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Synthesis and polymerization of β,β-dibromo-4-ethynylstyrene; preparation of a new polyconjugated, hyperbranched polymer

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The new monomer β,β-dibromo-4-ethynylstyrene was synthesized and polymerized by the Heck reaction to give a partially soluble, conjugated hyperbranched polymer. The polymer structure was elucidated using standard spectroscopic techniques and with the aid of model compound synthesis. Theoretical calculations using the AM1 method were carried out and they showed that conjugation in the polymer is partially disrupted by twisting of the benzene rings. Both the model compound and the polymer showed luminescence. Copyright © 1996 Elsevier Science Ltd.

(Keywords: Heck reaction; acetylenes; diacetylenes)

INTRODUCTION

There is growing interest in macromolecules with architectures that differ from those of the classical linear polymers as these new polymer architectures may exhibit unusual behaviour and possess properties that differ from those of linear materials. The synthesis of new macromolecular architectures where the ratio of branches to monomer units approaches unity can be conveniently divided into two separate fields. Major efforts have been directed towards the preparation of perfect dendritic macromolecules by stepwise divergent[1] or convergent[2,3] synthetic approaches. While highly defined structures are obtained which are excellent for investigation, they are obtained in only limited quantities after much effort. On the other hand, polymerization of AB_2 monomers[4,5] leads directly to hyperbranched macromolecules which, owing to their polydispersity and less perfect branching, can be considered as a separate field of study. One of the advantages of hyperbranched polymers is their high solubility as compared to their linear analogues.

It is also known that the polyconjugated polymers which show conductivity and non-linear optical properties are mostly insoluble unless they contain long aliphatic groups. These spacers decrease the non-linear optical properties of the polymer at the expense of diluting the polyconjugated chains with aliphatic groups. Consequently, it would be interesting to try to prepare a fully conjugated[4,5] hyperbranched polymer without aliphatic spacers and study its properties.

This paper reports on the synthesis and polymerization of the new AB_2-type monomer β,β-dibromo-4-ethynylstyrene. The polymerization of this monomer gave a polyconjugated, hyperbranched polymer. Also reported is the synthesis of the model compound 4,4′-bis[2,2-(diethynylylphenyl)vinyl]diphenyldiacetylene.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) and triethylamine (TEA) were distilled just before reaction. Methylene chloride was distilled over CaH_2. Other reagents were used as received (Aldrich). 4-Ethynylbenzaldehyde **1** was prepared according to a procedure given elsewhere[6].

Preparation of β,β-dibromo-4-ethynylstyrene **2**. Carbon tetrabromide (6.4 g, 19.2 mmol) was dissolved in 300 ml of CH_2Cl_2 and triphenylphosphine (TPP) (10.05 g, 38.3 mmol) was added under nitrogen to the solution. 4-Ethynylbenzaldehyde **1** (2.5 g, 19.2 mmol) was added to the orange solution over a period of 10 min at room temperature and the reaction was followed by thin layer chromatography (t.l.c.). After 5 h the reaction mixture was washed with a 5% solution of potassium hydrogencarbonate, the solvent was evaporated under vacuum and the residue was extracted twice with 200 ml of hot hexane. The extract was concentrated to 100 ml and then passed down a chromatography column packed with SiO_2 using hexane as eluent to give a 70% yield of monomer **2** (melting point 49°C). ^{13}C n.m.r. ($CDCl_3$), δ (ppm) 78.5 (s, $HC\equiv$), 83.2 (s, $\equiv C-$), 90.7 (s, $=CBr_2$), 122.2 (s, $>C-C\equiv$), 128.2 (s, *m*-aromatic), 132.0 (s, *o*-aromatic), 135.5 (s, $=C-C<$), 136.1 (s, $=C-$). Calculated for $C_{10}H_6Br_2$:

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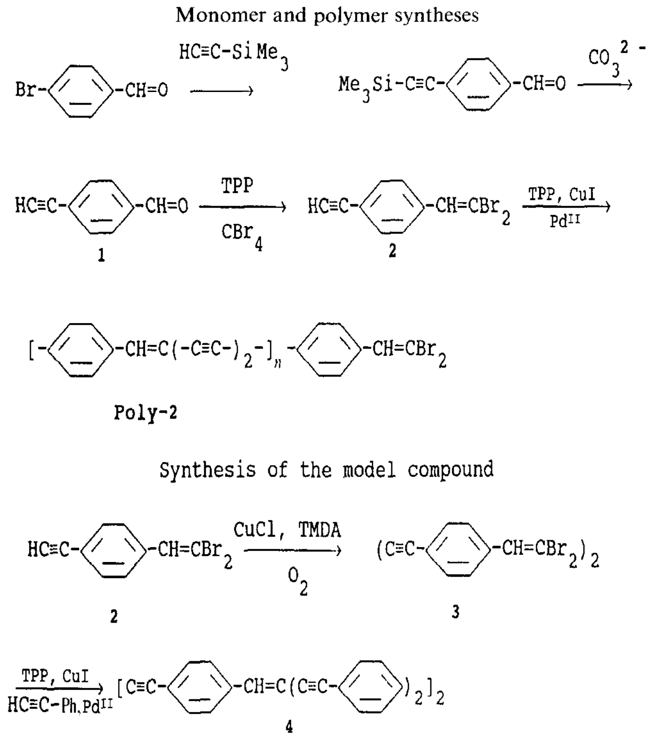

Scheme 1

C, 41.96; H, 2.10; Br, 55.94. Found: C, 41.99; H, 2.10; Br, 55.91.

Preparation of 4,4′-bis(2,2-dibromovinyl)diphenyldiacetylene 3. β,β-Dibromo-4-ethynylstyrene **2** (1.5 g) was dissolved in isopropanol (100 ml) and CuCl (0.05 g) and *N,N,N′,N′*-tetramethylethylenediamine (TMDA) (0.1 ml) were added to the solution. Oxygen was bubbled through the reaction mixture for 6 h at room temperature. The reaction mixture was poured into water acidified with HCl, and the precipitated solid was filtered off, washed with water, dried and crystallized from a 1 : 1 mixture of toluene and ethanol to give a 77% yield of pure product (melting point 191°C). I.r. (cm^{-1}) 2145, 2136 ($C \equiv C - C \equiv C$). ^1H n.m.r. ($CDCl_3$), δ (ppm) 7.40–7.60 (m). ^{13}C n.m.r. ($CDCl_3$), δ (ppm) 75.0 (s, $\equiv C - C \equiv$), 82.0 (s, $-C \equiv$), 91.0 (s, $= CBr_2$), 122.0 (s, $>C - C \equiv$), 128.2 (s, *m*-aromatic), 132.1 (s, *o*-aromatic), 135.4 (s, $= C - C<$), 136.0 (s, $= C-$). Calculated for $C_{20}H_{10}Br_4$: C, 42.11; H, 1.75; Br, 56.14. Found: C, 42.30; H, 1.68; Br, 55.99.

Preparation of 4,4′-bis[2,2-(diethynylylphenyl)vinyl]-diphenyldiacetylene 4. 4,4′-Bis(2,2-dibromovinyl)diphenyldiacetylene **3** (0.80 g, 1.4 mmol) was dissolved in a deoxygenated mixture of THF (25 ml) and TEA (25 ml). To this solution, TPP (0.08 g), CuI (0.02 g), phenylacetylene (0.6 g, 5.88 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.014 g) were added sequentially under nitrogen and the reaction mixture was refluxed for 24 h. Then the reaction solution was filtered, the solvent was evaporated under vacuum and the residue was purified by column chromatography (eluent hexane, then a 3 : 1 mixture of hexane and benzene to give an 84% yield of pure product (melting point 250°C (with decomposition)). I.r. (cm^{-1}) 2200 ($= C - (C \equiv C)_2-$), 2148 ($C \equiv C - C \equiv C$). ^1H n.m.r. ($CDCl_3$), δ (ppm) 7.13 (s, 2H), 7.3–7.45 (m, 16H), 7.5–7.6 (m, 20H). ^{13}C n.m.r. ($CDCl_3$), δ (ppm) 75.9, 82.4, 87.0, 95.8, 105.0, 122.3, 123.0, 128.5, 128.7, 129.0, 131.8, 132.5, 135.5, 141.9. Calculated for $C_{52}H_{30}$: C, 95.41; H, 4.59. Found: C, 94.06; H, 4.62.

