

Rapid Communication

SYNTHESIS AND CHARACTERIZATION OF A NOVEL BLUE LIGHT EMITTING ROD-COIL DIBLOCK OLIGOMER*

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Abstract Four new rod-coil diblock molecules, which had well-defined *para*-phenylene oligomers (PPP, from biphenyl to quinquiphenyl) as rigid segments and poly(ethylene oxide) (PEO, M_w ca. 750) as flexible segments, were synthesized. The chemical structure and the number of repeating unit in PEO coil and PPP rod were characterized by ^1H -NMR and MALDI-TOF mass spectrometry. The diblock oligomers showed good solubility in common organic solvents and aggregated in water as characterized by a blue shift in UV-vis absorption spectra, a red shift in emission spectra, quenching of the fluorescence and formation of the microfibrilla and fractal-like structures. The formation of different supramolecular structures meant that this effort might lead to commercial important highly organized functional materials.

Keywords Rod-coil diblock oligomer, MALDI-TOF mass spectrometry, Microfibrilla aggregate, Fractal-like pattern

INTRODUCTION

There has been intense interest in the development of materials with surprising properties based on designed molecules and their ordered supramolecular architectures^[1–6]. Rod-coil block oligomers are among the most studied self-assembling materials. Due to the simultaneous presence of orientational ordering of rod like segments and the microphase separation of covalently bonded stiff segments and flexible segments, they have been found to form a variety of well-defined self-assembled structures^[7–11]. However, only a few studies have addressed the preparation and properties of rod-coil block oligomers containing π -conjugated segments^[12–16].

The oligomers of *para*-phenylene are promising candidates for opto-electrical devices because of their blue light-emitting feature, chemical stability, high fluorescence efficiency and thin film processability by vacuum deposition techniques^[17–21]. One of the intriguing characteristics of these molecules is that the emission light radiates in the direction normal to the molecular axis. As a result, the manipulation of molecular orientation is critical in full exploration of their potential applications. Here we report for the first time the synthesis and characterization of four rod-coil diblock molecules, **16-n**, which consist of poly(ethylene oxide) (PEO) oligomers as flexible coils and poly(*p*-phenylene) (PPP) oligomers as rigid rods. It is expected that the unique molecular spatial orientation and packing of PPP can be achieved by self-assembly of these diblock oligomers.

EXPERIMENTAL

Solvents and Reagents

Tetrahydrofuran (THF) was refluxed over sodium and distilled off just before use. All other solvents and reagents

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were commercial products and used as received unless otherwise stated.

Characterization

^1H -NMR spectra were recorded on a Bruker ARX-400 spectrometer using CDCl_3 as solvent and TMS as standard. MALDI-TOF mass spectra were measured on a Bruker Biflex III Mass Spectrometer with dithranol as matrix. UV/vis and luminescence measurements were performed on a Varian Cary 1E UV-Vis Spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer respectively. The fluorescence micrographs were taken on a Leica DMLP Fluorescence Microscope.

Synthesis

The synthetic route for PEO-PPP diblock oligomers was shown in Scheme 1. As a typical example, the detailed procedures for **16-5** were described as follows.

Methyloxy poly(ethyleneoxy)ethyloxy tosylate (1)

Compound **1** was synthesized by etherification of poly(ethylene glycol methyl ether) (M_w ca. 750) with *p*-toluenesulfonyl chloride according to a literature method^[14] with a yield of 65%. ^1H -NMR (CDCl_3 , TMS): δ = 2.37 (s, 3H, CH_3 -phenyl), 3.31 (s, 3H, CH_3O), 3.55–4.10 (m, 64H, OCH_2), 7.28 (d, 2H, Ar-H), 7.72 (d, 2H, Ar-H).

4-[Methyloxy poly(ethyleneoxy)ethyloxy]-4'-biphenylboronic acid (2)

Compound **2** was obtained by refluxing a stirred mixture of 2.72 g (3.00 mmol) monotosylated PEO, 0.64 g (3.00 mmol) 4-(4-hydroxyphenyl)phenylboronic acid and 1.17 g (8.48 mmol) potassium carbonate in 30 mL ethanol. After 24 h, the reaction mixture was extracted with three 50 mL portions of dichloromethane, followed by washing with distilled water, drying over magnesium sulfate and evaporation of solvent. The crude product was purified by silica gel column using the mixed solvent of dichloromethane and methanol (V/V = 5:1) as eluent, resulting in 2.40 g pure compound in 83% yield. ^1H -NMR (CDCl_3 , TMS): δ = 3.38 (s, 3H, CH_3O), 3.55–3.79 (m, 60H, OCH_2), 3.88 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 4.15 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 6.95–7.89 (m, 8H, Ar-H), 8.04 (s, 2H, $-\text{B}(\text{OH})_2$).

