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.
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 ± 0.1°.

The glass transition temperatures ($T_g$'s) of the copolymers of styrene and acrylic