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generation dendrimer as a multifunctional monomer N. V. Kuchkina,^aM. S. Zinatullina,^aE. S. Serkova,^a P. S. Vlasov,^bA. S. Peregudov^a andZ. B. Shifrina^a†

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An A_6+B_2 approach was applied for the first time to synthesize novel hyperbranched pyridylphenylene polymers by Diels-Alder cyclocondensation reaction. For this, the pyridylphenylene dendrimer of the first generation with six ethynyl functionalities (A_6) was used as a branching core for the molecule growth. The phenyl-substituted bis(cyclopentadienone)s (B_2) of different structures were used as a co-monomer in the reaction. A careful choice of reaction conditions allowed us to obtain high molecular weight polymers without undesirable gelation. The molecular weight of the polymers varied in the range of 10-80 kDa with polydispersity degree of 1.69 to 4.07 according to SEC analysis. The ¹H and inverse-gated decoupling ¹³C NMR combined with Heteronuclear Single Quantum Correlation and Heteronuclear Multiple Bond Correlation measurements were used to estimate a branching degree of the polymers synthesized.

Hyperbranchedpyridylphenylene polymers based on the first

Introduction

polymers(HBP) received Hyperbranched considerable attention of academia researchers and industry in the last twenty years. They arecharacterized by higher solubility compared to that of linear polymers, low viscosity, and a generous amount of functional groups.¹⁻⁵ Typically, the HBP are obtained by an one-pot procedure, which limits the ability to control the molecular weight and leads to "heterogeneous" products with a broad molecular weight distribution and differences inbranchingcompared todendrimers which are monodisperse macromoleculesin regard of both size and structure.^bThe main advantages of HBPover dendrimers area facile synthesis and alow cost of the final product. HBP have been applied in catalysis,⁷⁻⁹opto-electronic materials,¹⁰ drug release¹¹⁻¹³ etc.There are two scenariosfor the synthesis of HBP:the single-monomer methodology (SMM) and the doublemonomer methodology (DMM).¹SMM is based on the use of AB_n monomer type (n \ge 2). According to the reaction mechanism, theSMM strategy includes at least four approaches: (1)polycondensation of AB_n monomers; (2) self-condensing vinyl polymerization (SCVP); (3) self-condensing ring-(4) proton-transfer openingpolymerization (SCROP); polymerization (PTP). A broad range of hyperbranched hyperbranchedpolyphenylenes,¹⁴⁻ polymers, including ¹⁶ polyethers, ¹⁷ polyesters, ¹⁸ polyamides, ^{19, 20} polycarbonates, ²¹

polyurethanes²² and polycarbosilanes²³ were synthesized by polycondensation of AB_n monomers. Various hyperbranched polyacrylates,²⁴⁻²⁶hyperbranched azobenzene-containing polymers,²⁷ hyperbranched glycopolymers²⁸ were prepared via SCVP. Hyperbranched polyamines,^{29, 30}hyperbranched polyethers^{31, 32} and polyesters^{33, 34} were synthesized through SCROP. Hyperbranched polyesters with epoxy or hydroxyl end groups³⁵ and hyperbranched polysiloxanes³⁶ were synthesized through PTP. DMM is based on the use of a pair of monomers such as A_n (n \ge 3) and B_2 . For example, hyperbranched aromatic polyamide,³⁷ pyrimidine-based hyperbranched polyimides,³⁸ hyperbranched polybenzoxazole³⁹ and hyperbranched polyacenaphthenequinones⁴⁰ were synthesied by A₃+B₂ approach. The $A_4+B_2^{41-43}$ and $A_3+B_3^{44}$ methods were also used for the synthesis of hyperbranched polymers.

