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The crystallization of piezoelectric vinylidene fluoride-tetrafluoroethylene and vinylidene fluoride-hexafluoropropylene copolymers was investigated. Several compositions of each copolymer were synthesized and the melting point depression was evaluated as a function of composition. Models were examined

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in which the comonomers were included as defects in the crystal lattice or in which they were excluded. The need to use several approaches before a conclusion can be reached is clearly seen. Our studies indicate that the exclusion model is a less accurate description of the crystallization of these two copolymers. Values for the enthalpy of defect incorporation are evaluated and shown to be reasonable.

Introduction

The homopolymer of 1,1-difluoroethylene (vinylidene fluoride) has received considerable attention because of the high piezo- and pyroelectricity it exhibits once it has been subjected to high electric fields.[1-5] The reason for this piezo- and pyroelectric behavior has not been determined with certainty. A dipole theory and a charge entrapment theory have been proposed. Discussions of these possibilities are given in recently published articles.[3,6]

Although the exact mechanism of piezo- and pyroelectricity is not known, it has been firmly established that the crystals of poly(vinylidene fluoride) are responsible for this phenomenon. Hence, the characterization of the crystal structure and its variation with comonomers could lead to a better understanding of piezoelectricity in the vinylidene fluoride homopolymer.

Two copolymers of vinylidene fluoride that exhibit piezoelectricity[7-10] are vinylidene fluoride-co-hexafluoropropylene and vinylidene fluoride-co-tetrafluoroethylene polymers. The thermodynamics of the crystallization of these two copolymers is the subject of the present article. Copolymers of vinylidene fluoride with tetrafluoroethylene have received some attention previously;[11,12] to the author's knowledge vinylidene fluoride-hexafluoropropylene copolymers have not.

The object of the present analysis was to determine whether the comonomer with vinylidene fluoride was incorporated in the crystal or excluded. Copolymers of varying composition were synthesized. Using the melting point depression behavior of these copolymers, an attempt was made to fit two predictive equations. The exclusion model formulated by Flory[13] is:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_u} \ln p_A \simeq -\frac{R}{\Delta H_u} \ln X_A \qquad (1)$$

where T_m is the melting point of the copolymer T_m° is the equilibrium melting point of the homopolymer of the crystallizing unit "A" (in this case vinylidene fluoride), ΔH_u is the heat of fusion per mole of the homopolymer crystalline units, and p_A is the probability that a vinylidene fluoride will add to the polymerizing molecule. The probability for a random copolymer is the mole fraction, X_A. The melting point depression with increasing non-crystallizing comonomer concentration is interpreted as a configurational entropic effect. The second equation was formulated for inclusion of the comonomers in the growing crystal lattice. It is given as[14]

$$T_m = T_m^\circ \{1 - \frac{2\sigma}{\Delta H_u} 1/\ell\} - \frac{\Delta H_d}{\Delta H_u} X_B T_m^\circ \qquad (2)$$

where ΔH_d is the excess enthalpy due to the defect in the crystal lattice caused by the comonomer, σ is the fold surface free energy, ℓ is the lamellar thickness, and $X_B = 1-X_A$, and the other symbols are the same as in equation 1.

Experimental

The vinylidene fluoride/tetrafluoroethylene copolymers were prepared by latex polymerization techniques. The reaction was initiated at 84°C and at 300 psig with sodium persulfate. For the vinylidene fluoride/hexafluoropropylene copolymer, the reaction was initiated at 75°C, 650 psig with isopropyl peroxy dicarbonate. Subsequent characterization of the coagulated and purified copolymers proved them to be of high molecular weight.

DSC measurements were made with a Perkin-Elmer Model DSC-1B. Scan rates of 10°/minute were used. The melting points reported are those measured after an initial melting and recrystallization cycle.

