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THERMAL ANALYSIS OF MACROMOLECULAR "HALOAMINES"

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The TG, DTG and DTA curves of macromolecular macroporous N-halogeno- and N,N-dihalogenosulfonamides are reported and interpreted. To compare their thermal behaviour with that of their unfunctionalized matrices, analogous studies were performed on the porous styrene-divinylbenzene (20%) copolymer and its sulfonamide derivative.

Styrene-divinylbenzene (St-DVB) copolymers are widely used in the manufacture of ion-exchangers and specific reactive polymers [1]. Starting from a macroporous sulfonic cation-exchange resin, Wofatit KS 10*, we have obtained [2] N-monohalogeno- and N,N-dihalogenopoly(St-DVB) sulfonamides containing the following functional groups:

$$\textcircled{\text{P}} - SO_2NXM \qquad \text{and} \qquad \textcircled{\text{P}} - SO_2NX_2$$

where $\textcircled{\text{P}}$ = St-DVB matrix, X = Cl, Br or I, and M = metal cation.

Owing to the presence of halogen atoms with oxidation number +1 covalently bound to the nitrogen atom, these copolymers have bactericidal, disinfectant and oxidative properties. In this respect they resemble the low-molecular chloramines, e.g. Chloramine T or Dichloramine B. Moreover, these copolymers can serve as halogenating reagents and some of them as cation-exchangers. Thus, macromolecular chloramines are interesting from both scientific and technological aspects. Their main advantage (in comparison to low-molecular halogenosulfonamides) is the possibility of easy separation from treated liquids.

The purpose of this study was to establish the thermal behaviour of the halogenosulfonamides obtained. Thermal analysis by means of thermogravimetric (TG, DTG) and differential thermal analysis (DTA) methods were performed. In order to obtain comparative data, similar studies were carried out on a non-halogenated copolymeric sulfonamide and on the unfunctionalized St-DVB matrix itself.

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Experimental

Materials

All the copolymers tested (spherical beads, Ø 0.8–1.0 mm) have a common matrix, i.e. St–DVB copolymer (ca. 20% DVB) with a macroporous structure. The preparation and the properties of the macromolecular halogenosulfonamides were reported earlier [3, 4]. The unfunctionalized St-DVB copolymer and Wofatit KS-10 were supplied by Chemiekombinat Bitterfeld, GDR. Samples of the resins were thoroughly powdered and vacuum-dried before each measurement.

Thermal measurements

The TG-DTG-DTA measurements were run with 200 mg samples in air at a heating rate of 10 deg $\min^{-1}$ in the range 20–1000° under a constant flow of air ($2\cdot 10^4$ cm^3 h^{-1}), on an OD 102 derivatograph (MOM, Budapest), using ceramic crucibles. Al_2O_3 was applied as reference substance.

Results and discussion

The DTG and DTA peak temperatures and peak widths and the TG plateaus are presented in Table 1. Kinetic parameters for all decomposition steps will be published elsewhere. Typical TG-DTG-DTA curves are given in Figs 1–8.

Table 1 Thermal behaviour of N-halogeno-poly/St-co-DVB/sulfonamides (Abbreviations: w=weak, s= strong, v=very, m=medium)

The kind of copolymer	Plateaus in TG, °C	Peaks in DTG, °C	Peak width in DTG, °C	Peaks in DTA, °C	Thermal effect	Peak width in DTA, °C
St-DVB	upto 140	200 w	140 260	200	endo	30–300
(20%)	480–560	420 vs	260–480	410	endo	300–490
		700 w	560–790	530	endo	490–600
				720	exo	600–810
			residue 0%			
Ⓟ–SO_2NH_2	upto 100	140 w	100–160	200	endo	60–340
	160–280	375 vs	280–460	380	endo	340–440
	above 460			480	exo	460–490
				above 500	exo	500–1000
			residue 6.9%			

