Solid-Supported Synthesis of Hyperbranched Polymer with Discrete Conjugated Units

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ABSTRACT: Novel hyperbranched polymer poly(4-(5-hexynyloxy)-β,β-dibromostyrene) was synthesized by Pd-catalyzed cross-coupling reaction of 4-(5-hexynyloxy)-β,β-dibromostyrene in solution and using an aromatic polyamide solid support. According to the NMR data the degree of branching of the polymer obtained in solution without solid support was of 30—35%, while when using solid support the degree of branching increased to 60—65%. However, molecular weight of detached **Poly-6** was lower that of the polymer obtained in solution. It seems that monomer molecules trapped in the vicinity of growing polymer chain by the polymeric support have more time to react with second bromine atoms of dibromovinyl groups, thus increasing branching of the polymer. Drop in molecular weight when using solid support is attributed to steric hindrance due to polymeric support, thus limiting the molecular weight of the attached polymer.
        KEY WORDS   Hyperbranched Polymers / Solid-Supported Polymerization /

Hyperbranched polymers obtained from AB_2 type monomers are taking on interest. There is growing interest in macromolecules with architectures differing from classical linear polymers as these new architectures may exhibit unusual behavior and possess properties that differ from those of linear polymers. Some advantages of hyperbranched polymers are high solubility compared to linear analogs and high concentrations of end groups even for high polymers.

The present authors are interested in the development of polymers with new chemical structures for photo-, electroluminescence and nonlinear optics and previously reported the synthesis and polymerization of a new AB_2 monomer β,β'-dibromo-4-ethynyl styrene by the Pd-catalyzed cross-coupling to produce fully aromatic conjugated polymer containing β,β-diethynylstyryl conjugated groups.[1] To increase the tractability of hyperbranched polymer, flexible aliphatic spacers were incorporated into polymer chain, resulting in hyperbranched polymer containing β,β-diethynylstyryl discrete conjugated units.[2] The polymers were readily soluble in chloroform, showing strong photo- and electroluminescence.

An undesirable feature of one-step AB_2 polymerization is loss of control in molecular weight accompanied by a broad molecular weight distribution.[3] Hyperbranched polymerization on an insoluble solid support provides polymers with polydispersity < 1.3 and good molecular weight control in the range 5—25 kDa.

This work developed solid-supported synthesis of polymers with discrete conjugated units and compares the properties of polymer prepared in solution with those of polymer synthesized using solid support.

EXPERIMENTAL

Materials
Terephthaloyl chloride was crystallized from hexane. All other reagents were used as received from Aldrich.

Solid Support and Monomer Synthesis
4,4'-Diamino-4''-hydroxy Triphenylmethane (**2**). A mixture of 4-hydroxybenzaldehyde (**1**) (10 g, 82 mmol), phenylammonium hydrochloride (1 g) and aniline (30 g, 340 mmol) was stirred at 120°C under nitrogen flow for 3.5 h. The reaction mixture was extracted with hot chlorobenzene, The solid precipitated was filtered off and crystallized from *o*-dichlorobenzene. Yield 46%, mp = 100—103°C. ^{1}H NMR (dimethyl sulfoxide (DMSO)-d_6) 9.14 (s, 1H, OH), 6.85 (d, 2H, $J=8.4$ Hz, *meta* to OH), 6.68 (d, 4H, $J=8.4$ Hz, *meta* to NH_2), 6.63 (d, 2H, $J=8.4$ Hz *ortho* to OH), 6.46 (d, 4H, $J=8.4$ Hz, *ortho* to NH_2), 5.01 (s, 1H, CH aliph.), 4.83 (s, 4H, NH_2). ^{13}C NMR, 155.5 (C_{ar}–O), 146.2 (C_{ar}–N), 136.2 (C_{ar} *para* to OH), 130.2 (C_{ar} *meta* to OH), 129.8 (C_{ar} *meta* to NH_2), 126.3 (C_{ar} *para* to NH_2), 114.5 (C_{ar} *ortho* to OH) 113.8 (C_{ar} *ortho* to NH_2), 54.1 (C aliph).

Poly(4,4'-diphenylene-4''-hydroxyphenyl methane) Terephthalamide (*SOH*). To a solution containing 3.800 g (13.10 mmol) diamine **2** and 50 ml *N*-methylpyrrolidone (NMP) terephthaloyl chloride (2.709 g, 13.34 mmol) was added slowly at 0°C. The viscous solution was poured into water. The polymer was filtered off, rinsed with water and dried in vacuum. Yield = 98%. ^{1}H NMR (DMSO-d_6), 10.4 (s, 2H, NH), 9.34 (s, 1H, OH), 8.09 (s, 4H arom, terephthaloyl), 7.73 (d, 4H, $J=8.4$ Hz, *ortho* to NH), 7.11 (d, 4H, $J=8.4$ Hz, *meta* to NH), 6.35 (d, 2H, $J=8.4$ Hz, *meta* to OH), 6.72 (d, 2H, $J=8.4$ Hz, *ortho* to OH), 5.46 (s, 1H, CH aliph), ^{13}C NMR, 164.7 (C=O), 155.6 (C_{ar}–O), 140.1 (C_{ar}–NH), 137.4, 137.0 (C_{ar}–CO, C_{ar} *para* to NH), 134.2 (C_{ar} *para* to OH), 129.9 (C_{ar} terephthaloyl), 129.1 (C_{ar} *meta* to NH), 127.7 (C_{ar} *ortho* to NH), 120.5 (C_{ar}

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meta to OH), 115.1 (C_{ar} *ortho* to OH), 54.15 (CH aliph).