Results

Tables I and II summarize the differential scanning calorimetry data, the calculated mole fractions of monomers, together with the p_A values. The probability, p_A, that a vinylidene fluoride unit will add to the growing chain was calculated using the equation[15]

$$p_A = \frac{r_A[M_A]}{r_A[M_A] + [M_B]} \qquad (4)$$

where r_A is the reactivity ratio of vinylidene fluoride in the copolymer system, calculated from the Q and e scheme.[15] The values used for Q and e are: for vinylidene fluoride $Q = 0.03$, $e = -0.5$, for tetrafluoroethylene $Q = 0.049$ and $e = 1.22$, and for hexafluoropropylene $Q = 0.002$ and $= 1.8$.[16] The reactivity ratio is calculated from[17]

$$r_A = \frac{Q_A}{Q_B} \exp[-e_A(e_A - e_B)] \qquad (4)$$

Without further knowledge the inequality of p_A and X_A cannot be resolved and both must be used for the evaluation of equation 1. This is especially true since the Q and e scheme itself is subject to criticism.

The Exclusion Model

When a linear regression is performed on the data of Table I a fit to equation 1 is achieved. If the mole fraction is used as a first approximation, the calculated equilibrium melting point of homopolymer, T_m°, is obtained as $T_m^\circ = 453°K$, and the slope of the least square line gives a value for the enthalpy of fusion per mole of crystalline vinylidene fluoride units, ΔH_u, of 525 cal/mole. In order to test the "goodness of fit" the standard deviation of the estimate of $1/T_m$ on $\ln X_A$ is calculated. Using

$$\hat{S}y,x = \hat{S}y\sqrt{1 - r^2} \qquad (5)$$

where $\hat{S}y$ is the standard deviation of $1/T_m$ from the mean and r^2 is the coefficient of the determination, $\hat{S}y,x$, the standard deviation of the estimated $1/T_m$ at any $\ln X_A$, is found to be 3.9×10^{-5}. Calculated at 400°K this value for the error gives a ± 6°K variation. Hence, the fit is fairly good. However, based on earlier work on the crystallization of vinylidene fluoride homopolymer[18,19] the ΔH_u was found to be 1425 cal/mole. Refinement of these calculations using the p_A values rather than the mole fractions yields $T_m^\circ = 452°K$ and $\Delta H_u = 115$ cal/mole. The standard deviation of temperature is ± 6°K as above. Although the data appear to fit equation 1, the error in the heat of fusion forces an examination of the inclusion model.

The identical data analysis was performed on the vinylidene fluoride-tetrafluoroethylene copolymer. For this calculation, only the first three data points in Table II were used since at about 80 mole % vinylidene fluoride further increase in tetrafluoroethylene content causes a rise in melting point. This behavior is not unusual and has been reported earlier.[11,12] When equation 1 is used with the p_A's a T_m° of 426°K and a ΔH_u of 4295 cal/mole result. The ΔH_u is much higher than the value of 1425 cal/mole expected. With the mole fraction values, a $T_m^\circ = 426°K$ and $\Delta H_u = 1407$ cal/mole result. The standard deviation of the estimate of T_m from equation 5 is ± 1°K; hence, a very good fit is indicated. The ΔH_u does agree with the value expected. An independent check for T_m° would give more confidence in the fit of equation 1. Figure 1 is based on a method due to Hoffman and Weeks[20] that is used to calculate the T_m° from melting point data versus annealing temperature. It is designed to eliminate the melting point depression due to the surface free energy of finite sized crystals. A sample of poly(vinylidene fluoride) is melted and then recrystallized by cooling at a controlled rate. After the recrystallization a predetermined annealing temperature, T_a, is set on the DSC, observing proper calibration techniques, and the sample is annealed for one hour. The melting point, T_m, is then recorded by scanning upward in temperature. The T_m° for this homopolymer from the data of Figure 1 is 466°K. It is obtained by fitting the data points to[2]

$$T_m = (1 - \phi)\, T_m^\circ + \phi\, T_a \qquad (6)$$

and using the slope and intercept to calculate T_m°. Equivalently the straight line of melting point depression can be extrapolated to the $T_m = T_{anneal}$ line as shown on Figure 1. The intercept is T_m°. ϕ is a factor containing the lateral and fold surface interfacial free energies. The difference in T_m° from equation 1 and equation 6 is sufficient to cause concern about the validity of the exclusion model.