A wide assortment of organic reactions is known for construction of HB polymers.⁴⁵⁻⁵¹ Among them the Diels-Alder reaction has been successfully used for the synthesis of HB polyphenylenes using the AB₂ or A₃+B₂ approaches.^{52, 53}

The main challenge in the HBP synthesisis to obtain the perfect dendritic polymer structure by aone-pot procedure; therefore, the known methods of synthesis are constantly improving. It was proposed to combine the advantages of dendrimers and hyperbranched polymers. In this way the synthesis is becoming much easier than that of high generation dendrimers and the polymer defects are becoming less pronounced than those of HBP synthesized via a routine monomer method. Dendrons have been used to design branched polymers, named "dendronized polymers".⁵⁴ Usually it is a linear polymer with dendritic units in side chains.^{54, 55}

In this paper for the first time we report the A_6+B_2 approach based on a Diels-Alder polycycloaddition of the first generation six-functional pyridine containing polyphenylene dendrimer with the aromatic bis(cyclopentadienone)s of different

^a A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov St., Moscow, 119991 Russia

 ^{b.} St. Petersburg State University, Department of Macromolecular Compounds, Universitetskyprospekt, 26, Petrodvorets, St. Petersburg, 198504, Russia
 ⁺ Corresponding author

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structures, leading to novel hyperbranchedpolyphenylenes with pyridine moieties. The structure of the HB polymers synthesized was characterized by NMR spectroscopy, while molecular weight and polydispersity degree were evaluated by size exclusion chromatography (SEC). The branching degree of the polymers synthesized was unambiguously defined by a combination of 1D and 2D NMR techniques.

Experimental section

Materials. 1,3,5-triethynylbenzene (98%), Bu₄NF (1M solution in tetrahydrofuran), N-methylpyrrolidone (99%), tetrahydrofuran (anhydrous, 99.9%), diphenyl ether (99%), oxylene (anhydrous, 97%) were purchased from Aldrich and used as received.

Measurements. ¹H NMR and ¹³C NMR spectra were recorded on Avance-IIIHD-500MHz NMR spectrometer operating at 500.13 MHz for ¹H and at 125.76 MHz for ¹³C. Chemical shifts are given in parts per million (ppm), using the solvent signal as a reference. CD₂Cl₂ was used as solvent for all standard 1D and 2D NMR measurements [δ (¹H)=5.35 ppm; δ (¹³C)=53.4 ppm]. 2D spectra: Heteronuclear Single Quantum Correlation(HSQC) and Heteronuclear Multiple Bond Correlation (HMBC) were recorded by using the standard pulse sequences of the Bruker software. The inverse-gated decoupling ¹³C NMR spectra were obtained at 25°C, 30° pulse angel, inverse-gated decoupling with 5.0 s delay, and 5,000 scans.

Size-exclusion chromatography (SEC) analyses were carried out using chromatograph Shimadzu LC-20AD equipped with TSKgel G5000H_{HR} 7.8 mm×30 cm (Tosoh Bioscience) and with TSKgel HHR-L. Detection was achieved with refractive index detector. SEC was performed in tetrahydrofuran at a flow rate of 1.0 mL/min with polystyrene as a standard.

The intrinsic viscosity $[\eta]$ measurements were performed with an Ubbelohde viscometer at 25°C in N-methylpyrrolidone (NMP). The samples were dissolved at room temperature.

Mass spectral analysis was carried out on the Bruker Biflex III MALDI-TOF instruments. MALDI-TOF mass spectra were measured by using a 337 nm nitrogen laser and tetracyanoquinodimethane (TCNQ) as a matrix.

Synthetic procedures.Synthesis of monomers.3,3'-(1,4-Phenylene)bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one)(1),3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopenta-2,4-

dien-1-one) (2), 3,3'-(carbonyldi-1,4-phenylene)-bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (3) (Scheme 1) were synthesized according to procedure described in paper.⁵⁶

First generation dendrimer G1-6N-(ethyn)₆(**4**) (Scheme 1) was synthesized according to procedure described by us elsewhere.⁵⁷

G1-6N-(ethyn)₆:¹H NMR spectrum (500 MHz, CD₂Cl₂): 8.64 (d, 3H, PyH), 8.02 (d, 3H, PyH), 7.81 (s, 3H, ArH), 7.45 -6.55 (m, 45H, ArH), 3.01, 2.97 (2s, 6H, acetylenes). MALDI-TOF, m/e: 1370 (M+, calcd. 1369.66). Elem. anal. found, %: C 88.65; H 4.35; N 6.05. Calcd. for $C_{102}H_{60}N_6$, %: C 89.45; H 4.42; N 6.14.

