

Dielectric and ^{13}C n.m.r. studies of various stereostructural forms of poly(*N*-vinyl carbazole)

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Three different stereostructural forms of poly(*N*-vinyl carbazole) (PVK) have been prepared using cationic (AlCl_3 and $\text{BF}_3(\text{CH}_2\text{CH}_3)_2\text{O}$) and radical (azobisisobutyronitrile) initiators. The dipole moment per repeat unit of PVK has been determined and correlated with ^{13}C n.m.r. spectra of the methine and methylene carbon absorptions for fractions of PVK in solution in 1,4-dioxan. The dielectric data for cationically prepared PVK appear to indicate a random coil configuration or possibly a rod-like structure in which the dipole moment vectors of the carbazole groups are randomly oriented but remain approximately perpendicular to the long axis of the molecule. For each type of PVK examined the repeat unit dipole moment was observed to be independent of molecular weight over the range 10^4 – 10^7 and insensitive to polydispersity.

(Keywords: poly(*N*-vinylcarbazole); carbazole; *N*-ethyl carbazole; synthetic route; dielectric permittivity; dipole moment, ^{13}C nuclear magnetic resonance; meso dyad; racemic dyad)

INTRODUCTION

Even a brief survey of the scientific literature reveals that poly(*N*-vinyl carbazole) (PVK) has been the subject of many investigations concerned with its potential as an electro-active material^{1–3}. Although one of the principal attractions of PVK lies in its interesting photo-electric properties^{4–7}, a great deal of effort has also been expended in the development of this polymer as an organic electrical conductor through the formation of acceptor–donor complexes with small molecules such as I_2 , AsF_5 and tetracyanodiquinomethane (TCNQ)^{1–3,8}. The results of these endeavours, involving polymers other than PVK, are now beginning to make an impact on a commercial level (e.g. solid state batteries). In addition to exposing novel areas of scientific research it is highly probable that the detailed study and development of electro-active materials will provide important insights into the electronic structure of molecules in the solid state. Such studies also promise to yield much valuable information relating to the nature of electronic interactions between molecules. The molecular structure of electrically conductive polymers and their morphology are areas of research assuming increasing importance^{9–11}. The stereochemistry of polymer molecules and their macroscopic structure are now considered in many instances to play an important role in determining the magnitude of electrical conductivity and the degree of electrical anisotropy¹². It is now generally accepted that the polymerization of *N*-vinyl carbazole, using different catalyst systems, produces a variety of polymers possessing different stereostructures. Although the exact nature of these various structures has been the subject of much discussion it is now generally accepted that there are several types of

stereostructures, as judged by n.m.r. spectroscopy^{13–19}, X-ray diffraction^{20–23} and the measurement of glass transition temperatures²⁴. For the majority of studies^{25–29} concerned with the dielectric properties of PVK in solution, relatively little was known about the stereostructures and distribution of molecular weights of the polymer samples. As far as the authors are aware the present study is the first to correlate dipole moments with ^{13}C n.m.r. spectra for fractions of different stereostructural forms of PVK characterized using gel permeation chromatography.

PREPARATION OF POLY(*N*-VINYL CARBAZOLE)

N-vinyl carbazole was polymerized in solution using three different types of initiator¹⁵. The polymerization reactions were carried out in purpose-built glass reaction vessels (approximately 250 cm³) fitted with gas-tight PTFE–glass joints and Suba seals. The reaction vessels could be attached to a vacuum line for charging with solvent. All the solvents were distilled, dried over alumina and re-distilled before use. The *N*-vinyl carbazole monomer (Fluka Ltd., Purum grade) was used as received. For all the polymerization reactions the concentration of the monomer was approximately 0.5 M (97 g l⁻¹).

Initiation using aluminium chloride

The vinyl monomer was placed in the reaction vessel and toluene was added by distillation under nitrogen. The solution was thermally equilibrated at 298 K before adding a suspension of aluminium chloride (0.20 g) in toluene. The aluminium chloride was purified by subliming the material twice under vacuum. The concentration of the initiator was 0.5 mol% (~0.0025 M) of the monomer concentration. Polymerization was allowed to proceed for 19 h at 298 K under dry nitrogen gas. The

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polymer sample prepared in this manner will be referred to as sample S1.

Initiation with boron trifluoride etherate

The vinyl monomer and freshly distilled toluene (150 cm^3) were placed in the reaction vessel. A small quantity (0.17 cm^3) of the initiator boron trifluoride etherate was injected into the reaction flask using a gas-tight syringe. The concentration of the initiator was $0.5\text{ mol}\%$ ($\sim 0.0025\text{ M}$) of the monomer concentration and the polymerization time was 19 h. All of these operations were conducted under an atmosphere of dry nitrogen. This procedure gave polymer sample S2.

