Molecular motions in poly(*N*-vinylsuccinimide)

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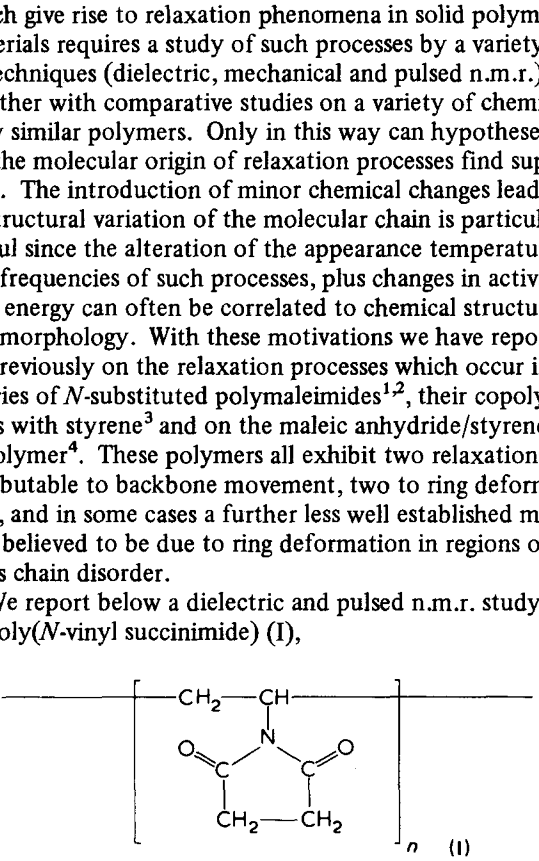
The dielectric and pulsed n.m.r. relaxation of poly(*N*-vinyl succinimide) has been investigated as a function of frequency and temperature. Five loss processes (α to ϵ) have been observed and assigned to main chain motion (α, β) and ring deformations (γ, δ, ϵ) on the basis of comparative work with chemically analogous polymers previously reported[1–4].

INTRODUCTION

The unravelling of the nature of the molecular processes which give rise to relaxation phenomena in solid polymeric materials requires a study of such processes by a variety of techniques (dielectric, mechanical and pulsed n.m.r.) together with comparative studies on a variety of chemically similar polymers. Only in this way can hypotheses for the molecular origin of relaxation processes find support. The introduction of minor chemical changes leading to structural variation of the molecular chain is particularly useful since the alteration of the appearance temperatures and frequencies of such processes, plus changes in activation energy can often be correlated to chemical structure and morphology. With these motivations we have reported previously on the relaxation processes which occur in a series of *N*-substituted polymaleimides[1,2], their copolymers with styrene[3] and on the maleic anhydride/styrene copolymer[4]. These polymers all exhibit two relaxations attributable to backbone movement, two to ring deformation, and in some cases a further less well established mode also believed to be due to ring deformation in regions of gross chain disorder.

We report below a dielectric and pulsed n.m.r. study of poly(*N*-vinyl succinimide) (I),



(I)

in the solid state covering the frequency range 10^{-5}–10^{7} Hz and temperature range −190° to 215°C. This material, has structural features similar to those polymers referred to above, and also exhibits five relaxation processes. For reasons outlined below, we believe the detailed assignment of these does not follow an exact one-to-one correspondence.

EXPERIMENTAL

Material

Poly(*N*-vinyl succinimide) was prepared by the free radical polymerization of vinyl succinimide using benzoyl peroxide (0.5% w/v) as initiator and benzene as solvent (monomer to solvent ratio, 1:2)[5]. After the careful removal of oxygen, the *'in vacuo'* ($<10^{-3}$ mmHg) polymerization was achieved at 80°C for 3 h. The precipitated polymer was well washed with benzene to remove excess monomer and vacuum dried at 80°C for several days. Elemental analysis: C, 54.9; H, 5.8; N, 10.7%. $(C_6H_7NO_2)_n$ requires C, 57.6; H, 5.6; N, 11.2%. I.r. spectra indicated the absence of monomer (disappearance of vinyl absorptions) and the existence of carbonyl bands at 1700 and 1760 cm^{-1}.

