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Synthesis of a novel liquid crystalline polymer, poly(2,5-didecyloxy-1,4-phenylenebutadiynylene)

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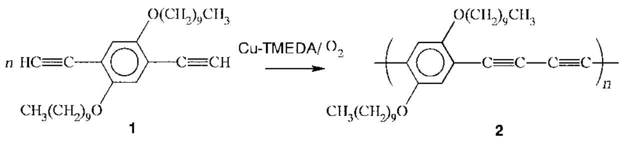
Oxidative polycondensation of 2,5-didecyloxy-1,4-diethynylbenzene with a Cu-amine catalyst gave a new soluble and fusible poly(2,5-didecyloxy-1,4-phenylenebutadiynylene) showing intense fluorescence, semiconducting properties upon doping with H_2SO_4, and thermotropic liquid crystalline properties.

The synthesis of linear carbon chains, carbynes, has been paid much attention as they represent a new carbon allotrope, although the syntheses have often not been successful due to unwanted side-reactions during the extension of the conjugation number and the instability of the product. The insolubility of the products has often led to ambiguous characterizations.[1] In order to overcome their lability, stabilization of the carbon chains could be achieved by means of end capping,[2–4] incorporation of inter-chain material,[5,6] and introduction of a stable unit in the conjugated carbon chain. Poly(arylene-*alt*-oligoethnylene)s, in which the arylene unit and the oligoethynylene unit are alternatively linked to form a rod-like polymer, belong to the last case. Although poly(aryleneethynylene)s have been noted as optoelectronic materials in recent years,[7–9] there have been few reports on the synthesis of polymers having polyyne segments longer than ethynylene, most of which involve metal–polyyne species.[10–12] Thus we report the synthesis and properties of a new soluble and fusible rod-shaped poly(arylenebutadiynylene) as an example of materials containing a linear carbon chain moiety.

The synthesis of poly(2,5-didecyloxy-1,4-phenylenebutadiynylene) **2** is shown in Scheme 1. The decyloxy substituent at the phenylene unit is incorporated to increase the solubility and fusibility of the polymer, since unsubstituted poly(1,4-phenylenebutadiynylene) is almost insoluble and infusible.[10] 1,4-Didecyloxy-2,5-diethynylbenzene **1**[7] (660 mg, 1.5 mmol in 8 mL of THF) was added in a THF solution (30 mL) of a Hay catalyst[13] [37 mg of CuCl and 44 mg of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA)] and reacted for 24 h at room temperature under O_2, giving a powdery yellow polymer. The polymer was soluble in hot $CHCl_3$ and THF, but the solubility was poor at room temperature. The crude polymer was purified *via* normal reprecipitation methods using MeOH–HCl and MeOH successively, and dried under vacuum. The polymer structure was confirmed by IR (disappearance of an absorption at 3286 cm^{-1} due to acetylenic $\nu_{C—H}$), Raman (appearance of a new peak at 2200 cm^{-1} due to $\nu_{C\equiv C}$), NMR and elemental analysis.‡ The number average molecular weight (M_n) of this polymer was 5400 ($M_w/M_n = 2.4$) *vs.* polystyrene standards *via* GPC analysis. The conjugation length (n) is estimated to be about 12 from the M_n value. The low degree of polymerization and the high polydispersity are due to the heterogeneous conditions toward the end of the reaction, brought about by the low solubility of the produced polymer in the reaction medium.

The polymer **2** shows an intense luminescence in solution (blue–green) even at a very low concentration (Fig. 1) and in the solid state (yellow). Similar fluorescent properties have been reported in the cases of poly(aryleneethynylene)s.[7–9] The fluorescent maximum was 475 nm and the UV–VIS absorption maximum was 424 nm in $CHCl_3$ solution, which is comparable to the corresponding poly(aryleneethynylene) showing a fluorescent maximum at 475 nm and a UV–VIS maximum at 419 nm.

Stimulated by reports that similar rod-like poly(aryleneethynylene)s exhibit thermotropic[7] or lyotropic[9] liquid crystalline properties, the thermal properties of the polymer **2** were investigated by differential scanning calorimetry (DSC) and thermo-controlled polarizing microscopy. In the DSC curves in Fig. 2, two sharp exothermic peaks are observed during cooling, suggesting that the former is an isotropic–liquid crystalline phase transition ($\Delta H = -74.6$ J g^{-1})§ and the latter is a liquid crystalline–crystalline phase transition ($\Delta H = -15.4$ J g^{-1})§. On the other hand, the total enthalpy of the two overlapping endothermic peaks is about 86 J g^{-1}, approximately corresponding to the total exothermic enthalpy



Scheme 1.

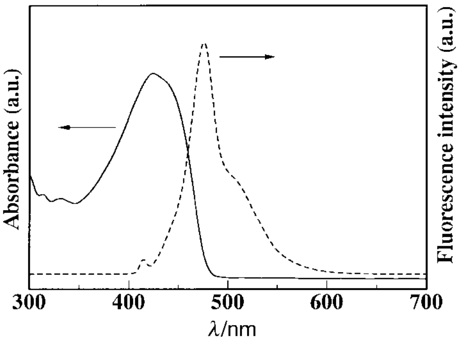


Fig. 1 Absorption (solid line) and fluorescence (broken line) spectra of polymer **2** in $CHCl_3$.

