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Synthesis and Characterization of Novel Hyperbranched Polymers with Discrete Conjugated Units *via* Heck Reaction

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ABSTRACT: A novel monomer β,β'-dibromo-4-(10-undecynoyloxy)styrene (**5**) was synthesized and polymerized to give a soluble hyperbranched polymer (**poly-5**) containing discrete conjugated units. Copolymerization of monomer **5** with β,β'-dibromo-4-ethynylstyrene (**6**) produced partially soluble hyperbranched copolymer **poly-56**. The average conjugated length was longer for **poly-56**. The polymer structure was determined by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The polymers were found to be photoluminescent with emission peaks correlated with absorption maxima. **Poly-56** was less thermally stable than **poly-5** due to higher concentration of the triple bonds.

KEY WORDS Hyperbranched Polymers / Heck Reaction / Photoluminescence /

Hyperbranched polymers obtained from AB_2 type monomers are taking on increasing interest. There is a growing interest in macromolecules with architectures differing from the classical linear polymers as these new polymer architectures may exhibit unusual behavior and posses properties that differ from those of linear materials. Some advantages of hyperbranched polymers are high solubility compared with their linear analogs and high concentrations of end groups even for high polymers. Currently, hyperbranched polymers are attracting attention as candidates for optoelectronics application. Thus, the preparation of a new AB_2 monomer 3,6-diformyl-9-(11-hydroxyundecyl)carbazole and polymerization to a new hyperbranched polymer intended for nonlinear optics have recently been reported.[1]

The present authors are interested in the development of polymers with new chemical structures for photo- and electroluminescent and nonlinear optics, and previously reported the synthesis and polymerization of a new monomer of AB_2 type; β,β'-dibromo-4-ethynylstyrene by the Heck reaction, resulting in conjugated hyperbranched polymer.[2] This polymer was partially soluble in hot chlorinated aromatic hydrocarbons, showed M_w of 70700 and exhibited intense photoluminescence with emission peak at 500 nm. Theoretical calculations and model compound synthesis indicated effective conjugation length in the polymer not to exceed a repeating unit due to steric hindrance. Therefore, we attempted to increase the solubility of the polymer introducing flexible spacers, thus obtaining a hyperbranched polymer containing discrete conjugated units. Some linear polymers containing discrete conjugated units such as fluorescein,[3,4] diethynylanthracene,[5] vinylphenylanthracene,[6] and arylenevinylideneethynylene[7] have been prepared at the laboratory. They showed photo- and electroluminescence and the third order harmonic generation up to 3×10^{-10} esu and gave films with good optical quality by casting.

This work is concerned with the synthesis of novel hyperbranched polymers with discrete arylenevinylideneethynylene groups by the Heck reaction of a novel monomer: β,β'-dibromo-4-(10-undecynoyloxy)styrene, and its copolymerization with β,β'-dibromo-4-ethynylstyrene.

EXPERIMENTAL

Materials

1,4-Dioxane and triethylamine (TEA) were distilled just before use, methylene chloride was distilled over CaH_2. Other reagents were used as received. β,β'-Dibromo-4-ethynylstyrene was prepared according to the literature.[2] The synthesis of the monomer and the polymers is shown in Scheme 1.

4-(10-Undecynoyloxy)benzaldehyde (**4**)

10-Undecynoic acid (**1**) (10 g, 55 mmol), 100 ml CH_2Cl_2 and $SOCl_2$ (16 g, 132 mmol) were refluxed for 8 h. The solvent and excess $SOCl_2$ were removed under vacuum at room temperature and crude acid chloride **2** was added to a solution of 4-hydroxybenzaldehyde (**3**) (6.7 g, 55 mmol) in 100 ml pyridine at 5°C and the reaction mixture was stirred for 4 h at room temperature. The reaction mixture was poured into a cool diluted hydrochloric acid and extracted with benzene. The extract was washed with water and dried over magnesium sulfate. The solvent was evaporated under vacuum and the residue was crystallized from hexane. Yield 47%, $T_m = 39$—40°C. IR (cm^{-1}) 3296 ($\equiv$C–H), 3070 (C–H, arom), 2934, 2856 (C–H, aliph.), 2115 (–C$\equiv$CH), 1763 (C=O, ester), 1701 (C=O, aldehyde).

