

STUDY ON LIQUID CRYSTALLINITY OF POLY(*N*-VINYLCARBAZOLE)*

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Abstract The liquid crystallinity of poly(*N*-vinylcarbazole) was studied by using powder X-ray diffraction, polarized optical microscopy, and differential scanning calorimetry. The results show that the lower molecular weight fractions of this polymer do not form a liquid crystalline phase, while the samples of sufficiently high molecular weight do form a mesophase at temperatures above the glass transition. The lowest value of the degree of polymerization for PVK to form a stable liquid crystalline phase was found to be in the range of 150 to 200, significantly higher than the value of 50 for most conventional side chain liquid crystalline polymers.

Keywords Poly(*N*-vinylcarbazole), Liquid crystalline polymers

INTRODUCTION

Poly(*N*-vinylcarbazole) (PVK) is a widely used photoconductor. Its synthesis, structure and properties have been investigated in detail since the 1960's. It is generally observed that PVK is amorphous as it is isolated from the polymerization solution, but the degree of order increases with heat-treatment. Kimura *et al.*^[1] studied a PVK powder sample which had been annealed at 300°C for 30 min in nitrogen by using an X-ray diffractometer. They found that the diffraction peak at $2\theta = 8.15^\circ$ became stronger with the annealing. They attributed this apparent increase of ordering to the crystallization of PVK during the heat treatment. Based on the X-ray diffraction data, they proposed that PVK molecules were packed approximately parallel to each other in a pseudo-hexagonal array with a lateral spacing of 1.07 nm, and that the PVK chains had a stereoblock array consisting of 3/1 and 2/1 helices. However, because no layer line diffraction was observed, they concluded that the crystalline PVK had no longitudinal order. Crystal^[2] examined the heat-treated PVK samples using fracture replica electron microscopy and found that PVK had a fibrous structure without substantial evidence for longitudinal order of PVK chains. Griffiths^[3] presumed that PVK was a disordered paracrystal after investigating the heat-treated samples using X-ray diffraction and electron microscopy. In the subsequent publication, Griffiths and Van Laeken^[4] established a dependence of the structure and morphology of PVK on its molecular weight (MW). They found that PVK with number-average molecular weight $M_n < 46,000$ was uncrystallizable. Prest^[5] studied melt-extruded samples of PVK by X-ray diffraction, densitometry and small angle laser scattering measurements. The results of these studies indicated that the melt extrusion of PVK produced a highly ordered, one-dimensional structure composed of closely packed oriented chains. He concluded that direct evidence of crystallization during extrusion was not found.

Although one-dimensional ordered structure was observed by the above investigators the notion of the formation of crystals of PVK is questionable. In particular, no X-ray diffraction pattern characteristic of a crystal was obtained. The X-ray patterns observed by these investigators showed only one strong reflection in the low angle region and its presence could be appropriately ascribed to a mesophase rather than to a crystal^[6–8]. For

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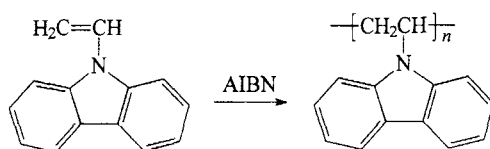
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instance, the wide angle X-ray diffraction (WAXD) pattern of poly(2,5-bis[(4-methoxy-benzoyl)oxy]styrene) displays a strong reflection at $2\theta \sim 5.89^\circ$ and a diffuse scattering at $2\theta \sim 21^\circ$ and was interpreted by Xu *et al.*^[6] to be a nematic structure with polymer chains oriented along the phase director. On the other hand, the X-ray diffraction pattern of another mesogen-jacketed liquid crystalline polymer, poly(2,5-bis[(4-butyl-benzoyl)oxy]styrene), has a sharp peak at $2\theta \sim 5^\circ$ and only a diffuse scattering at $2\theta \sim 20^\circ$, which was interpreted by a nematic structure by Pragliola and coworkers^[7]. More recently, Tu *et al.*^[8] studied the self-assembled supra-molecular structure of poly[di(4-heptyl)vinylterephthalate], or poly(2,5-bis[(4-heptyl)-oxycarbonyl]styrene). The powder pattern of this polymer also showed no obvious Bragg reflection in the wide-angle region of $2\theta > 10^\circ$ but a strong reflection in the low angle region of $2\theta = 5.6^\circ$. Together with the WAXD fiber experimental results the structure was characterized as a hexagonal columnar mesophase. As one may have noticed, PVK and the polymers studied by Xu, Pragliola, and Tu are alike in molecular structure. The four polymers all have a polyethylene backbone and a laterally substituted bulky side group at every second backbone carbon atom. It is therefore reasonable to suggest that they have a similar phase structure. In fact, Wu^[9] has considered PVK as a liquid crystalline polymer, although no experimental evidence was given. In this paper, we report our results that could suggest a nematic structure for high molecular weight PVK at temperatures higher than T_g but of course below its thermal decomposition temperature.

