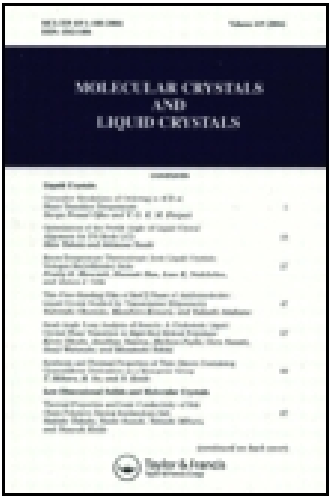

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DISCOTIC SIDE GROUP LIQUID CRYSTAL POLYMER ELECTROLYTES

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DISCOTIC SIDE GROUP LIQUID CRYSTAL POLYMER ELECTROLYTES

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The synthesis and characterization is reported of a novel discotic side group polymer based on a predominantly poly(ethylene oxide) backbone to which are attached triphenylene-based mesogenic groups via *flexible spacers. The thermal and mechanical behavior of this polymer and its complex with lithium perchlorate are compared. The addition of salt increased both the glass transition temperature and clearing point of the host polymer. The temperature dependence of the ionic conductivity of the polymer–salt complex is reported and reveals that ionic conduction can occur in essentially solid-like liquid crystal polymer electrolytes. Ion transport in this material presumably involves assistance from local segmental motions of the backbone but does not rely upon long range cooperative motions.*

Keywords: side group liquid crystal polymers; polymer electrolytes; discotic; ionic conductivity; ion transport mechanism

INTRODUCTION

A polymer electrolyte is an ionically conducting solid or elastomeric phase comprised of a salt dissolved in a polymeric solvent [1]. The demand for all solid-state electrochemical devices and, perhaps most notably, lithium batteries continues to stimulate interest in this class of materials, although it has not proved possible to design solvent-free solid polymers with ionic conductivities reaching the target level of *ca* $10^{-3}\,\mathrm{S\,cm^{-1}}$ at ambient temperature. To understand the root of this problem we must consider the mechanism of ion transport in polymer electrolytes, which typically consist of lithium salts in polyether systems. In such a system it is generally

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*Corresponding author. E-mail: c.t.imrie@abdn.ac.uk accepted that ion transport involves segmental motions of the host polymer and thus significant levels of ionic conductivity will exist only above the glass transition temperature, T_g [2]. We have described recently, however, a new class of liquid crystal polymer electrolytes which exhibit significant levels of ionic conductivity in the liquid crystalline and glassy states [3,4]. In these polymers, mesogenic (4-methoxybiphenyl) groups are attached via alkyl spacers to a predominantly poly(ethylene oxide)-based backbone containing isophthalate linking groups [5–7].

In order to investigate how the nature of the liquid crystalline phase effects ionic conductivity in this class of polymers, here we report the synthesis and characterization of a novel polymer electrolyte containing triphenylene-based discotic moieties attached via alkyl spacers to a predominantly poly(ethylene oxide) backbone Scheme 1.

