A New Thermal Analytical Technique for Acrylic Polymers

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SUMMARY. An unconventional thermal analytical technique
has been developed for acrylic polymers. By adding
water to the polymer the melting point is depressed
well below the onset temperature of cyclic thermal de-
gradation. This addition of water depresses the melt-
ing point of polyacrylonitrile from 320°C to 185°C. The
melting behavior of acrylic copolymers in the wet and
dry state is explained in terms of the Eby model of a
polymer crystal whereby the non-crystallizable comono-
mers enter the crystal lattice as defects. The melting
point and heat of fusion are interpreted as a measure
of the regularity and strength of the intermolecular
dipolar bonding that stabilizes the lattice.

INTRODUCTION

We have recently developed an unconventional thermal
analytical method for investigating the structure of
polyacrylonitrile (PAN) and its attendant fiber forming
copolymers. This technique involves the measurement of
melting endotherms and crystallization exotherms of
powder, film or fiber samples in the presence of water.
Precise measurements of melting points and heats of
fusion can be readily obtained without interference from
the cyclic exothermic thermal degradation reactions that
have previously limited the application of thermal
analysis to acrylic polymers (SLADE, 1970; BERGER,1973).
This capability is especially important in view of the
paucity of useful characterization methods for these
polymers.

The acrylic morphology is poorly understood and can be
said to bridge the amorphous and crystalline polymeric
states. Well-defined three-dimensional crystallinity
is lacking. Wide angle X-ray diffraction analysis of
oriented fibers (BOHN et.al., 1961) and solution-grown
single crystals (HOLLAND et.al., 1962; KLEMENT and GEIL,
1968) reveal several sharp reflections on the equator
and diffuse scattering on the quadrants. The absence
of sharp meridional reflections implies a low degree of

order along the chain axis direction. This can be attri-
buted to the low degree of stereoregulatiry (SCHAEFER,
1971) and the highly polar nitrile side groups. Confor-
mational energy calculations (KRIGBAUM and TOKITA, 1960)
predicted that no regular chain conformation would be stable,
even for pure syndiotactic and isotactic polymer. How-
ever, a high degree of intermolecular bonding is possible
though dipole-dipole attractions between nitrile groups
located on adjacent chains (HENRICI-OLIVÉ and OLIVÉ,
1979).

The equatorial X-ray reflections can be indexed in a two-
dimensional orthorhombic unit cell in which the intense
5.26 Å reflection arises from the average interchain
distance of 6 Å (BOHN et.al. 1961, COLVIN and STORR,
1974). Bohn, Schaefgen, and Statton (BOHN et.al. 1961)
proposed that the individual chains were forced into a
stiff extended and randomly kinked conformation by the
repulsion among the neighboring nitrile groups such that
on the average each chain occupied a cylindrical space
approximately 6 Å in diameter. The packing of these
cylinders in a psuedo-hexagonal fashion gives rise to the
equatorial reflections.

The validity of a two-phase model for PAN has been much
debated. The amorphous halo seen near 2 θ values of
17°-20° in wide-angle diffraction patterns of semi-
crystalline polymers is not seen in acrylics, though in
unoriented specimens the diffuse meridional scattering
at a 2 θ value of 29° does resemble this halo. The
acrylic structure has been characterized as a single
phase with disorder (BOHN et.al., 1961). However, small
angle X-ray patterns (WARNER, 1978), iodine sorption
(ANDREWS et.al., 1972) and dynamic mechanical spectra
(MINAMI et.al., 1972) have been interpreted as evidence
of a limited two-phase model.

EXPERIMENTAL

Polymer in the form of powder, film or fiber is placed
in a special stainless steel capsule that fits in the
sample holder of a Perkin-Elmer DSC II scanning calorim-
eter. Water is added and the capsule is sealed. The
capsule must be capable of withstanding the vapor pres-
sure of water up to 200°C. The melting point of the PAN
decreases continuously from 340°C to 185°C as the percent
of water (based on polymer) is increased from zero to
35%. Higher amounts of water form an inert phase and do not
suppress the melting point any farther. We have found
that 3 parts water per two parts polymer is a convenient
level, and have used this level in all wet-polymer
measurements reported here. The sealed capsule is
placed in the DSC and analyzed using heating and cooling

rates of 5°C/minute. The melting points and enthalpies were calibrated by placing indium metal into one of the sample capsules along with the same amount of water used for a polymer sample and generating the indium melting and cooling thermograms. By doing this the thermal lag and peak broadening caused by the weight of the capsule and water are accounted for in the determination of the polymer transition temperatures and enthalpies.

All of the polymers and copolymers used in this study were suspension polymerized in a continuous process reactor using the standard persulfate-bisulfate redox system as the free radical generator. The polymer $MW_{(n)}$ was approximately 100,000 grams/mole. The shape of the melting endotherm of copolymers is very sensitive to compositional homogeneity.

