NOTE

Solvent-tuned dual emission of a helical poly[3,5-bis (hydroxymethyl)phenylacetylene] connected with a π-conjugated chromophore

Zhichun Shi[1,2] · Giseop Kwak[3] · Young-Jae Jin[3] · Masahiro Teraguchi[2] · Toshiki Aoki[2] · Takashi Kaneko [2]

Abstract

For THF solutions of an optically active helical poly[3,5-bis(hydroxymethyl)phenylacetylene] derivative bearing a biphenyl group, photoexcitation of the terphenyl moiety at 300 nm led to photoluminescence at 390 nm. On the other hand, the photoluminescence resulting from excitation at 280 nm caused dual emission at 310 and 390 nm, whose intensities were tuned by the polar-solvent stimuli which induced the collapse of the intramolecular stack structure of the side groups, and the change in the emission wavelength accompanied disappearance of the optical activity.

Introduction

Recently, optically active synthetic helical polymers have attracted much attention in the field of intelligent polymer architectures [1–6]. In particular, optically active helical π-conjugated polymers will promise interesting technological applications in combination with optical, electronic and magnetic properties. Helix-sense-selective polymerization (HSSP) using chiral catalysts or chiral initiators is a promising method for preparing optically active functional helical polymers because the monomers do not need a chiral moiety, allowing flexibility in the molecular design [7–9]. We have already succeeded in the HSSP of achiral phenylacetylenes using the catalyst [Rh(nbd)Cl]$_2$ (nbd = 2,5-norbornadiene) in the presence of chiral 1-phenylethylamine (PEA), and 3,5-bis(hydroxymethyl)phenylacetylene derivatives (HPAs) gave the corresponding polymers (poly(HPA)s), whose rigid and one-handed helical conformation was kinetically stabilized in the solution

by intramolecular hydrogen bonds among the hydroxyl groups in the poly(HPA)s (Scheme 1) [10–17]. We have recently reported that the HSSP of HPAs connected with a rigid π-conjugated substituent gave the corresponding optically active helical poly(HPA)s whose side groups were also arranged helically with the preferential helical sense [16, 17]. Some π-conjugated oligomers have been envisaged as materials for multicolor photoluminescence (PL) switching on the basis of structural perturbation [18–21]. In this study, we found that a biphenyl-substituted poly(HPA) (poly(DBHPA)) showed dual emission, whose intensity was tuned by the polar-solvent stimuli.

Results and discussion

DBHPA was polymerized in the presence of the catalyst [Rh(nbd)Cl]$_2$ and chiral PEA by the same procedures as those used in our previous work [16, 17]. Yellow solid polymers were obtained from the polymerization mixtures by precipitation into methanol (Table 1). DBHPA gave the corresponding polymer with a high degree of polymerization, even though compared with 3,5-bis(hydroxymethyl)-4-dodecyloxyphenylacetylene (DHPA), DBHPA had a rigid
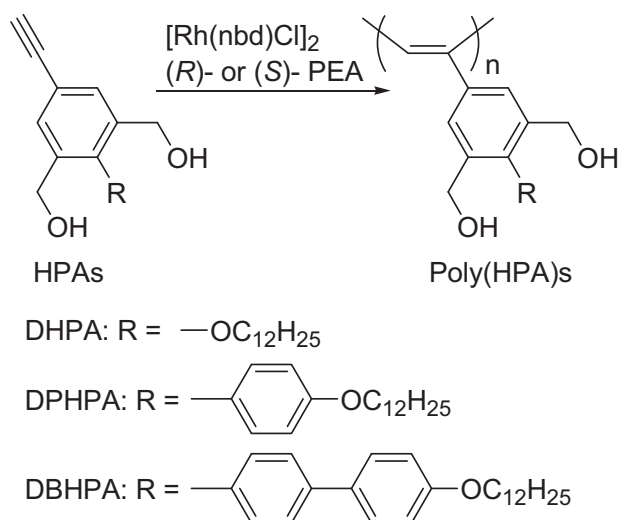
✉ Takashi Kaneko
    kanetaka@gs.niigata-u.ac.jp

1   College of Chemistry and Chemical Engineering, Qiqihar University, Wenhua Street 42, Qiqihar, Heilongjiang 161006, China