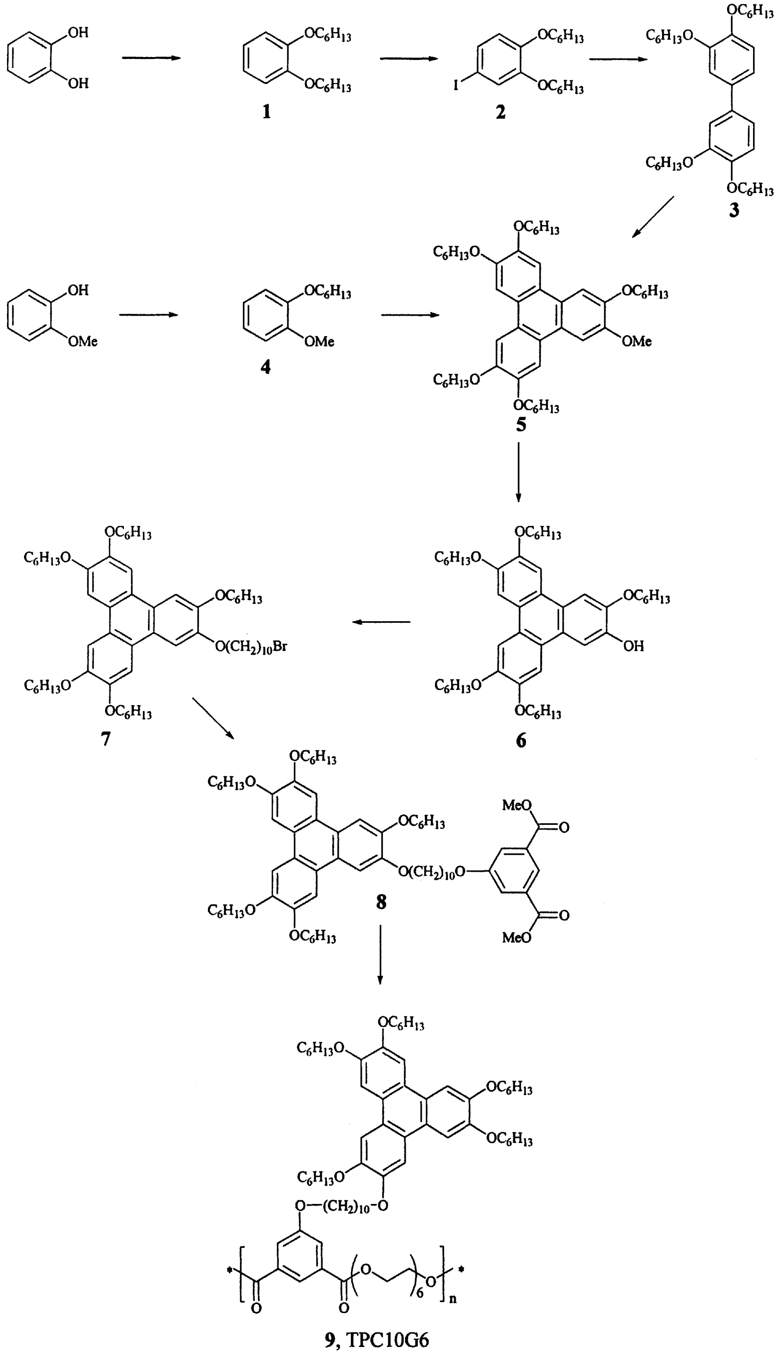
The acronym used to refer to this polymer is TPC10G6. The thermal, mechanical, and conducting properties of the 14:1 TPC10G6: $LiClO_4$ complex are also reported. The concentration of lithium ions in the complex is described as the ratio of active oxygens to lithium ions. An active oxygen is defined in terms of its ability to coordinate the lithium ion, which is influenced both by steric factors and donicities of individual oxygens. Rather arbitrarily, we have assumed that all the oxygen atoms in the polymer backbone may be counted except for the carbonyl oxygens. Thus, TPC10G6 contains 7 active oxygens per repeat unit.

EXPERIMENTAL

TPC10G6 was prepared using the synthetic route shown in Scheme 1. The syntheses of 1,2-dihexyloxybenzene, 1, [8] 1-hexyloxy-2-methoxybenzene, **4**, [9] 2-methoxy-3,6,7,10,11-pentahexyloxytriphenylene, **5**, [9] 2-hydroxy-3,6,7,10,11-pentahexyloxy-triphenylene, **6**, [9] and 2-(10-bromodecyloxy)-3,6,7,10,11-pentahexyloxy-triphenylene, **7**, [10] have been described in detail elsewhere.

4-Iodo-1,2-dihexyloxybenzene, 2

1,2-dihexyloxybenzene (55.7 g, 0.20 mol) was added to a solution of glacial acectic acid 150 mL), water (25 mL), dichloromethane (30 mL) and concentrated sulphuric acid (1.0 mL). Iodine (20 g) and then iodic acid (8 g) were added and the mixture heated with stirring at 40°C overnight. The reaction progress was monitored by ^{1}H NMR spectroscopy. After the reaction was complete, sodium hydrogensulphite solution (~5 g sodium metabisulphite in ~100 mL water) was added and the red color disappeared after stirring for 10 min. The product was extracted using dichloromethane and the organic layer rinsed with potassium carbonate



SCHEME 1 Synthetic route for the preparation of TPC10G6.

solution to neutralize the remaining acids. The organic layer was dried over magnesium sulfate, concentrated and passed through a short column (silica gel, dichloromethane) to give the product 4-iodo-1,2-dihexyloxybenzene, a yellow oil (76 g, 94%).