β,β′-Dibromo-4-(10-undecynoyloxy)styrene (**5**)

To a solution of CBr_4 (7.51 g, 22.6 mmol) in 100 ml CH_2Cl_2, triphenylphosphine (TPP) (11.85 g, 45.2 mmol) was added dropwise at room temperature. The orange solution formed was stirred for 15 min and compound **4** (6.47 g, 22.6 mmol) dissolved in 50 ml CH_2Cl_2 was slowly added to the solution. The reaction mixture was stirred for 24 h at room temperature, the solvent was removed under reduced pressure, the residue was extracted by hot hexane and chromatographed on SiO_2 (hexane). Yield 48%, $T_m = 36$—37°C. IR (cm^{-1}) 3300 ($\equiv$C–H), 3020 (C–H, arom), 2928, 2853 (C–H, aliph.),

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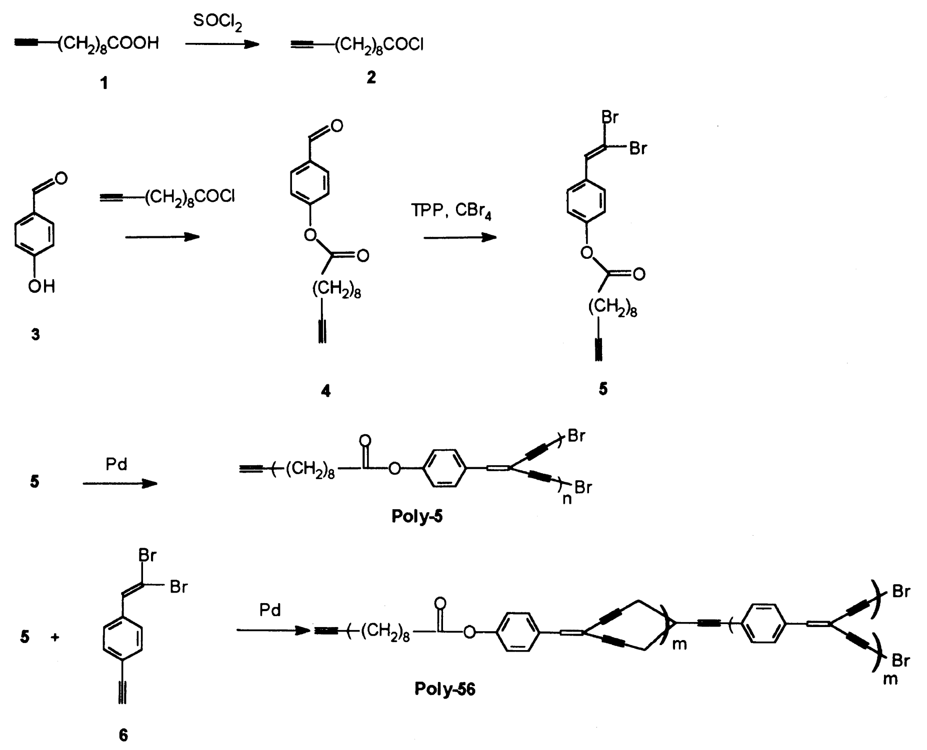

Scheme 1.

2115 (–C≡CH), 1747 (C=O, ester). ^{1}H NMR ($CDCl_3$) 7.55—7.50 (m, 2H, arom, *ortho* to dibromovinyl group), 7.42 (s, 1H olefinic) 7.08—7.05 (2H, arom, *metha* to dibromovinyl group), 2.52 (t, 2H, $J=7.5$ Hz, –(O)C–CH_2), 2.16 (t, d, 2H, $J_t=6.9$ Hz, $J_d=2.4$ Hz, –$\underline{C}H_2$–C≡CH), 1.93 (t, 1H, $J=2.4$ Hz, ≡CH), 1.74—1.30 (m, 12H, –$(CH_2)_6$–). ^{13}C NMR 171.4 (C=O ester), 150.5 (–O–C_{arom}), 135.7 (–$\underline{C}$H=CBr_2), 132.4 (Br_2C=CH–$C_{\underline{arom}}$), 129.3 (arom, *ortho* to dibromovinyl group), 121.4 (arom, *metha* to dibromovinyl group), 89.5 (=CBr_2), 84.4 (–C≡), 68.1 (≡CH), 34.1 (–(O)C–$\underline{C}H_2$–), 35—24 (–(CH_2)–), 18.2 (–$\underline{C}H_2$–C≡).

