

NOTES

*Investigation of Ionic Copolymers
by Thermal Volatilization Analysis*

Thermal volatilization analysis (TVA) has been described recently as a new method of studying polymer degradation.¹ We have used this technique, as modified in our laboratories, to study the degradation processes of ionic ethylene copolymers. We now wish to report the results obtained from acrylic acid ionic copolymers.

The TVA apparatus in this laboratory utilizes a National Research Corporation Model 701 thermocouple vacuum gage. The vacuum meter is connected to one axis of a Houston Instrument Company, Model HR 92-1, x-y recorder. The remaining axis is used to record the output of an iron-constantan thermocouple, which is located in close proximity to the sample tube. The sample tube is heated at a rate of approximately 10°C./min. The instrumental results are obtained directly in the form of a recording of the pressure as a function of sample temperature.

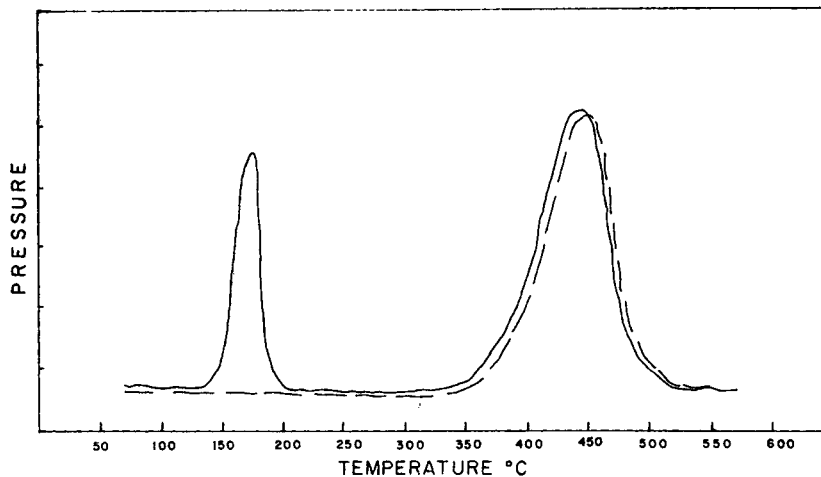


Fig. 1. Pressure-temperature data on hydrogen and salt forms of copolymer: (---) 8% acrylic acid-ethylene polymer; (—) same polymer modified by 20% conversion to sodium salt.

The results given in Figure 1 were obtained from experiments performed on an experimental ethylene-acrylic acid polymer which contained 8 wt.-% acrylic acid. In addition, a curve is shown for the same polymer modified by 20% conversion to the sodium salt. These results show the modified copolymer to have two distinct peaks, whereas the unmodified copolymer exhibits only one peak.

Figure 2 shows a plot of peak area as a function of the extent of modification. The points shown are for the acrylic acid copolymer and for samples in which 20, 60, and 80% of the available acrylic acid groups reacted to the sodium form. Mass spectro-

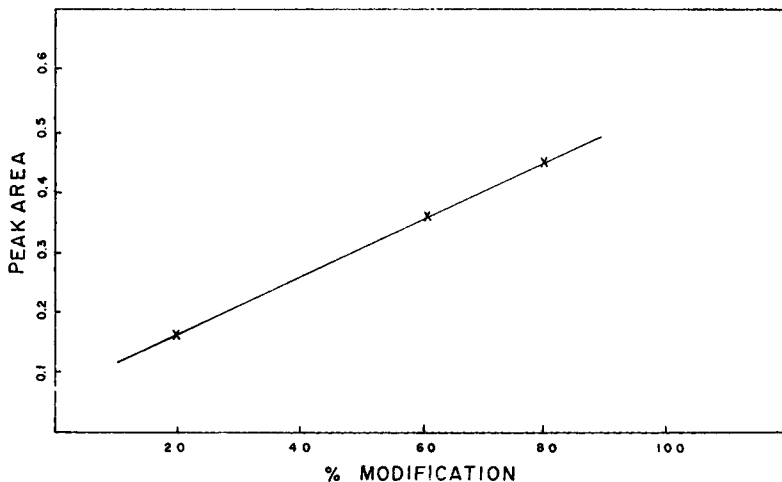


Fig. 2. Peak area versus per cent modification for an acrylic acid-ethylene polymer.

graphic analysis of the modified samples at -170°C . shows that the gases evolved during the -170°C . decomposition consist of water, CO_2 , and various hydrocarbon fragments.

It may be concluded that the ionic polymer in the salt form is less stable toward formation of gaseous thermal decomposition products than that in the hydrogen form.

Similar results have been found with experimental copolymers of higher acrylic acid concentration, modified to various degrees, and with commercially available ethylene-methacrylic modified polymers.

Reference

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