Synthesis of hyperbranched pyridylphenylene polymers. All procedures were performed using a Schlenk flask under an argon atmosphere in diphenyl ether at 160°C using total

monomer concentrations of $0.01 - 0.05 \text{mol} \cdot \text{L}^{-1}$, at various molar ratios of monomers. The amounts of reagents employed are given in Table 1. In typical procedure, 0.050 g (0.073 mmol) of 3,3'-(1,4-phenylene)-bis-(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (B₂) and 0.1 g (0.073 mmol) of first generation dendrimer G1-6N-ethyn (A₆) were dissolved in 14.6mL of diphenyl ether at 160°C (Table 1, entry 1, a). All reactions were carried out for 6.5 hrs, and then the mixture was allowed to cool. The cold reaction mixture was diluted with chloroform and added dropwise into ethanol. A white precipitate was filtered, washed with ethanol and reprecipitated twice from chloroform into ethanol. Polymers were dried in vacuum at 120°C.

Table 1. The synthesis parameters	for polymer	preparations
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N	A .D	A ~	D ~	D	C ^a	
IN	A ₆ :B ₂	A ₆ , g	B ₂ , g	В2	C, mol 1 ⁻¹	
	(molar	(mmol)	(mmol)		mol·L	
1	ratioj				2)0.010	
1		0.100	0.050		a)0.010	
	1:1	0.100	0.050		b)0.020	
		(0.075)	(0.075)		0.033	
2					a)0.050	
2		0.100	0.075		a)0.010	
	1:1.5	0.100	0.075		b) 0.020	
		(0.073)	(0.109)	1	c)0.033	
					d)0.050	
3	1:2	0.100	0.101		a)0.050	
		(0.073)	(0.146)		b)0.033	
4		0.100	0.151		a)0.010	
	1:3	(0.073)	(0.219)		b)0.033	
		. ,	. ,		c)0.050	
5	1:1	0.100	0.057		a)0.033	
		(0.073)	(0.073)		b)0.050	
6		0.100	0.085		a)0.010	
	1:1.5	(0.073)	(0.000)	2	b)0.020	
		(0.073)	(0.103)		c)0.050	
7	1:2	0.100	0.114		a)0.01	
		(0.073)	(0.146)		b)0.02	
8		0.100	0.050		a)0.010	
	1:1	0.100	0.058		b)0.033	
		(0.073)	(0.073)		c)0.050	
9					a)0.010	
	1:1.5	0.100	0.087		b)0.020	
		(0.073)	(0.109)	3	c)0.033	
					d)0.050	
10	1:2	0.100	0.116		a)0.01	
		(0.073)	(0.146)		b)0.02	
11		0.400	0.474	1	a)0.010	
	1:3	0.100	0.1/4		b)0.033	
		(0.073)	(0.219)		c)0.050	

^atotal concentration of monomers A_6 and B_2

Results and discussion

Polymer synthesis

Hyperbranched aromatic polymers were synthesized by a Diels-Alder reaction using an A_6+B_2 approach. For this, the

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pyridylphenylene dendrimer of the first generation with six terminal acetylene functionalities -monomer A_6 - was used as a branching point for the molecule growth (Scheme 1, compound 4). Bis(cyclopentadienone)s (B₂) of different structures (Scheme 1, compounds 1, 2, and 3) were used as a second monomer in the reaction. Dendrimer G1-6N-ethyn (4) was synthesized according to the protocol described by us previously.⁵⁷ The aromatic bis(cyclopentadienone)s were obtained by the Knoevenagel condensation of bis(*a*-diketones) with two-fold molar amounts of diphenylacetone according to the procedure described in ref.⁵⁶. In this way 3,3'-(1,4-phenylene)bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (1), 3,3'-(oxydi-1,4-phenylene)-bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (2) and 3,3'-(carbonyldi-1,4-phenylene)-bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (3) were synthesized.