Poly(β,β′dibromo-4-(10-undecynoyloxy)styrene) (**Poly-5**)

Monomer **5** (1.833 g, 4.147 mmol) was dissolved in a mixture of 1,4-dioxane (10 ml) and TEA (10 ml). Nitrogen was bubbled through the solution for 20 min, TPP (0.24 g), CuI (0.05 g), and $PdCl_2(TPP)_2$ (0.04 g) were added and the reaction mixture was refluxed under nitrogen for 24 h. The solution was filtered, and the polymer precipitated in water. The polymer was filtered off, washed with methanol and purified by the precipitation from chloroform to methanol. Yield 87%.

(**Poly-56**) monomer **5** (1.033 g, 2.337 mmol) and monomer **6** (0.684 g, 2.337 mmol) were dissolved in a mixture of 1,4-dioxane (10 ml) and TEA (10 ml). Nitrogen was bubbled through the solution for 20 min, then TPP (0.25 g), CuI (0.05 g), and $PdCl_2[(TPP)_2$ (0.05 g) were added and the reaction mixture was refluxed under nitrogen for 24 h. The solution was poured in water. The polymer was filtered off, washed with methanol and purified by the precipitation from chloroform to methanol. Yield 54%.

Poly(β,β′-dibromo-4-(10-undecynoyloxy)styrene-co-β,β′-dibromo-4-ethynylstyrene)

Measurements and Sample Preparation. The relative molecular weights of polymer **poly-5** and **poly-56** were determined using a Varian 9012 GPC instrument at 30°C in CH_2Cl_2 with polystyrene standard, universal column and a flow of 1 ml min^{-1}. DSC and TGA were performed at a heating rate of 10°C min^{-1}, under nitrogen with a du Pont 2100 machine. FT-IR-spectra were taken using a Nicolet 510p spectrometer. UV-visible spectra were taken using a Shimadzu UV-260 spectrometer in films spin coated onto quartz plates. (In the case of monomer **5**, chloroform solution was used.) ^{1}H NMR and ^{13}C NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. Photoluminescence was measured using a Perkin-Elmer 630-10S fluorimeter for films with excitation wavelength of 350 nm Excitation spectra of the films were measured with emission wavelength of 468 and 524 nm for **poly-5** and **poly-56**, respectively.

RESULTS AND DISCUSSION

The synthesis of monomer **5** and polymers **poly-5** and **poly-56** is shown in Scheme 1. The monomer was prepared from 4-hydroxybenzaldehyde (**3**) and 10-undecynoic acid (**1**). Acid **1** was converted to acid chloride (**2**) by $SOCl_2$, followed by reaction with 4-hydroxybenzaldehyde. Monomer **5** was obtained by the Wittig reaction of 4-(10-undecynoyloxy)benzaldehyde (**4**) with CBr_4 and TPP. Hyperbranched polymers **poly-5** and **poly-56** were prepared from monomer **5** by the Heck homopolycondensation of monomer **5** or copolycondensation of monomer **5** with monomer **6**. During the

