Polymer Vol. 37 No. 5, pp. 755–760, 1996

0032-3861/96/$15.00 + 0.00

Temperature dependence of static dielectric permittivity and dipole moments of poly(*N*-vinylcarbazole)

M. Fiaz* and M. S. Beevers†
Speciality Polymer Group, Chemical Engineering and Applied Chemistry, University of Aston in Birmingham, Aston Triangle, Birmingham B4 7ET, UK
(Received 13 April 1995)

The dipole moment has been measured for various stereostructural forms of poly(*N*-vinylcarbazole) (PVK) in solution in 1,4-dioxane and in toluene in the temperature range 288–338 K. The dielectric and dipole moment data were correlated with the stereostructure of PVK. The dipole moment behaviour of various types of PVK, prepared using different catalyst systems, may be explained in terms of 3/1, 2/1 or all-*trans* sequences of syndiotactic PVK. All PVK samples showed a positive temperature coefficient of dipole moment but to a different extent. PVK with lowest isotacticity (prepared with a free-radical catalyst) had the largest temperature coefficient, suggesting that this structure was more sensitive to changes in temperature. However, the dielectric data for cationically prepared PVK appear to indicate a more random coil-type of configuration or possibly a segmental, rod-like structure in which the dipole moment vectors of groups of carbazole groups are randomly oriented but remain approximately perpendicular to the long axis of the molecule, resulting in only a small temperature coefficient of dipole moment.

(Keywords: poly(*N*-vinylcarbazole); dielectric permittivity; dipole moment)

INTRODUCTION

A great deal of interest has been shown in the photo-induced electrical conductivity of bulk poly(*N*-vinylcarbazole) (PVK) and PVK systems doped with a variety of electron-acceptor molecules, such as 2,4,7-trinitro-9-fluorenone (TNF)[1]. Since PVK possesses a chiral centre in its repeat unit, an important question arises concerning the effect of tacticity on its various electrical and photo-conductive properties. It has been shown that the synthetic route used to prepare poly(*N*-vinylcarbazole) has a marked effect on its stereoregularity and crystallinity[2,3]. Thus, radical-based polymerizations are believed to lead to an increased racemic content while cationic systems result in the production of polymers possessing higher isotactic contents. However, it is recognized that the interpretation of ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) spectra is ambiguous. Thus, additional complementary experimental data on these materials, using techniques sensitive to their conformations, are essential if meaningful correlations are to be made between their physical properties and tacticity.

The dielectric permittivity and dipole moment is a popular method for characterizing the conformations of polymer molecules since the experimentation is not too demanding (cf. Kerr effect) and interpretation of the results is often relatively straightforward. Debye and Bueche[4] have shown that a comparison of the dipole moment of a polymeric molecule to that of one of its structural units can yield information concerning the average chain configuration. A variety of polymer types have been successfully studied using this technique. Therefore, along with the Kerr effect (the topic for a future publication), the determination of dipole moments makes an ideal complementary tool for the study of the average configurational structures of PVK in this investigation.

Previous studies of the dielectric properties of PVK have focused either on dielectric relaxation or have been performed on poorly characterized polymer samples[5–10]. Mumby and Beevers[11,12] have correlated dipole moment and electro-optic Kerr effect with the tacticity of PVK polymers. They concluded that as the isotacticity of the polymer increases the dipole moment and Kerr effect both increase. It was also shown that the dipole moment and Kerr effect are independent of the polymer molecular weight. Sundararajan[13] predicted a negative temperature coefficient for the dipole moment of poly(*N*-vinylcarbazole) using a conformational analysis based on pairwise rotation around the skeletal bonds. However, there is some disagreement between the theoretical results predicted by Sundararajan and the experimental results reported by Riande *et al.*[14]. The experimental work carried out by Riande *et al.* suggests a positive temperature coefficient for the dipole moment of samples of PVK prepared by a free-radical catalyst (azobisisobutyronitrile, AIBN). Riande *et al.* concluded that the discrepancy between theory and experiment may be