2   Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050, Niigata 950-2181, Japan

3   School of Applied Chemical Engineering, Major in Polymer Science and Engineering, Kyungpook National University, 1370 Sankyuk-dong, Buk-ku, Daegu 702-701, Korea

Scheme 1 HSSP of HPAs

Fig. 1 CD and UV-vis absorption spectra of poly(DBHPA), poly (DPHPA), and poly(DHPA) in THF at 20 °C

Table 1 Polymerization of HPAs using [Rh(nbd)Cl]$_2$ in the presence of chiral PEA[a]

No.	Monomers	PEA	Yield/ %	$M_n^{b}/10^5$	M_w/M_n^{b}	$[\theta]_{max}^{c}/10^4$ deg. cm^{2}dmol^{-1}
1	DBHPA	(R)	45	3.5	2.8	−2.5
2	DPHPA[d]	(R)	68	8.5	5.2	−3.3
3	DHPA[d]	(S)	62	5.7	2.4	−1.2

[a] [M]$_0$ = 0.2 M, [M]$_0$/[Cat]$_0$ = 100, [PEA]$_0$/[Cat]$_0$ = 400. In toluene, 25 °C, 3 h, precipitated with MeOH

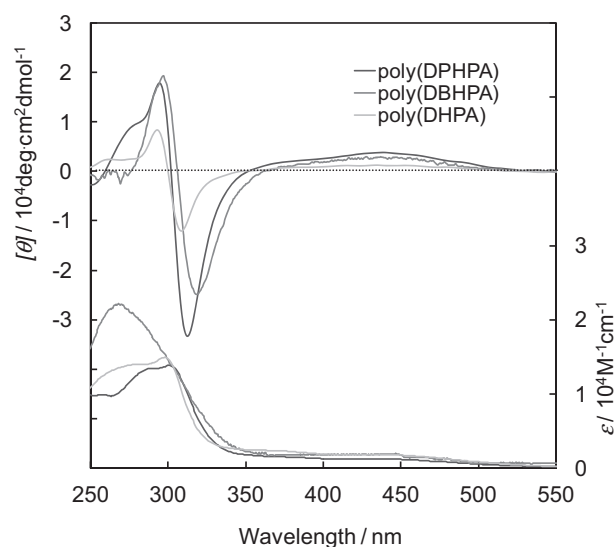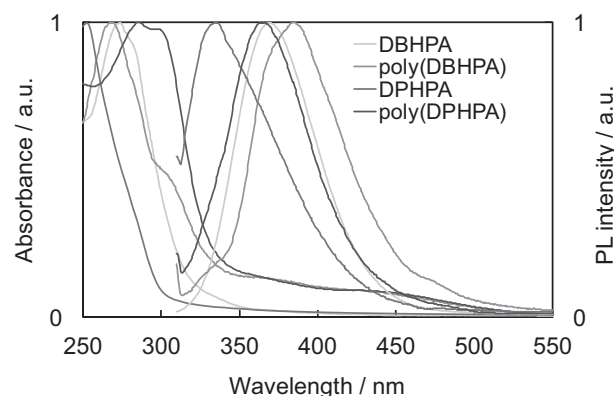[b] Determined from a GPC calibrated by PSt standards (eluent: THF)

[c] Molar ellipticity of the polymers in THF

[d] From Ref [16]

Fig. 2 UV-vis absorption and PL emission spectra of poly(DBHPA), poly(DPHPA), DBHPA, and DPHPA in THF at 20 °C (0.01 mM, λ_{ex} = 300 nm). Spectral intensities are normalized at their maxima

and bulky biphenyl group substituted between two hydroxymethyl groups. The solubility of poly(DBHPA) was maintained due to the peripheral alkyl chain. The polymer dissolved well in common organic solvents, such as chloroform, tetrahydrofuran (THF) and toluene.

The CD spectra of poly(HPA)s in THF exhibit split-type-induced CD signals at 300 nm and broad signals at 350–500 nm (Fig. 1). The isosbestic point of the CD signals for poly(HPA)s shifted bathochromically upon increasing the length of the π-conjugated side group. This fact indicates that the split-type-induced CD signals at 300 nm corresponded to the chromophore of the offset intramolecular stack structure including the π-conjugated side group. These CD patterns indicate that the static helical conformation is established by intramolecular hydrogen bonds because the polymers possess no chiral moieties except for helicity. The static stability of the helical conformation was diminished by the addition of polar solvents such as DMF and DMSO because the intramolecular hydrogen bonds were collapsed by the polar solvents, which was confirmed

by the disappearance of CD signal upon adding polar solvents (Supplementary Fig. S1) [17].

