polymer communications

Rigid backbone polymers: 22. Dielectric relaxation in lyotropic and highly concentrated isotropic solutions of poly(n-hexylisocyanate) in toluene

J. K. Moscicki, G. Williams
Edward Davies Chemical Laboratories, Aberystwyth, SY23 1NE, UK

and S. M. Aharoni
Allied Chemical, Morristown, New Jersey 07960, USA

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The recent studies by Aharoni and coworkers[1-8] have demonstrated that certain poly(n-alkylisocyanates) exhibit thermotropic mesomorphic behaviour in the bulk phase and lyotropic mesomorphic behaviour in concentrated solution. Hot-stage polarized-light microscopy studies[3,8] show that both thermotropic and lyotropic mesophases are nematic in character. Unfortunately thermal decomposition sets in near the temperatures at which the bulk materials exhibit the thermotropic nematic phase[8] (above 120°C) and makes the studies of the physical properties of that phase difficult. Some effects due to decomposition are also observed in solutions above 80°C, but there is sufficient stability for the solutions of poly(n-alkylisocyanates) in solvents such as toluene or carbon tetrachloride at, or around, room temperature to allow studies to be made in their isotropic and lyotropic solution phases.

The transformation from isotropic to nematic phase on increasing the polymer concentration, is not sharp. Polarized-light optical microscopy studies[3,6] reveal that isotropic and nematic phases coexist over a range of concentration, being the 'bi-phasic' regime. The shear viscosity shows a sharp maximum as concentration is increased[2-7,9]. It was noticed that the maximum occurred not at the concentration at which the nematic phase first appears but substantially within the bi-phasic range. The marked fall in viscosity on entering the nematic range of concentration implies a corresponding marked change of the molecular mobility of the polymer which should be detected by such techniques as dielectric or n.m.r. relaxation. It is well-known that the poly(n-alkylisocyanates) have a rod-like conformation for large sequences of the chain[10]. Since the dipole moment lies along the long axis of the chain and is extremely large[10,11] it was considered that a dielectric study of the isotropic and nematic phases would give useful information on the structure and dynamics of the chains in those phases.

This communication presents preliminary results of dielectric measurements made for poly(n-hexylisocyanate) in solution in toluene, covering both the isotropic and nematic phases. The measurements were made in the ranges 20°C to 55°C for nematic phase, from -10°C to $+60$°C for isotropic phase, and the frequency range 0.1 kHz to 90 kHz (using a Sullivan C3060 capacitance bridge together with a specially designed coaxial cell having an electrode capacitance of 15 pF and an inter-electrode gap of 1 mm). The cell was calibrated using benzene and toluene as standards, and the reproducibility of the dielectric permittivity and loss factor was about 1%. Temperature was controlled to ± 0.2°C using water or alcohol circulating systems. The poly(n-hexylisocyanate) sample was one of those used by Aharoni (see references 1, 3) and one nematic phase (42% polymer w/w) and several isotropic phase solutions (5, 10, 15% polymer w/w) were made with dry analar toluene as solvent using the preparation procedure described by Aharoni.

Figure 1 shows the imaginary part (ε'') of the dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) as a function of frequency at given temperatures for a 15% solution of PHIC in toluene, giving typical isotropic solution behaviour, and for the 42% solution, giving nematic behaviour. The marked

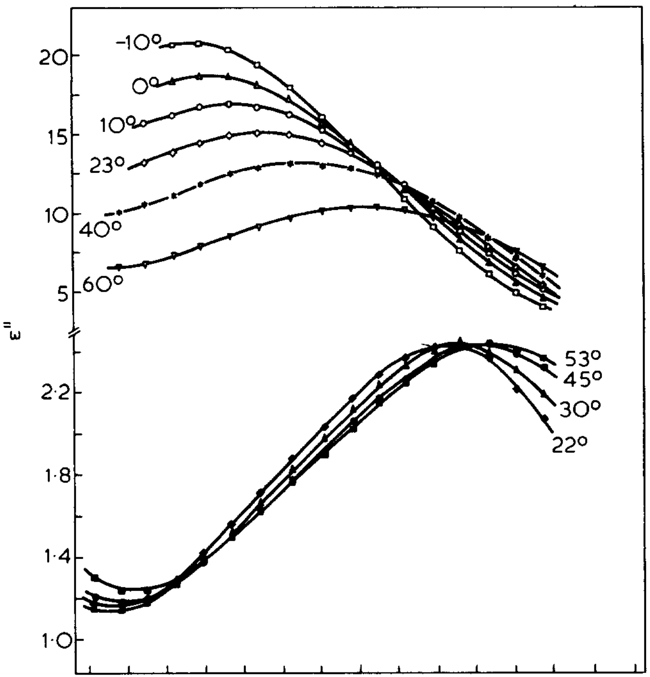

Figure 1 PHIC in Toluene. Dielectric loss factor, ε'', as a function of frequency (log ν) and temperature (°C) for 15% isotropic upper curves and 42% nematic lower curves solutions

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difference in behaviour is evident, and may be summarized as follows:

(a) the magnitude of the loss in these ranges of temperature, is far smaller for the nematic phase than for the isotropic phase, being the opposite of that expected on the basis of number of dipolar molecules per unit volume.

