Macromolecules **1980**, *13*, 989–994

servation of the amphoteric behavior of TMCQ is attributable to the anomalously strong electron-accepting character of TCNQ.

Acknowledgment. Grateful acknowledgment is made to Professor T. Sasaki, Nagoya University, for performing the ^{13}C NMR measurements.

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Inhomogeneous Thermal Degradation of Poly(vinylidene fluoride) Crystallized from the Melt

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ABSTRACT: Poly(vinylidene fluoride) crystallized from the melt at low undercoolings has been found to undergo an inhomogeneous degradation. Mixed (γ) spherulites, as well as regions of α-spherulites that have undergone a solid-state transformation to a higher melting form, discolor preferentially at high crystallization temperatures (~160 °C). This degradation was shown to proceed primarily by dehydrofluorination, with little chain scission or cross-linking. Degradation was also seen in films of the β phase prepared by uniaxial drawing, in which subsequent heating at ~160 °C caused pronounced discoloration. A feature that mixed spherulites, transformed regions in α-spherulites, and drawn β films share in common is incorporation of trans sequences within their crystalline segments. Elimination of HF and consequent degradation might occur preferentially in such sequences because of adverse electrostatic and van der Waals interactions along them.

A number of authors[1–4] have examined the morphology of melt-solidified poly(vinylidene fluoride) (PVF$_2$). Two spherulitic types were found to grow from the melt at high temperatures. The most common of the two is the α form, whose spherulites are characterized by their large sizes, high birefringence, and tight concentric banding. The spherulites of the second type are generally smaller and less birefringent than their α counterparts and exhibit some disorganization and adulteration of crystallographic features, as seen by electron-[5] and X-ray-diffraction[4] analyses; for this reason (and also as a result of the disturbed morphological and birefringent appearance of some of them) these spherulites have been called "mixed".[4] Their precise crystallographic identity is uncertain: while Gianotti et al.[1] originally identified them with the γ form, Prest and Luca[2] obtained infrared evidence associating them with the β phase. Recent electron- and X-ray-diffraction data[4,5] from such spherulites are consistent with a new unit cell for γ-PVF$_2$ reported by Weinhold et al.;[6] these data[4,5] also suggest the presence of small amounts of microcrystalline inclusions, most probably of the α phase. We identify these spherulites predominantly with the γ form.

In addition to these two spherulitic types, a third phase is obtained at high temperatures in melt-crystallized PVF$_2$ as a result of a solid-state transformation occurring in parts of α-spherulites.[1–4] Such transformations lead to a highest melting form, which has been variously associated with the β[1] or γ[2,3] phase. A detailed morphological study[7] has shown that the solid-state transformation in spherulites of α-PVF$_2$ is regularly initiated in those areas of their peripheries where their lamellae are directly intermeshed with those of mixed spherulites. From there, the transformation proceeds toward the nucleus by advancing along lamellae at a slow (~10^{-4} μm/s), linear "growth" rate; the transformation also takes place across lamellae, but at a much slower rate. As the temperature is raised, such transformations are also initiated with increasing frequency at spherulitic nuclei, from which they subsequently "grow" radially outward.[2] During the course of this study, it was discovered that the various spherulitic forms in PVF$_2$ degrade differently, causing an inhomogeneous discoloration of our samples. The physical characteristics of this degradation, possible mechanisms for it, and potential reasons for its inhomogeneous character are described herein.

Experimental Section

The PVF$_2$ resin used in this study was Kynar 821 of Pennwalt Corp.; molecular weight averages (calibrated against polystyrene fractions) were $\bar{M}_w$ = 541 000 and $\bar{M}_n$ = 337 000. The polymer was compression-molded in the form of films whose thicknesses covered a wide range (~10 μm to 2 mm) and then transferred to glass slides for thermal treatment. As is described later on, other resins were also briefly investigated for comparison purposes, as were films cast from solution in *N*,*N*-dimethylformamide (DMF). The samples were melted between 200 and 230 °C for up to 30 min and recrystallized between 156 and 164 °C for varying times ranging from 1 to 15 days. A number of different crystallization environments were used, including ambient atmosphere, dried nitrogen, vacuum, and deaerated silicone oil. Molecular weights of samples dissolved in DMF were determined by gel permeation chromatography in a Model 244 Waters liquid chromatograph employing a set of μ-Styrogel columns with pore sizes of 10^6, 10^5, 10^4, and 10^3 Å. Weight loss during degradation was investigated using a Du Pont 950 thermogravimetric analyzer

