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Kerr constant of poly(*N*-vinylcarbazole)

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Abstract

Electro-optical Kerr-effect data have been obtained for various stereostructural forms of poly(*N*-vinyl carbazole) in solution in 1,4-dioxane over the temperature range 298–338 K. All of the polymers had a negative Kerr constant which become more positive with increasing temperature. Polymer samples with the largest isotactic content also had molar Kerr constants with the largest temperature coefficients. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-vinylcarbazole); Tacticity; Molar Kerr constant; Dipole moment; Conformation; Temperature coefficient

1. Introduction

The electric dipole moment, a vector quantity and the tensor quantity, optical anisotropy, are usually the most convenient and sensitive parameters for investigating the conformationally depended properties of polymer chain molecules. Thus, the electro-optical Kerr constant, which depends both on polarity and polarisability (optical and electrical) is a much used parameter for studying the conformationally dependent properties of small molecules and polymer molecules in solution.

Although the majority of publications concerned with the utilisation of the Kerr effect and measurement of dipole moments have been confined to the conformational analysis of small molecules [1–5], much work (experimental and theoretical) has also been done on synthetic polymers and biopolymer systems [6–27]. Since for solutions of polymers the solvent can make a significant contribution to the measured Kerr effect it is important that accurate values of Kerr constants of the solvent are available [27,28].

In one of our earlier publications [29], it was shown that the dielectric permittivity and dipole moment of stereoregular poly(*N*-vinyl carbazole) (PVK) in solution were significantly affected by the synthetic procedure used to prepare the polymers, confirming earlier work on electro-optical properties of stereoregular PVK by Beevers and Mumby [30–32]. Since molar Kerr constants usually depend, in a sensitive manner, on the molecular optical anisotropy and the relative disposition of the dipole moment (a function of molecular geometry and conformation) the measurement of the electro-optical Kerr effect presents an interesting opportunity to study samples of PVK that have been prepared using different types of catalyst. In this paper the temperature dependences of the Kerr-effect data of samples of PVK are correlated with their isotactic content, the latter being determined using proton NMR.

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2. Experimental

N-vinylcarbazole monomer (Aldrich Chemicals, Poole, Dorset, UK) was polymerised (without further purification) in toluene to produce polymers of different stereostructures. The synthetic routes for the polymerisation of the *N*-vinylcarbazole monomer have been published in detail elsewhere [30]. Polymer F1 was prepared by polymerising the monomer with azobisisobutyronitrile (AZBN) at 343 K and polymers F2 and F3 using boron-trifluoride etherate and anhydrous aluminium trichloride, respectively, at 298 K. The polymers were purified by repeated precipitation from toluene using methanol as the non-solvent. The molecular weight distributions of these polymers were obtained using gel permeation chromatography (GPC) (RAPRA, Shawbury, UK). The number-average molecular weight of polymers F1, F2 and F3 were found to be 28.5×10^3, 30.9×10^3 and 23.7×10^3, respectively. For polymer F2 some fractions of very high molecular weight were excluded from the GPC columns. Proton NMR spectra of the polymers in deuterated toluene were obtained using a Bruker AC 300 MHz spectrometer at 393 K. The percentage isotacticity was obtained by comparing the areas of the methine and methylene peaks. The isotactic contents of F1, F2, and F3 were found to be 24%, 51% and 33%, respectively.

2.1. The Kerr effect apparatus

A diagrammatic representation of the apparatus used to measure the electrically-induced phase difference, is shown in Figs. 1–3 show the longitudinal and cross-section of the Kerr cell, respectively. A parallel, plane-polarised beam of monochromatic light is passed through the Kerr cell such that the plane of polarisation of light is at an angle of 45° relative to the direction of the applied electric field, E. In the presence of this electric field the light leaving the cell is generally elliptically polarised. After passing through a quarter-wave retarder orientated with its principal optical axis at 45° to the direction of the applied electric field, the resultant plane-polarised light can be nulled by rotating the analyser. The angular difference, α, between the principal planes of the polariser and the analyzer is equal to $\delta/4$ provided that the electric field is applied as a rectangular pulse.