RESULTS

The melting point, T_m, of dry PAN has been estimated to be near 320°C. The polymer degrades before this temperature is reached unless heating rates in excess of 1000°C/minute are used (HINRICHSEN, 1974). The thermogram of wet PAN polymer appears in Figure 1. A well-defined melting endotherm is observed at 185°C with a heat of fusion, ΔH_f, of 1050 cal/mole·AN. Two exothermic peaks differing greatly in area are observed upon cooling from 200°C, one at 167°C with a ΔH_f of 1100 cal/mole·AN and other at 138°C with a ΔH_f of approximately 50 cal/mole·AN. Reheating the sample reveals a small endotherm at 160°C in addition to the intense 185°C endotherm. The second cooling curve is identical to the first and a third heating curve again shows the two endotherms, though with each additional cycle the peaks become slightly broader. This is not unexpected since holding the sample above 185°C for one hour will convert the PAN to acrylamide, which is water soluble. When the sample capsule is opened after cooling from the melt a smooth cream-colored polymer is found surrounded by water. The pellet is soluble in typical PAN solvents and IR analysis of a film cast from solution shows no sign of extensive degradation. The intensity of the nitrile stretching based at 2240 cm^{-1} is unchanged and no increase in carbonyl content is detected. Therefore, we conclude that any interaction with the water is reversible.

X-ray analysis of the polymer pellet revealed a new reflection at 3.36 Å that was not present in the initial polymer. We determined that this reflection was characteristic of polymer that had been heated through the 184°C endotherm. Other groups have noted the presence of this reflection in fibers that have been subjected to intense thermal treatments (STEFANI et.al., 1960; SOTTON, 1973). When a previously
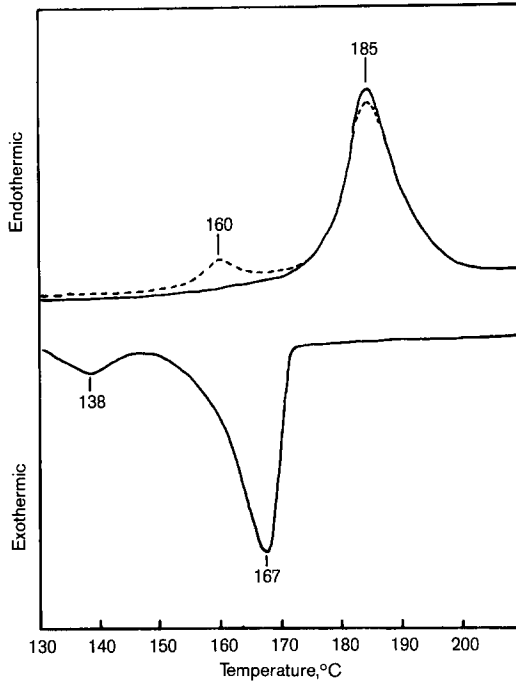
Fig.1. Melting and crystallization peaks of PAN-
       water mixture (150% water). Broken line
       corresponds to second heating.

melted sample is reheated in the DSC to a temperature just
beyond the 160°C endotherm and then cooled,only the 138°C
exotherm is observed. Therefore, we tentatively associ-
ate this double melting and crystallization phenomenon
with two distinct crystalline variants. The major
endotherm at 185°C probably corresponds to the two-
dimensional structure discussed previously and the 160°C
endotherm must be associated with an unknown structure
that forms upon cooling from the melt and gives rise to
the 3.36 Å reflection.

The addition of comonomers to the PAN chain strongly
suppresses both T_m and ΔH_f. Also, the endotherm half-
width increases. The decrease in T_m has been observed
previously in conventional DTA measurements (SLADE, 1970;
BERGER, 1973), but comes out more clearly using this
technique. In Figure 2 the reciprocal melting point of
AN-vinyl acetate copolymers is plotted against the mole
fraction of vinyl acetate. Both the dry-polymer and wet-
polymer melting points are given. The peak temperature
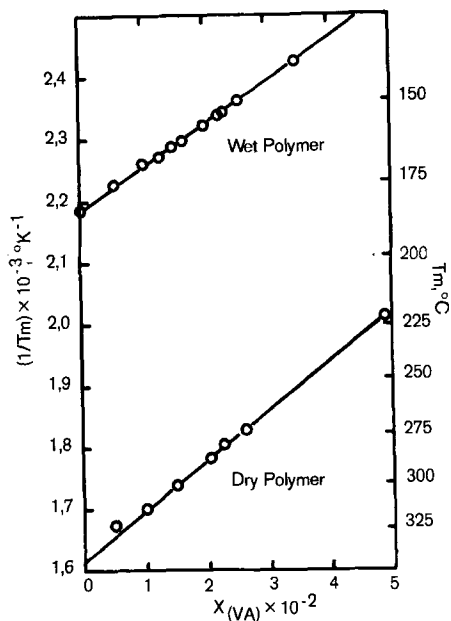of the endotherm was chosen as the melting point.