---

*Present address: Institute of Polymer Chemistry and Materials Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, UK

†To whom correspondence should be addressed

Table 1 Static dielectric permittivities of solutions of PVK polymers and *N*-ethylcarbazole (NEK) in 1,4-dioxane

Conc. $\times 10^4$ (mol cm^{-3})	ϵ_{12}					
	288 K	298 K	308 K	318 K	328 K	338 K
F1						
0.13	2.248	2.243	2.235	2.022	2.184	2.163
0.26	2.255	2.252	2.243	2.212	2.193	2.172
0.52	2.259	2.255	2.247	2.215	2.192	2.173
0.78	2.272	2.265	2.257	2.225	2.203	2.184
1.04	2.284	2.279	2.271	2.237	2.218	2.196
F2						
0.13	2.259	2.255	2.248	2.215	2.194	2.174
0.26	2.275	2.274	2.265	2.230	2.210	2.188
0.52	2.321	2.316	2.307	2.269	2.249	2.226
0.78	2.358	2.350	2.338	2.300	2.278	2.253
1.04	2.366	2.357	2.348	2.310	2.288	2.262
F3						
0.13	2.220	2.218	2.211	2.181	2.162	2.143
0.26	2.227	2.225	2.217	2.186	2.167	2.147
0.52	2.249	2.245	2.237	2.205	2.186	2.165
0.78	2.274	2.272	2.263	2.230	2.210	2.189
1.04	2.295	2.292	2.284	2.252	2.232	2.209
NEK						
0.13	2.250	2.245	2.236	2.199	2.179	2.158
0.26	2.285	2.276	2.266	2.227	2.205	2.181
0.52	2.314	2.302	2.294	2.253	2.228	2.206
0.78	2.348	2.336	2.325	2.283	2.257	2.233
1.04	2.373	2.360	2.349	2.305	2.282	2.256

attributed either to specific solvent effects or to significant errors involved in the experimental determination of the dipole moments. However, there appears to be no experimental data published on the dipole moments of various stereostructural forms of PVK determined over a range of temperature.

In this work, an attempt is made to further extend this area of research by studying the influence of temperature on the dielectric permittivity and dipole moment of samples of PVK produced using various catalyst systems. The results are interpreted in terms of tacticity and conformations of these polymers. The Debye–Guggenheim equation was employed in the calculation of molecular dipole moment from the dielectric constants of dilute solutions of polar molecules in non-polar solvents. The solvent 1,4-dioxane was chosen as an acceptable medium in which all the dielectric permittivity measurements on various stereostructural forms of PVK were carried out. The dipole moments were also measured in toluene, which is believed to be a 'poor' solvent for PVK. It is believed that PVK consists of rigid rod-like structures comprising 2/1 and 3/1 helices[3,15]. Therefore, 1,4-dioxane would be expected to favour the unwinding and opening up of the helices, when compared with toluene.

In some previous work, Sitaramaiah and Jacobs[16] characterized PVK by gel permeation chromatography, viscometry, light scattering and osmometry. The Mark–Houwink relations suggested that benzene ($a = 0.58$ at 298 K) is a poor solvent and tetrachloroethane ($a = 0.68$ at 298 K) is a good solvent for PVK. When they repeated the experiment in cyclohexanone they found $a = 0.61$ at 298 K. Another data source[17] also lists Mark–Houwink a and k parameters for PVK in different solvents. In toluene the theta temperature is 310 K ($a = 0.50$), supporting the view that toluene is a poor solvent for PVK when compared with polar solvents such as cyclohexanone.

EXPERIMENTAL

Materials and characterization

N-Vinylcarbazole monomer (purchased from Aldrich Chemicals Ltd, Poole, UK) was polymerized (without further purification) in toluene to produce polymers of different stereostructures. The synthetic routes for the polymerization of the *N*-vinylcarbazole monomer have been published in detail elsewhere[12]. Polymer F1 was prepared by polymerizing the monomer with AIBN 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 poor solvent.