The kind of copolymer	Plateaus in TG, °C	Peaks in DTG, °C	Peak width in DTG, °C	Peaks in DTA, °C	Thermal effect	Peak width in DTA, °C
Ⓟ–SO_2NClNa	upto 30	120 s	30–200	120	endo	30–170
	200–310	380 s	310–460	260	endo	170–360
		760 s	620–780	440	exo	360–480
	460–620			580	exo	480–620
	above 780			700	exo	620–760
			residue 14.9%			
Ⓟ–SO_2NClH	upto 50	120 m	50–200	125	endo	30–200
	200–300	380 vs	300–460	260	endo	200–330
	460–1000			370	endo	330–405
				800	exo	405–1000
			residue 0%			
Ⓟ–SO_2NCl_2	upto 60	120 m	60–160	140	endo	30–200
	220–305	200 m	160–220	170	endo	200–340
		370 s	305–480	370	endo	340–390
	above 480			720	exo	390–850
			residue 7.5%			
Ⓟ–SO_2NBrK	upto 60	120 m	60–180	120	endo	30–180
	180–270	340 s	270–400	250	endo	180–300
	400–450	530 w	450–570	400	exo	300–500
	570–670	740 w	670–760	530	exo	500–600
				700	exo	650–800
			residue 12.5%			
Ⓟ–SO_2NBr_2	upto 80	160 s	80–200	105	endo	30–180
	200–300	340 s	300–400	220	endo	180–300
	400–450	530 vw	450–600	550	exo	340–1000
	over 600					
			residue 14.5%			
Ⓟ–SO_2NINa	upto 40	140 m	40–230	120	endo	30–170
	230–300	360 s	300–440	270	endo	220–300
	440–540	570 w	540–600	420	exo	300–500
	600–720	760 m	720–790	570	exo	550–620
	above 780			760	exo	640–760
			residue 7.5%			

The highly porous St-DVB copolymer tested (Fig. 1) is stable up to 140°, where a slight weight loss can be noticed. This endothermic process is probably due to the evolution of the residual organic diluent used by the manufacturer to generate the macropores. This is accompanied by an endothermic process of pore breakdown. In the range 260–480°, the main endothermic destruction occurs, which is probably due to depolymerization of the copolymer and elimination of styrene vapour. The solid residue probably melts at 490–600° as indicated by the endothermic effect without weight loss. Above this temperature, the residue burns, showing an exothermic peak as expected, until no matter remains.

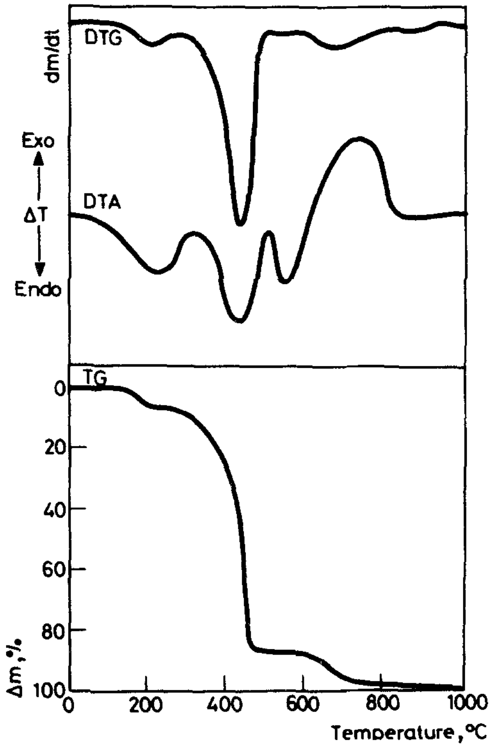

Fig. 1 TG, DTG and DTA curves of St-DVB copolymer Wofatit type

The *sulfonamidic derivative of the St-DVB copolymer* (Fig. 2) loses some volatile matter and the pores break down in an endothermic process. In this case, these processes proceed at a somewhat higher temperature than for the parent copolymer. Above 280°, the main destruction process takes place, similarly as for the parent copolymer, but in a smaller range of temperature, due to the activating effect of the functional groups. On the other hand, in the case of the sulfonamidic derivative a notable amount of solid matter remains, which contains sulfur and nitrogen. Afterwards, a short but marked exothermic effect is observed, without weight loss. This is a result of reoxidation of sulfur compounds, reduced during the earlier stage of depolymerization. Oxidative exothermic destruction then occurs, yielding a coke-like residue of 6.9% in which sulfur is still present.

