

Orientation in poly(*N*-vinyl carbazole) by melt extrusion

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The use of poly(*N*-vinyl carbazole) (PVK) in photoconductive devices and the potential correlation of its unusual electrical properties with structure have resulted in several investigations concerning its morphology. Recent work with annealed solvent cast and stretched PVK films suggests that the high temperatures and stresses present during the melt extrusion of high molecular weight PVK could produce highly ordered structures. In the present work, calorimetry, thermogravimetry, infra-red dichroism, X-ray diffraction, optical microscopy, densitometry and small-angle laser light scattering measurements are used to evaluate the ordering produced by the high temperature melt extrusion of thin PVK films. The results indicate the high stress fields present during extrusion produce a highly ordered one-dimensional structure composed of closely packed, oriented chains.

INTRODUCTION

N-vinyl carbazole is readily free radically or cationically polymerized into a high molecular weight polymer¹⁻³. Its early use was as a dielectric, heat resistive material but recently its electrical properties have been used in photoconductive devices³. These unusual properties and their potential correlation with structure have resulted in several investigations concerning the morphology of poly(*N*-vinyl carbazole) (PVK).

Highly ordered structures suggestive of crystallinity have been obtained in PVK by Griffiths⁴, Crystal⁵ and Su and Stein⁶⁻⁸. Griffiths showed that lamella-like structures are formed when solvent cast PVK films are annealed at elevated temperatures (270°–330°C) for hours. He determined the nominal percentage crystallinity of these annealed films from X-ray measurements and used the measured sample densities to determine the *c*-axis unit cell dimensions of this 'paracrystalline' state of PVK as illustrated in Figure 1. Su and Stein subsequently found that when PVK is oriented and held under stress at elevated temperatures, there is a time dependent change in both the birefringence and light scattering pattern that is analogous to what is observed during the stress induced crystallization of other polymers⁶⁻⁸. They determined the time and elongation dependence of the nominal degree of crystallinity of these films from the measured and calculated intrinsic birefringence of PVK as shown in Figure 2⁶⁻⁸. Compared to the crystallization time required in unoriented films, the Figure indicates that stresses accelerate the formation of the unusual degree of ordering in PVK. This suggests that similar structures could be formed quickly at the high temperatures and stresses present during the melt extrusion of high molecular weight PVK.

In the present work, calorimetry, thermogravimetry, infra-red dichroism, X-ray diffraction, optical microscopy, densitometry and small-angle laser light scattering measurements are used to evaluate the ordering produced by the high temperature melt extrusion of thin PVK films.

EXPERIMENTAL

The high molecular weight PVK used in this study was obtained from BASF Wyandotte Corporation (New York City, NY). The intrinsic viscosity in tetrahydrofuran at 25°C was 1.4 dl/g. The number- and weight-average molecular weights were 2.54×10^5 and 1.50×10^6 , respectively, as measured by gel permeation chromatography (g.p.c.) and the universal calibration curve. The original material contained 1.5% car-