Initiation with azobisisobutyronitrile

A solution of the monomer in benzene (140 cm^3) was evacuated and degassed several times. The initiator, azobisisobutyronitrile (0.123 g) in solution in benzene ($\sim 6\text{ cm}^3$) was injected into the reaction vessel through a Suba seal. The concentration of the initiator was $1.00\text{ mol}\%$ ($\sim 0.005\text{ M}$) of the monomer concentration. The polymerization reaction was allowed to proceed for 7 h at 343 K under the vapour pressure of the solution. This preparative route gave polymer sample S3.

All of the polymerizations were terminated by pouring the reaction mixtures into methanol (500 cm^3). The polymers were purified by repeated precipitation (at least three times) by the dropwise addition of a 1% w/v solution of the polymer in toluene into methanol (500 cm^3), while vigorously stirring the mixture. A thermally initiated sample of PVK was obtained from Polymer Consultants Ltd., London. This sample was also purified by several fractional precipitations in the manner previously described and will be referred to as sample S4.

Polymer samples S1–S4 had broad molecular weight distributions ($\bar{M}_w/\bar{M}_n > 9$) as judged by gel permeation chromatography, with the exception of sample S3 which was estimated to have a polydispersity index of *ca.* 2.9. The polymer samples S1–S4 were fractionated to produce fractions possessing a range of molecular weights and a variety of polydispersity indices. The polymers were dissolved in toluene to give an approximately 1% w/v solution and sufficient methanol was slowly added to produce a faint turbidity at 333 K . The temperature of the solution, which was controlled to within $\pm 0.05\text{ K}$, was slowly decreased by a few degrees until a portion ($\sim 10\%$) of the polymer had precipitated. The temperature was then kept constant for several hours during which time the flask was shaken regularly to permit the solution and the precipitated polymer to attain thermodynamic equilibrium. After allowing the system to form a well-defined boundary between the two phases the uppermost solution was carefully removed by decantation. The remaining layer represented the required fraction. This was dissolved in toluene, reprecipitated by adding methanol and dried. Further fractions were produced from the remaining solution by repeating the above procedure at successively lower temperatures down to a final temperature of 273 K .

Gel permeation chromatography

The fractions of poly(*N*-vinyl carbazole) were characterized in terms of number-average and weight-average polystyrene equivalent molecular weights, ${}_{\text{ps}}\bar{M}_n$ and ${}_{\text{ps}}\bar{M}_w$, respectively, using a Dupont gel permeation chromatograph fitted with a Waters detector. The column

porosities were 10^2 , 10^3 , 10^4 and 10^5 nm . This combination of columns produced a satisfactory separation for the majority of the PVK fractions. However, some of the higher molecular weight fractions were excluded from the columns and for these samples no reliable values of molecular weight and polydispersity index could be obtained. The molecular weight distribution curves shown in Figure 1 were calculated from g.p.c. data for various fractions of PVK samples S1–S4.

Determination of weight-average molecular weights

A low-angle light scattering (LALLS) unit, attached to the eluent output of the g.p.c. instrument, was used to measure the absolute weight-average molecular weights, \bar{M}_w , of samples S1–S4 and some of the fractions. Figure 2

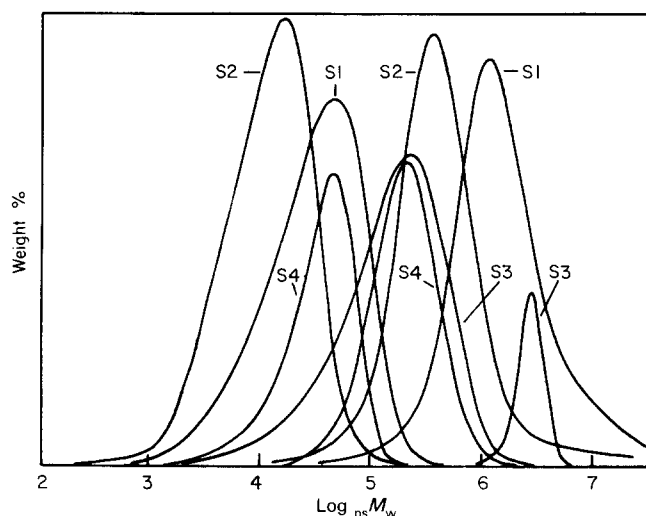


Figure 1 Molecular weight distributions for fractions of PVK obtained from sample types S1–S4 (see preparation section)

