

Water as a Melting Point Depressant for Acrylic Polymers

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SUMMARY

Water is known to strongly depress the melting point of polyacrylonitrile (PAN) and acrylic copolymers. A scanning calorimetric technique has been developed that utilizes this melting point depression in probing the structure of acrylic fibers. In this report the melting and crystallization of PAN and acrylonitrile-vinyl acetate copolymers is studied as a function of water content. Addition of water continually depresses the polymer melting point until a critical water level is reached where the molten polymer separates from the water and no further reduction in the melting point is observed. Both the minimum melting point and the critical amount of water required for phase separation decreases as the level of vinyl acetate comonomer is increased. The latter relationships are examined in terms of the acrylic polymer morphology and the possibility that the water molecules become associated with the nitrile group during the melting process.

INTRODUCTION

In a previous report (FRUSHOUR, 1981) a new scanning calorimetric technique for acrylic polymers and fibers was described that produced well-defined melting endotherms and crystallization exotherms of polymer-water mixtures. The technique provides structural information of acrylic fibers and polymers that is not provided by more conventional fiber characterization methods such as X-ray diffraction, infrared spectroscopy and density measurements. The structure of polyacrylonitrile (PAN) and attendant fiber-forming copolymers has been described as a highly imperfect two-dimensional structure in which clusters of chains pack together in a pseudo-hexagonal array (BOHN et al, 1961; WARNER 1978; KLEMENT and GEIL, 1968). Fiber wide angle X-ray patterns show little evidence of long-range order along the fiber axis, which is parallel to the chain axis, but a surprisingly high degree of order is found perpendicular to the fiber axis. This order is attributed to clustering of the chains into bundles that are stabilized by intermolecular bonds formed between the nitrile groups on adjacent

chains. In the previous report (FRUSHOUR, 1981) a model of the structure was proposed whereby the temperature and energy (heat of fusion) of the melting endotherms of the polymer-water mixtures were associated with the strength and regularity of these intermolecular bonding networks. In this report the dependence of the melting behavior on the water content is discussed for PAN and acrylonitrile-vinyl acetate (AN/VA) copolymers and compared to the behavior that would be predicted from application of the Flory theory of polymer-diluent systems.

EXPERIMENTAL

The differential scanning calorimetry (DSC) measurements were made using a Perkin-Elmer DSC II calorimeter and the Perkin-Elmer large-volume stainless steel capsules (Part 319-0218). Details of the instrument operation and polymer preparation have been discussed previously (FRUSHOUR, 1981). Polymer and water are uniformly mixed and approximately 70 mgs. of the mixture are packed into the bottom of the two-piece capsule. A rubber O-ring is fitted into the top of the capsule, which is then forced over the bottom in a crimping tool. A properly sealed capsule is capable of withstanding pressures up to 350 psig, which is the pressure generated by pure water at 220°C. Rupture of a capsule at such high pressure while in the DSC can damage the sensing cell and therefore the thermal scans were usually stopped at 200°C when analyzing the polymer-water mixtures.

The melting point, T_m , and crystallization point, T_c , are taken as the maxima in the endothermic and exothermic peaks, respectively. The quantity ΔH_f is the experimental heat of fusion in calories per gram of polymer and is calculated from the peak area using an indium standard.

The polymers were prepared by continuous aqueous dispersion polymerization using a redox initiator system. The M_n and M_w were approximately 55,000 and 100,000 grams/mole. The polymers were analyzed for vinyl acetate by measuring the intensity of the carbonyl infrared absorption at 1720 cm^{-1} .

DEPENDENCE OF MELTING BEHAVIOR ON WATER CONTENT

The melting of PAN in the presence of water can be observed by sealing a mixture of 20ml of H_2O and 1 g of polymer in a thick walled glass tube and then heating the tube in a clear oil bath. When the temperature reaches 180-190°C the polymer will begin to fuse and take on a molten appearance. This fused lump of polymer will be surrounded by H_2O , i.e., a distinct water-polymer phase separation will have occurred. The polymer will crystallize at approximately 170°C upon cooling and when the tube is opened a solid plug of PAN will be found. Fracture of the solid reveals a very porous interior with spherical pores indicating that water vapor must have evolved from the melt upon solidification. If the

total time in the melt is restricted to only several minutes then no significant irreversible chemical changes as measured by the infrared spectra will have occurred. However, holding the PAN above 185°C in the melt for prolonged periods of time will hydrolyze the polymer to water soluble polyacrylamide. Water is clearly an effective melting point depressant since PAN in the absence of water melts near 320°C (HINRICHSEN, 1974).