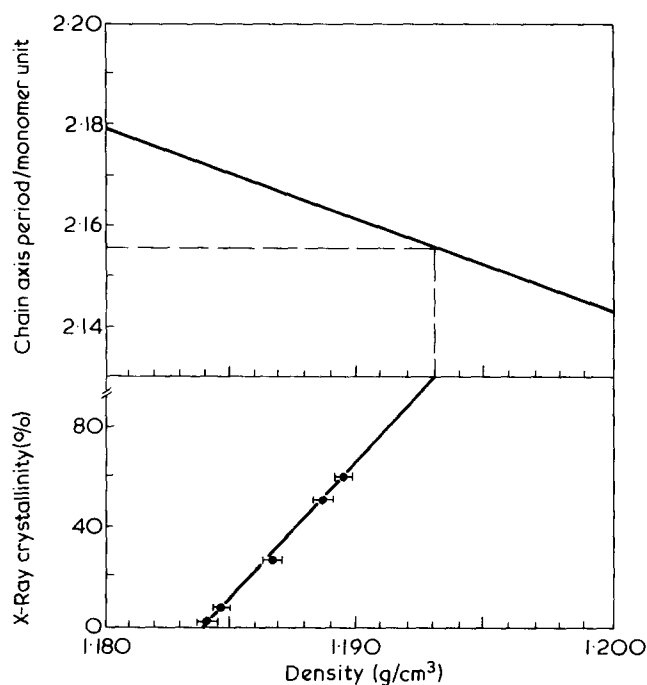


Figure 1 Percent crystallinity and chain axis period/monomer unit as functions of density. [Reproduced from Griffiths, C. H. *J. Polym. Sci.* 1975, 13, 1167 by permission of John Wiley and Sons, Inc. ©]

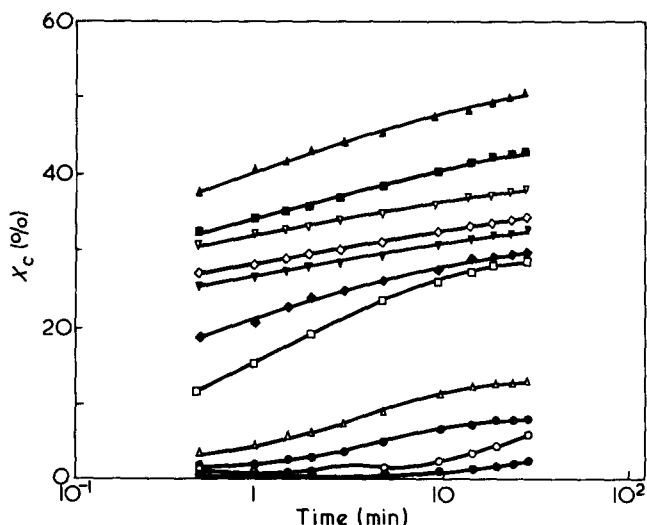


Figure 2 The variation of crystallinity with time at 275°C for extension ratios of 1.75 to 5. Reprinted with the permission of the author, (ref 8). Elongation ratio: \blacktriangle , 5.0; \blacksquare , 4.5; ∇ , 4.0; \diamond , 3.5; \blacktriangledown , 3.25; \blacklozenge , 3.1; \square , 3.0; \triangle , 2.25; \oplus , 2.1; \circ , 2.0; \bullet , 1.75

bazole and 3.5% vinyl carbazole, measured using a Hewlett-Packard 7620A gas chromatograph with a 3380A integrator.

Fifty micrometer films were extruded through a slit die attached to an Instron Capillary Rheometer. Heating rods were placed in the die and the temperature was monitored by a thermocouple placed within 1/8 in. of the slit. The temperature of the barrel was maintained at 286°C and the die at 320°C. The films were extruded at approximately 0.2 cm/sec at stresses exceeding 10⁶ dynes/cm² (10⁵ Pa).

The X-ray analysis was conducted with a Siemens Type F diffractometer and a Laue camera. Nickel-filtered CuK α radiation was used throughout. The infra-red dichroism was measured with a Perkin-Elmer IR257 equipped with a rotatable wire grid polarizer. The preferred directions of the sample and polarizer were aligned at 45° to the spectrometer's monochromator. Mass densities were measured with a 1 m KBr/H₂O density gradient column with a range of 1.100–1.200 g/ml. A Perkin-Elmer DSC-2 and TGS-2 were used to measure the temperature dependence of the heat capacity and the weight loss of the samples. The output of the DSC-2 was digitized at 0.2°C increments by a Datas 308 analog interface and stored on magnetic tape. Measurements of the thermal properties of the empty pan, the pan plus sapphire standard and the pan plus sample were combined with a time sharing system to provide the point by point calibrated heat capacity of the sample. The samples were weighed between each thermal cycle and the data corrected accordingly.

