Synthesis of ω-Pyrenyl-Functionalized Poly(1,3-Cyclohexadiene)

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ABSTRACT: ω-Pyrenyl-functionalized poly(1,3-cyclohexadiene) (PCHD) was successfully synthesized by the postpolymerization reaction of poly(1,3-cyclohexadienyl)-lithium (PCHDLi) with 1-chloromethylpyrene (ClMe-PY). This postpolymerization reaction consisted of two competitive reactions: the addition reaction of the pyrenyl group, and a hydrogen abstraction reaction (lithiation) as a side reaction. The degree of nucleophilicity of PCHDLi was a very important factor for suppression of the side reaction, and the PCHDLi/amine system, which has high nucleophilicity, produced high ω-pyrenyl-functionalization for PCHD. The UV/vis and fluorescence spectra for ω-pyrenyl-functionalized PCHD were bathochromically shifted, relative to that of pyrene. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2006–2010, 2009

Key words: anionic polymerization; fluorescence; functionalization of polymers; poly(1,3-cyclohexadiene); pyrene

INTRODUCTION

The synthesis of ω-functionalized polymers has been a very interesting research subject for polymer chemists, because it effectively imparts new properties to the original polymers. One of the attractive applications of ω-functionalized polymers is the fluorescent end-labeled polymer. In particular, it has been expected that ω-pyrenyl-functionalized polymers would have the ability to be more accurate fluorescent probes than pyrene, to reveal the structural, conformational, and dynamic properties of polymers, their blends and colloids.[1–10] A variety of ω-pyrenyl-functionalized polymers (e.g., polystyrene, polybutadiene, and poly(methacrylic) acid) has been prepared by living anionic polymerization[1–3,5] and living radical polymerization.[4,6–10]

Among the hydrocarbon polymers, poly(1,3-cyclohexadiene) (PCHD) has long been recognized as an attractive precursor for the synthesis of a new class of high-performance polymers.[11–13] Polymer chemists are well aware that (living) anionic polymerization is a suitable means of preparing ω-functionalized polymers by postpolymerization reactions with electrophilic reagents.[14–17] However, the (living) anionic polymerization of 1,3-cyclohexadiene (1,3-CHD), a monomer of PCHD, has been reported to be difficult under various polymerization conditions, and the polymers obtained under these conditions were of low-molecular weight or in low yield, and the molar ratio of 1,2-addition (1,2-CHD unit) and 1,4-addition (1,4-CHD unit) to the polymer chain could not be controlled.[18–24] Therefore, ω-pyrenyl-functionalized PCHD has not been obtained until now.

In previous articles, we have reported the first successful living anionic polymerization of 1,3-CHD, in addition to an effective method for controlling the 1,2-CHD/1,4-CHD unit molar ratio of the PCHD polymer chain.[25–27] Using this polymerization method, we have recently re-examined the reactivity of poly(1,3-cyclohexadienyl)lithium (PCHDLi) by the postpolymerization of PCHDLi with electrophilic reagents.[28] From the results obtained, ω-fluorenyl (and anthracenyl)-functionalized PCHD were synthesized.[29]

In this article, we report the first successful example of ω-pyrenyl-functionalized PCHD synthesis by the postpolymerization of PCHDLi, using 1-chloromethylpyrene (ClMe-PY) as an electrophilic reagent. The optical properties of obtained polymers are also discussed.

