Electro-optical studies of various stereostructural forms of poly(*N*-vinylcarbazole)

S. J. Mumby* and M. S. Beevers†
Speciality Polymer Group, Chemical Engineering and Applied Chemistry, University of Aston, Aston Triangle, Birmingham, B4 7ET, UK

(Received 18 August 1988; accepted 24 October 1988)

The electro-optical Kerr effect has been measured for various stereostructural forms of poly(*N*-vinylcarbazole) (PVK) in solution in 1,4-dioxan at 298 K. The electro-optic behaviour of various types of PVK, prepared using different catalyst systems, may be explained in terms of 3/1 helical sequences of isotactic PVK and all-*trans* sequences of syndiotactic PVK. The Kerr effect of 2/1 and 4/1 helical forms of syndiotactic PVK has also been considered.

(Keywords: poly(*N*-vinylcarbazole); carbazole; *N*-ethylcarbazole; Kerr effect; dipole moment; optical anisotropy; conformation)

INTRODUCTION

The electro-active properties of poly(*N*-vinylcarbazole), PVK, in its pure state and when complexed with suitable dopant molecules have attracted much attention[1–9]. Certain spectroscopic and photo-electric phenomena exhibited by PVK and their dependence on molecular configuration have been considered previously[1,4], but the effects of stereostructure on electro-optical properties has received relatively little attention. It is now well known that the stereostructure of PVK and a number of its physical properties are significantly affected by the synthetic method employed for its formation[1,4,10,11].

Earlier dielectric studies indicated that some forms of PVK may have a rod-like structure in solution[12,13]. A more recent dielectric study[14] has demonstrated that, depending on the synthetic route used in its preparation, PVK exists in solution in one of at least two different stereostructural forms. For these materials the effective electric dipole moment of the repeat unit of PVK was observed to be independent of molecular weight in the range 10^4–10^7 and was not significantly affected by polydispersity. In a previous Kerr effect study[15] of PVK in solution in 1,4-dioxan at 298 K it was possible to clearly distinguish between the various stereo-structural types of PVK produced by different catalyst systems. Here, we report on a more extensive study of the solution electro-optical behaviour of samples of PVK prepared using the catalysts azo-bis-isobutyronitrile (AIBN), $BF_3O(CH_2CH_3)_2$ and $AlCl_3$.

MATERIALS

Because the details of the synthetic routes used to prepare the various stereostructural types of PVK have been published elsewhere[14] only a brief description of the synthetic methods will be presented here.

Polymer sample I was obtained by polymerizing the monomer *N*-vinyl carbazole using AIBN in solution in benzene at 343 K. Polymer sample II was prepared by polymerizing the vinyl monomer in toluene at 298 K using the catalyst $BF_3O(CH_2CH_3)_2$. A third polymer type, polymer III, was prepared using an initiator system consisting of a suspension of finely powdered $AlCl_3$ in toluene at 298 K. The fourth polymer, (IV), was a commercial sample obtained from Polymer Laboratories, UK. The method used to prepare polymer sample (IV) is not certain but its dielectric and Kerr effect behaviour were found to be almost identical to polymer I. This suggests that it was prepared using a radical-catalysed polymerization. Each of the polymers (I–IV) was purified and separated into fractions of different molecular weight by repeated fractional precipitation from solution in toluene using methanol as the non-solvent. The distributions of molecular weights in the fractions derived from polymers (I–IV) were examined using gel permeation chromatography (g.p.c.)[14].

MEASUREMENT OF THE KERR EFFECT

Detailed descriptions of the apparatus for the measurement of the experimental Kerr constant, B (electrically-induced optical birefringence per unit electric field squared, E^2, per unit optical path length, l) have been presented in a number of earlier publications[16,17]. Thus, only the essential optical elements of the Kerr effect apparatus will be described. The source of plane-polarized, monochromatic light was a 2.6 mW helium/neon laser (Spectrophysics) emitting at 632.8 nm. The quality of the plane-polarized light was improved by passing the light through a Glan-type polarizer. The light then passed between the parallel, plane surfaces of the electrodes of the Kerr cell. A diagram of the Kerr cell is shown in *Figure 1*.