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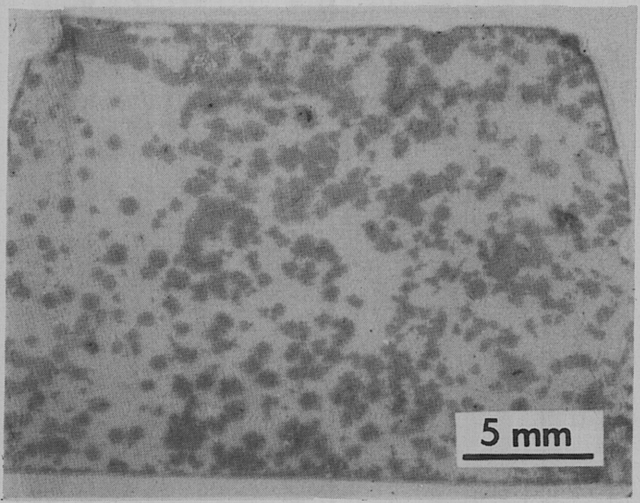

Figure 1. Macroscopic appearance of a PVF$_2$ specimen crystallized at 160 °C for 15 days in an atmosphere of dried N$_2$.

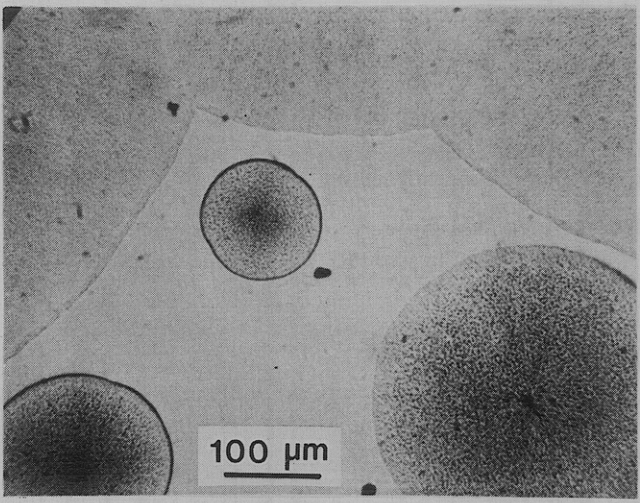

Figure 2. Transmitted light optical micrograph of α-type and mixed spherulites crystallizing from the melt at 160 °C.

in the isothermal mode. Detection and identification of gaseous degradation products were attempted by using a Varian MAT 112 gas chromatograph/mass spectrometer as well as a Model 901 Orion research microprocessor/ionanalyzer equipped with a fluoride ion specific electrode. Infrared spectra of degraded films were obtained with a Model 621 Perkin-Elmer infrared spectrometer.

Results and Discussion

While polymers typically degrade in a uniform manner (visible, for example, in the homogeneous discoloration of polyethylene and polypropylene films exposed to high temperatures for long times), PVF$_2$ samples crystallized from the melt at high temperatures were found to deteriorate in a uniquely nonuniform fashion. The macroscopic appearance of a representative specimen is seen in Figure 1. Although black-and-white photography cannot adequately reproduce the striking difference between highly discolored and totally clear areas in this sample, it is evident from Figure 1 that *only parts* of the specimen have visibly been degraded. At this very low magnification, the discolored areas appear to be spherulites or clusters of spherulites. This inhomogeneous degradation was seen in all samples irrespective of thickness or environment but appeared more pronounced in those treated in air or originating from DMF solution. We, therefore, infer that the degradation is fundamentally thermal in nature rather than oxidative; moreover, diffusion of gaseous products away from the polymer film is not a determining factor, as evidenced by the fact that the thickest samples (~2 mm) degraded as conspicuously as the thinnest.