Preparation of poly(β,β-dibromo-4-ethynylstyrene) (poly-2). β,β-Dibromo-4-ethynylstyrene **2** (2 g, 7 mmol) was dissolved in a deoxygenated mixture of THF (25 ml) and TEA (25 ml). To this solution, TPP (0.4 g,

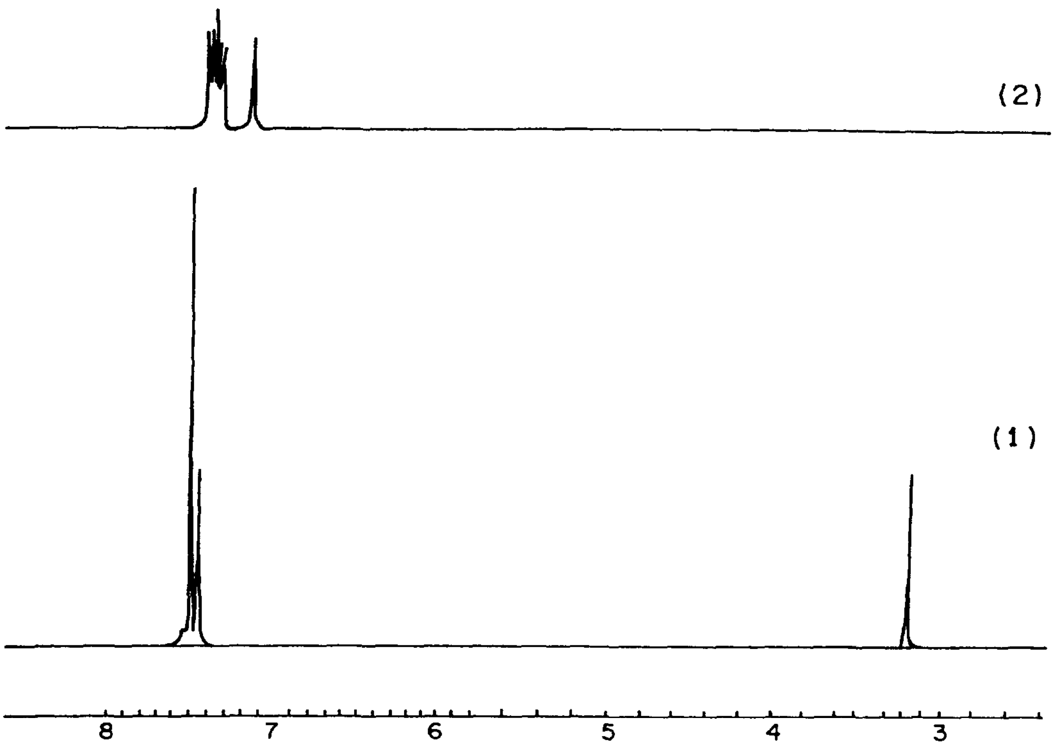

Figure 1 ^1H n.m.r. spectra of monomer **2** (1) and poly-**2** (2)