EXPERIMENTAL

All reagents except AIBN were used as purchased. AIBN was recrystallized from alcohol. The polymer used for fractionation was obtained by an AIBN-initiated free radical polymerization of *N*-vinyl carbazole (NVK) monomer in toluene solution (Scheme 1). The polymer was fractionated to give six fractions by fractional precipitation from THF solution using methanol as the precipitant. The MW and molecular weight distribution (MWD) were determined with a Waters 2401 gel permeation chromatograph using monodispersed polystyrenes as standards. Table 1 shows the results. The M_w s of the six fractions range from 1.9×10^4 to 7.9×10^4 and the MWD indices are all below 1.4. The sample used for WAXD experiments was obtained by AIBN-initiated free radical polymerization of NVK in benzene that had a higher M_n of 20.7×10^4 with M_w/M_n equal to 1.44. The thermograms were obtained by using a TA DSC 2010 instrument at a heating rate of 20 K/min under a nitrogen gas flow of 20 mL/min. The WAXD powder experiments were performed with a Rigaku Dmax-2400 diffractometer. The polarized optical microscope observations were made on a Leitz Laborlux 12 Pol microscope equipped with a Leitz 350 hot stage.



Scheme 1 Reaction pathway for the synthesis of PVK

Table 1. Some properties of PVK fractions

$M_n \times 10^4$	M_w/M_n	T_g (°C)	Liquid crystallinity
1.9	1.38	223	No
2.9	1.26	223	No
4.0	1.27	224	Yes
5.8	1.25	224	Yes
6.6	1.30	225	Yes
7.9	1.19	225	Yes

RESULTS AND DISCUSSION

PVK is thermally very stable. Either the original sample or the fractionated ones showed only a 2% weight loss at

400°C. Yet our subsequent experiments were conducted below 300°C (except otherwise indicated) in order to warrant reliable data.

Several investigators^[1-5] had carried out WAXD experiments for PVK. They stated that the PVK samples as synthesized were amorphous, but the degree of order could be increased by heat-treatment at high temperature. Thus, the WAXD pattern of the amorphous samples showed two diffused scattering peaks with one at $2\theta \sim 8^\circ$ and the other at $2\theta \sim 20^\circ$. However, the former scattering peak became stronger with heat-treatment. In our present WAXD experiments, we used a sample that had a very high molecular weight of $M_n = 20.7 \times 10^4$ in order to minimize the molar mass effect. Again, two experiments were carried out. One used the original sample, the other used the sample that had been heat-treated at 300°C under nitrogen for 30 min and then quenched in ice water. The results are shown in Fig. 1, in which the curve a is of the untreated sample, b is of the annealed sample. There is no distinct Bragg reflection but only a very diffused scattering can be observed in the wide-angle region for both samples. This indicates that no crystalline structure of close molecular packing can be detected in the original sample or in the annealed sample. Besides, there is no indication of increase in crystallinity by annealing if a comparison of the sharpness of the scattering peak at $2\theta \sim 20^\circ$ is made for the original and the heat treated samples. However, the diffused scattering peak at $2\theta = 7.46^\circ$ of the original sample did become much stronger and shifted to a larger $2\theta = 8.0^\circ$ (corresponding to a shorter d-spacing of 1.10 nm) after the sample was heat-treated. Thus the sample should possess a structure with a long-range order of a length scale of 1.1 nm. The shift of diffraction toward a larger angle indicates that the annealing also increases the density of molecular packing. These observations are actually the same as those reported by other investigators^[1-5]. As cited in the introduction, Kimura and coworkers have attributed the results to a pseudo-hexagonal array of PVK chains^[1]. However, the long range order in the annealed sample must have been formed at 300°C during annealing. As will be described below, at 300°C the sample was, however, viscous in its fluid state and shearable. Therefore, the long-range order structure should not be considered as the crystal but as the liquid crystal.