The molecular weight distributions of these polymers were obtained using gel permeation chromatography (RAPRA, Shawbury, UK). The number-average molecular weights of polymers F1, F2 and F3 were found to be 28.5×10^3, 30.9×10^3 and 23.7×10^3 g mol^{-1}, respectively, and their polydispersity ratios (M_w/M_n) were 2.63, 20.37 and 5.65, respectively. For polymer F2 some

Table 2 Static dielectric permittivity of solutions of PVK polymers and *N*-ethylcarbazole (NEK) in toluene

Conc. $\times 10^4$ (mol cm^{-3})	ϵ_{12}					
	288 K	298 K	308 K	318 K	328 K	338 K
F1						
0.13	2.423	2.380	2.373	2.334	2.312	2.281
0.26	2.421	2.382	2.382	2.332	2.313	2.290
0.52	2.431	2.391	2.393	2.335	2.320	2.302
0.78	2.442	2.403	2.404	2.364	2.353	2.343
1.04	2.463	2.421	2.404	2.373	2.341	2.332
F2						
0.13	2.420	2.392	2.371	2.342	2.313	2.303
0.26	2.432	2.391	2.370	2.350	2.325	2.301
0.52	2.452	2.412	2.402	2.362	2.343	2.312
0.78	2.461	2.443	2.412	2.384	2.371	2.342
1.04	2.493	2.450	2.430	2.402	2.390	2.364
F3						
0.13	2.423	2.334	2.374	2.334	2.312	2.291
0.26	2.431	2.392	2.382	2.341	2.311	2.293
0.52	2.442	2.412	2.392	2.353	2.342	2.324
0.78	2.462	2.420	2.410	2.384	2.351	2.331
1.04	1.480	1.442	2.432	2.391	2.374	2.342
NEK						
0.13	2.410	2.381	2.373	2.332	2.312	2.280
0.26	2.423	2.392	2.383	2.330	2.293	2.282
0.52	2.342	2.402	2.394	2.331	2.352	2.331
0.78	2.444	2.410	2.431	2.352	2.334	2.292
1.04	2.461	2.432	2.423	2.362	2.352	2.311

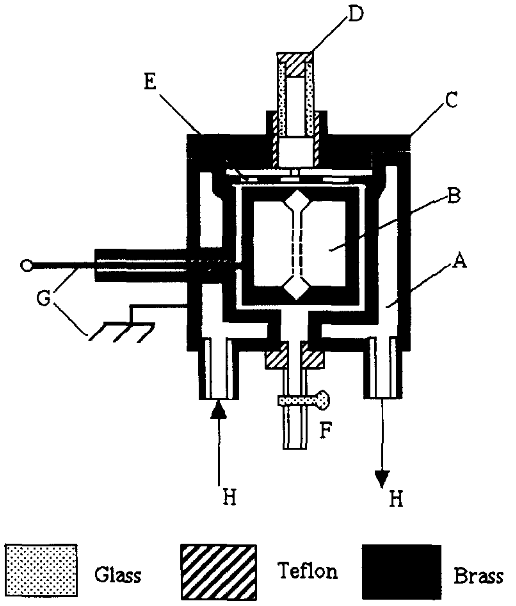

Figure 1 The dielectric cell comprising a cylindrical hollow cell body (earth electrode) (A), a cylindrical inner electrode (B), a screw-top lid (C), a filler cap (D), an inner perforated lid (E), a drain tap (F), connections to GenRad 1689 Bridge (G) and a coolant (H)

fractions of very high molecular weight were excluded from the h.p.l.c. columns. Proton n.m.r. 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[2]. The isotactic contents of F1, F2 and F3 were found to be 24, 51 and 33%, respectively. For PVK samples F1 and F2, tacticity was also estimated from ^{13}C n.m.r. spectra using a method outlined by Kawamura and Matsuzaki[18]. Isotactic contents were 30 and 59% for PVK samples F1 and F2, respectively. These results matched fairly closely the results obtained from proton n.m.r. A dipole moment study was also carried out on *N*-ethylcarbazole, which is close in structure to a single repeat unit of PVK.