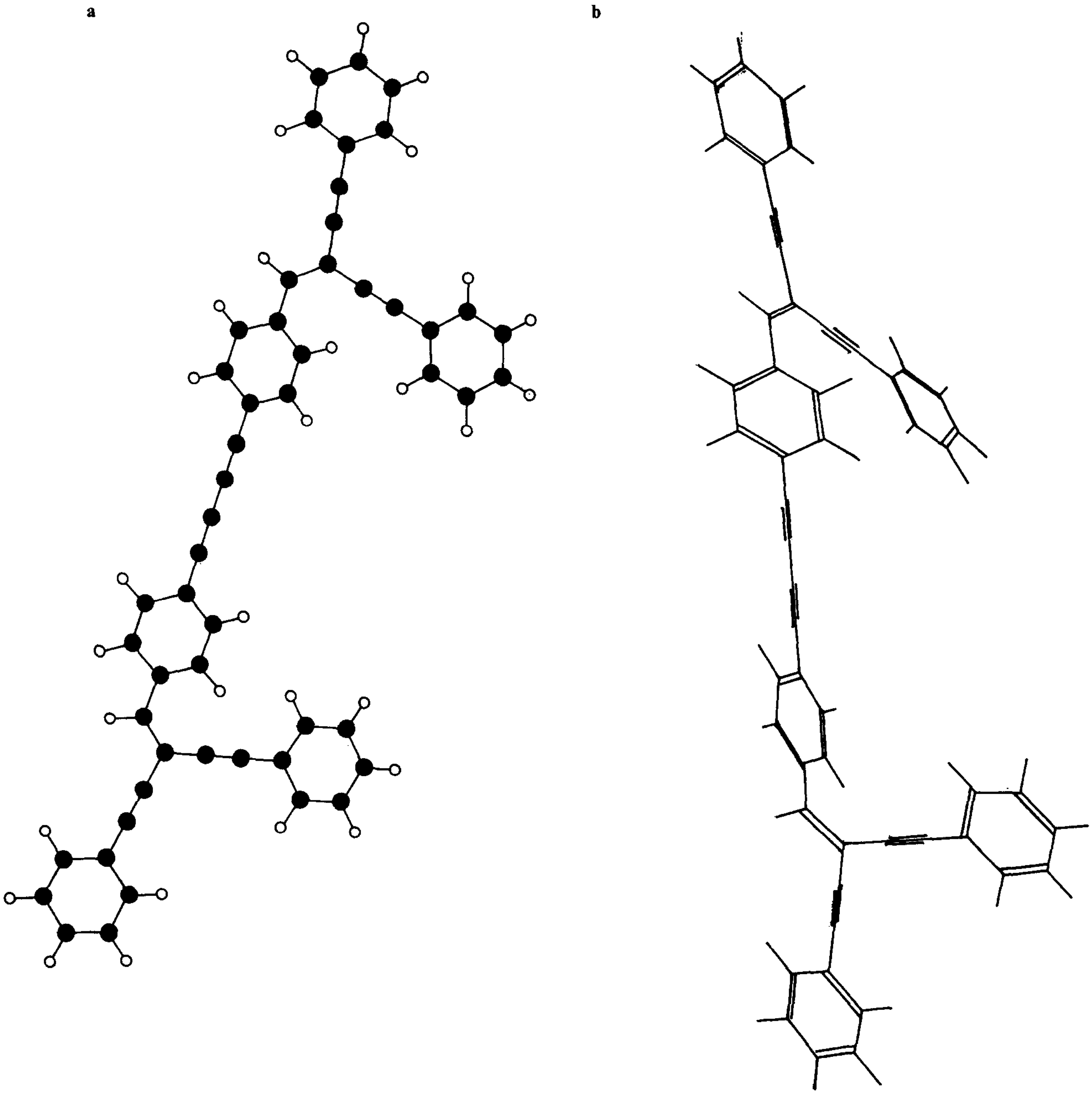

Figure 2 (a) Model compound; (b) non-planar geometry of model compound

1.55 mmol), CuI (0.05 g) and bis(triphenylphosphine)-palladium(II) dichloride (0.07 g) were added sequentially under nitrogen and the reaction mixture was refluxed. The polymerization was followed by t.l.c. for consumption of the monomer. After 24 h of reflux, t.l.c. showed that there was no monomer left, and the orange solid was precipitated by pouring the reaction mixture into water acidified with HCl. The polymer was filtered off, washed with methanol and dried under vacuum. Then the polymer was extracted with boiling *o*-dichlorobenzene and precipitated in methanol to give a 64% yield of soluble polymer. ^{13}C n.m.r. ($CDCl_3$), δ (ppm) 87.2, 91.1, 95.9, 105.2, 122.0, 122.8, 128.4, 128.6, 131.9, 132.3, 135.3, 135.5, 136.1, 141.5. Calculated: C, 58.60; H, 2.44; Br, 39.0. Found: 59.50; H, 2.55; Br, 37.95.

Measurements

^{1}H n.m.r. and ^{13}C n.m.r. spectra were recorded with a Varian 200 MHz n.m.r. spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. I.r. spectra were taken with a Nicolet 510p Fourier transform i.r. spectrometer. U.v. spectra were taken with a Shimadzu UV-260. Luminescence spectra were taken with a Perkin–Elmer u.v. spectrometer with excitation at $\lambda = 420$nm. X-ray diffractometry was performed using a Siemens D-500 diffractometer with CuK radiation of 1.540 Å (1 Å = 0.1 nm) wavelength. The relative molecular weight of the soluble fraction was determined using gel permeation chromatography (g.p.c.) on a Varian 9012 instrument at 30°C with THF as eluent, polystyrene standards, a universal column and a flow rate of 1 ml min^{-1}

All theoretical calculations were carried out using the AM1 method[7] included in the Cerius package[8]. The initial geometries were built using the Universal FF method[9] included in the same package.