Instrumentation

Dielectric studies were made on discs of polymer (51 x ~1 mm) prepared by pressing the powdered material at ~220°C in a die as previously described[3]. For the frequency range 10^2 to 10^6 Hz transformer ratio-arm bridges were employed and in the range 10^{-5} to 10^{-1} Hz recourse was made to the step-response technique using direct Fourier transformation of the decay current–time data[5]. Further experimental details have been described elsewhere[3]. Nuclear magnetic relaxation data were obtained by the use of a Polaron pulsed n.m.r. spectrometer operated at a resonance frequency of 21 MHz.

The pulse sequences used were 90°-τ-90° for T_1 measurements and for experiments in the rotating frame a 90° pulse was followed by a long (several msec) pulse, phase shifted by 90° relative to the initial pulse. Observation of the decay of the long pulse as a function of pulse length enables $T_{1\rho}$ measurements to be made from the latter sequence. There was evidence of non-exponential decay but the relaxation times were too close to permit accurate decomposition. Experimental details have been given elsewhere[2]. The glass–rubber transition temperature was estimated using a Perkin–Elmer DSC-1B differential scanning calorimeter operated at a scan rate of 32°C/min and employing small compressed pellets (~0.5 mm thickness) of polymer.

RESULTS AND DISCUSSION

Dielectrically, poly(*N*-vinyl succinimide) exhibits four relaxation processes which we label in the conventional man-

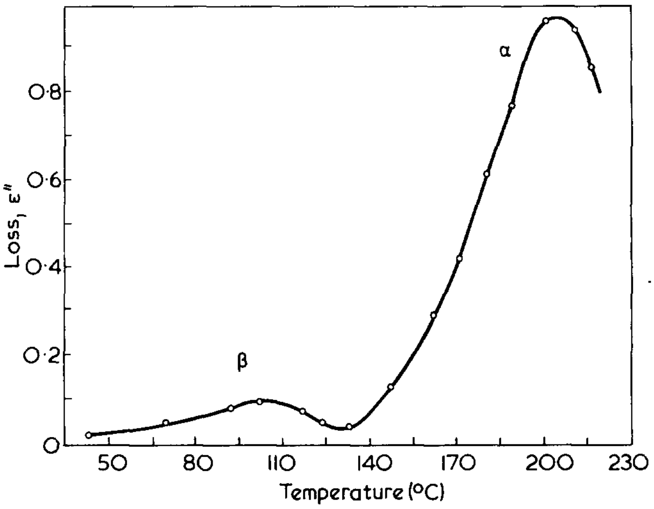


Figure 1 Dielectric loss vs. temperature at 10^{-3} Hz for the α- and β-relaxation processes

ner α, β, γ, δ in the order of high temperature–low frequency process first. These four processes occur in positionally neighbouring pairs, viz. α, β and γ, δ. The α- and β-processes are depicted in *Figure 1* at a frequency of 10^{-3} Hz and as can be seen the loss magnitude for the α-process is ten times larger than the β-process. *Figure 2* shows the temperature dependencies of frequency at maximum loss for these (and the remaining processes) in the form of an Arrhenius plot. The derived activation energy for the α-process is 730 kJ/mol and for the β-loss process 140 kJ/mol. The higher energy α-process we ascribe to the glass–rubber transition because of its high activation energy, which is commensurate with such gross main chain movement involved in glass–rubber transitions. Also, the T_g of 199°C, estimated from d.s.c. data corresponds well with the position of the Arrhenius plot for the α-process as indicated in *Figure 2*. The α-process appears to be kinetically controlled by an energy barrier process since the WLF free volume equations[8] do not adequately describe the frequency–temperature interdependence. Also, the α-process is quite narrow with a nearly, but not quite, symmetrical Cole–Cole[9] distribution (*Figure 3*) and is characterized by a distribution parameter of 0.99. This does suggest that some form of single, partly cooperative process is responsible for the glass–rubber transition in this polymer and that this process is controlled by interchain forces.

