organize to form a cooperative stack with a face-to-face arrangement.[7,16,17] This can be seen in the racemic mixture of PBLG and PBDG, in which the cooperative stack is preferentially formed between D and L molecules,[17,18] and its melt appears as a first-order transition at around 100 °C.[19] The dielectric and dynamic mechanical strengths in this film have been reduced,[20,21] as in this study, since relaxation occurs only in side chains free from the stack. We are thus led to the view that similar regular cooperative stacks of benzyl groups between adjacent molecules have been created in the present forms D and E. These stacks might be one of the factors stabilizing the specific association of 7 or 19 chains. Work is in progress to illustrate the packing structure of these novel forms in relation to the side-chain structure.

Registry No. PBLG (homopolymer), 25014-27-1; PBLG (SRU), 25038-53-3.

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Received January 6, 1986

On the Curie Temperature of Poly(vinylidene fluoride)

The existence and location of a Curie transition in poly(vinylidene fluoride) (PVF$_2$) have been issues of major importance in regard to the ferroelectric nature and the useful piezoelectric and pyroelectric properties of this polymer. While the first of these issues has now been resolved, the second remains controversial. Existence of Curie transitions in PVF$_2$ has been demonstrated primarily through studies of its copolymers with trifluoroethylene (F$_3$E).[1-9] However, trifluoroethylene introduces a new chemical species (–CHF–) that is absent in PVF$_2$, thus altering its chemical structure. It also introduces the possibility of stereoirregular defects (which, of course, does not exist for PVF$_2$); the resulting VF$_2$/F$_3$E copolymers have, in fact, been shown to be atactic.[1,10] We were the first to report on similar Curie transitions in a different copolymer of PVF$_2$, one containing ~19 mol % *tetra*fluoroethylene (F$_4$E).[11,12] This demonstration has been of importance in applying findings of Curie behavior to PVF$_2$ *homo*polymer, because the F$_4$E units introduce neither new chemical species nor tacticity defects but act simply as additional head–head linkages within PVF$_2$ (which typically contains ~3.5–6% of such units).

While the existence of a ferroelectric-to-paraelectric phase transition in PVF$_2$ is thus now generally accepted, its corresponding temperature is still a subject of controversy. The first reported values were given in 1980 by Micheron[13] and Herchenröder et al.[14] Micheron[13] suggested a Curie temperature of ~170 °C by extrapolation of data for the temperature dependence of the dielectric permittivity of PVF$_2$. This temperature lies just below the melting point of the piezoelectric β-phase of PVF$_2$, which is generally in the region ~175–185 °C (depending upon thermal treatment, polarization, orientation, etc.). The temperature proposed by Herchenröder and co-workers[14] is much lower (i.e., ~140 °C) but has been questioned because both piezoelectric constant (d_{31})[15] and remanent polarization[16] persist well above that temperature, and nearly saturated ferroelectric hysteresis loops are still observed at 140 °C.[17]

Further proposals of a Curie temperature for PVF$_2$ were made in 1983 by Tashiro and co-workers[18,19] and Lovinger et al.[7,8] Tashiro et al. showed that very small new peaks in IR absorbance[18] and X-ray diffracted intensity[19] are obtained at 172 °C during heating of β-PVF$_2$. These peaks were associated with adoption of a paraelectric-phase structure containing gauche and gauche$^-$ segments. Because the melting process is already well under way at this temperature, these peaks are very weak: for example, as seen in Figure 3 of ref 19, the (020) X-ray peak for the paraelectric phase appears only after ~80% of the room-temperature intensity of the corresponding (200,110) peak for the ferroelectric phase has been lost and does not rise above ~15% of that initial intensity. The Curie temperature that we proposed in our earlier work[7,8] was ~205 °C, which is significantly higher than any of the others. We obtained this estimate by extrapolating Curie temperatures from X-ray and dielectric data of VF$_2$/F$_3$E copolymers to 100 mol % VF$_2$. Our X-ray scans showed that the Curie transition for each of the copolymers is very broad (as are typically all transitions in polymers) and can thus encompass up to 40 °C from the first appearance of the paraelectric phase to complete disappearance of its ferroelectric counterpart. Accordingly, the Curie temperatures for each copolymer were reported as temperatures of maximal rate of transformation from the X-ray data and as peak maxima from dielectric spectra. As a result, we pointed out[7,8] that, if the Curie transition for PVF$_2$ is indeed centered at ~205 °C, its earliest manifestations should, in fact, be observable just below the melting point. We, therefore, consider the results of Tashiro et al.[18,19] consistent with ours, since their data show clearly that they observed only the *beginnings* of a transition that was in the process of being aborted by ongoing