The nature of discolored areas, as well as the morphogenesis of the degradative process, is evident from microscopic examination, as illustrated in Figure 2. This micrograph was taken with unpolarized transmitted illumination on a PVF$_2$ film which was crystallizing from the melt in a microscope thermal stage (Mettler FP 52). The growth fronts of three large α-type spherulites are seen at the top (left, center, and right) of this photograph; three smaller mixed spherulites have grown within the melt in the center, lower left, and lower right of this figure. While contrast is again unavoidably poor, the mixed spherulites appear unmistakably darker than either their α counterparts or the melt itself. In addition, the portions of mixed spherulites that are closer to the nuclei are observed to be progressively more discolored. Therefore, not only do mixed spherulites degrade preferentially but the extent of degradation appears to be proportional to the total residence time of their molecules in the crystalline state rather than to the overall duration of thermal treatment. The fact that the melt itself is not visibly discolored implies that this degradative process takes place predominantly in the crystalline regions of some PVF$_2$ molecules and not in their amorphous segments. This is quite surprising, because, as a rule, amorphous regions in polymers degrade more readily than their crystalline counterparts, as was shown by Winslow and co-workers in their extensive studies of the oxidation of polyolefins.[8-11]

Careful examination of fully crystallized samples in the optical microscope reveals another facet of the inhomogeneous degradation of PVF$_2$. This can be seen in Figure 3 which depicts the same region of a PVF$_2$ film between crossed polars (Figure 3a) and in unpolarized transmitted illumination (Figure 3b) after crystallization and annealing at 160 °C for 15 days. It is distinctly seen in these micrographs that the degraded regions encompass not only the small, mixed spherulites but also those parts of α-spherulites that were transformed to a higher melting form.[7] The fact that degradation accompanies the solid-state transformation without delay follows from the time-lapse series of micrographs shown in Figure 4. The large α-spherulite of Figure 4a is seen to have degraded in the immediate vicinity of the nucleus after thermal treatment at 162 °C for 3 days; since the small, mixed spherulite had only recently come in contact with its α counterpart (as evidenced from growth-rate data[4] and from the position of the two spherulitic peripheries relative to each other), no discoloration is yet apparent at the boundary. On the fifth day of heating (Figure 4b), the degraded region surrounding the nucleus is seen to have grown radially outward by ~35 μm, while a similar length of degraded area is seen advancing toward the center of the α-spherulite at the point where its lamellae are juxtaposed to those of its smaller counterpart. Both of these discolored fronts are seen to have further approached each other after 7 days of heating (Figure 4c), and finally to have fused together by the tenth day (Figure 4d). Figures 4c and 4d also show that in the area of contact between the two spherulites the degradative process has also advanced slowly across lamellae and then radially outward so as to surround the small, mixed spherulite; this is identical with the growth pattern typifying solid-state transformations.[7] Finally, the equivalence of these two processes is directly demonstrated by comparison of Figures 4d–f, the last two of which show the field of Figure 4d as it appears between crossed polars at 162 and 173 °C, respectively. Melting of the original α-spherulite in Figure 4f exposes the

