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Compositional Variation of the Structure and Solid-State Transformations of Vinylidene Fluoride/Tetrafluoroethylene Copolymers

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ABSTRACT: Random copolymers of vinylidene fluoride (VF_2) with tetrafluoroethylene (F_4E) have been synthesized over the full compositional range, and their crystalline structures have been studied at ambient temperature, as well as during heating to the melting point and subsequent cooling. The room-temperature structure changes from α-PVF_2 (for compositions with $\geq\sim 93$ mol % VF_2) to β-PVF_2 (for ~92–71 mol % VF_2), to β-PVF_2 and PTFE-like (for ~71–35 mol % VF_2), and eventually to PTFE (for ≤ 34 mol % VF_2). The interchain lattices expand as more F_4E units are incorporated into the molecules; the β-PVF_2 lattice does so at a rate ~6 times that of the PTFE-like structure. Thermal cycling of copolymers containing ≥ 83 mol % VF_2 between room temperature and the melting point shows no solid-state transformations. However, between ~82 and 72 mol % VF_2, discrete and reversible Curie transitions are obtained, of the same type as found earlier in VF_2 copolymers with *tri*fluoroethylene. When the VF_2 content is reduced to 71–35 mol %, such transformations are smeared out, with both phases coexisting over increasingly broader temperature ranges. These effects are explained by the influence of tetrafluoroethylene units in expanding the interchain packing, introducing random deviations from the all-trans conformation of the ferroelectric phase, and facilitating adoption of the disordered conformation of the paraelectric phase.

Introduction

Copolymers of vinylidene fluoride with tetrafluoroethylene (VF_2/F_4E) have been receiving increasing attention, particularly since the first report in 1983 of Curie transitions in these ferroelectric materials.[1] Such copolymers were shown by Lando and Doll[2] to be capable of crystallizing from the melt with the unit cell of the ferroelectric β phase, provided they contain at least 7 mol % of tetrafluoroethylene. Piezoelectricity and pyroelectricity in some VF_2/F_4E copolymers were investigated by a number of authors,[3-6] who demonstrated the attendant dipolar rotation[4] and the nonuniformity of the resulting polarization.[6]

Our initial reports[1,7] of a Curie transition in VF_2/F_4E copolymers were from specimens containing 81 mol % VF_2. Subsequent studies of copolymers in similar compositional ranges indicated the presence[8,9] or absence[10-12] of such a transition. Clearly, therefore, the *compositional dependence* of phase transformations in VF_2/F_4E over the full range (from PVF_2 to PTFE) ought to be examined. In addition, the crystalline structure of these copolymers as a function of composition also requires examination because of the lack of extensive data in the literature. The earliest such data are those of Leshchenko and co-workers,[13] who provided electron diffraction patterns of the compositional range 59–84 mol % VF_2. They interpreted their patterns as indicating essentially the same unit cell dimensions for all of these compositions, corresponding to a slightly expanded β-PVF_2 structure. Lando and Doll[2] subsequently showed that a copolymer containing 93 mol % VF_2 also crystallizes from the melt with a somewhat expanded β cell. More recently, Moggi et al.[14] obtained X-ray diffraction patterns of such copolymers, which indicated a structural change from β-PVF_2 to PTFE with decreasing VF_2 content.

We have prepared VF_2/F_4E copolymers over a wide range of composition, and we report here both their ambient-temperature structures and their phase transformations upon heating and cooling.

Experimental Section

The VF_2/F_4E copolymers were synthesized by emulsion polymerization at 60 °C as described previously.[15] Their molecular structures were determined by use of a variety of solution NMR techniques: ^1H NMR at 500 MHz, ^{19}F NMR at 470.7 MHz, and ^{13}C NMR at 50.3 MHz. Full regiosequence assignments through the heptad level indicated random addition with no blockiness, in agreement with a first-order Markov copolymerization model. For purposes of comparison with the literature, the ^{19}F NMR spectra of two commercial samples used in previous work,[5-7,10-12] were also examined together with that of one synthesized here and having the same nominal composition. The three spectra are seen in Figure 1 to be virtually identical, indicating no systematic differences among the samples in the literature.

For X-ray diffractometric studies, the copolymers were molded into thin films in a heated press and then rapidly cooled to ambient temperature. They were then placed on a resistive diffractometer heater whose temperature and uniformity had been calibrated by melting point standards to ±1 °C and scanned in the reflection mode at 0.5–2.0° 2θ/min, using nickel-filtered Cu $K\alpha$ radiation. For transmission fiber patterns, the specimens were oriented manually at room temperature because of the small quantities of material available.