(b) The magnitude of the loss maximum as indicated here by ε''_m, remains practically constant with changing temperature for the nematic phase. In contrast, ε''_m decreases markedly with increasing temperature for the isotropic material. Such behaviour for the isotropic phase was observed earlier for poly(n-hexylisocyanate) and poly(n-octylisocyanate) in carbon tetrachloride at much lower concentrations, and is interpreted as being due to variations in the mean-square dipole moment, $<\mu^2>$, of the chain with temperature, such that the chain goes from rigid-rod (with large dipole moment) to a multi-broken rod (with lower dipole moment) as temperature is increased (see Bur and Fetters[10] and Beevers, Garrington and Williams[11]). ε''_m was strictly proportional to polymer concentration for the 5, 10 and 15% solutions, *Figure 2*, indicating no special intermolecular orientational correlations in this range. We note that Coles, Gupta and Marchal[12] have suggested, on the evidence for their observed variation of dielectric permittivity and Kerr-constant with concentration, that PHIC molecules aggregate in toluene solutions for $c < 6\%$(w/w). We shall discuss these results and our studies of PHIC/toluene isotropic solutions in a future publication.

(c) The maximum loss frequency, f_m, varies appreciable with temperature for the isotropic phase, but hardly at all for the nematic phase. Derived apparent activation energies are Q (isotropic) $= 30$ kJ mol^{-1} and Q(nematic) $= 20$ kJ mol^{-1}. The value for Q(isotropic) is typical of that of a viscosity-controlled reorientation for which $\tau = (2\pi f_m)^{-1} = 3\eta V kT$ where η is the viscosity of the solution, T is temperature and V is the volume of the molecule. We note that f_m (nematic) occurs at much higher values than f_m (isotropic) for given temperatures.

The present dielectric data for the isotropic phase are entirely consistent with those obtained earlier by Bur and Fetters[10] and by Beevers, Garrington and Williams[11]. The molecules reorientate via Brownian diffusion, relaxing all of $<\mu^2>$ in that process, and the strength of the relaxation decreases with increasing temperature due to the increased tendency of molecules to depart from a rigid-rod conformation. The small values of dielectric loss-factor, the increased values of f_m and its small temperature dependence, relative to those values for the isotropic phase, indicate that in the nematic phase the molecules are unable to reorientate into the 4π solid angle, at least at frequencies accessible to us in this study. The permittivity values are in agreement with this observation. At 293K and 110Hz the permittivity approximates to the static value ε_0. We find values of 12.5 for the nematic material and 62.5 for the 15% isotropic solution. In the nematic phase the long axes of chains are preferentially aligned along common local directors and for molecular weights of PHIC studied here the overall reorientation of a given molecule is not possible. This is in direct contrast to small-molecule nematogens such as *N*-(*p*-methoxybenzylidene(-*p*-n-butyl aniline (MBBA). 4,4-n-heptyl cyanobiphenyl (NCB) and substituted alkyl cyanopyrimidines where the overall rotations of molecules occur in the nematic phase with preservation of the local director (for a review, see ref 13). Whilst overall motion of polymer chains is suppressed in the nematic phase, the solvent molecules between chains assist those chains to undergo angular motions through a limited solid angle leading to only a partial relaxation of $<\mu^2>$ and a fast motion (relative to the total reorientational process observed for the isotropic phase, *Figure 1*). Such a motion is fairly insensitive to changes in temperature.

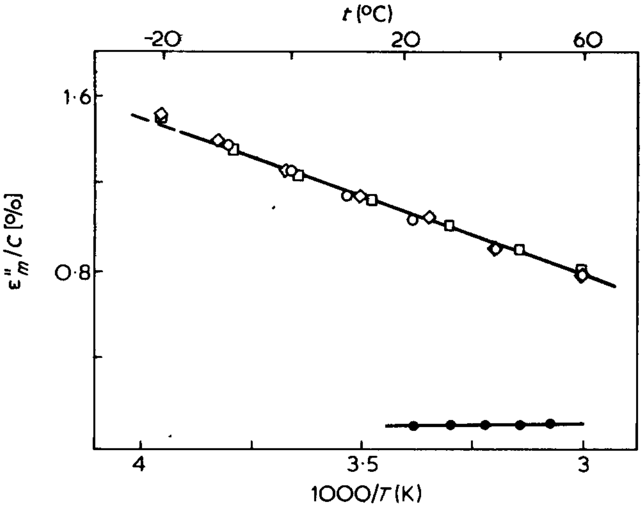

Figure 2 PHIC in toluene. Dielectric loss maximum normalized to the same concentration, ε''_m/C, as a function of temperature for isotropic and nematic solutions (●, 42%; ○, 15%; ◇, 10%; □, 5%)

The present data do not allow us to make more quantitative assessments of the motional processes but they provide evidence of restricted motions of chains in the lyotropic nematic phase of poly(alkylisocyanates). Further studies are in progress of the dielectric behaviour of this and other poly(alkylisocyanates), to include lower frequencies and a wider range of cencentration than those reported here and also to include Kerr-effect measurements as a means of gaining information on angular correlations between molecules in the isotropic phase at high concentrations.

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