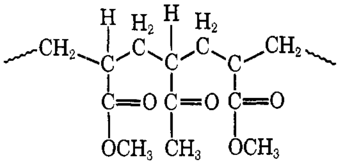
for the type II process in isolated methyl ketone groups in polymer systems.

If this explanation is correct, one would expect, therefore, to observe a similar increase in quantum yield for copolymers containing γ hydrogens. Accordingly, a copolymer was made of methyl vinyl ketone with methyl acrylate. In this case, the polymer structure would have the sequence shown in III. Photolysis of this copolymer in benzene solution by a similar method gave a value for ϕ_s of approximately 0.2,[12] which again is substantially higher than for poly-MVK.



III

On the basis of these results, we suggest that the quantum yield for main-chain scission in vinyl copolymers containing pendant methyl ketone groups adjacent to the main chain will be approximately 0.2 in systems where the carbonyl is isolated from similar groups along the chain and where the molecular mobility is high. In solid polymers, the quantum yield will be reduced to very low values at temperatures below the glass-transition temperature of the polymer because of the restriction in molecular mobility. We suggest that the scission mechanism in such copolymers involves the breaking of either α–β or β–γ carbon–carbon bonds through an intermediate transition state consisting of either a six- or a seven-membered ring through a γ- or δ-hydrogen atom. We further conclude that transfer of excitation energy along a polymer chain will be possible in systems where similar chromophores are located in adjacent positions along the backbone. When such is the case, one may expect to get substantial changes in the quantum yields for the observed photochemical processes.

Acknowledgment. The authors wish to acknowledge the generous financial assistance of the National Research Council of Canada and the many helpful discussions with F. Golemba, M. Heskins, and E. Dan.

---

[12] E. Dan and J. E. Guillet, unpublished work.

The Crystalline Morphology of Poly(*N*-vinylcarbazole)[1]

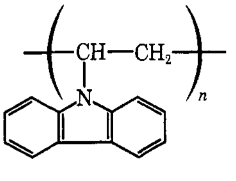
Richard G. Crystal

Research Laboratories, Xerox Corporation, Rochester, New York 14603.

Received August 23, 1970

ABSTRACT: The crystalline morphology of poly(*N*-vinylcarbazole), a polymer which exhibits interesting electrical properties, has been examined by optical microscopy, electron microscopy, electron diffraction, and X-ray diffraction. The unsheared polymer crystallized into fragmented "pseudo-spherulitic" structures at temperatures above 285° which then melted between 347 and 351°. Crystallization was markedly shear dependent, and shear-induced crystallization was noted at temperatures as low as 230°. The morphology of such crystallizations was characterized by bundles of fibrous entities approximately 250 Å in diameter oriented parallel to the shear direction, and bore a striking resemblance to the fibrous texture reported for polytetrafluoroethylene. Resultant poor mechanical properties were attributed to weak interfibrillar bonding. Two distinct single crystal morphologies were grown from dilute solution using several solvent systems. Below 115° rod-shaped crystals (which appear to be extended chain structures) were formed, while above approximately 115°, flat thin lamellar (presumably chain-folded) crystals were realized. Because of the large bulky pendant groups attached to the polymer, it is postulated that below approximately 115° the polymer in solution is too stiff to chain fold, while above 115° chain folding is possible. Electron diffraction from solution grown single crystals suggest that PVK molecules are isotactic, and form a 3/1 helical array in a hexagonal packing with $a_1 = a_2 = a_3 = 12.30$ Å and $c = 7.44$ Å.

Poly(*N*-vinylcarbazole) (PVK) was used very heavily during World War II as a substitute for mica because of its good dielectric properties and heat resistance. While further research into the polymer's high-temperature resistance continued after the war, its extreme brittleness and tendency to cause exzema-type rashes on personnel handling it has resulted in a drastic decrease in production.[2a] Interest today centers largely on PVK's electrical properties. Hoegl, *et al.*,[2b] identified the photoconductive properties of the polymer which have since been studied in detail.[3-5] Charge-transfer complexing between PVK and iodine has been reported by Hermann and Rembaum.[6] From a manufacturing point of view, the polymer is difficult to handle by conventional molding techniques, but is tractable in several organic solvents. The solution properties of PVK have been described by Naghizadeh and Springer[7] and more recently by



poly (*N*-vinylcarbazole) repeat unit

---

[1] Presented in part at the American Physical Society Meeting, Dallas, Texas, March 1970.