Scheme1.Synthesis of hyperbranchedpyridylphenylene polymers

The polycyclocondensation of multifunctional monomers may lead to rapid undesirable gelation which can be controlled by reaction parameters such as temperature, reaction time, concentration of monomers, etc. To establish dependences of the reaction parameters on the polymer structure, the Diels-Alder polycyclocondensation was carried out using a pair of 3,3'-(1,4-phenylene)-bis(2,4,5-triphenylmonomers: B₂, cyclopenta-2,4-dien-1-one) (1) and A₆, G1-6N-ethyn (4). Since we observed gelation at 180°C already in one hour, the synthesis of the polypyridylphenylenes was performed at 160°C for 6.5 hrs. The molar ratios of the A₆:B₂monomers employed were 1:1, 1:1.5, 1:2, and 1:3. When the $A_6:B_2$ molar ratio was 1:3, complete gelation occurred at all monomer concentrations (0.010-0.050 mol·L⁻¹) (Table 2, polymers 1, 2, and 3). However, when the reaction time was decreased to 3 hrs, a soluble polymer with a molecular weight 23500 (according to SEC) was obtained, at the total monomer concentration of 0.033 mol·L⁻¹ (Table 2, polymer 4). The same trend was observed for the $A_6:B_2$ molar ratio of 1:2. The gelation has occurred at the concentrations of 0.050 and 0.033 $mol \cdot L^{-1}$ (Table 2, polymers **5** and **6**), while a soluble polymer of the molecular weight 17900 was prepared, when the reaction time was decreased to 3 hrs, at the total monomer concentration of 0.033 mol· L^{-1} (Table 2, polymer **7**).

At the $A_6:B_2=1:1.5$ molar ratio the soluble polymer was obtained at $C_{total}= 0.02 \text{ mol} \cdot L^{-1}$ after the 6.5 h reaction with the

molecular weight 40300 (Table 2, polymer **10**). At higher concentrations the gelation was observed for the polymers (Table 2, polymers **8** and **9**). A further decrease of the concentration led to the polymer molecular weight drop at the same monomer ratio (Table 2, polymer **11**).

At the equimolar monomer ratio the soluble polymers were prepared at the total monomer concentration of 0.033 mol·L⁻¹ and below (Table 2, polymers 13, 14, and 15). Here the drop of the monomer concentrations led to lower molecular weights of the polymers as well.

Based on the above observations we determined that the monomer concentration dramatically effects the soluble polymer formation. Moreover, the effect is more pronounced for the high $B_2:A_6$ monomer ratio. In some cases, the soluble polymers were obtained only when the reaction time was reduced (Table 2, polymer 4 and 7).

Using the above findings we synthesized the polymers based on monomers A6 and B2 (compounds (2) and (3), Scheme 1) having bridging groups. At the monomer ratio 1:1, the polymers with higher molecular weights were obtained at C_{total} = 0.033 mol·L⁻¹ (Table 2, polymers 20 and 25) as compared to that based on monomer 1 (polymer 13). This effect can be ascribed to a more flexible structure of B₂ monomers, providing the favourable polymer growth due to lower steric constraints. At the same time, at a higher B₂ content (A₆:B₂=1:2 or 1:1.5) the soluble polymers were obtained only at C_{total} = 0.01mol·L⁻¹ (Table 2, polymers 17, 19, 22, and 24) for both B₂ monomers.

According to SEC the highest molecular weight polymer (80100) was obtained by reacting of 3,3'- (carbonyl-di-1,4-phenylene)-bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one) (3) with G1-6N-ethyn (4) (Table 2, polymer 25), probably due to the higher reactivity of the 3 compared with 1 and 2.

All polymers showed good solubility in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, toluene, benzene, and N-methyl-2pyrrolidone.

