

Molecular relaxation processes in poly(*N*-acryloyl-10,11-dihydrodibenz[*b, f*]azepine)

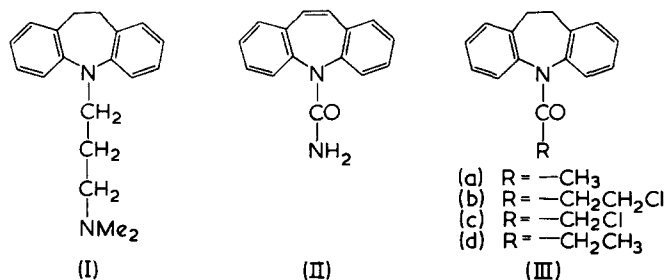
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The preparation and homopolymerization of *N*-acryloyl-10,11-dihydrodibenz[*b, f*]azepine is described. The relaxation behaviour is characterized using dielectric relaxation, pulsed n.m.r. and thermally stimulated depolarization (t.s.d.) techniques. In order to assist the assignment of relaxation data to molecular behaviour 5-chloroacetyl and 5-propionyl derivatives of iminobibenzyl were prepared and studied by dielectric relaxation in the matrix-isolated state. Comparison with *N*-ethyl carbazole under similar conditions revealed the existence of a relaxation in the polymer associated with nitrogen inversion in addition to a relaxation due to the glass transition. The data may be useful in studies relating to the pharmacological activity of the dibenz[*b, f*]azepine ring system.

Derivatives of the dibenz[*b, f*]azepine ring system¹ exhibit pharmacological activity as exemplified by the psychotropic drugs² imipramine (I) and carbamazepine (II).

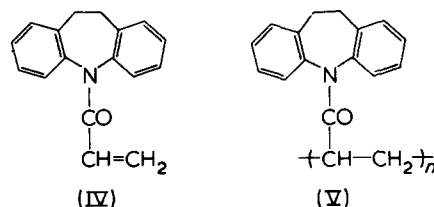


X-ray crystallographic studies³ show clearly that imipramine (I) is non-planar with the two aromatic rings twisted by rotation of the ethano bridge unit. The central ring nitrogen atom in imipramine and related molecules lies above the planes of the two aromatic rings and undergoes the usual trivalent nitrogen (flipping) conformational process. This central ring inversion process occurs readily in *N*-alkyldibenzazepine derivatives because of the essentially free rotation around the ring nitrogen-alkyl group bond and is too rapid for study by n.m.r. techniques. However, for *N*-acyl derivatives (e.g. II and III) hindered rotation about the *N*-acyl bond produces a concomitant decrease in the rate of ring inversion due to the buttressing effect of the dibenzo groups. Variable temperature ¹H and ¹³C n.m.r. spectroscopic studies⁴ have established that for *N*-acetyl-10,11-dihydrodibenz[*b, f*]azepine (*N*-acetyl-10,11-dihydrodibenz[*b, f*]azepine (*N*-acetyl-10,11-dihydrodibenz[*b, f*]azepine) (IIIa), the central ring conformation is about 50° buckled, and temperature effects on the coalescence spectra are consistent with a general picture of a concerted amide bond rotation-ring inversion mechanism. However it is not yet clear whether there is only one molecular rate process occurring or whether more than one is involved.

The study of conformational equilibria in polymers by

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the dielectric relaxation technique is now well established⁵ and it seemed that polymeric analogues of (III) would afford useful substrates for such studies and might also assist in resolving mechanistic details of the restricted amide bond rotation-ring inversion in compounds such as (II) and (III). Polymeric analogues of (III) were most easily obtained by homo- and copolymerization of *N*-acryloyl-10,11-dihydrodibenz[*b, f*]azepine [NADDBA, (IV)] and the present paper describes the synthesis, dielectric relaxation, ¹H n.m.r. relaxation and thermally stimulated depolarization (t.s.d.) behaviour of poly(NADDBA) (V).



In addition to the study of poly(*N*-acryloyl dibenzazepine) itself, certain model compounds were investigated to assist in assigning the polymer relaxation processes to their molecular origins. The 5-chloroacetyl (IIIc) and 5-propionyl (III d) derivatives were prepared and their dipole moments measured together with *N*-ethyl carbazole. These three compounds were also dispersed in a polystyrene matrix to determine their isolated rotational behaviour⁶.

