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Behavior

Melting Behavior of Polyacrylonitrile Copolymers

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SUMMARY: The melting behavior of acrylonitrile copolymers, ter- and tetrapolymers was studied in the dry state and in the presence of water. The melting point depression caused by the incorporation of a specific comonomer into the polyacrylonitrile chain was shown to be dependent on the molecular structure of the comonomer. Not all comonomers gave equivalent melting point depressions on a molar basis. The Eby theory of comonomer melting was used to model the melting behavior. This theory assumes that the non-crystallizing (non-AN) comonomers enter the crystal lattice as point defects rather than being relegated to the amorphous phase. An equation was developed for predicting the melting point of copolymers, terpolymers and higher order polymers as a function of the polymer composition and the specific melting point depression constant for each comonomer. The latter constants are derived from the copolymer melting point curves. The equation is applicable to both dry and wet polymers and excellent agreement between the observed and calculated melting points for wet terpolymers and tetrapolymers was observed.

INTRODUCTION: In a previous report we demonstrated that incorporation of comonomers into the PAN chain disrupted the crystalline structure and thereby reduced the melting point and heat of fusion (FRUSHOUR, 1981). The latter two quantities were interpreted as a measure of the strength and regularity of the intermolecular dipolar bonding networks that stabilize the crystalline structure.

We wish to establish two points in this communication. First, the melting point depression effected by a given comonomer is primarily a function of the molecular structure of that comonomer. Secondly, the latter dependence allows one to calculate very accurately the melting point of acrylic polymers having rather complex compositions, i.e., terpolymers and tetrapolymers.

EXPERIMENTAL: The DSC wet-polymer melting point method was described in previous reports and will be reviewed here very briefly (FRUSHOUR, 1981, 1982). A Perkin-Elmer DSC II scanning calorimeter and the attendant large volume stainless steel capsules (Perkin-Elmer part 319-0218) were used. A polymer-water paste was prepared by mixing sufficient water with the polymer to give a water weight fraction of 0.67 for the paste and then approximately 70 mgs. of this paste was sealed in the capsule. The wet-polymer melting points reported here are taken as the peak of the the first melting endotherm. They are reproducible to ±0.5°C. A heating rate of 5°C/min. was used.

The melting point of the dry polymers was measured using a scanning rate of 80°C/minute in an attempt to record the entire melting endotherm prior to the onset of the strong exothermic degradation reaction that is characteristics of acrylic polymers (HINRICHSEN, 1974). Even at this high scanning rate many of the polymers decomposed before the melting could be measured. It should be emphasized that the melting point was easily measured for these same polymers when water was added.

The polymers were made using a standard continuous reactor method that maintains good compositional homogeneity. The Mn and Mw were approximately 55,000 and 100,000 grams/mole, respectively. Details concerning polymerization and compositional analysis are available upon request.

The polymer type will be denoted by using the abbreviations for the monomers. For example, the acrylonitile-vinylidene chloride copolymer will be designated as AN/VCl_2. Additional abbreviations to be used are as follows: acrylonitrile, AN; vinyl acetate, VA; methyl acrylate, MA; ethyl vinyl ether, EVE; vinyl bromide, VBr; and vinyl chloride, VCl.

Dependence of Copolymer Melting Behavior on Composition

The dependence of both wet and dry-polymer melting points on the mole fraction of comonomer can be compared in Figure 1 where Tm^{-1} is plotted against mole fraction for the AN/VA, AN/EVE and AN/VCl_2 copolymers. The major effect of the water is to shift the curves along the reciprocal temperature axis without significantly altering the slope. In other words the water does not affect the dependence of Tm^{-1} on comonomer content. The water weight fraction for the comonomers was 0.67. This is well into the region of two-phase behavior where the melting point has been depressed the maximum amount possible by addition of water and becomes dependent upon comonomer composition alone (FRUSHOUR, 1981, 1982).