[2] (a) J. A. Brydson, "Plastics Materials," Van Nostrand, Princeton, N. J., 1966; (b) H. Hoegl, O. Sus, and W. Neugebauer, West German Patent 1,068,115 (1957).

[3] H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).

[4] M. Lardon, E. Lell-Doller, and J. Weigl, *Mol. Cryst.*, **2**, 241 (1967).

[5] D. Pai, *J. Chem. Phys.*, **52**, 2285 (1970).

[6] A. M. Hermann and A. J. Rembaum, *J. Polym. Sci., Part C*, **No. 17**, 107 (1967).

[7] J. Naghizadeh and J. Springer, *Kolloid-Z. Z. Polym.*, **215, 1**, 21 (1967).

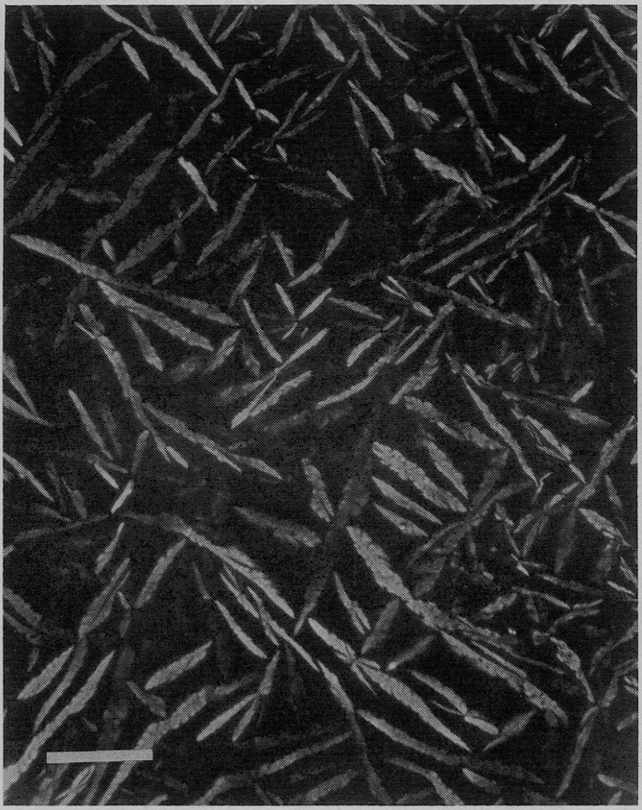


Figure 1. Optical micrograph of bulk crystallized (300°) unsheared PVK showing fibrillar or feathery structures, crossed polars. The bar is 50 μ.

Sitaramiah and Jacobs[8] while solution dielectric properties have been reported by North and Phillips.[9]

Reference to crystallinity in the polymer appeared primarily in the patent literature as early as 1940. Beck and Dorrer,[10] in their patent disclosure on a fabrication process for PVK, referred to a pearlike fibrous structure that, while not specified at the time, was apparently the crystalline form. A 1963 Montecatini patent[11] made definite reference to the crystalline form derived by annealing a "stereoregular" polymer above 250°. Recently, Kimura, *et al.*,[12] noted that X-ray data from annealed PVK indicate the presence of an isotactic 3/1 helix as well as a syndiotactic 2/1 helix in the crystalline form.

This paper describes the results of an investigation into the crystalline morphologies of PVK, morphologies which do not resemble spherulitic crystalline polymers. Data from X-ray and electron diffraction, electron microscopy, and optical microscopy are presented. Morphological structures are compared to other crystalline polymers. The PVK studied was a commercially produced polymer obtained from Borden Chemical Co. having a number average molecular weight $\overline{M}_n = 2.5 \times 10^5$ and a molecular weight distribution $M_w/M_n = 2.5$ as determined by gpc.

Results

Bulk Morphology. Crystallization from the Melt. PVK crystallized from the unsheared melt into a fragmented "pseudo-spherulitic" morphology. Figure 1 is an optical micrograph of a 10-μ film crystallized for 1 hr at 300° on a microscope hot stage and viewed through crossed polars. The negatively birefringent feathery structures, approximately 50 μ long and 10 μ wide, nucleated heterogeneously at temperatures above 285°. Unlike more common spherulites which fill spherical envelopes during growth, crystallization proceeded along a limited number of arms extending from the central nucleating source, resulting in the feathery appearance.

