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Relaxation in Poly(N-Vinylcarbazole) and Ring Chlorinated Derivatives

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Introduction

Relaxation experiments on PVK and poly(3-chloro-N-vinyl carbazole) have revealed four relaxations originating in the glass transition, carbazole wagging, carbazole rotational libration and localised backbone motions from high to low temperature respectively (POCHAN ET AL, 1975). The work was carried out on high molecular weight ($M_w \sim 1.4 \times 10^6$), bulk polymerised material. Recent evidence suggests (OKAMOTO ET AL. 1976) that such material is syndiotactic, but that the sequence lengths may be short in low molecular weight materials (WILLIAMS, FROIX 1977). In order to discover the influence of stereoregularity and molecular weight on relaxation behaviour we have studied the dielectric and nmr relaxation properties of materials prepared by cationic polymerisation in solution. The molecular weights are low and the polymers are thought to contain substantially more isotactic sequence than the commercial material.

Experimental

Two samples of PVK were separately prepared by tropylium perchlorate initiation in dichloromethane solution followed by precipitation into excess methanol. M_n values were 3.8×10^3 and 19×10^3 (Membrane Osmometer, toluene, 37°C) respectively. The lower molecular weight sample was ring chlorinated using 1-chlorobenzotriazole in the appropriate concentration in dichloromethane to produce 1:1, 1:2, 1:4 and 1:8 ratios of chlorine to carbazole rings in the substituted polymers (BOWYER ET AL, 1976). G.p.c. in toluene at 45° showed no changes from the original PVK in degree of polymerisation or molecular weight distribution due to this procedure. Elemental analysis confirmed the expected chlorination ratios. X-ray diffraction (Ni filtered CuKα) revealed two amorphous halos in all samples similar to those reported by KIMURA ET AL.(1970) and CRYSTAL (1971) corresponding to spacings of about 34Å (variable) probably reflecting interchain separation and 5.2Å (constant to ± 0.1Å between all polymers) corresponding to carbazole ring separation. This is consistent with an isotactic vinyl polymer with a 3_1

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helix (GRIFFITHS 1978).

Differential scanning calorimetry (16°C min^{-1}) exhibited traces characteristic of a glass transition at 238°C for the PVK samples and at 226 ± 2°C for all the chlorinated derivatives. The value for PVK is higher than the 227°C usually quoted but this may reflect the increased isotacticity (OKAMOTO ET AL. 1976).

Dielectric measurements in the 10^{-5} to 10^{-3} Hz range were performed using the step-response technique followed by Fourier transformation and in the 10^{2} to 10^{6} Hz regime by transformer ratio-arm bridge methods. The experimental details and those of sample preparation are given elsewhere (BLOCK ET AL. 1975). Nmr measurements using pulse techniques yielded spin-lattice relaxation times at a spectrometer frequency of 21 MHz and rotating frame data at an equivalent frequency of 5 x 10^{4} Hz (BLOCK ET AL. 1977). The dielectric and nmr results were transformed to the same frequency scale using established formulae (MCCALL 1966).

A sample of N-vinyl carbazole monomer was dispersed in a polystyrene matrix at 20% w/w concentration by co-dissolving the components in toluene followed by film casting on a mercury surface to produce a disc for dielectric studies. The residual solvent was removed in vacuo at room temperature.

Results and Discussion

Fig. 1 shows the results obtained from the step response experiments together with a line extrapolated from the α relaxation data of POCHAN ET AL.(1975). Clearly, despite the large five decade extrapolation, the same mechanism is involved and the glass-transition is being observed. There is no reliable trend in appearance temperatures among the chlorinated materials and the data are insufficiently accurate to add to the D.S.C. observations. One point to emerge, however, is that the α relaxation appears to be very little affected by dropping the molecular weight substantially. This is surprising when it is remembered that the Tg (and the associated relaxation) of amorphous polymers is usually considered to be independent of molecular weight only above a limit of about 10^{4}. The morphology must be such that the packing around the chain ends is little different to that about the main chain, thus supporting the view of GRIFFITHS (1978) that the carbazole "side-chain" is dominating and directing the main chain behaviour.

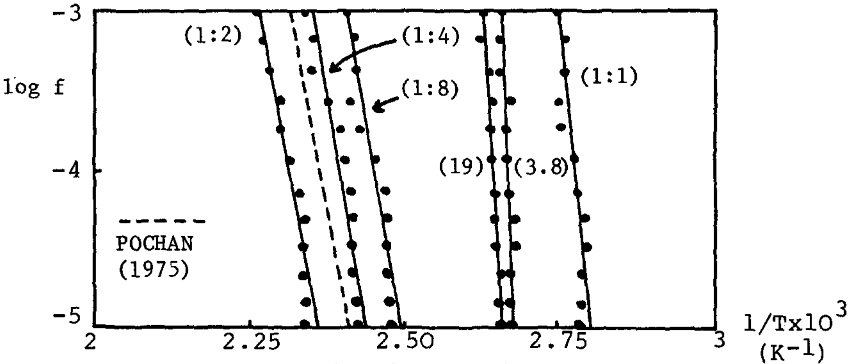

Fig.1 The α relaxation

We have found no evidence in any of our experiments for the existence of a β relaxation in the positions found by POCHAN (1975). This is unexpected if their assignment to a carbazole wagging motion is correct since changes in molecular weight or stereoregularity in the main chain will not change this motion substantially. It seems possible that the β relaxation originates in a local motion of backbone segments which, in the short polymer chains studied here will not be independently observed but subsumed into the α relaxation. This point is further explored later.

