Dielectric Properties of Poly-(*N*-vinylcarbazole) Solutions

By A. M. NORTH*
(*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow,* C.1)
and P. J. PHILLIPS
(*Donnan Laboratories, University of Liverpool, Liverpool*)

THE current interest in the dielectric, charge-transfer, or energy-transfer properties of poly-(*N*-vinylcarbazole) has focussed attention on the ease of rotation about backbone bonds in this polymer. It has been suggested[1] that, in solution, poly-(*N*-vinylcarbazole) chains are sterically hindered and undergo segmental motion only with difficulty. To examine this thesis we measured the dielectric properties, between 10^2 and 10^{10} Hz, of certain polymers in toluene as solvent, by experimental techniques previously described.[2]

The measured and the predicted[3] relaxation frequencies for polymers, with components of each monomer dipole arranged unidirectionally along the chain contour, are compared in Table 1. It can be seen that the low molecular-weight polymers show dielectric behaviour which accords with that expected for a rigid rod, but that the dielectric relaxation of the highest molecular-weight sample occurs at a higher frequency than that predicted for a perfectly rigid entity.

TABLE 1

Relaxation parameters for poly-(N-*vinylcarbazole) solutions* (10% *by wt.*) *in toluene at* 25°

Molecular weight $\times 10^{-3}$	$f_{\max}$ (MHz)	f_{relax} (rigid rod) (MHz)	f_{relax} (1st-mode non-free-draining coil) (MHz)
1·66	60	69	102
4·72	9	9·6	14·1
45·7	0·9	0·12	0·17

Dipole moments of a variety of polymers have been evaluated by the method of Guggenheim[4] and Smith,[5] and are presented in Table 2 where μ is the dipole moment and Z the number average degree of polymerization of the chain. At the lowest molecular weights, $\mu/Z^{\frac{1}{2}}$ increases as $Z^{\frac{1}{2}}$. However at molecular weights above about 10,000, $\mu/Z^{\frac{1}{2}}$ becomes independent of molecular weight, exhibiting a limiting value of about 2·1 D.

TABLE 2

Dipole moment parameters for poly-(N-*vinylcarbazole) in toluene at* 25°

$Z^{\frac{1}{2}}$	μ (D)	$\mu/Z^{\frac{1}{2}}$ (D)
isopropylcarbazole	2·96	—
2·93	4·51	1·54
4·97	8·62	1·74
15·4	34·7	2·16
21·1	40	2·00
21·8	42·5	1·95
23·9	49·9	2·09

The behaviour at low molecular weights can be explained only if the molecule behaves as a rigid rod with dipole moment component 0·10 D per monomer unit lying unidirectionally along the rod. The high molecular weight behaviour corresponds to a random coil in which each monomer has an unresolved dipole moment of about 2·1 D. Comparison of the results for very high and very low molecular weights suggests that about 400 monomer units are required to form an equivalent freely rotating chain segment.

Such dielectric behaviour has not previously been observed in vinyl polymers, and confirms the hypothesis that in solution poly-(N-vinylcarbazole) molecules form very stiff chains.

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