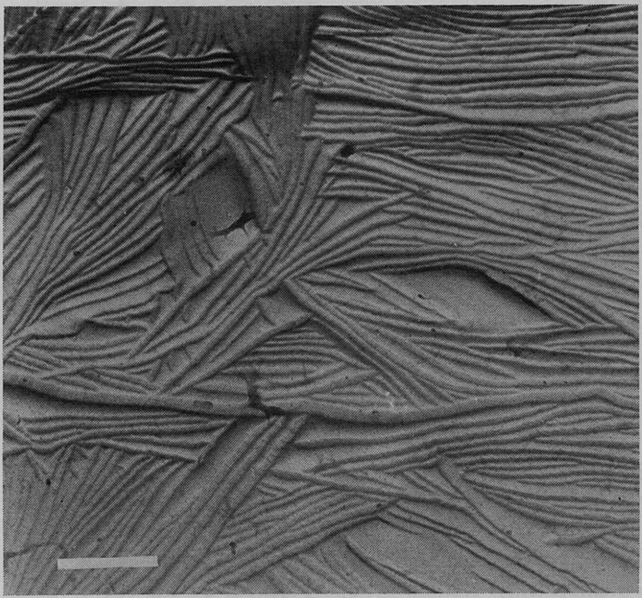


Figure 2. Fracture replica electron micrograph of melt crystallized (300°) unsheared PVK showing fibrillar texture; Pt–C two-step replica. The bar is 1 μ.

The morphology illustrated in Figure 1 was further examined by fracture replication electron microscopy. Figure 2 is an electron micrograph (Pt–C shadow) illustrating the marked fibrous substructure of crystalline fragments. Note the large unstructured regions between fiber bundles. Electron diffraction from small fiber fragments adhering to the stripped replicas indicated a considerable degree of order perpendicular to the fiber axis as illustrated by arc patterns corresponding to an approximately 5 Å spacing. As will be expanded upon later, this indicates molecular order parallel to the fiber axis. Molecular orientation could in part be explained by either extended chain crystallization or more plausibly by a high degree of molecular order along the fiber axis. To amplify this point further, Figure 3 is a replica of a sample subjected to compression (in a small vise) after crystallization in which numerous jogs in the fibrous texture are evident. Such jogs or kinks have been previously described by Speerschneider and Li[13] in their examination of deformed polytetrafluoroethylene bulk extended chain crystal morphologies. The PVK jogs were readily seen in several specimens and jog lines appeared to preferably run perpendicular to the fiber directions, suggesting that the kinks have crystallographic origin. In comparison to readily crystallizable polymers, such as high-density polyethylene and nylon 66, PVK crystallization was markedly slower. Since crystallizaion occurred near temperatures where the polymer degrades, hot stage optical microscopy experiments at higher temperatures (>340°) were difficult to perform. Constant purging

---

(8) G. Sitaramiah and D. Jacobs, *Polymer*, **11**, 165 (1970).

(9) A. M. North and P. J. Phillips, *Chem. Commun.*, **21**, 1340 (1968)

(10) H. Beck and E. Dorrer, U. S. Patent 2,215,573 (1940), assigned to General Aniline and Film Corp.

(11) British Patent 914,418 (1963), Montecatini Societa l'Industria Mineralia E Chemica.

(12) A. Kimura, S. Yoshimoto, Y. Akana, H. Hirata, S. Kusabayashi, H. Mikawa, and N. Kasai, *J. Polym. Sci., Part A-2*, **8**, 4, 643 (1970).

(13) C. J. Speerschneider and C. H. Li, *J. Appl. Phys.*, **33**, 1871 (1962).

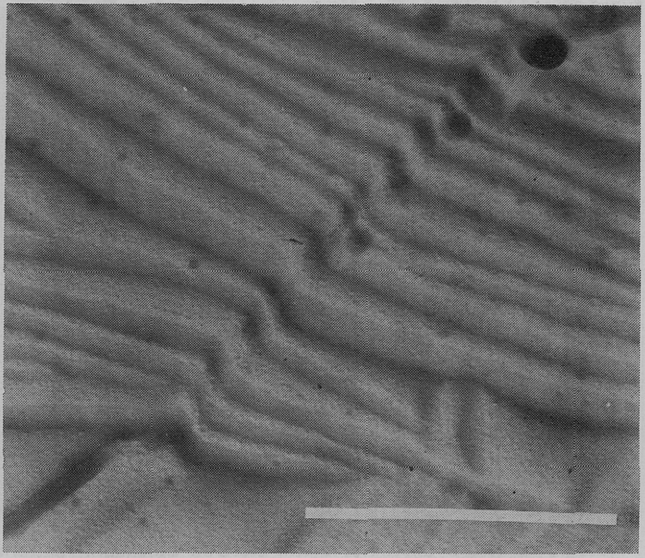


Figure 3. Electron micrograph of melt crystallized (300°) unsheared PVK subjected to compressive forces. Note jogs in the fibers; Pt–C two-step replica. The bar is 1 μ.

of the hot stage chamber with dry nitrogen, however, did slow degradation considerably.