The body of the cell was fabricated by milling a channel through one face of a rectangular shaped block of stainless-steel. The two electrodes, also of stainless-steel, are positioned in this channel. The high voltage electrode is

---

* AT & T Bell Laboratories, Whippany Road, Whippany, NJ 07981, USA

† To whom correspondence should be addressed

0032-3861/89/050860–06$03.00

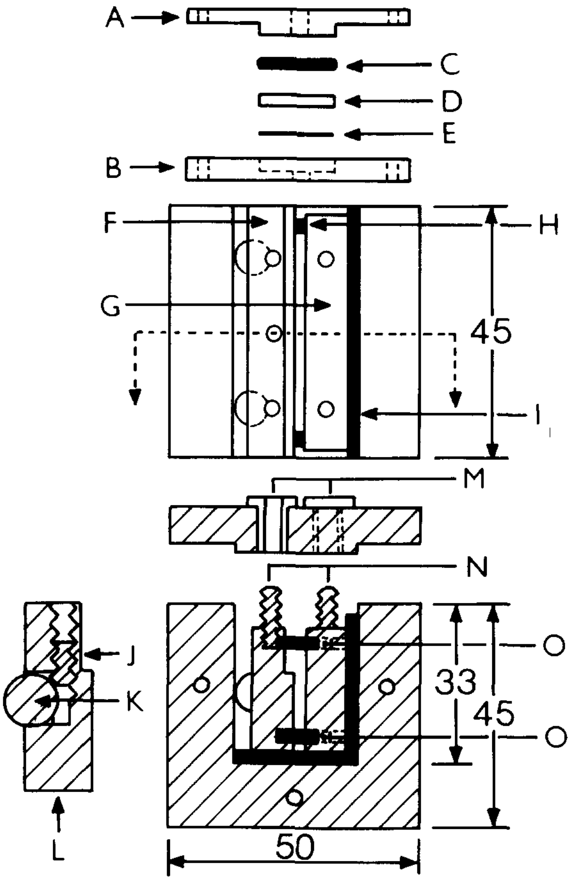

Figure 1 Electro-optic Kerr cell showing window retaining ring (A), window seating ring (B), O-ring (C), glass window (D), paper sealing washer (E), earthed electrode (F), high-voltage electrode (G), glass spacer rod (H), glass insulator (I), locking screw (J), ball bearing (K), earthed electrode (L), PTFE insulation (M), electrical connectors (N), adjuster screws (O). All dimensions in mm

isolated from the earthed body of the cell by two pieces of poly(tetrafluoro ethylene) (PTFE) that cover the bottom of the channel and the inside wall of the channel adjacent to the high-voltage electrode. The earthed electrode makes electrical contact with the body of the cell through stainless-steel ball bearings housed in the earthed electrode. The ball bearings are pressed firmly into contact with the inner wall of the cell by the means of two Allen key grub screws. This mechanism also serves to keep the electrode assembly rigid. The electrode gap is set by four spacers, fashioned from short lengths of 2 mm diameter glass rod seated in holes in the faces of the electrodes. The effective depth of the holes in the high-voltage electrode can be varied by adjusting four Allen key grub screws. This permits the electrode separation to be accurately set. The upper edge of the earthed electrode was cut back by 2 mm in order to prevent arcing between the electrodes above the level of the solution. The high-voltage electrode was 2 mm shorter than the earthed electrode to prevent arcing between the ends of the electrode and the window assembly of the cell. The length of the high-voltage electrode was taken to be equal to the optical path length between the electrodes. The stainless-steel seating rings for the windows were sealed onto the body of the cell using an epoxy resin and further secured by three screws.

The windows of the cell were optical quality quartz discs, chosen for their relative freedom from strain-induced birefringence. Each window was secured in the window assembly by a retaining ring and three screws. A leak-proof seal between the steel and the window was achieved using a paper gasket. A rubber O-ring cushioned the pressure exerted by the window retaining ring. The electrical connections to the electrodes passed through holes in the lid of the cell. Each hole was lined with a sleeve of PTFE. The temperature of the cell was controlled to better than ±0.05 K by means of a close fitting water jacket connected to a Churchill water pump and thermostat.

The optical path length and electrode gap of the Kerr cell were 50 mm and 1.2 mm, respectively. After passage of the light through the Kerr cell, a quarter-wave plate (cleaved for operation at 632.8 nm) and a rotatable Glan-type analyser, the light impinged on a photomultiplier tube, the output of which was displayed on a Tektronix 565M oscilloscope. The high-voltage required to induce the optical birefringence was supplied by a Brandenberg power supply. It was applied to the high-voltage electrode of the Kerr cell as a short duration (approximately 1 ms) rectangular-shaped pulse via two electronically controlled high-voltage reed switches. One switch served to apply the voltage, the other to connect the high-voltage electrode to ground potential after a suitable time delay. The magnitude of the applied voltage was measured using a digitial voltmeter to an accuracy of ±1 V.