4-[Methyloxy poly(ethyleneoxy)ethyloxy]-4'''-methylquinquephenyl (16-5)

The molecule **16-5** was prepared by the tetrakis(triphenylphosphine)palladium (0.14 g, 0.12 mmol) catalyzed Suzuki cross-coupling reaction of **2**, 2.40 g (2.53 mmol), with 4-bromo-4'''-methylterphenyl, 1.29 g (3.99 mmol), in 50 mL toluene and 10 mL 0.8 mol/L sodium carbonate aqueous solution under an argon atmosphere at 98°C for 24 h. The target molecule, 1.07 g in 36% yield, was obtained after purification by column chromatography (silica gel) using ethyl acetate, methanol and dichloromethane/methanol (V/V = 5:1) as eluents successively. ^1H -NMR (CDCl_3 , TMS): δ = 2.42 (s, 3H, CH_3 -phenyl), 3.38 (s, 3H, CH_3O), 3.56–3.76 (m, 60H, OCH_2), 3.90 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 4.19 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 7.00 (d, 2H, Ar-H), 7.28 (d, 2H, Ar-H), 7.58–7.84 (m, 16H, Ar-H). m/z : ($M + \text{Na}$)⁺ 932.5, 976.5, 1020.5, 1064.5, 1108.5, 1152.6, 1196.6, 1240.6, 1284.6, 1328.6, 1372.6, 1416.6; ($M + \text{K}$)⁺ 992.5, 1036.5, 1080.5, 1124.5, 1168.5, 1212.5, 1256.5, 1300.5, 1344.6, 1388.5.

4-[Methyloxy poly(ethyleneoxy)ethyloxy]-4'-methylbiphenyl (16-2)

^1H -NMR (CDCl_3 , TMS): δ = 2.38 (s, 3H, CH_3 -phenyl), 3.38 (s, 3H, CH_3O), 3.55–3.78 (m, 60H, OCH_2), 3.88 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 4.16 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 6.98–7.53 (m, 8H, Ar-H). m/z : ($M + \text{Na}$)⁺ 704.2, 748.2, 792.2, 836.2, 880.2, 924.3, 968.3, 1012.3, 1056.3, 1100.3, 1144.3, 1188.3; ($M + \text{K}$)⁺ 764.2, 808.2, 852.2, 896.2, 940.2, 984.2, 1028.2, 1072.2, 1116.3, 1160.3.

4-[Methyloxy poly(ethyleneoxy)ethyloxy]-4''-methylterphenyl (16-3)

^1H -NMR (CDCl_3 , TMS): δ = 2.40 (s, 3H, CH_3 -phenyl), 3.38 (s, 3H, CH_3O), 3.55–3.75 (m, 60H, OCH_2), 3.89 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 4.17 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 6.99–7.70 (m, 12H, Ar-H). m/z : ($M + \text{Na}$)⁺ 780.3, 824.3, 868.3, 912.3, 956.3, 1000.4, 1044.4, 1088.4, 1132.4, 1176.4, 1220.4, 1264.4; ($M + \text{K}$)⁺ 840.3, 884.3, 928.3, 972.3, 1016.3, 1060.3, 1104.3, 1148.3, 1192.4, 1236.4.

4-[Methyloxy poly(ethyleneoxy)ethyloxy]-4'''-methyltetraphenyl(**16-4**)

$^1\text{H-NMR}$ (CDCl_3 , TMS): δ = 2.41 (s, 3H, CH_3 -phenyl), 3.38 (s, 3H, CH_3O), 3.56–3.75 (m, 60H, OCH_2), 3.90 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 4.18 (t, 2H, $\text{CH}_2\text{CH}_2\text{O}$ -phenyl), 7.00–7.82 (m, 16H, Ar-H). m/z : $(\text{M} + \text{Na})^+$ 856.4, 900.4, 944.4, 988.4, 1032.4, 1076.5, 1120.5, 1164.5, 1208.5, 1252.5, 1296.5, 1340.5; $(\text{M} + \text{K})^+$ 916.4, 960.4, 1004.4, 1048.4, 1092.4, 1136.4, 1180.4, 1224.4, 1268.5, 1312.5.

