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Novel triphenylene-based ionic discotic liquid crystalline polymers

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The photopolymerization of triphenylene-substituted 1-vinylimidazole yielded a novel ionic discotic liquid crystalline polymer. The thermotropic liquid crystalline properties of both the monomer and polymer were investigated by polarizing optical microscopy and differential scanning calorimetry. The mesophase structure has been characterized by X-ray diffractometry. Both the monomer and polymer displayed columnar rectangular mesophase over a wide temperature range. However, the columnar order in the polymer was found to be small compared to the monomer. Such ionic discotic polymers are useful for unidirectional transport of ion and energy at nanoscale.

Ionic liquids are currently attracting considerable attention as "green" solvents for various chemical reactions (*1*). Additionally, it is well known that ionic molecules form amphotropic liquid crystals (LCs) (*2*). They have great potential as ordered reaction media that can impart selectivity in reactions by ordering reactants (*3*). The formation of supramolecular assemblies containing ionic liquids may find applications as heat carriers in solar-thermal energy generators and as electrolytes for batteries and capacitors (*4*). Alkali metal soaps were the first salts identified as displaying liquid crystalline properties, followed by alkylammonium, pyridinium, vinamidinium, phosphonium, imidazolium, etc., salts (*5*). The majority of ionic liquid crystals belong to the calamitic liquid crystals group, however, a few discotic ionic liquid crystals are also known (*6*).

For many years, ionic liquid crystalline polymers with the mesogen in the main chain or in the side group have been investigated intensively for their scientific and technological potentials (*7*). For example, Hara and co-workers (*8*) developed polymer liquid crystals by introducing ionic groups into the polymer main chain to obtain better tensile and compressive properties. Paleos and co-workers investigated the mesomorphic properties of oligomeric viologens (*9*). Main chain liquid crystalline viologen polymers have been intensively studied by Bhowmik et al (*10*). Bazuin and co-workers investigated tail-end amphiphiles of the type poly(ω-pyridinium alkyl methacrylates) with various 4-substituted pyridinium bromide groups (*11*). Haramoto and co-workers described high molecular weight ionic liquid crystalline polymers with a 4-(1,3-dioxan-2-yl) pyridinium group (*12*). Barmatov and co-workers investigated liquid crystallne ionomers containing alkali metal ions, alkaline-earth matal ions, transiton metal ions and rare-earth ions to establish the effect of the nature of the metal ion on the mesophase behavior (*13*).

Discotic liquid crystals (*14*) are renowned for their one-dimensional charge and energy migration properties. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction (*15*). These supramolecular assemblies are of fundamental importance not only as models for the study of energy and charge migration in organized systems but also as functional materials for device applications such as, one-dimensional conductors, photoconductors, light emitting diodes, photovoltaic solar cells, gas sensors, etc. (*16*). Recently, Yoshio *et al.* reported one-dimensional ion transport in self-organized columnar ionic liquids (*17*). Despite the non-discotic shape of the trialkoxybenzene substituted imidazolium salt, it forms a columnar phase in which the ionic conductivities parallel to the columnar axis were found to be higher than those perpendicular to the axis (*17*). Similarly, rod-shaped 3,5-diaryl-1,2-dithiolium salts were also reported to exhibit columnar mesophases (*18*). We have recently reported pyridinium and imidazolium-based ionic discotic liquid crystal and their dimers with a triphenylene moiety (*19*).

Polymers consisting of a triphenylene unit have been well explored. The Ringsdorf group (*20*) reported side chain discotic polysiloxane with penta-substituted triphenylene rings attached to the backbone via flexible spacers with ethers or esters as a linking group. Suitably substituted triphenylene