RESULTS AND DISCUSSION

X-ray

Flat plate (Laue) X-ray diffraction patterns of solvent cast amorphous and melt extruded films are presented in Figures 3a and 3b, respectively. Corresponding diffraction traces are shown in Figure 4. These Figures show a highly oriented, strong sharp peak at $2\theta = 8.25^\circ$, corresponding to a lattice spacing of 10.7 Å compared with a much diminished reflection at $2\theta = 7.9^\circ$ in the amorphous film. The relative intensities, shift in peak positions and sharpness of the reflection in the extruded film correlate directly with the primary evi-

dence for crystallization in solution (8.2°)⁵ and bulk (8.39°)⁴ crystallized PVK. This suggests that the high stresses and temperatures of the extrusion process have succeeded in rapidly producing comparable degrees of order.

Density

Table 1 compares the densities of the extruded films, Griffith's⁴ thermally ordered structures and the oriented and stress annealed samples of Su and Stein⁶⁻⁸. All measurements were made under identical conditions in the same density gradient column. The extremely high densities of the extruded films, which are the highest yet reported for PVK, indicate that a substantial degree of ordering has been achieved by the extrusion process. Attempts to anneal these films above 270°C only succeeded in reducing the apparent density (Table 1). This effect is discussed further in the thermal behaviour section. The extent to which Griffith's model can be applied to the stress-induced ordering of PVK can be judged by comparing the nominal percentage crystallinities determined from the birefringence (Figure 2) and the density (Figure 1) of Su's films. The calculated values listed in

