



SYNTHESIS OF A NEW HYPERBRANCHED PYRIDYLPHENYLENE POLYMER BASED ON AN AB₂ MONOMER AND A PAIR OF AB/AB₂ MONOMERS

Cite this: *INEOS OPEN*, 2020, 3 (5), 172–175
DOI: 10.32931/io2020a

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Received 18 July 2020,
Accepted 2 September 2020

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Abstract

A hyperbranched pyridylphenylene polymer with the weight average molecular mass of 56000 Da is synthesized for the first time from an AB₂ monomer bearing one diene and two internal triple bonds. The introduction of a linear AB comonomer into the reaction system leads to an increase in the yield of the polymer which has the weight average molecular mass of 21400 Da. Due to the limited degree of intramolecular cyclization, the high content of functional groups facilitates the formation of defect-free structures and provides an opportunity to modify the resulting polymers.

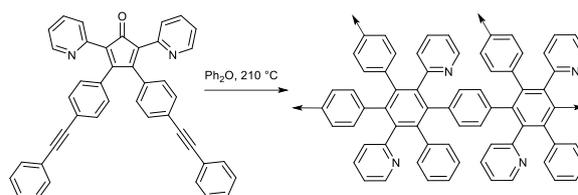
Key words: hyperbranched pyridylphenylene polymer, Diels–Alder reaction, AB₂ monomer, AB monomer.

Introduction

Hyperbranched polymers (HBPs) attract strong interest owing to their unique characteristics, which open the way to different application fields. For example, they are used as additives for linear polymers to improve their rheological properties [1]. Earlier we have shown that HBPs can serve as efficient stabilizing agents for catalytically active nanoparticles [2, 3]. Furthermore, they find use in microelectronics [1].

HBPs refer to dendritic macromolecules with irregular structures, in which the dendritic and linear moieties are distributed randomly. The unique properties of HBPs stem, first of all, from their molecular branched architectures, which define their high solubility, and the possibility of synthesis of macromolecules with terminal functional groups, which enable further modification [4, 5]. These features of HBPs allow for their comparison with ideally branched dendrimers. Dendrimers represent the objects which molar masses and branching degrees can be controlled during stepwise synthesis. At the same time, their synthesis is more tedious due to the intermediate steps of isolation of each generation. However, this provides monodisperse macromolecules with clearly defined structures. In the case of HBP, one-step synthesis affords polydisperse macromolecules featuring nonideal branching. Nevertheless, the one-step synthetic procedure is an important advantage that encourages the application of new materials in the case when the final cost of a product is a crucial factor [1]. Therefore, HBPs are preferred from the viewpoint of saving the raw materials and energy.

As a rule, hyperbranched polymers such as polyphenylenes [6, 7], polyesters [8], polyamides [9], polycarbonates [10], polyurethanes [11], polycarbosilanes [12] are synthesized using an AB₂ monomer or a pair of AB/AB₂ monomers.



In this report, we used these approaches to produce HBPs based on new substituted aromatic cyclopentadienones bearing phenylene and pyridine units and internal triple bonds. The possibility of synthesis of new HBPs by the Diels–Alder reaction using an AB₂ monomer and a pair of AB/AB₂ monomers was studied. The reaction conditions, including the temperature, monomer concentration, and duration, were optimized. The molar masses and polydispersity indices of the resulting polymers were defined by the gel permeation chromatography (GPC).

Results and discussion

The target pyridylphenylene polymers were obtained by the polycondensation of an AB₂ monomer or copolycondensation of a pair of AB and AB₂ monomers. The structures of the monomers are presented in Fig. 1. These monomers were synthesized by the Knoevenagel reaction according to the published procedure [13].