The source of light was a 5 mW He/Ne laser (Scientifica and Cook, model SLH/2) emitting at 632.8 nm. The degree of polarisation of the light entering the Kerr cell (15 cm optical path length) was improved by passing the beam through a high quality polariser. Both the polariser and analyser were Glan-type prisms (Ealing Beck) mounted in brass tubes. The analyser could be rotated by means of a series of gears allowing rotations as small as 0.005° to be read with an accuracy of ±0.002°. The quarter wave retarder was of mica (F. Wiggins and Sons), used at 632.8 nm and mounted between glass discs.

A Wallis (Worthing) model S103/3 power pack was used to supply the high-tension voltage, which was continuously variable in the range 0–10 kV. The voltage applied to Kerr cell was measured on a Thurlby digital multiplier (Model 1503-HA). The optical signal,

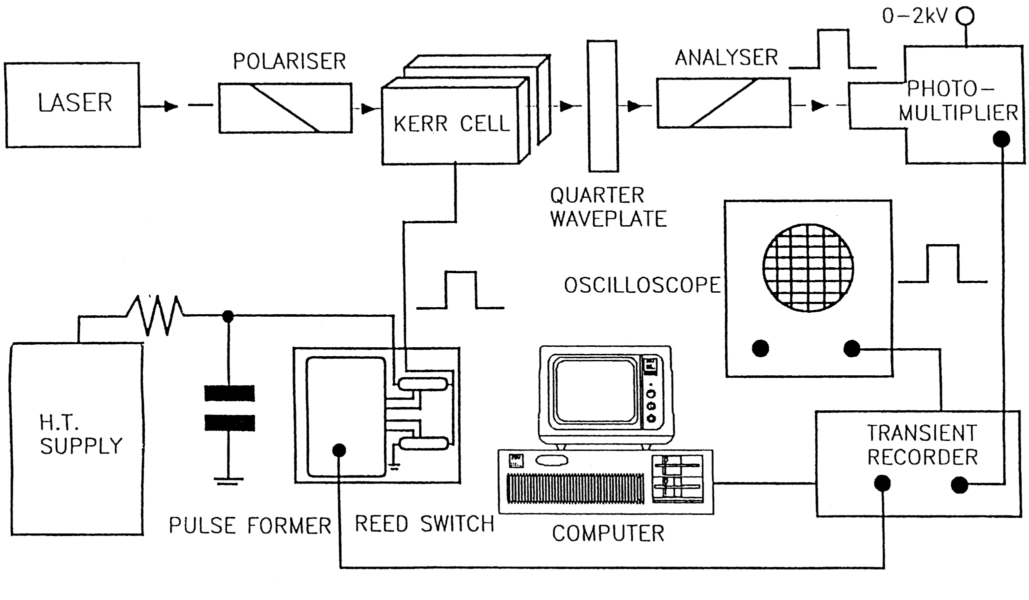

Fig. 1. Apparatus used to measure the electrically induced phase difference.