Evidence is presented for the existence of two relaxations in the polymer which may be associated with the glass transition and with inversion about the iminobibenzyl nitrogen respectively.

EXPERIMENTAL

Preparation of materials

5-(3-chloropropionyl) iminobibenzyl (IIIb). To a stirred solution of 48.7 g (0.4 mol) of iminobibenzyl in 500 ml of sodium-dried benzene was added slowly 31.6 g (0.4 mol)

of 3-chloropropionyl chloride. The reaction mixture was refluxed for 7.5 h and allowed to cool. After pouring into water and extracting several times with chloroform, the organic layer was washed twice with water and dried over MgSO_4 . Evaporation of the solvent and recrystallization from absolute ethanol yielded 58.4 g (82.7%) of (IIIb) as slightly off-white crystals: m.p., 106.5–107.5°C; ν_{max} , 1670 (C=O), 1600, 1580, 1310, 1270, 970, 950, 780 and 750 cm^{-1} ; τ [CDCl_3], 2.25 (8H, s, ArH), 6.15 (2H, t, J = 13 Hz, $-\text{CH}_2\text{Cl}$), 6.58 (2H, two d, J = 4 Hz, $-\text{COCH}_2-$) and 7.15 (4H, m, ethano bridge).

5-Acryloyliminobibenzyl (IV), NADDBA. To a stirred solution of 15.0 g (0.053 mol) of (IIIb) in 280 ml of dry dimethyl sulphoxide was added 8.1 g (0.053 mol) of DBU (1,8-diazabicyclo[5, 4, 0]undec-7-ene). The solution was stirred at 90°C for 4 h and then allowed to cool. The solution was then poured into water in small portions and extracted with dichloromethane. The combined extracts were washed several times with large volumes of water, then dried over MgSO_4 . Evaporation of the solvent and recrystallization from propan-2-ol (charcoal) yielded 9.8 g (75%) of the monomer, (IV), as white crystals, m.p., 101–102°C. Found: C, 81.7%; H, 6.0%; N, 5.8%; O, 6.5%. $\text{C}_{17}\text{H}_{15}\text{NO}$ requires: C, 81.9%; H, 6.1%; N, 5.6%; O, 6.4%. ν_{max} 1680 (C=O), 1610, 1580, 1495, 1410, 1335, 1270, 975, 795, 780 and 755 cm^{-1} . τ [CDCl_3], 2.81 (8H, s, ArH), 3.59 and 3.64 (2H, two d, $J_a = 4.2$ Hz, $J_b = 9.0$ Hz, two vinyl protons), *t,t*3 (1H₂m, $J_a = 4.0$ Hz, $J_b = 9.0$ Hz, one vinyl proton), and 6.93 (4H, m, ethano bridge). *m/e* 249 (M^+ , 30%), 221 (M-bridge 5), 195 (M-COC₂H₂, 100), 180 (10), 167 (10), 165 (7), *m** 166 (195 → 180), *m** 153 (249 → 195).

Polymerization of NADDBA (IV). The polymerizations were performed in heavy-walled glass polymerization vessels that had been thoroughly cleaned and then oven-dried (110°C). Recrystallized monomer, and a solution of initiator (AIBN) in dried methanol were placed in the tube and the vessel degassed through four freeze-thaw cycles on a high vacuum line (10⁻³ mmHg). The vessel was removed from the vacuum line and placed in a thermostatically controlled constant temperature bath at 70 ± 0.1°C. After polymerization the vessel was opened and the solution poured into a large excess of petroleum ether. The polymer was filtered, washed, dried and weighed. The following were the conditions used: monomer, 5 g; 13.3 mg AIBN in 12.5 ml methanol; time, 9.5 h; yield, 40%. Seven such polymerizations were performed. The polymers were combined by dissolving them in approximately 100 ml of dichloromethane. One homogeneous polymer was then collected by precipitation into a ten-fold excess of petroleum ether. In this way, around 17 g of poly(NADDBA) was produced for use in the dielectric relaxation studies. The polymer was found to have a number-average molecular weight, M_n , of 38 000.