Dielectric measurements

All the dielectric permittivities, listed in *Tables 1* and *2*, were obtained using a GenRad 1689 Bridge apparatus operating at a frequency of 1 kHz. The dielectric cell comprised two cylindrical blocks of brass (*Figure 1*). The external surfaces were nickel-plated and the internal surfaces in contact with the sample were gold-plated. The outer cylinder was hollow to allow passage of a coolant liquid. The cell was fitted with an external screw-top lid through which the cell could be filled. An internal perforated lid ensured that the effective sample volume of the dielectric cell was reproducibly constant and independent of the exact sample volume (approximately 20 cm^3) provided that the liquid level was above the internal lid. The height and diameter of the inner cylindrical electrode were 35 and 33 mm, respectively. The electrode gap was approximately 1.5 mm. The temperature of the cell could be controlled to better

Table 3 Gradients (Δ/C) [see equation (1)] for various samples of PVK and *N*-ethylcarbazole (NEK) in solution in 1,4-dioxane

Temperature (K)	(Δ/C) (cm^3 mol^{-1})			
	F1	F2	F3	NEK
288	374	1260	844	601
298	362	1184	839	561
308	365	1153	822	554
318	356	1099	802	518
328	333	1082	787	499
338	335	1022	753	484

Table 4 Gradients (Δ/C) [see equation (1)] for various samples of solutions of PVK and *N*-ethylcarbazole (NEK) in solution in toluene

Temperature (K)	(Δ/C) (cm^3 mol^{-1})			
	F1	F2	F3	NEK
288	444	741	643	526
298	429	744	661	514
308	445	768	637	514
318	424	688	670	528
328	486	822	688	553
338	481	671	591	391

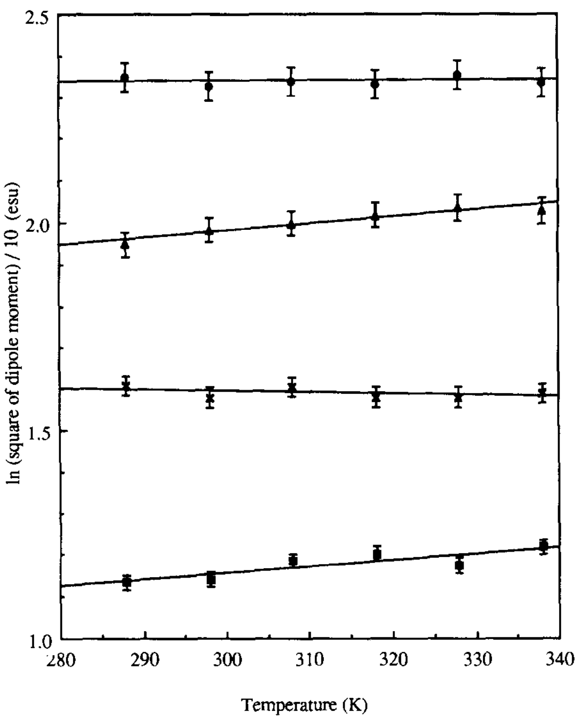

Figure 2 Temperature coefficients of average dipole moment per repeat unit of stereoregular forms of PVK (■, F1; ●, F2; ▲, F3) and *N*-ethylcarbazole (×) measured in 1,4-dioxane

Table 5 Temperature dependence of dipole moments per repeat unit (esu = electrostatic units) of various stereoregular forms of PVK and *N*-ethylcarbazole (NEK) in solution in 1,4-dioxane

Temperature (K)	$10^{18}\langle\mu\rangle$ (esu)			
	F1	F2	F3	NEK
288	1.764	3.236	2.644	2.235
298	1.768	3.200	2.694	2.202
308	1.810	3.216	2.716	2.230
318	1.825	3.208	2.741	2.202
328	1.799	3.245	2.766	2.203
338	1.840	3.214	2.758	2.212