The β-process has a lower activation energy whose estimate is in greater error than the α-process because of the problems of resolving this process from the large α peak. Nevertheless the α- and β-processes exhibit similar activation energies, magnitudes, and appearance temperatures, as the maleimide homopolymers and copolymers with styrene[1,3]. By analogy we assign the β-process to a local mode process involving backbone movement but not involving such major chain reorientation as corresponds to the glass–rubber transition.

The second group of processes γ and δ are much more facile than the α- and β-processes. They are dielectrically active in the frequency region 10^2–10^6 Hz and at much lower temperature (*Figure 4*). In magnitude the δ-process is of the same order as the β-process but the γ-process is again reduced in intensity. Difficulties of resolving the γ-process from the δ-process render activation energy estimates for the former impossible using the dielectric data alone, since without the use of curve resolving procedures the position of the γ peak cannot be reliably located. Indeed, as can be seen in *Figure 2*, the apparent position of the γ-relaxation moves to higher frequencies as the temperature is reduced. However the n.m.r. experiments help in this respect. *Figure 5* shows a clear minimum in T_1 and

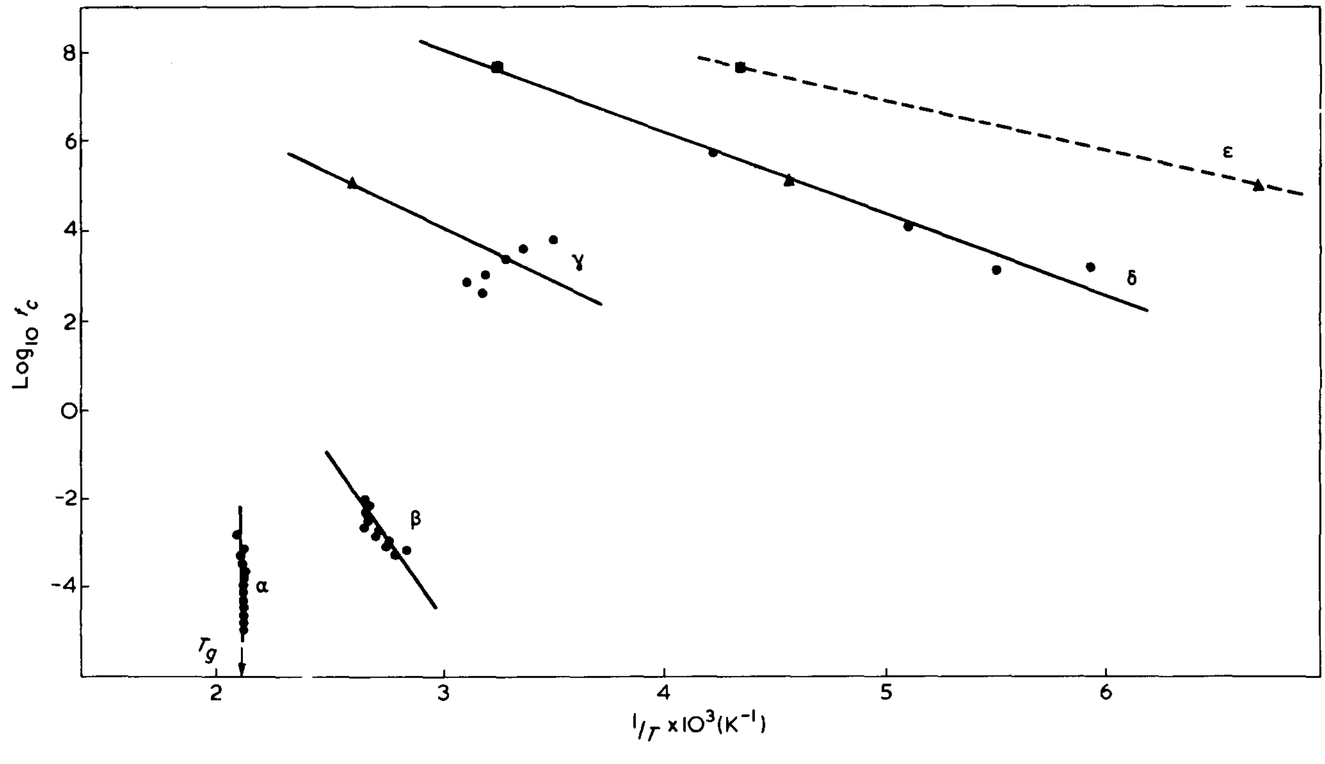


Figure 2 Arrhenius plot of five relaxation processes: ●, dielectric data; ■, n.m.r. T_1; ▲, n.m.r. $T_{1\rho}$