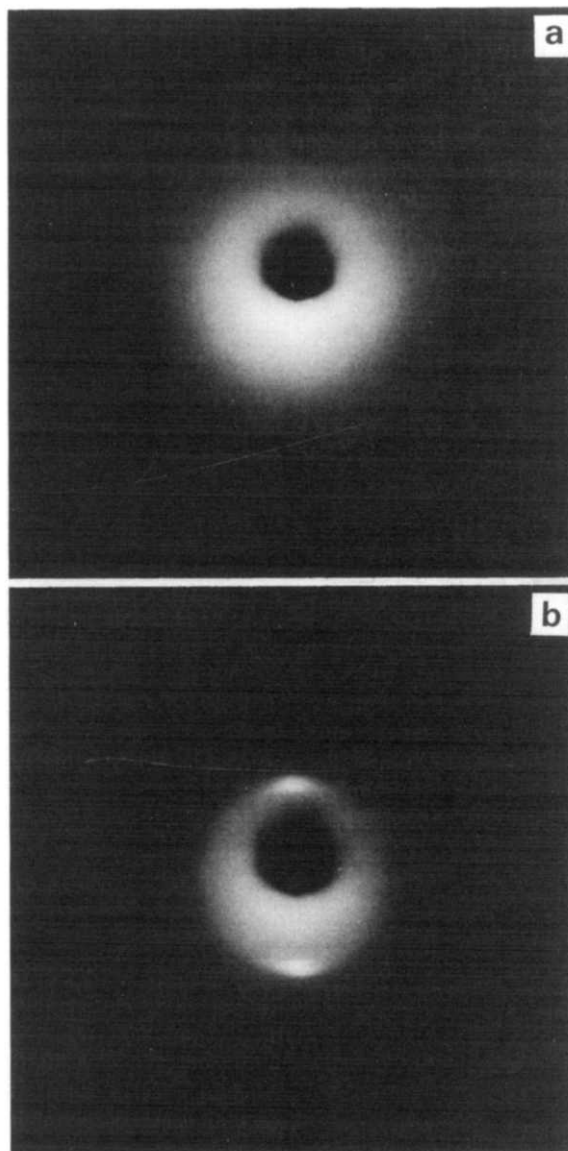


Figure 3 X-ray diffraction patterns of amorphous (a) and extruded (b) PVK

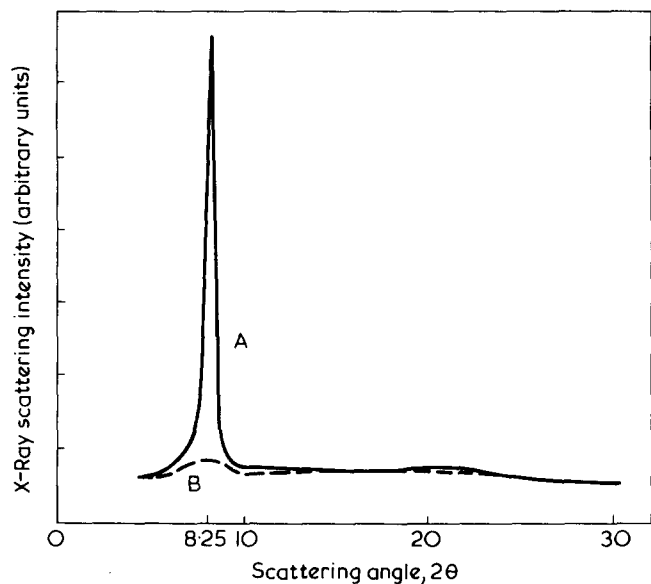


Figure 4 X-ray diffraction scans of amorphous and extruded PVK. A, Extruded PVK; B, solvent cast PVK

Table 1 Density, crystallinity and average orientation function of amorphous and oriented PVK

Sample	ρ (g/cm ³)	X_p (%) (ref 2)	X_Δ (%) (ref 3)	f_{925} [=(D-1)/(D+2)]
Amorphous	1.1840	0.0		0.0
Extruded:				0.21
(a)	1.1911	79		
(b)	1.1910	78		
(c)	1.1903	71		
Extruded, annealed (330°C, 15 min)	1.1876	40		0.20
Thermally annealed ²	1.1868	26		
	1.1888	51		
	1.1895	60		
Stretched ¹ :				
275°C, 3.0x	1.1874	38	28	0.159
3.5x	1.1876	40	34	0.168
4.0x	1.1880	44	38	0.172

¹ Samples obtained from T. K. Su and R. S. Stein; ² ref 4; ³ ref 8

Table 1 are in surprisingly good agreement considering the diversity of the two techniques. If this model is also applicable to the extruded films, the experimental densities indicate an unusually high degree of crystallinity of the order of 70–80%.

I.r. characterization

The degree of molecular orientation that is achieved during the extrusion process can be determined by measuring the infra-red dichroism of the resulting films. While the band assignments for PVK have not been made, the polarized infra-red spectra for different orientations of carbazole single crystals have been published⁹. A comparison of the spectra shows that there is a direct correspondence between the major absorption bands of the molecular crystal and the polymer. The polarizations of the vibrational bands in melt drawn PVK films support this identification. Carbazole possesses C_{2v} symmetry. In the crystal, strong infra-red active, out-of-plane absorptions are observed at 438, 570,

720, 742 and 924 cm^{-1} ⁹. In the oriented polymer, the only prominent parallel polarized bands are found at 425, 725, 745 and 925 cm^{-1} . All of the other vibrational bands associated with the polymer are perpendicularly polarized.

The parallel dichroism of the out-of-plane vibrational modes of the carbazole ring indicates that the uniaxial orientation of PVK films preferentially aligns the plane of the aromatic ring normal to the orientation direction and thus perpendicular to the chain backbone. This result is consistent with the negative sign of the experimentally determined stress-optical coefficient⁸ and is analogous to behaviour observed in polymers with bulky planar pendant groups such as polystyrene¹⁰. For example, it has been shown that for all stereochemical conformations, the steric constraints between the adjacent phenyl rings in polystyrene force the plane of the ring to be nearly perpendicular ($\pm 20^\circ$) to the chain direction¹⁰. This effect can be expected to be even more pronounced in polymers with substantially larger pendant groups such as PVK.

On the basis of the calculated normal modes of the carbazole crystal⁹, the 924 cm^{-1} vibrational band corresponds to the symmetric out-of-plane bending mode of the carbazole ring. The relative intensity and the unambiguous identification of the corresponding vibrational band in the polymer (925 cm^{-1}) makes it an ideal absorption for measuring the orientation of the polymer. Collaborative evidence can be obtained (with a lesser degree of confidence) from the perpendicular dichroism of the in-plane, aromatic C–H stretch modes at 3060 cm^{-1} .

