

MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Thermal Properties of Copolymers of Sodium
2-Acrylamido-2-methylpropanesulfonate
with *N*-Vinylpyrrolidone

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Abstract—Thermal transformations of sodium 2-acrylamido-2-methylpropanesulfonate–*N*-vinylpyrrolidone copolymers of various chemical compositions were studied by thermogravimetric, differential thermal, and thermomechanical analyses within 20–600°C in air. The thermal degradation parameters in various temperature ranges were estimated, as well as the heat resistance of the copolymers.

Random copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (Na-AMS) with *N*-vinylpyrrolidone (VP) are of great technical and medical importance owing to high flocculation [1] and adhesion and antistatic [2], as well as thickening and complexing powers. During preparation, dissolution, and application, these copolymers can be subjected to various thermal impacts, but thermal properties of the copolymers are studied inadequately. Only thermal degradation of poly-2-acrylamido-2-methylpropanesulfonic acid (H-PAMS) [3, 4] and its salts with single- and double-charged cations [5], as well as of poly-*N*-vinylpyrrolidone (PVP) [6, 7], was reported.

In this work, we characterize the thermal properties of Na-AMS–VP copolymers of various compositions in the temperature range 20–600°C and compare them with those for homopolymers, Na-PAMS and PVP.

EXPERIMENTAL

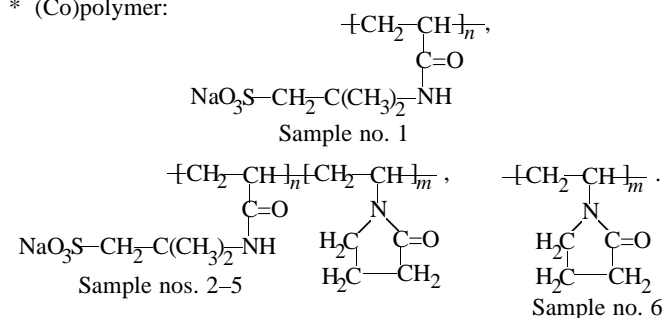
Copolymers of Na-AMS with VP, as well as Na-PAMS, were prepared by radical (co)polymerization in aqueous solutions at pH 9 and 50°C, initiated with potassium persulfate, and PVP, by bulk polymerization at 60°C, initiated with azobis(isobutyronitrile). The procedure of synthesis of (co)polymers was identical to that described in [8]. The resulting (co)polymers were precipitated into acetone, washed with acetone, and vacuum-dried at 50°C to constant weight. Table 1 presents the molecular characteristics of the (co)polymers.

The content of the Na-AMS units in the Na-AMS–VP copolymers was estimated from the sulfur content determined by elemental analysis [9]. The molecular weight MW of the copolymers was estimated from the intrinsic viscosity $[\eta]$, for which the Mark–Houwink equation $[\eta] \sim MW$ holds. The intrinsic viscosity $[\eta]$ was measured in 0.5 M NaCl at 25°C in a VPZh-3 capillary viscometer (capillary diameter 0.56 mm). The intrinsic viscosity $[\eta]$ was determined from the

Table 1. Molecular characteristics of the (co)polymers

(Co)polymer	Sample no.	Content of units, mol %		$[\eta]$, cm ³ g ⁻¹
		Na-AMS	VP	
Na-PAMS	1	100	0	180
Na-AMS–VP	2	52.8	47.2	230
	3	44.1	55.9	120
	4	21.4	78.6	172
	5	8.9	91.1	37
	6	0	100	30

* (Co)polymer:



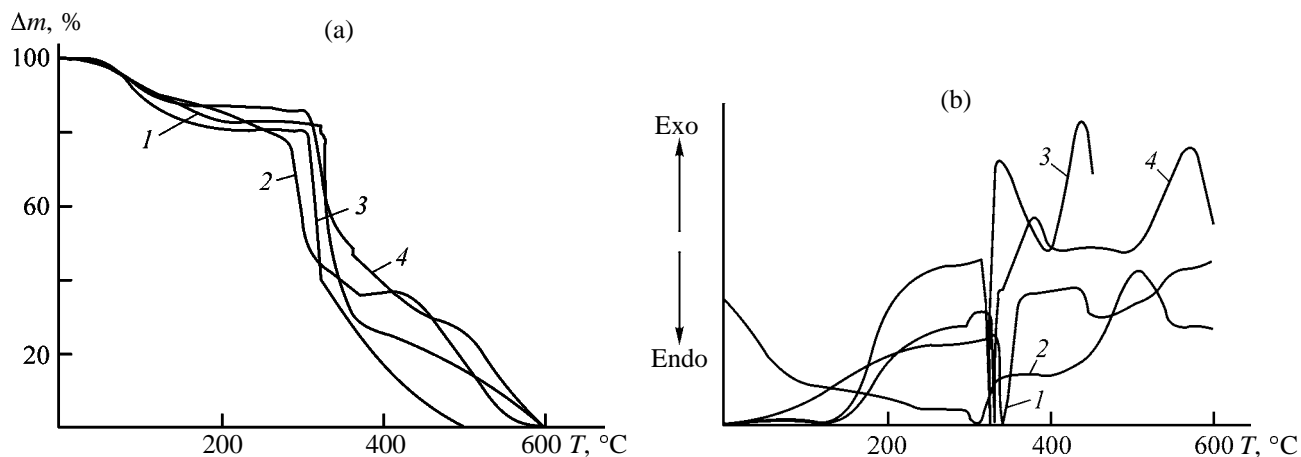


Fig. 1. (a) TG and (b) DTA curves for Na-AMS-VP copolymers. (Δm) Mass loss and (T) temperature; the same for Fig. 2. Sample no.: (1) 2, (2) 3, (3) 4, and (4) 5.

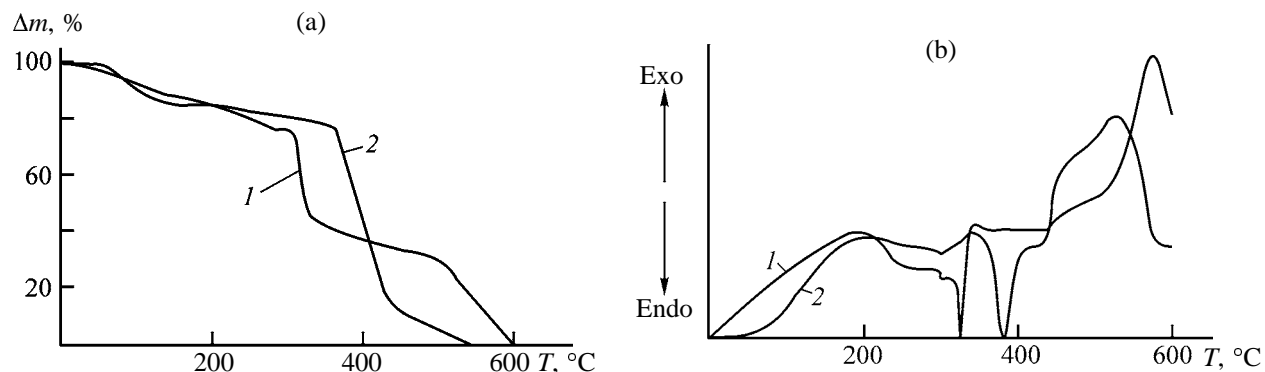


Fig. 2. (a) TG and (b) DTA curves for (1) Na-PAMS and (2) PVP. Sample no.: (1) 2 and (2) 6.

linear plot of (η_{sp}/c_p) vs. c_p , where c_p is the copolymer concentration, and $[\eta] = \lim(\eta_{sp}/c_p)$ at $c_p \rightarrow 0$.

The differential thermal (DTA) and thermogravimetric (TG) analyses were carried out on an MOM derivatograph (heating rate 3 deg min⁻¹ in air; 20-mg weighed portion).

Thermomechanical analysis (TMA) was carried out on a modified Kargin balance at a load of 100 g mm⁻² and a heating rate of 3 deg min⁻¹ in air. The (co)polymer samples were 2-mm-thick films.

The qualitative and quantitative transformations of the (co)polymers in air at 20–600°C were determined from analysis of the DTA and TG curves (see Figs. 1a and 1b for copolymers of Na-AMS with VP and Figs. 2a and 2b for Na-PAMS and VP homopolymers). Table 2 presents the temperature ranges and the mass loss percentages for thermal degradation of the polymer samples. Figures 1 and 2 and Table 2 suggest that thermal transformations of Na-AMS-VP copolymers and PVP include two, and those of Na-PAMS,

three stages. According to the TG curves (Figs. 1a and 2a) and to Table 2, heating of the polymer and copolymer samples is accompanied by gradual mass loss from 40–50 to 150°C, followed by a plateau extending to 295–350°C, depending on the specific polymer sample.

The mass loss recorded in the first stage of degradation for all the polymer samples can, evidently, be due to release of water and volatiles, as well as to partial thermal and (possible in air) thermooxidative degradation of the (co)copolymers. These assumptions were confirmed by identification of the products of thermal degradation of H-PAMS [3, 4] and of depolymerization of PVP within 230–270°C [6]. Also, we did not rule out release of ammonia, yielded by imidization, in the first stage of degradation. This assumption was confirmed by identification of the products of thermal degradation of H-PAMS [3] and polyacrylamide [10].