Poly-(4,4'-diphenylene-4"-(4-bromobenzoyloxy)phenyl methane) Terephthalamide (S-OOCPhBr). Polymer SOH (5.27 g) was treated with equimolar amount of 4-bromobenzoyl chloride in a mixture of methylene chloride (40 ml) and pyridine (30 ml) for 24 h. The solid was filtered off, washed with diluted HCl and dried in vacuum to give 6.72 g of product (89% yield). The polymer was not soluble any longer in common organic solvents. IR (cm^{-1}) 3321 (N–H), 1736 (C = O ester), 1664 (C = O amide), Elemental analysis ($C_{34}H_{23}N_2O_4Br$)$_n$ Calc (%) Br 13.3 Found (%) Br 11.1.

5-Hexynyl Toluene Sulfonate (4). A mixture of 5-hexyne-1-ol (3.9 g, 39.7 mmol), TsCl (9.1 g, 47.3 mmol), methylene chloride (40 ml) and pyridine (10 ml) was stirred 24 h at room temperature, The reaction mixture was poured into dilute HCl. The product was taken into chloroform and dried with $MgSO_4$. Excess solvent was removed in vacuum. The product was yellowish oil. Yield = 81%. ^1H NMR ($CDCl_3$); 7.76 (d, 2H, J = 8.1 Hz, *meta* to CH_3), 7.32 (d, 2H, J = 8.1 Hz, *ortho* to CH_3), 4.05 (t, 2H, J = 6.3 Hz, OCH_2), 2.41 (s, 3H, CH_3), 2.12 (m, 2H, $\equiv C-CH_2-$), 2.00 (m, 1H, HC$\equiv$), 1.74—1.65 (m, 2H, CH_2O–CH$_2$–CH_2), 1.55—1.49 (m, 2H, $\equiv C-$CH$_2-$). ^{13}C NMR; 144.9 ($C_{ar}-SO_2$), 133.1 ($C_{ar}-CH_3$), 129.6, 127.9 (C_{ar}), 83.7 (–$C\equiv$CH), 70.1 (OCH_2), 69.3 (–$C\equiv$CH), 27.8 (–$OCH_2CH_2CH_2-$), 24.3 (–$OCH_2CH_2-$$CH_2-$), 21.7 ($CH_3$), 17.7 (–$CH_2-C\equiv$CH).

4-(5-Hexynyloxy)benzaldehyde (5). A mixture of tosylate 4 (12.85 g, 50.98 mmol), 4-hydroxybenzaldehyde (6.22 g, 50.98 mmol), K_2CO_3 (14.2 g, 102 mmol) and NMP (40 ml) was stirred for 24 h at 70°C. The reaction mixture was poured into dilute HCl and the product was taken into chloroform and washed with 2% NaOH solution. Excess solvent was evaporated and the residue was crystallized from hexane and then from methanol. Yield = 70%, mp = 38—39°C. ^1H NMR ($CDCl_3$); 9.90 (s, 1H, CH = O), 7.82 (d, 2H, J = 8.7 Hz *ortho* to CHO), 6.98 (d, 2H, J = 8.7 Hz, *meta* to CHO), 4.74 (t, 2H, J = 6.3 Hz, OCH_2), 2.29 (dd, 2H, J_1 = 6.6 Hz, J_2 = 2.7 Hz, –$CH_2-C\equiv$), 1.99—1.90 (m, 3H, HC$\equiv$C–, –OCH_2CH$_2-$), 1.80—1.70 (m, 2H, –CH_2CH$_2$–C$\equiv$). ^{13}C NMR; 190.8 (CH = O), 164.0 ($C_{ar}-O$), 132.0 (C_{ar} *ortho* to CHO), 129.9 ($C_{ar}-$CH = O), 114.7 (C_{ar} *meta* to CHO), 83.6 (–$C\equiv$CH), 68.8 (–$C\equiv$CH), 67.7 (OCH_2), 28.1 (–$OCH_2CH_2CH_2-$), 24.9 (–$OCH_2CH_2CH_2-$), 18.1 (–$CH_2-C\equiv$CH).

Poly-(4,4'-diphenylene-4"-(4-(6-(4-formylphenyloxy)-hexyn-1-yl))benzoyloxy)phenyl Methane (7). 1.3 g S-OOCPhBr was dispersed in a mixture of triethylamine/dioxane = 1/1.3 under nitrogen. Triphenylphosphine (TPP) (0.163 g), CuI (0.064 g), Pd(TPP)$_2$Cl$_2$ (0.091 g) and compound 5 (0.44 g, 2.16 mmol) were added to the reaction and the mixture was refluxed overnight. The solid precipitate was filtered off, washed with methanol and water and dried in vacuum. Yield = 87% (according to the weight uptake) IR (cm^{-1}) 3400 (N–H), 2850 (C–H aldehyde), 2230 (–$C_{ar}-C\equiv C-CH_2$), 1736 (C = O ester), 1680 (C = O aldehyde) 1655 (C = O amide).