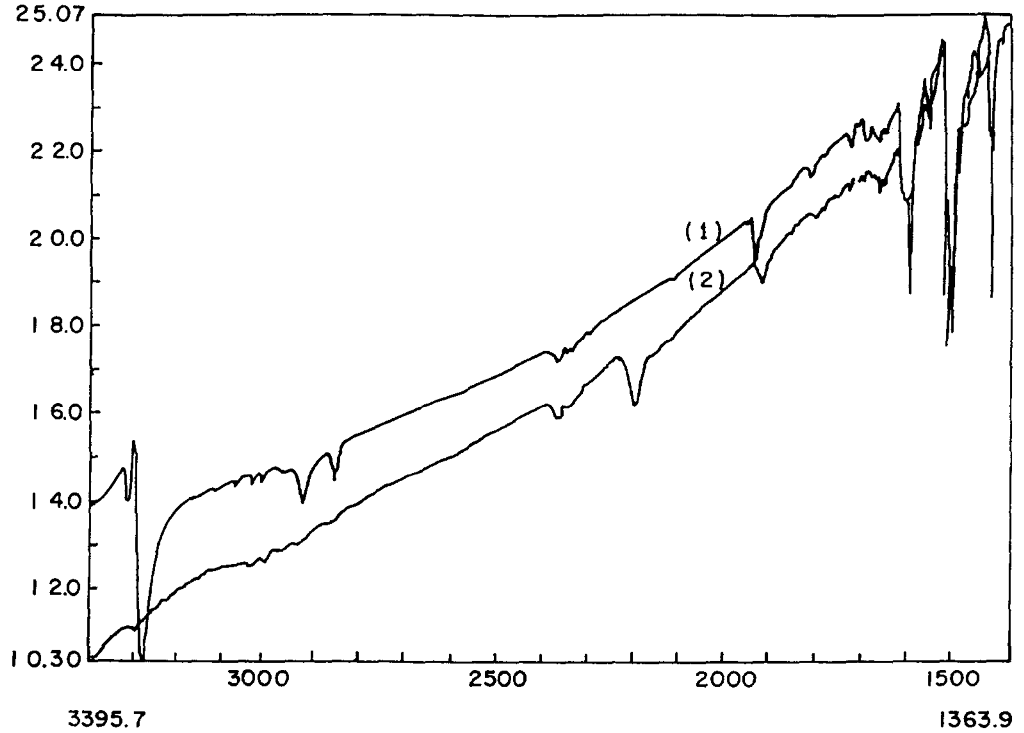

Figure 3 *FT* i.r. spectra of monomer **2** (1) and poly-**2** (2)

RESULTS AND DISCUSSION

The monomer and polymer syntheses are shown in *Scheme 1*. Monomer **2** was prepared from 4-ethynylbenzaldehyde **1** by the Wittig reaction. ^{1}H n.m.r. spectra are presented in *Figure 1*. As can be seen from the ^{13}C n.m.r. data of **2**, the signal for $= CBr_2$ is located at 90.7 ppm, indicating a rather high electron density at this atom and suggesting a fairly low reactivity of this group in the Heck reaction[10]. This was confirmed by theoretical calculations using the AM1 method. The negative charge was calculated for the terminal atom of the double bond of monomer **2** and was −0.306 against a poor −0.045 for the other carbon atom on the double bond.

The theoretical simulation of the model compound **4** shows that there is no planarity at all. This result indicates low conjugation near the triple bonds, allowing free rotation of the single bonds. This feature accounts for the acceptable solubility of **4**. The shape and geometrical conformation of this molecule are shown schematically in *Figure 2*.

Some interesting thermodynamic results obtained in the same calculation were a heat of formation of 486.25 kcal mol^{-1} (1 cal = 4.2 J), a total energy of −7056.346 eV and an ionization potential (Koopman's theory) of 8.315 eV.

In order to correlate the properties of poly-**2** with its structure, we prepared the model compound **4** by oxidative coupling of monomer **2** followed by Heck reaction of the tetrabromo derivative **3** with phenylacetylene (*Scheme 1*). The model compound **4** was yellow and strongly luminescent.