5-Chloroacetyliminobibenzyl (IIIc). 14 ml of chloroacetylchloride was added to a stirred solution of 29.25 g (0.15 mol) of iminobibenzyl in 100 ml of dry benzene and the solution refluxed for 4 h. After cooling, the solvent was removed and the resulting oil taken up into 100 ml of 1:2 (v/v) petrol (60–80°C): EtOH; 35.7 g (88.9%) of the chloroacetyl derivative were collected as slightly off-white crystals m.p. 96–97°C. The compound was recrystallized twice before use, and its identity and purity was checked by i.r. and n.m.r. spectroscopy.

5-Propionyliminobibenzyl (III d). 12 g of propionyl chloride was added to a stirred solution of 19.5 g (0.1 mol)

of iminobibenzyl in 100 ml of dry benzene and the solution refluxed for 3 h. After cooling the solution was poured into dichloromethane, washed three times with water and then dried over MgSO_4 . The oil obtained by evaporation of the solvent was recrystallized from ethanol. 14.5 g (58%) of the propionyl derivative was collected as white crystals (m.p. 72–74°C). The compound was recrystallized twice before use and once again its identity and purity was checked by i.r. and n.m.r. spectroscopy.

Instrumental technique

Polymer samples for dielectric studies were prepared by compression (1 h at a pressure of $\sim 10^7$ N/m²) at room temperature to form a disc 5.08 cm in diameter and approximately 1.5 mm thick. The surfaces were coated with tin foil (25 μm) affixed by purified petroleum jelly and placed in a specially constructed dielectric cell. Full details of the apparatus have been given elsewhere⁸. Measurements were made from 10⁵ to 10⁶ Hz using Wayne-Kerr B221 and B601 bridges over a temperature range of from -100° to +200°C. The material was also studied by the same techniques after quenching in liquid nitrogen after being held for a period of 5 h at a temperature of 200°C.

The model compounds were prepared in matrix form for dielectric studies by co-dissolving the compound with polystyrene (previously purified by reprecipitation) in THF. The solvent was then stripped on a rotary evaporator and the matrix chips thoroughly dried in a vacuum oven at 60°C to constant weight (approximately 3 h). Dielectric samples were then prepared by compression moulding at 130°C for ½ h using a pressure of $\sim 10^6$ N/m² again producing discs approximately 1.5 mm thick. The concentration of small molecules in the matrix was determined by the need to ensure the maximum observable dielectric response consistent with maintaining compatibility between the two components. Ultimately the concentrations used were all approximately 17% by wt.

Thermally stimulated depolarization (t.s.d.) experiments were kindly performed on the polymer by Dr J. M. Pochan of Xerox. Gold-coated pressed powder samples (1.3 mm thick) were polarized at 150°C and 1.3 kV for 1¼ h. The depolarization scan was initiated at -196°C and continued at a rate of 2.31°C/min.

Dipole moments of the model compounds were calculated by the method of Guggenheim⁹ from room temperature permittivity measurements in successively diluted toluene solutions. Refractive indexes were obtained by using an Abbé refractometer.

Nuclear magnetic relaxation measurements were carried out on the polymer using a Polaron pulsed n.m.r. spectrometer operating at 21 MHz. T_1 data were obtained from the 90- τ -90 sequence and rotating frame data, at an equivalent frequency of 5×10^4 Hz, from the spin locking technique. Full experimental details have been given elsewhere⁸.

A Perkin-Elmer DSC-1B differential scanning calorimeter operating at a scan rate of 16°C/min on compressed pellets was used to estimate the glass transition temperature. X-ray powder diffraction photographs were taken using nickel filtered $\text{CuK}\alpha$ radiation.

RESULTS

The dielectric relaxation spectrum of poly(NADDBA) exhibits two loss peaks as shown in *Figure 1*. In the untreated

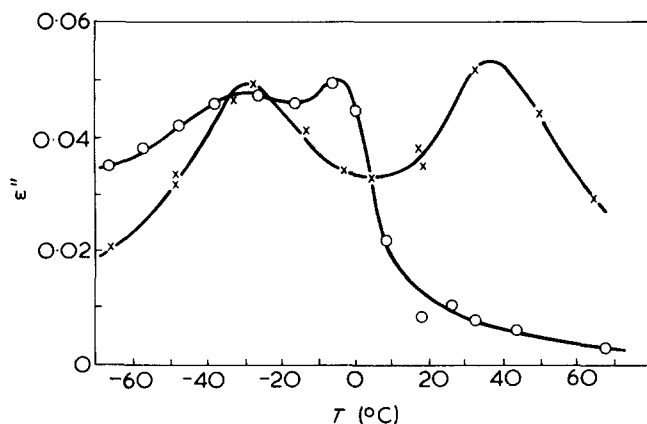


Figure 1 Dielectric loss behaviour of poly(NADDBA) as a function of temperature at 10^4 Hz: X, fresh sample; O, quenched sample