Poly-(4,4'-diphenylene-4"-(4-(6-(β,β-dibromo-4-styryloxy)hexyn-1-yl))benzoyloxy)phenyl Methane: (SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH = CBr$_2$). To a solution containing dibromotriphenylphosphorane prepared from CBr$_4$ (5.59 g, 7.81 mmol), and TPP (4.10 g, 15.6 mmol) in 70 ml

CH_2Cl_2 polymer 7 (1.14 g) was added under nitrogen. The reaction mixture was stirred overnight at room temperature. The solid was filtered off, washed with methylene chloride and dried in vacuum. Yield = 100% (according to the weight uptake). IR (cm^{-1}) 3400 (N–H), (C–H aldehyde), 2230 (–$C_{ar}-C\equiv C-CH_2$), 1736 (C = O ester), 1655 (C = O amide) Elemental analysis: ($C_{48}H_{36}N_2O_5Br_2$)$_n$ Calc (%) Br 18.18 Found (%) Br 16.0.

4-(5-Hexynyloxy)-β,β-dibromostyrene (6). To a solution containing dibromotriphenylphosphorane prepared from CBr$_4$ (11.71 g, 35.3 mmol) and TPP (18.5 g, 70.6 mmol) in 30 ml CH_2Cl_2 compound 6 (7.13 g, 35.3 mmol) dissolved in 40 ml CH_2Cl_2 was added slowly at room temperature under nitrogen and stirred for 3 h. Excess solvent was removed under reduced pressure and the residue was extracted twice with hot hexane. The solid precipitated from hexane solution was filtered off and purified column chromatography on SiO_2 (hexane), Yield = 58%, mp = 27—28°C. ^1H NMR ($CDCl_3$) 7.51 (d, 2H, J = 9.3 Hz, *ortho* to CH = CBr_2), 7.39 (s, 1H, CH = Br_2), 6.85 (d, 2H, J = 9.3 Hz, *meta* to CH = CBr_2), 4.00 (t, 2H, J = 5.7 Hz, OCH_2), 2.30 (dd, 2H, J_1 = 6.6 Hz, J_2 = 3.0 Hz, $\equiv C-$CH$_2$), 1.80 (t, 1H, J = 3.0 Hz, H$\equiv$C–), 1.78—1.70 (m, 2H, OCH_2-CH$_2$), 1.60—1.50 (m, 2H, $\equiv C-$CH$_2C$H$_2$), ^{13}C NMR; 159.1 ($C_{ar}-O$), 136.3 (CH = CBr$_2$), 129.9 (C_{ar} *ortho* to CH = CBr_2), 127.7 ($C_{ar}-$CH = CBr$_2$), 114.3 (C_{ar} *meta* to CH = CBr_2), 87.2 (CH = CBr$_2$), 84.0 (HC$\equiv$$C-$), 68.7 (H$C\equiv$C–), 67.3 ($OCH_2$), 28.2 ($OCH_2CH_2$), 25.0 ($CH_2CH_2C\equiv$), 18.1 ($CH_2CH_2C\equiv$).

Polymerization

Polymerization of Monomer 6 without Support. To monomer 6 (1.48 g mmol) dissolved in 30 ml dioxane/triethylamine mixture = 1/1, TPP (0.24 g), CuI (0.05 g), and Pd(TPP)$_2$Cl$_2$ (0.04 g) were added under nitrogen. The reaction mixture was stirred for 15 h under reflux. The reaction mixture was poured into methanol, the fibrous precipitate was filtered off, washed with methanol, purified by reprecipitation from chloroform to methanol and dried in vacuum Yield = 88%.

Polymerization of Monomer 6 in the Presence of Solid Support. S-OOCPhBr: To a reaction mixture containing S-OOCPhBr (0.674 g, 1.12 mmol), TPP (0.022 g), CuI (0.0065 g), Pd(TPP)$_2$Cl$_2$ (0.0087 g) triethylamine (15 ml) and dioxane (10 ml) monomer 6 (2.0 g, 5.59 mmol), dissolved in dioxane (30 ml) was added during 2 h at 80°C under nitrogen. The reaction was stirred under reflux overnight. The solid was filtered off, washed with methanol and dried in vacuum. To cleave the polymer bound material, the product was stirred with 1.5 g K_2CO_3 in 150 ml methanol for 24 h. The solid was filtered off and extracted with chloroform.

(SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH = CBr$_2$): To a reaction mixture containing (SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH = CBr$_2$) (1.01 g, 1.12 mmol), TPP (0.079 g), CuI (0.0115 g), Pd(TPP)$_2$Cl$_2$ (0.0150 g) triethylamine (15 ml) and dioxane (10 ml), monomer 6 (2.0 g, 5.59 mmol), dissolved in dioxane (30 ml) was added during 2 h at 80°C under nitrogen. The reaction was stirred under reflux overnight. The solid was filtered off, washed with methanol and dried in vacuum. To cleave the polymer bound material,

the product was stirred with 1.5 g K_2CO_3 in 150 ml methanol for 24 h, solid was filtered off and extracted with chloroform.