The magnitude of the electrically induced optical retardation, δ, was determined using the nulled-pulse technique[17]. The retardations were measured to an accuracy of ±0.01°.

RESULTS

Graphs of the electrically induced optical phase retardation, δ, plotted as a function of the square of the applied electrical field, E^2, were found to be linear, within experimental error, for all of the sample types I–IV of PVK when measured in solution in 1,4-dioxan at 298 K. Solution Kerr constants defined by references 18–20 as

$$B_{12}=\delta/(2\pi l E^2) \qquad (1)$$

were calculated for the solutions of PVK in 1,4-dioxan by comparing the magnitude of the Kerr effect to that measured for the solvent, 1,4-dioxan. For this purpose the Kerr constant of 1,4-dioxan, B_{12} was taken to be $0.60\times10^{-14}\,\mathrm{m\,V^{-2}}$ at 298 K (ref. 21). *Figure 2* shows plots of solution Kerr constant as a function of the weight fraction of solute, w_2, for a series of fractions of different molecular weight for PVK type 1. For each series of fractions for a particular type of PVK the Kerr effect was observed to be virtually independent of molecular weight and data could be fitted to a single straight-line graph, within experimental error. However, for the sake of clarity the data acquired for the different molecular weights have been successively displaced in a negative direction along the ordinate by equal intervals in order of increasing weight-average molecular weight, M_w. Master plots of the solution Kerr constants, B_{12}, presented in *Figure 3*, enable a comparison to be made of the relative magnitudes of the Kerr effect for the various types of PVK I–IV.

The effect of solvent on the Kerr constants was briefly examined by remeasuring sample IV in solution in benzene at 298 K. The solution Kerr constant (B_{12}) was observed to increase by about 5% in going from 1,4-dioxan to benzene.

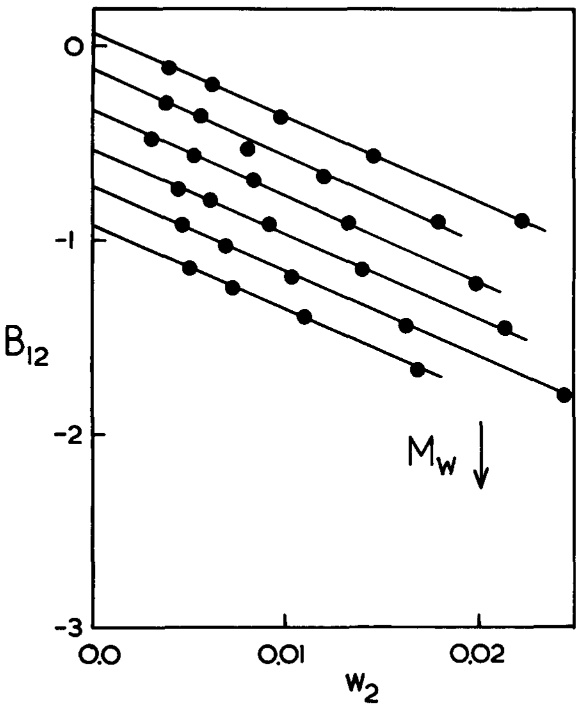

Figure 2 Solution Kerr constant $B_{12} \times 10^{14}$ mV^{-2} for fractions of PVK (I), prepared using AIBN, in 1,4-dioxan at 298 K. The polystyrene equivalent weight-average molecular weights, PSM_w, and the polydispersity indices, (PSM_w/PSM_n), are 41 000 (4.4), 84 000 (1.3), 102 000 (1.3), 150 000 (1.4), 180 000 (1.6) and 250 000 (1.7) in the order indicated