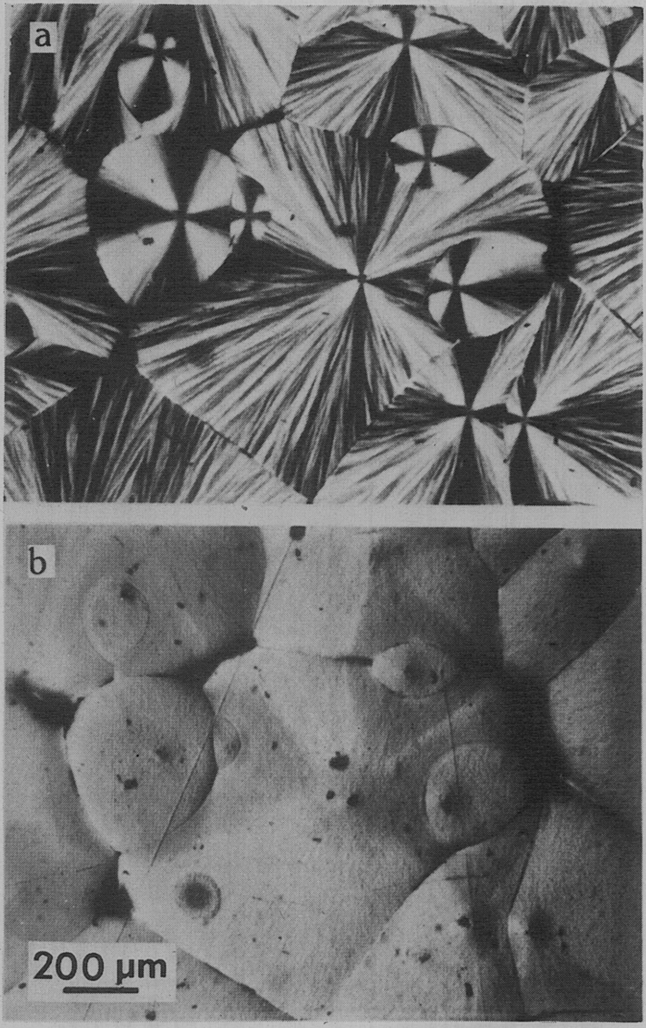

Figure 3. Appearance of PVF_2 spherulites crystallized at 160 °C for 15 days: (a) between crossed polars; (b) in unpolarized transmitted illumination.

transformed area, which is seen to coincide almost exactly with the degraded region in Figure 4d. It is by taking advantage of this equivalence that radial growth rates of the solid-state transformation could be estimated continuously as a function of time without resorting to repeated melting and recrystallization.[7] Scouting for discolored nuclear regions in unpolarized transmitted illumination (with the possible aid of a blue filter to increase contrast) also circumvents the previously[2] encountered problem of not being able to predict a priori which α-spherulites would transform to the highest melting phase.

Having seen that degradation occurs preferentially in mixed spherulites and regions transformed to a highest melting form, we should now consider (a) what these two may have in common, (b) in what way they differ from α-PVF_2, and (c) how their shared features might lead to increased thermal deterioration. Although their exact crystallographic identity is somewhat clouded (both have been variously referred to as β and γ phases[1–4]), their crystalline structures are quite similar. Actually, both β and γ forms had for years been considered to contain chains in identical conformations (all trans[12] or slightly distorted therefrom[13,14]) but packed with different symmetries (orthorhombic and monoclinic, respectively).[13,14] However, Weinhold et al.[6] have recently found that the c-axis length in γ-PVF_2 is 9.18 Å and is thus incompatible with a TT conformation; the same authors have shown[15] the actual conformation to be $T_3GT_3\bar{G}$. In this case, the chain conformation in the γ phase may be viewed either as a combination of α and β conformations [$TGT\bar{G}$ and TT, respectively] or as an all-trans conformation containing alternating kinks after every third carbon atom. On this basis, a common feature of mixed spherulites and regions of the solid-state transformation is that they both contain TT sequences within their crystalline stems; such sequences are absent in untransformed areas of α-spherulites.

In order to determine whether such TT sequences could be responsible for the inhomogeneous deterioration of melt-crystallized PVF_2, we should now examine the mechanism of this process. The thermal degradation of poly(vinylidene fluoride) has been investigated by a number of authors in the past 2 decades: Madorsky et al. studied it at intermediate[16] (~300–500 °C) and high[17] (up to 800 °C) temperatures by weight-loss analysis and mass spectrometry. Rates of volatilization and thermal stabilities of PVF_2 both under vacuum[18] and in oxygen[19] up to ~600 °C have also been reported by Cox and coworkers. An infrared study of PVF_2 decomposed in air has been performed by Wentink et al.[20] All of these studies have shown that degradation in PVF_2 proceeds overwhelmingly by elimination of HF from the molecular chains, in a manner analogous to the dehydrochlorination of poly(vinyl chloride).[21] In these polymers, dehydrohalogenation involves reactions with lower activation energies than those required for chain scission.