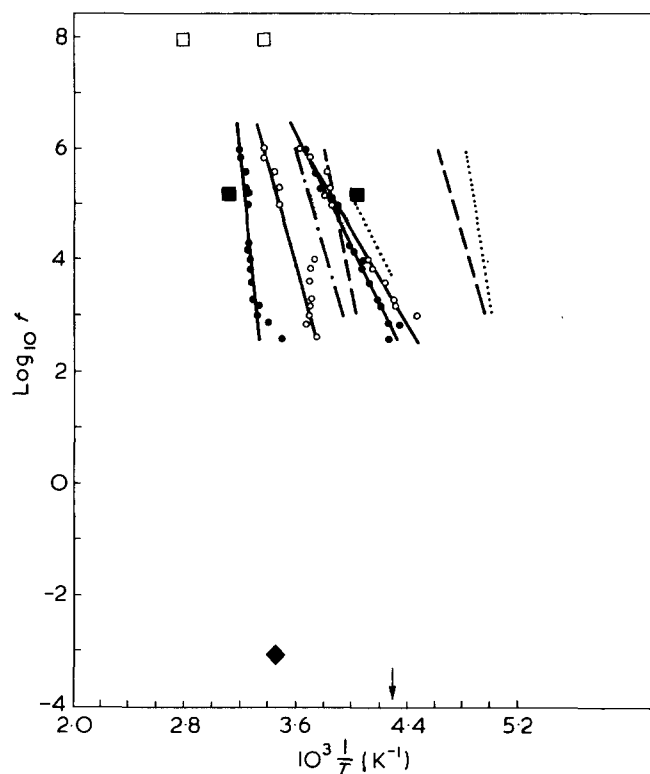


Figure 2 Arrhenius presentation of the relaxation behaviour of poly(NADDBA) and the model compound matrixes. ●, Dielectric data on poly(NADDBA) fresh sample; ○, dielectric data on poly(NADDBA) quenched sample; □, n.m.r. T_1 data on poly(NADDBA); ■, n.m.r. $T_{1\rho}$ data on poly(NADDBA); — — —, dielectric data on *N*-ethyl carbazole matrix; - · - ·, dielectric data on 5-chloroacetylaminobibenzyl matrix; · · · ·, dielectric data on 5-propionyliminobibenzyl matrix; ◆, t.s.d. data on poly(NADDBA); ↓, d.s.c. transition on quenched poly(NADDBA)

sample these are close and difficult to resolve in the frequency plane, but representation as a function of temperature clearly indicates two processes. No evidence was found for dielectric activity outside this relatively narrow temperature region despite the wide temperature range employed for the experiments. Quenching the sample produced a marked change in the separation of the loss peaks (Figure 1) with the high temperature process moving to substantially lower temperatures and overlapping considerably with the second peak which appears to have been only marginally shifted by the heat treatment. Indeed, resolu-

tion of the two peaks is now so difficult that it is impossible to be certain about the positional changes (if any) shown by the lower temperature process. The complete range of frequency-temperature data have been plotted in Figure 2 in the form of a Arrhenius diagram from which the activation energies recorded in Table 1 have been derived.

The n.m.r. results on the polymer indicated the presence of three relaxations within the temperature range -196° to $+180^\circ\text{C}$ as shown in Figure 3. There was some evidence for non-exponential decays in the magnetization in the rotating frame but the proportion of the minor component was insufficiently large to permit accurate resolution¹⁰. Figure 3 therefore shows only the major or long component of the decays. The two highest temperature relaxations have also been plotted on the relaxation map (Figure 2) using well established relations for the correlation frequencies at the temperature minima¹¹ and for translating

Table 1 Activation energies of the transitions (kJ/mol)

System	High temperature relaxation	Low temperature relaxation	Methyl rotation
Poly(NADDBA)			
Fresh sample	241 (dielectric) 156 (n.m.r.) 127 (t.s.d.)	93 (dielectric) 79 (n.m.r.)	8.7 (n.m.r.)
Quenched sample	165 (dielectric)	75 (dielectric)	
Matrixes			
5-Propionyliminobibenzyl (III d)		109*	
5-Chloroacetylaminobibenzyl (III c)		153*	
<i>N</i> -ethyl carbazole		522*	

* Only the higher temperature transition is quoted (see text).