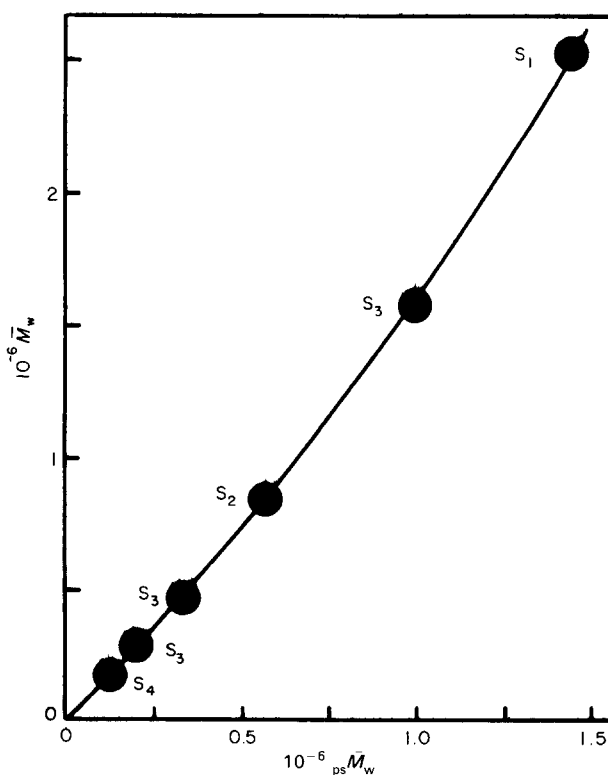


Figure 2 Weight-average molecular weights \bar{M}_w from low-angle light scattering vs. g.p.c. polystyrene equivalent weight-average molecular weights ${}_{\text{ps}}\bar{M}_w$ derived for various samples of PVK

shows the absolute weight-average molecular weight, \bar{M}_w , plotted against the corresponding weight-average polystyrene equivalent molecular weight calculated from g.p.c. data. Although the data in this plot can be approximately represented by a straight line it appears that a slight curve represents the data more accurately. This calibration curve was used to calculate the absolute weight-average molecular weights from polystyrene equivalent molecular weights derived from g.p.c. data.

^{13}C nuclear magnetic resonance spectroscopy

It has been demonstrated by a number of workers that proton and carbon nuclear magnetic resonance spectroscopy may be used to distinguish between the various stereostructural forms of PVK in solution¹³⁻¹⁹. The ^{13}C n.m.r. spectra of the samples of PVK prepared in this study were recorded with a Jeol FX90Q Fourier transform n.m.r. spectrometer. The instrument was fitted with a spectrum computer having a memory capacity of 16k and was operated at 22.5 MHz. The spectra were all broadband decoupled to remove the magnetic effects of directly and indirectly bonded protons. A pulse width of 15 μs ($\cong 60^\circ$) and a spectral width of 5000 Hz were employed. The data were analysed using a trapezoidal-exponential window which although causing a slight line broadening gave an improved signal-to-noise ratio. The free-induction decay signals were accumulated in the memory every 50 pulses after transformation. A total of approximately 2×10^5 pulses were used to produce acceptable spectra and each spectrum required 65 h for its completion. When recording the peaks of the methylene and methine ^{13}C absorptions, all the other peaks were allowed to go off scale. All measurements were made on solutions in 10 mm diam. glass tubes at 332 K without degassing. The solvent was 1,4-dioxan and the concentration of the polymer was approximately 10% w/v. Hexamethyldisiloxane (HMDS) was employed as an internal reference and chemical shifts are reported on the δ -scale in ppm with respect to tetramethylsilane (TMS). The chemical shift of HMDS was 1.950 ppm downfield relative to TMS. A ^{13}C n.m.r. spectrum recorded for a fraction of PVK prepared using the initiator AlCl_3 is shown in Figure 3. This spectrum is typical of those recorded for all of the unfractionated and fractionated samples of PVK. Figures 4 and 5 show the ^{13}C n.m.r. absorption peaks of the methine and methylene carbons