In our samples, the discoloration of PVF_2 was seen to occur at temperatures much below those investigated by the above authors;[16–21] it could therefore not be assumed a priori that elimination of hydrogen fluoride is again involved in the chemical mechanism of this degradation. Initial attempts to determine the presence of fluoride ions by using an appropriate ion analyzer did not detect any measurable signal. Clearly, gas evolution at these temperatures (ca. 160 °C) is exceptionally small, as was also confirmed by thermogravimetric analysis (samples crystallized at 160 °C failed to show any detectable weight loss (i.e., anything over ~0.05%) during thermal treatment at ~160–165 °C for 18 h). Similar results have also been obtained for PVC, in which severe darkening had been observed well before hydrogen chloride elimination of 0.1% by weight was attained.[21] Of course, it should be kept in mind that since melt-crystallized samples are composed primarily of large α-type spherulites, only a relatively small fraction of the material would be expected to yield degradation products. Finally, evolution of HF from our specimens was detected by its specific reaction with the zirconium chelate of Morin (2′,3,4′,5,7-pentahydroxyflavone[22]). Films of PVF_2 containing discolored areas were heated at 160 °C under nitrogen for 1 h with the gas bubbling into a solution of the chelate. Fluorescence measurements then showed a decrease in the original intensity which was due to the reaction of fluoride with the chelate, a reaction which is known to be specific for fluoride. Volatilization of HF at relatively low temperature is also supported by the results of Ishii,[23] who observed dehydrofluorination of PVF_2 at ~200 °C. In a separate paper,[24] we also report gas chromatographic–mass spectrometric evidence for HF evolution at temperatures of 60 °C and above. Loss of HF results in formation of the conjugation CH=CF—CH=CF along the chains, which would cause absorption of electromagnetic radiation in the visible region of the spectrum, consistent with the observed discoloration.

While elimination of HF is the primary mechanism of degradation in our PVF_2 samples, some evidence has been

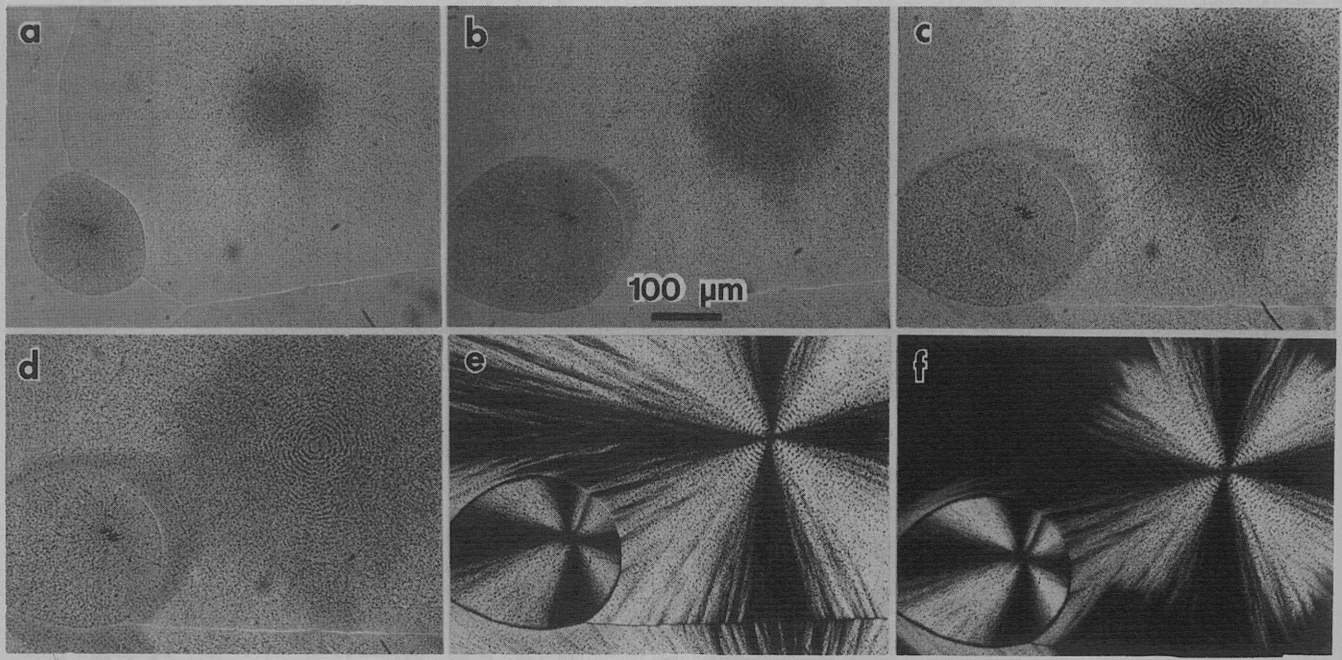

Figure 4. Appearance of an α-type and of a mixed spherulite crystallizing from the melt at 162 °C, viewed in unpolarized transmitted illumination after (a) 3, (b) 5, (c) 7, and (d) 10 days. The same spherulites of d are seen between crossed polars at (e) 162, and (f) 173 °C.