The region of the γ relaxation is illustrated in Fig. 2, including the results of POCHAN ET AL.(1975). As previously reported by them, this relaxation is dielectrically inactive in PVK but the chlorinated (or oxidised) material exhibits a substantial loss. As expected, the nmr experiment responds to the molecular motion in all materials. On the basis of the oxidation work POCHAN (1975) interpreted this relaxation as originating in rotational libration of the carbazole unit and we have confirmed this assignment using the carbazole/polystyrene matrix. It is known (WILLIAMS, HAINS 1975) that the incorporation of small polar molecules into predominantly non-polar polymeric matrices can yield significant information on the guest's molecular motion, which may be used as a diagnostic aid in interpreting polymer behaviour (LEDWITH ET AL. 1978). We have observed N-vinyl carbazole rotation in the matrix at about 0°C (Fig. 3) and this is shown in Fig. 2 to correspond very closely in position and activation energy to the polymeric γ relaxations. The effective relaxing dipole in the matrix calculated from the Onsager equation is 1.47×10^{-30} Cm which compares favourably with the solution monomer dipole of 1.97×10^{-30} Cm calculated using the Guggenheim method. With the exception of the dielectric data on the matrix and the 1:1 chlorinated material, the activation energies are based on the two point nmr measurements and are

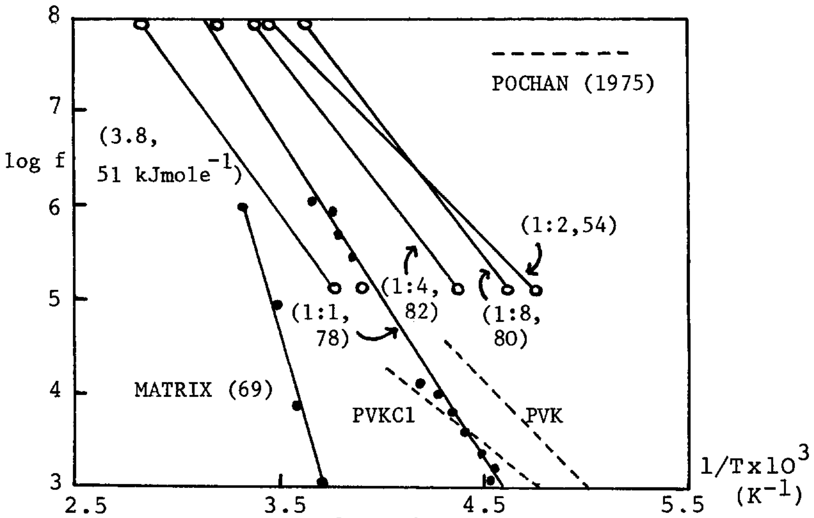

Fig.2. The γ Relaxation.

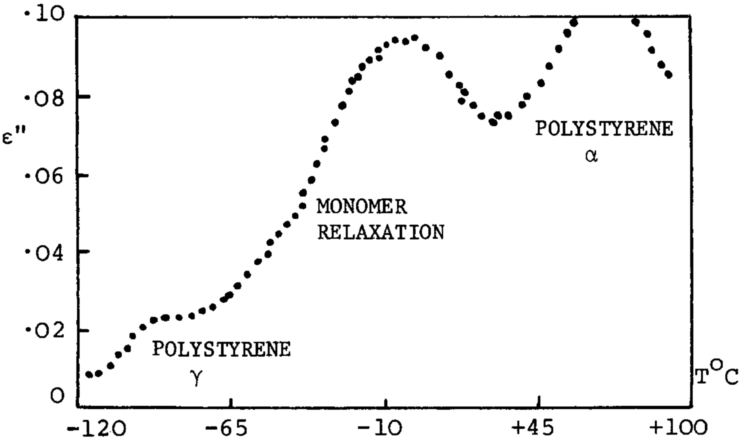

Fig.3. Dielectric loss in the matrix at 10^3Hz.

not sufficiently accurate to warrant discussion. However, the dielectric measurements clearly indicate that the carbazole libration is considerably more hindered than in the high molecular weight polymers. We are not yet sure of the reason for this. In view of this effect it may be that the carbazole wagging motion is similarly hindered thus shifting the β relaxation of POCHAN (1975) into the region dominated by the α relaxation where it cannot be separately observed.

There is nmr evidence of further relaxations to lower temperatures (∿ -150^{o}C) which may correspond with the δ relaxations but an evaluation of this requires further experimental consideration.

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