EXPERIMENTAL

Materials

Cyclohexane (99.5%), toluene (99.8%), 1,3-CHD (97%), and *N,N,N′,N′*-tetramethylethylenediamine

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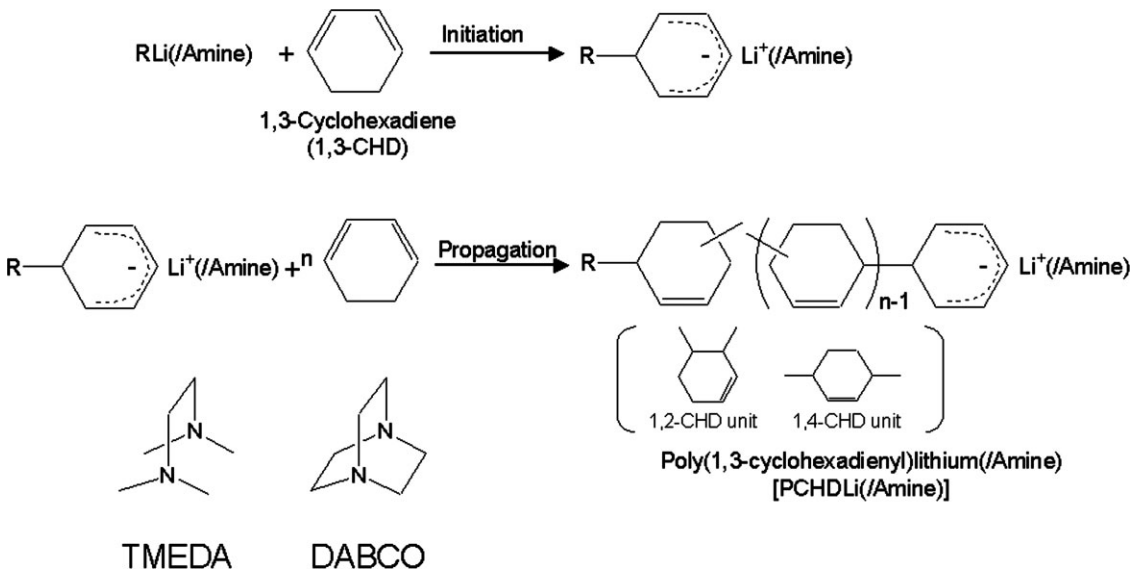


Scheme 1 Preparation of poly(1,3-cyclohexadienyl)lithium(/amine).

(TMEDA, >99.5%) were refluxed over calcium hydride and then distilled under dry argon. 1,4-Diazabicyclo[2,2,2]octane (DABCO, 98%) and ClMe-PY (≥97%, Tokyo Chemical) were dried under reduced pressure in dry argon. All other reagents were purchased from Aldrich and were used as received unless otherwise stated.

Polymerization (preparation of PCHDLi)

A well-dried 50-mL Schlenk tube was purged with dry argon, and then cyclohexane and alkyllithium (RLi) [*n*-butyllithium (*n*-BuLi, 1.60 mol/L in *n*-hexane) or *sec*-butyllithium (*s*-BuLi, 1.40 mol/L in cyclohexane)] were added at room temperature (~ 25°C) using syringes. Amine (TMEDA or DABCO) was then added to this solution under dry argon and the mixture was stirred for 10 min. 1,3-CHD was supplied to this solution using a syringe, and the reaction mixture was magnetically stirred under dry argon at room temperature, resulting in the preparation of PCHDLi. The consumption of 1,3-CHD was confirmed by gas chromatographic analysis.

