

Properties of Bound Water in Poly(Acrylic Acid) and its Sodium and Potassium Salts Determined by Differential Scanning Calorimetry

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Synopsis

The thermal transitions occurring in poly(acrylic acid) and its sodium and potassium salts were investigated over a large range of water content using differential scanning calorimetry at temperatures below the normal melting temperature of water. The bound water was identified as nonfreezing (type I), freezing with a constant melting temperature (type II), and freezing with a melting temperature dependent on the water content (type III). The transition temperatures of the freezing states of the water were determined. Two constant melting temperatures were observed for the type II water in the sodium and potassium polyacrylates, while a single transition of this type was observed for poly(acrylic acid). The sodium polyacrylate absorbed more water in the nonfreezing state than the potassium polyacrylate, and both polyelectrolytes absorbed about three times as much water in this state as the nonionic poly(acrylic acid). The effects of water content on the occurrence of an exotherm at low temperature in the melting scans of the polyelectrolytes are described.

INTRODUCTION

The effects of water content on the barrier properties of polymer coatings and the permeabilities of gases and vapors through polymer membranes are often significant. This investigation arose from an interest in the use of hydrophilic membranes containing either polyelectrolyte components or polar groups in hyperfiltration and in vapor permeability applications.^{1,2} Knowledge of the states of water in the hydrophilic polymers would enable better selection of membrane components for specific applications.

The states of water in polymers have been investigated using a variety of methods, including sorption and desorption experiments, infrared and NMR spectroscopy and calorimetric techniques. This article describes an investigation of poly(acrylic acid) and its sodium and potassium polyelectrolyte forms using differential scanning calorimetry (DSC).

Several hydrophilic polymer-water systems have been investigated using DSC. Ohno et al.³ reported DSC scans of poly(acrylic acid) (PAA) at different water contents in their investigation of polyelectrolytes and interpolymer complexes. Hiraoka et al.^{4,5} included poly(acrylic acid) and sodium and potassium polyacrylate at selected degrees of neutralization in their investigation of the hydration of polyacrylates by sorption techniques. They suggested that three polymer repeat units (p.r.u.) were coordinated with each alkali

metal ion and an excess of this amount of neutralization was needed before significant amounts of water were absorbed.

The water absorbed in the polymers will be discussed in terms of three identifiable types. The bound water component that does not exhibit a melting transition is type I, or primary bound, water, i.e., nonfreezing water. This type of water is present at water contents below the amount required to observe a melting transition peak in the subfreezing DSC scan. The water content is given quantitatively as the mole ratio r [mol water/mol polymer repeat unit (p.r.u.)]. Type II, or secondary bound water, exhibits a melting transition at a constant temperature well below the normal melting temperature of water and the size of the transition peak is constant, or changes very little, when r is sufficient to obtain the transition peak. Type III, or tertiary bound water, exhibits a melting temperature below 0°C, when r is just large enough to produce the transition peak, and then increases with r and eventually approaches the normal melting temperature of water. The area of the type III melting transition peak increases linearly with r .

EXPERIMENTAL

Materials

The poly(acrylic acid) (PAA) was Rohm and Haas Acrysol A3, with a weight-average molecular weight of about 150,000. It was purified by precipitating with sulfuric acid, dialyzing with a membrane having a molecular weight cutoff of 6000–8000 to remove the small ionic species, and freeze-drying. The sodium and potassium polyacrylates (NaPa and KPA) were prepared by neutralizing the purified PAA with the appropriate hydroxide, dialyzing to remove the excess ionic species and freeze-drying. All the polymers were stored in a desiccator before use. The PAA was atactic and no crystallinity was detected by X-ray of the dry powder. The reagents used in preparing the polymers were reagent grade. The water was deionized, with conductivity less than 2×10^{-4} S/m, and filtered.

Sample Pans

Standard DSC aluminum sample pans supplied by Perkin-Elmer were used. The samples were sealed between two of the pans, without tops, using the pan crimper. The resulting sample container exhibited only a slow rate of water loss, slowly enough to permit DSC measurements after several days.