The intrinsic viscosity $([\eta])$ of the polymers synthesized measured in N-MP at 25 °C was rather low (Table 2) which is characteristic of hyperbranched polymers. It is well known that the intrinsic viscosities of the hyperbranched polymers are much lower compared to that of linear polymer of the same molecular weight. For linear polymers in a good solvent $[\eta]$ increases monotonically with a molecular weight following the Mark-Houwink equation with α =0.7.⁵⁸ On the other hand, dendrimers and hyperbranched polymers demonstrate unusual viscosity behaviour. For example, $[\eta]$ of some dendrimers increases initially and then decreases after a maximum is reached at a certain generation.⁵⁹ The intrinsic viscosity of star and hyperbranched polymers generally has a lesser dependence on the molecular weight than that of corresponding linear polymers.^{60, 61} A small dependence of $[\eta]$ on the molecular weight was also observed for the polymers synthesized (Table 2). The $[\eta]$ values of these polymers are quite low and the increase of the molecular weight of the polymers obtained at the same molar concentrations but at the different molar ratio of monomers (compare pairs 4 and 7,

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10 and **14**, **17** and **19**, **22** and **24**, Table 2) does not lead to a significant change in $[\eta]$, indicating the formation of macromolecules of a compact shape.⁶²

It is worth noting that the average yields of the polymers are in the range of 63-79% (Table 2). We assume that these comparatively low yields can be because monomer A_6 does not fully participate in the reaction with B_2 due to lower solubility or slow solubilization of the former. Indeed, during the workup procedure A_6 is isolated in practically all cases. This effect is especially pronounced for polymers obtained at the 1:1 molar ratio. Instead of expected predominantly linear polymers, a branched polymers are formed apparently as a result of disturbance of the initial monomer loading ratio.

More accurate assessment of the polymer branching has been obtained from NMR data.

Table 2. The synthesis conditions and characterization data of different hyperbranched pyridylphenylene polymers

Poly- mer ^a	A ₆ :B₂(molarr atio)	B ₂	C ^b , mol·L ⁻¹	[η] ^c , dL·g ⁻¹	M _w ×10 ⁻³ , g·mol ⁻¹	M _w /M _n	Yield %
1 ^d	1:3		0.050	-	-	-	-
2 ^d	1:3]	0.033	-	-	-	-
3 ^d	1:3		0.010	-	-	-	-
4 ^e	1:3		0.033	0.32	23.5	3.10	75
5 ^d	1:2		0.050	-	-	-	-
6 ^d	1:2		0.033	-	-	-	-
7 ^e	1:2		0.033	0.30	17.9	2.15	77
8 ^d	1:1.5	1	0.050	-	-	-	-
9 ^d	1:1.5		0.033	-	-	-	-
10	1:1.5		0.020	0.46	40.3	4.07	78
11	1:1.5		0.010	0.1	13.4	2.44	75
12 ^d	1:1		0.050	-	-	-	-
13	1:1		0.033	0.72	33.7	3.27	69
14	1:1		0.020	0.49	22.1	2.11	68
15	1:1		0.010	0.13	10.8	2.15	66
16 ^d	1:2		0.02	-	-	-	-
17	1:2		0.01	0.11	29.1	1.84	78
18 ^d	1:1.5	2	0.02	-	-	-	-
19	1:1.5		0.01	0.12	17.1	1.69	79
20	1:1		0.033	0.29	40.3	2.94	63
21 ^d	1:2		0.02	-	-	-	-
22	1:2		0.01	0.19	35.1	2.69	69
23	1:1.5	3	0.02	-	-	-	-
24	1:1.5		0.01	0.17	18.4	1.85	70
25	1.1		0.022	0.27	90.1	2 00	66