Measurements

Molecular weights of the polymers were determined by GPC using a Varian 9012 instrument at 30°C in CH_2Cl_2 with polystyrene standard, universal column and flow of 1 ml min^{-1} and by end group analysis using ^{1}H NMR. In the case of solution prepared polymers a signal of terminal acetylene (1.80 ppm) and that OCH_2 protons as a reference were used to determine number average molecular weight, while for polymers prepared using solid support a signal of methoxy terminal protons (3.90 ppm) was taken. ^{1}H and ^{13}C NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in DMSO-d_6, or $CDCl_3$ with tetramethyl-silane (TMS) as the internal standard. Absorption, emission and excitation spectra were measured with an automated Spex-FluoroMax spectrofluorimeter in $CHCl_3$ solution. ^{1}H and ^{13}C isotropic shielding tensors of **A**, **B**, **C**, and **D** model compounds were computed by the Gauge-Independent Atomic Orbital (GIAO) method[4] for NMR spectra simulation at 3-21G(d) level of theory. Excitation energies of **A**, **B**, **C**, and **D** model compounds were calculated using geometries optimized at HF/3-21G(d) followed by a single point energy calculations at B3LYP/6-31G(d) with Gaussian 94.[5] The energies of long wave absorption maxima were taken as energy difference between lowest unoccupied (LUMO) and highest occupied (HOMO) orbitals. LUMO–HOMO energy difference obtained with the Becke three parameter hybrid (B3) exchange functional in combination with Lee–Yang–Parr (LYP) correlation functional yield excitation energies in good agreement with experimental values.[6]

RESULTS AND DISCUSSION

Monomer **6** was synthesized starting from 4-hydroxybenzaldehyde (**1**) and 5-hexyne-1-ol (**3**) in 3 steps (Scheme 1). Tosylation of **3** with TsCl produced tosylate **4**. The alkylation of **1** with tosylate **4** gave compound **5** which was converted to monomer AB_2 type (**6**) by the Wittig reaction with dibromotriphenylphosphinephosphorane.

The synthesis of solid supports is shown in Scheme 1. Aromatic polyamide SOH bearing phenolic hydroxyl on each repeat unit was synthesized by low temperature solution polycondensation in NMP starting from diamine **2** and terephthaloyl chloride. Soluble polymer was obtained with well defined structure when the exact stochiometric ratio of monomers is used. Diamine **2** was prepared in one step from aniline and benzaldehyde. Hydroxy-containing polyamide SOH was used to prepare two solid supports. The first one (S-OOCPhBr) was prepared by treating SOH with 4-bromobenzoyl chloride. The reaction produced polymer with about 80% substitution according to elemental analysis and the polymer lost solubility in common organic solvents attributed to unfavorable change in hydrophobic/hydrophilic balance after functionalization. The second support (SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH=CBr_2) was prepared from S-
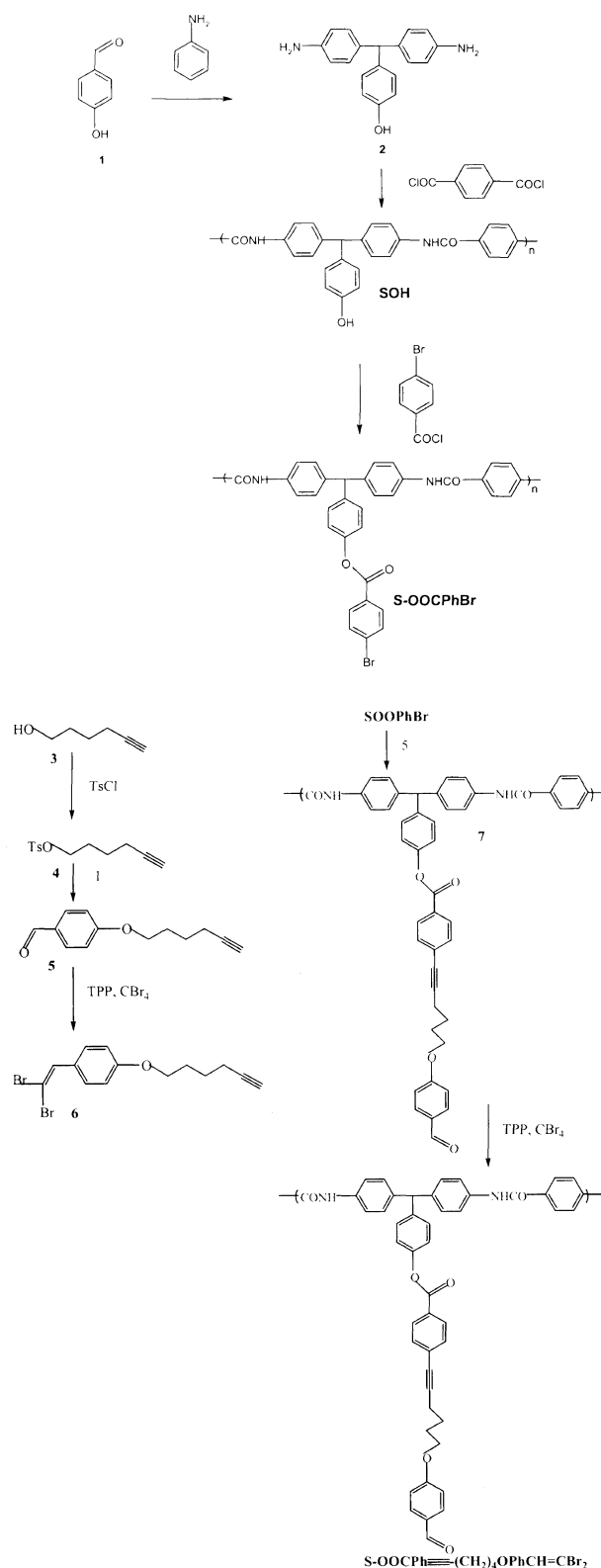