δ_H: 7.14 (dd, $J^3 = 8.3$ Hz, $J^4 = 2.0$ Hz, 1H), 7.12 (d, $J^4 = 2.0$ Hz, 1H), 6.58 (d, $J^3 = 8.3$ Hz, 1H), 3.99 (4H, t, ArOCH_2, $J = 6.7$), 1.81 (4H, m, ArOCH$_2$CH_2), 1.2–1.6 (12H, m, ArOCH$_2$CH$_2$(CH_2)$_3$), 0.90 (6H, t, CH_3, $J = 6.9$).

3,3′,4,4′-Tetrahexyloxybiphenyl, 3

4-iodo-1,2,-dihexyloxybenzene (19.9 g, 49.2 mmol) was added to copper powder (20 g) and mixed thoroughly. The mixture was heated carefully to ~270°C, and the temperature increased to ~310°C due to the exothermic reaction. After cooling, the product was extracted with dichloromethane and concentrated under vacuum. Ethanol was added to initiate crystallization to give 3,3′,4,4′-tetrahexyloxbiphenyl (5.9 g, 43%, m.p. 68–70°C).

δ_H: 7.04 (4H, m, ArH), 6.90 (2H, d, ArH, $J = 6.9$), 4.03 (8H, t, ArOCH_2, $J = 7.3$), 1.82 (8H, m, ArOCH$_2$CH_2), 1.2–1.6 (24H, m, ArOCH$_2$CH$_2$(CH_2)$_3$), 0.89 (12H, t, CH_3, $J = 6.7$).

Discotic Monomer, 8

A mixture of 2-(10-bromodecyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (8.0 g, 8.3 mmol), dimethyl-5-hydroxyisophthalate (2.0 g, 9.5 mmol) and potassium carbonate (4.7 g, 34 mmol) in acetone (50 mL) was heated at reflux with stirring for 48 h. The cooled reaction mixture was poured into water and filtered. The residue was recrystallized from hot ethanol. Due to the low melting point of the product, an oil tended to form, and form this mixture, crystals were decanted off. This procedure was repeated several times giving white crystals of **8**.

δ_H: 8.24 ppm (1H, s, ArH), 7.82 (6H, s, ArH), 7.72 (2H, s, ArH), 4.22 (12H, t, ArOCH_2, $J = 6.6$), 4.02 (2H, t, ArOCH_2, $J = 6.7$), 3.92 (6H, s, ArCOOCH_3), 1.93 (14H, m, ArOCH$_2$CH_2), 1.3–1.6 (42H, m, CH_2), 0.92 (15H, t, CH_3, $J = 6.9$). There was some ethanol exchange with the methyl ester groups, which gave rise to a quartet at 4.4 ppm. IR(KBr) v 1723 cm^{-1} (CO stretch). Melting point (DSC) 37°C, a glass transition observed at −17°C.

TPC10G6 Polymer, 9

8 (5.1 g, 4.7 mmol) and freshly distilled PEG 300 (1.3 g) were flushed with argon. This mixture was heated with stirring until fully molten (~100°C).

Two 0.5 mL portions of catalyst (10%v/v titanium(IV) isopropoxide in 2-methoxyethyl ether) were added approximately an hour apart and the temperature increased to 120°C. The pressure was then reduced over 5 h to 1 mmHg; finally the temperature was increased to 150 °C. The reaction was held at this temperature and pressure for 24 h until the production of a liquid was no longer evident. The polymer was purified by dissolving the reaction mixture in a small volume of chloroform and precipitating into a large volume of hexane.