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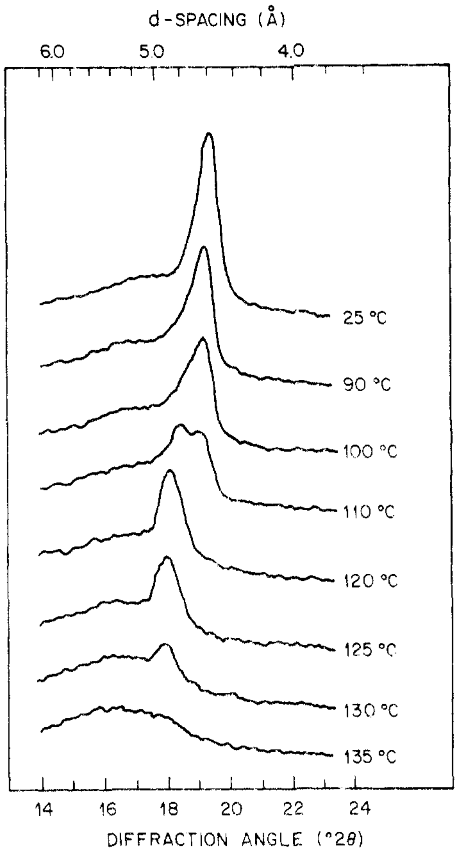

Figure 1. X-ray diffractometric scans during heating of a 76 mol % VF_2 copolymer with tetrafluoroethylene.

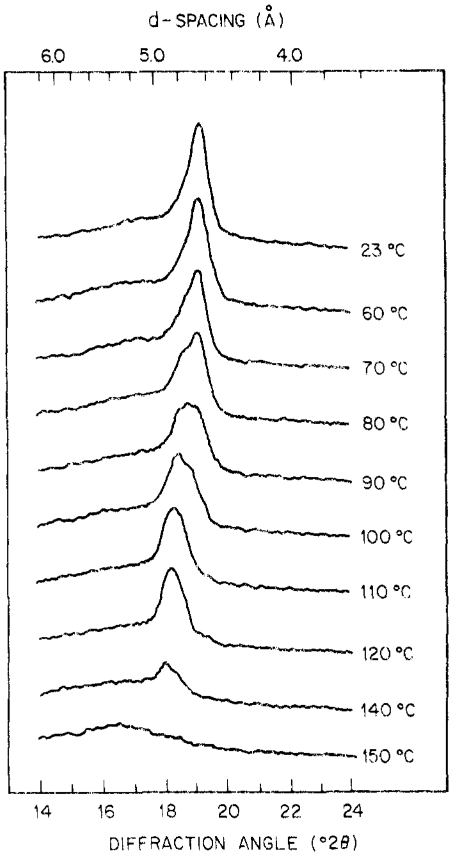

Figure 2. X-ray diffractometric scans during heating of a 71 mol % VF_2 copolymer with tetrafluoroethylene.

melting. In this context, it should be noted that the nature of the transition observed by Tashiro and co-workers[18,19] is not unequivocally associated with a Curie process but can also be a result of melting of β-PVF_2 followed by partial recrystallization of the α- or γ-polymorphs.[20]

In an attempt to provide a new, independent approach toward establishment of the Curie temperature of PVF_2, we report here our results from a study of such transitions in VF_2 copolymers with *tetra*fluoroethylene. Although we had earlier reported a Curie transition for one such copolymer containing 81 mol % VF_2,[11,12] other studies[21-23] of copolymers of similar composition did not find evidence for such transitions. We have, consequently, investigated the *compositional* dependence of Curie transitions in VF_2/F_4E copolymers, using samples synthesized for this purpose.[24] Their synthesis and structural characterization are described separately;[24,25] here, we discuss specifically our findings of Curie transitions and their implications on the Curie temperature of PVF_2 homopolymer.

Our experimental procedure involved synthesis of random copolymers of vinylidene fluoride and tetrafluoroethylene by an emulsion technique as described elsewhere;[24,25] their composition was determined by ^{19}F NMR at 470.7 MHz. Thin-film samples were prepared by molding slightly above the melting point of each copolymer and then rapidly cooling to room temperature. The specimens were then placed on a specially constructed X-ray heating stage and examined diffractometrically during various heating and cooling programs at a scanning rate of 2 °2θ/min, using Ni-filtered Cu Kα radiation.