The striking dependence of the PAN melting point depression on the molecular structure of the comonomer is demonstrated in Figure 1

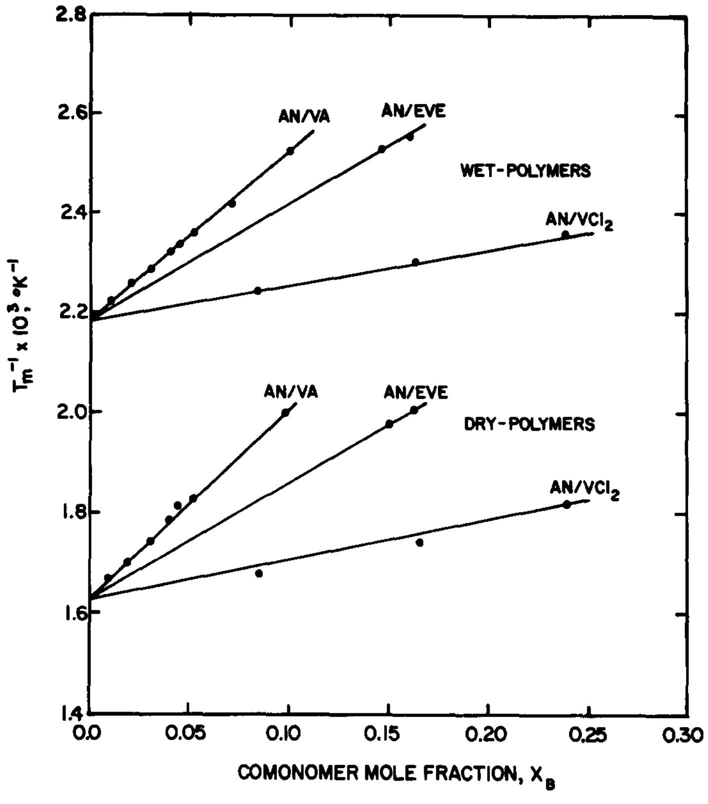

Figure 1. A comparison of the dependence of the wet and dry-polymer melting points on comonomer type and mole fraction.

and also in Figure 2 where more extensive wet-polymer melting point data is shown. The slope of the melting point curve is a good measure of the degree to which a comonomer will depress the melting point and therefore the slopes will be referred to as the melting point depression constants. One can immediately see the strong dependence of the melting point depression on the size of the comonomer. It is possible to estimate the molar volume of the comonomer substituent groups using the tabulated values of the molar volumes of common functional groups (VAN KREVELAN, 1972). The comonomers having the largest and smallest substituent groups are the AN/MA and AN/VCl comonomers, respectively. The estimated molar volumes of the acrylate and chloride groups are 36 cm^3/mole and 7.5 cm^3/mole, respectively and the corresponding melting point depression constants for the AN/MA and AN/VCl comonomers are 3.37 x 10^{-3} °K^{-1} and 0.51 x 10^{-3} °K^{-1}. The difference in the degree to which these two comonomers depress the PAN melting point is large. At a comonomer mole fraction of 0.1 the melting point of the wet PAN homopolymer is depressed from 184°C to 122°C for the AN/MA copolymer but only depressed to 172°C for the AN/VCl copolymer.

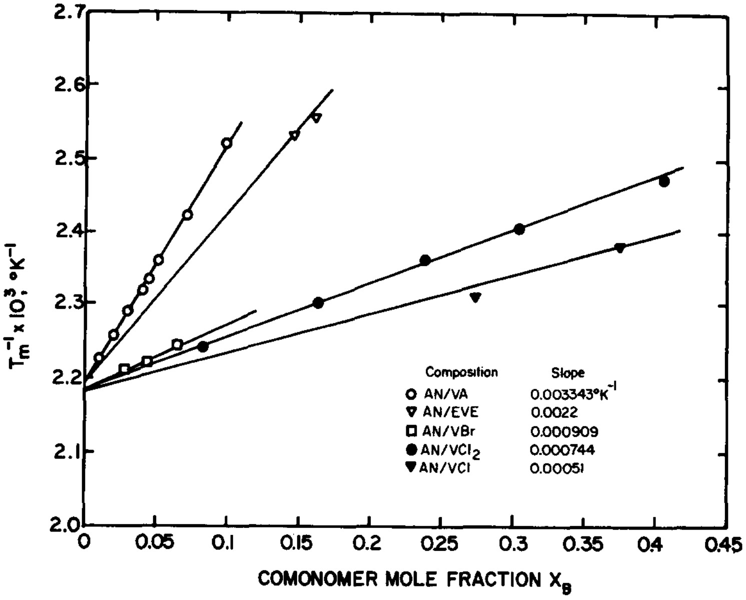

Figure 2. More extensive series of melting point curves for wet-polymers.