δH: 8.23 ppm (1H, ArH), 7.81 (6H, ArH), 7.71 (2H, ArH), 4.46 (4H, COOCH_2), 4.21 (12H, ArOCH_2), 4.0 (2H, ArOCH_2), 3.8 (4H, COOCH$_2$-CH_2O), 3.6 (16H, PEG OCH_2), 1.7–2.0 (14H, ArOCH$_2$CH_2), 1.3–1.7 (42H, (CH_2)$_{21}$), 0.91 (15H, CH_3). IR(KBr) ν 1723 cm^{-1} (CO stretch). GPC (polystyrene standards) $M_w = 10{,}800\ \mathrm{gmol}^{-1}$, $M_n = 5{,}200\ \mathrm{gmol}^{-1}$.

Preparation of TPC10G6:LiClO$_4$ Complexes

The polymer TPC10G6 and salt LiClO$_4$ were codissolved in freshly distilled THF. The mixture was stirred and flushed with argon until most of the solvent was removed. The complex was dried by heating under vacuum for at least a week. The conductivity cells were prepared by melting the complex onto the electrode by heating under vacuum for a week, to ensure the sample was dry.

Characterization

The proposed structures of all the intermediates and the final polymer have been verified using ^{1}H-NMR and IR spectroscopy. The thermal characterization of TPC10G6 and its salt complex was performed by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). DSC measurements were made using a Mettler Toledo 821 DSC equipped with a liquid nitrogen cooling system and calibrated using indium as a standard. All heating and cooling rates were 10°C min^{-1}. The DMTA measurements were made using a PC-controlled Rheometric Scientific DMTA equipped with a Mk III analyzer operating in the shear mode. Measurements were recorded at a heating rate of 2°C min^{-1}. Phases were studied using polarized light microscopy using an Olympus BH2 polarized light microscope equipped with a Linkam THMS heating stage, LNP2 cooling pump and TMS control unit.

The ionic conductivity of the polymer salt-complex was measured by standard ac impedance methods using a Schlumberger 1260 impedance analyzer over a frequency range 1–10^6 Hz. Complex impedance plots were obtained using Zview software.

RESULTS AND DISCUSSION

The DSC trace for the initial heat of TPC10G6 is shown in Figure 1. A weak glass transition occurs at −17°C, and an endotherm is observed at 47°C with an associated enthalpy change of 33.4 J g^{-1}. On Cooling from the isotropic phase a poorly defined birefringent texture is observed when viewed under the polarizing microscope (see Figure 2(a)). This texture remained unchanged after annealing for prolonged periods and was not suitable for the assignment of the phase. The phase is highly viscous, strongly suggesting either a highly ordered columnar phase or a disordered crystal phase.

The 14:1 TPC10G6:$LiClO_4$ complex shows a glass transition at −11°C and a clearing transition at 52°C with an associated enthalpy change of 24.0 J g^{-1}, (see Figure 1). A broad week peak is also evident with a maximum at 21°C. A characteristic optical texture could not be obtained for the mesophase (see Figure 2(b)), and again it is probable that the phase is a