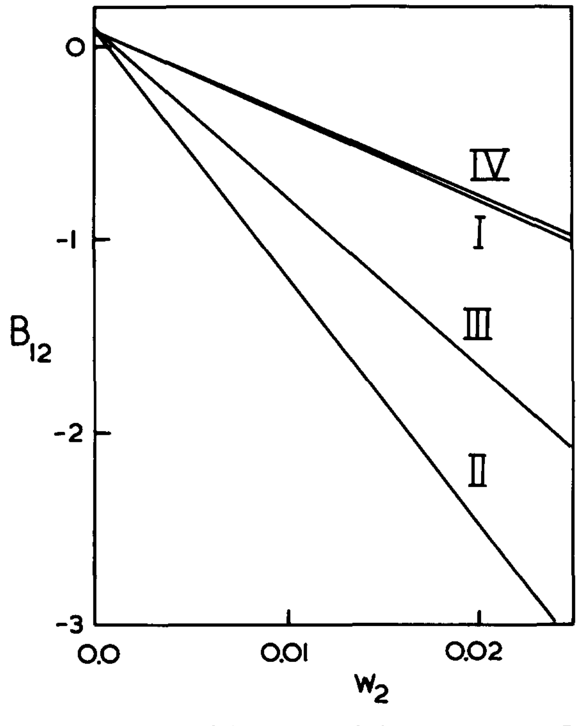

Figure 3 Comparison of the average solution Kerr constants $B_{12} \times 10^{14}$ mV^{-2} of PVK samples I–IV in solution in 1,4-dioxan at 298 K. The ranges of polystyrene equivalent molecular weight (heterodispersity index) for PVK types I, II, III and IV are respectively, 41 000–250 000 (1.3–4.4), 18 000–7 800 000 (2.0–11), 240 000–3 100 000 (1.7–6.1) and 200 000–3 940 000 (2.0–5.1)

In addition to the Kerr effect data obtained for the various samples of PVK, Kerr constants were measured for carbazole and *N*-ethyl carbazole in solution in 1,4-dioxan at 298 K (see *Figure 4*). The Kerr effect of these molecules is of interest because they are both related structurally to the repeat unit of PVK.

From an examination of the Kerr effect data presented in *Figure 3* it is clear that the synthetic routes employed in this study have resulted in the formation of three different types of PVK. For each type of PVK the sign of the Kerr constant of their respective solutions in 1,4-dioxan was always observed to be negative and substantially greater than the small positive Kerr constant of the solvent. Samples of PVK (II), prepared using the cationic system, $BF_3O(CH_2CH_3)_2$, exhibited the largest Kerr effect. Solutions of PVK (I), prepared using the radical system, AIBN, showed the smallest Kerr effect. The use of the catalyst, $AlCl_3$, gave samples of PVK (III) that possessed Kerr constants that were almost halfway between those measured for PVK types I and II.

An interesting observation concerns the sign of the experimental Kerr constants of solutions of *N*-ethyl carbazole and carbazole in 1,4-dioxan at 298 K, which were both found to be positive and therefore opposite in sign to that observed for all of the polymer samples considered in this study. The significance of the difference in the signs of the Kerr constants observed for *N*-ethyl carbazole, a molecule that possesses a similar structure to the repeating unit of PVK, and the various stereostructural forms of poly(*N*-vinylcarbazole) will be discussed in detail subsequently.

Calculation of specific Kerr constants

From a knowledge of the static permittivity, ε_{12}, refractive index, n_{12}, experimental Kerr constant, B_{12} (n_{12} and B_{12} are measured using light of wavelength λ), and density, d_{12}, measured for solutions of PVK, *N*-ethylcarbazole and carbazole the specific Kerr constants of these solutes may be calculated using the expression[18–20]

$$_sK = 6\lambda n B/(\varepsilon+2)^2(n^2+2)^2 d \qquad (2)$$

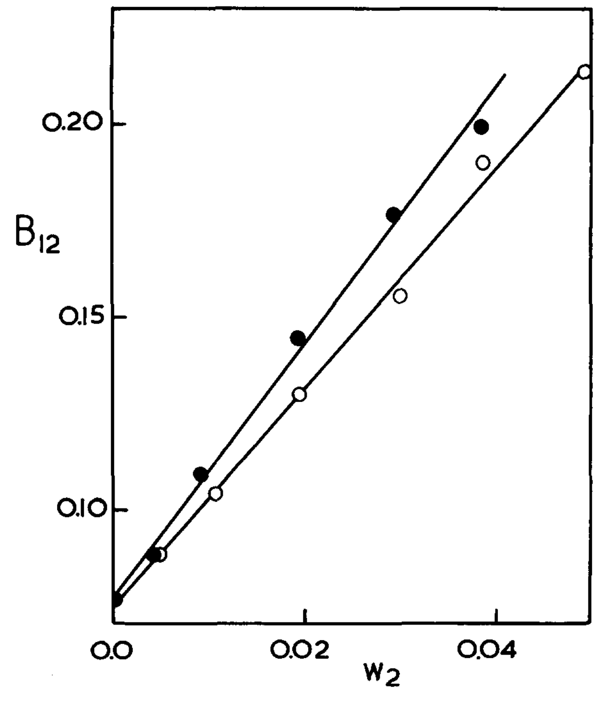

Figure 4 Solution Kerr constant $B_{12} \times 10^{14}$ mV^{-2} for 9-ethyl carbazole (●) and carbazole (○) in 1,4-dioxan at 298 K