Representative polarized infra-red spectra of the 800–1100 cm^{-1} and 2800–3500 cm^{-1} region of an extruded PVK film are shown in Figure 5. The orientation functions of the extruded films, calculated from the dichroic ratio of the 925 cm^{-1} band, are compared with similar measurements on uniaxially oriented films in Table 1. Similar results are also obtained from the dichroism of the 3060 cm^{-1} absorption. These results demonstrate that the high shear and stress fields present during the extrusion process create a molecular alignment that is even greater than that achieved by melt drawing PVK to four times its original length.

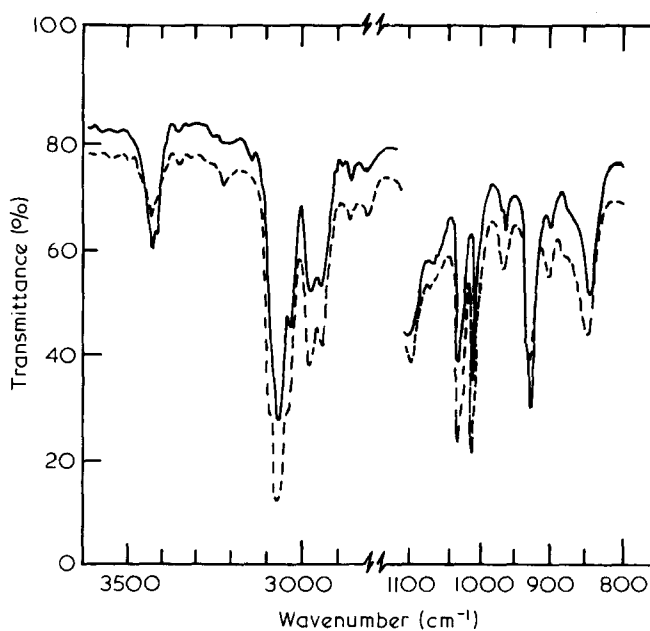


Figure 5 Polarized infra-red spectra of extruded PVK. —, //; ---, \perp

The polarization of the 3420 cm^{-1} band (Figure 5) results from the selective orientation of the dispersed carbazole impurity (N–H stretch). Surprisingly, the parallel dichroism of this band indicates that the long axes of these free carbazole rings are oriented perpendicular to the extrusion direction. This is in contrast to what is normally observed for the alignment of planar molecules in stretched polymeric matrices¹¹. Separate orientation experiments on similarly doped polycarbonate and purified PVK films reinforce this disparity. In the oriented polycarbonate films the N–H stretch is perpendicularly polarized, indicating that the planes of the carbazole groups are, as expected, parallel to the host chain direction. However the carbazole dispersed in oriented PVK films is oriented in the opposite direction in the same manner as shown in Figure 5 for the extruded films. These results indicate the existence of a specific interaction between the dispersed carbazole rings and the pendant carbazole groups of the PVK chains.

This suggests that a similar interaction may exist between the pendant carbazole groups of adjacent polymer chains. Such an assumption could contribute to the observed ordering in a manner analogous to that observed in other polymers with bulky pendant groups¹².

Light scattering

The small-angle laser light scattering patterns of the extruded films support the i.r. dichroism conclusion of the presence of highly oriented parallel chains. Su and Stein have shown that the H_v light scattering patterns of oriented PVK films change from that normally seen for shish-kebab-like structures (four leaf clover plus perpendicular scattering) at moderate elongations (2–3x) to that associated with oriented rods at high elongations^{6,8}. The H_v light scattering of the extruded films show only the strong perpendicular scattering indicative of a highly oriented rod-like structure.

Mechanical properties

The tensile modulus of the extruded films was 597 000 ($\pm 4\%$) p.s.i. (4.12×10^9 Pa) and the strain at failure was $1.1 \pm 0.1\%$. Reported values for amorphous PVK are 580 000 p.s.i. (4.00×10^9 Pa) and $0.3\%^2$. The extruded films are more flexible in the extrusion direction but more brittle than amorphous films when stressed perpendicular to this direction. The degree of interchain ordering implied above apparently does not extend over a sufficient region normal to the principle direction to improve the biaxial behaviour of the extruded film.