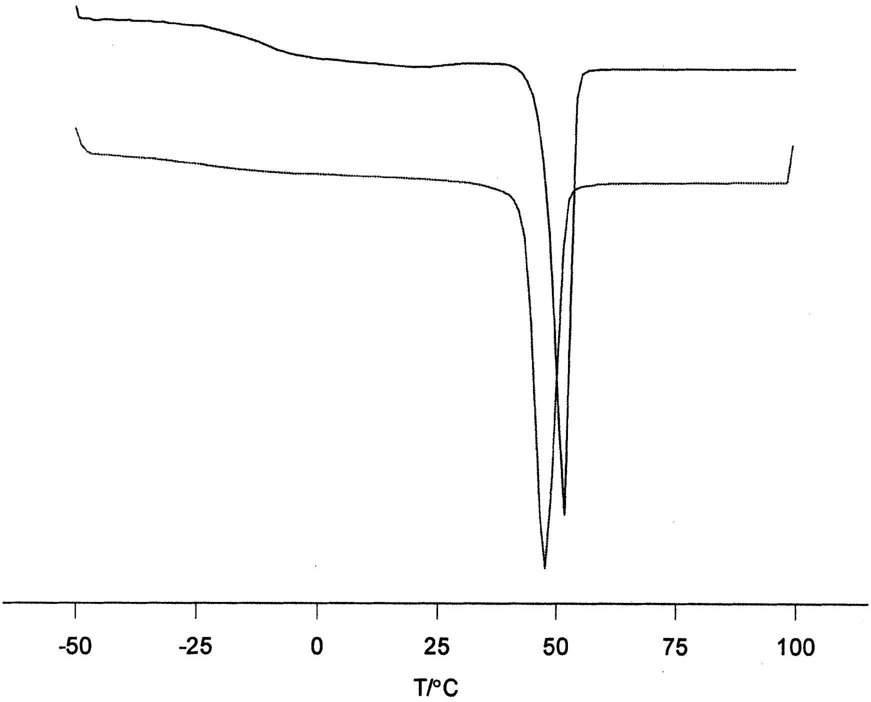
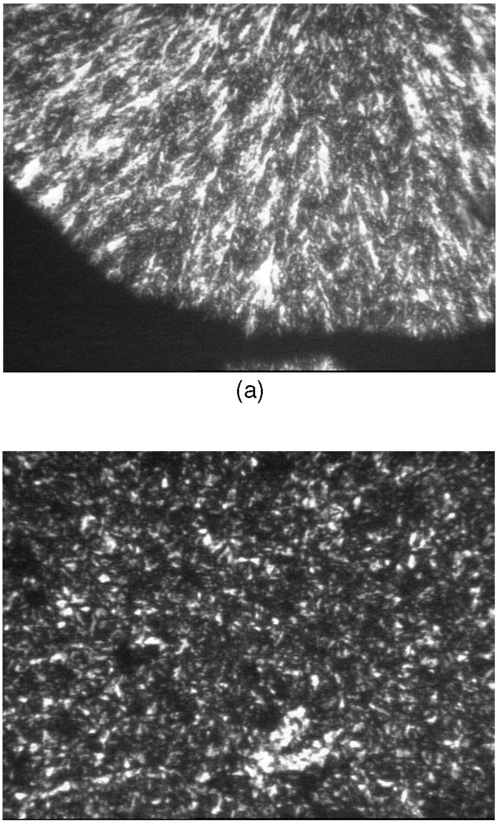


FIGURE 1 DSC reheat traces for TPC10G6 (initial heat, lower trace) and 14:1 TPC10G6:$LiC1O_4$ complex (reheat, upper trace).

highly ordered columnar arrangement. X-ray diffraction experiments are in progress to determine the phase structure.

The addition of salt increased both the glass transition temperature and clearing point of the host polymer. Similar effects were observed for calamitic liquid crystal polymer electrolytes [5–7]. The increase in the glass transition temperature reflects the loss of segmental mobility arising from the coordination of lithium ions by the ether oxygens of the backbone. The concurrent increase in the clearing point may be accounted for in terms of the preferential dissolution of the ions in the backbone domains, which serves to reinforce the microphase separation between the backbones and discotic side groups that drives mesophase formation.


(a)

(b)

FIGURE 2 Optical textures for (a) TPC10G6 and (b) 14:1 TPC10G6:$LiClO_4$ complex. (See COLOR PLATE I)

The temperature dependence of the real component of the shear modulus for TPC10G6 is shown in Figure 3. A softening of the polymer is seen at −10°C presumably associated with the glass transition. The major decrease in the modulus, however, occurs at the clearing temperature. A shoulder is evident on the trace, suggesting that there is a relaxation just below the clearing point. The addition of salt shifts the onset of softening to ca 0°C (see Figure 3), consistent with the observed increase in the glass transition temperature observed using DSC. Again the sudden decrease in modulus is associated with the clearing transition, only now the change in modulus associated with the second event is more pronounced than that seen for the host polymer (Figure 3). This change in modulus is presumably associated with the transition observed at 21°C by DSC.