Birefringent fragments were observed on the hot stage at temperatures as low as 226°, but no appreciable crystal growth ensued. Heterogeneous nucleation occurred at 285° and above followed by detectable crystal growth, resulting in the morphology shown in Figure 1. Sizes of "fragments" varied from 0.5×10 to $10 \times 50\ \mu$, the latter being favored by higher crystallization temperatures where nuclei densities were lower. Melting occurred in the 347–351° temperature range as noted by loss of birefringence. Degradation (discoloration) was noted above 340° in spite of the nitrogen atmosphere.

Shear-Induced Crystallization. PVK crystallization was found to be extremely shear dependent. Subjecting films to slight shear on the hot stage by displacement of the cover glass resulted in shear-induced row nucleation at temperatures as low as 230°. When compression molded under moderate pressures at 240°, PVK underwent marked crystallization into a fibrous material having the friability of mica, *i.e.*, the films readily fractured in planes parallel to the plane of molding. Examination of freshly cleaved surfaces by replication electron microscopy revealed the fibrous morphology illustrated in Figure 4. Their radial orientations indicated that fibers grew parallel to shear lines in the mold.

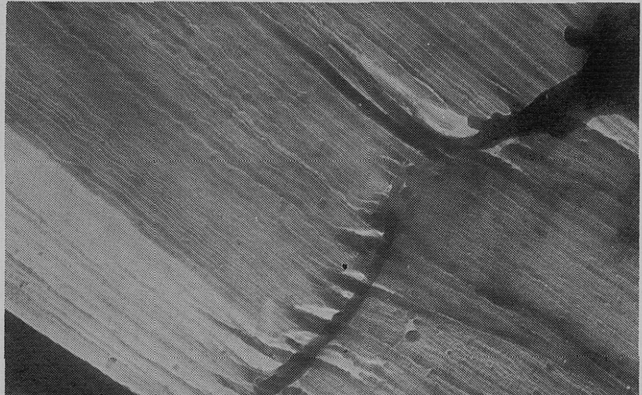


Figure 4. Electron micrograph of compression molded PVK showing fibrous substructure. Pt–C replica.

Figure 5. Electron micrograph of compression molded PVK. Fibrous substructure has been splayed apart. Pt–C replica.

Upon closer inspection, substructure in the form of striations oriented approximately perpendicular to the fibril axis was evident. We could hypothesize that such striations are caused by folded chain crystallization nucleating epitaxially on a central extended chain core, but evidence is not conclusive. The entire morphology, however, was remarkably similar to that observed by O'Leary and Geil[14] in compression molded polytetrafluoroethylene, a polymer known to crystallize in an extended chain morphology. Interfibril bonding in PVK was apparently weak as indicated by the splaying of fibrils as seen in Figure 5, an electron micrograph of a specimen rubbed lightly with a pencil eraser. It should be pointed out that while the macroscopic material failed quite easily, the individual fiber elements, usually tens of microns long, maintained their integrity. The friability of molded samples is in direct contrast to the nonfriable melt crystallized polymer. We believe that in the latter (Figure 2) crystallization has not gone to completion and thus uncrystallized polymer between fibrils prevent interfibrillar failure.

X-Ray Diffraction. Melt crystallized PVK did not give strong X-ray diffraction patterns. Figure 6 superimposes

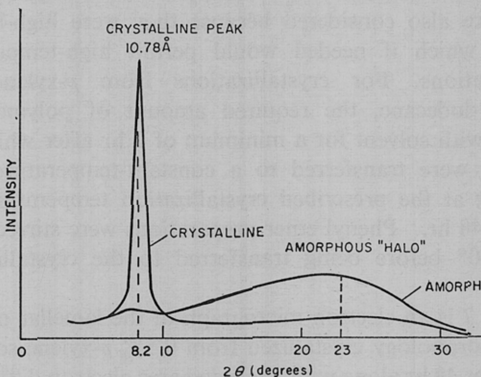


Figure 6. X-Ray diffraction traces for both crystalline and amorphous PVK.

---

[14] K. O'Leary and P. H. Geil, *J. Appl. Phys.*, **38**, 11, 4169 (1967).