Microscopy

The extruded films are optically inhomogeneous. A microscopic examination shows that they are composed of a series of closely packed, cigar-shaped, highly birefringent regions 5–20 μm wide and 50–200 μm long. Within each region the birefringence is nearly uniform but at each boundary there is a sudden shift to a different phase. This effect is the result of large scale variations in the local degree of orientation rather than changes in film thickness. An examination of the microscopic birefringence of uniaxially oriented PVK films as a function of elongation shows the precursor of this effect. At moderate elongations, striations appear parallel to the orientation direction. At high elongations these striations are extended to form a tightly woven network. However, it is only in the extended films that the regions between these striations become sufficiently birefringent to appear coloured without the assistance of a first order waveplate.

The existence of these distinctly separated, highly birefringent regions indicate that an unusual non-uniform flow occurs in these extruded films.

These microscopic inhomogeneities do not extend to the submicrometer level. Electron micrographs of the extended films are featureless in contrast to the irregularly stacked lamella-like structures that are observed in the thermally crystallized samples⁴. This observation and the infra-red and light scattering results, then, imply that the unusually high densities of these films result from large domain extended-chain ordering.

Thermal behaviour

The literature contains a number of conflicting values for the glass transition temperature of PVK. While T_g values as low as 150°C ¹³ have been reported, more recent work has shown that $T_{g\infty}$ is 227°C and the Fox–Flory coefficient [$K = (T_{g\infty} - T_g)/M_n$] is of the order of 2.5×10^5 ^{3,14}. Since most commercial materials have $M_w > 10^6$ and $M_n > 10^5$, the T_g values of these materials should be relatively independent of molecular weight distribution (*MWD*). However, in contrast to this relative insensitivity to *MWD*, the T_g of PVK is very sensitive to the presence of residual solvent and impurities that are commonly found in this polymer (i.e., carbazole, vinyl carbazole and anthracene). For example, the addition of 5% carbazole to high molecular weight commercial (impure) PVK depresses the T_g by 30°C . It is this plasticization effect that is responsible for the spread in the reported transition temperature. Conversely this effect can also be used to monitor the processing-induced changes in the low molecular weight components in the sample.

Table 2 lists the molecular weight, *MWD* and the impurity content of both the virgin and extruded PVK samples. Note that the extrusion process only slightly reduced the carbazole and vinyl carbazole content and does not significantly change the molecular weight or *MWD*. However, the thermal properties of the samples suggest that the extrusion process has had a more profound effect on the polymer.

The original, pre-extruded sample exhibits a broad T_g with the midpoint in ΔC_p at 182°C . The thermal treatment associated with this initial d.s.c. scan, in which the sample was heated at 230°C at $20^\circ\text{C}/\text{min}$ and then quenched, drives off enough of the low molecular weight impurities to decrease the sample weight by 2%. The loss of these mobile species reduces the measured heat capacity of the glass and raises the apparent T_g to 188°C . As shown in the thermograms of Figure 6, subsequent thermal cycling to and quenching from 270° , 350° and 350°C for 5 min continues the process, decreasing the weight of the sample by a total of 5% and the apparent heat capacity of the glass by a corresponding amount. This deplasticization effect gradually increases the T_g of the sample to a limiting value of 223°C . Thermal gravimetric analysis (t.g.a.) shows this same effect. The

Table 2 Molecular weight and impurities in pre-extruded and extruded PVK

Sample	$M_w \times 10^{-6}$	$M_n \times 10^{-5}$	<i>MWD</i>	Vinyl carbazole (%)	Carbazole (%)
Pre-extruded	1.50	2.54	5.91	3.1	1.6
Extruded	1.56	2.35	6.64	1.6	1.2