Hyperbranched polymer **3** was obtained from the AB₂ monomer bearing one diene and two internal triple bonds by the

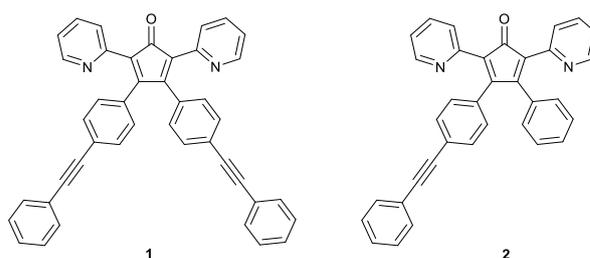
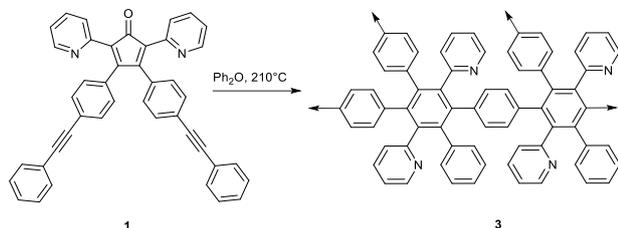


Figure 1. AB₂ (**1**) and AB (**2**) monomers used in the synthesis of new HBPs.

Diels–Alder reaction (Scheme 1). The reaction conditions suggested by Morgenroth and Müllen [7] for the polyphenylenes afforded an insoluble product (Table 1, sample I). A reduction in the monomer concentration and reaction temperature provided a considerable increase in the yield of the soluble polymer.



Scheme 1. Synthesis of the HBP based on the AB₂ monomer.

Table 1. Conditions for the polycondensation of the AB₂ monomer

Sample	T, °C	Time, h	c, mol/L	M _w , Da	M _n , Da	MMD
I	260	72	0.330	–	–	–
II	260	45	0.170	8500	2400	3.54
III	220	148	0.068	1300	1000	1.30
IV	220	72	0.034	1200	900	1.33
V	200	72	0.032	1400	1300	1.08
VI	180	72	0.010	2000	1800	1.11
VII	180	72	0.005	1400	1300	1.08
VIII	210	99	0.005	56000	25000	2.24

In most cases, the reactions afforded, besides the insoluble product, the low-molecular-weight compounds (Table 1, samples II–VII). This evidences the low reactivity of internal triple bonds in oligomeric compounds as well as the probable steric hindrances that may arise during the synthesis of this polymer. Furthermore, the reaction rate is caused by the low concentration of the monomers.

The high-molecular-weight reaction product (sample VIII) was obtained upon an essential reduction in the monomer concentration compared to sample I (from 0.330 mol/L to 0.005 mol/L) and a considerable increase in the reaction temperature (from 180 to 210 °C) and time (from 72 to 99 h) compared to sample VII. The characteristic viscosity of the resulting polymer was 0.4 dL/g. According to the GPC data (Fig. 2), the weight average molecular mass of polymer VIII was 56000 Da, and its polydispersity was 2.24. The polymer was obtained in 53% yield.

In order to improve the polymer yield, an alternative synthetic route was suggested that was based on the

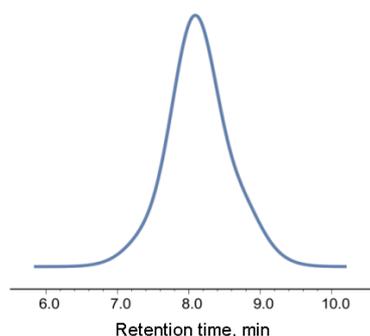
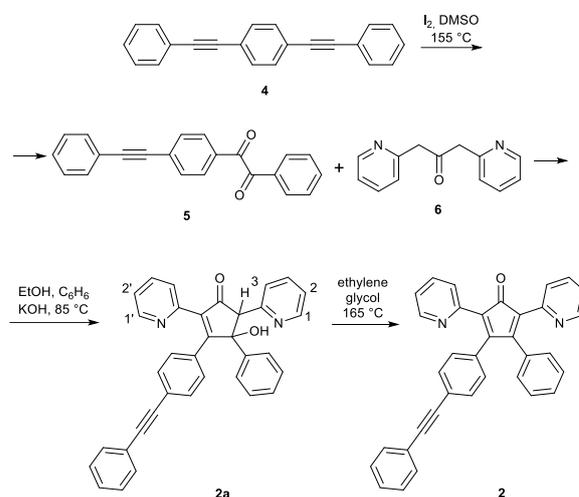


Figure 2. GPC data for polymer 3.

copolycondensation of the AB₂ and AB monomers. The use of the AB monomer—a tetrasubstituted pyridyl-containing cyclopentadienone with one internal triple bond (Fig. 1, compound 2)—facilitated a reduction in the steric hindrances during growth of a macromolecule. The synthetic route for the enol (2a) and diene (2) forms of the AB monomer is presented in Scheme 2.