In Table I the melting point depression constants are listed for each comonomer along with the calculated substituent molar volumes and the literature values of the dipole moments. The values for the melting point depression constants obtained from the wet and dry polymer measurements are in close agreement. Dry polymer melting points could not be obtained for the AN/VCl and AN/VBr copolymers due to polymer degradation prior to melting during the DSC scan. A correlation between the magnitude of the melting point depression constant and the comonomer substituent molar volume was determined by fitting the wet-polymer data in Table I to a linear least squares regression. The results of this analysis are included in Table I. The r^2 value, which is the degree of fit, was 0.83. This means that approximately 80% of the variation in the melting point depression constants can be accounted for by the variation in the molar volumes of the substituent groups. This result supports our previous position that the comonomers enter the lattice as point defects rather than being relegated to an amorphous phase (FRUSHOUR, 1981, 1982) and that the Eby model of crystalline copolymer should be used for acrylonitrile copolymers (EBY, 1963). This model predicts that larger comonomers will disrupt the crystal more than the smaller ones.

These results do not rule out the possibility that features of the comonomer in addition to the molar volume may affect the magnitude of the melting point depression constant. All of the comonomers included in this study had dipole moments between 1.0 and 2.0 Debyes, and one could argue that the presence of the dipole on the comonomer would affect the degree to which the comonomer disrupts the crystal lattice. Dipole-dipole interactions between the comonomer and the nitrile groups will exist and these interactions could offset the degree to which the bulky side-groups disrupt the lattice. A logical extension of this work will be the examination of a series of AN copolymers in which the volume, flexibility and polarity of the substituent groups is systematically varied. One might then be able to develop a more complete explanation of the dependence of the melting behavior on comonomer molecular structure.

Melting Behavior of AN Ter- and Tetrapolymers

The defect model of the copolymer structure as originally proposed by Eby (EBY, 1963) suggests that the influence of individual defects on the final melting point should be additive. A general expression for the melting point of acrylic polymers that takes into account this additivity of defects is given below:

$$\frac{1}{Tm} - \frac{1}{Tm^{\circ}} = \sum_{i=1}^{n-1} KiXi$$

where n is the copolymer order (n is two for copolymers, three for terpolymers, etc.), X_i is the mole fraction of the i^{th} monomer, K_i is the corresponding melting point depression constant, and Tm° is the melting point of the PAN homopolymer.

This equation can be used to predict the melting point of wet and dry polymers. The vertical shift in the melting point curves observed upon addition of water, as seen in Figure 1, is simply the difference in Tm° for the wet and dry polymers. A value of 456.8°K was used for Tm° of the wet homopolymer. This was obtained from a direct measurement of the wet homopolymer. A reliable value for Tm° of the dry homopolymer is more difficult

TABLE 1

Melting Point Depression Constants for Acrylic Copolymers

Comonomer	$K_B \times 10^3 (°K)^{-1}$ Wet Polymer	Dry Polymer	Molar Value of[1] Comonomer Side Chain	Dipole Moment[2]
Methyl Acrylate	3.370	-----	36 cm^3/mole	1.7 Debyes
Vinyl Acetate	3.343	3.923	39	1.7
Ethyl Vinylether	2.20	2.40	39	1.2
Vinyl Bromide	0.909	-----	11	1.3
Vinylidene Chloride	0.744	0.710	15	1.3
Vinyl Chloride	0.510	-----	7.5	1.4

[1] Volume of R side-chain on monomer ($CH_2 = CHR$). Volumes calculated from tabulated values of the molar volumes of common functional groups (VAN KREVELEN, 1972). The correlation between the K_B values and the side chain molar volumes is given below:

$$K_B = 8.5 \times 10^{-5}(M.V.) - 1.5 \times 10^{-4} \qquad r^2 = 0.83$$

[2] Dipole moments from (MC CLELLAN, 1963)

TABLE II

Comparison Between Observed and Calculated Melting Points

Composition	Weight Percent	$Tm_{(obs.)}$	$Tm_{(calc.)}$	Error
	Copolymers			
AN/VA	98.36/1.64	176	176.8	-0.8
AN/VA	96.75/3.25	169.8	170.1	-0.3
AN/VA	95.20/4.80	163.9	163.7	0.2
AN/VA	93.65/6.35	157.9	157.5	0.4
AN/VA	92.95/7.05	155.2	154.6	0.6
AN/VA	91.94/8.06	150.7	150.7	0.0
AN/VA	88.95/11.05	140.0	139.0	1.0
AN/VA	15.06/84.94	123.2	124.1	-0.9
AN/VCl_2	85.73/14.27	173.1	171.2	1.9
AN/VCl_2	73.69/26.31	161.3	159.8	1.5
AN/VCl_2	63.64/36.36	150.5	149.7	0.8
AN/VCl_2	55.63/44.37	142.8	141.1	1.7
AN/VCl_2	44.28/55.72	131.7	128.3	2.4