THF solutions of poly(DBHPA) and poly(DPHPA) exhibited a PL maximum at 390 and 370 nm, respectively, when excited at 300 nm (Fig. 2). The PL maximum wavelength of the former polymer was longer than that of the latter one by 20 nm. Moreover, the PL intensity of poly(DBHPA) was stronger than that of poly(DPHPA) at the same concentration. The corresponding monomers also exhibited the same tendency in their PL properties. Thus, the difference in PL between the two polymers is probably due to the difference in π-conjugation length between the chromophore side groups. This means that the PL emission upon excitation at 300 nm originates from the chromophore side groups.

Quite interestingly, the PL emission of the polymers was highly variable depending on the excitation wavelength, while the corresponding monomers did not show such a
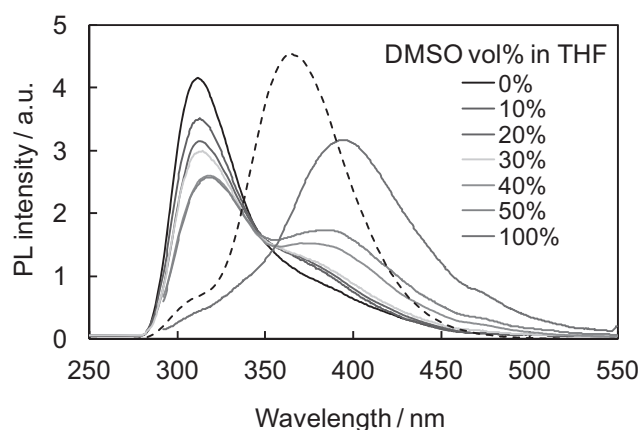
Fig. 3 PL emission spectra of poly(DBHPA) (solid line) and DBHPA (dotted line) in THF/DMSO mixed solvent systems at 20 °C (0.01 mM, λ_{ex} = 280 nm)

dependency. As shown in Fig. 3, poly(DBHPA) excited at 280 nm emitted PL at 310 nm, which is quite different from its behavior upon excitation at 300 nm (Supplementary Fig. S2). On the other hand, when excited at 280 nm, the monomer DBHPA emitted PL at 370 nm, which is almost the same as that exhibited by the polymer when excited at 300 nm. This indicates that our polymers have at least two excited states. Where do these multiple excited species come from? They are closely related to intramolecular hydrogen bonding. To elucidate this idea, we examined the PL emission change accompanying the addition of polar solvent. Adding DMSO to the THF solution of poly(DBHPA) weakened the PL emission at 310 nm but significantly enhanced the PL emission at 390 nm (Fig. 3), as well as increasing the absorption at approximately 450 nm attributed to the extended π-conjugation of the polymer backbone (Supplementary Fig. S3). Similarly, according to a previous study, poly(DHPA), which has a shorter π-conjugated chromophore in its side group, emitted quite strong PL at 310 nm in THF solution when excited at 280 nm, while the emission disappeared in a polar solvent such as piperidine [22]. It was also found that the PL of poly(DHPA) originates from the excimer based on the intramolecular stack structure of the side phenyl rings which are locked tightly through intramolecular hydrogen bonding. In this respect, it was assumed that the intramolecular hydrogen bonding was broken in the presence of a polar solvent and that the intramolecular stack structure was then readily collapsed. This led to a significant PL quenching of the excimer emission. This is true in the case of poly(DBHPA), as described above. Consequently, the shorter wavelength emission band at 310 nm originates from the intramolecular excimer of the side phenyl rings, while the longer wavelength band at 390 nm comes from the π-conjugated chromophore of the side group. Although the side group of poly(DBHPA) consisted of the terphenyl group, the biphenyl