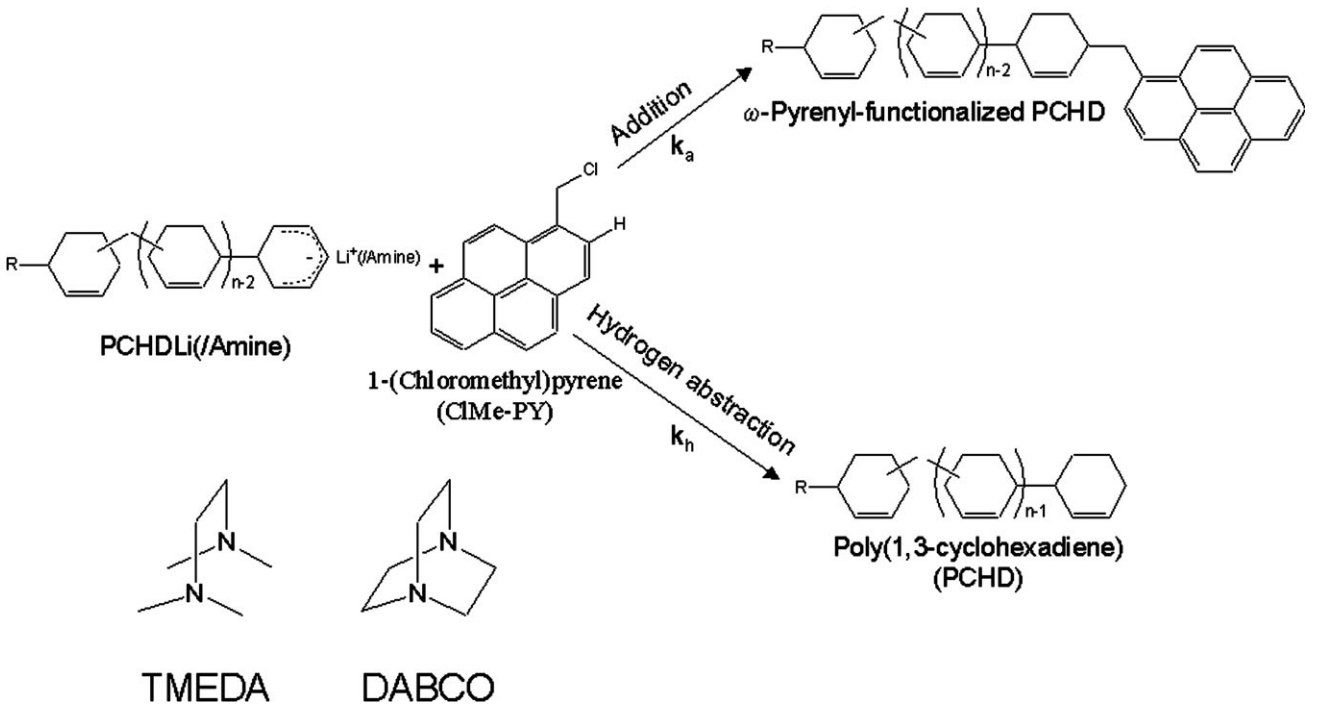
Postpolymerization reaction*

A solution of PCHDLi(/amine) in cyclohexane (10 wt %) was placed in a well-dried 50-mL Schlenk tube under dry argon at room temperature (ca. 25°C). A solution of ClMe-PY in toluene (10 wt %) was then added to this solution with a syringe, and the reaction mixture ($[PCHDLi]_0/[ClMe\text{-}PY]_0$ = 1.00/1.20) was magnetically stirred under dry argon at room temperature for 10 min. After the postpolymerization reaction, dry methanol was added to the reaction mixture in an equimolar amount to the total of lithium atoms present in the reaction mixture. The reaction mixture was then poured into a large volume of ethanol to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure in dry argon at room temperature for 24 h, resulting in a light yellow powdery polymer.

*The post-polymerization reactions of PCHDLi and ClMe-PY could be also performed "in-situ" after the preparing of PCHDLi.

Measurements

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI, M_w/M_n) were determined using gel permeation chromatography (GPC) equipment with a differential refractometer detector (Shimadzu RID-6A), a UV detector (Shimadzu SPD-6A), and a Shimadzu Shim-pack GPC-80*M* column at 40°C. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene standards. ^{1}H-NMR spectra of the polymers were measured in deuterated chloroform ($CDCl_3$) at 500 MHz, using a Jeol JNM LA-500 spectrometer. UV/vis spectroscopic measurements were performed in THF using a Shimadzu UV-3101 PC spectrophotometer with quartz cells. Fluorescence spectra of the polymers were measured in THF with quartz cells using a Jasco FP-777 spectrofluorometer. Gas chromatography (GC) was carried out using a Shimadzu



Scheme 2 Postpolymerization reaction of poly(1,3-cyclohexadienyl)lithium(/amine) with 1-chloromethylpyrene (ClMe-PY).