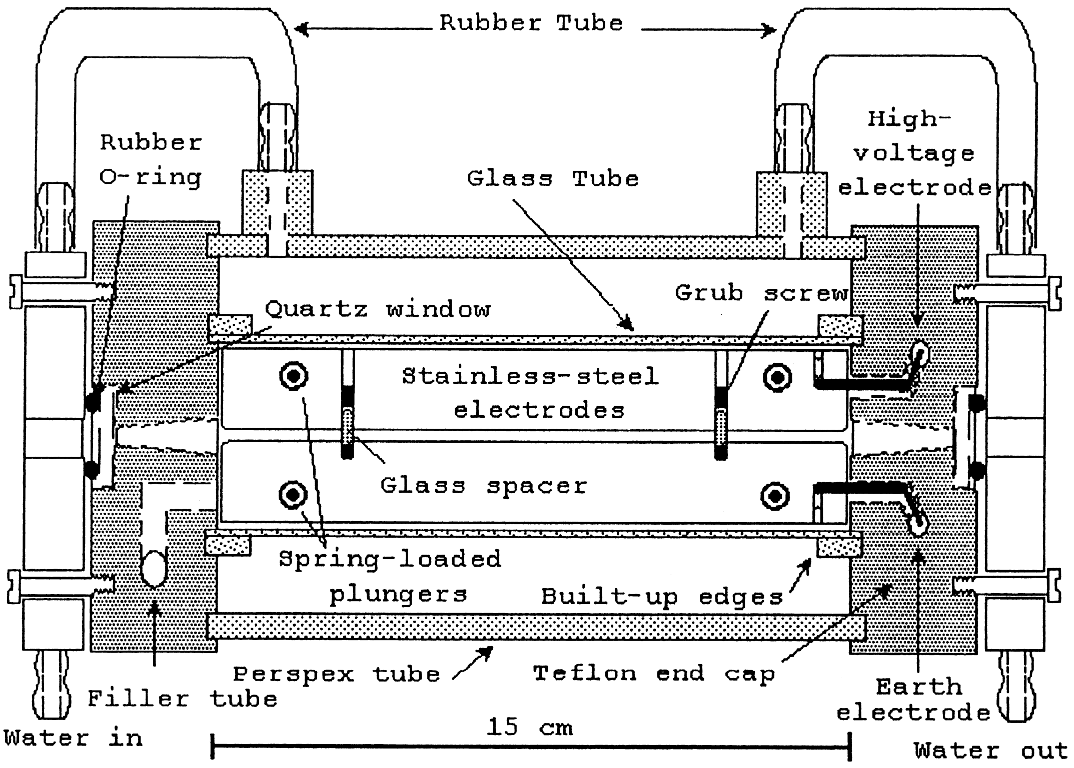

Fig. 2. Longitudinal section of Kerr cell.

is captured by a transient recorder and displayed continuously on an oscilloscope before transferring digital data to the computer.

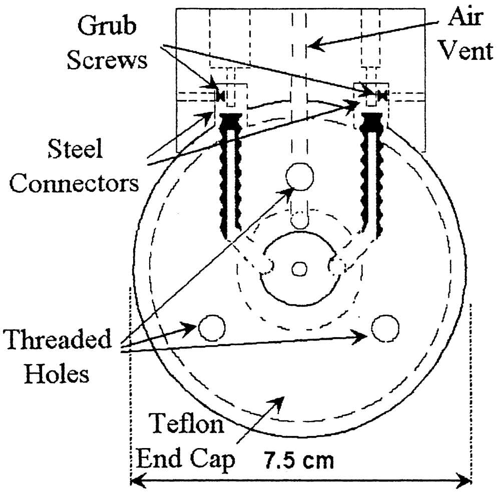

Fig. 3. Cross-section of Kerr cell showing electrodes connections.

2.2. Measurement of experimental Kerr constants (B)

The molar Kerr constant ${}_{\mathrm{m}}K$ of a substance may be visualised as the difference in the molecular refraction along directions parallel to the major and minor axis of the polarisability ellipsoid of the molecule. An important quantity, required for the calculation of ${}_{\mathrm{m}}K$, is the experimental Kerr constant (B), defined by

$$B = \frac{n_{\mathrm{p}} - n_{\mathrm{s}}}{E^2 \lambda} \tag{1}$$

where n_{p} and n_{s} are the refractive indices for the component of the light in the medium parallel and perpendicular to the applied electric field E. The wavelength of light is denoted by λ and l is the optical pathlength.

The experimental Kerr constant B, may also be conveniently defined by

$$B = \frac{\delta d^2}{2\pi l V^2} \tag{2}$$

where δ is the electrically-induced phase difference between the components of plane polarised light possessing electric vectors parallel and perpendicular to the applied electric field E. The quantities V and d are

Table 1
Experimental Kerr constant of toluene

Temperature (K)	Calibration constant for cell using toluene	Gradient (α/V^2) for toluene	Experimental Kerr constant, B_1 (10^{-14} mV^{-2})
298	1389	0.05689	0.790
308	1389	0.05489	0.762
318	1389	0.05303	0.736
328	1389	0.05128	0.712
338	1389	0.04965	0.689

the applied voltage and electrode separation, respectively.