in conjunction with the alligation formula[19]

$$ {}_{s}K_{1,2} = w_1\,{}_{s}K_1 + w_2\,{}_{s}K_2 \qquad (3) $$

where the subscripts 1, 2 and 1, 2 denote the physical properties associated with the solvent, solute and solution, respectively. The molar Kerr constants ${}_{m}K$ ($= {}_{s}K \times$ molar mass, M), may also be readily calculated. The static permittivities of the solutions of these materials and that of the solvent, 1,4-dioxan, all specified at 298 K, have been reported in a previous publication[14]. Since the solutions are dilute ($C \approx 1\%$ w/v) the approximations $n_{12} \approx n_1$ and $d_{12} \approx d_1$ may be employed without incurring a serious loss of accuracy in the calculation of the experimental specific Kerr constants[19].

The negative Kerr constants, observed for the different types of PVK can be accounted for by recognizing that the dipolar term[18], θ_2, must be negative and greater in magnitude than the positive, induced term (the anisotropy term)[18], θ_1, in the expression for the specific Kerr constant[20].

$$ {}_{s}K = N_{\mathrm{L}}(\theta_1 + \theta_2)/18M\varepsilon_0 \qquad (4) $$

The induced and dipolar terms, θ_1 and θ_2 may be written as a function of the electrostatic polarizabilities b_x, b_y and b_z and the corresponding components, μ_x, μ_y and μ_z, of the permanent electric dipole moment, μ, that is

$$ \theta_1 = P_{\mathrm{D}}[(b_x - b_y)^2 + (b_y - b_z)^2 + (b_z - b_x)^2)]/45kTP_{\mathrm{E}} \qquad (5) $$

$$ \theta_2 = [(\mu_x^2 - \mu_y^2)(b_x - b_y) + (\mu_y^2 - \mu_z^2)(b_y - b_z) + (\mu_z^2 - \mu_x^2)(b_z - b_x)]/45k^2T^2 \qquad (6) $$

where N_{L}, k, ε_0 and T are the Avogadro number, Boltzmann constant, permittivity of a vacuum and absolute temperature, respectively. P_{D} is the distortion polarization and P_{E} is the electronic polarization. For a large number of organic compounds the ratio $P_{\mathrm{D}}/P_{\mathrm{E}}$ has a value lying in the range 1.0–1.1 (refs. 18, 19). Exceptions to this general observation have been noted for some dialkylsiloxane materials[22]. The permanent dipole moments, and the specific Kerr constants, ${}_{s}K_2$ of the various sample types of PVK, I–IV, measured in solution in 1,4-dioxan at 298 K, are presented in *Table 1*. Also included in this table are data for the solutes carbazole and *N*-ethylcarbazole measured using the same solvent conditions.

DISCUSSION

Both carbazole and *N*-ethylcarbazole have a positive electro-optic Kerr effect when measured in solution in 1,4-dioxan at 298 K. Because the direction of the dipole moment (7.0×10^{-30} C m) of carbazole lies along the N–H bond, and the Kerr effect of carbazole is positive, it can be concluded that the axis of maximum polarizability of carbazole must also lie along the N–H bond. A similar conclusion can be drawn for the relative directions of the dipole moment and the axis of maximum polarizability for *N*-ethyl carbazole. The replacement of the nitrogen proton of carbazole by an ethyl group significantly reduces the magnitude of the Kerr effect. The hypothetical replacement of the N–H bond by a C–N bond would be expected to enhance the Kerr effect of *N*-ethylcarbazole with respect to carbazole. This is because the longitudinal, b_{L}, transverse, b_{T} and vertical, b_{V}, polarizabilities ($\times 10^{40}$ C m V^{-1}) of the N–H and C–N bonds are 0.45, 0.98, 0.98 and 0.89, 0.57, 0.57, respectively[20]. However, the C–C bond of the ethyl group, because it lies only 20° from the direction normal to the dipole moment, introduces components of polarizability that result in a decrease of the optical anisotropy of the molecule. This diminution of the Kerr effect of *N*-ethyl carbazole relative to the parent compound carbazole is also affected by their different dipole moments. These are 7.0×10^{-30} C m for carbazole and 6.9×10^{-30} C m for *N*-ethylcarbazole[14].

It has been argued that the optical anisotropy of the C–H bond may be assumed to be very small and that its contribution to the optical anisotropy of organic molecules can be neglected[23]. As a direct consequence of this assumption the electro-optic behaviour of the repeat unit of PVK can be represented by the tensorial sum of the electro-optic polarizability tensors of *N*-ethylcarbazole and a single C–C bond.