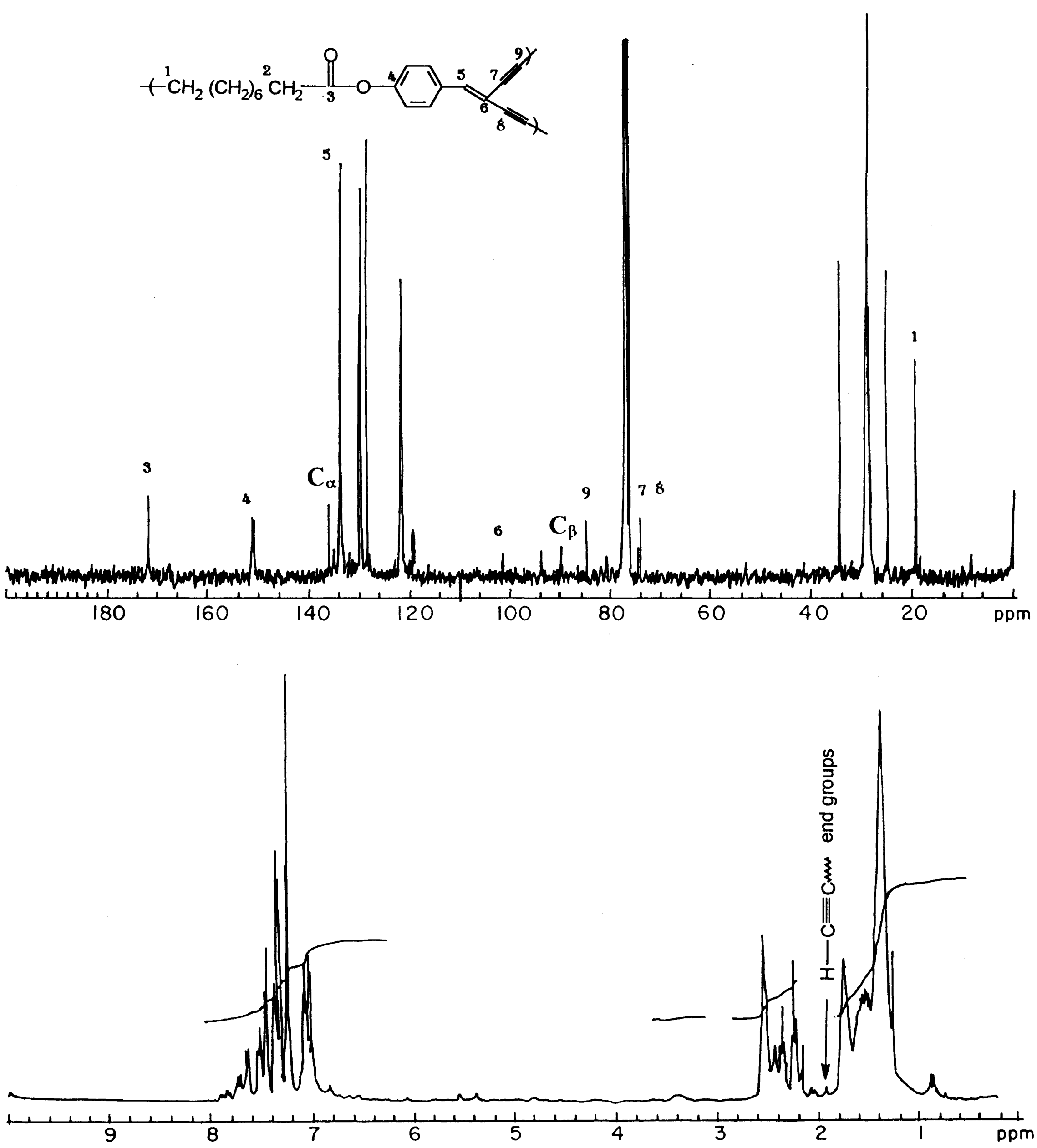

Figure 1. ^{13}C NMR and ^{1}H NMR spectra of **poly-5**.

homopolycondensation of monomer **5**, no gel formation was observed and **poly-5** was completely soluble at room temperature in chlorinated aliphatic hydrocarbons such as chloroform and methylene chloride, giving transparent amorphous and flexible films on casting. GPC gave for **poly-5** $M_w = 11500$ with the polydispersity index of 1.7. Spectroscopy data confirmed the general structure of hyperbranched polymer **poly-5**. In the IR spectra of the polymer, two peaks disappeared: at 3300 and 2115 cm^{-1}, corresponding to the ≡C–H and C≡CH stretches, respectively, and two new bands were observed at 2248 and 2211 cm^{-1}, due to the stretches of $=C-(C\equiv C)_2-$ group. In the ^{1}H NMR spectra of **poly-5** (Figure 1) aromatic protons appeared in the region of 8—7 ppm, while the protons of aliphatic spacer were observed between 2.6 and 1.2 ppm. The signal of olefinic proton of $(-C\equiv C)_2-C=CH-$ group which should appear[2] at 7.14 ppm overlapped with the signals of aromatic protons. It is noteworthy that the triplet of acetylenic proton at 1.93 ppm practically disappeared in the spectra of **poly-5**. ^{13}C NMR spectra provided more information on the structure of the polymer. In the case of **poly-5** the spectra were the superposition of signals of terminal $Br_2C=CH-Ph-OOC-(CH_2)_8-$ groups in large quantities due to hyperbranched structure of the polymer and polymer repeating units $(-C\equiv C)_2-C=CH-Ph-OOC-(CH_2)_8-$. The signal of terminal acetylene carbon at 68.1 ppm disappeared completely due to the polymerization and two new peaks (7, 8) appeared at 77.4 and 77.0 ppm, corresponding to two different *sp*-carbons connected directly to the double bond. The positions of *sp*-carbons connected to the aliphatic spacer in **poly-5** (9) were unaffected, compared with the monomer and observed at 84.4 ppm. A carbon atom of ester carbonyl (3) and C_{ar}–O carbon (4) appeared in **poly-5** at 171.4 and 150.5. The signals of C_α(6) and C_β(5) carbons of di-