When the experiment is repeated using a copolymer containing 7.3% VA the melting and crystallization temperatures are shifted to 157°C and 140°C, respectively. It is these transitions in the homopolymer and copolymers that give rise to the melting endotherms and crystallization exotherms that are observed when the polymer-water mixtures are heated and cooled in the DSC. The dependence of these transitions on the water content for the homopolymer and two copolymers will now be discussed.

Polymer-water mixtures covering a range of water weight fraction, $W(H_2O)$, from zero (dry polymer) to 0.67 (1 part polymer: 2 parts water) were prepared. Copolymers having vinyl acetate comonomer weight fractions of 7.3% and 11% were used in addition to the homopolymer. Thermograms were obtained by heating the polymer-water mixtures at 5°C/min. from 75°C up through the melting endotherm followed by cooling at the same rate through the exotherm and then repeating the cycle. The differences between the first and second melting endotherms are small, but consistent. The T_m is shifted approximately 1°C higher in the second melt and the endotherm is skewed to the low temperature side.

The dependence of T_m on $W(H_2O)$ for the three polymers are compared in Figure 1. In each case T_m decreases very sharply as water is added until a plateau region of constant T_m is reached. The plateau region coincides with the polymer-water phase separation that was previously described. Once the critical water level that is required for phase separation is reached the T_m remains constant, as predicted by the phase rule, because the additional phase reduces the number of degrees of freedom available to the system by one. This has long been observed in polymer-diluent systems where the interactions between the two components is repulsive, i.e. the polymer-solvent interaction parameter has a large positive value (FLORY, MANDELKERN, and HALL, 1951). In the following discussion the two-phase region will refer to measurements in which T_m is independent of $W(H_2O)$ and similarly the one-phase region refers to measurements where T_m is dependent on $W(H_2O)$.

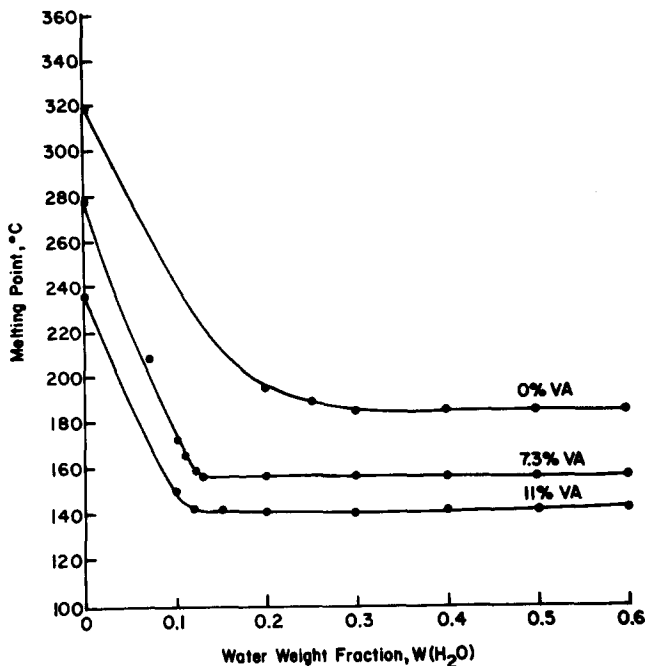


Figure 1. Dependence of polymer melting point on water content for different acrylic copolymers

Once the two-phase region has been reached the melting behavior becomes dependent only on the chain microstructure. By microstructure we mean chain defects including chain ends, chain branches and comonomers. Due to the high molecular weight and linear nature of these acrylic polymers we can assume that the melting behavior will be controlled almost entirely by the comonomer content. Incorporation of VA into the PAN chain causes a pronounced reduction in T_m and ΔH_f , and the peaks broaden, as seen in Figure 2. The values of T_m and ΔH_f for the PAN homopolymer and the 7.3% VA and 11% VA copolymers are 185°C, 18.5 cal/g; 157°C, 8.5 cal/g; and 142°C, 5.3 cal/g, respectively. It is thought that the endotherms become smaller and shift to lower temperature as more vinyl acetate is incorporated into the polymer because a vinyl acetate monomer enters the crystalline lattice as a defect and disrupts the intermolecular bonding (FRUSHOUR, 1981). The thermograms in the two-phase region are extremely reproducible. T_m can be reproduced to $\pm 0.2^\circ\text{C}$, which makes these measurements attractive for analytical applications.