Differential Scanning Calorimeter

A DuPont DSC/DTA 900 thermal analyzer was used with a DSC cooling attachment. The DSC was purged with nitrogen and the subambient temperature was attained with liquid nitrogen. The cell constant was determined by the manufacturer's standard procedure using a sapphire disc. The temperature scale of the DSC cell was calibrated using indium (mp = 156.6°C), water (0°C), cyclohexane (6.5°C), and the crystallization temperature of cyclohexane (–87.1°C). With careful calibration and weighing, precisions of $\pm 2\%$ for the enthalpy of transition and $\pm 1^\circ\text{C}$ for the transition temperature were expected.

Sample Preparation

A sample, 4–8 mg, of the freeze-dried polymer was placed in a DSC pan. The sample was heat treated for 15 min at 100°C and then for 10 min at 115°C under dry nitrogen. The dry mass of the polymer sample was recorded. The precision of the balance was ± 0.005 mg. The sample was then exposed to steam to obtain low water-content samples, or to liquid water to obtain high water-content samples, and weighed after sealing with another pan used as a cap. All samples were then equilibrated for at least 10 h at room temperature before the DSC experiment. The samples were weighed before and after the DSC experiment to evaluate the mass of water in the sample and to detect any loss of water resulting from a faulty seal.

DSC Experiments

The standard experiment consisted of quench cooling the sample to -100 to -110°C with liquid nitrogen. The scan was carried out at a constant heating rate of $10^\circ\text{C}/\text{min}$ to 50°C .

TREATMENT OF DATA

The glass transition temperature T_g was defined as the onset temperature of the transition. The temperature of an exothermic or endothermic transition peak was taken as the peak maximum. A straight base line was drawn from the onset to the end of the peak and the area enclosed in the peak was measured with a Salmoiraghi 236 planimeter. The precision of the planimeter was $\pm 2\%$ for areas greater than 1 in.^2 and $\pm 2\text{--}5\%$ for the smaller areas. The enthalpy associated with the peak was calculated using the equation

$$\Delta H = A(251BE\Delta q_s)/m$$

where A is the peak area (in.^2), m is the mass of the dry sample (mg), B is the time base setting ($\text{min}/\text{in.}$), E is the cell calibration coefficient at the temperature of the experiment (dimensionless), Δq_s is the y -axis range [$(\text{mcal}/\text{s})/\text{in.}$], and ΔH is the transition enthalpy (J/g).

RESULTS

Poly(acrylic Acid)

Figure 1 shows the effects of absorbed water, indicated as the mole ratio of water to polymer repeat unit (p.r.u.), r , on the DSC scans of water–PAA samples. The curves are not normalized to a constant mass of PAA, but the variation of the masses of the samples was less than 25%. The glass transition of the dried PAA was 118°C . Absorption of modest amounts of water by the PAA reduced the glass transition temperature into the scanning range, e.g., the glass transition at $r = 0.5$ was about 10°C , before a melting endotherm was detected. At higher r (> 1.6) the melting endotherms representing two distinguishable types of water, type II and type III, became apparent. The melting temperature of the type II water occurred at about -17°C and remained constant as r increased. Ohno et al.³ reported a constant melting

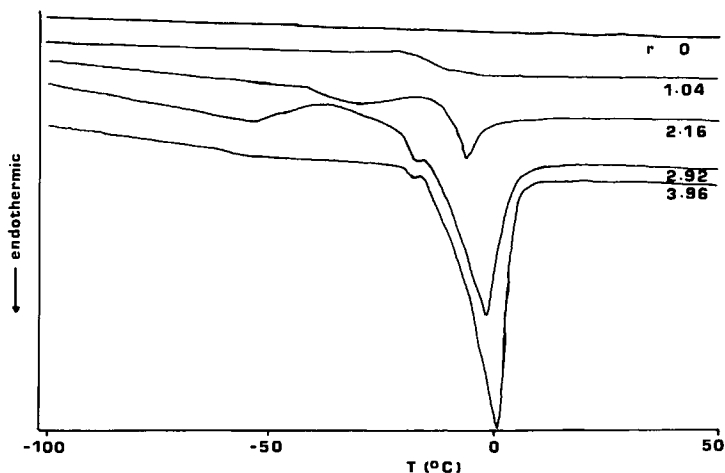


Fig. 1. DSC melting scans of PAA-water at selected r vs. temperature.