Type 14A gas chromatograph, with ethylbenzene used as an internal standard.

RESULTS AND DISCUSSION

Synthesis of ω-pyrenyl-functionalized PCHD

The synthesis of ω-pyrenyl-functionalized PCHD was attempted by the postpolymerization reactions of PCHDLi(/amine) with ClMe-PY as an electrophilic reagent. In a previous article,[28] the following order was determined for the nucleophilicity of PCHDLi(/amine): PCHDLi/DABCO > PCHDLi/TMEDA > PCHDLi, and we reported that the nucleophilicity of PCHDLi strongly affected the postpolymerization reactions of PCHDLi with an electrophilic reagent. Therefore, three types of PCHDLi(/amine), i.e., PCHDLi/DABCO, PCHDLi/TMEDA, and PCHDLi, were again evaluated in this study to determine the effect of nucleophilicity on the postpolymerization reaction with ClMe-PY.

As shown in Scheme 1, three types of PCHDLi (/amine) were synthesized by the anionic polymerization of 1,3-CHD, using *s*-BuLi or RLi/amine (i.e., *n*-BuLi/TMEDA and *s*-BuLi/DABCO) systems as an initiator. Subsequently, the postpolymerization reactions of PCHDLi(/amine) with ClMe-PY were conducted to synthesize ω-pyrenyl-functionalized PCHD (Scheme 2). The rate of the postpolymerization reaction of PCHDLi(/amine) with ClMe-PY was considerably fast, and was complete within 10 min. The color resulting from the anion in the reaction mixture disappeared, indicating the complete consumption of the PCHDLi(/amine) active end.

For the postpolymerization reaction of PCHDLi(/amine) with ClMe-PY, the conversion from PCHDLi(/amine) to ω-pyrenyl-functionalized PCHD can be estimated by ^{1}H-NMR measurement.[28]

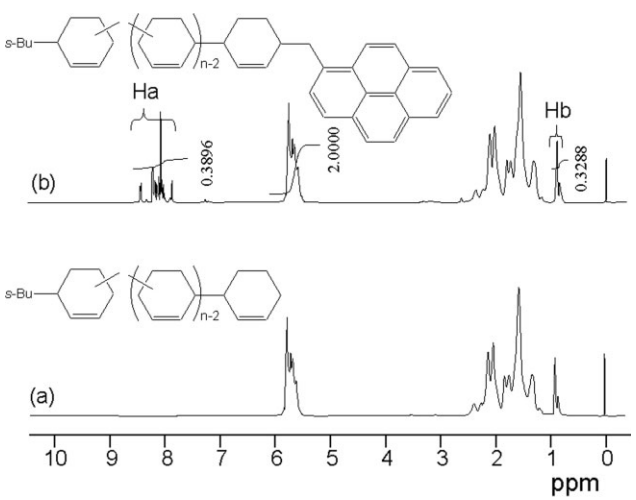


Figure 1 ^{1}H-NMR spectra of poly(1,3-cyclohexadiene) (a), and ω-pyrenyl-functionalized poly(1,3-cyclohexadiene) (b) in a 5.0 wt % solution of $CDCl_3$ at 50°C. Ha: Aromatic protons on the pyrenyl end-group. Hb: Methyl protons in the butyl residues from *s*-BuLi.