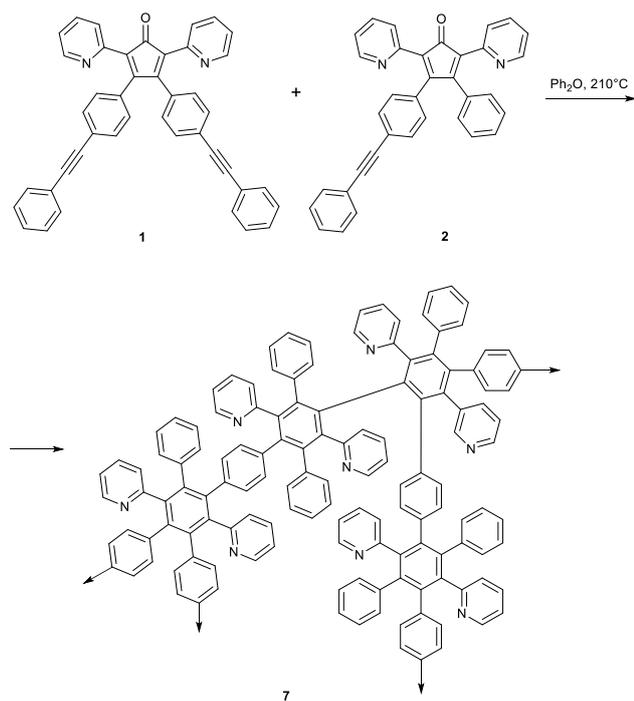


Scheme 2. Synthesis of the AB monomer.

At the first step, the oxidation of 1,4-(diphenylethynyl)benzene (4) afforded compound 5 [14]. The synthesis was carried out for 17 h; the product yield reached 70%. Then, compound 5 was introduced into the Knoevenagel condensation with 1,3-di(pyridin-2-yl)propan-2-one 6, which resulted in the enol form of the AB monomer (Scheme 2, compound 2a) as a mixture of diastereomers. As it was shown earlier, the enol form of the target product can be converted *in situ* to the corresponding cyclopentadienone (2) under the conditions of the Diels–Alder reaction [15]. Therefore, the dehydration in ethylene glycol at 165 °C was not required, which significantly simplified the synthesis of the target polymer.

The structure of compound 2a was confirmed by the ¹H and ¹³C NMR spectroscopic data. Thus, the ¹H NMR spectrum of the resulting product shows the doublets at δ = 8.70 (*J* = 4.3 Hz) and 8.57 ppm (*J* = 5.0 Hz), which correspond to 1 and 1' α-protons of the nonequivalent pyridine rings, and the multiplets in the ranges of 7.61–7.66 and 7.74–7.78 ppm, which correspond to 2 and 2' β-protons of the pyridine rings. Moreover, the characteristic signals of proton 3 of the enol form are observed at 4.22 and 4.20 ppm. The diene form of the AB monomer was formed *in situ* under conditions of the copolycondensation. Scheme 3 depicts the synthetic route for the HBP based on the AB₂ and AB monomers.

The introduction of the AB monomer facilitated the formation of soluble product IX (Table 2) and a reduction in the content of the insoluble fraction compared to sample I (Table 1) obtained under analogous conditions. A further decrease in the monomer concentrations led to growth of the weight average molecular masses of samples X and XI, whereas an extension of the reaction time from 72 to 99 h afforded polymer XII (Table 2) with the weight average molecular mass of 21400 Da and polydispersity index of 1.80.



Scheme 3. Synthesis of the HBP based on a pair of the AB/AB₂ monomers.