obtained to suggest a limited presence of other degradative processes, e.g., chain scission, cross-linking, and cyclization.[24] Discolored areas which were melted and recrystallized in the α form exhibited a subsequent melting point that was typically a few tenths of a degree lower than that of nondegraded regions. The polydispersity of samples treated at 160 °C for 13 days was also seen to increase somewhat from 1.60 to 1.87, with molecular weight averages not deviating much from the original range. Parts of discolored areas in PVF_2 films were also found to be practically insoluble in DMF at all temperatures up to its boiling point. This contrasts sharply with the ready solubility of undegraded PVF_2 in DMF even at low temperatures and suggests that some cross-linking may have taken place. Of course, when PVF_2 is allowed to degrade in the presence of air, other mechanisms involving hydroperoxide formation are also expected to occur.[8]

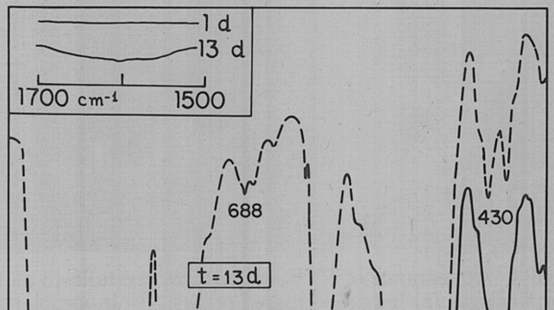

Figure 5. Infrared spectra of PVF_2 films crystallized for 1 day and for 13 days.

Partly degraded films were also examined by infrared spectroscopy in an attempt to determine the compositional and conformational effects of this heat treatment upon the molecular chains. The characteristic absorption bands of the polymorphs of PVF_2 are concentrated in the region below ~1000 cm^{-1}, which is presented in Figure 5 for two specimens crystallized at 160 °C for different periods of time. Since most of both samples is in the α form irrespective of the duration of the heat treatment, the vibrational spectra are dominated by absorption bands of this major polymorph (e.g., those at 408, 531, 612, 677, 766, and 795 cm^{-1}). In addition, the sample that was heated for 13 days exhibits extra absorption bands at 430, 510, 688, 778, 812, and 834 cm^{-1} characteristic of the polar forms of PVF_2. Of these, the bands at 430, 510, 778, 812, and 834 cm^{-1} have been attributed to the γ form[2,26] (those at 510 and 834 cm^{-1} being common with β-PVF_2[25]), while the weak band at 688 cm^{-1} is new. The band at 482 cm^{-1} (or, more generally, the region between 480 and 490 cm^{-1}) is essentially common to α-, β-, and γ-PVF_2.[2,25] All these features of the vibrational spectra are consistent with previous observations of Prest and Luca[2] and support their[2] conclusion that the solid-state transformation yields the γ phase; however, this region of the spectrum contains no information on the accompanying degradation. Some inference regarding degradation may be made from the presence of a very broad and shallow band ranging from ~1500 to 1700 cm^{-1} in some samples subjected to prolonged heat treatment

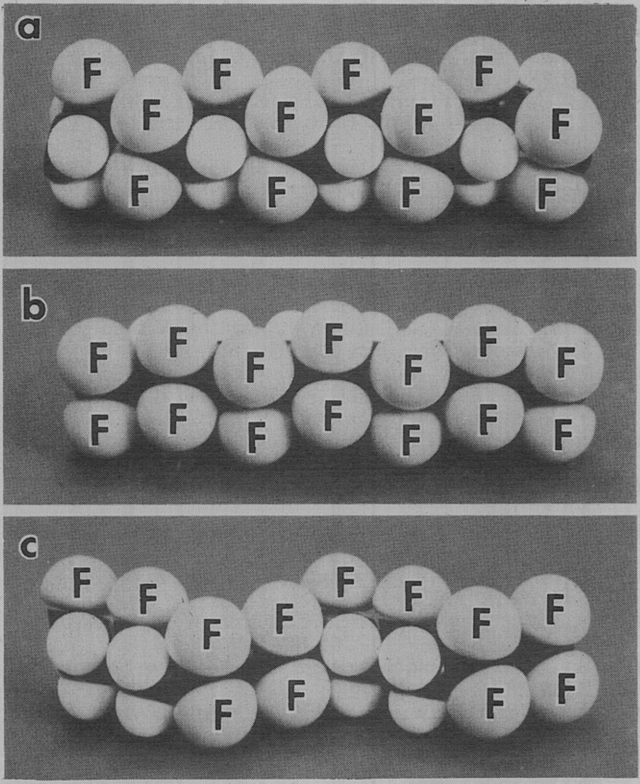

Figure 6. Molecular models of chain conformations in crystalline segments of (a) α-PVF_2, (b) β-PVF_2, and (c) γ-PVF_2.