Results and Discussion

1. Room-Temperature Structure. X-ray diffraction patterns of our VF_2/F_4E copolymers at ambient temperature are seen in Figure 2. The reciprocal-space region depicted here is deliberately restricted between 15° and 25° 2θ because we want to discuss the fine features of the major intermolecular peak, which have eluded previous investigations;[13,14] the region beyond ~25° 2θ is as pres-

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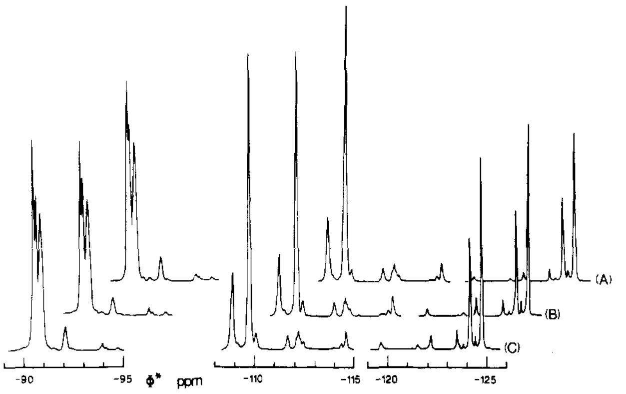

Figure 1. Comparison of the 470.7-MHz ^{19}F NMR spectra of three VF_2/F_4E copolymers having the same nominal composition (80 mol % VF_2): (A) from Daikin Kogyo Co., Ltd.; (B) from Pennwalt Corp. (Kynar 7200); (C) from our laboratory. Actual molar VF_2 contents determined by our NMR analyses: (A) 80.8%, (B) 80.3%; (C) 79.5%.

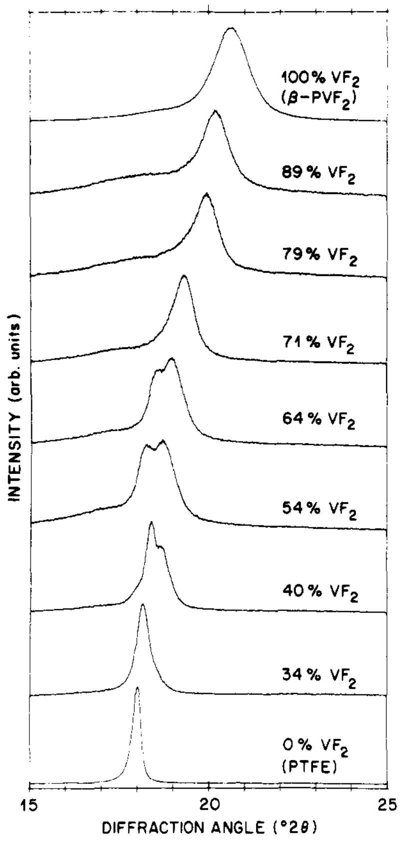

Figure 2. Variation of X-ray diffractograms of VF_2/F_4E copolymers with composition at $T = 26$ °C.

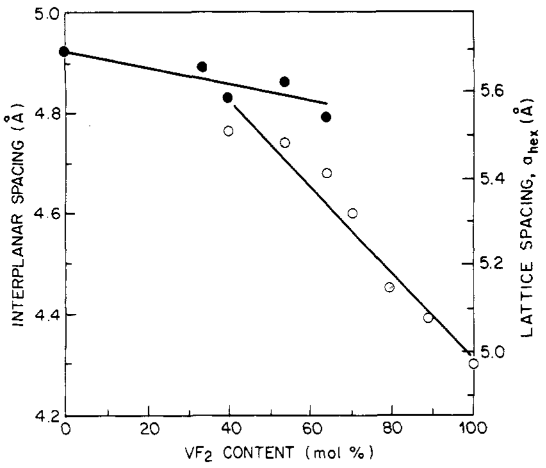

Figure 3. Dependence of interplanar and lattice spacings (the latter in terms of metrically hexagonal axes) of VF_2/F_4E copolymers on composition.

