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

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The thermal stabilities of copolymers of styrene and acrylic acid and their alkali metal salts have studied.

The thermal stability properties T_i and T_s, and the kinetic parameters n, E, ΔS and Z were determined and the results are discussed. It was found that the thermal stabilities of the investigated copolymers of styrene and acrylic acid are somewhat lower than that of polystyrene and decrease with increase of the quantity of acrylic acid introduced into the copolymers.

The thermal stabilities of the sodium salts of these copolymers are somewhat higher than those of the initial copolymers, and are almost equal to that of polystyrene.

The thermal stabilities of the investigated ionomers depend on the nature of the alkali metal introduced into the copolymer.

During the past 20 years, ionomers have developed into a distinct and promising branch of the polymer field. These are ion-containing polymers, generally copolymers, in which typically the ionizable protons of the acid side-groups are replaced by metal cations.

It has been shown that the incorporation of a relatively small amount of ionic groups into the polymer matrix profoundly changes the structure and physical properties of the material as compared with its non-ionic counterpart [1–4].

In such copolymers, the low dielectric constant of the major component (ethylene, butadiene or styrene) leads to the formation of ion-pairs, which are thought to aggregate further into multiplets of a few ion-pairs or into somewhat larger entities called clusters [5].

The studies [6–9] have shown that in styrene-based ionomers containing methacrylic acid salts the clusters are formed when the concentration of the ionic component exceeds about 6 mol%.

Despite the intensive study of ionomers, in the literature there are relatively few papers concerning the thermal stabilities of ionomers and the copolymers used to obtain these ionomers.

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The thermal degradations of copolymers of styrene and methyl methacrylate [10] and of methyl methacrylate and methacrylic acid [11] have already been studied.

Investigations [12] of the thermal degradation of a copolymer of ethylene and acrylic acid indicated that the degradation mechanism of the acrylic acid portion of the polymer involved dehydration of the acid to give the anhydride, and decarboxylation of the anhydride, leading to unsaturation. The resultant unsaturation reduced the stability of the copolymer towards both thermal and oxidative degradation.

Study of the degradation of some ionomers [13–15] indicated the influence of the composition of the macromolecules on the yield and on the mechanism of the degradation.

The thermal and thermooxidative degradation of copolymers of styrene and acrylic acid and its sodium salts have also been studied [16]. The thermooxidative resistance was found to depend on the amount of introduced acid and on the degree of neutralization.

The investigations performed by Bukin [17] and Jegorov [18] on styrene-based ionomers revealed that the thermal and thermooxidative resistance of these ionomers may or may not depend on the amount and nature of the introduced metal ion.

It has been found [19] that the thermal stability can be influenced by the use of polymer samples with different structures, different molecular distributions or different histories of formation.

It has also been demonstrated that the properties of ionomers depend on the sample history [20].

These purpose of the present study was to establish the correlation between the kinetic thermal stabilities of styrene and acrylic acid copolymers obtained by copolymerization in the mass, their alkali metal salts and the amount of acid or salt introduced into the copolymer.

Experimental

The copolymers of styrene and acrylic acid were obtained by copolymerization in the mass [8, 21].

Suitable ionomers were then obtained by neutralization [8, 21] and were freeze-dried.

All the polymers were dried to constant weight at 50° in vacuum.

The limiting viscosity number (LVN) of the initial copolymers was determined in tetrahydrofuran at $25\pm0.1°$.

The glass transition temperatures (T_g's) of the copolymers of styrene and acrylic acid were determined on a Perkin–Elmer differential scanning calorimeter (model DSC–1) at a heating rate of 8 deg/min.

Thermal methods and calculations

TG, DTG and DTA curves were recorded simultaneously with a Paulik–Paulik–Erdey OD–102 derivatograph (MOM, Budapest). 70 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.

The thermogravimetric and DTG curves were used to determine the following features: T_i (IDT), the initial decomposition temperature, and the DTG peak temperature (T_s) where the rate of non-isothermal transformation is highest. The order of reaction n was evaluated by the Horowitz–Metzger method [22]. 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 $n=1$, a plot of $\log\frac{1-\left(\frac{W-W_f}{W_0-W_f}\right)^{1-n}}{1-n}$ *vs.* Θ was drawn, and a straight line with the same slope as in the previous case was obtained.

$\Theta = T-T_s$,
W_0= initial mass loss,
W_f= mass loss at the completion of the main reaction stage, and
W = mass loss up to the DTG peak temperature (T_s).

The pre-exponential factor Z was then calculated from the equation

$$\frac{E}{RT_s^2}=\frac{Z}{\Phi}nc_s^{n-1}\,e^{-E/RT_s},$$

where Φ = heating rate.

For $n=1$, this reduces to

$$\frac{E}{RT_s^2}=\frac{Z}{\Phi}e^{-E/RT}$$

The entropy of activation (ΔS) was calculated from the equation [23]

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

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

Results and discussion

The properties of the copolymers used in the studies appear in Table 1.