For the pulsed electric field method of measuring the Kerr effect the rotation of the plane of polarisation, α, is related to the phase difference, δ, by

$$\alpha = \frac{\delta}{4} \tag{3}$$

Eliminating δ from Eqs. (2) and (3) and rearranging gives:

$$\alpha = \frac{\pi l V^2 B}{2d^2} \tag{4}$$

If the Kerr law is obeyed, a plot of α versus V^2 should give a straight line graph passing through the origin with a gradient of $(\pi l B)/2d^2$, from which the experimental Kerr constant B may be determined. If l, d and V are accurately known then a so-called absolute Kerr constant B may be obtained from Eq. (4). However, in practice it is more convenient to calibrate the Kerr cell using a liquid of known Kerr constant. If the gradients of plots of α verses V^2 for the unknown and standard liquids are denoted by M_x and M_s, respectively, then the experimental Kerr constant of the unknown material B_x can be readily calculated using the simple relationship

$$B_x = \frac{M_x}{M_s} B_s \tag{5}$$

2.3. Preparation of solutions of PVK

Solutions of PVK samples F1–F3 and model compound, *N*-ethylcarbazole (1% w/v) were prepared by dissolving accurately weighed quantities (approximately 0.5 g) of polymer in 50 cm^3 of 1,4-dioxane. Agglomerates of the polymers were first crushed into powders to aid the dissolution and, in some cases, mild sonification was employed to aid the dissolution of the polymers. Generally, the solutions were allowed to stand for at least 24 h to ensure that all the material has gone into solution. The solutions were transparent and viscous. All the solutions were filtered through paper filters (Type SS 3.0 μm).

2.4. Experimental Kerr constants of poly(N-vinylcarbazole)

Before the experimental Kerr constant of polymers and their complexes were measured, the Kerr cell had to be calibrated at different temperatures using a liquid of known experimental Kerr constant. Pure toluene (HPLC grade) ($B = 0.80 \times 10^{-14}$ mV^{-2} at 298 K) was used for this purpose. The experimental Kerr constants of toluene at 308, 318, 328 and 338 K were obtained by plotting the electrically-induced rotation, α, against the square of the applied voltage. Table 1 lists the Kerr constants measured for toluene at different temperatures.

The solution experimental Kerr constants (B_{12}) of each polymer and that of the model compound, *N*-ethylcarbazole were determined at 298, 308, 318, 328

Table 2
Experimental and molar Kerr constants of 1,4-dioxane

Temperature (K)	Experimental Kerr constant, B_1 (10^{-16} mV^{-2}	Molar Kerr constant, ${}_{m}K_1$ (10^{-21} m^{5}V^{-2} mol^{-1})
298	8.98(1)	1.30(0)
308	7.94(3)	1.16(9)
318	7.68(1)	1.16(4)
328	7.48(1)	1.15(9)
338	7.63(4)	1.21(2)

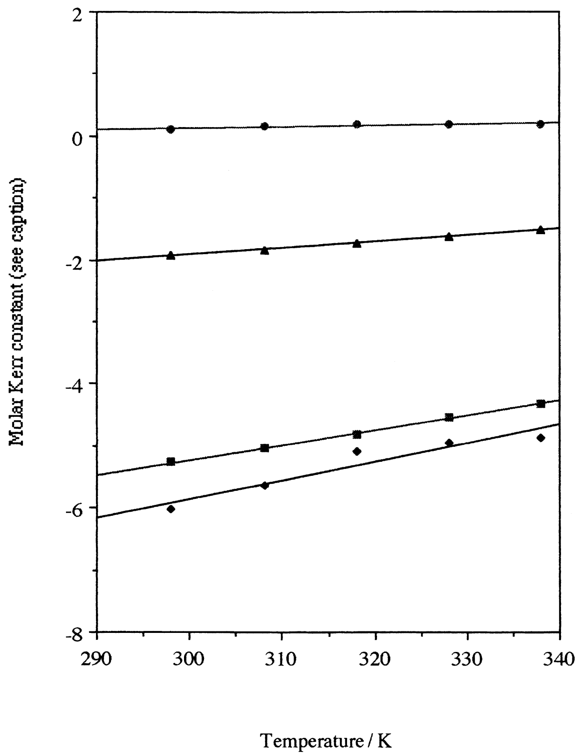

Fig. 4. Molar Kerr constant ${}_{\mathrm{m}}K_2 \times 10^{24}$, per repeat unit for various stereostructural forms of PVK. (▲ F1, ◆ F2, ■ F3 and ● *N*-ethylcarbazole) in solution in 1,4-dioxane.