Table I
Interplanar Spacings of Oriented VF_2/F_4E (Å)

	reflection		
VF_2, mol %	A (200, 110)	B (001)	C (201, 111)
100	4.28	2.56	2.22
89	4.36	2.55	2.21
79	4.49	2.56	2.23
71	4.61	2.56	2.24
64	4.75[a]	2.57	2.26
54	4.82[a]	2.58	2.27

[a] Unresolved doublet.

ented by Moggi and co-workers.[14] In Figure 2, the combined (200, 110) peak of β-PVF_2 is seen gradually to shift to lower angles as VF_2 content is decreased to 71%; this is consistent with the incorporation of the bulkier F_4E units into the lattice. Moreover, below 71% VF_2, a second peak is seen at lower angles, its intensity increasing at the expense of the higher angle peak as the specimen becomes richer in F_4E. Eventually, for VF_2 content ≤34 mol %, the PTFE structure is adopted. We should also notice the diminishing peak half-widths as the F_4E content is increased; this reflects the significant improvement in intermolecular coherence lengths as the cross-sectionally anisometric β-PVF_2 conformation is changed to the cylindrical one of PTFE, which allows much more efficient hexagonal packing. The splitting of this strongest reflection at intermediate composition has not been noted before except in the case of a 35% VF_2 copolymer, where it was attributed to "presence of the low-temperature PTFE phase".[14] This is clearly not plausible in light of the data of Figure 2, which show a smooth and consistent variation of both the positions and the intensities of the two individual reflections with composition (also, the low-temperature phase of PTFE does not persist above 19 °C).

The *d* spacings of these reflections and the dimensions of the corresponding intermolecular lattices (referred to metrically hexagonal axes, which approximate reasonably the packing of both β-PVF_2 and PTFE) are seen in Figure 3. The distances can be described by two straight lines corresponding to compositions rich in PVF_2 and PTFE, respectively; the slope of the first is almost 6 times that of the second. This is qualitatively expected, because the expanding effects of F_4E units will be more pronounced in the smaller β-PVF_2-like lattice than in the already PTFE-like structure.

The doublet in the major intermolecular reflection observed at intermediate compositions may arise for reasons other than the coexistence of two metrically hexagonal lattices. Specifically, the two peaks may represent the (200) and (110) planes of a single nonhexagonal phase, as has been proposed by Tashiro et al.[16] for similar compositions of VF_2 copolymers with *tri*fluoroethylene. We can investigate this possibility by examining X-ray diffraction patterns of oriented specimens, as seen in Figure 4. The major reflections are identified in the accompanying Table I. All these patterns exhibit a clear β-PVF_2 structure, uniquely identified by the trans conformation implied by the exactly meridional (001) peak. As the VF_2 content drops to 71–54%, an additional diffuse reflection is observed in the region of the meridian between the (001) and (201, 111), at $d \simeq 2.36$ Å. Its location and spacing are consistent with coexistence of a *second*, paraelectric phase,

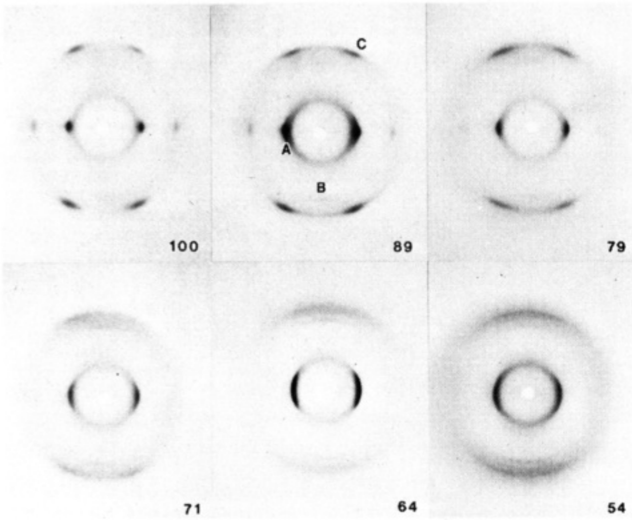

Figure 4. X-ray diffractograms at 26 °C of VF_2/F_4E copolymers containing the indicated mole percent of VF_2. The specimens had been uniaxially oriented in the vertical direction.