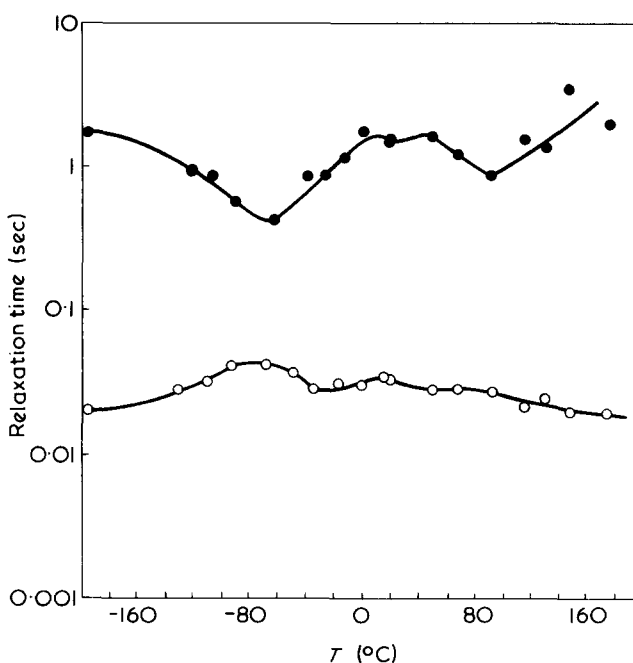


Figure 3 N.m.r. relaxation times as a function of temperature for poly(NADDBA): ●, T_1 data; ○, $T_{1\rho}$ data

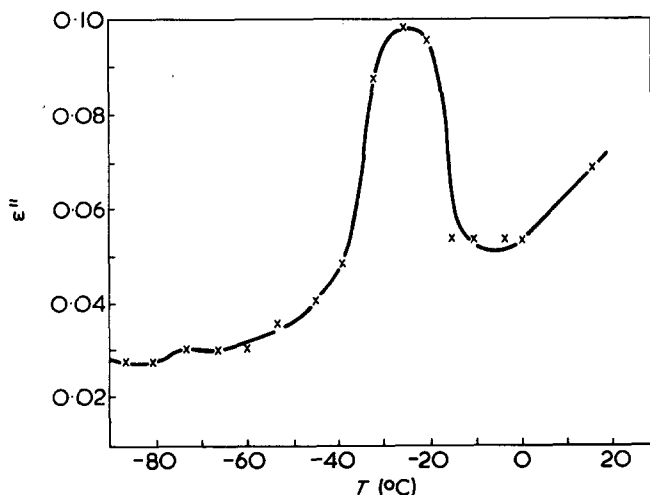


Figure 4 Dielectric loss as a function of temperature at 10^3 Hz (below ambient only) for the *N*-ethyl carbazole matrix. The scaling necessary to accommodate the matrix relaxation has substantially reduced the polystyrene γ peak.

n.m.r. and dielectric data onto the same frequency scale¹². The very low temperature relaxation is clearly associated with methyl rotations¹³ of the polymer end-groups present as a result of AIBN initiation. This relaxation will not be discussed.

Thermally stimulated depolarization work revealed two peaks near room temperature. Of these, the lower peak, occurring at 6°C is attributed to surface water while the peak at 18°C originates in a molecular relaxation. Analysis by the method of Bucchi¹⁴ enabled the activation energy to be calculated (Table 1) whilst the Schwarzl approximation¹⁵ additionally allows this peak to be plotted on the relaxation map of Figure 2. The appropriate relations are:

$$t_m = skT_m^2/E$$

and

$$\nu_m = 0.113/t_m$$

Where t_m , ν_m and T_m are the time, frequency and temperature at which the peak maximum occurs, E is the activation energy and s , the inverse heating rate.

Differential scanning calorimetry showed no evidence for any transition in the fresh polymer over the temperature range -100° to $+250^\circ\text{C}$. In the quenched material however there was a consistent tendency for slope changes to occur at about -45°C . Unfortunately, in this temperature region, the apparatus is neither particularly sensitive nor stable and both the existence and position of this transition must be regarded as tentative. Nevertheless Figure 2 incorporates this information.

