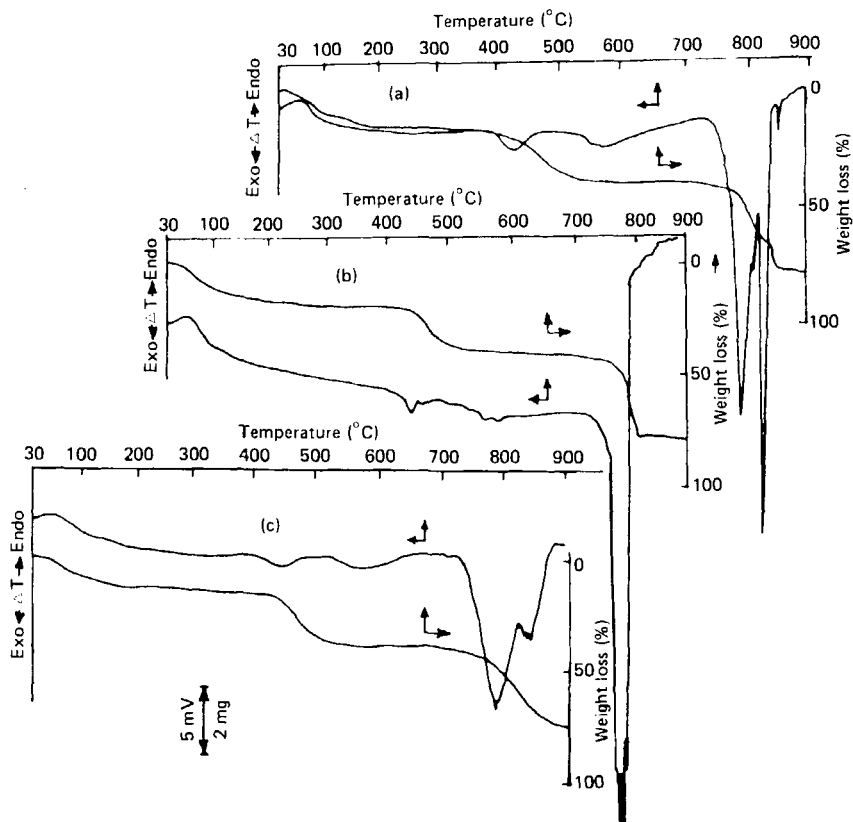
FIG. 6.   DTA and TGA curves: Na form of PSPAS (a), Na form of
PSTMAS (b), and Na form of PSTHPAS (c).

occur at higher temperatures than the corresponding reactions of the
H form resins. Similarly, in the present case, all degradations are
expected to occur at elevated temperatures while the nature of the
degradation reactions involved should remain essentially the same
as in the cases with H-form resins.

Isothermal Decomposition in Water

Table 7 presents relevant data on the isothermal decomposition
of PSPAS, PSTMAS, and PSTHPAS resins at 60, 80, and 100°C. All
the resins undergo losses in ion-exchange capacity in the presence
of water, apparently due to the hydrolysis of the ionogenic groups
[14, 15]:

TABLE 6. DTA Characteristics of the Resins (Na forms)

	DTA peak at temperatures (°C)	
	Endotherm	Exotherm
Resin	60	430 (small 780 and 820 sharp)
PSTMAS	60	440 (small) 560-580, 770 (sharp)
PSTHPAS	50-60	440 (small) 580 (small) 780 (sharp)
PSPMDAS[a]	150	460 (sharp) 755 (sharp)

[a]DTA recorded in a MOM Derivatograph in oxygen [4, 5].

TABLE 7. Isothermal Stability[a] of PSPAS, PSTMAS, PSTHPAS, and PSPMDAS[b] in the Presence of Water

Resin	Temperature (°C)	Total ion-exchange capacity (meq/g)		% Loss in ion-exchange capacity
		Before heating	After heating	
PSPAS	60	5.80	5.75	0.87
	80	5.80	5.02	13.50
	100	5.80	4.80	17.24
PSTMAS	60	5.69	5.49	No loss
	80	5.49	4.71	14.2
	100	5.49	4.66	15.11
PSTHPAS	60	5.74	5.64	1.70
	80	5.74	4.75	17.31
	100	5.74	4.75	17.31

[a]All samples were heated with deionized water in sealed ampules for 24 h.
[b]PSPMDAS undergoes ~3.5% ion-exchange capacity loss after isothermal heating in water at 100°C for 24 h [5].

resin-SO_3H + H_2O $\rightleftharpoons$ resin + H_2SO_4

The loss in the ion-exchange capacity at $100°C$ amounts to $\sim 17\%$ in all cases except for PSPMDAS [5] where only a $\sim 3.5\%$ loss is realized under otherwise identical conditions. This implies that the above reaction is less favored in the PSPMDAS matrix due to its highly cross-linked nature which discourages the diffusion of water to a greater extent at the sites of sulfonation in the polymer matrix.

CONCLUSION

Sulfonic acid resins processed from PS modified electrophilically with PA, PMDA, TMA, and THPA generally exhibit higher thermal stability than PS. PMDA-modified PS sulfonated resin possesses the highest thermal stability in the series due to its more cross-linked structure. DTA studies reveal exothermic oxidative degradation for these resins beyond $400°C$, in contrast to the endothermic reactions undergone by conventional S-DVB sulfonated polystyrene.

ACKNOWLEDGMENTS

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