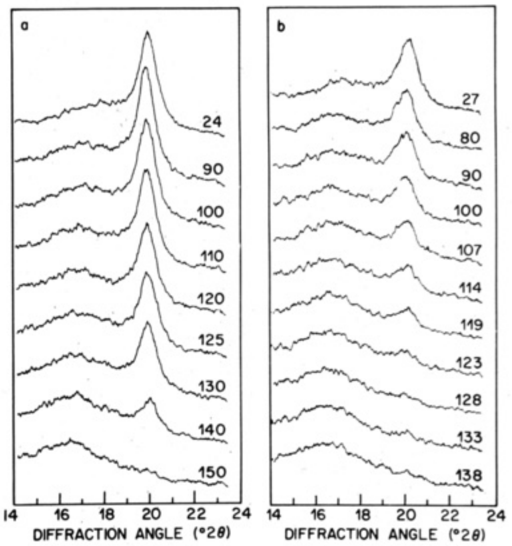

Figure 5. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 89 mol % VF_2.

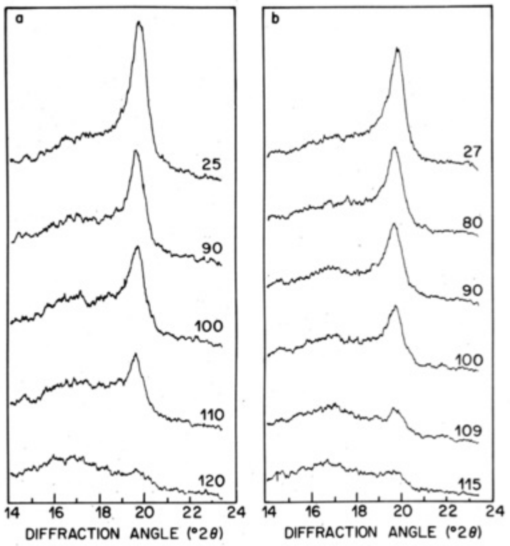

Figure 6. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 83 mol % VF_2.

which is known from VF_2 copolymers with trifluoroethylene[16-18] (F_3E) to incorporate tg^+ and tg^- groups with a repeat of ~2.30 Å (the increased repeat in F_4E copolymers may reflect the larger volume of the CF_2 group). In its metrically hexagonal packing, rotational disorder,[19] and lattice dimension, this paraelectric phase is in fact very similar to the high-temperature phase of PTFE. As VF_2 content is further decreased below 54 mol %, the full diffraction patterns at room temperature become even more closely characteristic of PTFE (e.g., through appearance of reflections at ~2.86, 2.46, and 2.23 Å). Deviation from strict all-trans conformations and introduction of gauche bonds have also very recently been invoked by Murata[20] to explain the observation of *c*-axis disorder in copolymers containing 75 and 69 mol % VF_2.

2. Curie Transitions. Having described the structure of VF_2/F_4E copolymers as a function of composition at *ambient* temperature, we now discuss its phase transformations during heating and cooling. The solid-state structural behavior of these copolymers varies with composition, falling into five categories.

(a) VF_2 Content ≥93 mol %. These compositions are known from the literature[2,13] to crystallize with the antipolar α unit cell rather than with that of the ferroelectric β phase. Their behavior was not examined further in this study.

(b) VF_2 Content between ~92 and 83 mol %. These are the highest compositions for which the β phase is obtained directly from the melt. Our thermal investigations show that this phase remains dominant at all temperatures up to the melting point and that no solid-state transformations are obtained. This may be seen for the higher end of this compositional range (i.e., for a VF_2 content of 89 mol %) in Figure 5, where the (200, 110) intermolecular peak is observed to decrease gradually as the melting point is approached and to increase again during subsequent cooling. No additional crystalline peaks are seen at any temperatures. This behavior continues down to 83 mol % VF_2 (Figure 6), although there is a hint of a shoulder at ~18° 2θ in the 100 °C scan; this would suggest transient emergence of a small amount of the paraelectric phase prior to melting.

(c) VF_2 Content between ~82 and 72 mol %. In this compositional region, the behavior is characterized by reversible Curie transitions in the manner described previously.[1,7] This may be seen in Figure 7 for a 79 mol % VF_2 copolymer. During heating, a distinct paraelectric peak is observed at ~18° 2θ as the ferroelectric peak almost disappears at 120 °C. Melting at higher temperatures interferes with this ferroelectric-to-paraelectric transformation. Upon cooling, the paraelectric phase grows from the melt and then undergoes a discrete solid-state transformation to the ferroelectric (e.g., at 110 °C the populations of the two phases are seen in Figure 7b to be approximately equal). This reversible behavior has also been documented in a copolymer of similar composition (81 mol % VF_2) by DSC and dielectric techniques.[7] The structural identity of the paraelectric phase is as described previously,[1] i.e., reflects internal disorder as a result of deviations from the all-trans conformation through introduction of gauche ± bonds, leading to irregular *tt*, tg^+, and tg^- sequences.