X-ray powder photographs showed no evidence for order in either the freshly prepared polymer or in the quenched material.

The dielectric studies of the matrixes revealed broadly similar features in all three cases, with differences of degree rather than kind. An example is given in Figure 4 showing the temperature dependence of the dielectric loss below ambient in *N*-ethyl carbazole. Two peaks are presented and a third (not shown) occurs at $\sim 100^\circ\text{C}$ associated with the polystyrene matrix glass transition⁶. Discussion and analysis of these will be deferred until later. 5-propiony-

liminobibenzyl (IIIId) exhibited very similar features but the chloroacetyl (IIIc) derivative possessed a substantial Maxwell-Wagner contribution to the conductivity¹⁶ at high temperatures and low frequencies that obscured the glass transition. The transitions are plotted on the relaxation map of Figure 2 and the activation energies are entered into Table 1. The transitions at $\sim -70^\circ\text{C}$ are relatively small and often obscured by the peaks at $\sim -30^\circ\text{C}$. For this reason reliable activation energies cannot be quoted. From the permittivity data we can calculate, with the aid of the Onsager equation¹⁷, the effective relaxing dipole associated with the two transitions shown in Figure 4. The results are shown in Table 2. In order to compare these data with those for the free model compounds, dipole moment measurements are also collected together in this Table.

DISCUSSION

High temperature relaxation

In relaxation work it is customary to label the highest temperature process as α , progressing through the alphabet in order of decreasing occurrence temperature or increasing frequency. In most amorphous polymers the α -relaxation originates in the micro-Brownian movement associated with the glass transition and the two have become virtually synonymous. Although this relaxation exhibits many of the characteristics of such α -relaxations in other materials we do not have sufficiently conclusive evidence to label it as glass transition.

Figure 2 demonstrates clearly that the transition is active both as a dipole and as a proton movement. Furthermore the t.s.d. experiment is clearly responding only to this process. The discrepancy in the n.m.r. T_1 point either reflects a genuine difference in that the proton and dipole motions responsible are somewhat different, or that the transition shows a variable activation energy resulting in a curve. This latter view would seem to be the more probable in that the n.m.r. T_{1p} and t.s.d. points are in agreement with the dielectric data. If this is so then this relaxation is almost certainly associated with the glass transition where free volume changes, following the WLF principle¹⁸, are responsible for the curvature. The known sensitivity of t.s.d. to glass transitions¹⁹ supports the concept. Further

Table 2 Dipolar properties of the model compounds $Cm \times 10^{30}$

Compound	System	Dipole moment
5-Propionyliminobibenzyl (IIIId)	Solution dipole	11.92
	Matrix relaxing high temperature dipole	1.17
	Matrix relaxing low temperature dipole	0.93
5-Chloroacetyliminobibenzyl (IIIc)	Solution dipole	13.95
	Matrix relaxing high temperature dipole	4.41
	Matrix relaxing low temperature dipole	1.44
<i>N</i> -ethyl carbazole	Solution dipole	5.87
	Matrix relaxing high temperature dipole	1.07
	Matrix relaxing low temperature dipole	0.87

support derives from the quenching experiment where the creation of free volume by heat treatment has facilitated this process quite considerably as shown by the marked drop in apparent activation energy and the shifting to lower temperatures. The differences in apparent activation energy in *Table 1* can be explained partially as a result of this curvature and also in the assumption of a single relaxation time for the analysis of the t.s.d. data. A distribution of relaxation times, which is almost certainly present, would increase the value shown in *Table 1*.

In contrast we have to recognize that a glass transition has not been observed calorimetrically in freshly prepared material, nor is the small slope change in the quenched sample sufficiently indicative of such a process. Although the marked temperature shift in dielectric work on quenching has been used in support of this hypothesis, the X-ray data do not lend morphological support to the argument. There is no apparent order, even at short range, in the polymer that might be destroyed by heat treatment. Furthermore, on microstructural grounds, it is difficult to reconcile an apparent T_g of $\sim 0^\circ\text{C}$ with the inevitably rigid system imposed by the bulky substituent.