Several other facts also argue against the exclusion model. Firstly, as little as 5 mole % of tetrafluoroethylene is known to cause a morphology change in the vinylidene fluoride lattice.[2] The change is from the α phase with trans-gauche-trans-gauche chain configuration to a β form with an all trans configuration of the chains. The unit cell is also altered. Secondly, X-ray diffraction data taken on the vinylidene fluoride-tetrafluoroethylene polymers of Table II show an increase in the (200) spacing with increasing tetrafluoroethylene content, which can be attributed to the opening of the lattice dimension to accommodate the somewhat larger fluorine atoms that are replacing hydrogen atoms. Figure 2 shows the X-ray data obtained on unoriented copolymer films. Figure 3 is a representation of the crystal lattice sliced perpendicular to the crystallographic c axis. The (200) and (110) planes contribute to the spacing plotted in Figure 2. In view of these facts, the exclusion model should be put aside despite the accurate ΔH_u determination, and the inclusion model should be examined.

The Inclusion Model

For this model the melting point is a linear function of the mole fraction of comonomer. Figures 4 and 5 are graphs of the observed melting point plotted against the mole fraction of vinylidene fluoride for the hexafluoropropylene and tetrafluoroethylene copolymers, respectively.

The values for the intercept and slope [equation 2] obtained by linear regression for the vinylidene fluoride-hexafluoropropylene copolymer system are

$$T_m^\circ \left\{ 1 - \frac{2\sigma/\ell}{\Delta H_u} \right\} = 450.6 \tag{7A}$$

and

$$- \frac{\Delta H_d}{\Delta H_u} T_m^\circ = -677.6 \tag{7B}$$

The standard error of the estimate of T_m by equation 5 is ± 6°K; hence, the regression equation is a fair predictor. Using the values of $T_m^\circ = 466°K$ and $\Delta H_u = 1425$ cal/mole, equations 7A and 7B give values for σ/ℓ and ΔH_d. The surface area free energy per unit lamella thickness is 23.6 cal/mole. The excess enthalpy of defect inclusion, ΔH_d, is 2072 cal/mole. Similar analysis of the vinylidene fluoride-tetrafluoroethylene yields for the intercept and slope in this system

$$T_m^\circ \left\{ 1 - \frac{2\sigma/\ell}{\Delta H_u} \right\} = 426.3 \tag{8A}$$

$$\frac{-\Delta H_d}{\Delta H_u} T_m^\circ = -254.4 \tag{8B}$$

The standard error of the estimate of T_m is 0.2°K indicating a very good fit of the data points. Using T_m° = 466°K and ΔH_u = 1425 cal/mole values for σ/l and ΔH_d are 60.7 and 778 cal/mole, respectively.

Although at present we have no means of comparing the σ/ℓ and ΔH_d values, they are reasonable when compared to those reported in the tetrafluoroethylene-hexafluoropropylene copolymer system.[23] In fact, with this latter system and the vinylidene fluoride-tetrafluoroethylene copolymer system in the present work a Hess's Law calculation can be performed to calculate the ΔH_d of hexafluoropropylene in vinylidene fluoride crystals.