As the VF_2 content is reduced to 76 mol % (Figure 8), a discrete Curie transition is seen upon heating, centered at ~110 °C. In contrast to the other compositions, this solid-state transition approaches completion before the competing effects of melting become dominant; thus, the paraelectric phase can be obtained in essentially pure form

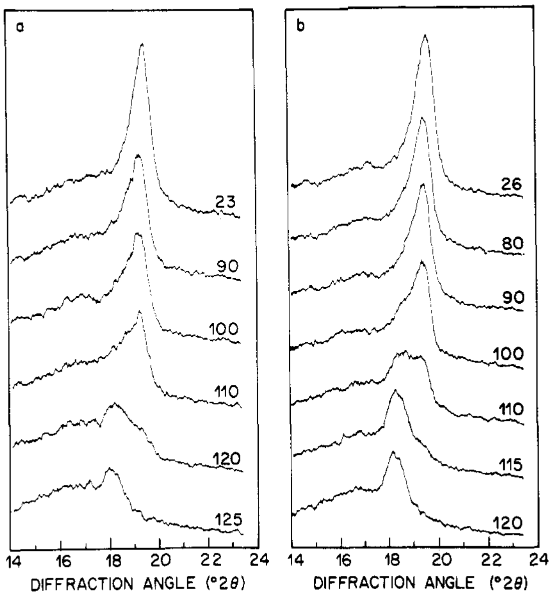

Figure 7. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 79 mol % VF_2.

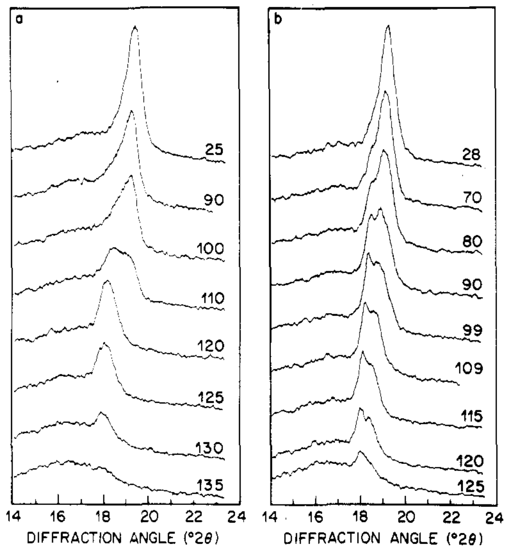

Figure 8. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 76 mol % VF_2.

at ~120 °C. However, when the specimen is cooled from the melt, a *double* peak is seen that does not change substantially in relative proportion until ~90 °C. This indicates coexistence of the two phases to similar extents down to that temperature, at which point a distinct shift in favor of the ferroelectric peak becomes apparent. Full return to the ferroelectric phase is attained near ambient temperature.

(d) VF_2 Content between ~71 and 35 mol %. This broad compositional region is characterized by the coexistence of the ferroelectric and paraelectric phases over a *wide* range of temperature; this range increases steeply with F_4E content. The behavior of 71 mol % VF_2 is seen in Figure 9. During heating, a shoulder at higher spacings is apparent already at 60 °C. The shift from ferroelectric to paraelectric structure, which begins at that temperature, is seen to be smooth and gradual, extending close to the melting point. This is in marked contrast to the more discrete transitions exhibited by copolymers richer in VF_2 content (i.e., up to ~82 mol %). The cooling behavior is also remarkable: Crystallization from the melt yields directly a double peak in the intermolecular packing region of the diffraction pattern (Figure 9b), indicating the presence of both phases. While both grow as temperature decreases, their relative magnitudes do not change until about 70 °C, whereupon a very gradual shift to the ferroelectric phase begins. However, a distinct shoulder at low angles is seen even at room temperature, implying survival of some paraelectric crystals.

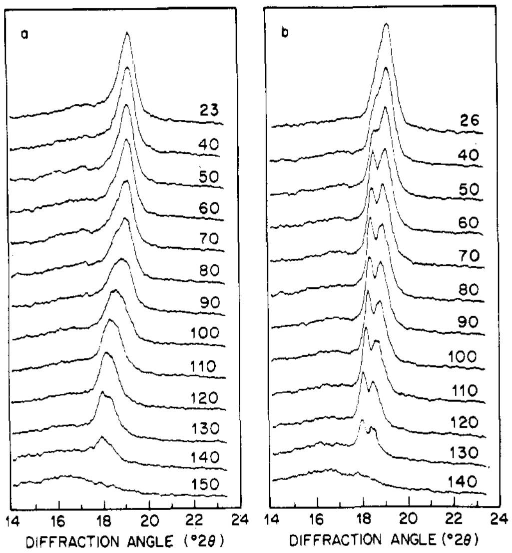

Figure 9. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 71 mol % VF_2.