Clear Curie transitions were obtained for specimens containing ~64–81 mol % VF_2 (and possibly even down to 54 mol % VF_2). At VF_2 contents of ~83 mol % or higher, only the ferroelectric phase was observed at all temperatures between 25 °C and the melting point, both during heating and cooling. The behavior at the upper limit for the transition (~81 mol % VF_2) was described previously:[11,12] the ferroelectric-to-paraelectric phase transition during heating was seen only fleetingly because of incipient melting, while the reverse transition occurred *fully* upon cooling as a result of the metastability of the paraelectric phase.[11,12]

As the relative amount of tetrafluoroethylene increases, the transition is shifted to lower temperatures, so that it is no longer significantly thwarted by melting. This is seen for a 76 mol % VF_2 copolymer in Figure 1, where the peak at ~4.6 Å (arising from the intermolecular spacing of the ferroelectric phase) begins to be asymmetric already at 90 °C, as a result of a small contribution from the emerging paraelectric phase. The two peaks become of approximately equal intensity at 110 °C, while further heating to 120 °C brings all of the crystallographic scattering in this region to the peak of the paraelectric phase (at ~4.9 Å). Additional heating to 135 °C causes this paraelectric phase to melt, and subsequent cooling (not shown) leads to the expected paraelectric-to-ferroelectric transition.

To demonstrate the rapid decrease of the Curie temperature with increasing tetrafluoroethylene content, we show in Figure 2 diffractograms obtained during heating of a 71 mol % VF_2 copolymer. The transition is already well under way at 70 °C, and at 90 °C the two phases are present to approximately the same extent. This solid-state transformation is seen to be completed at ~110 °C, while melting of the resulting paraelectric phase occurs only at much higher temperature. Similar behavior (only at even lower temperatures) was also obtained for a 64 mol % VF_2 copolymer with tetrafluoroethylene. We have indications that the same process persists to even lower VF_2 contents, at least as low as 54 mol %; however, at this composition, the transition is very indistinct and appears to be centered

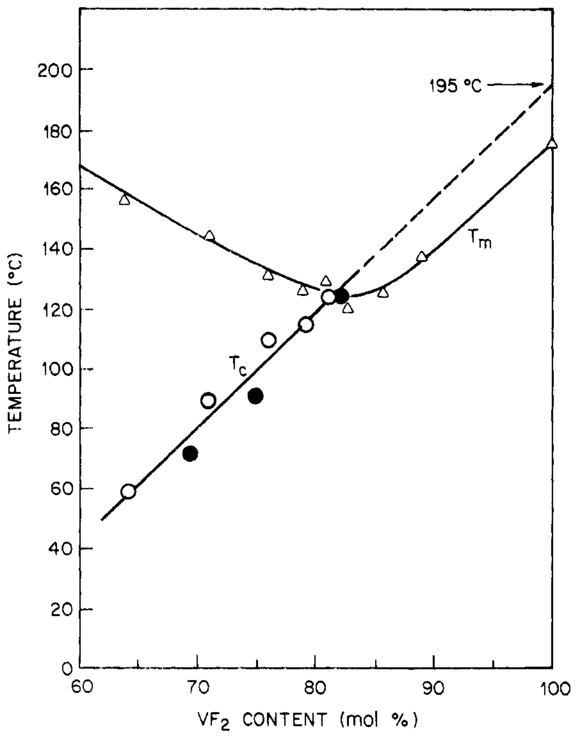

Figure 3. Compositional variation of the Curie temperature, T_c, and the melting temperature, T_m, in copolymers of vinylidene fluoride with tetrafluoroethylene: (○) our data; (●) data from ref 26.

just slightly above room temperature.

We believe that these results substantiate over a wide compositional range our earlier claim of Curie transitions in VF_2/F_4E copolymers, despite the existence of other reports[21-23] in which no Curie transition was detected. In the works by Hicks et al.[21] and Tasaka and Miyata[23] the copolymer used contained 80–81 mol % VF_2, for which, as discussed above, melting interferes and thwarts the ferroelectric-to-paraelectric transition at an early stage. With respect to the study of Koizumi et al.,[22] absence of a Curie transition is somewhat more puzzling, because three compositions were examined dielectrically, ranging from ~69 to ~82 mol % VF_2. However, after publication of our reports,[11,12] Murata and Koizumi reexamined their copolymers and, in a recent communication,[26] propose Curie transitions based upon mechanical and DTA experiments. While such experiments establish the presence (but not the nature) of transitions, our X-ray results described above provide the first crystallographic evidence for Curie transitions in VF_2/F_4E copolymers over a range of composition.