Table I
Conditions for PVK Single Crystal Growth and Type of Resultant Morphologies

Solvent	Polym concn, wt %	Temp, °C	Morphology
p-Xylene	0.5	100	Rods
		115	Rods + lamellae
		125	Lamellae
	0.25	100	Rods
p-Xylene/dodecane (50/50)	0.5	100	Rods
		115	Rods
		125	Lamellae
Phenyl ether	0.5	100	Rods
		125	Lamellae

diffractometer traces for both a substantially crystalline and an amorphous PVK sample. Only one distinct crystalline reflection at $2\theta = 8.2°$ was observed in the crystalline form. The amorphous form was characterized by a strong amorphous "halo" in the region $2\theta = 20$–$25°$ and a weaker amorphous "halo" in the vicinity of the crystalline peak. X-Ray diffraction studies with a transmission Laue camera indicated that the 10.78 Å ($2\theta = 8.2°$) spacing was oriented perpendicular to the fibrils in compression molded materials. Assuming molecular orientation parallel to shear lines, the 10.78 Å spacing should then be attributed to an intermolecular distance. This assumption will be confirmed in a subsequent section describing diffraction from solution grown single crystals. X-Ray examination of drawn amorphous films[12] also confirm that the 10.78 Å spacing is intermolecular.

Single Crystal Morphology. In order to elucidate further PVK molecular structure, single crystals were successfully prepared from dilute solution. From the literature[15] and past experience, conditions favoring polymer single crystal growth are (1) dilute solution, *i.e.*, less than 1% polymer, (2) a solvent medium which is a poor solvent at the desired crystallization temperature, but in which the polymer has appreciable solubility at higher temperatures, and (3) a crystallization temperature not more than 50–75° below the melting point.

The latter condition, requiring 275–300° crystallization, was not feasible since PVK degrades readily at elevated temperatures. Crystallizations below 150° were most desirable both from an equipment and a degradation point of view. Table I lists the conditions under which PVK single crystal growth was successful along with the type of morphology obtained. After screening several solvent systems, *p*-xylene looked most attractive because of limited solubility. Dodecane and phenyl ether were also considered because they were high-boiling solvents which if needed would permit high-temperature crystallizations. For crystallizations from *p*-xylene and *p*-xylene–dodecane, the required amount of polymer was refluxed with solvent for a minimum of 2 hr after which the solutions were transferred to a constant-temperature bath operating at the prescribed crystallization temperature and held for 48 hr. Phenyl ether preparations were stirred for 4 hr at 160° before being transferred to the crystallization bath.

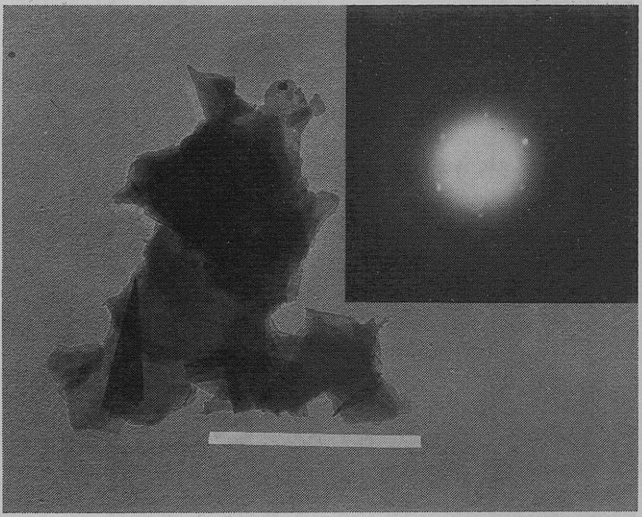


Figure 7. Electron micrograph and electron diffraction pattern of lamellar type PVK single crystal morphology grown at 125° in *p*-xylene. The bar is 1 μ.

Figure 7 is an electron micrograph of the lamellar or "flat sheet" morphology crystallized from 0.5% *p*-xylene solution at 125° for 48 hr along with a selected area electron diffraction pattern from identical unshadowed crystals. Such diffraction patterns disappeared after several minutes of electron beam exposure, thus indicating loss of crystallinity with irradiation. The sixfold symmetry in the electron diffraction pattern obtained from these crystals suggests that the unit cell is hexagonal (although a pseudohexagonal pattern as seen in polyethylene single crystals[15] is possible). Kimura, *et al.*,[12] arrived at a similar conclusion based on bulk X-ray data and concluded that the *c* axis or the polymer chain backbone is oriented in the [0001] direction. Accordingly, the chain backbones in these lamellar crystals are oriented perpendicular to the path of the electron beam, and thus, these crystals must be chain folded. In this morphology, the chains apparently fold back and forth to form chain-folded lamellae.