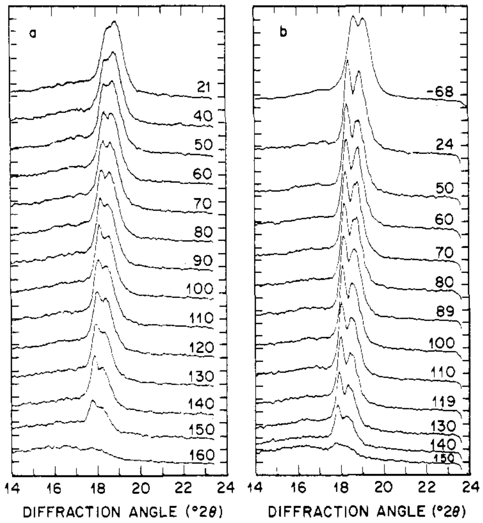

Figure 10. X-ray diffractograms at the indicated temperatures, obtained during (a) heating and (b) cooling of a VF_2/F_4E copolymer containing 64 mol % VF_2.

This tendency for coexistence of both phases increases with content of tetrafluoroethylene units. The situation is depicted for the 64 mol % VF_2 copolymer in Figure 10. Here, during both heating and cooling, two peaks are seen for room temperature to the melting point, with only gradual and limited changes in relative intensities. This is especially so in the cooling part of the cycle, where the relative proportions of the two peaks remain essentially unchanged even at temperatures as low as −68 °C (the lowest attainable with our equipment). Similar behavior is also exhibited by specimens richer in F_4E (i.e., 54 mol % VF_2), whose X-ray diffraction patterns are not reproduced here for the sake of brevity.

We should note here again that these two peaks might conceivably arise not only from two coexisting phases but

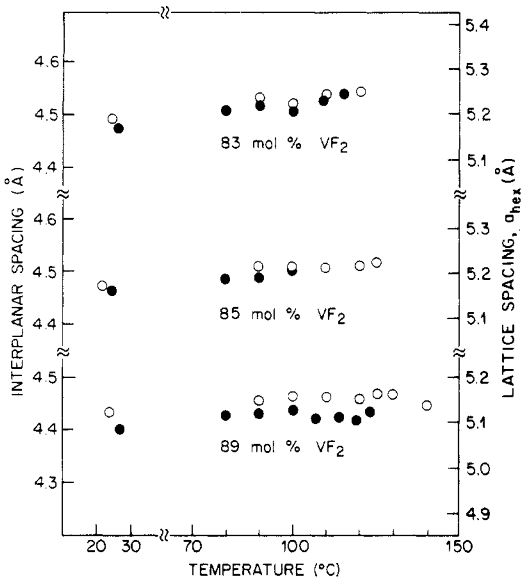

Figure 11. Intermolecular lattice dimensions for copolymers containing 83–89 mol % VF_2, during heating (○) and cooling (●).

also from a *single* phase with an intermolecular symmetry lower than hexagonal.[16] However, we reject the latter possibility on the basis of Raman spectroscopic results by Green and Rabolt,[21] which show distinct absorption bands characteristic of the *tt* and *tg*$^{\pm}$ groups at all temperatures, even as far down as −248 °C. Initial assignments of these bands to the ferroelectric and paraelectric phases was made[22] on a widely studied VF_2/F_4E copolymer (81/19), in relation to DSC results, and by extension from similar, well-documented findings from VF_2/F_3E copolymers.[23]

(e) VF_2 Content <~35 mol %. In this compositional region, as seen in Figure 2, the room-temperature structure begins to approach closely that of polytetrafluoroethylene. Therefore, no ferroelectric–paraelectric phase transformations are expected, and these materials were not investigated further.