First, we assume only enthalpic effects and neglect, for simplicity, crystal surface effects. The enthalpy of fusion per mole of monomer units in a copolymer is given as[14]

$$\Delta H = \Delta H_u - X_B \Delta H_d \qquad (9)$$

where ΔH_u is the enthalpy of fusion of crystalline units and X_B is the mole fraction of included comonomer. The abbreviations VF_2 for vinylidene fluoride, TFE for tetrafluoroethylene and HFP for hexafluoropropylene will be used as well as the subscripts "c" and "m" for monomers located in the crystal and melt, respectively. From the present work, the melting of a VF_2 lattice with TFE defects at a 50/50 molar ratio can be written as

$$1/2(VF_2)_c + 1/2(TFE)_c \rightarrow 1/2(VF_2)_m + 1/2(TFE)_m \quad \Delta H = 1425-.5(778) \qquad (10A)$$

The incorporation of HFP defects in a TFE lattice can be represented, from the work of Colson and Eby,[23] as

$$1/2(TFE)_c + 1/2(HFP)_m \rightarrow 1/2(TFE)_c + 1/2(HFP)_c \quad \Delta H_d = 1/2(1084) \qquad (10B)$$

Using the fusion of TFE homopolymer

$$1/2(TFE)_c \rightarrow 1/2(TFE)_m \qquad \Delta H = 1/2(1430) \qquad (10C)$$

we may substract equations 10B and 10C from 10A and obtain

$$1/2(VF_2)_c + 1/2(HFP)_c \rightarrow 1/2(VF_2)_m + 1/2(HFP)_m \qquad (10D)$$

which is the equation for the melting of the VF_2/HFP copolymer.

Algebraically summing the ΔH's of equations 10A - 10C and using equation 9, a value of ΔH_d = 3296 cal/mole is obtained for the defect energy of hexafluoropropylene incorporated in a vinylidene fluoride lattice. When compared to the values of 2117 cal/mole determined from the melting point data the agreement is fair, given the gross assumptions and experimental error.

It is also of interest to note without elaboration that Colson and Eby[23] used a first order elasticity model to calculate the dilatational energy caused by an HFP insertion in a TFE lattice. Their value was .08 ev/defect or 1844 cal/mole. Given that the HFP should cause a proportionally larger volume change on the smaller VF_2 lattice we see that the value of 2117 cal/mole is not unreasonable.

Conclusion

Using the results of several types of measurements the exclusion model is seen to be a less accurate one for the vinylidene fluoride-tetrafluoroethylene and vinylidene fluoride-hexafluoropropylene copolymer system. The need to be cautious is shown by the deceptively good mathematical fit of the data to this model. The comonomers entering as defects in the vinylidene fluoride lattice will be used as a working hypothesis in future efforts to elucidate the role of the defects, if any, in influencing piezo- and pyroelectricity in this fluoropolymer system.

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TABLE I

The Vinylidene Fluoride-Hexafluoropropylene Copolymer System

Mole Fraction Vinylidene Fluoride (X_A)	pa	Tm(°K)
.967	.993	427
.96	.991	427
.96	.991	421
.94	.987	415
.935	.986	404
.935	.986	410
.93	.984	391
.92	.982	404
.91	.980	388

TABLE II

The Vinylidene Fluoride-Tetrafluoroethylene Copolymer System

Mole Fraction Vinylidene Fluoride (X_A)	pa	Tm(°K)
.96	.8614	416
.90	.6998	401
.85	.5948	388
.78	.4787	387
.70	.3767	405
.60	.2798	430