and 338 K in solution in 1,4-dioxane (Table 2). The molar Kerr constants (${}_{\mathrm{m}}K_2$) of the polymer samples and model compound were then calculated using

$$ {}_{\mathrm{m}}K_2 = \frac{{}_{\mathrm{m}}K_{12} - f_1 {}_{\mathrm{m}}K_1}{f_2} \qquad (6)$$

where, f_1 is mole fraction of solvent and f_2 is mole fraction per PVK repeat unit. The molar Kerr constant of the solvent (${}_{\mathrm{m}}K_1$) is given by

$$ {}_{\mathrm{m}}K_1 = \frac{6\lambda n_1 B_1 M_1}{\left(n_1^2+2\right)^2(\varepsilon_1+2)^2 d_1} \qquad (7)$$

B_1, ε_1, M_1, n_1, and d_1 are the experimental Kerr constant, dielectric permittivity, relative molar mass, refractive index and density of the solvent, respectively. The molar Kerr constant of the solution is given by

$$ {}_{\mathrm{m}}K_{12} = \frac{6\lambda n_{12} B_{12} M_{12}}{\left(n_{12}^2+2\right)^2(\varepsilon_{12}+2)^2 d_{12}} \qquad (8)$$

where B_{12}, ε_{12}, M_{12}, n_{12}, and d_{12} are the experimental Kerr constant, dielectric permittivity, relative molar mass, refractive index and density of the solution, respectively.

Since the concentrations of polymer solutions were low (1% w/v) the refractive index and density of the solutions was assumed to be approximately equal to the refractive index and density of the solvent (1,4-

Table 3
Experimental and molar Kerr constants for 1% w/v solution of various stereostructural forms of PVK measured in 1,4-dioxane at various temperatures

Sample	Temperature (K)	Experimental Kerr constant, B_{12} (10^{-15} mV^{-2})	Molar Kerr constant, ${}_{\mathrm{m}}K_{12}$ (10^{-26} m^{5}V^{-2} mol^{-1})	Molar Kerr constant, ${}_{\mathrm{m}}K_2$ (10^{-24} m^{5}V^{-2} mol^{-1})
F1	298	−4.63	−0.74	−1.92
	308	−4.52	−0.72	−1.85
	318	−4.18	−0.68	−1.75
	328	−3.86	−0.63	−1.64
	338	−3.46	−0.57	−1.51
F2	298	−16.91	−2.61	−6.01
	308	−15.86	−2.46	−5.64
	318	−13.98	−2.21	−5.08
	328	−13.46	−2.14	−4.94
	338	−13.07	−2.11	−4.86
F3	298	−14.19	−2.26	−5.26
	308	−13.63	−2.18	−5.04
	318	−12.83	−2.09	−4.82
	328	−11.96	−1.96	−4.54
	338	−11.17	−1.85	−4.31
NEK	298	1.21	0.19	0.10
	308	1.26	0.20	0.15
	318	1.33	0.21	0.19
	328	1.32	0.21	0.20
	338	1.30	0.21	0.20

dioxane) 1.4202 and 1.028 kg/m^3, respectively. This is normally an acceptable approximation if the dipole moment of the solute is not too small. To minimise the error in the measurement of ${}_{\mathrm{m}}K_2$ solutions of PVK samples were prepared by dissolving accurately weighed quantities in 1,4-dioxane. Granular forms of polymers were first crushed into fine powder to aid the dissolution. In some cases, sonification was employed to ensure complete dissolution of the polymers. This procedure allows the experimental Kerr constants to be reproduced within error limits of ±2%.

Dielectric permittivities of various stereostructural forms of PVK and model compound *N*-ethylcarbazole measured in solution in 1,4-dioxane at different temperatures were reported in our earlier publication [29]. These values were used to calculate solution experimental Kerr constants (B) and molar Kerr constants of the polymer samples F1, F2, F3 and *N*-ethylcarbazole listed in Table 3.