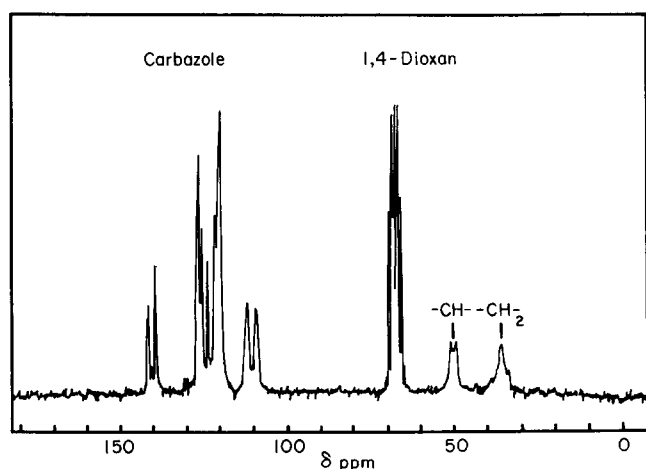


Figure 3 ^{13}C n.m.r. spectrum of PVK (S1) in solution in 1,4-dioxan at 333 K

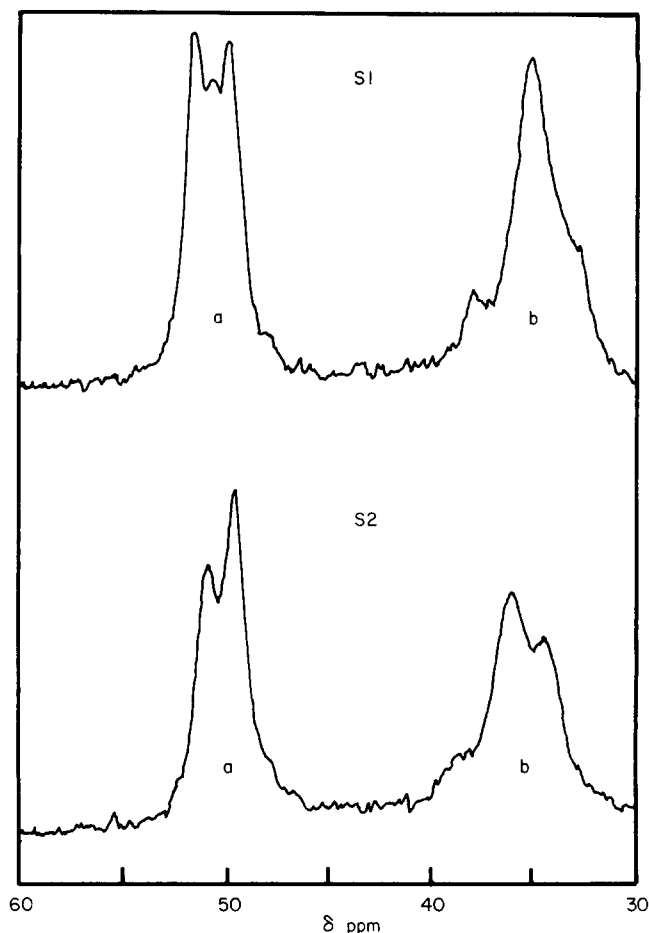


Figure 4 ^{13}C n.m.r. spectrum of the methine (a) and methylene (b) absorptions of PVK prepared using AlCl_3 (S1) and BF_3 etherate (S2)

of PVK samples S1-S4. The spectrum presented in Figure 5 for the AZBN initiated polymer S3 is very similar to the spectrum (Figure 5) obtained for a fraction prepared from the thermally initiated sample of PVK. The n.m.r. spectra of these two fractions are also similar to the spectra published by Kawamura and Matsuzaki¹⁹ and to those published by Williams and Froix¹⁸ for PVK prepared by radical polymerization. The spectra presented in Figure 4 for PVK fractions prepared by initiation with AlCl_3 and boron trifluoride etherate, respectively, also closely resemble the corresponding spectra reported by Kawamura and Matsuzaki¹⁹. It is interesting that the spectrum reported by Williams and Froix¹⁸, for a sample of PVK prepared using BF_3 etherate, is very similar to the spectrum published by Kawamura and Matsuzaki¹⁹ for $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ initiated PVK and to the spectrum obtained in the present study for an AlCl_3 initiated sample of PVK. The assignments made in Figures 4 and 5 follow those proposed by Williams and Froix¹⁸ (see below).

Static dielectric permittivities

The dielectric cell (manufacturer is unknown) comprised two cylindrical blocks of brass. The external surfaces were nickel plated and the internal surfaces were gold plated. The outer cylinder was hollow to allow passage of the coolant liquid. To permit recovery of the samples a glass stopcock was fitted to the base of the dielectric cell by means of a Teflon sleeve. The cell was equipped with an external, screw-type lid and an internal,

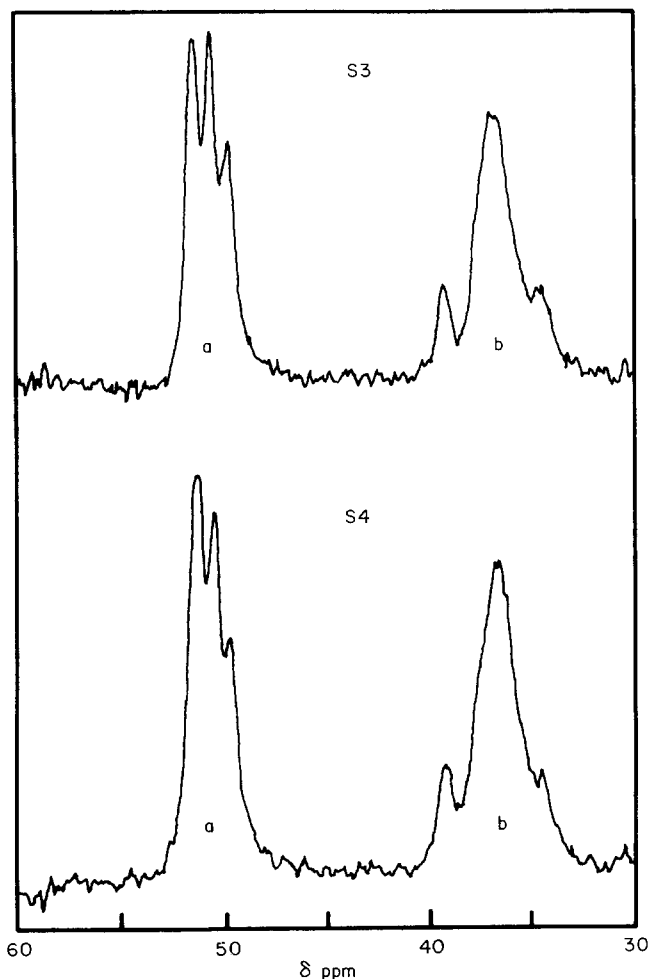


Figure 5 ^{13}C n.m.r. spectrum of the methine (a) and methylene (b) absorptions of PVK prepared using AZBN (S3) and thermal (S4) initiation