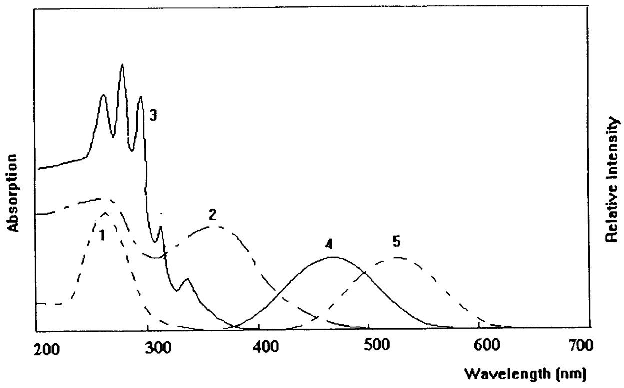

Figure 2. Absorption spectra of monomer **5** (1), **poly-56** (2), and **poly-5** (3). Emission spectra of **poly-5** (4) and **poly-56** (5) ($\lambda_{ex}=350$ nm).

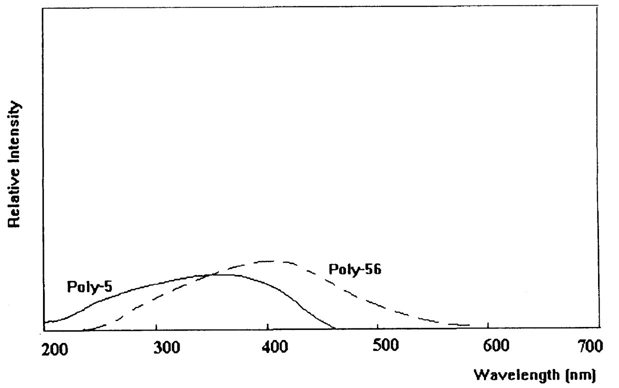

Figure 3. Excitation spectra of **poly-5** and **poly-56** ($\lambda_{em}=468$ and 524 nm, respectively).

bromovinyl end groups were seen at 136 and 89.5 ppm, respectively, similarly to these of monomer. The signals of C_α and C_β carbons of diethynylvinyl groups formed during the polycondensation were detected at 101.9 and 134 ppm. Two more new signals were detected in the ^{13}C NMR spectra of **poly-5**, at 94 and 82 ppm. These may correspond to C_β carbon and *sp*-carbon, respectively, connected to the double bond of ethynylbromovinyl group $(\text{-(C}\equiv\underline{\text{C}})\text{Br}\underline{\text{C}}=\text{CH-)-}$ formed when only one bromine reacted with acetylenic group resulting in imperfections of polymer structure. The branching degree could be calculated using the difference in chemical shifts of the protons disubstituted vinylic groups[2] (7.13 ppm) and monosubstituted one. Taking into account the position of the proton signal in dibromovinylic group (7.42 ppm), the proton of monosubstituted vinylic group should appear in the region of 7.13—7.42 ppm, reflecting the contribution of the linear structure. Unfortunately, we were not able to assign this proton due to overlapping with the aromatic protons and broadness of the signal. However, peaks at 94 and 82 ppm in the ^{13}C NMR spectra assigned as C_β carbon and *sp*-carbon, respectively, connected to the double bond of ethynylbromovinyl group $(\text{-(C}\equiv\underline{\text{C}})\text{Br}\underline{\text{C}}=\text{CH-)-}$ formed when only one bromine reacts with acetylenic group demonstraded the contribution of the linear structure exists in the polymer.

Figure 2 shows UV-visible absorption spectra of monomer **5** and polymers **poly-5** and **poly-56**. Monomer **5** shows the only absorption peak at 263 nm, while the spectra of **poly-5** exhibited a vibrational structure, characteristic of polyene and polyene moieties with general bathochromic shift due to the expansion of conjugated system during the polymerization. It is noteworthy that **poly-5** showed intense blue photoluminescence due to the presence of rigid discrete conjugated β,β'-diethynylstyrene units. Figures 2 and 3 show the emission and excitation spectra of polymer films. As can be seen from the spectra, the film of **poly-5** showed a broad emission peak at 468 nm when excited at 350 nm. The excitation spectra exhibited a maximum at 360 nm ($\lambda_{em}=468$ nm) which differs significantly from he absorption maximum. We suggest that this is due to the reabsorption of the emitted light by the polymer film.