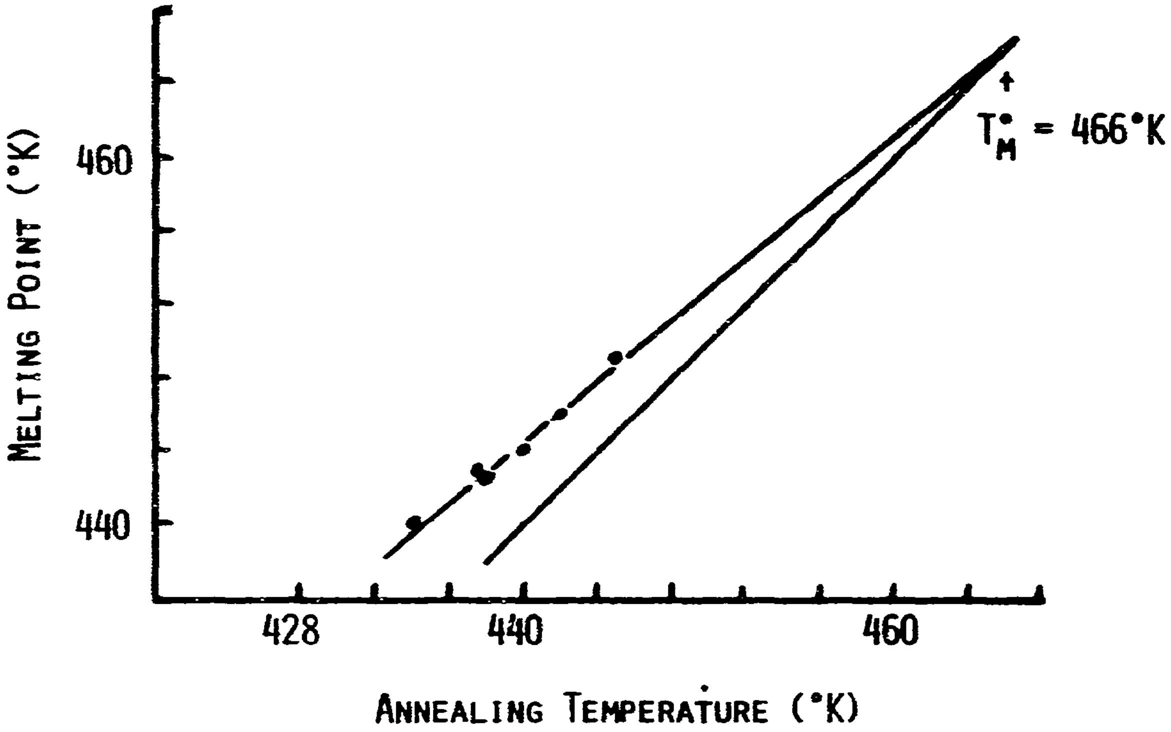

Figure 1. Melting point as a function of annealing temperature for a poly(vinylidene fluoride) homopolymer.