According to the n.m.r. studies of Okamoto *et al.*[24], Williams and Froix[25] and Cho and Choi[11] samples of PVK prepared using cationic catalysts may be considered to be 'isotactic-rich', while samples of PVK prepared using radical-based catalyst systems may be regarded as 'syndiotactic-rich'. From an analysis of n.m.r. spectra Okamoto *et al.*[24] deduced that 'isotactic-rich' samples of PVK were comprised, on average, of 50% isotactic sequences and 50% syndiotactic sequences. A similar analysis of n.m.r. spectra obtained for samples of 'syndiotactic-rich' PVK indicated that these materials may be regarded as being constituted of 75% syndiotactic sequences and 25% isotactic sequences[24].

It has been suggested in the literature that for isotactic sequences of PVK the most favourable conformation is the 3/1 helix[26–30]. Indeed, the examination of a space-filling model, adjusted for minimum steric hindrance, indicates that the 3/1 helix is a strongly preferred conformation for isotactic PVK. Such a conformation, if permitted to extend over a large number of repeat units, would impose a rod-like shape on the polymer molecule. From an inspection of models of isotactic PVK it can be seen that for minimum steric interaction the planes of the carbazole groups are approximately perpendicular to the long axis of the molecule. The overall structure resembles a spiral staircase in which each step is a carbazole side-group. Because the direction of maximum polarizability of each carbazole group lies within its plane the axis of maximum polarizability of the 3/1 helical form of isotactic PVK is perpendicular to the long axis of the helix. A more detailed analysis of the orientation of the carbazole side-groups reveals that each carbazole ring system is tilted by about 20° from the direction normal to the long axis of the helix. This modification of the helical

Table 1 Dipole moments and specific Kerr constants of carbazole, *N*-ethylcarbazole and different types of poly(*N*-vinylcarbazole) measured in solution 1,4-dioxan at 298 K

Material	10^{30} μ (C m)	10^{25} ${}_{s}K_2$ (m^5 V^{-2} kg^{-1})
PVK (I) (AIBN)	5.7	−81
PVK (II) (BF_3OEt_2)	7.2	−234
PVK (III) ($AlCl_3$)	7.2	−158
PVK (IV) (AIBN ?)	5.6	−80
Carbazole	7.0	6.0
N-ethylcarbazole	6.9	5.1

[a] Reference 13

arrangement of polar side-groups will give rise to a cumulative dipole moment that is parallel to the long axis of the helix.

The presence of three-fold symmetry about the long axis of the helix excludes the possibility of a cumulative off-axis dipole moment. Thus, for molecules of isotactic PVK adopting the 3/1 helical form, the permanent dipole moment is parallel to the long axis of the molecule and therefore perpendicular to the axis of maximum polarizability. The Kerr effect of isotactic PVK would, therefore, be expected to be strongly negative (see equations (3)–(5)). This conclusion is supported by the experimental observations. Thus, for samples of PVK that are rich in isotactic sequences the specific Kerr constants are observed to be strongly negative (e.g. PVK II in *Table 1*).

Generally, the conformational preferences for syndiotactic vinyl polymers are more diverse and therefore more difficult to predict without recourse to rigorous statistical calculations[31]. However, for syndiotactic PVK a number of possible conformations (e.g., the 4/1 and 2/1 helical forms) are likely to be excluded because of severe, unfavourable steric interactions between the very bulky carbazole side-groups[26,27,30,31]. From an examination of a space-filling model of syndiotactic PVK it can be deduced that the all-*trans* form is likely to be the most stable conformation, provided that steric interactions are assumed to be dominant over all other possible interactions. The recent n.m.r. studies of Natansohn[32] have supported previous suggestions[26,27,29] that syndiotactic sequences of PVK are dominated by the all-*trans* configurations. For molecules of syndiotactic PVK adopting all-*trans* conformations the axis of maximum polarizability of the molecule and the cumulative permanent dipole moment are parallel to each other and perpendicular to the long axis of the molecule. This situation would give rise to a positive Kerr effect (refer to equations (4)–(6)).