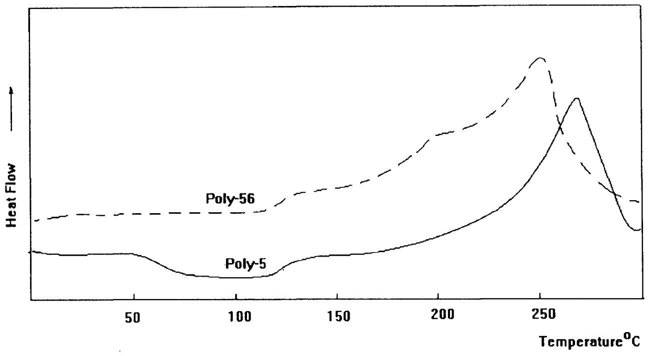

Figure 4. DSC curves of **poly-5** and **poly-56**.

In spite of its highly unsaturated β,β'-diethynylstyrene moieties and aliphatic groups **poly-5** was found rather thermostable, probably due to the network formation on heating which increases thermostability. It showed 10% weight loss at 280°C. Figure 4 shows the DSC curve of **poly-5**. It exhibits a glass transition at around 60°C and an exotherm started at 150°C with maximum at 272°C related to the thermal cross-linking of the triple bonds of the polymer together with the decomposition which started above 270°C.

In the case of the copolymerization of monomer **5** with monomer **6** the polymer (**poly-56**) was completely soluble in the reaction mixture. However, it was only partially soluble after the precipitation. A soluble fraction of **poly-56** was about 50—60% and had M_w of 11800 with a polydispersity index of 1.8 according to GPC. The polymer was soluble in hot chlorinated solvents such as chlorobenzene and o-dichlorobenzene. The FT-IR and ^1H NMR spectra of **poly-56** are shown in Figure 5. The ^{13}C NMR spectra of **poly-56** were of very poor quality due to the low solubility of the polymer. The FT-IR spectra of **poly-56** were similar to those of **poly-5**. They exhibited doublet peaks corresponding to stretches of triple bonds of $CH=C(C\equiv C)_2$ system at 2247 and 2202 cm^{-1}. The ^1H NMR spectra of **poly-56** were similar to those of **poly-5** with the aromatic to aliphatic proton ratio corresponding to the feeding monomer ratio. The absorption and emission spectra of **poly-56**, differed significantly from those of **poly-5**. As can be seen from Figure 2 a long wave absorption maximum of **poly-56** (360 nm), was significantly red shifted compared with that of **poly-5** reflecting a longer average conjugation in the former. It is noteworthy that fully conjugated homopolymer of monomer **6** exhibited a long wave