Figure 8 illustrates schematically a cross section of the rodlike molecules arranged in a hexagonal array. The d spacing associated with the sharp spots in Figure 7 is 5.41 Å. In comparison to X-ray data, we assign the 5.41 Å reflections to the second-order reflections of the $\{10\bar{1}0\}$ family of planes in a hexagonal net. Because of equipment limitations, we were not able to detect the first-order reflections seen in X-ray analysis as it was apparently too close to the beam. In addition, faint diffraction spots were detected between the $\{10\bar{1}0\}$ reflections at a spacing of 6.15 Å, which we assign

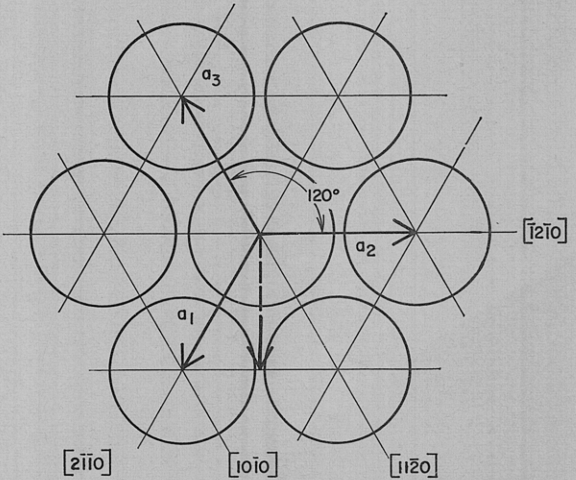


Figure 8. Schematic diagram of a cut through PVK rodlike molecules arranged in a hexagonal array, indicating key crystallographic orientations.

---

(15) P. H. Geil, "Polymer Single Crystals," Interscience, New York, N. Y., 1964.

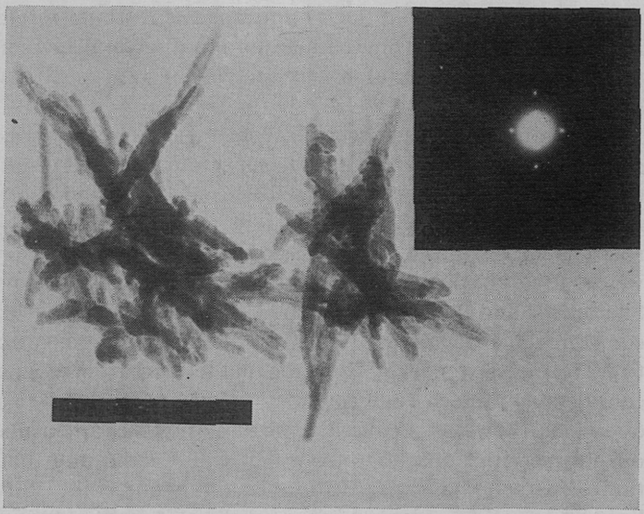


Figure 9. Electron micrograph and electron diffraction pattern of rod type PVK single crystal morphology grown at 100° in p-xylene. The bar is 0.5 μ.

to the first-order reflections of the $\{11\bar{2}0\}$ family of planes. These data on single crystals confirm the $(10\bar{1}0)$ assignment of Kimura, *et al.*, and indicate that the rodlike PVK chains form into a hexagonal net with $a_1 = a_2 = a_3 = 12.30$ Å. While it appeared surprising to find a regular electron diffraction pattern from a polymer containing such large pendant groups, the phenomenon can be rationalized by considering that both stereoregularity and the planar nature of these pendant groups can lead to a regular crystal structure in which the pendant groups play an important role in stabilizing the crystal lattice.

Figure 9 is a transmission electron micrograph (Pt–C shadowing) and a corresponding selected area electron-diffraction pattern from the rod-type morphology crystallized from 0.5% p-xylene solution at 100° for 48 hr. By reducing the crystallization temperature 25°, the flat tablet crystals are no longer realized. The rod-shaped entities, approximately 500 Å in diameter and 5000 Å long, are similar to the fibrils pointed out in the description of compression molded PVK. The lengths of these rods approximate the expected molecular chain length from molecular weight data. The sharp spot electron diffraction pattern obtained by tilting around the crystal long axis indicates that the rods are single crystals, but these patterns show no sixfold symmetry. The previously mentioned 5.41 Å spacing is observable, however, and is oriented perpendicular to the rod long axis. From the crystal relative shape and appearance and the observed orientation of the 5.41 Å spacing, it is assumed that the rods are extended chain crystals in which the molecules are oriented parallel to the long axis of the rods.