temperature of -15°C for type II water in PAA. The melting temperature of the type III water occurred at about -10°C when r was just large enough to produce a measurable transition peak and approached 0°C at high r . The area of the transition peak also increased as r increased. The effects of the amount of absorbed water on the transition temperatures of the type II and type III water in PAA are shown in Figure 2.

Figure 3 is a graph of the enthalpy of fusion of freezing water, type II plus type III, per mol p.r.u. vs. r . The intercept of the line on the r -axis represents the maximum mole ratio of type I, i.e., nonfreezing water to p.r.u., $r(\text{I})$ -maximum. The value of $r(\text{I})$ -maximum for PAA, 1.4 ± 0.4 , agrees well with the value of 1.2, reported by Ohno et al.³ The slope of the line gives the enthalpy

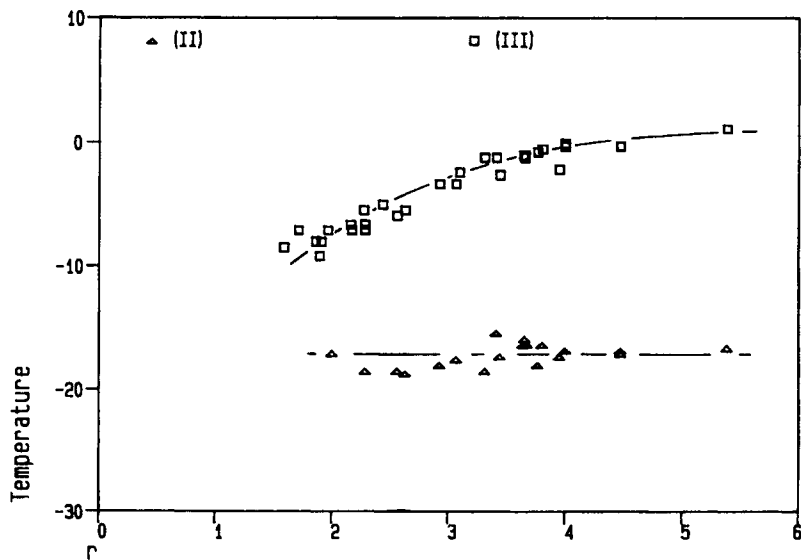


Fig. 2. Melting temperatures of type II (Δ) and type III (\square) water in PAA vs. r .

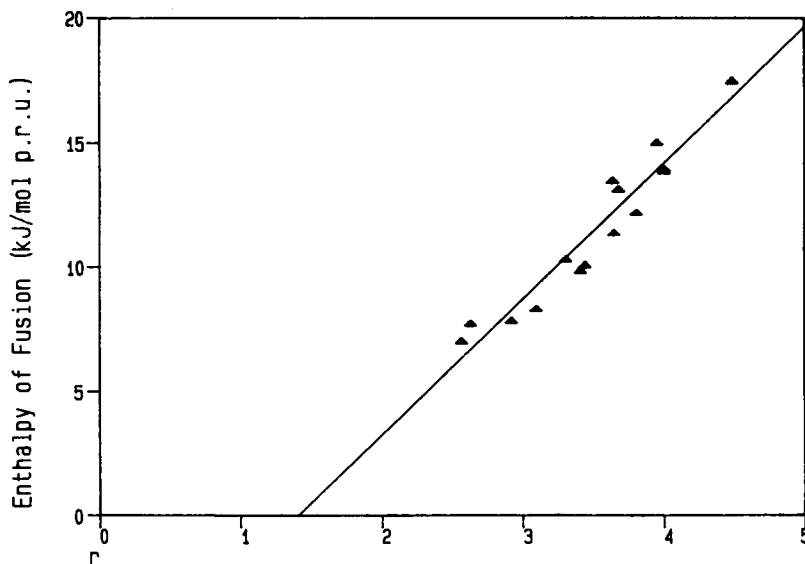


Fig. 3. Enthalpy of fusion of freezing water, type II plus type III in PAA per mole of p.r.u. vs. r .