perforated lid. The latter ensured that the effective volume of the dielectric was reproducible and independent of the total volume ($\sim 20\text{ cm}^3$) of liquid sample in the cell, provided that the level of the liquid was just above the lower surface of the internal lid. The height and diameter of the inner cylindrical electrode were 35 mm and 33 mm, respectively. The electrode gap was approximately 1.5 mm and the vacuum capacitance of the cell was determined to be 47 pF. The cell acted as one of the principal capacitive elements of a variable frequency oscillator (VFO). The frequency of the VFO ($\sim 100\text{ kHz}$) was monitored using a precision frequency counter (Venner Electronics Ltd. Type T5A 6636/2M) with an accuracy of 1 part in 10^5 . To determine the dielectric permittivity of a solution the frequency of the VFO was measured for the empty cell (f_0), for the cell filled with the solvent 1,4-dioxan (f_1) and for the cell filled with solutions of PVK (f_{12}) in the concentration range 0–1.0%. The temperature was maintained at 298 K.

The static dielectric permittivities, ϵ_{12} , of the solutions were calculated using the expression

$$\epsilon_{12} = 1 + \frac{1/f_{12}^2 - 1/f_0^2}{1/f_1^2 - 1/f_0^2} (\epsilon_1 - 1) \quad (1)$$

where $\epsilon_1 = 2.2090$ for 1,4-dioxan at 298 K (ref. 30).

Plots of ϵ_{12} against weight fraction of solute, w_2 , for fractions of PVK are shown in *Figures 6* and *7*. For any

given type of sample, S1–S4, the data appear to be described by the same line of regression within experimental error. Gradients ($d\epsilon_{12}/dw_2$) of the plots for S1 and S2 were found to be equal to one another, within experimental error, as were those of samples S3 and S4 prepared by

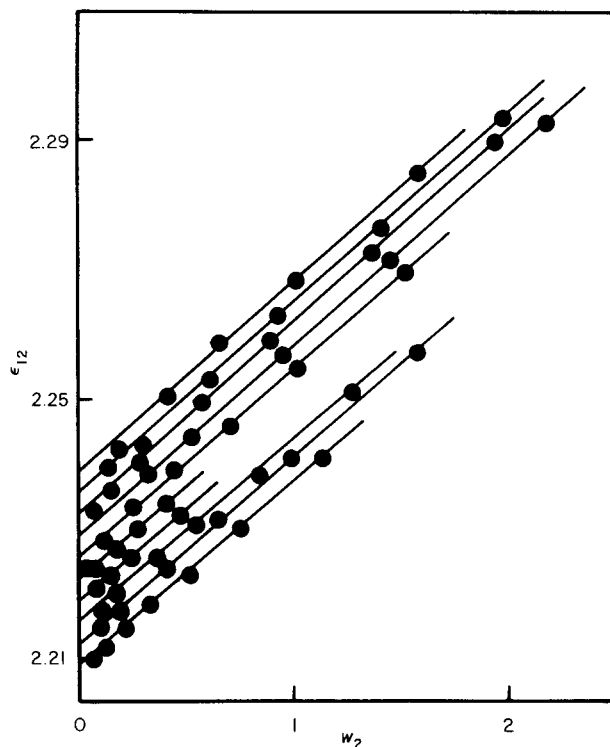


Figure 6 Dielectric data for fractions of PVK (S1– AlCl_3) in solution in 1,4-dioxan at 298 K. For clarity the curves are displaced upwards in order of increasing molecular weight over the approximate range 10^4 – 10^7 . Similar gradients were observed for PVK prepared using BF_3 etherate

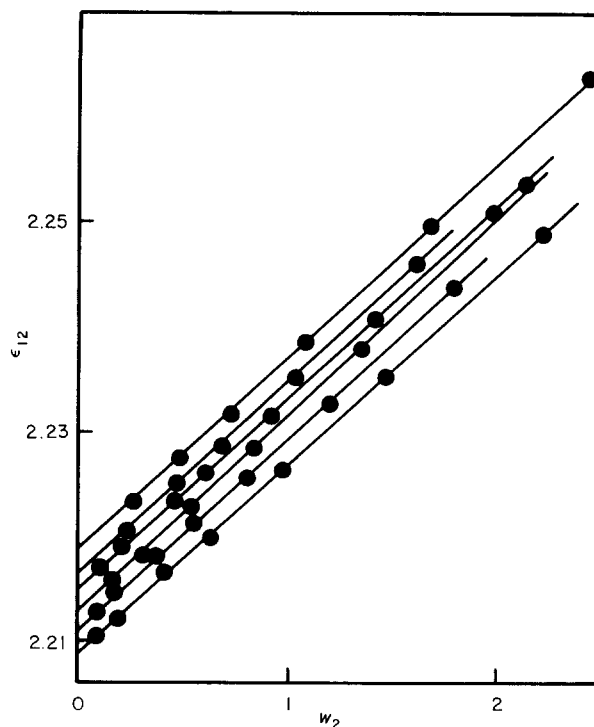


Figure 7 Dielectric data for fractions of PVK (S3–AZBN) in solution in 1,4-dioxan at 298 K. For clarity the curves are displaced upwards in order of increasing molecular weight over the approximate range 10^4 – 10^7 . Similar gradients were observed for PVK prepared using thermal initiation