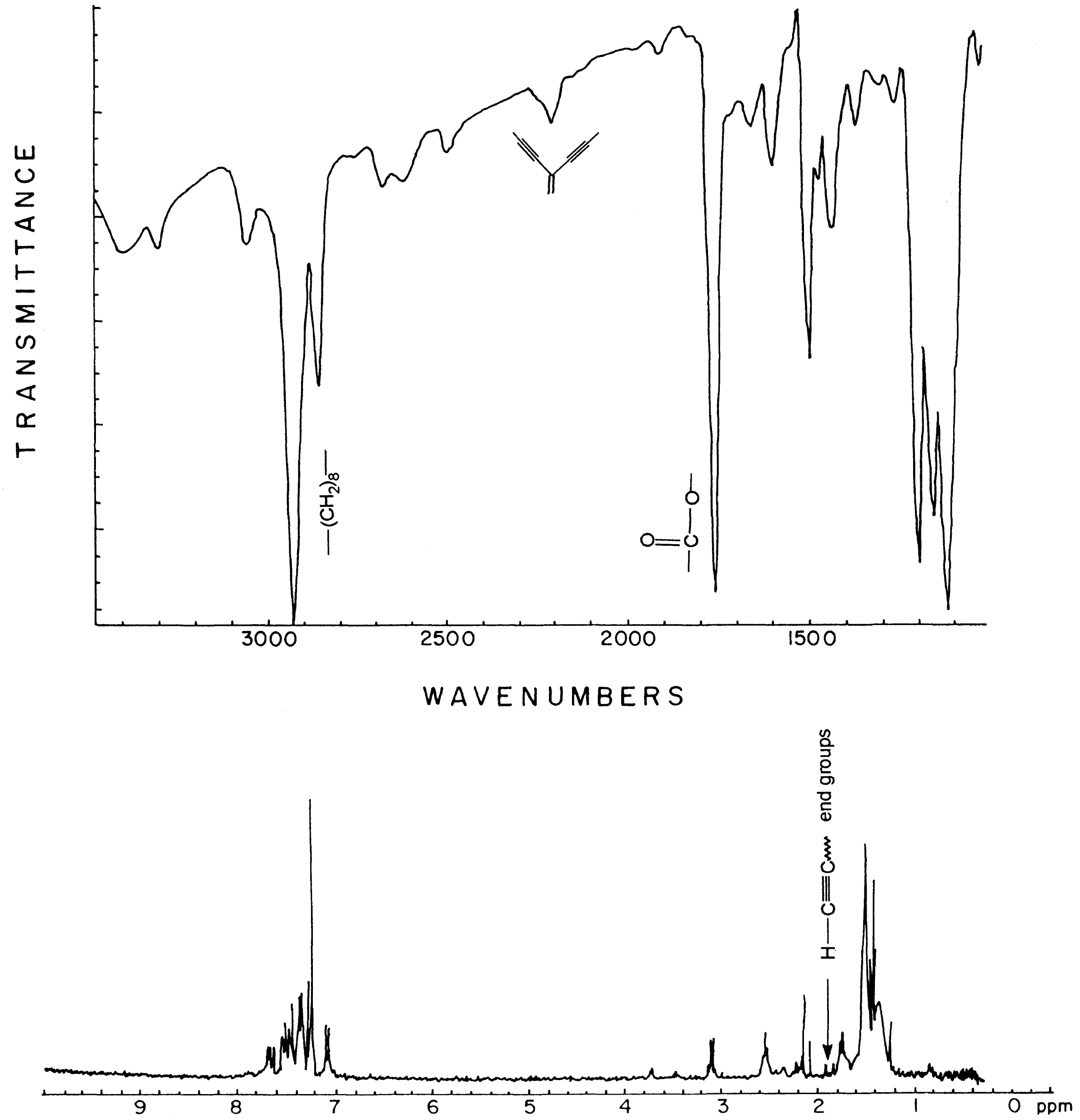

Figure 5. FT-IR and ^{1}H NMR spectra of **poly-56**.

absorption maximum at 377 nm, thus showing relatively small difference with **poly-56**.[2] This means that average conjugation in homopolymer of monomer **6** does not exceed a repeating unit due to steric hindrances.

Poly-56 showed intense green-yellow photoluminescence. Figures 2 and 3 show emission and excitation spectra of films of **poly-56**. The films showed a single emission band with a maximum at 524 nm when excited at 350 nm, indicating a bathofluoric shift of 56 nm compared with **poly-5** films due to the lower π–π^* energy transition in the former. The excitation spectrum of film of **poly-56** is presented in Figure 3 showing a single band with a maximum at 400 nm ($\lambda_{em} = 524$ nm), which represents a 40 nm red shift compared to **poly-5**. This was due to the lower π–π^* energy transition in **poly-56**.

Poly-56 was less thermostable than **poly-5** probably due to the higher concentration of triple bonds in the former. It showed 10% weight loss at 230°C. Figure 4 shows DSC curve of **poly-56**. No glass transition could be detected, probably, due to the rigidity of macromolecules. An intense exotherm peak was observed at 250°C related to the thermal cross-linking of the triple bonds. It is noteworthy that **poly-5** has an exotherm maximum 22°C above that of **poly-56**, which is probably related to the higher concentration of the triple bonds in the latter.

In conclusion, a novel monomer β,β'-dibromo-4-(10-undecynoyloxy)styrene (**5**) was synthesized and polymerized to give a soluble hyperbranched polymer (**poly-5**) containing discrete conjugated units. Copolymerization of monomer **5** with β,β'-dibromo-4-ethynylstyrene (**6**) produced partially soluble hyperbranched copolymer **poly-56**. Average conjugated length was longer for **poly-56**. The polymer structure was determined by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The polymers were found photoluminescent with emission peaks correlated with absorption maxima. **Poly-56** was less thermally stable than **poly-5** due to the higher concentration of the triple bonds.

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