of fusion of freezing water per mole of freezing water. The value obtained is 5.61 ± 0.85 kJ/mol water; comparable to the value of 6.01 kJ/mol for free water.⁶ Ohno et al.,³ did not provide a value, but indicated that the enthalpy of fusion of freezing water in the water-PAA system was less than free water.

Assuming the enthalpy of fusion for type II water is 6.01 kJ/mol, the amount of type II water can be estimated from the area of the constant endotherm peak. This calculation gives $r(\text{II})$ of 0.1, much smaller than the 1.5 reported by Ohno et al.³ This discrepancy is puzzling because all the other results are in good agreement with their results. Likely it is the result of differences in procedures in obtaining the area of a small shoulder on the large asymmetric peak for type III water. Despite this single discrepancy the general agreement between the two investigations supports the value of DSC experiments in examining states of water in polymers.

Sodium and Potassium Polyacrylate

Figure 4 shows the effects of absorbed water on the DSC scans of NaPA. These curves are not normalized to a constant mass of NaPA, but variations in the masses of the samples was less than 25%. Again, the initial absorbed water reduced the glass transition temperature from about 250°C for dry NaPA to the scanning region as r was increased before the type II and type III water melting transitions were observed. The results differed from the PAA results in two respects. In a rather high region of r , a large exotherm occurred that was not observed for PAA and there were two, rather than one, small shoulders on the type III melting peak. The nature of the exotherm will be discussed later in this text. The two shoulder peaks are designated type IIA and type IIB. The transition temperatures of these two peaks were independent of r , characteristic of type II water in hydrophilic polymers. Although

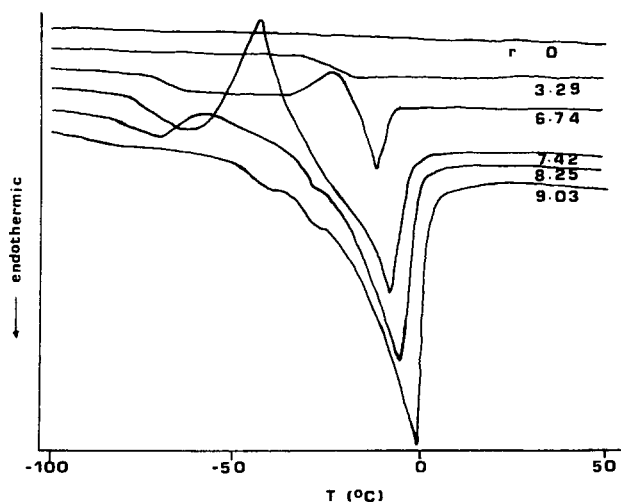


Fig. 4. DSC melting scans of NaPA-water at selected r vs. temperature.

these shoulders were quite small, and the accuracies of the peak areas were poor, it appeared that as the water content increased, the total area first increased slightly before it became a constant value. The characteristics of the DSC scans of the KPA-water system were very similar to those seen in Figure 4 for NaPA, differing only by displacement of the transition temperatures and r values.