The thermal degradation of the investigated polymers takes place in one stage, as indicated by the mass loss, accompanied by an endothermic peak in the range 365–400° in the DTA curve.

Table 2 gives the thermal stabilities of the copolymers of styrene and acrylic acid and their sodium salts. These data indicate that the initial decomposition temperatures, T_i, and the DTG peak temperatures, T_s, of the copolymers of styrene and acrylic acid show a general weak tendency to decrease with increasing acrylic acid content. These results support the mechanism of degradation described by Gaugh and Kottle [12], for copolymers of ethylene and acrylic acid, and indicate the somewhat lower thermostabilities of the investigated copolymers than that of polystyrene.

Table 1 Data on resulting polymers

mol%, AA	T_g, °C	LVN, dl/g
—	100	1.10
3.85	108	1.12
5.16	111	1.16
6.41	115	1.18
11.67	122	1.18
14.05	126	1.20
22.37	140	1.40

AA = acrylic acid

Table 2 Thermal stabilities of copolymers of styrene and acrylic acid and their sodium salts

mol%, AA	T_i, °C	T_s, °C	mol%, ANa	T_i, °C	T_s, °C
—	335	397	—	—	—
3.85	310	385	3.85	310	395
5.16	310	382	5.16	295	390
6.41	310	380	6.41	295	388
11.67	300	375	11.67	295	387
14.05	300	370	14.05	295	390
22.37	290	368	—	—	—

AA = acrylic acid,
ANa = sodium acrylate,
T_i = initial decomposition temperature,
T_s = temperature of highest rate of non-isothermal transformation

Table 2 shows that for the sodium salts T_i and T_s remain practically constant, independently of the sodium acrylate content. The T_s values are somewhat higher than those for the initial copolymers. These results also indicate that the thermal stabilities of the sodium salts of the copolymers of styrene and acrylic acid are almost equal to that of polystyrene.

Similar results were obtained previously [16] for copolymers of styrene and acrylic acid prepared by copolymerization in an emulsion and for their sodium salts. These results are similar to those obtained for the sodium salts of the copolymers of styrene and methacrylic acid [24] and to those obtained by Bukin [17] and Jegorov [18], who showed that the thermal resistance of a copolymer of styrene and methacrylic acid (9 : 1) is independent of the amount of sodium ions introduced.

Table 3 reveals that the order of reaction for the decomposition of the copolymers of styrene and acrylic acid is equal to 1 and is independent of the amount of acrylic acid introduced into the copolymer.

Table 3 Kinetic parameters of thermal decomposition of copolymers of styrene and acrylic acid

mol%, AA	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
—	1	271	4.17×10^{18}	104.8
3.85	1	280	5.62×10^{19}	126.6
5.16	1	277	4.09×10^{19}	109.3
6.41	1	261	2.38×10^{18}	100.4
11.67	1	214	4.64×10^{14}	29.4
14.05	1	211	3.61×10^{14}	27.4
22.37	1	189	5.92×10^{12}	−6.8

n = order of reaction,
E = activation energy,
Z = pre-exponential factor,
S = entropy of activation

Sodium salts of these copolymers containing below 6 mol% of sodium acrylate have an order of reaction of 3/2, and those containing above 6 mol% have a reaction order of 2 (Table 4). The higher n values for the sodium salts of the copolymers of styrene and acrylic acid suggests a difference in the mechanisms of degradation of the initial copolymers and their sodium salts. Further, the increase in the order of reaction with increasing sodium acrylate content suggests a change in the mechanism of degradation of the salts. This may be due to a change in the state of aggregation of the ions with increasing salt content.

It is known [25] that similar reaction orders indicate the breaking of chemical bonds of the same energy, and in fact the same type of reaction.

Table 4 Kinetic parameters of thermal decomposition of styrene-based sodium ionomers

mol%, ANa	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
3.85	3/2	304	1.95×10^{21}	155.9
5.16	3/2	270	6.03×10^{18}	108.5
6.41	2	281	5.27×10^{19}	126.0
11.67	2	273	1.45×10^{19}	115.3
14.05	2	269	5.14×10^{18}	106.6

It is seen from Table 3 that the activation energies of the main decomposition stage show a tendency to decrease with increasing acrylic acid content.

Table 4 indicates that the activation energies of the sodium salts of the copolymers of styrene and acrylic acid also show a general weak tendency to decrease with increasing sodium acrylate content. A comparison of the data in Tables 3 and 4 shows that the activation energies of the sodium salts at a given content of sodium acrylate are slightly higher than the corresponding values for the copolymers. This may be due to the fact that in the salts the energy of dissociation of the bond that breaks during the transition state is higher than that for the initial copolymers.

Table 3 shows that the pre-exponential factor (Z) and entropy of activation (ΔS) values for the copolymers of styrene and acrylic acid decrease with increasing acrylic acid content. This may suggest a higher ordering of the transition state with increasing acrylic acid content, probably due to the partial immobilization of neighbouring COOH groups [23, 26].