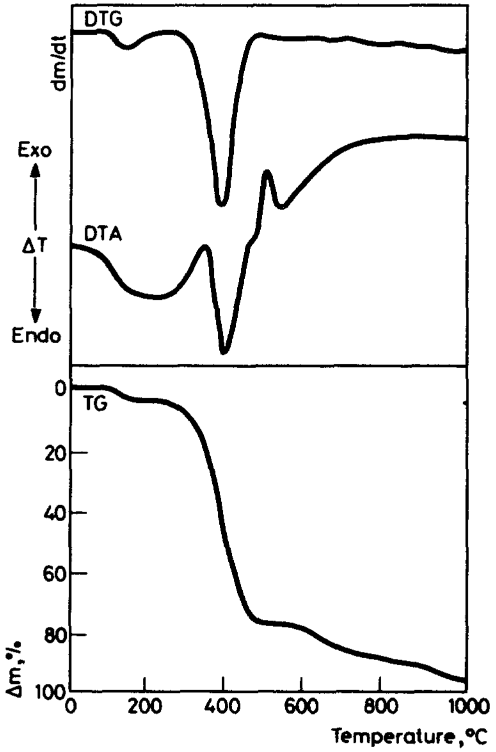

Fig. 2 TG, DTG and DTA curves of poly(St-co-DVB)sulfonamide

The *sodium salt of macromolecular "monochloramine"* (Fig. 3) shows a marked endothermic weight loss of 18.4% in the interval 30° to ca. 200°. This is connected with the evolution of water molecules linked with the functional groups. This water loss is followed by an endothermic peak combined with a very small mass decrease, which is due to the low molecular matter evolution, and the breakdown of pores. The subsequent exothermic process, with a marked weight loss of 20.2%, comprises a complicated simultaneous depolymerization and chlorination process, where the chlorine remains in the solid phase. Thus, the mass loss is much smaller than