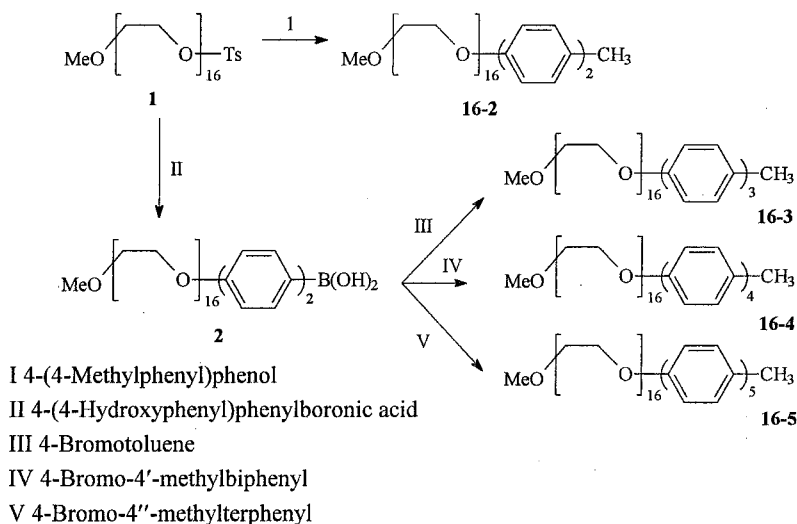
Film Preparation

The thin films were cast onto carefully cleaned cover glass from $1.00 \times 10^{-4} \text{ mol L}^{-1}$ aqueous solutions. The solvent was slowly evaporated at room temperature in a solvent-saturated atmosphere.

RESULTS AND DISCUSSION

Synthesis

The synthesis of **16-n** was based on standard synthetic transformations (Scheme 1). The chemical structure of target molecules and the number of repeating units in PEO coil and PPP rod were characterized by $^1\text{H-NMR}$ and MALDI-TOF mass spectroscopy. All of the analytical data were in full agreement with the values expected. As an illustration, the mass spectrum of **16-5** is depicted in Fig. 1. There are two series of equidistant mass peaks, indicating that different molecular ions were formed. The main series of mass peaks centered at 1108.5 Da can be assigned to the sodium ion adducts of **16-5**. The second series is shifted by 13 Da with respect to the first, which corresponds to the mass of the potassium ion adducts of molecules.



Scheme 1 Synthetic route for PEO-PPP diblock oligomers

Characterization of UV-vis and Fluorescence Spectra

The absorption and the emission features of **16-n** in tetrahydrofuran (THF) and water were examined, respectively. The UV-vis spectra of THF solutions of **16-n** at concentration of $1.00 \times 10^{-5} \text{ mol L}^{-1}$ showed similar π - π^* transitions with little or no resolved vibronic structure as expected for molecularly dissolved chromophores (Fig. 2). The molecule **16-2** had an absorption maximum at 262 nm, **16-3** at 293 nm, **16-4** at 308 nm and **16-5** at 316 nm. In unsubstituted PPP or end-substituted PPP, there is a 23° twist between adjacent phenylene units^[19]. Because the π -overlap is a function of the cosine of the twist angle, a fair amount of conjugative interaction remains. Therefore, the progressive red shift in the absorption maxima is presumably because of increasing π -conjugation as the number of phenyl units increases. Upon irradiating with a UV lamp, these solutions were blue-fluorescent. The emission spectra of **16-2**, **16-3** and **16-4** were qualitatively similar, save for the intensity of the

latter two (including **16-5**) which was much stronger than that of the first one. The fluorescence spectrum of **16-5** split into two well-resolved bands, which displayed maxima at 382 and 396 nm, respectively, when excited at 316 nm. The emission maxima were independent of the wavelength of the excitation, indicating they originated from the same chromophore. The absence of aggregation of molecules in this solvent was again supported. The Stokes shifts for **16-n** are in the range from 66 nm to 76 nm.