The effects of the amount of absorbed water on the melting temperatures of types IIA, IIB, and III water are shown in Figure 5 for NaPA and in Figure 6 for KPA. The melting temperatures of the type IIA and type IIB are independent of r . The type IIA melting temperatures differed very little in

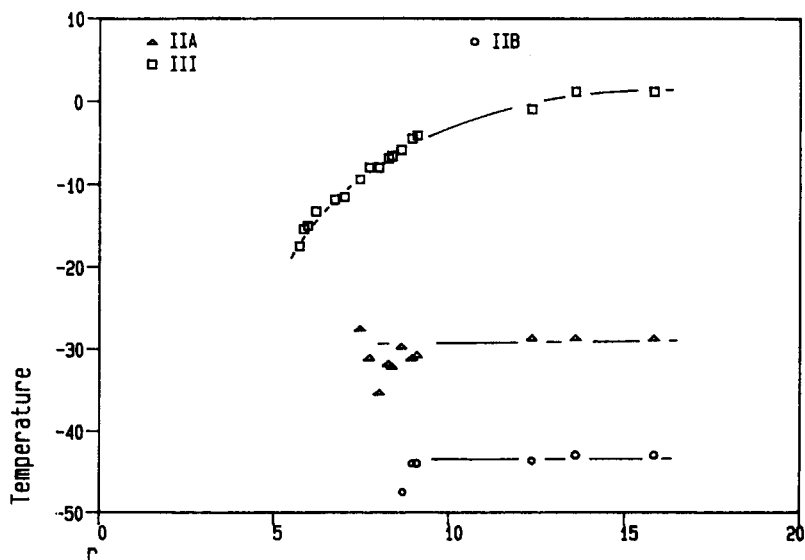


Fig. 5. Melting temperatures of type IIA (Δ), IIB (\circ), and III (\square) water in NaPA vs. r .

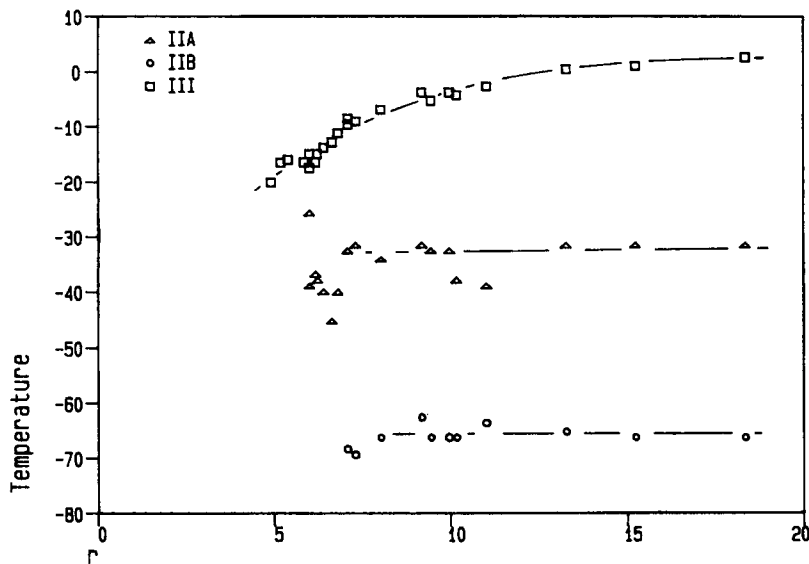


Fig. 6. Melting temperatures of type IIA(Δ), IIB (\circ), and III (\square) water in KPA vs. r .

the two polyelectrolytes, -30 and -32°C , but were significantly lower than the -17°C obtained in the nonionic PAA. The values for type IIB melting temperatures were very low, -45°C for NaPA and -66°C for KPA, and differed for the two cation forms. The melting temperature of the type III water began at about -20°C at smaller r and increased to 0°C at higher r for both polyelectrolytes.

The dependence of the enthalpy of fusion of freezing water, type II plus type III, per mole p.r.u. on r for NaPA and KPA is displayed in Figure 7. The intercepts of the lines on the r -axis give the $r(\text{I})$ -maxima for the two polyelectrolytes and the slopes give the enthalpies of fusion of freezing water per mole of freezing water. These results and other transition temperatures are summarized in Table I. The $r(\text{I})$ -maximum is greater for NaPA than for KPA and the enthalpies of fusion of types II and III water are approximately equal to the value for free water.