Fig. 2. Dependence of melting point
on the mole fraction of vinyl
acetate.

We wish to comment on several salient features of the
copolymer melting behavior seen in Figure 2. First, the
reciprocal melting points fall on parallel straight lines
that extrapolate to dry and wet PAN melting points of
183.8°C and 344.2°C, respectively. When the vinyl
acetate is substituted with a smaller comonomer such as
vinyl chloride one again observes parallel lines but the
slopes have decreased. The separation of the curves in
units of reciprocal degrees remains the same. We find
this behavior to be general. On a molar basis the
efficacy of a given comonomer to depress the PAN melting
point is proportional to the specific volume of the
comonomer side chain. In Table I the slopes, which we
call the melting point depression constants, are tabu-
lated for common comonomers along with the specific
volumes of the side chains.

Eby (EBY, 1963) proposed a defect model for semi-crystal-
line polymers whereby chain defects such as comonomers
and end groups enter the crystalline lattice as point
defects rather than being relegated to the amorphous
phase. The comonomer volume dependence of the acrylic

TABLE I

Melting Point Depression Constants
for Common AN-B Copolymers

B Comonomer	k_B x 10^3 $(°K)^{-1}$	Molar Volume of Side Chain(1)
Methyl acrylate	3.370	36 cm^3/mole
Vinyl acetate	3.343	36
Ethyl vinylether	2.2	39
Vinyl bromide	0.909	11
Vinylidene chloride	0.744	15
Vinyl chloride	0.51	7.5

(1) Volumes calculated from Table 4.2 (Exner) in the
following reference: D. W. Van Krevelen, Proper-
ties of Polymers, Elsevier Publishing Company,
N. Y. 1972, p. 43.

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melting behavior seems entirely consistent with this
model. When more than one type of comonomer is present
the effect on the melting point depression is additive.
The following equations are based on the Eby theory and
give the melting point as a function of composition for
acrylic copolymers of any order. We have used them to
predict the wet and dry polymer melting points of copoly-
mers up to order five (pentapolymers) to within several
degrees of the measured value (see note in References).

Wet polymer
$$\frac{1}{T_{m(H_2O)}} = \frac{1}{T_{mo(H_2O)}} + \sum_{i=1}^{n-1} K_i X_i, \quad T_{mo(H_2O)}$$
$$456.8°K$$

Dry polymer
$$\frac{1}{T_{m(dry)}} = \frac{1}{T_{mo(dry)}} + \sum_{i=1}^{n-1} K_i X_i \quad T_{mo(dry)}$$
$$617°K$$

where $T_{M(H_2O)}$, $T_{m(dry)}$ are the calculated melting
points of the wet and dry polymer; $T_{mo(H_2O)}$,
$T_{mo(dry)}$ are the wet and dry PAN melting points,
X_i is the mole fraction of comonomer i, K_i is the
respective melting point depression constant from
Table I and n is the copolymer order (n equals 2
for a comonomer, 3 for a terpolymer, etc.).

The reciprocal melting points of the wet and dry copoly-
mers differ by the quantity $(1/T_{mo(H_2O)} -
1/T_{mo(dry)})$. Therefore the dry polymer melting point can
be calculated from the wet polymer value, and vice versa.
This relationship is useful when thermal degradation

prevents the direct determination of the dry polymer melting point.

We believe that the melting temperature and heat of fusion, ΔH_f, reflect the regularity and strength of the intermolecular dipolar bonding networks that stabilize the laterally bonded two-dimensional crystalline phase. The DSC and X-ray techniques should be regarded as complementary for acrylics since they are probably sensitive to entirely different levels of order. Support for this statement comes from comparing the responses of the thermal and X-ray parameters to the addition of vinyl acetate to the chain. In Table II we compare the response of the wet-polymer T_m and ΔH_f with the half-width of the major equatorial reflection ([200]) at 5.26 Å) and the crystalline index. The [200] reflection is sensitive to the average interchain distance. The crystalline index is defined here as the diffractometer scattering intensity under the sharp [hko] reflections divided by the total intensity from $2 \theta = 0$ to 40°. The diffuse meridional reflection is treated as non-crystalline. Very little change in the two X-ray parameters is detected until the vinyl acetate level has reached approximately 12%. By this point significant reductions in T_m and ΔH_f have occurred. Once the ΔH_f has been reduced below about 150 cal/mole·AN the X-ray structure begins to become disordered. The distribution of the interchain distance broadens and the crystalline index decreases. The response in the thermal parameters over the vinyl acetate range from zero to 12% correlates extremely well with corresponding changes in fiber properties. One observes significant reduction in the hot-wet modulus and tenacity and increases in dyeability and hot-water shrinkage. We find the thermal parameters to be much more useful predictors of commercially important fiber properties than the X-ray parameters.