(see inset in Figure 5). Wentink et al.,[20] who have conducted a detailed infrared study of pyrolyzed PVF_2, have detected weak bands centered at 1600 and 1728 cm^{-1} which are characteristic of double bonds along the macromolecular backbone. The fact that these bands are weak even in a heavily charred specimen accounts for the shallowness of the absorption band in our films which, by comparison, are much less degraded. The nature of this absorption band is consistent with the preceding conclusion attributing the thermal degradation of PVF_2 samples to dehydrofluorination.

As has been discussed above, establishment of TT sequences in PVF_2 molecules, whether by crystallization from the melt or by solid-state transformations of $TGT\bar{G}$ chains, may be associated with degradation involving loss of HF. At this point we shall examine possible reasons for this tendency of TT sequences toward dehydrofluorination. While no firm conclusions can yet be drawn from available evidence, the origin of this phenomenon may presumably be found in intramolecular contributions to the stabilities of the three types of conformation. As has been shown by the detailed calculations of Hasegawa et al.,[13] the $TGT\bar{G}$ conformation of the α form has a low intramolecular potential energy (i.e., −1.46 kcal/mol of monomeric unit) as a result of favorable van der Waals and electrostatic interactions. This may be qualitatively visualized with the aid of the space-filling Corey–Pauling–Koltun-type model[27] of the $TGT\bar{G}$ chain in Figure 6 which shows the hydrogen atoms to be surrounded by fluorine atoms (and vice versa); therefore, each atom appears to be electrostatically stabilized on its macromolecular chain, which, furthermore, suffers no significantly adverse steric interactions.[14] On the other hand, trans-planar chains characteristic of β-PVF_2 were shown by Hasegawa's group[13] to have a much higher intramolecular potential energy (−0.48 kcal/mol of monomeric unit) due to very unfavorable electrostatic and van der Waals interactions, as may be seen with the aid of Figure 6b. In this case, every single fluorine atom is under steric strain because of its atomic volume which is large compared to that of hydrogen: even with partial relief via statistical deflections[14] about the chain backbone, the distance between adjacent fluorine atoms cannot be increased to more than 2.60 Å, whereas the sum of their van der Waals radii is 2.70 Å. In addition, instead of the electrically stabilizing effects seen in α chains, these fluorine atoms suffer strong electrostatic repulsions (as do their hydrogen counterparts) which bring the electrostatic intramolecular potential energy of the TT conformation to +0.71 kcal/mol.[13] As a result, it may not be surprising that sterically strained atoms of an all-trans conformation, which are at the same time electrostatically repelled within their own molecules, could be particularly vulnerable to abstraction from the chain backbone. Once dehydrofluorination has thus occurred at one point in the β chain, adjacent hydrogens become allylic and are therefore particularly susceptible to further abstraction because of their reduced bond dissociation energies. Consequently, once this degradative process has been initiated, it is likely that it will continue extensively within the same chain, probably until it is interrupted at positions of reversed monomeric units ("head-to-head", "tail-to-tail") which relieve both electrostatic and steric strain.[28]

The effect of such "head-to-head", "tail-to-tail" (HHTT) defects on stability of the α and β phases has been examined in detail by Farmer et al.[29] Because such defects introduce great strain to the $TGT\bar{G}$ chain but relieve the strain of an all-trans conformation,[28,29] the latter becomes energetically more favorable when the concentration of these defects is increased beyond 11%.[29] For the Kynar 821 samples used in our study, the HHTT defect concentration is 5.2%,[30] while in the Kureha materials it is known[13] to be even lower. Therefore, these defects are expected to reduce only very slightly the high potential energy of TT sequences in our samples. On the average, such defects will provide some steric and electrostatic relief at every nineteenth monomeric unit along the chain, without alleviating the adverse environment in the remainder of the macromolecule.