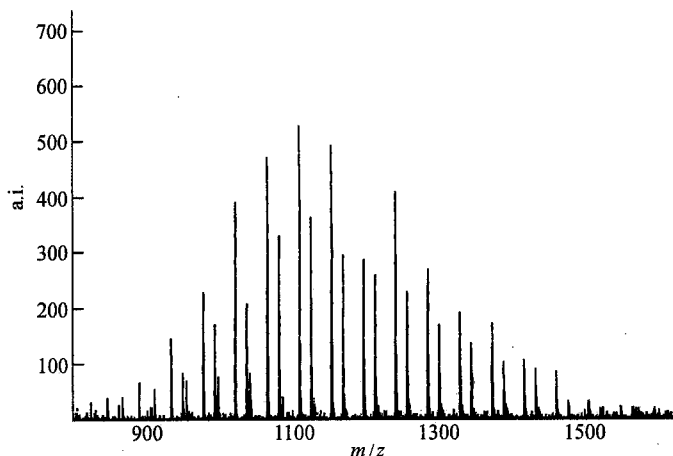


Fig. 1 MALDI-TOF mass spectrum showing the sodium and potassium adducts of **16-n**, respectively

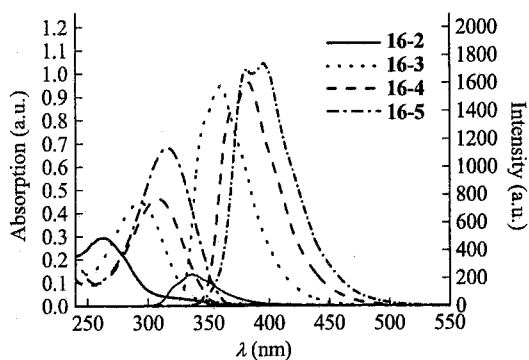


Fig. 2 UV-vis absorption (left) and emission spectra (right) of rod-coil molecules **16-n** in THF
Chromophore concentration = 1.00×10^{-5} mol L⁻¹

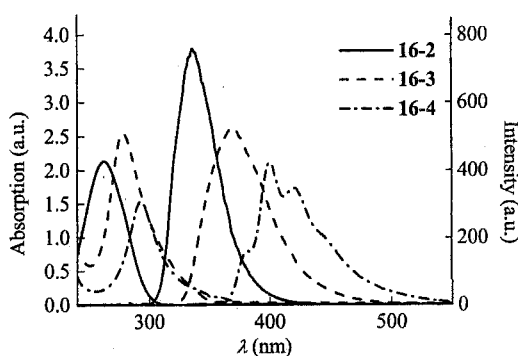


Fig. 3 UV-vis absorption (left) and emission spectra (right) of rod-coil molecules **16-n** in water
Chromophore concentration = 1.04×10^{-4} mol L⁻¹

Although the molecules **16-n** proved soluble in organic solvents such as chloroform and THF, only **16-2**, **16-3** and **16-4** could dissolve in water at a limited concentration. As shown in Figure 3, the UV-vis absorption and fluorescence spectra of **16-2** in THF and water were identical with the strongest band located at $\lambda_{\text{max}} = 262$ nm and 335 nm, separately. It implied that **16-2** was molecularly dissolved in water. It was worth noting that the absorption maxima of both **16-3** and **16-4** in water exhibited a blue shift by $\Delta\lambda = 15$ nm compared to THF solutions. The PL spectrum of **16-3** in water also showed a featureless, broad emission as in THF, but the peak maxima shifted from 360 nm to 370 nm. The emission spectrum of **16-4** showed more fine structure in water than in THF. It exhibited three clearly resolved bands and a shoulder at 380, 401, 420 and 442 nm, respectively. In addition, the emission from aqueous solutions of **16-3** and **16-4** was weaker when compared to THF solutions.

The blue shift in absorption spectra and the red shift in fluorescence spectra together with the greatly reduced emission intensity suggested that some aggregates were formed. These solvent dependent UV-vis absorption and fluorescence phenomena are common for conjugated polymers and oligomers, which has been explained as an effect of interchain π -stacking^[12–16].

Microfibrilla and Fractal-like Aggregates

The aggregation of **16-2**, **16-3** and **16-4** in water was studied primarily by fluorescence microscopy. Both **16-2** and **16-3** clearly displayed fibrillous morphologies (Fig. 4 and 5, respectively). The average width of the filaments was 1.5–4.0 μm for **16-2** and 12.0–34.1 μm for **16-3**. Their aspect ratio could be as high as several hundred. On the contrary, the molecule **16-4** formed fractal-like aggregates instead of flexible fibers (Fig. 6). Under a fluorescence microscope, many objects with highly irregular and ramified branches were observed.