Scheme 1. Solid support and monomer synthesis.

OOCPhBr in two steps. The first was Pd-catalyzed cross-coupling of compound **5** with S-OOCPhBr to give polymer **7** which was converted to SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH = CBr_2 by the Wittig reaction with dibromo-triphenylphosphinephosphorane. Both polymeric supports have Br atoms active in Pd-catalyzed cross-coupling with terminal acetylenes. However, vinylic bromine of SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH = CBr_2 is more reactive in cross-coupling reaction than aromatic bromine of S-

OOCPhBr which makes differences between them. In the case of solid supported polymerization of monomer **6**, it is the cross-coupling reaction that tethers growing hyperbranched molecules to the polymeric support. Support-bound hyperbranched polymer is cleaved by a simple K_2CO_3 catalyzed transesterification in MeOH as shown in Scheme 2.

The polymerization of monomer **6** without support produced polymer (**Poly-6**) completely soluble in chloroform. Figure 1 shows ^{1}H NMR and ^{13}C NMR spectra of **Poly-6**. To assign these spectra ^{1}H and ^{13}C shielding tensors of model compounds were computed with the GIAO method at HF/3-21G(d). The geometry of the model compounds was also optimized at HF/3-21G(d). The results of calculation are presented in Table I. Compounds **A** and **B** represent models for terminal groups and perfectly branched repeat units of **Poly-6** while

Scheme 2.
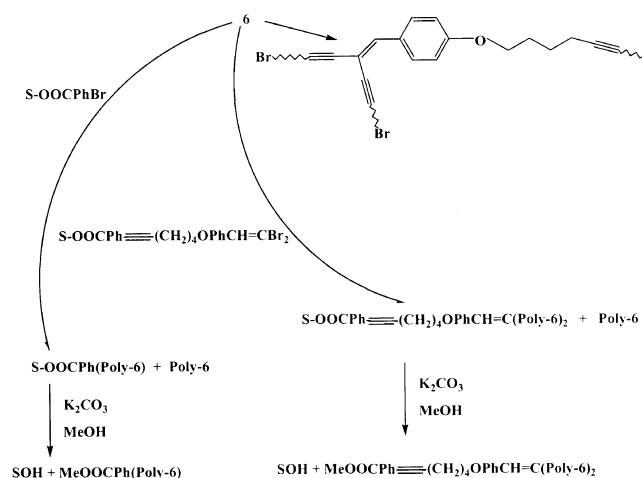
structures **C** and **D** are models of two possible defects resulting from incomplete branching. As seen from Table I, there is a reasonably good agreement between computed and measured chemical shift for structure **A** (experimental chemical shifts were taken from NMR of monomer **6**) making reliable other computed chemical shifts. Careful analysis of ^{1}H NMR spectrum of **Poly-6** leads us to the conclusion that branching in the polymer is not perfect. Taking into account calculated chemical shifts, a doublet at 7.50 ppm ($J = 9.0$ Hz) should be assigned to aromatic protons *ortho* to terminal CH = CBr_2 groups (H^3 of structure **A**) while a doublet at 7.62 ppm ($J = 9.0$ Hz) is due to H^3 of linear defect of type **D** ($\delta_{calc} = 7.70$ ppm). A low field doublet at 7.72 ppm should be a superposition of H^3 of two structures. Perfectly branched **B** and linear defect **C** ($\delta_{calc} = 7.98$ ppm). ^{13}C NMR spectra of **Poly-6** also confirm the existence of linear defects in the polymer. A signal at 136.3 ppm is due to C^α of terminal dibromovinyl groups (structure **A**) while three closely located signals at 134.9, 134.1, and 133.2 should belong to C^α of structures **B**, **C**, and **D**. This agrees reasonably well with calculated C^α chemical shifts (Table I). Assuming similar reactivity for two bromine atoms in dibromovinyl group (the number of linear defects of **C** and **D** type is the same) the degree of branching (DB) of **Poly-6** can be estimated as follows:

$$DB = (I_1 - I_2)/(I_1 + I_2) \qquad (1)$$

Where I_1 and I_2 are integrals of doublets at 7.72 and 7.62 ppm, respectively (terminal $= CBr_2$ not considered as branching). According to this calculated DB of **Poly-6** is 30—35%. A multiplet at 7.00—6.50 ppm is composed of H^2 signals of all four possible structures and H^α signals of structures **B** and **C** and integrated for 2.5 protons. This agrees well with that calculated for DB of 30—35%
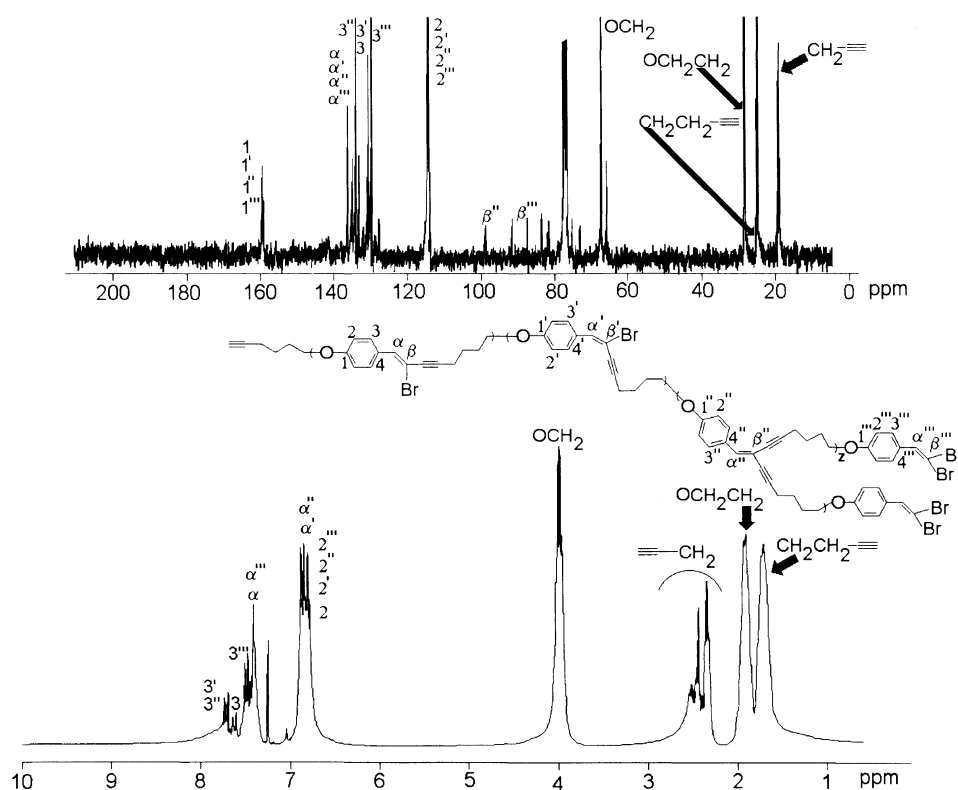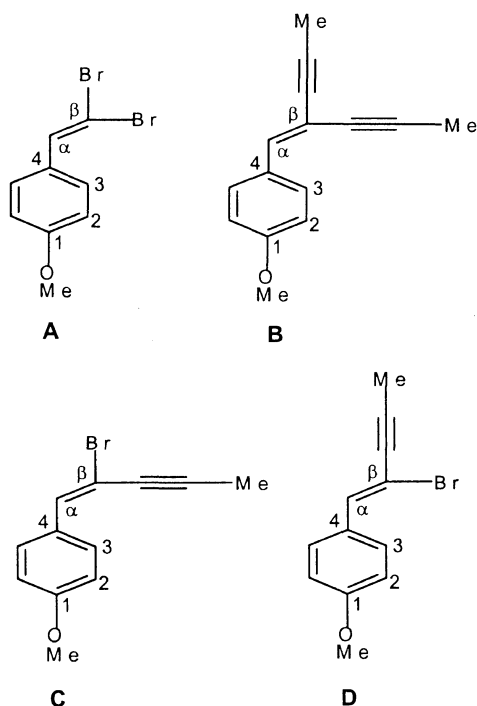
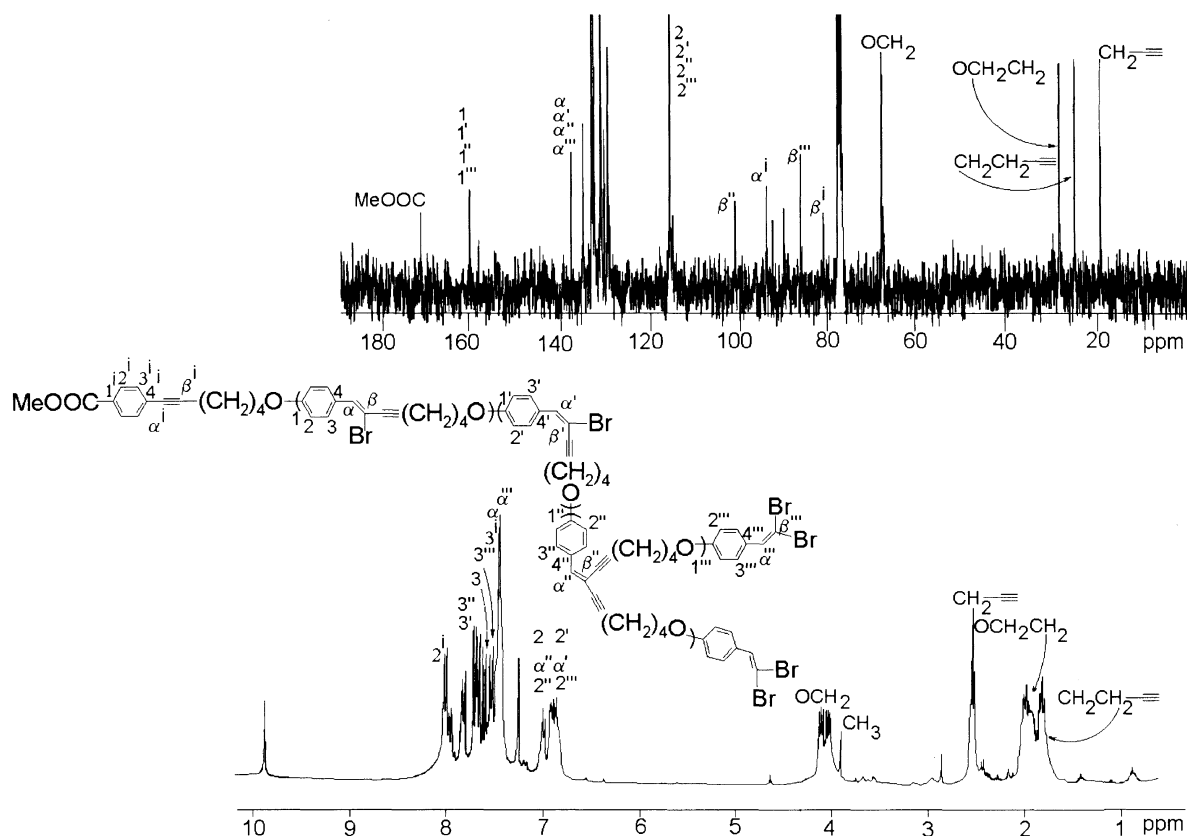**Figure 1.** ^{1}H NMR and ^{13}C NMR spectra of **Poly-6** obtained in solution.