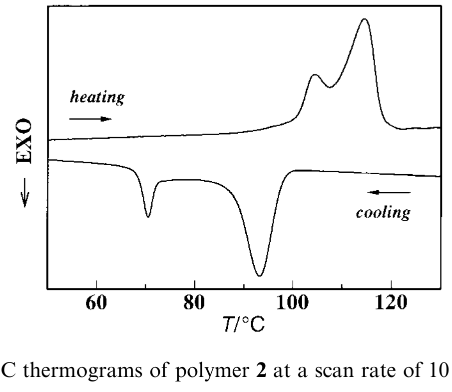


Fig. 2 DSC thermograms of polymer **2** at a scan rate of 10 °C min^{-1}.

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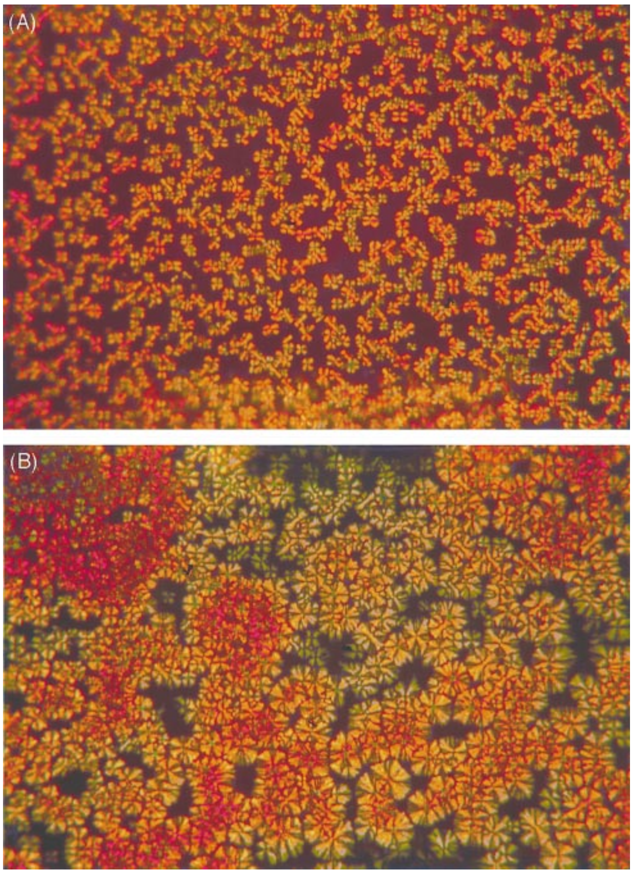

Fig. 3 Optical micrographs of polymer **2** observed between crossed polarizers at 200 × magnification (A) in a liquid crystalline state at 105 °C and (B) in a crystalline state at room temperature.

(90 J g^{-1}). These enthalpies are ascribed to orientation of the rod-like polymer molecules. The polymer **2** melts at 125 °C, and when it cools to 105 °C, birefringent droplets with poor fluidity appear and a mesomorphic texture with a Maltese cross is observed [Fig. 3(A)], which is frequently observed for rigid backbone polymers in a homeotropic nematic state.[11,14] With further cooling of the sample below 75 °C, the mesophase changes to a crystalline phase exhibiting a spherulitic texture [Fig. 3(B)]. In spherulites, the molecular axes of the crystals are thought to be perpendicular to the radii of the spherulite.[15] Thus the crystalline phase grows outwards in all directions from a point with a continual side-by-side accretion of the rod-like polymer chains. The thermo-controlled X-ray analysis of the sample shows a broad peak around $2\theta = 15–25°$ ($d = 6–3.5$ Å) in the liquid crystalline state and a sharp peak at $2\theta = 23.4°$ ($d = 3.8$ Å) in the crystalline state. These peaks are due to the molecular distances, and peaks due to a layer distance typical of smectic phases were not be observed. From DSC, microscopic and XRD analyses, the liquid crystalline phase is concluded to be a columnar nematic phase consisting of rod-like polymer molecules.

Thin film samples can be prepared by casting from a $CHCl_3$ or a THF solution on a glass plate but they are brittle, which is characteristic of low molecular weight rigid polymers.

The electrical conductivity of a pellet sample prepared from the as-prepared powdery product under a pressure of 400 kg f cm^{-2} was of the order of 10^{-8} S cm^{-1} without I_2 doping, but it increased to the order of 10^{-5} S cm^{-1} after H_2SO_4 doping. A pellet sample of unsubstituted poly(*p*-phenylenebutadiynylene) synthesized by the Hay method[10] showed similar conductivity of the order of 10^{-8} S cm^{-1} and 10^{-6} S cm^{-1} after H_2SO_4 doping, respectively. The higher conductivity of the doped polymer might be due to the alkoxy substituents, which play a role in lowering the ionization potential of the polymer by analogy with the case of poly(*p*-phenylenevinylene).[16]

Consequently, it has been shown that the inherently rod-like polymer **2** having the flexible decyloxy side chains exhibits intense fluorescent, semiconducting, and thermotropic liquid crystalline properties. Furthermore, the polymer solidifies as a crystalline material *via* a liquid crystalline–crystalline phase transition. Introduction of the linear butadiynylene unit in the polymer main chain explains the increase in crystallinity. Further investigations on the synthesis of polymers with high-molecular weight and good processability for thin films and on structural analysis of the polymer in the mesophase and the crystalline phase are currently under way.

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Notes and references

‡ Elemental analysis: Found: C, 82.2; H, 10.3. Calc. for $(C_{30}H_{44}O_2)_n$: C, 82.5; H, 10.15%.

§ Molar enthalpy values are $\Delta H = -32.5$ kJ mol^{-1} and -6.7 kJ mol^{-1}, respectively, taking the repeat unit of the polymer as a molar unit. Mean enthalpies per mole of polymer molecules can be estimated by multiplying the molar enthalpies by the average number of conjugation ($n = 12$).

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