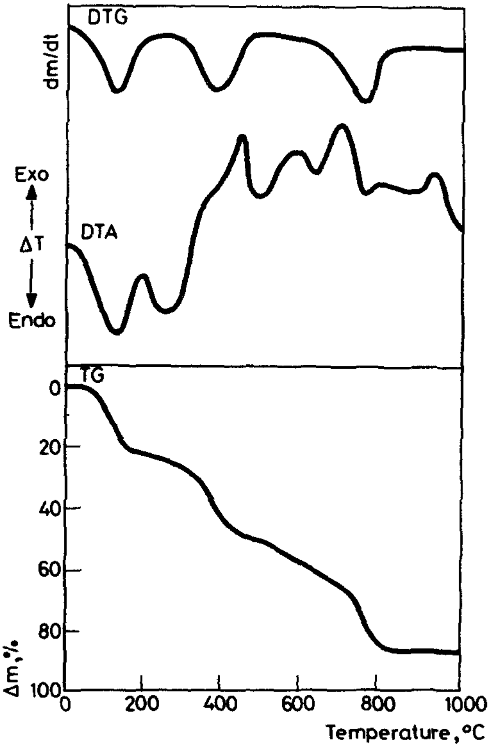

Fig. 3 TG, DTG and DTA curves of sodium N-monochloro-poly(St-DVB) sulfonamide

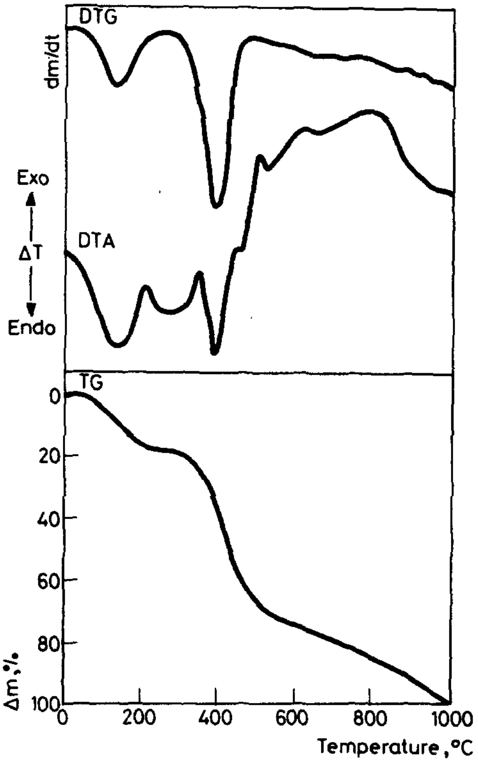

Fig. 4 TG, DTG and DTA curves of hydrogen N-monochloro-poly(St-DVB) sulfonamide

in Figs 1 and 2. An exothermic destruction process follows, separated by non-exothermic isomerization processes. Finally, at 760°, "burning-out" takes place and NaCl remains as residue (14.9%) in the crucible.

Figure 4 gives the thermal curves of the hydrogen form of the functionalized copolymer presented in Fig. 3. In this case, no solid residue was recorded at 1000°, since no mineral substances were present in the tested sample and the active chlorine helps to oxidize all organic matter. Up to 300°, this copolymer behaves similarly to the corresponding sodium form: it loses water linked with the functional groups. Next, the effects are similar to those in Figs 1–3. However, during the depolymerization step, volatile products arise, and hence there is a mass loss.

The *macromolecular "dichloramine"* (Fig. 5) displays a TG step at ca. 120°, like all the other copolymers. Further, a short DTG peak occurs

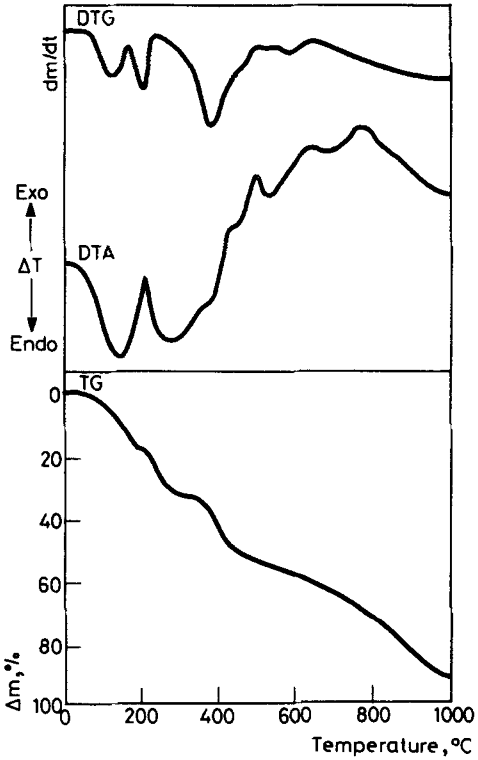

Fig. 5 TG, DTG and DTA curves of N,N-dichloro--poly(St-DVB) sulfonamide

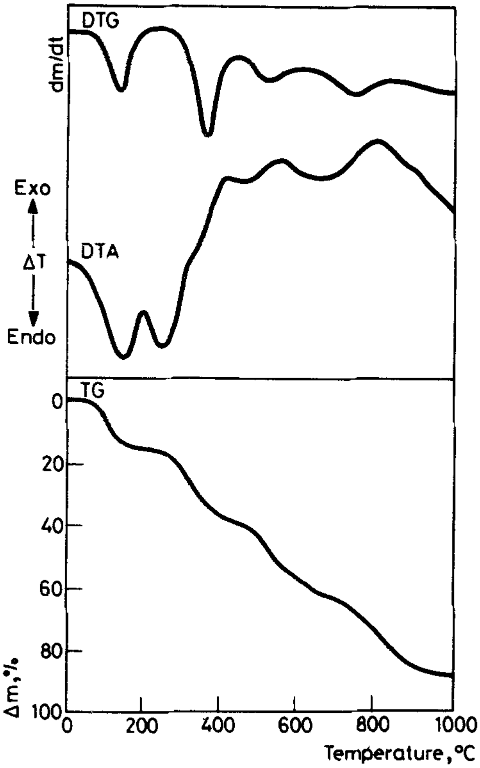

Fig. 6 TG, DTG and DTA curves of potassium N-monobromo-poly(St-DVB) sulfonamide

without any DTA effect, whereafter the known endothermic effect at 200–340° with a small weight loss is observed. The endothermic DTA peak at 340–390°, accompanied by a strong mass loss, corresponds to the depolymerization process. Subsequently, the curves resemble those of Fig. 4.