Fig. 4 Fluorescence micrograph of fibrilla morphology **16-2** deposited from aqueous solution on cover glass with magnification of 100



Fig. 5 Fluorescence micrograph of fibrilla morphology of **16-3** deposited from aqueous solution on cover glass with magnification of 100

The supramolecular structure of molecules on substrate depends on several factors, including the interaction between the absorbed molecules and the substrate, the intermolecular interactions, and mobility of the absorbed material^[22]. When the mobility for the molecules to diffuse on the surface is big enough, isolated structures are formed. Otherwise, uniform morphologies will be observed. The variety in the types of self-assembling behavior of **16-2**, **16-3** and **16-4** was a complex interplay between molecule-substrate and intermolecular interactions. The



Fig. 6 Fluorescence micrograph of fractal-like morphology of **16-4** deposited from aqueous solution on cover glass with magnification of 100

formation of microfibrilla structure suggested that the surface mobility of **16-2** and **16-3** on cover glass was considerable. The formation of self-similar domain may be due to a strong tendency for **16-4** to aggregate. Further study of the internal structures of these aggregates and the effects of solvent and substrate on the hierarchical self-assembly of **16-n** is in progress using atomic force microscopy and transmission electron microscopy.

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REFERENCES

- 1 Laibinis, P.E., Whitesides, G.M., Allara, D.L., Tao, Y.T., Parikh, R.G. and Nuzzo, R.G., *J. Am. Chem. Soc.*, 1991, 113: 7152
- 2 Terech, P. and Weiss, R.G., *Chem. Rev.*, 1997, 97: 3133
- 3 Nelson, J.C., Saven, J.G., Moore, J.S. and Wolynes P.G., *Science*, 1997, 277: 1793
- 4 Won, Y.Y., Davis, H.T. and Bates, F.S., *Science*, 1999, 283: 960
- 5 Van Esch, J., Schoonbeek, F., De Lous, M., Kooijman, H., Spek, A.L., Kellogg, R.M. and Feringa, B.L., *Chem. Eur. J.*, 1999, 5: 937
- 6 Menger, F.M. and Caran, K.L., *J. Am. Chem. Soc.*, 2000, 122: 11679
- 7 Stupp, S.I., LeBonheur, V., Walker, K., Li, L.S., Huggins, K.E., Keser, M. and Amstutz, A., *Science*, 1997, 276: 384
- 8 Zubarev, E.R., Pralle, M.U., Li, L.M. and Stupp, S.I., *Science*, 1999, 283: 523
- 9 Lee, M., Cho, B.K., Kim, H. and Zin, W.C., *Angew. Chem. Int. Ed.*, 1998, 37: 638
- 10 Lee, M., Cho, B.K., Jang, Y.G. and Zin, W.C., *J. Am. Chem. Soc.*, 2000, 122: 7449
- 11 Cho, B.K. and Lee, M., *J. Am. Chem. Soc.*, 2001, 123: 9677
- 12 Marsitzky, D., Klapper, M. and Mullen, K., *Macromolecules*, 1999, 32: 8685
- 13 Kilbinger, A.F.M. and Feast, W.J., *J. Mater. Chem.*, 2000, 10: 1777
- 14 Lee, M., Kim, J.W., Hwang, I.W., Kim, Y.R., Oh, N.K. and Zin, W.C., *Advanced Materials*, 2001, 13: 1363
- 15 Kilbinger, A.F.M., Schenning, A.P.H.J., Goldoni, F., Feast, W. J. and Meijer, E. W., *J. Am Chem. Soc.*, 2001, 122: 1820
- 16 Schenning, A.P.H.J., Kilbinger, A.F.M., Biscarini, F., Cavallini, M., Cooper, H.J., Derrick, P.J., Feast, W.J., Lazzaroni, R., Leclerc, Ph., McDonnell, L.A., Jeijer, E.W. and Meskers, S.C.J., *J. Am Chem. Soc.*, 2002, 124: 1269

- 17 Yanagi, H. and Okamoto, S., *Appl. Phys. Lett.*, 1997, 71: 2563
- 18 Mikami, T. and Yanagi, H., *Appl. Phys. Lett.*, 1998, 73: 563
- 19 Scherf, U., *Topics in Current Chemistry*, 1999, 201: 163
- 20 Kim, D.Y., Cho, H.N. and Kim, C.Y., *Prog. Polym. Sci.*, 2000, 25: 1089
- 21 Yanagi, H., Ohara, T. and Morikawa T., *Adv. Mater.*, 2001, 13: 1452
- 22 Gunther, J. and Stupp, S.I., *Langmuir*, 2001, 17: 6530