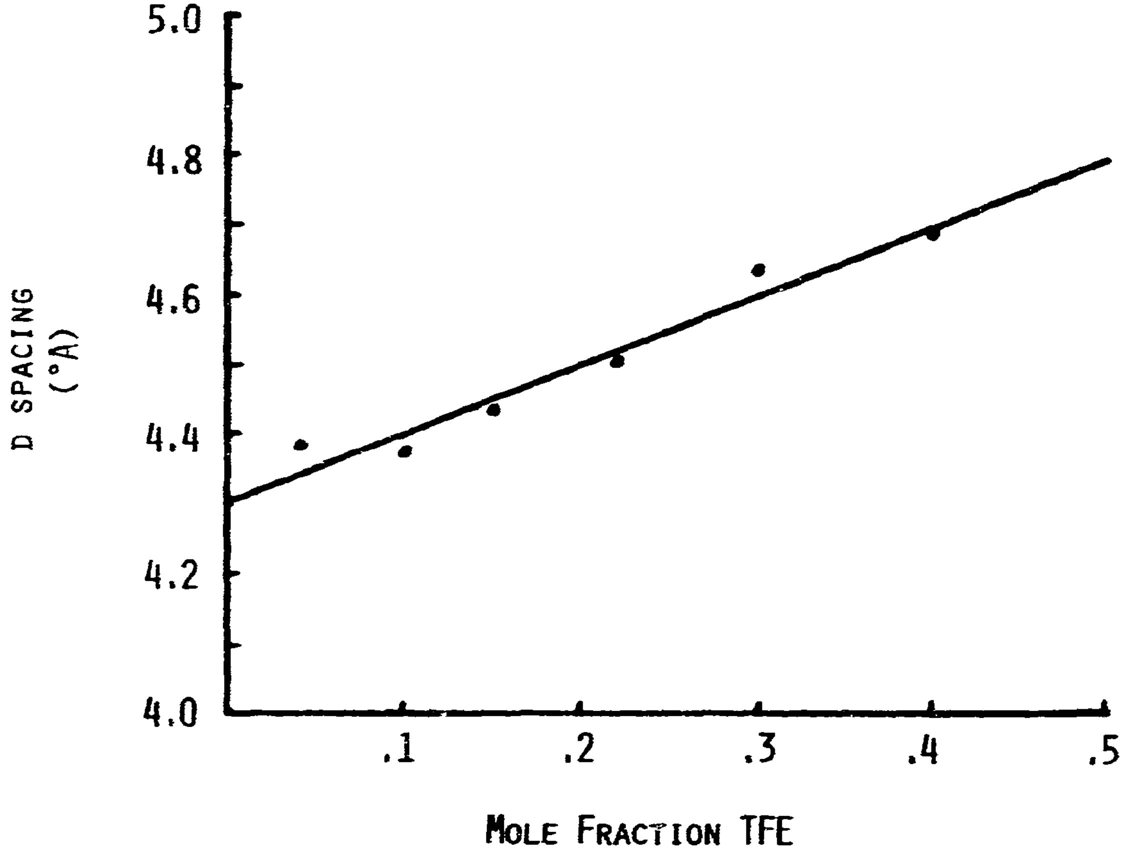

Figure 2. The dependence of the (110), (200) spacing on tetrafluoroethylene content in the vinylidene fluoride-tetrafluoroethylene copolymer.