3. Lattice Dimensions. The three compositional regions of primary interest are those described in (b), (c), and (d) above, i.e., where the ferroelectric phase exists alone, where it transforms discretely to the paraelectric, and where the two phases coexist over a wide range of temperature. The intermolecular lattice dimensions in the first region are seen in Figure 11 as functions of temperature for copolymers with 83–89 mol % VF_2. The behavior is essentially linear and reversible. Both the lattice spacings at each temperature and their rates of expansion during heating increase with content of the bulkier tetrafluoroethylene unit; the latter range from 3.8×10^{-4} Å/°C for 89 mol % VF_2 to 7.4×10^{-4} Å/°C for 83 mol % VF_2.

At the compositional region where discrete Curie transitions are obtained, the changes in lattice dimensions during heating and cooling are exemplified in Figure 12 by the 76 and 79 mol % VF_2 copolymers. Hysteresis between the heating and cooling curves is clearly seen here, resulting from the different stabilities (and metastabilities) of the phases. For both compositions, the paraelectric phase has a significantly larger spacing, and expands also at a higher rate, than the ferroelectric; these effects are attributable to the introduction of gauche$^{\pm}$ groups into the trans chains.

Lattice spacings for copolymers containing 54–71 mol % VF_2 are seen in Figure 13. The 71 mol % composition shows some analogy to the behavor in Figure 12; i.e., it exhibits an increase in the rate of expansion after initiation of the ferroelectric-to-paraelectric transition, as well as

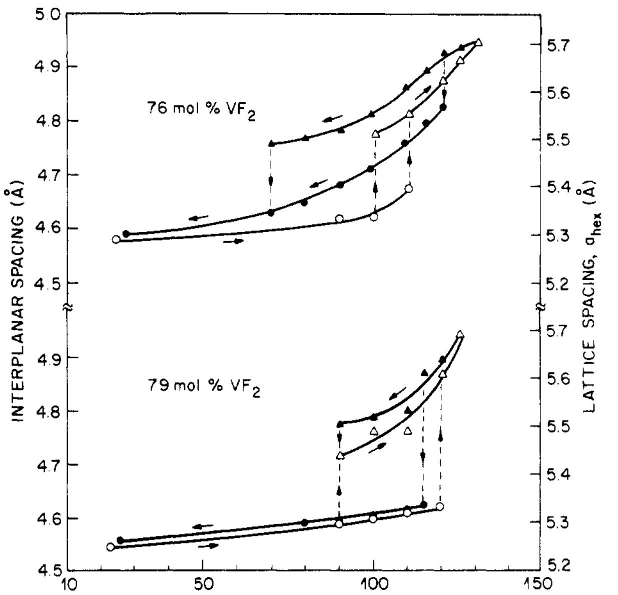

Figure 12. Intermolecular lattice dimensions for copolymers containing 76 and 79 mol % VF_2, during heating (○, △) and cooling (●, ▲): (○, ●) ferroelectric phase; (△, ▲) paraelectric phase.

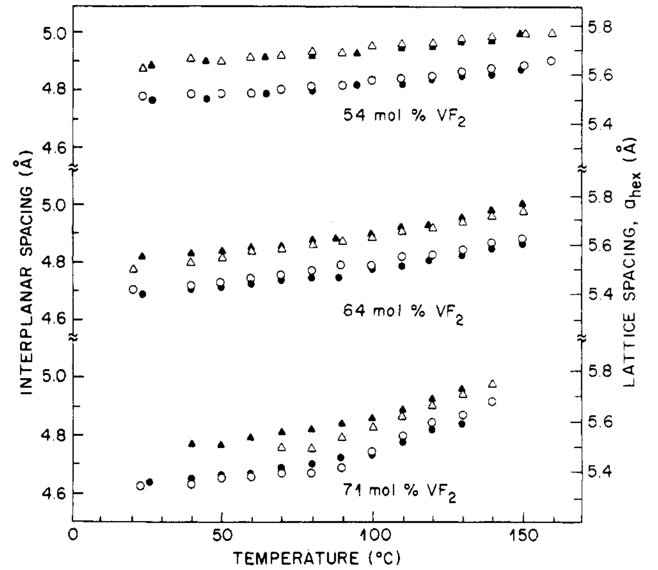

Figure 13. Intermolecular lattice dimensions for copolymers containing 54, 64, and 71 mol % VF_2, during heating (○, △) and cooling (●, ▲): (○, ●) ferroelectric phase; (△, ▲) paraelectric phase.

some hysteresis between heating and cooling. As the VF_2 content is reduced and the two phases coexist over the full temperature range, the heating and cooling behavior becomes increasingly more reversible, and the rates of change of lattice dimensions approach linearity and decrease in magnitude. Moreover, the spacings of both lattices at all temperatures increase with decreasing VF_2 content, and the difference between ferroelectric and paraelectric lattice dimensions is considerably smaller here than in the VF_2-richer polymers of Figure 12. Incorporation of larger proportions of the bulkier F_4E groups into both lattices is at the root of these phenomena.