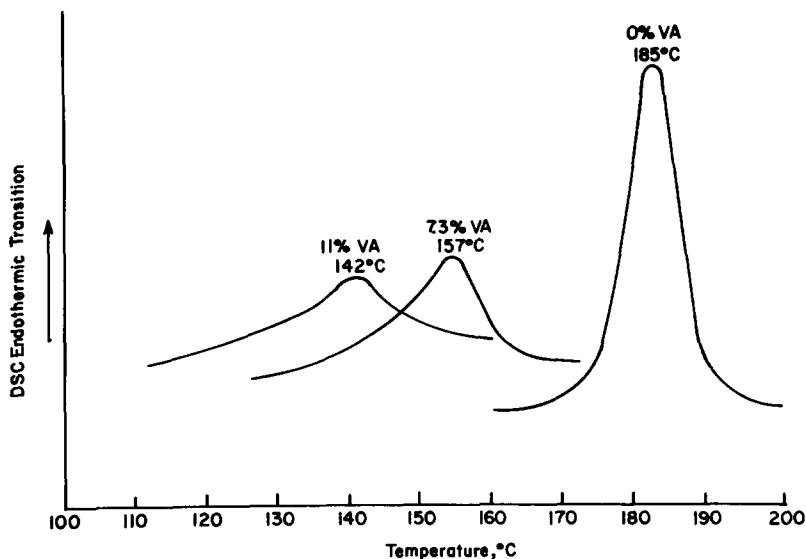


Figure 2. Melting endotherms of acrylic copolymers mixed with water (one part polymer: two parts water)

The thermograms in the single-phase region are characterized by melting endotherms that become progressively broader, more distorted and decrease in area as $W(H_2O)$ is decreased below the critical value for phase separation. The endotherm peak definitely shifts to higher temperatures. The accessible range in $W(H_2O)$ is limited because the T_m rapidly approaches the 200°C upper limit that was imposed to prevent damage to the DSC cell. Obtaining good data on the dry polymer requires very fast heating rates to insure that the polymer melts before it undergoes the characteristic exothermic degradation reaction. The T_m 's for the dry copolymers were obtained using a heating rate of 80°C/minute. A melting endotherm for PAN could not be obtained even at 320°C/minute. HINRICHSSEN (1974) determined that the T_m of PAN was near 320°C by immersing fibers into molten metal and then examining them under a microscope. This value is used in Figure 1 for PAN.

The behavior of the crystallization exotherms with respect to $W(H_2O)$ provides information about the polymer-water interaction. The exotherms are much sharper than the endotherms for all values of $W(H_2O)$ and even in the single-phase region the exotherms are not distorted. When $W(H_2O)$ falls below the critical value for phase-separation the exotherm responds by shifting to higher temperature while becoming broader and decreasing in area. This progression is shown in Figure 3 for the 7.3% VA copolymer. Curve A is typical for the two-phase region. The value of T_c is 130°C. Recall that T_m for this polymer in the two-phase region was 157°C, which

indicates a supercooling of 27°C. This amount of super-cooling is typical for all of the acrylic copolymers we have examined to date.

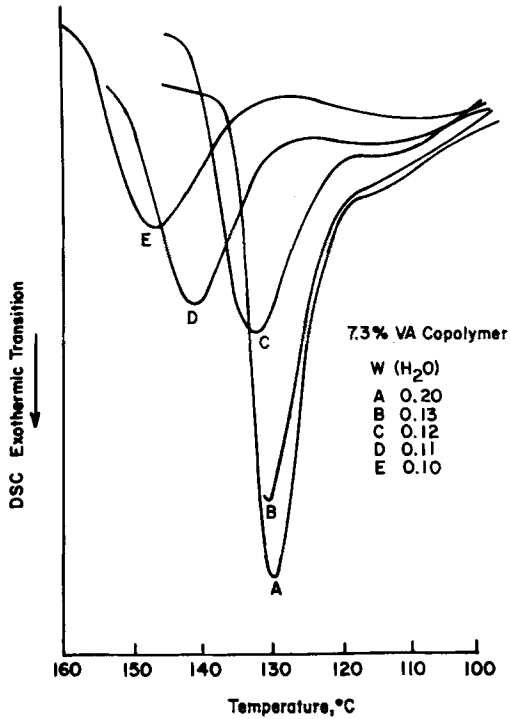


Figure 3. Dependence of acrylic copolymer crystallization temperature on water weight fraction $W(H_2O)$