Summarizing, we can report that the relaxation data support the hypothesis that the high temperature relaxation is associated with a glass transition but that this is unconfirmed by more conventional techniques for determining such processes.

Low temperature relaxation

This relaxation is well-defined by both dielectric and n.m.r. experiments but does not appear to respond to t.s.d. investigations, although this may be a reflection of the sensitivity of the apparatus. The magnitude of the activation energy⁵ and the insensitivity to heat treatment suggest a 'side-chain' type mechanism for this process.

It has been reported⁴ that 5-substituted iminobibenzyls exhibit molecular inversion about the nitrogen atom when investigated in solution by high resolution n.m.r. In the 5-chloroacetyl derivative (IIIc) for example, the activation energy barrier to this motion is quoted as approximately 80 kJ/mol. Since there is little possibility of full rotation of the iminobibenzyl substituent in the polymer and libration would be expected to occur at lower temperatures with a substantially lower associated dielectric loss than found here, nitrogen inversion may be causative in this case. In order to test this assumption we have carried out matrix studies on two substituted iminobibenzyls of differing dipole properties and a substituted carbazole which cannot display such inversion. Such experiments have been shown to reveal both conformational⁶ and whole molecule rotational effects²⁰. Williams *et al.*⁶ state that at low concentrations of small molecules in the matrix (typically up to ~ 50 wt %) the composites exhibit relaxations both peculiar to the guest molecules (rotations and/or conformational changes) and also reflect the host polymer behaviour where the guest molecules are 'bound' to the polymer chains. In the absence of matrix restriction only molecular rotation is observed as conformational changes have a very low dipole relaxation efficiency. In the present work all three guest molecules exhibit relaxations at $\sim 100^\circ\text{C}$ reflecting the host T_g process and at $\sim -70^\circ\text{C}$ reflecting the γ -relaxation in polystyrene²¹. At intermediate temperatures ($\sim -20^\circ\text{C}$) a further loss peak is evident which must be characteristic of the guest molecules only. Comparison of these intermediate relaxations with the homopolymer

(*Figure 2*) shows that there is a close positional correlation between them. For the substituted iminobibenzyls the activation energies are similar to the polymer, being somewhat higher in the matrixes as might be expected. In the case of the carbazole, however, the activation energy is very high and there is no doubt that a different mechanism must be operative in this molecule. We postulate that the iminobibenzyls are exhibiting conformational interconversion while the rigid carbazole is experiencing a highly hindered motion involving molecular rotation.

From the changes in permittivity accompanying these relaxations we can estimate the effective relaxing dipole contributing to the observed process in the matrixes using the Onsager equation (*Table 2*). These can be interpreted utilizing the measured dipole moments of the molecules together with the known structure of the iminobibenzyl system³. From X-ray crystallographic data³ it is clear that the two benzene rings are twisted with respect to each other with a pyramidal nitrogen between them and in the two derivatives used here, the amide group is constrained to adopt a planar conformation at low temperatures in solution⁴. Thus in unsubstituted iminobibenzyl the dipole will lie in the N-H bond direction but not coincident with the bond. Nitrogen inversion in this molecule would produce a substantial movement of the dipole with rotation about the C-N bond producing a minor change. In the 5-propionyl derivative (IIId) the carbonyl group naturally increases the molecular dipole but the direction is considerably altered into the plane of the amide moiety. Nitrogen inversion now involves a much smaller movement of the molecular dipole and it is possible that C-N bond rotation, or molecular rotation, would produce a larger effective dipole change. In the chloroacetyl derivative (IIIc) the chlorine and carbonyl dipoles are to a large extent in opposition producing only a small increment in the molecular dipole but once again returning the direction into the N-C bond direction. Thus nitrogen inversion would again relax the major part of the dipole. This analysis is supported by the results in *Table 2*. The guest molecule-influenced polystyrene γ -relaxation directly reflects the magnitude of the guest dipole while the guests own relaxations are not in this proportion. The propionyl derivative is exhibiting a relaxing dipole little different from the rigid carbazole despite its greater magnitude, showing how little movement of the molecular dipole is involved. In contrast, the chloroacetyl derivative (IIIc) has a substantially greater relaxation than can be accounted for simply by the magnitude of its dipole. We conclude that the important conformational change in the iminobibenzyls involves nitrogen inversion and it is this process that is responsible for the low temperature relaxation in poly (NADDBA).

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