moiety connected to the bis(hydroxymethyl)-substituted phenyl moiety would be highly twisted by the steric hindrance induced by the ortho-substituent. This highly twisted structure was supported by MO calculation and the blueshift of the absorption spectra compared to that of the simple alkoxyterphenylacetylene monomer (Supplementary Fig. S4 and Fig. S5) (see the Supplementary Information for more detailed experimental procedures). The torsional angle of the simple biphenyl structure is distributed around 45° [23, 24]. The torsional potential of DBHPA was calculated by AM1 to exhibit a minimum at 90°, which did not conflict with the theoretical calculations of other o-substituted biphenyls [25]. For DBHPA with a torsional angle of 90°, the HOMOs were isolated from each other at the twisted C–C bond. Therefore, similar to poly(DHPA), poly(DBHPA) with a torsional angle of 90° was excited at 280 nm in THF to give the excimer PL at 310 nm. When the intramolecular stack structure was collapsed by the addition of polar solvent, the moderately twisted excited terphenyl chromophore was formed by the rotation of the excited species with a highly twisted structure and/or by the energy transfer from the species excited at 280 nm instead of forming the excimer state, and the moderately twisted excited terphenyl chromophore emitted fluorescence at 390 nm (Fig. 4).

Conclusions

Optically active helical poly(DBHPA) has two chromophores: the phenyl moiety, which partially includes the π-conjugated backbone excited at 280 nm (Chromophore P), and the moderately twisted terphenyl moiety excited at 300 nm (Chromophore T). Photoexcitation of Chromophore T at 300 nm led to PL at 390 nm. On the other hand, photoexcitation of Chromophore P at 280 nm resulted in dual emission at 310 and 390 nm, whose intensities were tuned by the polar-solvent stimuli. That is, the photoexcitation at 280 nm of Chromophore P of optically active helical poly(DBHPA) in THF solution generated excimer PL at 310 nm based on the intramolecular stack structure which is locked tightly through intramolecular hydrogen bonding. Furthermore, the addition of a polar solvent induced the transformation and/or energy transfer from Chromophore P to Chromophore T, causing fluorescence emission at 390 nm accompanied with collapse of the intramolecular stack structure and optically active helical structure instead of the excimer PL. This solvent-tuned dual emission is a very unusual and unique phenomenon in optically active helical π-conjugated polymers. In other words, the excimer PL appeared at a shorter wavelength than another PL, while they were different species, and the change in the emission wavelength was accompanied by disappearance of the optical activity. This offers promise for more advanced functions and applications.