During the polymerization of monomer **2**, the reaction solution turned first yellow and then orange, indicative of the formation of a polyconjugated structure, and then the polymer started precipitating. Poly-**2** was not completely soluble even in hot *o*-dichlorobenzene. The

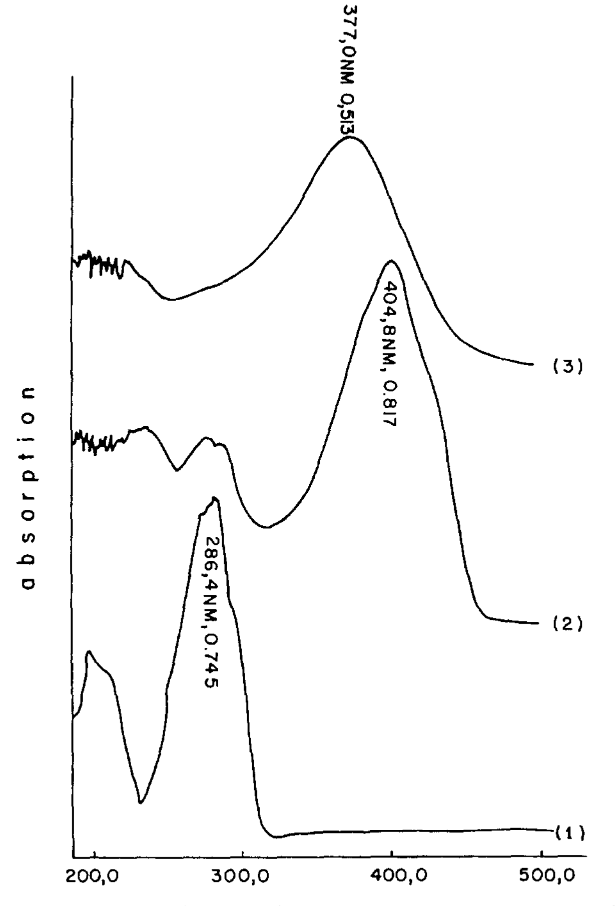

Figure 4 U.v.-visible absorption spectra of monomer **2** (1), model compound (2) and poly-**2** (2)

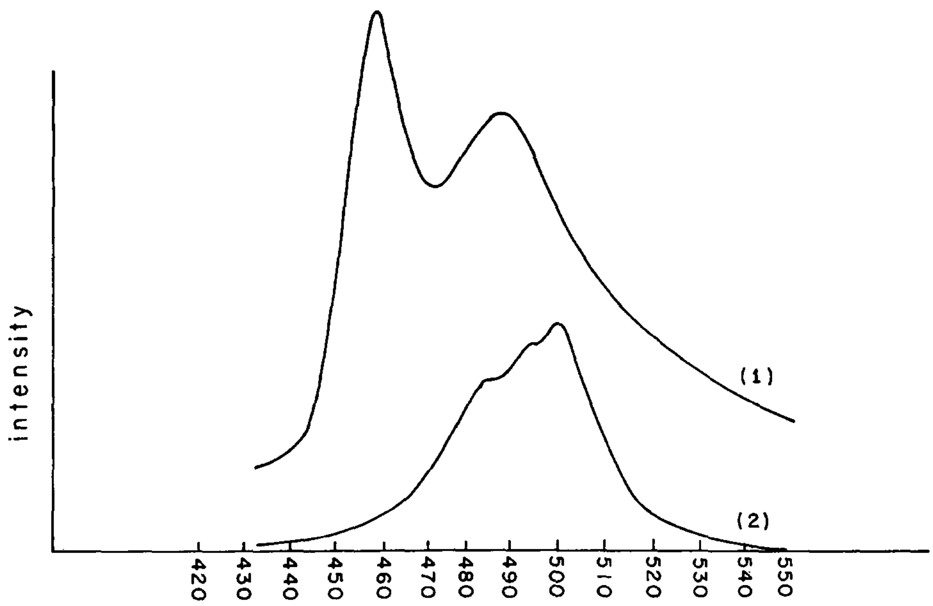

Figure 5 Luminescent spectra of the model compound (1) and poly-2(2). $\chi_{ext} = 420$ nm

soluble fraction of the polymer was isolated and analysed. This reaction was soluble at room temperature in chlorinated and aromatic solvents such as $CHCl_3$ and toluene, and the solubility increased on heating. The weight average molecular weight of the soluble fraction of poly-**2** was found to be as high as 70 722 with a polydispersity index of 1.76.