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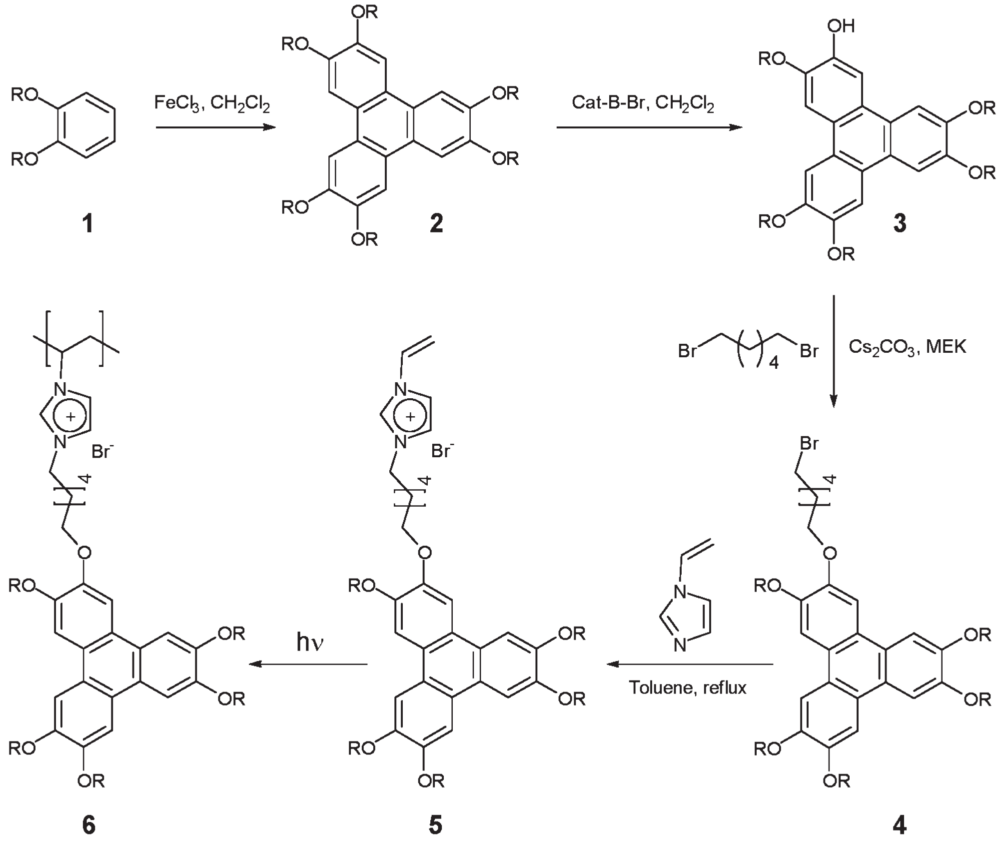
polyacrylates and polymethycrylates have been extensively studied (*21*). Very recently Imrie and co-workers prepared triphenylene-based side chain polymer by melt polycondensation of the triphenylene substitute isophthalate with polyethylene glycol (PEG 300) (*22*). The chemistry of triphenylene-based discotic dimers, oligomers and polymers has recently been covered in a review article (*23*). To the best of our knowledge ionic triphenylene polymers based on imidazolium ionic liquids has not yet been explored. Hybridization of ionic liquids and triphenylene discotics may lead to novel materials with interesting properties. In this communication we describe the synthesis and characterization of the first example of triphenylene-imidazole based ionic discotic liquid crystalline polymer.

The ionic polymer **6** was synthesized by the route shown in Scheme 1. Hexalkoxytriphenylenes **2**, monohydroxytriphenylenes **3** and ω-bromo-substituted triphenylenes **4** were prepared following literature methods (*24*). Liquid crystalline imidazolium salt **5** was obtained by reacting the bromo-substituted Compounds **4** with 1-vinylimidazole. Thus 0.1 g of Compound **4** was dissolved in 2.5 ml of toluene. To this, 2 ml of 1-vinyl imidazole was added and the reaction mixture was heated at 80°C for 8 hours under nitrogen with stirring. The solvent and excess of 1-vinyl imidazole were removed under vacuum and the residue was recrystallized twice from dry diethyl ether to afford the quaternized product **5** (80 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.3 (s, 1H), 7.82 (m, 6H), 7.37 (q, 1H), 7.30 (s, 1H), 7.21 (s, 1H), 5.78 (dd, 1H), 5.35 (dd, 1H), 4.43 (t, 2H), 4.24 (m, 6H), 1.02-2.03 (m, 49H). Elemental analysis: calculated for $C_{49}H_{69}O_6N_2Br$, C 68.29, H 8.06, N 3.25 %; found C 67.89, H 8.08.

For the preparation of polymer the monomer **5** and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (5 wt % to the monomer) were mixed thoroughly and sandwiched between two glass substrates, heated to the isotropic phase at 100 °C, and then cooled to room temperature at a cooling rate of 1°C min^{-1}. Photopolymerization was carried out under the exposure of UV light (400W, mercury vapour lamp) for one hour at room temperature. The polymer was dissolved in dichloromethane and precipitated by adding methanol. **^{1}H NMR** (400 MHz, $CDCl_3$, all the signals were quite broad in nature): δ 11.4 (s), 7.8 (m), 7.53 (s), 7.0 (s), 3.85–4.30 (m), 0.8–2.0 (m).

Gel permeation chromatography (GPC) was taken to characterize the polymer further. The



Scheme 1. Synthetic route of triphenylene-based ionic polymers.

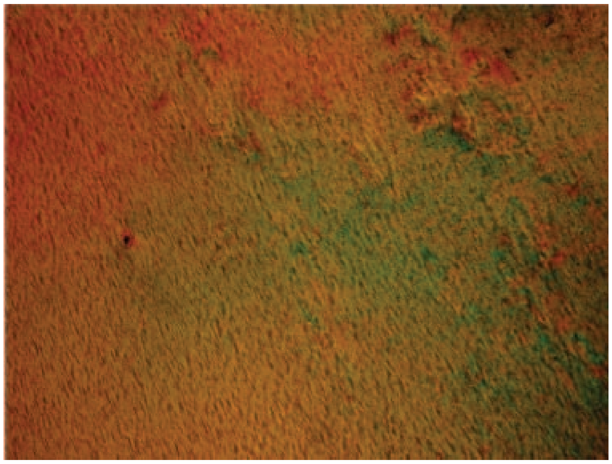


Figure 1. Optical photomicrograph of Compound **6** at 195 °C on cooling from isotropic liquid.

polymer showed a very broad peak near THF signal which corresponds to low molecular weight oligomers. The calculated weight-average molecular weight is around 5352 and number-average molecular weight is nearly 1192 with respect to polystyrene standard. Therefore, the polydispersity index comes around 4.