In the case of γ-PVF_2, the $T_3GT_3\bar{G}$ chain conformation would be intermediate between those of the α and β forms and would consist of trans sequences interrupted by the two types of gauche bond as seen in Figure 6c. Therefore, dehydrofluorination in γ-PVF_2 would be expected to occur to an extent greater than in the α phase, but not quite approaching that in the β form. This rationale for inhomogeneous degradation is supported by visual observation of PVF_2 films predominantly in the β form, prepared by mechanical drawing and subsequent thermal treatment under the same conditions as films crystallized from the melt; the former were seen to discolor more prominently than any region of the latter.

A further point of interest in this regard involves comparison of the extent of degradation in different resins. Other resins from the same manufacturer (i.e., Kynar 881 and 901) having similar molecular weight averages and distributions as Kynar 821 degraded in the same manner described above. Comparison with Kureha resins cannot be made directly because morphologies and growth rates equivalent to those of the Kynar materials are obtained at *different* crystallization temperatures[2,4] (specifically ∼5–7 °C higher than those of the Kynar resins); however, discoloration in melt-crystallized Kureha KF-1100 films appeared visually similar to that found in Kynar samples.

A more interesting point concerning these two types of resin may be made on their different extents of discoloration in the melt; KF-1100 discolors earlier and more

Macromolecules **1980**, *13*, 994–998

pronouncedly than its Kynar counterparts. One possible reason for this may lie in the greater chain perfection of the Kureha resin which is known[29] to contain a smaller percentage of reversed monomeric units. As was mentioned above, such units may interrupt dehydrofluorination along the chain, a process which has been recorded[23] at intermediate melt temperatures (~200 °C).

The difference in discoloration between Kynar and Kureha polymers is even more impressive in solution: As soon as KF-1100 is added to distilled DMF at room temperature, the solution immediately assumes a yellow or orange color. On the other hand, solutions of the Kynar polymers in DMF show no visible discoloration for days. With increasing temperature, solutions of both resins in DMF discolor much earlier, with the Kureha solution again becoming the darker one. Of course, DMF is a typical aprotic solvent; as such, it acts as a base, promoting attack on alkyl halides, which results in dehydrohalogenation. Such elimination of HF may again proceed more extensively along PVF$_2$ molecules that have fewer head-to-head and tail-to-tail units, thus increasing discoloration. On the other hand, solvents such as acetone and cyclohexanone, which are much weaker bases than DMF and which promote nucleophilic addition to their carbonyl groups, do not discolor upon dissolution of PVF$_2$ at any temperature.

Finally, other factors that might be of relevance to the inhomogeneous degradation of PVF$_2$ may be considered by extension from the much richer literature on the degradation of poly(vinyl chloride).[31] It is of interest to note that the rate of thermal dehydrochlorination in PVC is known to depend upon the tacticity of its chains, with syndiotactic sequences degrading more markedly.[32-34] This enhanced dehydrochlorination has been interpreted as arising from faster propagation of polyene sequences in the all-trans molecules of syndiotactic PVC[32,33] or from a decreased rate of termination in this polymer.[33,34] Clearly, therefore, the role that similar effects might play in the inhomogeneous degradation of PVF$_2$ is of considerable interest for further research.

Acknowledgment. We are grateful to Mrs. M. Y. Hellman for molecular weight determinations, to Mr. A. M. Mujsce for chemical analyses, and to Drs. H. D. Keith and W. H. Starnes, Jr., for helpful discussions.

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Block Copolymer Theory. 6. Cylindrical Domains

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ABSTRACT: Formulas are presented for the free energy of diblock and triblock copolymer systems which develop cylindrical microdomain structure. These algebraic equations are used to determine the domain sizes and periodicity distances in such systems. Comparisons with experiments are presented.

When a phase separation occurs in block copolymer systems, a spherical, cylindrical, or lamellar pattern of microdomains forms. The geometry and size of these microdomains are such as to minimize the free energy. Thus, the object of an equilibrium theory of microdomain structure in block copolymer systems is the determination of the free energy as a function of domain size and geometry. A general theory of inhomogeneous polymeric systems, developed earlier,[1] has been applied previously to block copolymers in lamellar[2,3] and spherical[4] arrays. The picture is completed in this paper with a study of diblock copolymers, AB, and triblock copolymers, ABA or BAB,

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