DISCUSSION

The classical description of the melting point depression of a polymer by addition of a diluent is provided by the Flory theory (FLORY, 1949). This theory states that a polymer melts when the chemical potential of the polymer in the crystalline and melt phases becomes equal. The addition of a diluent reduces the melting temperature, T_m , by reducing the chemical potential of the melt phase through entropy of mixing. Furthermore, it is tacitly assumed that the crystalline phase of the polymer can be described by a three-dimensional unit cell. One should appreciate that the latter is not completely fulfilled for acrylic polymers since the crystalline phase is highly disordered. KRIGBAUM and TOKITA (1960) reported that the Flory theory adequately described the melting behavior of PAN gels and therefore we shall utilize the Flory theory as a framework for the interpretation of the melting data.

The Flory equation for the polymer-diluent is given below:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} (\bar{v}_1 - \chi \bar{v}_1^2)$$

where T_m and T_m^0 are the melting points of the polymer in the presence and absence of the diluent, R is the gas constant, ΔH_u is the polymer heat of fusion in cal/mole of repeat unit, V_u and V_1 are the molar volumes of the polymer repeat unit and diluent, respectively, \bar{v}_1 is the volume fraction of the diluent and χ is the polymer-solvent interaction parameter.

When the reciprocal of the melting point is plotted against \bar{v}_1 the initial slope can be used to evaluate ΔH_u and the curvature of the line provides information about χ . Favorable polymer-solvent interactions are associated with a negative value of χ and give curves that are concave upwards and conversely unfavorable interactions give the opposite curvature. As described earlier a very positive value of χ will lead to phase separation at a critical value of \bar{v}_1 , and T_m will remain constant as \bar{v}_1 is increased beyond this critical value. One can replot the data in Figure 2 by calculating the reciprocal melting points and converting the water content from weight fraction to volume fraction using a polymer density of 1.20g/cm³. With increasing volume fraction of water one observes a linear increase in the reciprocal melting point until the point of phase separation is reached. The transition from straight lines of positive slope to zero slope with increasing \bar{v}_1 would be consistent with the Flory theory if the interaction parameter χ increased from near zero to a very positive value at a critical value of \bar{v}_1 and thereby induced a phase separation. This behavior might be expected if some type of complex or association between the polymer and water were being formed during the melting process. If this complex were insoluble in water then the phase separation would occur after \bar{v}_1 exceeded the value needed to complete the formation of the complex. The insolubility in water of such a complex seems entirely reasonable since the only component of the polymer molecule that is not hydrophobic is the nitrile group.

Recall from the introductory comments on the fiber structure that attractive interaction among the nitrile groups on adjacent chains are thought to stabilize the two-dimensional acrylic structure, and we have previously interpreted T_m and ΔH_f data of the acrylics as an indicator of the strength and regularity of these dipolar bonding networks (FRUSHOUR, 1981). If the water molecules were to become associated with the nitrile groups then the potential of the latter to interact and stabilize the structure would be reduced. One could even imagine the nitrile-water complex to be a non-crystallizing comonomer in the sense that the nitrile group to which the water molecule was bound could no longer participate in the intermolecular bonding. The critical value of $\bar{W}(\text{H}_2\text{O})$ required

for two-phase behavior could then be interpreted as the point at which all of the nitrile groups that were participating in dipolar bonding networks in the dry polymer had become complexed with the water. One can see from Figure 1 that the critical value of $W(H_2O)$ required to achieve phase separation decreases along with ΔH_f and T_m when VA is incorporated into the polymer chain. This reflects the reduction in size and strength of the dipolar bonds resulting from inclusion of the VA units in the crystalline lattice as defects (FRUSHOUR, 1981).

Direct evidence for association between the water and nitrile groups is claimed in a patent (GOODMAN and SUWYN, 1972) where the Raman active nitrile stretching vibration, ($C\equiv N$) is reported to have shifted from 2234 cm^{-1} to 2050 cm^{-1} upon melting in the presence of water. We attempted to follow the polymer-water interaction with the use of wide-line proton NMR. The melting process was accompanied by an extreme narrowing of the polymer proton resonance line, which simply indicates an increase in the polymer segmental mobility. This was expected. However, we did not observe any concomitant broadening of the water resonance signal. Such a broadening might have been expected if the water molecules were tightly bound to the nitrile groups in the melt. Clearly much more work needs to be done to better define the molecular basis of the polymer-water interaction.

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