A tentative model for the acrylic copolymer structure can now be presented. We assume that the crystalline phase is stabilized by intermolecular dipolar bonds as proposed by Bohn et.al. though the well-defined endotherms suggests that the bonding may be more regular than previously supposed. Comonomers are incorporated into the structure as defects at the expense of these intermolecular bonds. The crystalline structure is sufficiently imperfect to incorporate up to 12 weight percent vinyl acetate (or a correspondingly higher amount of a smaller comonomer) before significant changes in the X-ray parameters are observed. However, the thermal parameters respond to the disruption of the dipolar bonding networks at much lower levels of incorporation.

TABLE II

Comparison of the Response of Thermal and
X-ray Parameters to Vinyl Acetate Comonomer Level

Vinyl Acetate Mole Fraction	Wet-Polymer T_m	Wet-Polymer ΔH_f cal/mole·AN	Half-Width [200] Reflection	Crystal-line Index
0	185°C	1150	1.4 2 θ	0.39
0.0092	177	860	1.4	0.40
0.0294	166	550	1.4	0.37
0.0404	158	500	1.5	0.37
0.0509	153	420	1.6	0.37
0.0708	142	300	1.8	0.38
0.0981	125	205	2.4	0.33
0.130	108	70	3.1	0.29
0.150	102	50	4.1	0.20
0.178	None	None	4.6	0.12
0.240	None	None	8.0	--

The DSC technique is also responsive to the morphological changes that occur during commercial fiber production. A typical acrylic wet-spinning operation consists of three stages: fiber formation, orientation and relaxation. The fibers are formed by extruding filaments of concentrated polymer solution into a non-solvent bath. The coagulated filaments are then washed free of solvent and stretched in steam or hot water. A final relaxation step in steam or hot water is required to reduce fiber fibrillation and increase dyeability. Interesting changes are observed in the wet-fiber melting endotherms at various parts of the process. Here we consider a fiber spun from an acrylic copolymer containing 7% vinyl acetate by weight. When the orientation stretch ratio is increased from 1X to 6X two changes in the melting endotherm are observed. First, the ΔH_f increases continuously from 450 cal/mole·AN to 600 cal/mole·AN. This indicates an increased formation of dipolar bonds. Secondly, at a 1X stretch ratio a single endotherm is observed at 156°C, but as the stretch ratio is increased above 3X a small endotherm appears at 147°C. The melting endotherms of fibers spun at different stretch ratios is shown in Figure 3. Saturated steam relaxation at temperatures between the two endotherms cause the temperature of smaller endotherm to increase and approach the one at 156°C, which remains constant. We interpret the appearance of the 147°C endotherm to indicate disruption of the crystalline phase at the high threadline stress levels. The reversal or coalescence upon steam relaxation then is

analogous to the annealing process by which semicrystal-
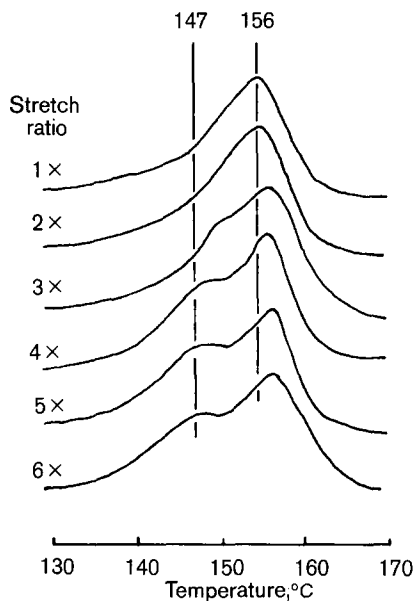line fibers increase their crystalline perfection.

Fig.3. Melting endotherms of copoly-
mer fiber (7% vinyl acetate)
at different stretch ratios.

CONCLUSIONS

The wet-polymer thermal technique promises to yield much
new information about acrylic copolymers. We have al-
ready seen that the technique is extremely sensitive to
morphological changes brought about by polymer composi-
tional variations and fiber processing operations. Future
publications will concentrate   on the nature of the
polymer-water interaction, the copolymer melting behavior
and the response to changes in fiber morphology.

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NOTE - The average absolute difference between the observed and calculated $T_{m(H_2O)}$ was 0.5, 1.5, and 2.3°C for co-, ter-, and tetrapolymers. This information will appear in a paper that is in preparation.