Table 6 Temperature dependence of dipole moments per repeat unit (esu = electrostatic units) of various stereoregular forms of PVK and *N*-ethylcarbazole (NEK) in solution in toluene

Temperature (K)	$10^{18}\langle\mu\rangle$ (esu)			
	F1	F2	F3	NEK
288	1.841	3.271	2.211	2.002
298	1.850	3.352	2.253	2.020
308	1.922	3.480	2.220	2.060
318	1.921	3.371	2.291	2.121
328	2.090	3.773	2.333	2.231
338	2.050	3.483	2.171	1.912

than ±0.05°C. The instrument was calibrated at every working temperature with air ($\epsilon_0 = 1.000$) and using liquids with well-known dielectric constants ($\epsilon_{\text{toluene}} = 2.379$ and $\alpha_{\text{cyclohexane}} = 2.015$ at 298 K)[19]. Dielectric increments of solutions of F1, F2, F3 and *N*-ethylcarbazole were measured at several temperatures in the temperature range 288 to 338 K. Dielectric permittivity of solvents, 1,4-dioxane and toluene, was also measured at this temperature range.

Mean-square dipole moments $\langle\mu^2\rangle$ per repeat unit of the polymer chain were calculated using the Guggenheim–Debye equation[20]:

$$\langle\mu^2\rangle = \frac{27kT}{4\pi N_{\text{L}}(\epsilon_1 + 2)(n_1^2 + 2)}(\Delta/C)_{c\to 0} \qquad (1)$$

where ϵ_1 is the dielectric permittivity of pure solvent, ϵ_{12} is the dielectric permittivity of solutions of the polymer dissolved in the same solvent, n_1 is the refractive index of the solvent, k is the Boltzmann constant, N_{L} is Avogadro's number, $\Delta = (\epsilon_{12} - n_{12}^2) - (\epsilon_1 - n_1^2)$, and $(\Delta/C)_{c\to 0}$ is the limiting gradient of the plot of Δ *versus* concentration (mol cm^{-3}) (see *Tables 3* and *4*).

The refractive index of 1,4-dioxane and toluene was measured at 632.8 nm over the temperature range 288–338 K. Since the polymers were dissolved in these solvents at very low concentration (0.25–2.0% w/v) it was assumed that the solution refractive index was equal to that of the solvent, normally an acceptable approximation if the dipole moment of the solute is not too small.

RESULTS AND DISCUSSION

From *Table 1* and *Figure 2* it is evident that all PVK samples have negative temperature coefficients of dielectric increment, i.e. as the temperature rises the dielectric permittivity falls. This suggests that the dielectric permittivity is significantly affected by temperature and that this is related to the degree of tacticity of the polymers. The dielectric permittivity of the polymer solutions increases with increasing isotactic content of the polymer. The highest dielectric permittivities of sample F2 are correlated to the higher isotacticity of this polymer. Therefore, F3 with an isotactic content lower than that of F2, would be expected to exhibit gradients lower than those of F2, but higher than F1, and this is found to be the case.

By substituting values of $(\Delta/C)_{c\to 0}$ (*Tables 3* and *4*)