^asyntheses were carried out in diphenyl ether at 160°Cfor 6.5 hrs

^btotal concentration of monomers A₆ and B₂

^cintrinsic viscosity of the polymer solution in NMP at 25°C

^dinsoluble polymer

^esynthesis was carried out in diphenyl ether at 160°C for 3 hrs

NMR analyses of polymers

The degree of branching (DB) is the most important characteristic of hyperbranched polymers. NMR spectroscopy has been proven to be the most powerful tool for the direct assessment of the DB.⁶³ Typically, the DB of polymers is determined by comparing the NMR spectra of suitable model compounds and a polymer.^{64, 65} For this, model compounds mimicking branched, linear, and terminal polymer fragments should be synthesized. In order to determine the DB of hyperbranched polypyridylphenylenes it was necessary to synthesize partially substituted monomer A₆, i.e., models containing from one to five terminal acetylene groups (Figure S1, the Electronic Supplementary Information, ESI). While mono- or disubstituted monomers A₆ (Figure S1, a and b, respectively) were obtained with a high yield and purity, the further substitution (Figure S1, c, d, and e) led to the mixture of differently substituted compounds that could not be separated by column chromatography. Therefore, in this study we used the NMR spectroscopy to estimate the relative amount of free (unreacted) functional groups in the repeating unit of the polymers synthesized that is directly related to the branching degree of the polymer.

As a proof of concept, we demonstrated the effect of the molar ratio of monomers on the branching of the polymers synthesized, for the pair of monomers A_6 and B_2 (compound 1) (Table 2). For this study, the polymers 4, 7, 10 and 13 obtained at the molar ratios of monomers $A_6:B_2=1:3$, 1:2, 1:1.5 and 1:1, respectively, were chosen.

All ¹H NMR spectra of polymers 4, 7, 10, and 13 (Figure 1a and Figure S2, a-c in ESI) show three groups of signals. The signals at 8.61 (or 8.64) and 8.07 (or 8.01) ppm belong to α -protons H(1) and H(1') of nonequivalent pyridine moieties of the polymer, the signals at 3.08 (or 3.02), 3.04 (or 2.99), and 3.00 (or 2.95) ppm correspond to the protons H(2) of the terminal acetylene groups, while signals in the range of 7.7-6.25 ppm are assigned to other aromatic protons of the polymer. According to the integral ratio of the signals of the acetylene protons and α -protons of pyridine fragments their ratio in polymer **13** ($A_6:B_2=1:1$) is 3:6, in polymer **10** ($A_6:B_2=1:1.5$) it is 2.34:6, in polymer 7 ($A_6:B_2=1:2$) it is 2:6, and in polymer 4 (A₆:B₂=1:3) it is 1.23:6. Therefore, an increase of the monomer B₂ content led to the decrease of the number of the unreacted acetylene groups in polymers. Because every repeating unit of polypyridylphenylenes contains six pyridyl moieties that come from the branching monomer A_{6} , the ratio of the pyridyl fragments and unreacted acetylene groups (which did not participate in the growth of macromolecules) is directly related to the branching of the polymers. Ideally, if the polymer growth occurs in six directions (this might be accomplished at $A_6:B_2=1:3$), the structure of the repeating unit of the polymer would be similar to the structure shown in Figure 2. In this case, no signal of acetylene protons should be observed int he ¹H NMR spectrum, and the branching degree should be 100%.

However, as it is discussed above, in the most branched polymer **4** the ratio of the acetylene and pyridine fragments is 1.23:6, revealing that the macromolecule growth occurred mostly in five directions (Figure 1) . Accordingly, for polymer **7**, macromolecule growth occurred mostly in four directions, for polymer **10**, in three or four directions, and for polymer **13**, in three directions, respectively. Here, it should be noted that the NMR signal ratio is an average value and a mixture of different

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possible repeating units may coexist in polymers (see Figures S3-S6, ESI for illustration).

¹H NMR (CD₂CI₂, 500MHz)

Figure 2. Proposed ideal structure of the repeating unit of the polymers.