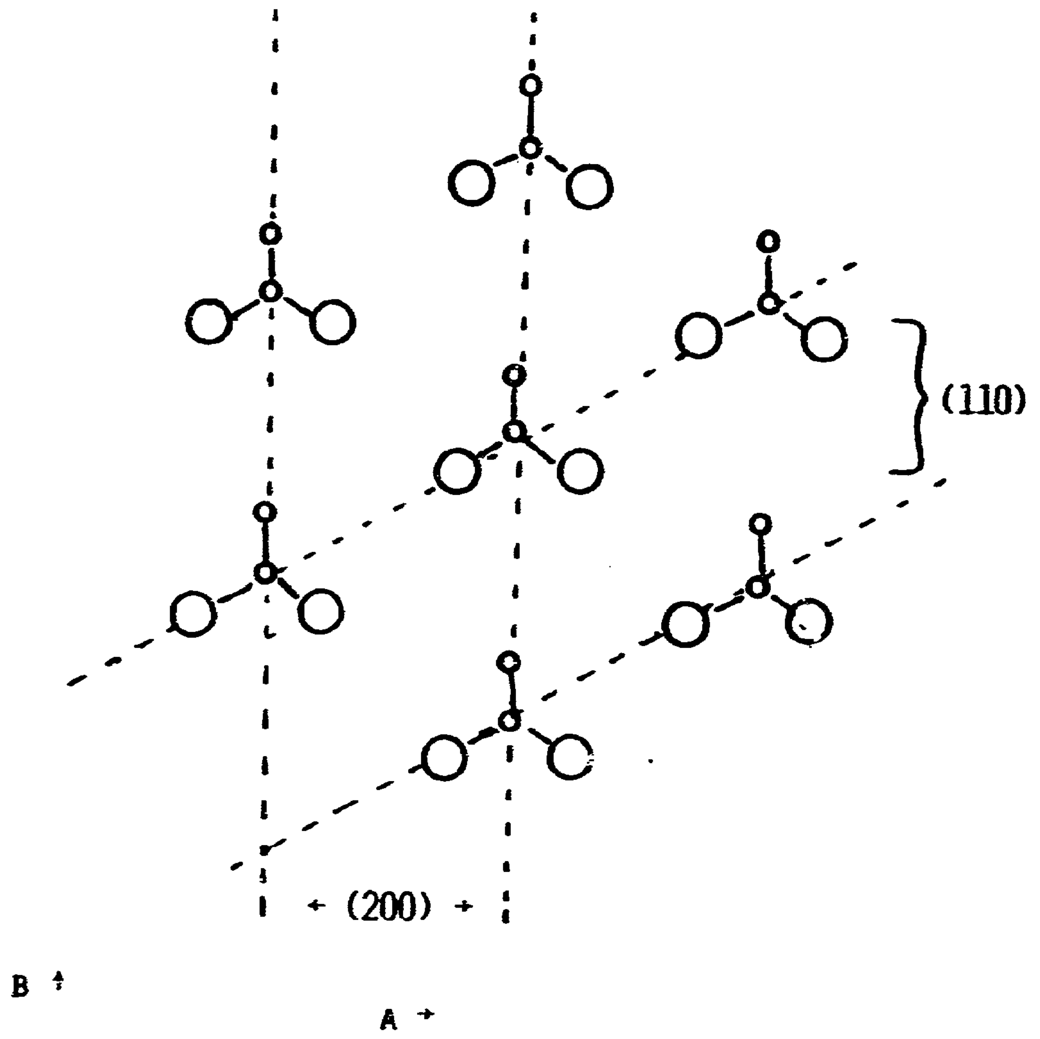

Figure 3. The "c" axis projection of the lattice of the form I (β) vinylidene fluoride copolymer. The large circles are fluorines, the small are carbons.