The nonfreezing water content per p.r.u. is greater for NaPA than for KPA; 4.9 ± 0.3 for NaPA and 4.3 ± 0.3 for KPA. The trend is consistent with the water of hydration for sodium and potassium ion in dilute aqueous solution where the hydration number for a sodium ion is 4–5 and for a potassium ion is 3–4.⁷ It is also notable that the difference between the $r(\text{I})$ -maximum values for these polyelectrolytes and the nonionic PAA is approximately 3, the presence of ionic groups increasing the type I water content as expected.

An exothermic transition occurred in the lower range of r in which type II and type III water melting transitions were observed. As r increased from the minimum value giving rise to the exotherm, the area of the transition peak increased and the transition temperature decreased. At higher r the peak eventually broadened and disappeared. Figures 8 and 9 give the enthalpy of the exothermic transition peak per mole of p.r.u. and the temperature at which the exotherms occur vs. r for NaPA and KPA, respectively. The range

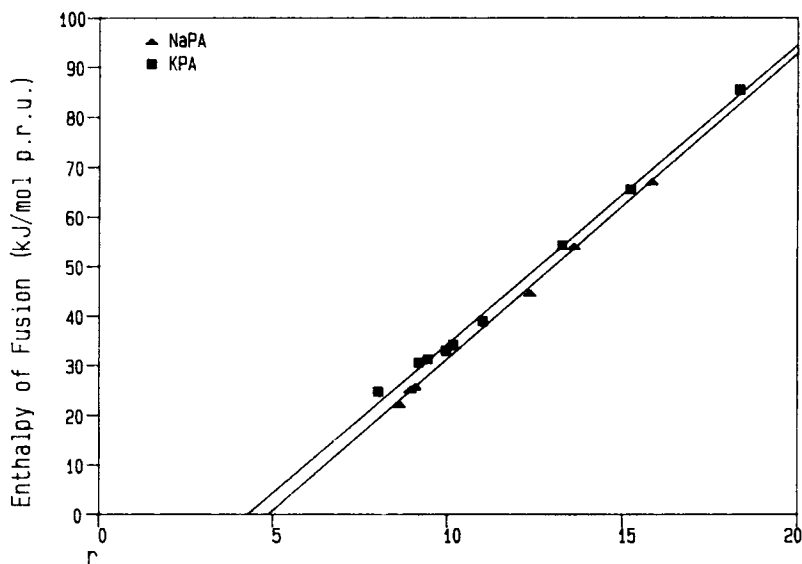


Fig. 7. Enthalpy of fusion of freezing water, type II plus type III, in NaPA (\blacktriangle) and KPA (\blacksquare) per mole of p.r.u. vs. r .

in r for the occurrence of the exotherm is approximately 5.7–8.4 for NaPA and 4.9–7.1 for KPA. The exotherm is likely the result of crystallization of the supercooled water developed at the time of quench cooling the sample. The occurrence of the exotherm in only a limited region of r and the persistence of the exotherm in repeated DSC scans is not consistent with the presence of an exothermic reaction. By cooling the samples slowly or holding the temperature during cooling at about -20°C for 10–20 min, the area of the exotherm peak was reduced significantly, i.e., about 35%, from the value obtained from the melting scans of quench cooled samples. This alteration of the cooling procedure reduced the area of the endotherm for the melting of type III water by only about 5%. No reduction of the endotherm for type II water was detected. These results support the hypothesis that the exothermic transition is crystallization of supercooled water. Similar exothermic transitions have been reported for poly(ethylene glycol)^{8,9} and cellophane¹⁰ and attributed to crystallization of supercooled water. The shift of the transition temperature to lower values as the water content increased and the absence of the

TABLE I
Transition Temperatures and Enthalpies, and r Values for Sodium Polyacrylate (NaPA)
and Potassium Polyacrylate (KPA)

Bound water type	Parameter	NaPA	KPA
I	$r(\text{I})$ -maximum	4.9 ± 0.3	4.3 ± 0.3
IIA	T (melting)	-30	-32
IIB	T (melting)	-45	-66
II + III	Enthalpy of fusion ^a	6.01 ± 0.21	6.01 ± 0.26

^a kJ/mol water.