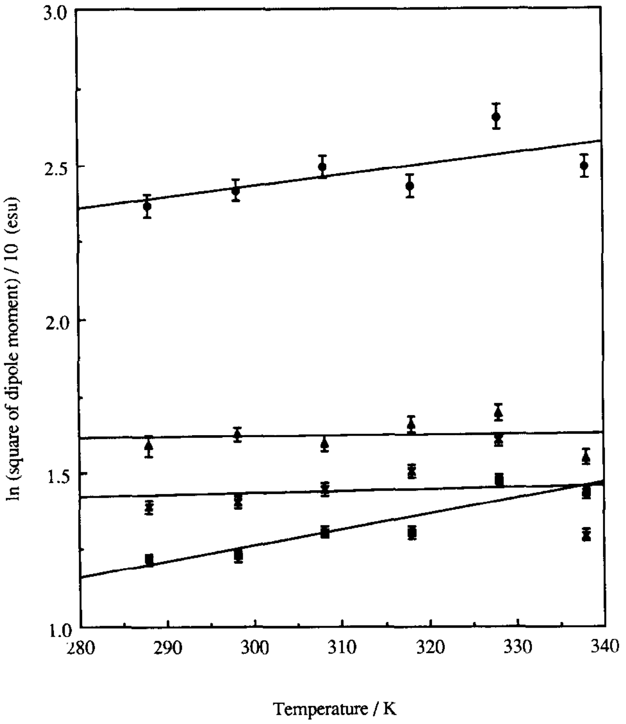

Figure 3 Temperature coefficients of average dipole moment per repeat unit of stereoregular forms of PVK (■, F1; ●, F2; ▲, F3) and N-ethylcarbazole (x) measured in toluene

into the Guggenheim–Debye equation, the average dipole moment per repeat unit of each of the PVK samples and that of N-ethylcarbazole were calculated (*Tables 5* and *6*). The temperature coefficient of the dipole moments is defined experimentally as the quantity

$$\frac{\mathrm{d}(\ln\langle\mu^2\rangle)}{\mathrm{d}T} \qquad (2)$$

Graphs of $\ln\langle\mu^2\rangle$ *versus* temperature are presented in *Figure 3*. These graphs show three important features. First, sample F1, with the least isotactic content, shows the smallest average dipole moment per repeat unit but the largest positive temperature coefficient. The polymers F1 and F3 (synthesized using AIBN and $AlCl_3$ catalysts respectively), as judged by n.m.r. data, possess mainly syndiotactic stereostructures. Space-filling models and computer-simulated structures show the possibility of forming 2/1 helices that are not as sterically hindered as the 3/1 helices believed to be formed in isotactic-rich F2[3,15]. 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 pendent 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 a decrease in the cancellation of the dipole moments of the repeat units.

The second point concerns sample F2, the polymer with the 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 helices and that the polymer chains are fairly rigid. At lower temperatures the chains are more 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 helices (where the pendent 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 helices. 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.

Table 7 Temperature coefficients of dipole moments of various PVK polymers and N-ethylcarbazole (NEK) measured in solution in 1,4-dioxane and in toluene

	$10^3(\ln\langle\mu^2\rangle)/\mathrm{d}T$ (K)	
Sample	1,4-Dioxane	Toluene
F1	1.7 ± 0.5	9.2 ± 2.2
F2	0.2 ± 0.2	3.6 ± 2.5
F3	1.8 ± 0.4	8.5 ± 0.8
NEK	−0.2 ± 0.3	0.4 ± 5.0

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.

It is interesting to note that sample F2 has an average dipole moment per repeat unit that is larger than that of 9-ethylcarbazole, whereas samples F1 and F3 have smaller values. These observations reflect accumulative or attenuating effects, respectively, of dipole moment vectors. Consequently, in this study, it was found that the highly isotactic polymers had dipole moments that were larger than those of the syndiotactic polymers. The temperature coefficient for polymer F1 (0.0017 K^{-1}) compares well with the results obtained by Riande *et al.*[14] (0.0021 K^{-1}) measured under similar conditions. As far as the authors are aware, the temperature coefficients of the dipole moments of PVK polymers with different tacticities have not been published by these or any other workers.

The temperature coefficients (*Table 7*) for all the PVK polymers measured in toluene are larger than the values measured using the solvent 1,4-dioxane. This observation probably reflects the fact that toluene can be considered as a poor solvent: the PVK molecules are 'crumpled up' and there are minimal van der Waal's interactions between repeat units and solvent molecules. 1,4-Dioxane, on the other hand, is believed to be a better solvent and thought to have stronger van der Waal's interactions with the PVK molecules. In the latter case the polymer molecules are induced to expand and, as a consequence it is possible that the helices start to unwind, i.e. tend to form random coil configurations at increased temperature.