Table 2. Conditions for the polycondensation of a pair of the AB/AB₂ monomers

Sample	<i>T</i> , °C	Time, h	<i>c</i> , mol/L	<i>M_w</i> , Da	<i>M_n</i> , Da	MMD
IX	260	72	0.330	4900	4000	1.23
X	210	72	0.170	7000	5100	1.37
XI	210	72	0.005	11300	8000	1.41
XII	210	99	0.005	21400	11900	1.80

Polymer **3** was used as a stabilizing macromolecule in the synthesis of a ruthenium-containing magnetically separable catalyst based on magnetite. As can be seen from the micrograph obtained by transition electron microscopy (TEM) (Fig. 3), the ruthenium nanoparticles are uniformly distributed over the polymer matrix without formation of aggregates, which is an important criterion for the production of active nanoparticles. Subsequently, the resulting catalyst will be tested for the oxidation of betulin which is used for the production of antiviral, antitumor, and antiseptic agents [16–18].

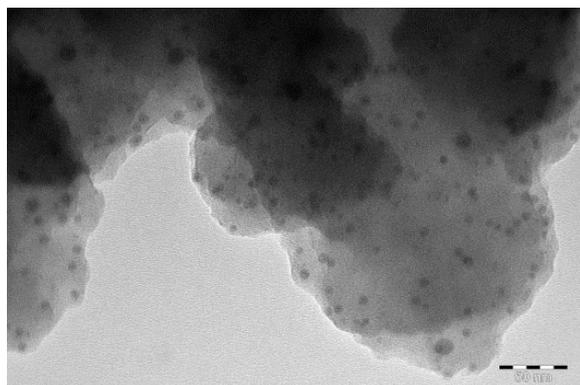


Figure 3. TEM micrograph of the ruthenium-containing magnetic catalyst based on polymer **3**.

Experimental

Methods

The ¹H and ¹³C NMR spectra were registered on Bruker Avance 500 and Avance 400 spectrometers.

The elemental analyses were obtained with a Carlo-Erba 1106 automated CHN-analyzer.

Thin-layer chromatography was carried out on ALUGRAMSILG/UV254 silica gel 60 (0.2 mm) plates with a fluorescent indicator (254 nm).

The molecular masses of the polymers were defined by GPC. The measurements were carried out on a chromatographer of Shimadzu production equipped with a RID-20A refractive index detector and a Phenogel 500A (300 × 7.8 mm) column. The analyses were performed using tetrahydrofuran as an eluent at the temperature of 40 °C and the flow rate of 1.0 mL/min. The polymer solution in tetrahydrofuran (concentration 35 mg/mL) was filtered through polytetrafluoroethylene membrane filters (0.45 μm). The relative molecular masses (*M_w* and *M_n*) and polydispersity indices were calculated with Shimadzu LC solution software based on the calibrating dependence using polystyrene standards.

The characteristic viscosity was determined by extrapolating the concentration dependence of the reduced viscosity to the zero concentration. The flow times of the polymer solution and a solvent (*N*-methylpyrrolidone) were measured using an Ubbelohde viscometer at 25 °C.

The transmission electron microscopic studies were carried out with a JEM 1400 plus microscope equipped with an OSIS Quemesa 11 MPix camera at the accelerating voltage of 120 kV.

Syntheses

Synthesis of 3,4-bis(4-(phenylethynyl)phenyl)-2,5-di(pyridin-2-yl)cyclopenta-2,4-dien-1-one (1). The enol form of monomer **1** was obtained according to the published procedure [13].

Synthesis of the HBP based on the AB₂ monomer (3). A solution of the enol form of monomer **1** (0.050 g, 0.083 mmol) in diphenyl ether (16.5 mL) was heated under an argon atmosphere at 210 °C for 99 h. After cooling to room temperature, the reaction mixture was poured into hexane. The resulting precipitate was filtered off, washed with hot ethanol, and dried under vacuum at 60 °C until the constant mass to give the target polymer. Yield: 0.020 g (53%).