Fig. 4 Schematic diagram of the PL emission of poly(DBHPA)
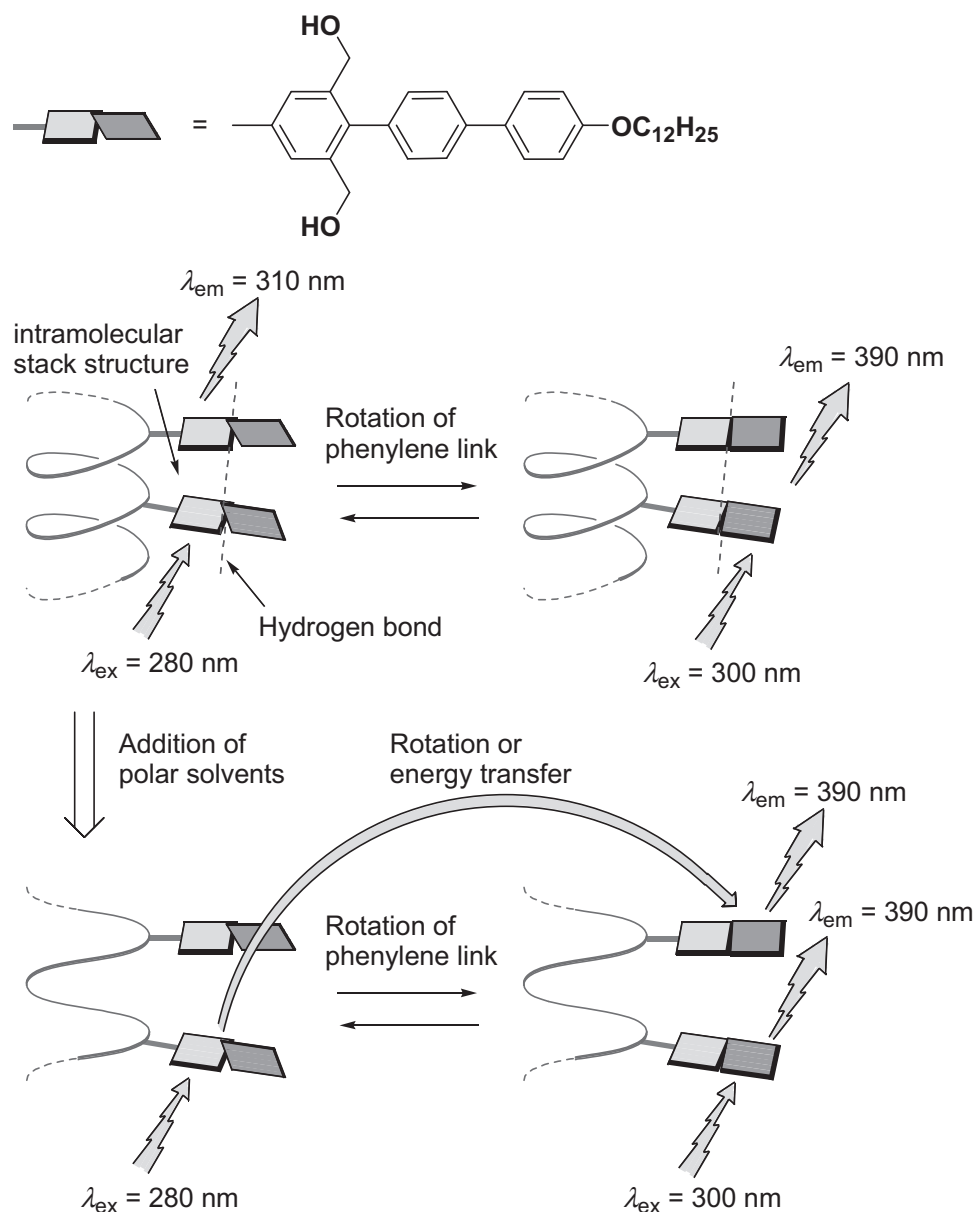
Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Aoki T, Kaneko T, Teraguchi M. Synthesis of functional π-conjugated polymers from aromatic acetylenes. Polymer. 2006;47:4867–92.
2. Akagi K. Helical polyacetylene: asymmetric polymerization in a chiral liquid-crystal field. Chem Rev. 2009;109:5354–401.
3. Liu J, Lam JWY, Tang BZ. Acetylenic polymers: syntheses, structures, and functions. Chem Rev. 2009;109:5799–867.
4. Ho R-M, Chiang Y-W, Lin S-C, Chen C-K. Helical architectures from self-assembly of chiral polymers and block copolymers. Prog Polym Sci. 2011;36:376–453.
5. Yashima E, Ousaka N, Taura D, Shimomura K, Ikai T, Maeda K. Supramolecular helical systems: helical assemblies of small molecules, foldamers, and polymers with chiral amplification and their functions. Chem Rev. 2016;116:13752–990.
6. Liu L, Zang Y, Jia H, Aoki T, Kaneko T, Hadano S, Teraguchi M, Miyata M, Zhang G, Namikoshi T. Helix-sense-selective polymerization of achiral phenylacetylenes and unique properties of the resulting cis-cisoidal polymers. Polym Rev. 2017;57:89–118.
7. Umeda Y, Kaneko T, Teraguchi M, Aoki T. Helix-sense-selective polymerization of a phenylacetylene bearing an achiral and bulky galvinoxyl moiety. Chem Lett. 2005;34:854–5.
8. Kaneko T, Umeda Y, Yamamoto T, Teraguchi M, Aoki T. Assignment of helical sense for poly(phenylacetylene) bearing

achiral galvinoxyl chromophore synthesized by helix-sense-selective polymerization. Macromolecules. 2005;38:9420–6.

9. Liu L, Zhang G, Aoki T, Wang Y, Kaneko T, Teraguchi M, Zhang C, Dong H. Synthesis of one-handed helical block copoly(substituted acetylene)s consisting of dynamic cis-transoidal and static cis- cisoidal block: chiral teleinduction in helix-sense-selective polymerization using a chiral living polymer as an initiator. ACS Macro Lett. 2016;5:1381–5.