Several additional reflections corresponding to 3.72 Å (moderate), 7.44 Å (strong, partially masked by the beam), 6.57 Å (weak), and several other very weak spacings are detectable from Figure 9. If the 5.41 Å spacing is assigned to the second-order reflection of $(10\bar{1}0)$, then the 7.44 and 3.72 Å spacings, oriented perpendicular to $(10\bar{1}0)$ and parallel to the rod long axis, would then be assigned to the first- and second-order (0001) reflections, respectively. It would then follow that the weak 6.57 Å spacing could then be assigned to the $(10\bar{1}1)$ reflection. We believe that several other very weak reflections that cannot be readily assigned to a hexagonal array are a consequence of regular packing of the planar carbazole groups.

Diffraction from the rod morphology indicates that the c axis is oriented parallel to the rod long axis, thus strengthening an argument for extended chain crystallization. It should be pointed out that assignment of the 3.72 Å spacing to (0002) strongly indicates that, in light of previous arguments,[12] PVK is isotactic with a 3/1 helix configuration. Construction of molecular models (Figure 10) confirms that a 3/1 isotactic helix results in a 7.4 Å chain periodicity. Kimura, *et al.*,[12] noted that rodlike chain structure with reasonable inter-carbazole group distances seemed to be limited to either a 3/1 isotactic conformation of a 2/1 syndiotactic confirmation. Construction of molecular models in our laboratory confirms this hypothesis and indicates that the repeat units along the chain backbone, the distances between white markers in Figure 10, are approximately 7.4 Å for the 3/1 isotactic model (Figure 10a) and 5.2 Å for the 2/1 syndiotactic model (Figure 10b).

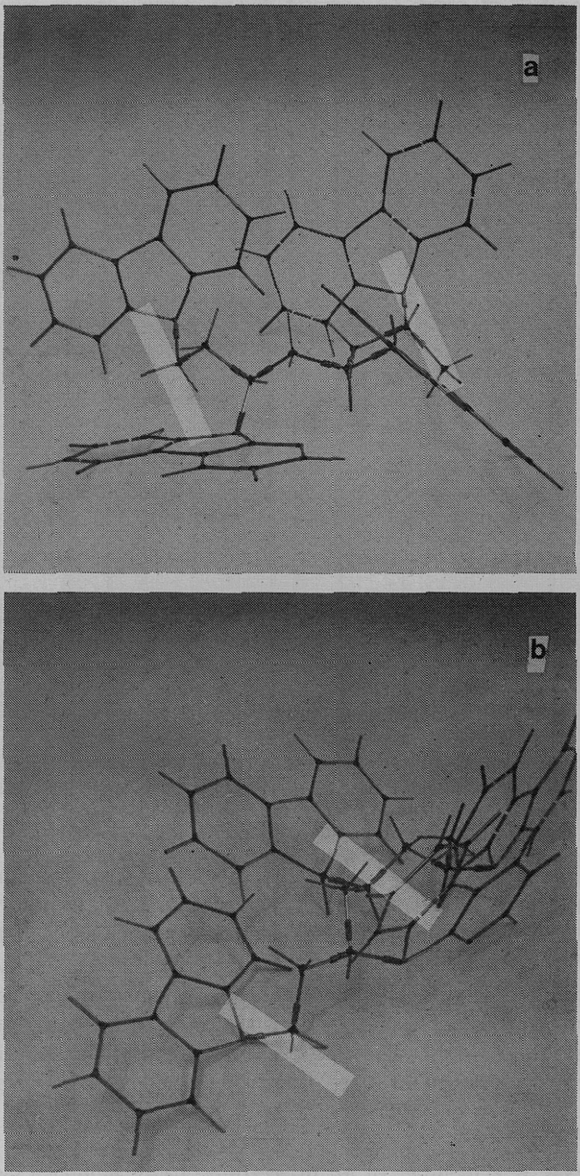


Figure 10. Molecular models of PVK showing (a) a 3/1 helical isotactic arrangement with a 7.4 Å repeat distance, and (b) a 2/1 helical syndiotactic arrangement with a 5.2 Å repeat distance. White markers signify repeat distances along the chain.

Figure 11 is an electron micrograph of a mixture of crystals obtained from a 0.5% p-xylene solution crystallized at 115° for 48 hr. From this micrograph it is evident that both rod type (white arrows) and lamellar type (black arrows) are realized.