The ionic conductivity of the 14:1 TPC10G6:$LiClO_4$ complex is shown as an Arrhenius plot in Figure 4. Two regions of Arrhenius behavior can be seen with a kink separating these at a temperature essentially coincident with the clearing point. The Arrhenius plot is steeper below the clearing temperature, i.e., the activation energy for ion transport is larger, which suggests that the onset of self-assembly is bad for ionic conductivity. It is

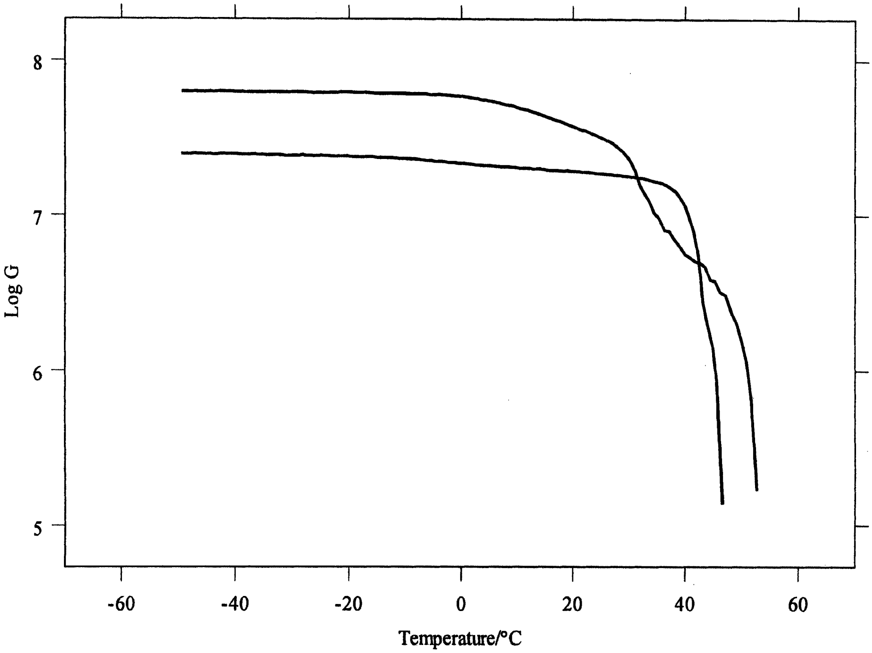


FIGURE 3 Temperature dependence of the real component of the shear modulus of TPC10G6 (lower trace) and the 14:1 TPC10G6:$LiClO_4$ complex.

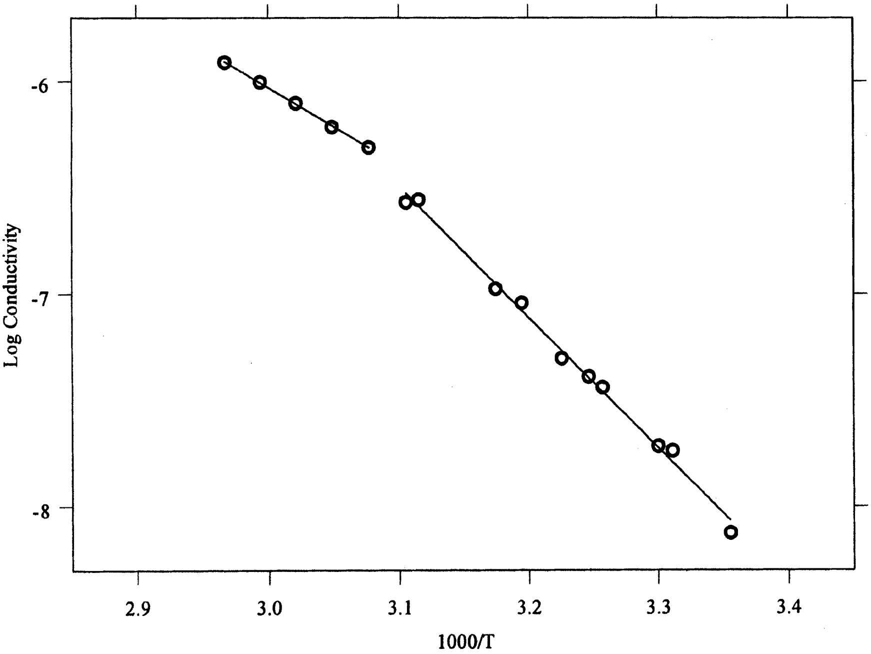


FIGURE 4 Arrhenius plot for conductivity of the 14:1 TPC10G6:$LiClO_4$ complex.