Synthesis of 1-phenyl-2-(phenylethynyl)phenylethane-1,2-dione (5). A mixture of 1,4-bis(phenylethynyl)benzene (**4**) (0.280 g, 1.006 mmol) and iodine (0.005 g, 0.02 mmol) in DMSO (10 mL) was heated at 155 °C for 17 h. After cooling to room temperature, the reaction mixture was poured into 1% aq. Na₂S₂O₃. The resulting precipitate was filtered off, washed with water, and dried under vacuum at 55 °C to give compound **5**. Yield: 0.219 g (70%). ¹H NMR (CDCl₃, 400 MHz): δ 7.38–7.40 (m, 3H), 7.52–7.58 (m, 4H), 7.65–7.71 (m, 3H), 7.97–8.01 (m, 4H) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 88.43, 94.08, 122.34, 128.45, 129.04, 129.78, 129.94, 130.10, 131.80, 131.93, 132.01, 132.85, 134.97, 193.58, 194.18 ppm.

Synthesis of 4-hydroxy-4-phenyl-3-(4-(phenylethynyl)phenyl)-2,5-di(pyridin-2-yl)cyclopenta-2-en-1-one (2a). A mixture of 1-phenyl-2-

(phenylethynyl)phenyl)ethane-1,2-dione (**5**) (0.100 g, 0.322 mmol) and 1,3-di(pyridyn-2-yl)propan-2-one (**6**) (0.082 g, 0.387 mmol) was dissolved in ethanol (2 mL) and benzene (5 mL) at 85 °C under an argon atmosphere. After dissolution of the reagents, a solution of KOH (0.018 g) in water (2 mL) was added for 3 h. The reaction course was controlled by thin-layer chromatography (eluent: chloroform–ethanol (25:1)). The resulting precipitate was filtered off, washed with ethanol, and dried under vacuum at 50 °C until the constant mass to give compound **2a**. Yield: 0.122 g (75%). Mp: 152–154 °C. ¹H NMR (CDCl₃, 500 MHz): δ 4.20 (s, 1H), 4.22 (s, 1H), 6.97–7.78 (m, 40H), 8.57 (d, 2H, *J* = 5.0 Hz), 8.70 (d, 2H, *J* = 4.3 Hz) ppm. ¹³C{¹H} JMOD NMR (CDCl₃, 125 MHz): δ 65.72, 65.90, 82.90, 89.20, 89.24, 89.71, 91.15, 122.14, 122.50, 122.62, 122.72, 122.77, 123.06, 123.13, 123.28, 124.37, 125.52, 125.63, 125.68, 127.02, 127.33, 127.90, 128.05, 128.27, 128.41, 128.47, 128.52, 128.58, 128.71, 129.08, 129.21, 129.36, 129.69, 129.78, 130.14, 130.25, 130.92, 131.13, 131.29, 131.70, 131.73, 131.96, 132.88, 133.01, 136.05, 136.13, 136.54, 136.58, 138.04, 138.08, 139.09, 139.17, 144.37, 144.81, 147.79, 147.81, 149.61, 149.65, 149.92, 150.00, 151.77, 151.88, 155.90, 156.01, 172.49, 173.07, 201.09, 201.22 ppm. Anal. Calcd. for C₃₅H₂₄N₂O₂: C, 83.31; H, 4.79; N, 5.55. Found: C, 83.10; H, 4.84; N, 5.33%.

Compound **6** was synthesized according to the published procedure [19].

Synthesis of polymer 7 based on a pair of the AB/AB₂ monomers. A mixture of the enol form of the AB₂ (0.026 g, 0.043 mmol) and AB (compound **2a**) (0.011 g, 0.0215 mmol) monomers in diphenyl ether (3 mL) was heated under an argon atmosphere at 210 °C for 99 h. After cooling to room temperature, the reaction mixture was poured into hexane. The resulting precipitate was filtered off, washed with hot ethanol until the filtrate decoloration, and dried under vacuum at 60 °C until the constant mass to give the target polymer. Yield: 0.007 g (72%).

Conclusions

The polycondensation of the AB₂ trifunctional monomer and copolycondensation of a pair of the AB₂ and AB monomers afforded the polymers with the weight average molecular masses of 56000 and 21400 Da, respectively. The introduction of the AB monomer led to an increase in the polymer yield from 53% to 72%. The resulting polymer was used for stabilization of magnetite and ruthenium nanoparticles during the synthesis of a magnetically separable ruthenium catalytic system, which will be further tested for the oxidation of betulin in order to produce biologically active substances.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project no. 18-33-00609. The NMR spectroscopic studies and elemental analyses were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

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