TABLE I
Synthesis of ω-Pyrenyl-Functionalized Poly(1,3-cyclohexadiene)

Polymer	Polymerization[a] Initiator system (molar ratio)	Postpolymerization[b] Alkylhalide	Conversion[c] (%)	M_n[d]	PDI[d]	1,2-CHD/1,4-CHD unit z(molar ratio)[e]
PY-PCHD-1	*s*-BuLi	ClMe-PY[f]	38	1960	1.29	2/98
PY-PCHD-2	*n*-BuLi/TMEDA(4/5)	ClMe-PY	77	2140	1.23	53/47
PY-PCHD-3	*s*-BuLi/DABCO (4/5)	ClMe-PY	79	2070	1.26	5/95

[a] Polymerization was carried out in cyclohexane (10 mL) for 2.0 h (PY-PCHD-3) and 1.0 h (PY-PCHD-2 and -3) 1,3-CHD/solvent = 10/90 (vol/vol). $[1,3\text{-CHD}]_0/[\text{Li}]_0 = 24.0/1.00$ (molar ratio).
[b] Postpolymerization was carried out for 10 mm $[\text{Li}]_0/[\text{ClMe-PY}]_0 = 1.00/1.20$ (molar ratio).
[c] From PCHPLi to ω-pyrenyl-functionalized PCHD.
[d] Obtained by measuring the reaction products after Postpolymerization.
[e] Estaimated by ^{1}H-NMR spectra.[28]
[f] 1-chloromethylpyrene.

Figure 1(a,b) show typical ^{1}H-NMR spectra of PCHD (1,2-CHD/1,4-CHD unit = 6/94, M_n = 1910)[†] and ω-pyrenyl-functionalized PCHD (PY-PCHD-3), respectively. The peaks at around 8.0 ppm (Ha) are assigned to the aromatic protons on the pyrenyl end-groups. The peak at ~ 0.9 ppm (Hb) is assigned to methyl protons in the butyl residues from *s*-BuLi. Under the polymerization conditions of this study, each molecule of *n*-(*s*-)BuLi produces one molecule of PCHDLi(/amine).[27] Therefore, the conversion from PCHDLi(/amine) to ω-pyrenyl-functionalized PCHD can be estimated by comparing the Ha and Hb peak areas [i.e., (Ha/number of aromatic protons)/(Hb/number of methyl protons)]. The results obtained are summarized in Table I.

With regard to PCHDLi (PY-PCHD-1 in Table I), the conversion from PCHDLi to ω-pyrenyl-functionalized PCHD did not exceed 40%. As shown in Scheme 2, the postpolymerization reaction of PCHDLi(/amine) with ClMe-PY seems to consist of two competitive reactions (i.e., the addition reaction of the pyrenyl group, and an hydrogen abstraction reaction (ortho-lithiation) as a side reaction).[28] That is, for the postpolymerization of PCHDLi with ClMe-PY, the hydrogen abstraction reaction seems to be predominant due to the insufficient nucleophilicity of PCHDLi. Therefore, the increase of nucleophilicity on the C—Li bonds seems to be a very important factor for the synthesis of ω-pyrenyl-functionalized PCHD with high conversion.

To suppress the hydrogen abstraction reaction, the postpolymerization reactions of the PCHDLi/TMEDA and PCHDLi/DABCO systems with ClMe-PY were attempted instead of the postpolymerization reaction of PCHDLi with ClMe-PY. As shown in Table I (PY-PCHD-2 and -3), the postpolymerization reactions of the PCHDLi/TMEDA and PCHDLi/DABCO systems with ClMe-PY both achieved successful conversions of over 75% (PY-PCHD-2 and -3). However, the conversions obtained through both systems were not so different, although the order of nucleophilicity was PCHDLi/DABCO > PCHDLi/TMEDA.[28] For the cases of the PCHDLi/TMEDA and PCHDLi/DABCO systems, the nucleophilicity of the C—Li bonds is thought to be sufficiently high for ClMe-PY. This is the reason why the PCHDLi/amine system was converted to ω-pyrenyl-functionalized PCHD with high conversion.

From the results obtained, it is concluded that the anionic polymerization of 1,3-CHD followed by the postpolymerization of PCHDLi/amine system with ClMe-PY is an effective method to synthesize ω-pyrenyl-functionalized PCHD.