For the model compound N-ethylcarbazole, it is reasonable to assume that there should be no increase in the dipole moment as the temperature increases. In fact, as the temperature increases the dipole moment of *N*-ethycarbazole does show a slight increase over the temperature range of 288–338 K, but this is probably attributable to experimental deficiencies.

CONCLUSIONS

It can be concluded that the temperature coefficients of dipole moments of PVK samples are highly dependent on the stereostructure and tacticity of the polymers. Sample F1 with the least isotactic content (prepared with a free-radical catalyst) possesses the smallest dipole moment per repeat unit but has the largest positive temperature coefficient. The dielectric data may be explained if it is assumed that the polymer possesses mainly syndiotactic stereostructures with 2/1 helices that are not as sterically hindered as 3/1 helices formed in sample F2. At low temperatures, the chains are very much restricted in their movement, and hence maintain their basic helical conformation. This conformation enables the cancellation of dipole moments to some extent, resulting in lower dipole moments at low temperatures. As the temperature increases, there is more thermal energy and hence rotation of the pendent groups and polymer chain movement also increase, resulting in some disruption of the helical structure. This change in the helical structure leads to a decrease in the cancelling of the side-group dipole moments and a consequential increase in the mean dipole moment per repeat unit. Polymer type F2 with 3/1 helical chains appears to be sufficiently sterically hindered and less affected by increases in temperature. Thus, samples of F2 tend to retain their basic helical configurations and as a consequence their temperature coefficients are lower than those measured for polymers F1 and F3. The model compound, *N*-ethylcarbazole, shows no significant temperature coefficient. In the present study, $\langle \mu^2 \rangle$ values were not found to depend on molecular weight or polydispersity, but it is possible that such a dependence might be observed for PVK samples possessing sufficiently low molecular weight.

ACKNOWLEDGEMENT

The authors would like to thank the Engineering and Physical Science Research Council, EPSRC, for a research grant to M. Fiaz.

REFERENCES

1 Shaffert, R. *IBM J. Res. Dev.* 1971, **15**, 75
2 William, D. J. and Froix, M. F. *Polym. Prepr.* 1977, **18**, 445
3 Griffiths, C. H. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 1167
4 Debye, P. and Bueche, F. *J. Chem. Phys.* 1951, **19**, 589
5 North, A. M. and Phillips, P. J. *Chem. Commun.* 1968, **21**, 1340
6 North, A. M. and Phillips, P. J. *J. Br. Polym.* 1969, **1**(2), 76
7 Dev, S. B., Lochhead, R. Y. and North, A. M. *Faraday Soc.* 1990, **49**, 244
8 Pochan, J. M., Hinman, D. F., Froix, M. F. and Nash, R. W. *Polym. Prepr.* 1975, 570
9 Froix, M. F., Williams, D. J., Pochan, J. M. and Geodde, A. O. *Polym. Prepr.* 1975, 576
10 Pochan, J. M., Hinman, D. F. and Nash, R. W. *J. Appl. Phys.* 1975, **46**(10), 4115
11 Mumby, S. J. and Beevers, M. S. *Polym. Commun.* 1984, **25**, 173
12 Mumby, S. J. and Beevers, M. S. *Polymer* 1985, **26**, 2013
13 Sundararajan, P. R. *Macromolecules* 1980, **13**, 512
14 Riande, E., Barrales-Rienda, J. M., Molina, M. R. and Saiz, E. *Macromolecules* 1984, **17**, 2728
15 Mikawa, H., Kasai, K., Kusahoyashi, S., Hirata, H. and Kimura, A. *J. Polym. Sci. Pt A-2* 1970, **8**, 613
16 Sitaramaiah, G. and Jacobs, D. *Polymer* 1970, **11**, 165
17 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', 3rd Edn, Interscience, New York, 1989
18 Kawamura, T. and Matsuzaki, K. *Makromol. Chem.* 1978, **179**, 1003
19 Lide, R. D. 'Handbook of Chemistry and Physics', 75th Edn, CRC Press, London, 1994
20 Guggenheim, E. A. *Trans. Faraday Soc.* 1949, **45**, 714