Fig. 4 indicates a variation of molar Kerr constant ${}_{\mathrm{m}}K_2$ per repeat unit of polymer with temperature. The plots shows the following interesting features: (1) The molar Kerr constant of *N*-ethylcarbazole is positive whereas a negative molar Kerr constant is obtained for the polymer samples, (2) the molar Kerr constants of the polymers increases in magnitude as the isotactic content increases. Thus, polymer F2 (prepared by boron trifluoride etherate) shows the largest negative Kerr constant, whereas, sample F1, synthesised with azo-bisisobutyronitrile, shows the smallest negative molar Kerr constant. This trend is consistent with the dipole moment data [29] where the largest dipole moment per repeat unit was obtained for polymer F2 whereas polymer F1 showed the smallest dipole moment per repeat unit, and (3) as the isotactic content in the polymer increases the temperature coefficient increases.

These observations may be discussed in terms of the Kerr effect factors θ_1 and θ_2. The anisotropy term, θ_1, may be expanded as

$$\theta_1 = \frac{(a_1 - a_2)(b_1 - b_2) + (a_2 - a_3)(b_2 - b_3) + (a_3 - a_1)(b_3 - b_1)}{45kT} \tag{9}$$

and the dipolar term, θ_2, expanded as

$$\theta_2 = \frac{\left\{(\mu_1)^2 - (\mu_2)^2\right\}(b_1 - b_2) + \left\{(\mu_2)^2 - (\mu_3)^2\right\}(b_2 - b_3) + \left\{(\mu_3)^2 - (\mu_1)^2\right\}(b_3 - b_1)}{45kT^2} \tag{10}$$

The electro-optic parameters in Eqs. (9) and (10) are the electrostatic polarisabilities, a_1, a_2, and a_3, electro-optical polarisabilities, b_1, b_2, and b_3 and the dipole moment components μ_1, μ_2, and μ_3, all referenced to the principal axes (1, 2, 3) of the molecular polarisability ellipsoid.

The algebraic sign of the Kerr constant gives information concerning the disposition of the resultant molecular dipole moment with respect to the principal axes of polarisability. It is interesting to note that whilst the molecular Kerr constant of *N*-ethylcarbazole is positive the values for all the polymer samples are negative. The positive Kerr constant of the *N*-ethylcarbazole indicates that the angular displacement of the resultant molecular dipole moment vector from the principal axis of maximum polarisability is less than 54.7°. For PVK polymers, it is believed that there is a strong tendency for the polymer to exist as a series of straight rigid helical sections [33,34], because rotations about bonds in PVK are severely sterically restricted, such that the planes of the carbazole units lie approximately normal to the longitudinal axis of the helix. This means that the axis of maximum polarisability will be along a direction perpendicular to the helix axis, since individual group polarisabilities are greatest in their planes. However, the overall repeat unit dipole moments of the carbazole groups are approximately perpendicular to the chain axis for PVK, and will cancel because of symmetry along directions perpendicular to the long axis of the helix thereby yielding a resultant molecular dipole moment that is parallel to the helix axis. The nett effect, therefore, is that the resultant dipole moment of the molecule tends to be approximate perpendicular to the principal axis of polarisabilty, thus resulting in a negative Kerr constant.

The results obtained for the temperature coefficients measured for solutions of PVK are difficult to interpret quantitatively, because as the temperature rises the polymer chains may no longer be rigid and rod-like but, instead, have some tendency to becoming more flexible. In simplistic terms, supported by NMR [35–37] and X-ray [34,38] data, it is suggested that polymer F2 consists largely of 3/1 helices and that sample F1, contains mostly 2/1 helices. As the temperature increases it is proposed that the helices tend to “unwind” and adopt a structure closer to that of a random coil. The nett effect, in terms of polarisabilty is that the direction of the resultant dipole moment of the polymer molecule tends to deviate from being approximately perpendicular to the principal axis of polarisabilty, thus resulting in a less negative molar Kerr constant. This temperature induced change in molar Kerr constant is smallest for polymer F1, since it contains the least 3/1 helical content, and consequently its molar Kerr constant is the least sensitive to changes in temperature.

Theoretical analysis of polymer conformation is not simple since the flexibility of the macromolecules allows the chains to attain various conformations. The rigid polymers move inside the solution in order to orientate by the effect of the electric field, whereas flexible molecules not only move, but also can change their shape. Consequently, the treatment becomes more complicated as the flexibility of the polymers increases. A complete treatment of rigid polymers has been published by Wegener and co-workers [20,21]. Moderately flexible molecules such as bent rods requires the use of either approximate [22,23] or simulation procedures [24]. The realistic treatment of flexible polymers was started by Nagai and Ishikawa [25] to the point that all calculations carried out previously were of simplified models such as freely jointed or freely rotating chains.