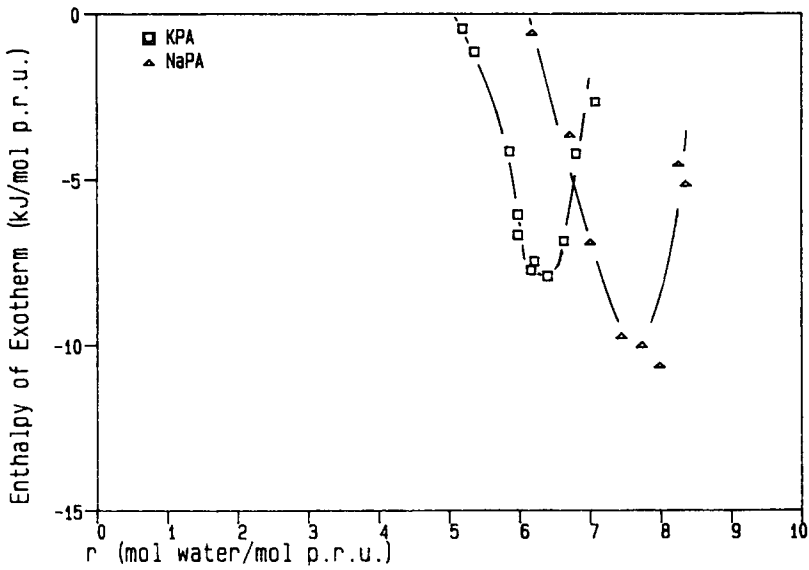


Fig. 8. Enthalpy of the exothermic transition per mole of p.r.u. for NaPA (Δ) and KPA (\square) vs. r .

exotherm at very high r could be the result of a decrease in the effect of the polymer on the constrained mobility of the water as more type III water is absorbed and the polymer swells. It is suggested that as the quantity of water is increased, more water crystallizes during the cooling cycle and at some high content the crystallization is complete enough to eliminate further crystallization during the heating cycle.

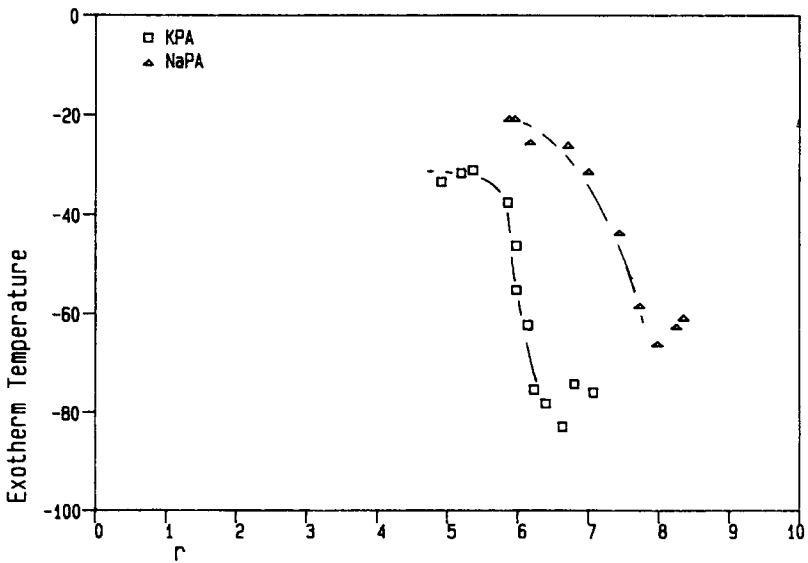


Fig. 9. Temperature of the exothermic transition for NaPA (Δ) and KPA (\square) vs. r .

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