10. Aoki T, Kaneko T, Maruyama N, Sumi A, Takahashi M, Sato T, Teraguchi M. Helix-Sense-selective polymerization of phenylacetylene having two hydroxy groups using a chiral catalytic system. J Am Chem Soc. 2003;125:6346–7.

11. Liu L, Namikoshi T, Zang Y, Aoki T, Hadano S, Abe Y, Wasuzu I, Tsutsuba T, Teraguchi M, Kaneko T. Top-down preparation of self-supporting supramolecular polymeric membranes using highly selective photocyclic aromatization of cis-cisoid helical poly(phenylacetylene)s in the membrane state. J Am Chem Soc. 2013;135:602–5.

12. Katagiri H, Kaneko T, Teraguchi M, Aoki T. Copper(I) iodide accelerates catalytic activation in rhodium complex-catalyzed helix-sense-selective polymerization of achiral phenylacetylene monomers. Chem Lett. 2008;37:390–1.

13. Liu L, Zang Y, Hadano S, Aoki T, Teraguchi M, Kaneko T, Namikoshi T. New achiral phenylacetylene monomers having an oligosiloxanyl group most suitable for helix-sense-selective polymerization and for obtaining good optical resolution membrane materials. Macromolecules. 2010;43:9268–76.

14. Teraguchi M, Tanioka D, Kaneko T, Aoki T. Helix-sense-selective polymerization of achiral phenylacetylenes with two n-alkylamide groups to generate the one-handed helical polymers stabilized by intramolecular hydrogen bonds. ACS Macro Lett. 2012;1:1258–61.

15. Zang Y, Nakao K, Yotsuyanagi H, Aoki T, Namikoshi T, Tsutsuba T, Teraguchi M, Kaneko T. Living-like helix-sense-selective polymerization of an achiral substituted acetylene having bulky substituents. Polymer. 2013;54:1729–33.

16. Shi Z, Murayama Y, Kaneko T, Teraguchi M, Aoki T. Helix-Sense-selective polymerization of 3,5-bis(hydroxymethyl)phenylacetylene connected with a rigid and π-conjugated substituent. Chem Lett. 2013;42:1087–9.

17. Shi Z, Teraguchi M, Aoki T, Kaneko T. Helical conformation stability of poly[3,5-bis(hydroxymethyl)phenylacetylene]s depending on the length of their rigid and linear π-conjugated side groups. Chem Lett. 2015;44:1413–5.

18. Becker K, Lupton JM. Dual species emission from single polyfluorene molecules: signatures of stress-induced planarization of single polymer chains. J Am Chem Soc. 2005;127:7306–7.

19. Shi J, Wu Y, Sun S, Tong B, Zhi J, Dong Y. Tunable fluorescence conjugated copolymers consisting of tetraphenylethylene and fluorene units: from aggregation-induced emission enhancement to dual-channel fluorescence response. J Polym Sci Part A Polym Chem. 2013;51:229–40.

20. Montalti M, Battistelli G, Cantelli A, Genovese D. Photo-tunable multicolour fluorescence imaging based on self-assembled fluorogenic nanoparticles. Chem Commun. 2014;50:5326–9.

21. Yeo H, Tanaka K, Chujo Y. Synthesis of dual-emissive polymers based on ineffective energy transfer through cardo fluorene-containing conjugated polymers. Polymer. 2015;60:228–33.

22. Jin Y-J, Kim H, Miyata M, Yin G, Kaneko T, Teraguchi M, Aoki T, Kwak G. Influence of a hydrodynamic environment on chain rigidity, liquid crystallinity, absorptivity, and photoluminescence of hydrogen-bonding-assisted helical poly(phenylacetylene). RSC Adv. 2016;6:36661–6.

23. Beenken WJD, Lischka H. Spectral broadening and diffusion by torsional motion in biphenyl. J Chem Phys. 2005;123:144311.

24. Campanelli AR, Domenicano A, Ramondo F. Transmission of electronic substituent effects through a benzene framework: a computational study of 4-substituted biphenyls based on structural variation. J Phys Chem A. 2012;116:8209–17.

25. Pan J-F, Chua S-J, Huang W. Conformational analysis on biphenyls with theoretical calculations: modeling torsions in poly(paraphenylene)s with side chains. Thin Solid Films. 2000;363:1–5.