Compound **5** exhibited a broad melting peak at 88°C in the first heating run in the DSC. On cooling, a well-defined texture of a columnar mesophase appeared at 75°C and remained stable down to room temperature. The DSC first cooling run showed the isotropic phase to columnar mesophase peak centered at 72°C and no other crystallization peak was observed up to room temperature. During the second heating, the mesophase to isotropic phase transition appeared at 77°C with a much lower heat of transition indicating a mesophase to isotropic transition. On second cooling, the isotropic phase to columnar mesophase peak again appeared at 72°C. On the other hand the ionic polymer which is glassy at room temperature showed a very broad melting at around 224°C and finally went to isotropic phase at 244°C. On cooling mesophase appeared at around 209°C and remains stable down to room temperature. However, the material was not deformed at room temperature. Probably, it vitrified and formed a stable super cooled glassy columnar phase. Optical microscopy displayed birefringent but undefined texture (Figure 1), which is very common in liquid crystalline polymers.

The nature of the mesophase was confirmed from X-ray diffraction studies. Compound **5** showed 7 reflections which can be indexed in a simple rectangular lattice with lattice parameter a=3.68 nm, b=1.49 nm. In case of polymer the

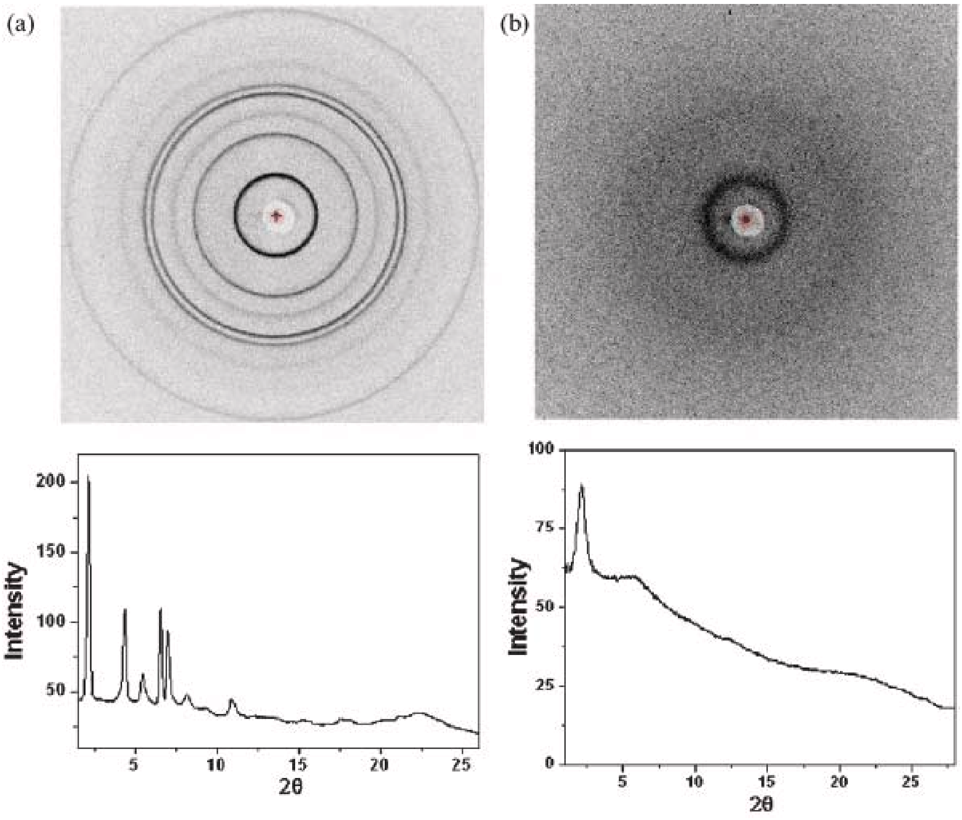


Figure 2. X-ray diffraction patterns obtained for monomer and polymers at 60°C and room temperature, respectively.

sample was heated to isotropic state and diffraction pattern was recorded at room temperature. Here, the lattice parameters were found almost same (a=3.71 nm, b=1.54 nm) as in the case of monomer, only peaks have broadened. This supports that columnar rectangular lattice is maintained in the polymer. The X-ray diffraction pattern and intensity *vs.* 2θ of both monomers and polymers have been shown in figure 2.

In conclusion, we have prepared and characterized a novel ionic discotic liquid crystalline polymer consisting of triphenylene and imidazole moieties. X-ray diffraction study indicates the columnar order is small in polymer compare to monomer. GPC showed that the polymer is actually a mixture of low molecular weight oligomers. This is probably due to steric hindrace of triphenylene units into the side chain. This finding is not only important for new possibilities of polymeric molten salts in materials science, but also contributes to the development of novel anisotropic soft materials for directional ion conductivity and charge transport.

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