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THERMAL STABILITIES OF COPOLYMERS OF STYRENE AND METHACRYLIC ACID AND THEIR SALTS

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The thermal stabilities of copolymers of styrene and methacrylic acid and their sodium salts have been studied. The values of the thermal stability IDT, T_s and the kinetic parameters n, E, ΔS and Z have been determined and the results are discussed. It has been found that the thermal stabilities of the investigated copolymers of styrene and methacrylic acid and their sodium salts are practically independent of the amount of methacrylic acid or sodium methacrylate introduced.

The copolymers of styrene and methacrylic acid are used to obtain ionomers. The application of the latter materials demands a knowledge of their thermal stabilities and those of the initial copolymers. The thermal degradations of copolymers of styrene and methyl methacrylate [1] and methyl methacrylate and methacrylic acid [2] have already been studied. Study of the degradation of some ionomers [3–5] indicated the influence of the composition of the macromolecules on the yield and mechanism of the degradation.

The thermal and thermooxidative degradations of copolymers of styrene and acrylic acid and the sodium salts obtained have also been studied [6]. The thermooxidative resistance was found to depend on the amount of introduced acid and the degree of neutralization. The investigations performed by Bukin [7] and Jegorov [8] on styrene ionomers revealed that the thermal and thermooxidative resistance of these salts may or may not depend on the amount and kind of the introduced metal ion.

The purpose of the present study was to establish the correlation between the kinetic thermal stabilities of styrene and methacrylic copolymers and their sodium salts and the amount of acid or salt introduced into the copolymer.

Materials and methods

The copolymers of styrene and methacrylic acid were obtained by copolymerization in emulsion [9]. Suitable salts were then obtained by neutralization [9].

TG, DTG and DTA curves were recorded simultaneously using a Paulik–Paulik–Erdey derivatograph (type OD–102, MOM, Budapest). 100 mg of powdered sample was heated in a Pt crucible over the temperature range 25 to 500° at a constant heating rate of 2.5 deg/min. A controlled dynamic atmosphere of nitrogen (20 l/h) was used in the furnace.

On the basis of the thermogravimetric and DTG curves the following were determined: IDT = initial decomposition temperature, and T_s = temperature where the rate of non-isothermal transformation is highest. The order of reaction n was evaluated according to the Horowitz–Metzger method [10]. The activation energy of decomposition (E) for the polymer was then determined by applying the appropriate Horowitz–Metzger equation. For $n=1$ a plot of log $\log\frac{W_0-W_f}{W-W_f}$ against θ resulted in straight line. The activation energy was calculated from the slope, which was equal to $E/2.303\ RT_s^2$. For $n\neq 1$ a plot of $\log\left[\frac{1-\frac{W-W_f}{W_0-W_f}}{1-n}\right]$ vs. θ was drawn and a straight line of the same slope as in the previous case was obtained.

θ = $T-T_s$,
W_0 = initial mass loss,
W_f = mass loss at the completion of the main reaction stage,
W = mass loss up to temperature T_s.

The preexponential factor Z was the calculated from the equation $\frac{E}{RT_s^2}=\frac{Z}{\Phi}n\, C_s^{n-1}\, e^{-E/RT_s}$, where
Φ = heating rate.

For $n=1$, this reduces to $\frac{E}{RT_s^2}=\frac{Z}{\Phi}e^{-E/RT_s}$.

The entropy of activation (ΔS) was calculated from the equation [11]

$$\Delta S = R\,2.303\log\frac{Zh}{KT_s}$$

where k = Boltzmann's constant, and
h = Planck's constant

Results and discussion

The thermal degradation of the investigated polymers usually takes place in one stage, as indicated by the mass loss, accompanied by an endothermic peak in the DTG curve in the range 390–400°. Table 1 gives values of the thermal stabilities of the copolymers of styrene and methacrylic acid and their sodium salts. These data indicate that the initial decomposition temperatures IDT and temperatures T_s of the copolymers of styrene and methacrylic acid remain almost constant, independent of the amount of methacrylic acid introduced.

Table 1 Thermal stability of the copolymers of styrene and methacrylic acid and their sodium salts

mol, % MA	*IDT*, °C	T_s, °C	mol, % MNa	*IDT*, °C	T_s, °C
—	313	396			
0.78	315	395	0.78	320	395
3.59	315	395	3.59	316	398
6.62	316	395	6.62	316	400
9.95	318	403	9.95	316	398

MA – methacrylic acid
MNa – sodium methacrylate

Table 1 shows that for the sodium salts too *IDT* and T_s remain nearly constant, independently of the amount of sodium methacrylate introduced. These data reveal that the copolymers of styrene and methacrylic acid and their sodium salts in the investigated range of composition have thermal stabilities almost equal to that of polystyrene. This may be due to the contents of acid or salt units, which are not very high in these copolymers. These results are similar to those obtained by Bukin [7] and Jegorov [8], who showed that the thermal resistance of the copolymer of styrene and methacrylic acid (9 : 1) is independent of the amount of sodium ions introduced.

Table 2 shows that the order of reaction for the decomposition of the copolymers of styrene and methacrylic acid is 1/2. All the styrene sodium ionomers have an order of reaction equal to 1 (Table 3).

It is seen from Table 2 that the activation energy of the main decomposition stage remains almost constant, independently of the content of methacrylic acid.

Table 3 indicates that the activation energy values of the sodium salts also remain nearly constant, independently of the amount of sodium methacrylate monomer units. A comparison of the data in Tables 2 and 3 shows that the activation energy values of the sodium salts at a given content of sodium methacrylate are slightly higher than the corresponding values for the copolymers. This may be due to the

Table 2 Kinetic parameters of the thermal decomposition of copolymers of styrene and methacrylic acid

mol, % MA	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
—	1	307	2.49×10^{21}	157.9
0.78	1/2	198	6.89×10^{12}	$-$ 5.82
3.59	1/2	199	8.32×10^{12}	$-$ 4.27
6.62	1/2	190	1.51×10^{12}	$-$ 18.46
9.95	1/2	186	4.44×10^{11}	$-$ 28.75

Table 3 Kinetic parameters of thermal decomposition of styrene sodium ionomers

mol, % MNa	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
0.78	1	251	1.22×10^{17}	75.47
3.59	1	251	9.90×10^{16}	73.70
6.62	1	240	1.14×10^{16}	55.77
9.95	1	219	2.78×10^{14}	24.86

fact in the case of the salts the energy of dissociation of the bond that is breaking during the transition state is higher than for the initial copolymers.

Table 2 shows that the preexponential factor and entropy of activation values of the copolymers of styrene and methacrylic acid decrease with inreasing methacrylic acid content. The ΔS values are negative; this suggests a high ordering of the transition state, probably due to the partial immobilization of neighbouring COOH groups [11, 12].

It is seen from Table 3 that the entropies of activation of the sodium salts have positive values and decrease with the sodium methacrylate content.

The performed studies indicate that the thermal stabilities of the investigated copolymers of styrene and methacrylic acid and their sodium salts are practically independent of the amount of methacrylic acid or sodium methacrylate introduced.

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