Utilizing the ideas expounded above the specific Kerr constants of isotactic and syndiotactic sequences of PVC may be estimated using the simple alligative relationship.

$$ {}_{s}K_{\mathrm{exp}} = w_{\mathrm{i}}\,{}_{s}K_{\mathrm{i}} + w_{\mathrm{s}}\,{}_{s}K_{\mathrm{s}} \tag{7}$$

Here, ${}_{s}K_{\mathrm{exp}}$, ${}_{s}K_{\mathrm{i}}$ and ${}_{s}K_{\mathrm{s}}$ represent the specific Kerr constants of the solute, the isotactic form of PVK and the syndiotactic form of PVK. The weight fractions of isotactic and syndiotactic sequences are denoted by w_{i} and w_{s}, respectively. Thus, for 'isotactic-rich' forms of PVK prepared in the present study

$$ -81 \times 10^{-25} = w_{\mathrm{i}}\,{}_{s}K_{\mathrm{i}} + w_{\mathrm{s}}\,{}_{s}K_{\mathrm{s}} \tag{8}$$

for which $w_{\mathrm{i}} = 0.5$ and $w_{\mathrm{s}} = 0.5$ (ref. 24). Similarly, for samples of 'syndiotactic rich' PVK

$$ -234 \times 10^{-25} = w_{\mathrm{i}}\,{}_{s}K_{\mathrm{i}} + w_{\mathrm{s}}\,{}_{s}K_{\mathrm{s}} \tag{9}$$

where $w_{\mathrm{i}} = 0.25$ and $w_{\mathrm{s}} = 0.75$ (ref. 24). Solving equations (8) and (9) yields equivalent experimental values of -570×10^{-25} SI units for the specific Kerr constant of isotactic sequences of PVK and $+99 \times 10^{-25}$ SI units for the specific Kerr constant of syndiotactic sequences of PVK. The specific Kerr constant of -158×10^{-25} SI units measured for samples of PVK prepared using $AlCl_3$ as the catalyst implies that the syndiotactic content of these materials lies somewhere between 50% and 75%. Using the equivalent experimental specific Kerr constants calculated for isotactic and syndiotactic sequences of PVK the fractions of isotactic and syndiotactic sequences in samples of PVK prepared using $AlCl_3$ are calculated to be 0.40 and 0.60, respectively.

The experimental specific Kerr constants of 'isotactic-rich' and 'syndiotactic-rich' samples of PVK are strongly negative, when measured in solution in 1,4-dioxan at 298 K. However, the specific Kerr constants measured for 'syndiotactic-rich' samples of PVK are markedly less negative than those measured for 'isotactic-rich' samples of PVK. If the various stereostructural forms of PVK are regarded as random intramolecular mixtures of isotactic and syndiotactic sequences, then the experimental Kerr effect data obtained for the various types of PVK can be rationalized in the following manner.

According to Okamoto *et al.*[24] the fraction of isotactic and syndiotactic sequences are approximately equal for samples of 'isotactic-rich' PVK. This particular stereostructural form of PVK (e.g. type I in *Table 1*) has a negative Kerr effect which indicates that the negative Kerr effect of the 3/1 helix for the isotactic sequences outweighs the positive Kerr effect associated with the all-*trans* syndiotactic sequences. For the 'syndiotactic-rich' samples of PVK in which the syndiotactic content (positive Kerr effect component) has risen to about 75% the net Kerr effect has become much less negative.

It is interesting to consider the possible effects on the Kerr constant of PVK arising from the inclusion of the 2/1 and 4/1 helical forms of syndiotactic PVK. Preliminary calculations indicate that the Kerr effect of 2/1 helical PVK is more negative than that calculated for the 3/1 helical form of isotactic PVK. It follows that if the 2/1 helical form of syndiotactic PVK is preferred to the all-*trans* form of syndiotactic PVK then the specific Kerr constants of 'syndiotactic-rich' PVK would be expected to be more negative than the specific Kerr constants of 'isotactic-rich' samples of PVK. Experimentally, the opposite is observed, i.e., the specific Kerr constants of 'syndiotactic-rich' samples of PVK are more positive than the specific Kerr constants of 'isotactic-rich' samples of PVK. From an examination of a model of the 4/1 helical form of syndiotactic PVK it is concluded that the dipole moment of a single turn of the helix is very close to zero and that as a consequence the specific Kerr constant of syndiotactic PVK adopting this particular conformation would be expected to be positive and significantly less in magnitude than the specific Kerr constants observed for *N*-ethylcarbazole and therefore much less than the equivalent specific Kerr constant of 99×10^{-25} SI units calculated for syndiotactic sequences of PVK (see above). It is concluded that for 'isotactic-rich' and 'syndiotactic-rich' samples of PVK considered in the present study the proportion of the 4/1 helix present in sequences of syndiotactic PVK is small compared to the planar all-*trans* conformation.