radical mechanisms. A statistical analysis indicated non-overlapping error bars for samples S3 and S4, suggesting a slight difference in their dielectric behaviour although ^{13}C n.m.r. spectroscopy was unable to differentiate between the original unfractionated samples or between the fractionated samples of S3 and S4. However, it is quite apparent that the effective dipole moment associated with individual repeat units is greater for the polymers (S1–S2) prepared using cationic catalyst systems. None of the samples of PVK exhibited dielectric relaxation at frequencies below 100 kHz.

Static dielectric data were also obtained for carbazole and *N*-ethyl carbazole in solution in 1,4-dioxan at 298 K (Figure 8).

The Guggenheim rearrangement of the Debye equation required for the calculation of solute dipole moments, μ_2 , may be written in the form³¹

$$\mu_2^2 = \frac{27\varepsilon_0 kT}{N(\varepsilon_1 + 2)(n_1^2 + 2)} \left(\frac{\Delta}{C} \right)_{c \rightarrow 0} \quad (2)$$

where ε_0 (8.8541×10^{-12} Fm) is the permittivity of free space, k (1.38062×10^{-23} J K $^{-1}$) is Boltzmann's constant, T is the absolute temperature, N (6.02217×10^{23} mol $^{-1}$) is the Avogadro number. C is the concentration of the solute expressed in units of mol m $^{-3}$ and Δ is given by

$$\Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^2) \quad (3)$$

where the single and double subscripts denote a property of the solvent and solution, respectively. For sufficiently

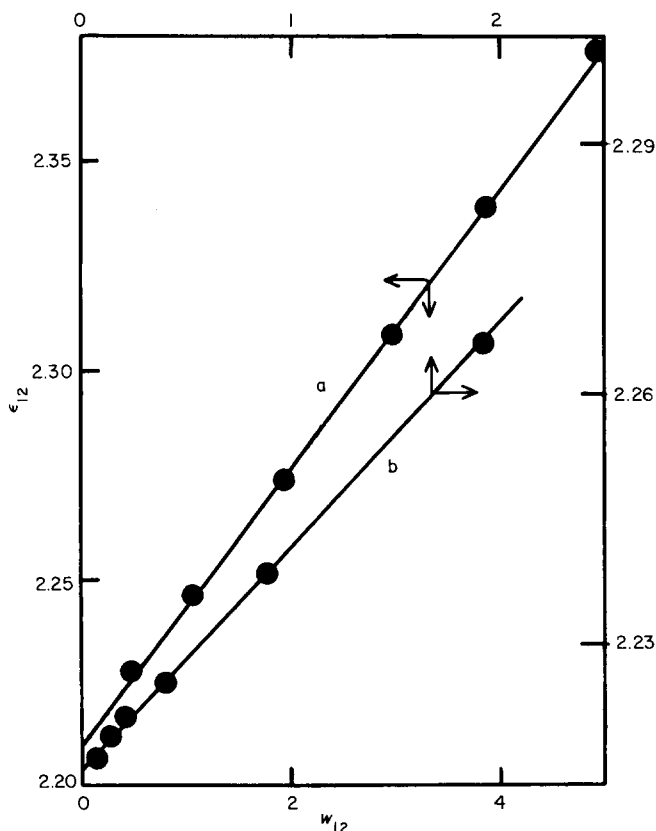


Figure 8 Dielectric data for carbazole (A) and *N*-ethyl carbazole (B) in solution in 1,4-dioxan at 298 K

Table 1 Static dielectric data and mean dipole moment per repeat unit for various stereostructural forms of poly(*N*-vinyl carbazole) in solution in 1,4-dioxan at 298 K

Solute	$d\varepsilon_{12}/dw_2$	μ (10^{-30} C m)
S1 (anhydrous AlCl_3)	2.89	7.24
S2 ($\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$)	2.83	7.16
S3 (AZBN)	1.81	5.73
S4 (Thermal)	1.75 ^a	5.63
Carbazole	3.16	7.04
<i>N</i> -ethyl carbazole	2.63	6.94

^a 1.71 in benzene at 298 K

dilute solutions of polar molecules in non-polar solvents Δ may usually be approximated to $(\varepsilon_{12} - \varepsilon_1)$ and

$$\left(\frac{\Delta}{C} \right)_{c \rightarrow 0} = \left(\frac{d\varepsilon_{12}}{dw_2} \right)_{w_2 \rightarrow 0} \left(\frac{M_2}{\rho_1} \right) \quad (4)$$

where M_2 is the molecular weight of the solute and ρ_1 is the density of the solvent. Equations (1)–(4), together with values of $d\varepsilon_{12}/dw_2$, were used to calculate the mean dipole moment per repeat unit of the various stereostructural forms of PVK. The dipole moment per repeat unit for samples S1–S4 and the molecular dipole moments of carbazole and *N*-ethyl carbazole are listed in Table 1.