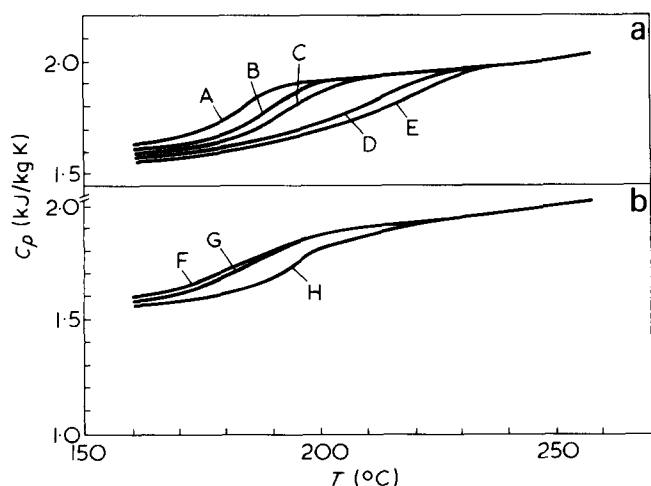


Figure 6 Heat capacities of thermally cycled PVK films. (a): A, Initial run, subsequently heated to B, 230; C, 270; D, 350 and E, 350°C (5 min). (b): Extruded film, subsequently heated to F, 230; G, 270; and H, 350°C (5 min)

sample weight decreases above the initial T_g , reaching a maximum rate of change at 270°C and a limiting value at 350°C.

In contrast to the behaviour of the starting material, the weight and apparent glass transition of the extruded material (Figure 6b) remain virtually unchanged as long as the sample is not heated above 270°C. Thermal treatments at higher temperatures do succeed in raising the T_g of the extruded films but only to 198°C, a value slightly higher than achieved by heating the original material to 270°C. In addition, the change in heat capacity associated with this well defined transition (0.11 kJ/kg/K) is significantly less than that normally observed in non-extruded samples (0.18 kJ/kg/K). This is caused by differences between the absolute heat capacities of the differently processed materials that persists until 220°C. At higher temperatures the heat capacities of the extruded and non-extruded samples are equal and remain so without any indication of a higher temperature transition. This is a surprising result in view of the degree of order suggested by the birefringence, X-ray scattering and densities of the extruded films and the models of the paracrystalline state of PVK. These effects will be discussed in detail in a forthcoming paper.

Infra-red measurements of heat cycled films show that this deplasticization effect is primarily associated with the diffusion and vaporization of the carbazole impurity. The carbazole N-H stretching band at 3420 cm^{-1} (see Figure 5) begins to vanish after the virgin samples are heated above T_g but persists in the extruded films until 270°C. In spite of these changes, the measured orientation functions (Table 1) are essentially unaffected by short thermal treatments up to at least 330°C. These results suggest that the highly ordered morphology produced by the extrusion process significantly restricts the mobility of the low molecular weight components. In the non-extruded films the lowest molecular weight impurities are able to diffuse out of the sample soon after it is heated above T_g . Further heat treatment allows

the diffusion and/or degradation and subsequent vaporization of larger impurities and low molecular weight components. This deplasticization effect raises the T_g of the sample. In the extruded films this diffusion process is significantly retarded by the highly ordered morphology. The low molecular weight impurities such as carbazole are now retained in the film until it is heated well above its T_g while the larger molecular fragments remain indefinitely trapped in the ordered matrix.

These results provide an explanation for why annealing decreases the apparent density of the extruded films without affecting the molecular orientation functions (see Table 1). The tightly bound carbazole that is driven out of the films at high temperatures leaves microvoids that are not accessible to the fluid in the density gradient column. The apparent lower density could then be an artifact of the thermally-induced defects in the sample.

CONCLUSIONS

The melt extrusion of PVK produces a very highly oriented film. Density measurements indicate that an unusual degree of order is achieved. The i.r. dichroism orientation functions, X-ray diffraction and light scattering patterns and the mechanical anisotropy support this observation. The calorimetric data suggests that the ordered regions restrict the mobility of dispersed low molecular weight components.

The results indicate the high stress fields present during extrusion produce a highly ordered, one-dimensional structure composed of closely packed oriented chains. Direct evidence of crystallization during extrusion was not found.

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