On the basis of these results, we can now plot the variation of Curie temperature in these tetrafluoroethylene copolymers as a function of VF_2 content, in the same manner as we have done previously for copolymers with *tri*fluoroethylene.[7,8] Such a plot is seen in Figure 3. As before,[7,8] these transitions encompass a wide temperature range at each composition; therefore, the points defined as Curie temperatures in Figure 3 correspond to the temperatures at which the peak heights for the ferroelectric and the paraelectric phases are equal. Curie points from Murata and Koizumi,[26] defined as the peak temperatures of the observed secondary endotherms, are also included. Figure 3 also shows the melting temperature of VF_2/F_4E copolymers as a function of composition, from DSC measurements of our samples at a heating rate of 5 °C/min (the datum for 100% VF_2 was obtained from an oriented sample of β-PVF_2). Figure 3 demonstrates remarkable linearity in the increase of Curie temperature with VF_2 content, both for our samples and for those of Murata and Koizumi.[26] These two sets of data can both be fitted well to a single straight line yielding an extrapolated transition temperature for PVF_2 of 195 °C. If only our own data are included, the extrapolated Curie transition for PVF_2 is 197 °C (the three data points by Murata and Koizumi[26] would also lead to an extrapolated transition temperature of 197 °C).

We consider these results as a significant confirmation of our earlier proposal that the Curie temperature for PVF_2 is centered above the melting point. This confirmation is particularly pertinent, because it arises from a family of copolymers that do not differ chemically from PVF_2 and that do not include tacticity defects (as was the case with trifluoroethylene copolymers). Precisely because of the greater chemical and structural similarity of these tetrafluoroethylene copolymers to β-PVF_2, we consider the extrapolated value of 195–197 °C a more reliable estimate for the Curie transition of PVF_2 than our previous one (~205 °C) obtained from copolymers with trifluoroethylene. As before, we find this estimate more appropriate than alternative proposals[13,18,19] for the Curie temperature in the range 170–172 °C, because X-ray and infrared results indicate that the latter corresponds either to the earliest stages of a transition that is thwarted by melting[18,19] or to a melting-and-recrystallization process.[20] Finally, we do not find our results consistent with the 140 °C proposals,[14,27] for reasons[15-18] already discussed by others.[17,18]

In conclusion, we have presented the first crystallographic evidence for Curie transitions in copolymers of vinylidene fluoride with tetrafluoroethylene over a *range* of composition. We found that the ferroelectric-to-paraelectric transition temperature increases linearly with VF_2 content up to 81–82 mol % VF_2, where it is aborted by melting. By extrapolating these transition temperatures to 100 mol % VF_2, we propose a Curie temperature for β-PVF_2 at 195–197 °C, which supports our previous claim that this transition is centered *above* the melting point of the homopolymer. This conclusion is of particular significance because it arises from materials that are chemically PVF_2 with increased head–head (although not tail–tail) content. We are now in the process of studying PVF_2 where the content of the *full* regiodefect group (head-head *and* tail-tail) can be varied over a wide range.[28] Preliminary X-ray results, to be published separately, show that even these PVF_2 polymers exhibit unequivocal Curie transitions both during heating and during cooling.

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Received February 6, 1986

CORRECTIONS

Donald J. Mitchell and Roger S. Porter*: Characterization of Poly(ethylene oxide) Drawn by Solid-State Extrusion. Volume 18, Number 6, June 1985, p 1218.

Due to a scaling error, we wish to correct Figure 1 in our paper. The numbers on the right-hand scale need to be divided by a factor of 1.4 to bring the limit to the obvious theoretical limit of 1.0. All the corresponding values given in the text for orientation factors are correct and are properly addressed relative to this figure.

Tadakazu Maeda and Satoru Fujime*: Dynamic Light-Scattering Study of Suspensions of fd Virus. Application of a Theory of the Light-Scattering Spectrum of Weakly Bending Filaments. Volume 18, Number 12, December 1985, p 2430.

In the left column of p 2431, $\sum_j a_j(m)Q(m,s)$ should read $\sum_j a_j(m)Q(j,s)$.

In the right column of p 2432, $\tau_{\mathrm{m}} = (\pi^4/24\gamma L)$... should read $\tau_m^{-1} = (\pi^4/24\gamma L)$.... In the right column of p 2433, $Y_m(\tau) - B = \beta[\exp(-\bar{\Gamma}\tau)\{1 - (\mu_2/2)\tau^2 + (\mu_3/6)\tau^3\}]^2$ should read $Y_m(\tau) - B = \beta[\exp(-\bar{\Gamma}\tau)\{1 + (\mu_2/2)\tau^2 - (\mu_3/6)\tau^3\}]^2$.