The thermal behaviour of the *salt of the macromolecular monobromosulfonamide* (Fig. 6) is similar to that of the corresponding chloro- (Fig. 3) and iodo- (Fig. 7) derivatives. Whereas the amount of residual NaCl agrees with the theoretical prediction, the NaBr and NaI residues are much smaller, than predicted. The reason for this is that bromine and iodine undergo intramolecular halogenation, forming volatile compounds.

The thermoanalytical curves of the *dibromosulfonamide* (Fig. 8) resemble those of the dichlorosulfonamide (Fig. 5).

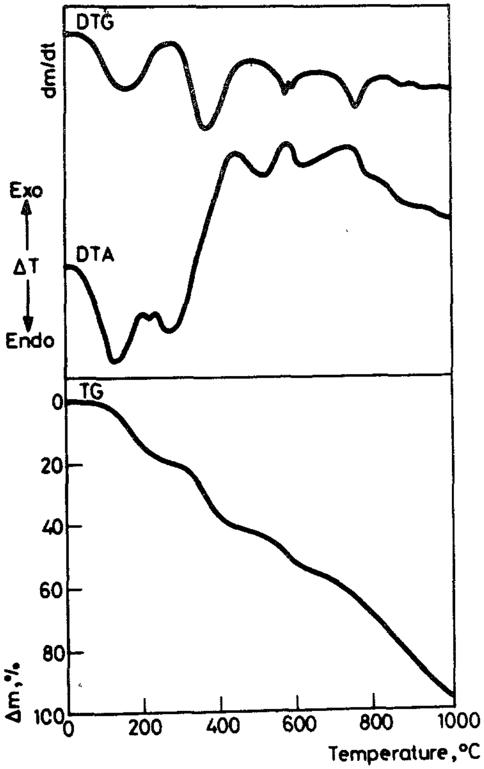

Fig. 7 TG, DTG and DTA curves of sodium N-monoiodo-poly(St-DVB) sulfonamide

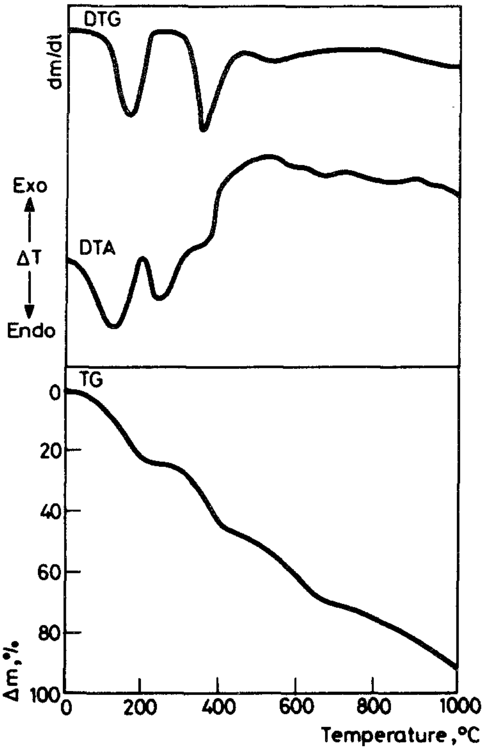

Fig. 8 TG, DTG and DTA curves of N,N-dibromo-poly(St-DVB) sulfonamide

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Zusammenfassung – Die TG-, DTG- und DTA-Kurven makromolekularer makroporöser N-Halogen- und N,N-Dihalogensulfonamide werden beschrieben und gedeutet. Zum Vergleich wurde das thermische Verhalten des unsubstituierten porösen Styren-(20%)Divinylbenzen-Copolymeren und seines Sulfonamids in gleicher Weise untersucht.

РЕЗЮМЕ — Приведены и обсуждены ТГ, ДТГ и ДТА кривые для макромолекулярных макропористых N-гологен- и N,N-дигалокенсульфамидов. С целью сопоставления их термического поведения с их неактивными незамещенными производными, были проведены аналогичные исследования пористого сополимера стирола и дивинилбензола и его сульфамидного производного.