DISCUSSION AND CONCLUSIONS

One of the earliest ^{13}C n.m.r. spectra of poly(*N*-vinyl carbazole) was that published by Tsuchihashi *et al.*¹⁷. They assigned most of the absorption peaks by comparing the spectrum of the polymer with those obtained for the model compound *N*-ethyl carbazole. Kawamura and Matsuzaki¹⁹ completed the assignment of the peaks in the ^{13}C spectrum of PVK and observed that the shapes and relative intensities of the methine and methylene carbon absorptions depended on the method of polymerization. The absorptions of the methine carbon of samples of PVK prepared by radical routes were observed to be split into a 'triplet', while those for samples of PVK obtained by cationic methods were split into a 'doublet'. It was tentatively assumed that the polymers of *N*-vinyl carbazole, obtained via radical polymerization, possessed a high proportion of syndiotactic sequences, and that PVK prepared using BF_3 etherate was mainly isotactic and that PVK synthesized by using $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ comprised stereoblock structures. Williams and Froix¹⁸ have reported ^{13}C spectra for samples of PVK prepared using synthetic methods similar to those described previously. However, the spectrum obtained by these authors for PVK initiated by BF_3 etherate, closely resembles the n.m.r. spectrum published by Kawamura and Matsuzaki¹⁹ for PVK prepared using $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$. Williams and Froix¹⁸ deduced that the methine peak was composed of absorptions due to *mr*, *rr* and *mm* triads (where *m* and *r* respectively denote meso and racemic dyads of consecutive repeat units) and that the methylene ^{13}C peak was the sum of absorptions associated with *rmr*, *mrm*, *rrr*, *mrr*, *mmr* and *mmm* tetrad stereostructures. By measuring the relative intensities of these various contributions these authors were able to draw certain conclusions regarding the spatial distribution of the pendant carbazole groups. Williams and Froix refuted the notion that PVK molecules consist of long blocks of either isotactic or

syndiotactic sequences. However, the text of their paper notes that there is an increase in racemic content for cationically prepared PVK whereas the accompanying n.m.r. data apparently indicate a decrease in racemic content, in agreement with the observations of Okamoto *et al.*¹⁵.

It is interesting to compare the chemical shifts of methine absorptions observed in the present study for PVK in solution in 1,4-dioxan, with those reported by Williams and Froix¹⁸ for PVK in solution in pyridine- d_5 at 378 K. For PVK in 1,4-dioxan the methylene ^{13}C absorptions are shifted downfield by approximately 4.5 ppm relative to the corresponding peaks for PVK in pyridine- d_5 , whereas the chemical shifts for the ^{13}C absorptions of PVK in either of these solvent systems are not significantly different from one another. This behaviour probably reflects the relatively greater accessibility of the methylene carbon atoms to the solvent molecules.

Theoretical developments in the early 1970s utilising arguments based on symmetry, suggested that for many types of polymer structure the mean-square molecular dipole moment would be unaffected by excluded volume^{32,33}. However, recent studies³⁴⁻³⁶ have shown that these predictions may fail in certain instances where the side-chain contributes to the dipole moment of the repeat unit, as is the case for many mono substituted vinyl polymers, $-(\text{CH}_2\text{CHX})-$, such as PVK. Therefore, it would appear imprudent to compare experimental and theoretical dipole moments if the latter were calculated assuming an absence of excluded volume effects. This restriction would not be expected to apply to dipole moments measured under theta point conditions.

The dipole moment of 7.04×10^{-30} C m, obtained for carbazole in the present study is close to the value of 6.97×10^{-30} C m reported by Cowley and Partington³⁷ but is somewhat larger than the value of 6.7×10^{-30} C m published by Liptay³⁸ for carbazole in solution in 1,4-dioxan. Replacement of the amino proton of carbazole by an ethyl group leads to a slightly smaller molecular dipole moment of 6.94×10^{-30} C m for *N*-ethyl carbazole. The repeat unit dipole moment of 5.73×10^{-30} C m found for sample S3 (AZBN initiated) is significantly lower than the value of 6.84×10^{-30} C m reported by North and Phillips^{25,27} using the same type of initiator. However, the dielectric data recorded by these authors was for relatively concentrated (10% w/v) solutions of PVK in toluene. North and Phillips^{25,27} also published dielectric data for two samples of PVK prepared using auric chloride (AuCl_3) as the initiator. Because these samples had a low molecular weight (1.66×10^3 and 4.72×10^3) and also exhibited smaller dipole moments (5.14×10^{-30} C m and 5.80×10^{-30} C m, respectively) per repeat unit than the higher molecular weight species prepared using different initiators these workers concluded that for molecular weights below about 4×10^3 PVK molecules are rod-like in solution.