TABLE II (continued)

Comparison Between Observed and Calculated Melting Points

Composition	Weight Percent	$\mathrm{Tm}_{(obs.)}$	$\mathrm{Tm}_{(calc.)}$	Error
AN/VBr	94.44/5.56	179.5	178.5	1.0
AN/VBr	91.6/8.4	177.0	175.7	1.3
AN/VBr	87.7/12.3	172.8	171.8	1.0
AN/VCl	71/29	159	158	1.0
AN/VCl	58.5/41.5	147	147	0.0
AN/EVE	81.03/18.97	122	125	-3.0
AN/EVE	79.25/20.75	118	120	-2.0
AN/MA	93.8/6.2	159.3	157.9	1.6
AN/MA	92.5/7.5	154.9	152.6	2.3
AN/MA	91.7/8.3	150.7	149.4	1.3
		Terpolymers		
AN/VA/VBr	87.6/6.87/5.53	152.8	149.8	3.0
AN/VA/VBr	85.8/8.38/5.79	143.8	143.5	0.3
AN/VA/VBr	90.7/7.15/2.12	152	152.2	-0.2
AN/VA/VBr	89.1/8.52/2.37	145.5	146.5	-1.0
AN/VA/VBr	83.1/4/12.9	154.7	154.0	0.7
AN/VA/VBr	86.1/8,28/7.61	141.6	142.1	-0.5
AN/VA/VBr	85.9/6.17/7.9	150.8	150.2	0.6
AN/VBr/VCl_2	65.9/10.4/23.7	150.8	150.8	0.0
AN/VBr/VCl_2	68.2/11.1/20.7	154.4	153.1	1.3
AN/VA/VCl_2	77.11/2.45/20.44	154.1	154.7	-0.6
AN/VA/VCl_2	79.93/3.49/16.58	152.8	154.0	-1.2
AN/MA/VBr	76.5/5.5/18	143.8	141	2.8
AN/MA/VBr	74.8/6.7/18.5	136	135	1.0
AN/MA/VBr	80.1/6.5/13.4	167	169	-2.0
		Tetrapolymers		
AN/VBr/VCl_2/ VA	65.7/11.4/21.9/ 1	142	145	-3.0
AN/VBr/VCl_2/ VA	78.9/9.08/11.25/ .8	157	159	-2.0

to obtain since the melting cannot be observed in the DSC. An extrapolated value of 617°K is obtained using the dry AN/VA copolymer melting points.

In Table II the calculated and observed wet-polymer melting points are compared for numerous polymers including ter- and tetrapolymers. Good agreement between the observed and calculated values is observed. The experimental error is within the range predicted from standard error calculations that take into consideration the error propagation in the calculated values. We made no attempt to obtain the corresponding dry polymer melting points on these ter- and tetrapolymers since many of them degrade prior to melting.

Conclusions

We have demonstrated that the degree to which a comonomer depresses the melting point of an acrylonitrile copolymer is strongly dependent on the comonomer structure. The effect can be quantified to a high degree of accuracy by measuring the melting point depression constants. This quantification allows one to accurately calculate the melting points of random ter-, tetra and even higher copolymers that are useful as fiber-forming polymers. This means that if one constructs a simple empirical correlation between a fiber property and the melting point, then one can calculate how that property will change with respect to comonomer composition. In future communications examples of this application will be presented.

REFERENCES

1. EBY, R. K.: J. App. Physics 34, 2442 (1963).

2. FRUSHOUR, B. G.: Polymer Bulletin 4, 305-314 (1981).

3. FRUSHOUR, B. G.: Polymer Bulletin 7, 1-8 (1982).

4. HINRICHSEN, G: Angew. Makromol. Chem. 20, 121 (1974).

5. MC CLELLAN, A. L.: Tables of Experimental Dipole Moments, W. H. Freeman and Company, San Francisco, 1963.

6 VAN KREVELAN, D. W.: Properties of Polymers, Elsevier Publishing Company, NY, 1972. Table II (Exner) pg. 43.

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