Figure 11. Electron micrograph of mixture of rod type (white arrows) and lamellar type (black arrows) PVK single crystals grown at 115° in *p*-xylene.

As indicated by the data summarized in Table I, the transition from rod to lamellar single crystals occurs in the vicinity of 115°. This change in single crystal morphology with crystallization temperature will be further discussed in the next section. It should be pointed out that the sharp single crystal electron diffraction patterns, in contrast to the weak melt crystallized X-ray diffraction patterns, suggest that solution grown crystals are far more ordered than melt grown crystals.

Discussion

PVK is a member of an interesting family of linear vinyl polymers having large, bulky pendant groups. Because of steric hindrance effects, tacticity should play a very critical role in crystallization. For polystyrene, with a much smaller pendant group, only the isotactic configuration is crystallizable. We have found that PVK polymerized by several routes including thermal and ionic polymerization has approximately the same propensity for crystallization, suggesting that all *N*-vinylcarbazole polymerizations lead to stereoregular polymers. From studies of molecular models of both isotactic and syndiotactic configurations, the planar pendant groups lie close to and parallel to one another, which could result in π overlap attraction between pendant groups. If true, we could expect that such bonding would make the PVK molecule quite stiff, resulting perhaps in a rod conformation in dilute solution. Because of steric effects from the bulky pendant groups and possible resultant barriers to rotation, a π overlap phenomenon might not be necessary to explain chain stiffness. Assignment of PVK to a hexagonal array with $c = 7.44$ Å is a strong indication of isotacticity and a 3/1 helix configuration. Such an arrangement would result in a carbazole group lying parallel to and directly below its third nearest neighbor along the polymer chain backbone (see Figure 10a).

North and Phillips[9] concluded from their dielectric measurements that PVK in dilute toluene solution is a very stiff molecule, low molecular weight PVK is rodlike, and 400 monomer units are required to form an equivalent freely rotating chain segment. They assume that higher molecular weight PVK chains assume a random coil conformation. Sitaramiah and Jacobs[8] determined that the "σ" steric or conformational factor of PVK in solution is 2.8 (compared to 2.2 for polystyrene) and conclude that the carbazole groups considerably hinder free rotation. Their Mark–Houwink exponents, however, deduced from viscosity measurements on polymer fractions, vary from 0.5 to 0.8, indicating that the dilute solution conformation is a random coil. Williams'[16] nmr measurements indicated that hindered rotation exists in PVK resulting from the steric restraints of the polymeric environment. Nmr results show that a large upfield shift occurs for one or more of the aromatic protons and this is attributed to shielding effects of neighboring carbazole groups on the polymer chain with restricted (temperature sensitive) internal rotation. The nmr results of Yoshimoto, *et al.*,[17] agree with this view.

The formation of both rod shaped and lamellar shaped crystals from dilute solution and its apparent temperature sensitivity is intriguing. To undergo chain folding, a molecule must be flexible enough to bend back upon itself. Without such flexibility extended chain crystallization is likely. We believe that as the barriers to rotation are overcome with increasing temperature, the flexibility of the molecule increases to a sufficient level to accommodate chain folding. Thus, at approximately 115° the single crystal morphology changes from rodlike to the kinetically preferred[18] folded-chain crystals.

Our morphological observations indicate that a fibrous crystalline morphology is grown from the melt. Assuming that migration of a stiff molecule to a crystal growth face is more difficult than migration of a flexible chain, then both slow crystallization rates and high temperature requirements for crystallization are understandable. Then, too, crystallization shear sensitivity would be expected since shearing would orient these long stiff molecules, thus increasing the chances for adjacent molecules to come together and crystallize. Finally, since both PTFE and PVK are apparently stiff molecules, similarities between the crystalline morphologies of these polymers is not surprising.

Acknowledgment. The author wishes to thank Mr. F. J. Walton for his invaluable assistance during this study, Dr. D. R. Wilson for PVK specimens polymerized by several routes, Dr. P. F. Erhardt for the initial compression molded specimens, and Dr. D. J. Williams for making nmr data available prior to publication.

---

(16) D. J. Williams, *Macromolecules*, 3, 5, 602 (1970).

(17) S. Yoshimoto, Y. Skana, A. Kimura, H. Hirata, S. Kasubayashi, and H. Mikawa, *Chem. Commun.*, 987 (1969).

(18) J. D. Hoffman and J. L. Lauritzen, Jr., *J. Res. Nat. Bur. Stand., Sect. A*, 65, 4, 297 (1961).