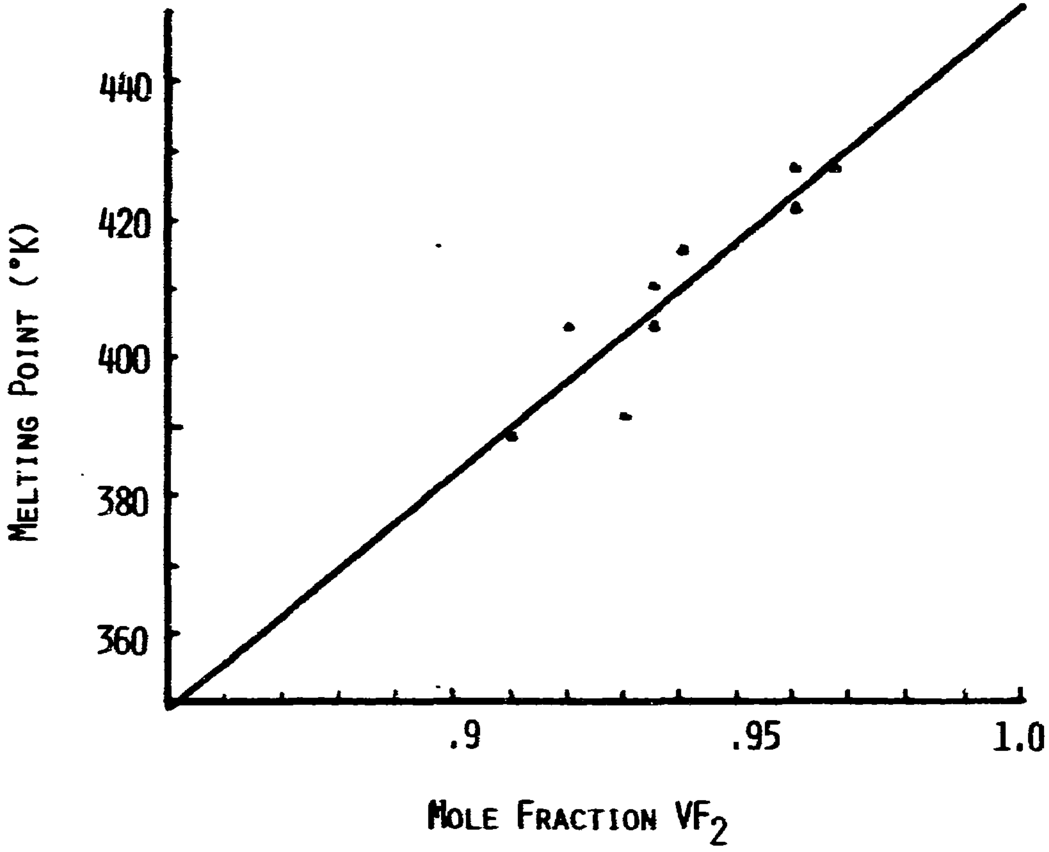

Figure 4. The melting point depression as a function of composition in the vinylidene fluoride-hexafluoropropylene copolymer.

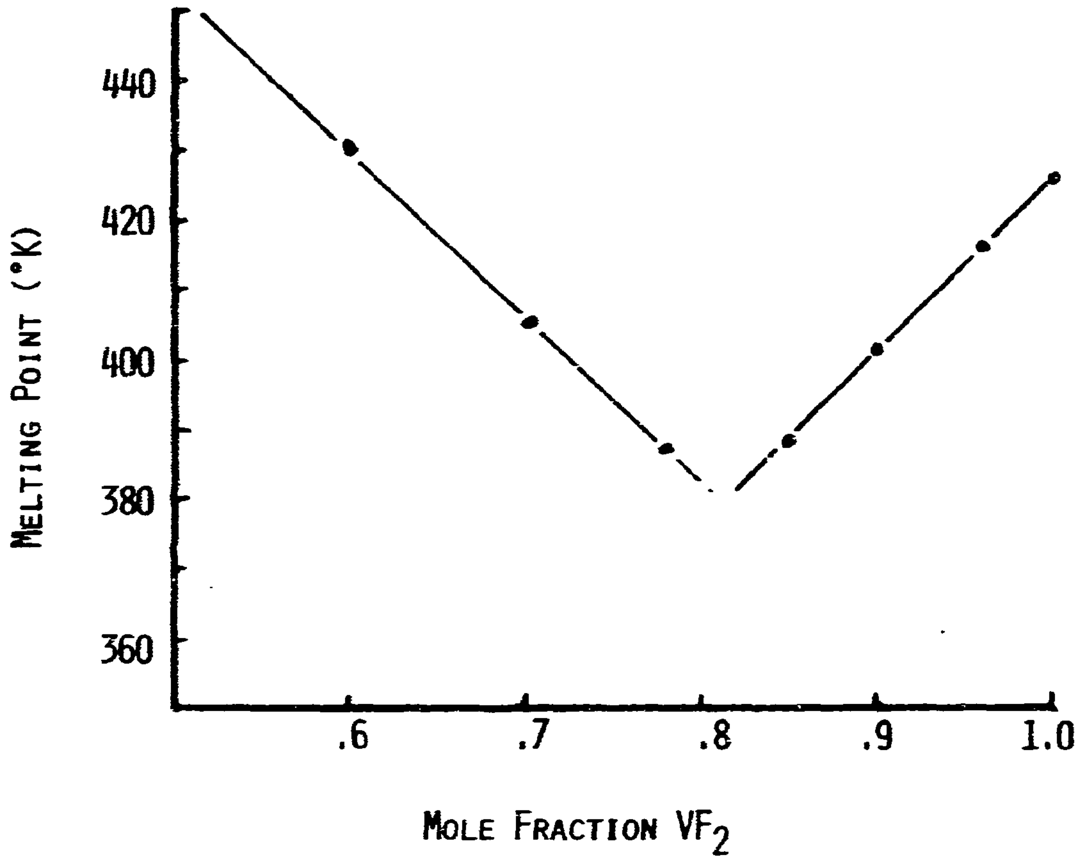

Figure 5. The melting point behavior as a function of composition in the vinylidene fluoride-tetrafluoroethylene copolymer.

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