Under the polarized optical microscope the powder sample of the unfractionated PVK ($M_n = 20.7 \times 10^4$) did not show birefringence. However, when the temperature was raised to 260°C, the sample became highly birefringent. This birefringence remained strong with increasing temperature within the experimental limit of 330°C. Figure 2 is a cross-polarized optical micrograph of the sample film that had been kept at 300°C for 10 min before the picture was taken. From the picture, we see a schlieren texture characteristic of a nematic liquid crystal. However, the shearing of the sample failed to result in a banded texture^[10, 11] because of the difficulties arising from the high experimental temperature and the high melt viscosity of the sample.

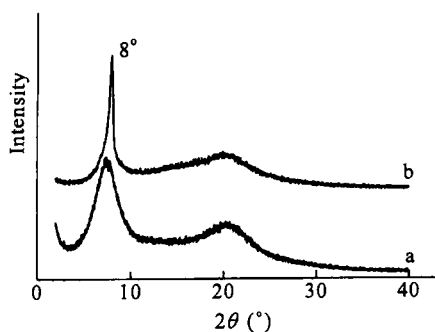


Fig. 1 X-ray diffraction pattern of the unfractionated PVK
a) Sample without heat-treatment
b) Sample annealed at 300°C and quenched

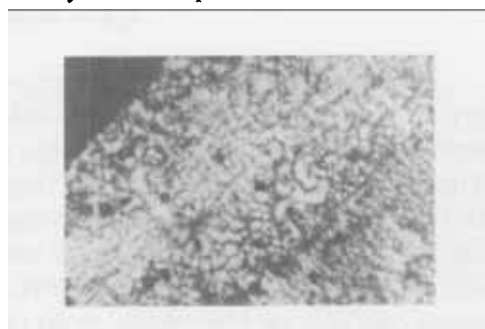


Fig. 2 Optical micrograph of unfractionated PVK (300°C) taken under crossed polarizers (× 150)

The fractionated samples with different MW showed different behaviors under polarized optical microscopy. Among them, the four samples with higher MW ($M_n = 40,000$ and above) behaved similarly to the unfractionated sample described above, while the two lower MW fractions ($M_n = 19,000$ and $M_n = 29,000$) were

isotropic and showed no birefringence from room temperature to 300 °C. Besides, in the thermal annealing experiments at ~250 °C or above, no development of birefringence was observed for these two samples. Therefore, the properties of this polymer have a strong dependence on MW. This dependence was also observed by Griffiths and Van Laeken^[4]. However, they concluded that PVK with MW smaller than 46,000 did not crystallize which is somewhat different from our experimental results. Our observations indicate that the polymer with M_n of 40,000, though not crystallizable, is already capable of forming a stable liquid crystalline phase. Therefore, we assume that the lowest MW of PVK must be as large as 30,000–40,000 in order to form a stable mesophase.