It is seen from Table 4 that the entropies of activation of the sodium salts also decrease with the sodium acrylate content, and are somewhat higher than those for the initial copolymers.

Tables 5 and 6 indicate that the temperatures T_i for the salts with different alkali metals are practically constant and are almost equal to that for the initial copolymer.

Table 5 Temperatures T_i and T_s and kinetic parameters of thermal decomposition of ionomer containing 5.16 mol of salt

	r cationic*, Å	T_i, °C	T_s, °C	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
H^+	—	310	382	1	277	4.09×10^{19}	109.3
Li^+	0.60	312	420	3/2	272	1.13×10^{18}	94.0
Na^+	0.95	295	390	3/2	270	6.03×10^{18}	108.0
K^+	1.33	300	407	3/2	246	2.09×10^{16}	60.7
Cs^+	1.69	300	413	3/2	215	5.70×10^{13}	11.5

* L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960.

Table 6 Temperatures T_i and T_s and kinetic parameters of thermal decomposition of ionomer containing 11.67 mol% of salt

	r cationic, Å	T_i, °C	T_s, °C	n	E, kJ mole^{-1}	Z, s^{-1}	ΔS, J mole^{-1} K^{-1}
H^+	—	300	375	1	214	4.64×10^{14}	29.4
Li^+	0.60	300	412	2	282	1.03×10^{19}	112.1
Na^+	0.95	295	387	2	273	1.45×10^{19}	115.3
K^+	1.33	300	412	2	259	1.75×10^{17}	78.3
Cs^+	1.69	300	425	—	224	4.61×10^{13}	9.6

The temperatures T_s for the salts increase with increase in the radius of the introduced cation and are higher than those for the initial copolymer. This may suggest the higher thermal stabilities of these salts than that of the copolymers.

The studies performed by Krzyszowska [27] indicated that the thermal decomposition of potassium polymethacrylate occurs at lower temperature than that of sodium polymethacrylate. She explained this by a weaker ionic bond between the acid radical and K^+ than in the case of Na^+, since the ionic radius of the former is larger than that of the latter.

Our results may be due to the fact that the introduced ions may form ion-pairs and aggregate further into multiplets of a few ion-pairs into somewhat larges entities (clusters).

Ionomers containing Li^+ ions have distinctive values among the studied polymers. This may be due to the fact, that, as indicated by other authors [28, 29], in the lithium salts the lithium cations and anionic groups are covalent in nature.

It is seen from Tables 5 and 6 that the values of E, Z and ΔS decrease with increase in the radius of the introduced cation. These data indicate that n, E, Z and ΔS change in the same manner below and above 6 mol% of salt, according to the nature of the alkali metal salt.

A comparison of the data in Tables 5 and 6 shows that the introduction of alkali metal ions with increasing cation radius causes a larger increase in T_s for a copolymer with a larger content of acrylic acid.

The studies conducted indicate that the thermal stabilities of the investigated copolymers of styrene and acrylic acid are somewhat lower than that of polystyrene and decrease with increase of the acrylic acid content in the copolymer.

The thermal stabilities of the sodium salts of the copolymers of styrene and acrylic acid are somewhat higher than those of the initial copolymers, and are almost equal to that of polystyrene.

The thermal stabilities of the investigated ionomers depend on the nature of the alkali metal introduced into the copolymer.

These studies may also suggest that, at above 6 mol% of sodium acrylate in the copolymer, the degradation occurs according to a different mechanism.

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Zusammenfassung — Es wurde die thermische Stabilität von Kopolymeren aus Styrol und Acrylsäure bzw. Acrylsäurealkalimetallsalzen untersucht. Die Werte T_i und T_s für die thermische Stabilität sowie die kinetischen Parameter n, E, ΔS und Z wurden bestimmt und die Ergebnisse diskutiert. Man fand, daß die thermische Stabilität der untersuchten Kopolymere aus Styrol und Acrylsäure etwas niedriger ist als die von Polystyrol und daß sie mit einer Zunahme des Anteiles an Acrylsäure an den Kopolymeren absinkt. Die thermische Stabilität der Natriumsalze dieser Kopolymere erwies sich als etwas höher als die die ursprünglichen Kopolymere, erreicht aber nur die von Polystyrol. Die thermische Stabilität der untersuchten Ionomere hängt von der Art der in die Kopolymere eingebrachten Alkalimetalle ab.

Резюме — Изучена термоустойчивость сополимеров стирола и акриловой кислоты и их солей со щелочными металлами. Определены и обсуждены значения термической устойчивости T_i, T_s, а также кинетические параметры E, n, ΔS и Z. Найдено, что термоустойчивость исследованных сополимеров иногда ниже, чем самого полистирола и уменьшается с увеличением содержания акриловой кислоты в сополимере. Термическая устойчивость натриевых солей этих сополимеров иногда выше, чем исходных сополимеров, но почти равна термоустойчивости полистирола. Термоустойчивость исследованных иономеров зависит от типа щелочного металла, введенного в сополимер.