Table I. Computed chemical shifts (δ) of model compounds

A   B

C   D

Atom	Computed chemical shifts/ppm				
	A	A_{exp}	B	C	D
H^2	6.65	6.85	6.58	6.59	6.59
H^3	7.55	7.51	7.98	7.98	7.70
H^x	7.21	7.39	6.78	6.68	7.22
C^x	133.0	136.3	134.1	131.9	131.4

(2.6—2.7).

The number average molecular weight of **Poly-6** determined from ^1H NMR using the signal of terminal acetylenic proton was 26000 while that measured by GPC gave 17500 with polydispersity of 3.5. Both values are lower than that of poly(β,β-dibromo-4-ethynyl styrene)[2] obtained by Pd-catalyzed cross-coupling polymerization of β,β-dibromo-4-ethynyl styrene ($M_n = 36000$). This is due to the fact that aromatic acetylene of β,β-dibromo-4-ethynyl styrene is more active in the cross-coupling reaction than aliphatic acetylene of monomer **6**. Low reactivity of aliphatic acetylene in monomer **6** could account for the relatively low DB of **Poly-6** and probably is responsible for relative low DB of **Poly-6**.

The polymerization of monomer **6** in the presence of support SOOCPhBr followed by cleavage of attached **Poly-6** gave no polymer at all. The only compound isolated after the cleavage was 4-bromomethylbenzoate formed due to the methanolysis of ester bond of SOOCPhBr as followed from NMR spectra. All monomer **6** was polymerized outside the support. This may be explained by difference in reactivity between aromatic and vinylic in the cross-coupling reaction. Increased reactivity of dibromovinyl bromine of monomer **6** led solely to homopolymerization. To solve this problem SOOCPhBr was converted to SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH$=CBr_2$. (Scheme 1) Similar to monomer **6**, support SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH$=CBr_2$ bears a dibromovinyl function. On polymerization of monomer **6** in the presence of SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH$=CBr_2$ (monomer/support ratio $= 5/1$) followed by cleavage of attached **Poly-6** gave detached polymer with 10% yield. Figure 2 shows ^1H NMR and ^{13}C NMR