Conclusions

Copolymers of vinylidene fluoride and tetrafluoroethylene adopt room-temperature structures that span the spectrum defined by the two homopolymers. Above ~92 mol % VF_2, the copolymers crystallize with the antipolar α-PVF_2 unit cell, whereas between ~92 and 71 mol % the ferroelectric β-PVF_2 structure is adopted. Below ~71 mol % VF_2, a second structure reflecting the increasing influence of tetrafluoroethylene groups is also seen; the relative population of this phase increases at the expense of the β-PVF_2 structure as the VF_2 content drops, and below ~35 mol % the structure becomes characteristic of PTFE.

In terms of solid-state transformations, these copolymers also exhibit a continuous spectrum of behavior. Compositions containing ≥83 mol % VF_2 do not undergo phase transformations but retain their ferroelectric β-structure at all temperatures between ambient and the melting point, during both heating and cooling. Between ~82 and 72 mol % VF_2, discrete and reversible Curie transitions are obtained, of the same type as seen previously in trifluoroethylene copolymers and involving the same kind of paraelectric structure (i.e., disordered through the introduction of $g^{\pm}$ bonds). Below ~72 mol %, the increasing F_4E content introduces more disorder into the lattice and reduces the stability of the ferroelectric phase. This results from expansion of the interchain lattice as a result of the larger van der Waals volume of the CF_2 group; not only are successive CF_2 units sterically restricted from adopting exact trans arrangements, but the accompanying intermolecular expansion also renders energetically easier the introduction of gauche$^{\pm}$ rotations in the remainder of the chain. This manifests itself in smearing out of the Curie transitions and in coexistence of the two phases over broad ranges of temperature. Eventually, in the region below ~35 mol % VF_2, the structure becomes typical of PTFE and the ferroelectric phase is no longer obtained.

As described recently,[9] in the compositional range where Curie transformations are observed, the ferroelectric-to-paraelectric transition temperatures increase linearly with VF_2 content and coincide with the melting temperature in a copolymer of ~82 mol % VF_2. This explains the absence of Curie transformations at higher VF_2 contents and allows extrapolation to 100 mol % VF_2. Such extrapolation led[9] to a temperature of 195–197 °C as that where the Curie transition of PVF_2 homopolymer would be centered and was in qualitative agreement with previous predictions from VF_2 copolymers with trifluoroethylene.[17]

Registry No. $(VF_2)(F_4E)$ (copolymer), 25684-76-8.

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Quantitative Investigation of the Amorphous and Crystalline Components in *trans*-1,4-Polyisoprene from Solution

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ABSTRACT: *trans*-1,4-Polyisoprene structures in the α and β crystalline forms with various morphologies were prepared by using different crystallization procedures. The effects of molecular weight, crystallization temperature, and annealing treatment on the crystalline stem length and the noncrystalline traverse length were investigated by using epoxidation in suspension followed by carbon-13 solution NMR. Preliminary studies were carried out to determine the optimum conditions for quantitative reaction of the double bonds at the lamellar surfaces. Results were obtained suggesting that for many liquids penetration of partially reacted lamellas can take place from the lateral surfaces; reactant concentration and time were also shown to be important and conditions were found that gave agreement between the fraction reacted and the noncrystalline fraction from infrared and density measurements. Interlamellar traverses were detected in multilamellar structures with the amount increasing with increasing molecular weight. The nature of chain folding in the *trans*-polydienes is discussed.

Introduction

trans-1,4-Polyisoprene, TPI, crystallizes from solution in either the α or the β form as single folded-chain lamellas, overgrown curved lamellas, or more complex structures that include lamellar stacks and spherulites.[1-6] Determination of crystallinity by density[3,4] and by solid-state carbon-13 NMR[7] measurements showed that a sizable noncrystalline component (35–50%) is present in dried crystal mats. In single lamellas this noncrystalline component is expected to be at the lamellar surfaces as chain folds and noncrystallizing chain ends. For multilamellar structures interlamellar chain traverses may also be present. The amount of the total surface component in TPI samples can be quantitatively evaluated in suspension

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