Further heating leads to the second stage of degradation, when the DTA curves for all the copoly-

Table 2. Temperature characteristics of the (co)polymers*

(Co)polymer	Sample no.	DTA			TG		TMA, T_{soft}
		degradation stage	T , °C	Δm , %	T_{10}	T_{50}	
					°C		
Na-PAMS	1	1	40–307	26	110	320	55
		2	307–500	70			
		3	500–600	100			
Na-AMS–VP	2	1	50–322	18	125	340	57
		2	322–600	100			
	3	1	40–295	25	125	310	61
		2	295–600	100			
	4	1	50–307	19	115	318	60
	2	307–500	100				
PVP	5	1	50–307	15	115	360	–
		2	307–600	100			
	6	1	40–350	21	115	400	57
		2	350–560	100			

* T_{10} , T_{50} are temperatures corresponding to 10 and 50% mass loss, respectively; T_{soft} is the softening point.

meric (Fig. 1b) and polymeric samples (Fig. 2b) exhibit clear endothermic peaks with maxima at various temperatures within 300–405°C, depending on the specific sample. This results in substantial acceleration of the mass loss by copolymers (Fig. 1a) and polymers (Fig. 2a). Above 310–435°C, depending on the specific sample, the mass loss by Na-AMS–VP copolymers and PVP tends to decelerate. At the same time, for Na-PAMS, the third stage of degradation began above 500°C, and the mass loss accelerated again.

More profound, compared to the first stage, transformations of the (co)polymers in the second stage of thermal degradation suggest intensified thermal and thermooxidative degradation, as seen from the DTA and TG curves. This process involves cleavage of the main chains of the macromolecules and imide rings formed in the first stage of degradation. This is accompanied by release of various liquid and gaseous products, in accordance with the published data on thermal degradation of H-PAMS [3, 4] and its salts [5], as well as of PVP [6, 7]. At 500–600°C we observed formation of an insoluble carbon-like powder in all cases.

From the TG curves (Figs. 1a and 2a), we determined the temperatures corresponding to 10 (T_{10}) and 50% (T_{50}) mass loss as the characteristics of the heat resistance of the (co)polymers. The T_{10} and T_{50} parameters are listed in Table 2. Comparison of the T_{10} parameters shows that, at low degradation tempera-

tures, sample nos. 2 and 3 of Na-AMS–3VP copolymers are the most thermally stable among the (co)polymer samples studied by us. Evidently, enhanced thermal stability of sample nos. 2 and 3 having approximately equimolar composition is due to the donor–acceptor interactions between the Na-AMS and VP units in the macromolecules (Na-AMS has a medium electron-acceptor, and VP, a medium electron-donor power). At higher temperatures, as judged from the T_{50} parameters (Table 2), the copolymers become less stable than the homopolymers [except for sample no. 2 having the highest MW among the samples studied by us (Table 1), which is responsible for its slightly higher T_{50} compared to Na-PAMS]. A decrease in the thermal stability of the copolymers at high temperatures is, evidently, due to degradation of the donor–acceptor complexes between the Na-AMS and VP units in the macromolecules.

Figure 3 shows the TMA curves recorded at 20–200°C. It is seen that the strain tends to increase in the course of heating for all the samples. This is due to “defrosting” of the segmental activity of the macromolecules, when softening occurs at the softening point and co(polymer) converts from the glassy to hyperelastic state. Further heating does not change the strain, and the polymer degradation temperature corresponds to the upper limit of the hyperelastic state. Based on Fig. 3, we estimated the softening points (Table 2), which proved to be slightly higher for the copolymers than for the polymers. The highest

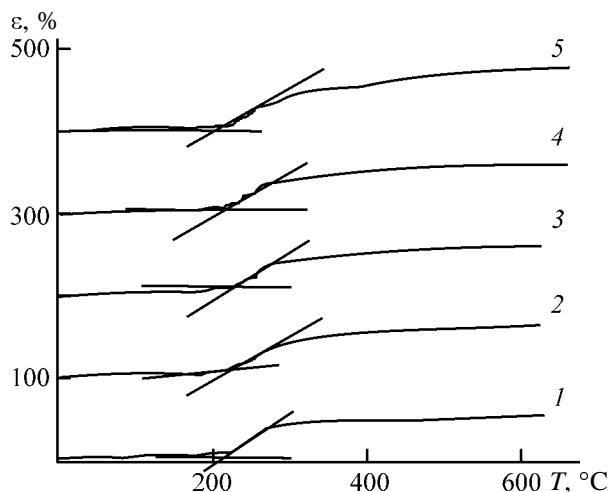


Fig. 3. TMA curves for (1) Na-PAMS, (2–4) Na-AMS–VP copolymers, and (5) PVP. (ϵ) Strain and (T) temperature. Sample no.: (1) 1, (2) 2, (3) 3, (4) 4, and (5) 6.

softening points were recorded for copolymeric sample no. 2. This can be due to formation of donor–acceptor complexes between the Na-AMS and VP units in the macromolecules. However, it is difficult to derive a correlation between the softening point and the chemical composition of the copolymer macromolecules because of the difference in the MWs of the samples (Table 1).

CONCLUSION

The differential thermal, thermogravimetric, and thermomechanical analyses of the copolymers of sodium 2-acrylamido-2-methylpropanesulfonate with

N-vinylpyrrolidone and of the corresponding polymers in air at 20–600°C showed that, at low temperatures, the thermal stabilities and softening points of the copolymers with approximately equimolar compositions are higher than for the other samples studied, but at high temperatures this trend is lost.

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