CONCLUSIONS

The electro-optic Kerr effect together with dielectric and ^{13}C n.m.r. data shows that there are at least three different stereostructural types of PVK and that these may be regarded as intramolecular combinations of isotactic and syndiotactic sequences of PVK present in proportions that depend on synthetic route. The electro-optic data is consistent with the view that isotactic PVK exists mainly in the 3/1 helical conformation and that syndiotactic PVK favours the all-*trans* conformation.

A theoretical study of the electric polarizability and permanent electric moments of PVK is currently in progress.

ACKNOWLEDGEMENTS

The authors would like to thank the Science and Engineering Council for a research grant (SJM). The late H. Jolly (Univesity College of Aberystwyth, Wales) and the late P. McGuire are acknowledged for their construction of Kerr cells.

REFERENCES

1 Hoegl. H. *J. Phys. Chem.* 1965, **69**, 755

2 *Encyclopedia of Polymer Science and Technology*, John Wiley, Chichester, 1972, **11**, 338

3 Penwell, R. C., Ganguly, B. N. and Smith, T. W. *J. Polym. Sci. Macro Reviews* 1978, **13**, 63

4 Block, H. *Adv. Polym. Sci.* 1979, **33**, 94

5 Yan, J., Zhang, Q. and Wen, T. *J. Mol. Sci.* 1987, **5**, 191

6 Giro, G., Di Marco, P. G., Chiellini, E. and Solaro, R. *Conv. Ital. Sci. Macromol. (Atti), 6th* 1983, **2**, 145

7 Itaya, A., Okamoto, K. and Masuhara, H. *Zairyo Gijutsu* 1986, **4**, 273

8 Chudacek, I. *Potsdamer Forsch. Paedagog. Hochsch. 'Karl Liebnecht' Potsdam, Naturwiss. Reihe.* 1983, **37**, 126

9 Drazheva, L. and Grigorov, K. *Dokl. Bolg. Akad. Nauk.* 1987, **40**, 43

10 Vandendriessche, J., Palmans, P., Toppet, S., Boens, N., De Schryver, F. C. and Masuhara, H. *J. Am. Chem. Soc.* 1984, **106**, 8057

11 Cho, H. N. and Choi, S. K. *J. Polym. Sci., Part A* 1987, **25**, 1769

12 North, A. M. and Phillips, P. J. *Br. Polym. J.* 1969, **1**, 76

13 Molina, M. S., Barrales-Rienda, J. M. and Riande, E. *Macromolecules* 1984, **17**, 2728

14 Mumby, S. J. and Beevers, M. S. *Polymer* 1985, **25**, 2014

15 Beevers, M. S. and Mumby, S. J. *Polym. Commun.* 1984, **25**, 173

16 Beevers, M. S., Garrington, D. C. and Williams, G. *Polymer* 1977, **18**, 540

17 Beevers, M. S. and Khanarian, G. *Aust. J. Chem.* 1979, **32**, 263

18 Le Fevre, C. G. and Le Fevre, R. J. W. *Rev. Pure and Applied Chem.* 1955, **5**, 261

19 Le Fevre, C. G. and Le Fevre, R. J. W. *J. Chem. Soc.* 1953, **823**, 4040

20 Aroney, M. J. *Angew. Chem.* 1977, **16**, 663

21 Le Fevre, C. G. and Le Fevre, R. J. W. in 'Physical Methods of Chemistry' (Ed. A. Weissberger) Wiley-Interscience, New York (1972) **1**, 399

22 Beevers, M. S. and Mumby, S. J. *Polymer* 1983, **24**, 1565

23 Le Fevre, R. J. W., Orr, B. J. and Ritchie, G. L. D. *J. Chem. Soc.* 1966, **B**, 273

24 Okamoto, K.-I., Yamada, M., Itaya, A., Kimura, T. and Kusabayashi, S. *Macromolecules* 1976, **9**, 645

25 Williams, D. J. and Froix, M. F. *Polym. Preprints* 1977, **18**, 445

26 Sundararajan, P. R. *Macromolecules* 1980, **13**, 512

27 Privratska, J. and Havranek, A. *Acta Polymerica* 1980, **31**, 130

28 Griffiths, C. H. *J. Polym. Sci. Polym. Lett.* 1978, **16**, 271

29 Crystal, R. G. *Macromolecules* 1971, **4**, 379

30 Kimura, K., Yoshimoto, S., Akana, Y., Hirata, H., Kusabayashi, S., Mikawa, H. and Kasai, N. *J. Polym. Sci.* 1970, **8**, 643

31 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York (1953)

32 Natansohn, A. *Polym. Preprints* 1988, **29**, 162