Figure 2. ^1H NMR and ^{13}C NMR spectra of **Poly-6** obtained using solid support SOOCPh–$\equiv$–$(CH_2)_4$–OPhCH$=CBr_2$.
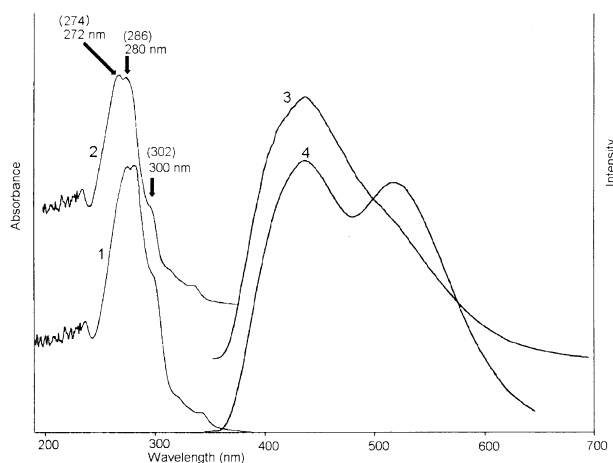
Figure 3. Absorption spectra of $CHCl_3$ solutions of **Poly-6** prepared without (1) and with (2) support SOOCPh— $\equiv$ —$(CH_2)_4$—OPhCH $=CBr_2$. Emission spectra of $CHCl_3$ solutions of **Poly-6** prepared without (3) and with (4) support SOOCPh— $\equiv$ —$(CH_2)_4$—OPhCH $=CBr_2$ (Excitation at 358 nm).

spectra of detached **Poly-6**. Similar to **Poly-6** prepared in solution **Poly-6** synthesized using solid support is not perfectly branched. This follows from proton NMR spectra where the doublet at 7.60 ppm is present along with other signals corresponding to monosubstituted structure **D**. However, DB of detached **Poly-6** was of 60—65% when calculated by formula 1 which is twice that for **Poly-6** synthesized in solution. M_n of detached **Poly-6** obtained by GPC and from ^1H NMR spectra was 7300 with polydispersity of 1.8 and 12000, respectively. The fact agrees with Moore *et al.* work[3] who were the first to observe self-limiting growth in solid supported hyperbranched polymerization. The origin of the phenomenon is steric hindrance due to polymeric support increase with molecular weight of the attached polymer. The increase of DB in solid-supported **Poly-6** is attributed from our point of view to the cage-effect. Monomer **6** molecules trapped in the vicinity of growing polymer chain by the polymeric support have more time to react with second bromine atoms of dibromovinyl groups, thus increasing DB of **Poly-6**. The molecular weight measured by GPC is consistently lower than that calculated from ^1H NMR spectra due to more compact conformation of hyperbranched molecules compared to linear polystyrene.

Figure 3 shows absorption and emission spectra of **Poly-6** synthesized with and without the solid support. All absorption spectra show shoulders at 300 nm and 3 maxims between 235 and 286 nm. Long wave absorption maxims of the structures **A**, **B**, **C**, and **D** were calculated theoretically using geometries optimized at HF/3-21G(d) level of theory followed by a single point energy calculations at B3LYP/6-31G(d) and shown in the Figure 3 in brackets. As seen from the Figure 3 there is good agreement between observed and calculated positions of peaks which allows us to assign a shoulder at 300 nm to the contribution from structure **B** ($\lambda_{max\,(calc)} = 300$ nm) while two close peaks at 270—272 ($\lambda_{max\,(calc)} = 274$ nm)

and 278—280 nm ($\lambda_{max\,(calc)} = 282$ nm) could be due to monosubstituted structures **B** and **C**, respectively. The peak from dibromostyryl terminal groups (structure **A**) ($\lambda_{max\,(calc)} = 248$ nm) which should appear at around 250 nm cannot be distinguished clearly due to high absorption of solvent ($CHCl_3$) in this region. The absorption spectra of **Poly-6** obtained with and without the solid support are similar and agree reasonably with NMR data. The emission spectra of **Poly-6** obtained in solution with and without solid support are alike. Both are blue emitters emitting the light at 437—442 and 527 nm when excited at 358 nm The second maxim is concentration depended and can be attributed to eximer formation.

CONCLUSIONS

Novel hyperbranched polymer poly(4-(5-Hexynyloxy)-β,β-dibromostyrene) was synthesized by Pd-catalyzed cross-coupling reaction of 4-(5-hexynyloxy)-β,β-dibromostyrene in solution and using aromatic polyamide solid support. According to NMR data, the degree of branching of the polymer obtained in solution without solid support was of 30—35%, while when using solid support the degree of branching increased to 60—65%. M_n of detached **Poly-6** calculated from ^1H NMR spectra was lower than that of the polymer obtained in solution. It seems that monomer molecules trapped in the vicinity of growing polymer chain by the polymeric support have more time to react with second bromine atoms of dibromovinyl groups, thus increasing of the polymer. Drop in molecular weight when using solid support results from steric hindrances due to polymeric support increase with molecular weight of the attached polymer, thus limiting the molecular weight of the attached polymer.

REFERENCES

1. L. Fomina and R. Salcedo, *Polymer*, **37**, 1723 (1996).
2. L. Fomina, S. Fomine, R. Salcedo, and T. Ogawa, *Polym. J.*, **28**, 1076 (1996).
3. P. Bharathi and J. Moore *J. Am. Chem. Soc.*, **119**, 3391 (1997).
4. K. Wolinski, J. Hilton, and P. Pulay *J. Am. Chem. Soc.*, **112**, 8251 (1990).
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
6. U. Salnzner, J. Lagowski, P. Pickup, and R. Poirier, *J. Comp. Chem.*, **18**, 1943 (1997).