Generally, the application of the Kerr constant to conformational analysis arises from the great sensitivity of this property to the variations of molecular geometry and environment [26]. The standard procedure used in these studies consists of a critical comparison between theoretical and experimental values of the molar Kerr constants, ($_{\mathrm{m}}K$). In many cases, this comparison is done with the assistance of a similar analysis of some other conformation-dependent property [27] such as dipole moments. In one of our earlier publications [29] temperature dependence of static dielectric permittivity and dipole moments of poly(*N*-vinylcarbazole) was discussed in detail. It was shown that sample F1, with the least isotactic content, had the smallest average dipole moment per repeat unit but the largest positive temperature coefficient. The polymers F1 and F3 (synthesised by using AZBN and $AlCl_3$ catalysts, respectively) as judged by NMR data, possess mainly syndiotactic stereostructures. Space filling models and computer simulated structures [33,34] show the possibility of forming 2/1 helixes that are not as sterically hindered as the 3/1 helixes believed to be formed in isotactic rich F2. At the lower temperatures considered in this study, the chains are restricted in their movement, and hence tend to occupy a helical conformation. Molecular models show that this conformation results in the partial cancellation of dipole moments of the polar carbazole groups. As the temperature increases, there is more thermal energy and hence a greater degree of freedom of the pendant groups and as a consequence this results in the formation of a great proportion of non-helical structures. This change in the fraction of helical structures leads to decrease in the cancellation of the dipole moments of the repeat units.

The second point concerns sample F2, polymer with the most largest isotactic content. This sample has the largest average dipole moment per repeat unit but the lowest temperature coefficient. A literature survey shows that it is generally believed that isotactic PVK consist of 3/1 helixes and that the polymer chains are fairly rigid. At low temperatures, the chains are very much restricted in their movement, and hence maintain their basic helical conformation. Generally, in a 3/1 helical conformation the cancellation of dipole moments is not as complete as that occurring in 2/1 helixes (where the pendant groups are almost trans to each other). As a result, the average dipole moment per repeat unit is higher than that observed for the 2/1 helixes. In addition, polymers with 3/1 helical chains are so sterically hindered that they are less affected by an increase in temperature and tend to retain their configurations, and as a consequence the temperature coefficient of the dipole moment is lower than that found for syndiotactic rich samples of PVK.

The final important observation is that the model compound, *N*-ethylcarbazole has a temperature coefficient close to zero. *N*-ethylcarbazole may be regarded approximately as a single rigid repeat unit of PVK. There will of course be little or no increase in the dipole moment of the *N*-ethylcarbazole as the temperature increases and indeed this was found to be the case.

3. Conclusions

Electro-optical birefringence (molar Kerr constants) of poly(*N*-vinylcarbazole) prepared with cationic and free radical catalysts were measured in solution in 1,4-dioxane over the temperature range of 298–338 K. It is confirmed that the Kerr constant for PVK systems are sensitive to stereostructure. All of the polymers had a negative Kerr constant in contrast to the model compound *N*-ethylcarbazole which had a positive molar Kerr constant.

Polymer F2, prepared using a boron trifluoride etherate catalyst, showed the highest isotactic content and exhibited the highest molar Kerr constant whereas polymer prepared with azo-bisisobutyronitrile had the lowest molar Kerr constant. Dipole moment trends for PVK were also similar where they increase with an increase of isotactic content of polymer. Thus, the molar Kerr constants could be used alongside dipole moments to differentiate the stereostructures of PVK chains.

Positive temperature coefficients of Kerr constant were measured for each of the different stereostructural types of PVK and were found to be largest for polymer sample F2. This could be due to a large dipole moment and/or anisotropy. However, the dielectric data [29] indicates that the temperature coefficient of the dipole moment of polymer sample F2 is very small. Therefore, it appears that the dipole moment contributions to Kerr constants are relatively insignificant and that changes in optical anisotropy mainly account for the differences in the Kerr constants of the various types of PVK.

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