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For more accurate signal assignment, we chose polymer 25 with highest molecular weight and combined 1D and 2D NMR techniques. All signal assignments in the inverse-gated decoupling ¹³C NMR spectrum of the polymer (Figure 3a) are made with the help HSQC and HMBC spectra (Figures S7-S10, ESI). The spectrum contains the signal at 196.4 ppm which corresponds to the carbon C(3) of the carbonyl group in the benzophenone unit of the polymer. The signal at 159.4 ppm is assigned to quaternary carbon atoms C(4) and C(5) in the pyridine fragments of the polymer. The signals at 149.6 and 148.9 ppm refer to the carbon atoms C(1, 1') located at the $\alpha\text{-}$ position of the pyridine fragments. The signals at 122.1 and 121.5 ppm are ascribed to the carbon atoms C(6) and C(7) in pyridine, while the signals at 120.2 and 119.7 ppm refer to the carbon atoms C(8) in phenyl rings bound to the acetylene group of the polymer. The signals at 83.9 and 77.5 ppm refer to the quaternary carbon atoms C(9) and the carbon atoms C(2) of the terminal acetylene groups, respectively.



Figure 3. 13 C NMR spectrum (a) and the proposed structure of polymer 25 (b).

Because the signal of a carbonyl group of cyclopentadienone unit at about 200 ppm is not detected (signal at 196.4 ppm belongs to the bridging carbonyl group of B₂) and considering

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Figure 1. ¹H NMR spectrum (a) and the proposed structure of the polymer 4(b). For polymers 7, 10, and 13, see ESI.



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the functionality of the monomers and the monomer loading ratio, we concluded that there are no unreacted functional groups from the B_2 monomer in polymer 25. To allow for accurate integration of the ¹³C signals, the ¹³C spectrum was recorded with proton decoupling only during the acquisition period to avoid non-uniform enhancement of carbon signals from proton (Nuclear Overhauser Effect). Thus, the integration of the aromatic and acetylene carbon signals in the spectrum in Figure 3a allows us to estimate the ratio of the terminal acetylene and pyridine fragments in the polymer as 3:6. The same ratio was obtained from the ¹H NMR data (see Figure S11, ESI).

The special attention is paid to the splitting in a "triplet" of the signal at 3.00 ppm.The HSQC spectrum (Figure S8, ESI) demonstrated that the "triplet" of acetylene protons gives intensive correlation signals with at least four signals of carbon at 77.5 ppm (position 2 in the polymer structure, Figure S8, ESI). Moreover, the poor correlation signals are observed with acetylene carbons at 83.9 ppm (position 9 in the polymer structure, Figure S8, ESI) due to geminal spin-spin interactions ¹H-C=¹³C. In the HMBC spectra there are also correlations of acetylene protons with at least four *ipso*¹³C nuclei of phenyl fragments, connected with the acetylene group, at 120.2 ppm (position 8, Figure S10, ESI). Thus, in the polymer there are a few acetylene groups, which indicator nuclei have different magnetic shielding. It should be noted that in the polymer with the symmetric structure of the repeating unit the magnetic shielding is similar. Possible conformation impact and/or deviation from the plane of conjugation of aromatic groups due to steric reasons should not effect shielding of acetylene H and C atoms that are spatially separated from the aromatic rings. Obviously, there are structurally different repeating units in the polymer (Figure S3, ESI) for which the magnetic shielding of indicator nuclei of acetylenes differs that leads to the splitting in a "triplet" of the signal at 3.00 ppm.

Thus, the detailed NMR study allows us to propose the structure of the polymers synthesized and estimate their branching degree.

Conclusions

In this work, the efficient and facile A_6+B_2 approach to hyperbranched pyridylphenylene polymers was proposed using Diels-Alder polycycloaddition of the first generation sixfunctional pyridine-phenylene dendrimer (A_6) and the aromatic bis(cyclopentadienone)s (B_2). A thorough screening of the reaction conditions allowed us to find optimal conditions for the formation of high molecular weight polymers as confirmed by SEC. The low intrinsic viscosity of polymers combined with high molecular weights was another proof of polymer branching whereas the detailed NMR study of the polymers clearly demonstrated that the growth of the polymer macromolecule occurs spatially in several directions, depending on the $A_6:B_2$ molar ratio, leading to hyperbranched polypyridylphenylenes. The approach developed paves the way for the one-pot synthesis of well-defined polymers bearing perfect dendritic fragments in the polymer backbone.

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