The composition of poly-**2** and the bromine content, in particular, are related to the molecular weight. Unlike linear polymers, hyperbranched polymers, even those with high molecular weights, have many end-groups. Thus, upon increasing the molecular weight, the bromine content changes from 55.94% for monomer **2** to 39.0% for poly-**2** having an infinitely high molecular weight. Poly-**2** with an infinitely high molecular weight should contain 58.60% carbon, 2.44% hydrogen and 39.0% bromine. The elemental analysis of poly-**2** showed 59.50% carbon, 2.55% hydrogen and 37.95% bromine. These results are beyond the sensitivity of an end group determination technique and agree reasonably well with the g.p.c. data, which gave a rather high molecular weight for poly-**2**.

Fourier transform i.r. spectra of monomer **2** and poly-**2** are shown in *Figure 3*. The absorption band at $2190\,cm^{-1}$ in the spectrum of poly-**2** corresponds to conjugated internal triple bonds. Similarly, the poly-**2** model compound **4** also has an absorption band at $2200\,cm^{-1}$. Absorption bands at 2108 and $3275\,cm^{-1}$ corresponding to $HC \equiv C-$ and $H-C\equiv$ stretches, respectively, are completely absent from the spectrum of poly-**2**.

The ^1H n.m.r. spectrum of poly-**2** is shown in *Figure 1*. The signal of the acetylenic proton at 3.13 ppm is completely absent from the spectrum of poly-**2**, and it can be seen that the signal at 7.13 ppm corresponds to the olefinic proton. In the ^1H n.m.r. spectrum of monomer **2**, the signal of the olefinic proton appeared together with the signals of the aromatic protons in the region 7.4–7.6 ppm. Because of this overlap in signals, we cannot calculate the branching degree of poly-**2**. The ^1H n.m.r. spectrum of model compound **4** is very similar to that of poly-**2** in the region 7.0–7.6 ppm. The signal of the olefinic proton occurs at 7.13 ppm, exactly the same as in poly-**2**, thus supporting the proposed structure of the polymer.

The ^{13}C n.m.r. spectrum of poly-**2** differs from that of monomer **2**. The signals of the terminal acetylenic group at 78.5 and 83.2 ppm are absent and the signals of the internal acetylenic groups appeared for poly-**2** at 87.2 and 95.9 ppm. By comparison with the spectrum of model compound **4**, the new signals at 105.2 and 141.5 ppm in the spectrum of poly-**2** were attributed to carbon atoms of double bonds substituted with two ethynyl groups. The signals of the terminal olefin can also be seen at 91.1 and 136.1 ppm, coinciding closely with those signals of monomer **2** (90.7 and 136.0 ppm).

Figure 4 shows the u.v.–visible absorption spectra of monomer **2**, poly-**2** and model compound **4**. As can be seen from the spectra, a long wavelength absorption maximum at 377 nm appeared on polymerization, indicating the formation of a conjugated structure. However, the model compound **4** has an absorption maximum at 404 nm, indicating a more expanded conjugation system in this case. This suggests that the conjugation in hyperbranched poly-**2** is disrupted by steric hindrance. To prove this suggestion, we calculated the most stable geometry of poly-**2** using the AM1 method. The most stable conformation of poly-**2** is shown in *Figure 5*. It is clear that the π-orbitals of poly-**2** do not lie in a plane, thus disrupting the conjugation system.

Both model compound **4** and poly-**2** showed luminescence in solution (*Figure 6*). The luminescence spectrum of poly-**2** has a maximum at 500 nm and a shoulder at 460 nm (excitation at 420 nm). The luminescence spectrum of **4** has maxima at 460 and 485 nm for the same excitation wavelength of 420 nm. Compound **4** shows stronger luminescence than poly-**2** which may be a result of luminescence quenching by the terminal bromine atoms in poly-**2**.

CONCLUSIONS

The new monomer β,β-dibromo-4-ethynylstyrene was synthesized and polymerized by the Heck reaction to give a partially soluble, conjugated, hyperbranched polymer. The soluble part of the polymer showed a rather high molecular weight in both g.p.c. and end-group analysis. The structure of poly-**2** was confirmed by n.m.r., Fourier transform i.r., elemental analysis and model compound synthesis. Both the model compound **4** and poly-**2** were luminescent in solution with long wavelength maxima at or near 500 nm for excitation with light of 420 nm wavelength.

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