The thermally initiated sample (S4) of PVK examined in the present study was found to possess a dipole moment per repeat unit of 5.63×10^{-30} C m, a value similar but slightly lower than that found for the polymer, S3, produced using the initiator AZBN. Samples of PVK obtained via cationic mechanisms using either AlCl_3 or BF_3 etherate gave dipole moments per repeat unit that were significantly larger than those determined for the

polymers prepared using radical methods. Thus, the dipole moment per repeat unit for S1 (AlCl_3 initiated) and S2 ($\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$) was found to be 7.24×10^{-30} C m and 7.16×10^{-30} C m, respectively. It is interesting that both of these values are quite close to the value determined for *N*-ethyl carbazole. The near equality of these values suggests that the dielectric behaviour of PVK, prepared using cationic catalysts, corresponds to either that of an atactic, random-coil polymer or that of a rod-like molecule in which the carbazole substituents are randomly oriented but remain approximately perpendicular to the long axis of the molecule.

Privatska and Havranek³⁹ and Sundararajan⁴⁰ have published theoretical conformational energy maps for syndiotactic and isotactic sequences of PVK chains. Although the overall details and conclusions of these two studies were similar (i.e. comparable energy contours in the vicinity of *trans-trans* (*tt*), *trans-gauche* (*tg*) and *gauche-gauche* (*gg*) conformations) the energies assigned to the various minima, expressed relative to the *tt* state of the racemic dyad differed quite substantially. Despite these quantitative discrepancies both sets of workers concluded that for isotactic and syndiotactic forms of PVK the rotational states of pairs of skeletal bonds flanking methylene carbon atoms are heavily weighted in favour of *tt* sequences. The broad implications of these observations on the static dielectric behaviour of PVK in solution can be ascertained by examination of scale models of meso and racemic forms of PVK. Restricting the backbone of PVK to the all-*trans* conformation results in the addition of dipole moment vectors of adjacent carbazole sidegroups for the meso dyads and substantial cancellation of sidegroup dipole moment vectors for the racemic dyads. Taking the dipole moment of a repeat unit to be μ_0 and oriented perpendicular to the long axis of the chain, the resultant dipole moments for meso and racemic dyads, locked in *tt* conformations, will be $2\mu_0$ (dipole moment components of adjacent carbazole groups parallel) and $1.2\mu_0$ (dipole moment components of adjacent carbazole groups 109° apart), respectively. Assuming, for the purpose of illustration only, that the resultant dipole moment vectors of meso and racemic dyads can orientate independently of each other then the ratios of meso to racemic dyads, deduced from ^{13}C n.m.r. spectra may be used to derive an estimate of the effective dipole moment per repeat unit of PVK. The n.m.r. spectra published by Williams and Froix¹⁸, supported by those presented in the present study, indicate that cationically prepared PVK possesses 54% meso dyads and 46% racemic dyads and that radically prepared PVK is composed of 41% meso dyads and 59% racemic dyads. The effective dipole moment per repeat unit, calculated using $\mu_0 = 6.94 \times 10^{-30}$ C m (*N*-ethyl carbazole) was found to be 8.2×10^{-30} C m (cf. experimental value of 7.2×10^{-30} C m) and 7.6×10^{-30} C m (cf. experimental value of 5.63×10^{-30} C m) for cationic and radical catalysed forms of poly(*N*-vinyl carbazole), respectively. Although it would be unwise to over interpret this crude model it does appear that there is a satisfactory agreement between estimated and experimental dipole moments for cationic types of PVK but substantial disagreement for samples of PVK derived using AZBN (S3) and thermal (S4) initiator. For the latter types of polymer a close match between calculated and experimental dipole moments can be achieved by using a value of 1.7 for the ratio of meso dyads

to racemic dyads, respectively. The rather simplistic nature of the conformational model adopted for PVK prohibits a more detailed analysis.

In the present study it has been demonstrated that although the static dielectric properties of solutions of poly(*N*-vinyl carbazole) prepared using cationic and radical initiators are discernably different from one another there was no significant evidence for any dependence of the repeat unit dipole moment on molecular weight in the range 10^4 – 10^7 . Thus, for fractions of PVK prepared using a particular initiator system the ratio Δ/C was observed to be effectively constant, within experimental error, and insensitive to polydispersity.

Although it is quite clear, from an inspection of high resolution ^{13}C n.m.r. spectra of the methine and methylene absorptions, that there are at least three types of stereostructures of PVK, measurements of static dielectric permittivities of their solutions in 1,4-dioxan are unable to clearly differentiate between fractions of PVK prepared using AlCl_3 and those prepared using $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$. However, a previous communication⁴¹ has indicated that the electro-optical Kerr effect (electrically-induced birefringence) is able to discriminate between the various stereostructural forms of poly(*N*-vinyl carbazole) considered in the present study. Further studies, concerning the electro-optic properties of poly(*N*-vinyl carbazole) are presently being undertaken.

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