A detailed DSC study of PVK was given by Griffiths and Van Laeken^[4]. They stated that the glass transition temperature T_g of PVK increased with MW from 152 °C for $M_n = 3,700$ to 225 °C for $M_n = 157,000$. The highest T_g of 227 °C was attainable by the sample with $M_n = 2.7 \times 10^6$. Similar results were obtained in our study. The DSC thermograms of PVK fractions were shown in Fig. 3 and the data of T_g together with the MW of each sample were collected in Table 1. From Fig. 3 it seems that for the higher MW and liquid crystalline fractions (curve c to f) there is one additional transition at 203 °C in addition to the T_g at 224 °C or 225 °C. This interesting transition was not observed for the lower MW and non-liquid crystalline fractions (curve a and b), but was repeatedly observed for those high MW fractions with repetitive heating and cooling. We are not able to interpret this observation at present, but we presume that it may be related to certain molecular or supra-molecular order in the mesophase.

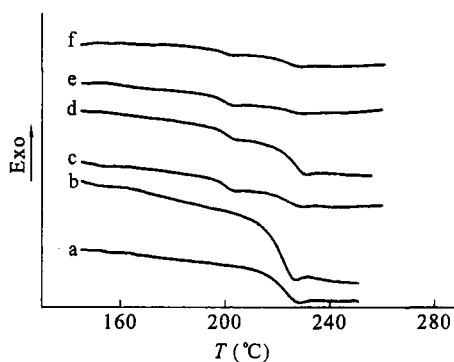


Fig. 3 DSC thermograms of the fractionated PVK
a) $M_n = 19,000$; b) $M_n = 29,000$; c) $M_n = 40,000$;
d) $M_n = 58,000$; e) $M_n = 66,000$; f) $M_n = 79,000$

The study of the structure and properties of PVK is still far from completion, even though this polymer has very interesting electro-optical properties and has been widely used and studied. In this study we found that PVK can be a liquid crystal if its molecular weight is high enough. The lowest molar mass demanded for the formation of the mesophase was found to lie in the range of 30,000 to 40,000 corresponding to a degree of polymerization (DP) of 150 to 200. This value seems very high if one considers that a DP of only ~50 is needed for conventional side-chain liquid crystalline polymers to form a stable liquid crystalline phase (Pugh and Kiste^[12]). North *et al.*^[13–15] studied the chain property of PVK in solution and found that there was a transformation from the random-coils of lower MW samples to the rigid-rods of higher MW samples. The M_n of PVK at this transition was ~50,000 corresponding to a DP of ~250. Because in the liquid crystalline phase of PVK the chain orientation is a must, it is understandable that a sufficiently high MW is necessary for the formation of a liquid crystalline phase, otherwise the rigid-rod conformation required by the liquid crystalline phase will not be adopted. As for the somewhat lower value of 150–200 of the degree of polymerization we observed for PVK to form a liquid crystalline phase compared to the value of 250 given by North *et al.*^[13–15] for PVK chains in solution to become rigid-rods, it may be understandable if we are allowed to assume that the molecular weight needed for formation of rigid-rods in the bulk melt state is lower than what is needed in solution.

CONCLUSION

We found that the lower MW fractions of PVK do not form a liquid crystalline phase, and only the samples with sufficiently high MW can form the mesophase. The lowest degree of polymerization for PVK to form a stable liquid crystalline phase is in the range of 150 to 200. This result is understandable if we assume, as we have done for the self-assembly-induced supramolecular hexagonal columnar liquid crystalline phase structure of poly[di(4-heptyl) vinylterephthalate]^[8], that the liquid crystalline phase is formed not by the parallel orientation of the carbazole side groups but by the parallel orientation of PVK chains that have a rigid-rod conformation. In other words, PVK is not of the side-chain type of liquid crystalline polymer, but has some similarity to a main-chain type of liquid crystalline polymer. This presumption could be put forward if a comparison is made between PVK and other polymers with similar molecular constitution such as poly(2,5-bis[(4-methoxy-benzoyl)oxy]styrene)^[6], poly(2,5-bis[(butyl-benzoyl)oxy]styrene)^[7], and poly[di(4-heptyl)vinylterephthalate]^[8]. Of course, this presumption needs to be proven.

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