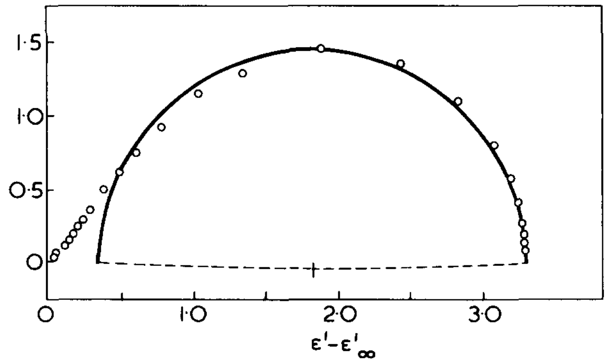


Figure 3 Cole–Cole plot of the dielectric data for the α-relaxation process at 200°C

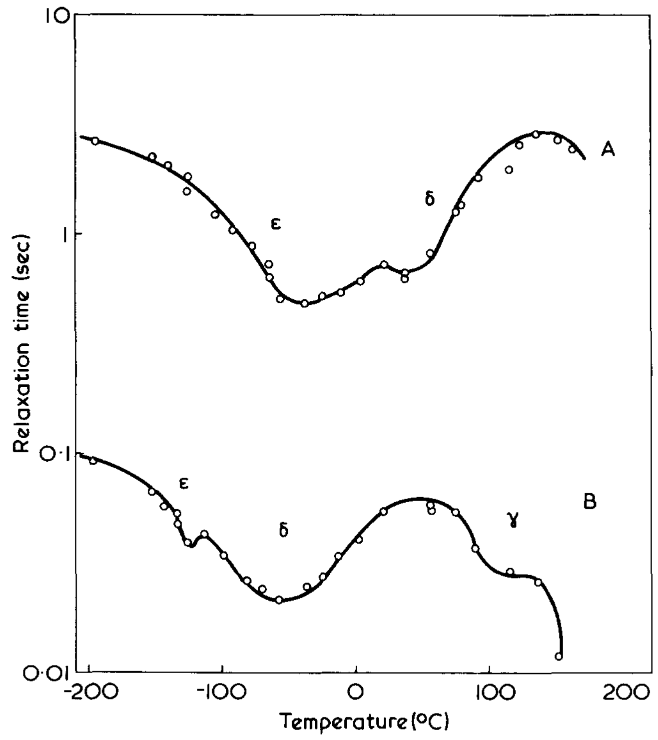


Figure 5 Plot of n.m.r. relaxation times vs. temperature. T_1 measured at 21 MHz; $T_{1\rho}$ measured at 10^5 Hz

two minima in $T_{1\rho}$. Furthermore, additional small discrepancies in the plots are found consistently when several runs are performed. *Figure 5* shows one such typical run with these discrepancies tentatively assigned to relaxation mechanisms. Two of the three transitions thus identified correlate well with the dielectric γ- and δ-transitions as shown in *Figure 2*. Estimates for the activation energies are thus much more reliable than would have been possible using either of the two techniques alone. The values obtained are 45.1 ± 20 kJ/mol for the γ-process and 35.6 ± 4 kJ/mol for the δ-process. In neither case are the energies involved suggestive of main chain motions and we conclude that dipole changes in the pendant succinimide rings are responsible for both these losses. Ring inversion of a non-planar succinimide ring system[10] has been proposed as causative in similar relaxations observed in poly(*N*-substituted maleimides)[1,2], copolymers with styrene[3] and the styrene/maleic anhydride copolymer[4], and we believe this to be the case here also. However, the low activation energy for the processes does suggest that the free volume available to the ring, or the energetic restraints preventing inversion, are much less than in those polymers where the ring forms an essential part of the backbone. In their energetic requirements the γ- and δ-processes observed in poly(*N*-vinyl succinimide) parallel much more closely the weak ε-process observed in the maleimides and tentatively ascribed in those systems to regions of gross chain conformational disorder. Whether this δ-process is indeed occurring in disordered regions and the γ-process in regions of local chain order for poly(*N*-vinyl succinimide) or whether both processes are occurring in two differing conformational environments of local chain order, as is the case in the maleimide and maleic anhydride based polymers[1-4] cannot be conclusively decided on the present evidence. Experiments in which samples of poly(*N*-vinyl succinimide) were rapidly quenched after heating to T_g did not exhibit any differences in behaviour from those not so treated. This is in contrast to the behaviour of the majority of those polymers with the maleimide ring as part of the backbone unit in which the behaviour after quenching is consistent with the view that the γ- and δ-relaxations are occurring in differing local chain environments, possibly 3_1 and 4_1 helices.