remarkable, however, that given the first-order nature of this transition in terms of both the thermodynamic and mechanical properties a step change in ionic conductivity is not clearly evident in these data.

The atypical behavior of the TPC10G6:$LiClO_4$ complex is further emphasized when the thermal, mechanical, and conductivity data are overlaid (Figure 5). It seems again that there is no clear discontinuity in the conductivity data at the clearing point. Furthermore, appreciable conductivities are observed at temperatures for which the shear modulus is approaching that of a solid-like material.

We have suggested in the past that the decoupling of ion transport from the segmental motions of the polymer matrix in calamitic side group crystal polymer electrolytes stems from the suppression of helix formation involving the poly(ethylene oxide)-based backbones, the suppression arising from the jacketing effect of the mesogenic side chains [4]. The resulting open structure and multiplicity of ion sites may be giving rise to a conductivity mechanism somewhat analogous to that found in inorganic glasses. It may seem reasonable to invoke a similar mechanism to account for the ionic conductivity of the discotic material seen here at low temperatures.

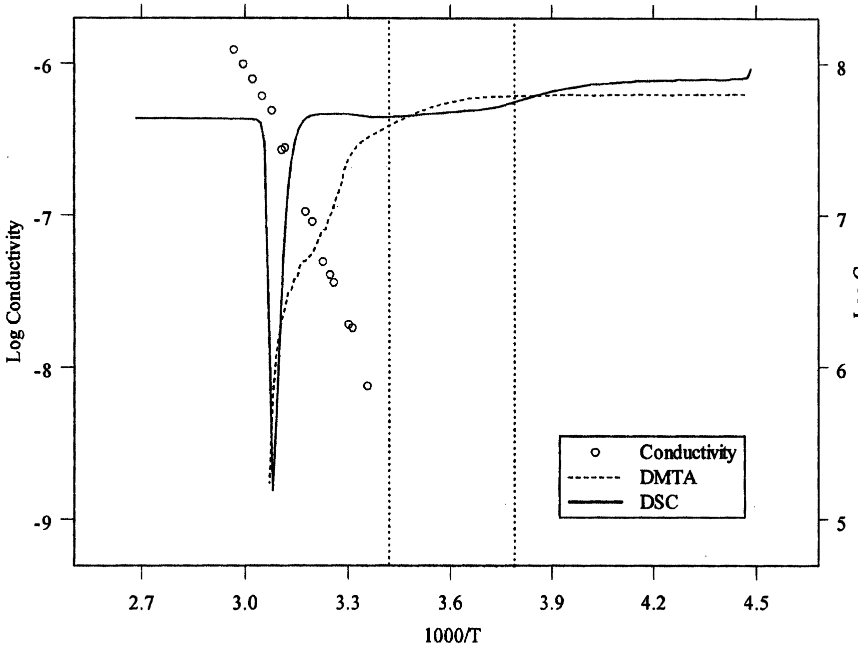


FIGURE 5 Dependence of the log (ionic conductivity) (open circles), log (real component of the shear modulus) (dashed line), and heat flow in the DSC experiment (solid line) on reciprocal temperature of the 14:1 TPC10G6:LiClO$_4$ complex.

CONCLUSIONS

We have shown that ionic conduction can occur in essentially solid-like liquid crystal polymer electrolytes. The challenge is now to establish the mechanism of ion transport in these systems, which presumably involves assistance from local segmental motions of the backbone but does not involve long-range cooperative motions. To clarify this further we are now undertaking measurements of the ionic conductivity as a function of pressure, where we will gain further insights from variations in activation volume [11].

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