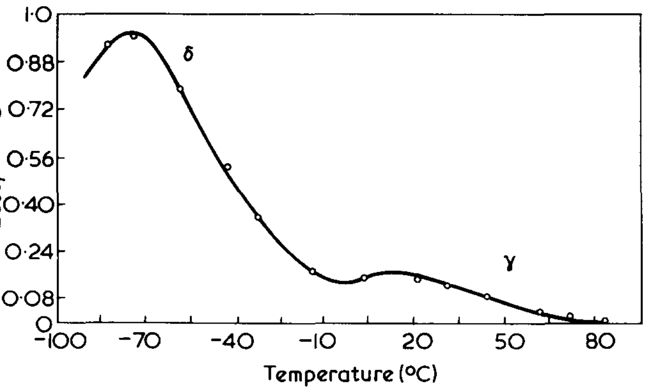


Figure 4 Dielectric loss vs. temperature at 10^4 Hz for the γ- and δ-relaxation processes

The n.m.r. evidence suggests the existence of a further (ε) relaxation process in the temperature range from about −125° to −35°C. Since this region, or a portion of it, is accessible to the dielectric technique, it can be concluded that the ε-process does not include dipole reorientation. Nor can it be ascribed to methyl end-group rotation, commonly found in the n.m.r. spectra of polymers in this temperature region, since the polymerization initiator was a peroxide. Both the relaxation position and activation energy (19.5 kJ/mol) correspond to the ε-relaxation observed in many similar polymers[1,3] but, in view of the absence of dipole movement, cannot have its origin in the same molecular process. The low activation energy suggests a very fast, relatively unhindered, process that is probably taking place in the ring. A possible explanation would involve twisting of the $-CH_2-CH_2-$ ring methylenes without dipole motion. A mechanism of this type is supported by the very shallow associated $T_{1\rho}$ minimum. While all three $T_{1\rho}$ minima are an order of magnitude too large, the ε-region is particularly shallow suggesting a significant spin diffusion mechanism[11,12] which also results in the inability to identify and resolve separate decays from differing environments.

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REFERENCES

1. Block, H., Groves, R. and Walker, S. M. *Polymer* 1972, **13**, 527
2. Bailey, J., Block, H., Cowden, D. R. and Walker, S. M. *Polymer* 1973, **14**, 45
3. Block, H., Lord, P. W. and Walker, S. M. *Polymer* 1975, **16**, 739
4. Block, H., Collinson, M. E. and Walker, S. M. *Polymer* 1973, **15**, 68
5. Nikolaev, A. F., Ushakov, S. N. and Krasnosel'skaya, I. G. *Acad. Sci. USSR* 1959, 1564
6. Block, H., Groves, R., Lord, P. W. and Walker, S. M. *JCS Faraday Trans. II* 1972, **68**, 1890
7. Bailey, J. and Walker, S. M. *Polymer* 1972, **13**, 561
8. Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
9. Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1949, **9**, 341
10. Balta-Calleja, F. J., Ramos, J. G. and Barrales-Rienda, J. M. *Kolloid Z.* 1972, **250**, 474
11. McBrierty, V. J., McCall, D. W., Douglass, D. C. and Falcone, D. R. *J. Chem. Phys.* 1970, **52**, 512
12. Douglass, D. C. and McBrierty, V. J. *J. Chem. Phys.* 1971, **54**, 4085