Optical properties of ω-pyrenyl-functionalized PCHD

To reveal the optical properties of ω-pyrenyl-functionalized PCHD, the UV/vis and fluorescence spectra of the polymers were measured in THF.

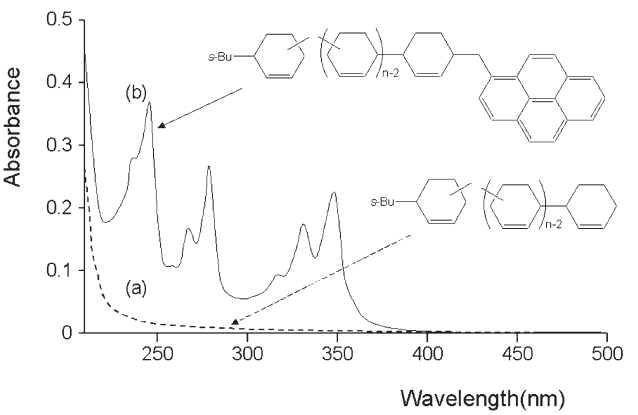


Figure 2 UV/vis spectra of poly(1,3-cyclohexadiene) (a), and ω-pyrenyl-functionalized poly(1,3-cyclohexadiene), (b) Polymer/THF = 0.1 mg/10 mL.

[†]PCHD with no functional group was prepared according to the synthetic route reported in our previous paper.[27] Initiator system: *s*-BuLi/DABCO=1.00/1.25 (molar ratio). 1,3-CHD/solvent=10/90 (vol/vol). $[1,3\text{-CHD}]_0/[\text{Li}]_0$=24.0/1.00 (molar ratio).

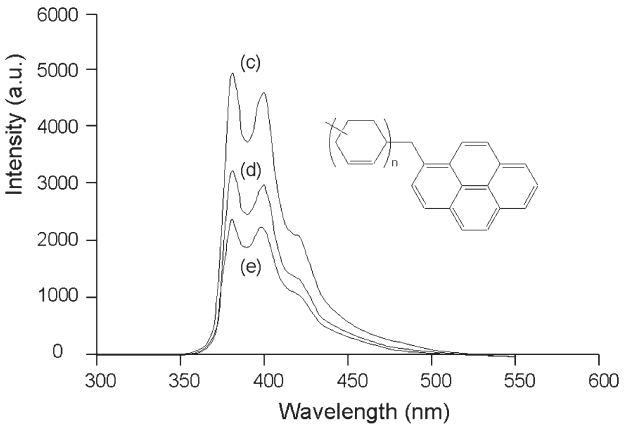


Figure 3 Fluorescence spectra of ω-pyrenyl-functionalized poly(1,3-cyclohexadiene) at excitation wavelengths of (c) 244 nm, (d) 278 nm, and (e) 347 nm. Polymer/THF = 0.1 mg/10 mL.

Figure 2 shows a comparison of the UV/vis spectra for (a) PCHD (1,2-CHD/1,4-CHD unit = 6/94, M_n = 1910)† and (b) ω-pyrenyl-functionalized PCHD (PY-PCHD-3 in Table I).

For PCHD with no pyrenyl end-group, there was almost no absorption in the wavelength region over 220 nm [Fig. 2(a)]. Thus, the absorption from PCHD can be ignored in ω-pyrenyl-functionalized PCHD. Multiple UV absorption peaks were observed in ω-pyrenyl-functionalized PCHD (PY-PCHD-3 in Table I) at 244, 267, 278, 330, and 347 nm, and are caused by the pyrenyl end-group in PY-PCHD-3 [Fig. 2(b)], which are bathochromically shifted relative to the corresponding bands of pyrene (240, 262, 274, 321, and 336 nm) measured under the same condition.

Figure 3 shows the fluorescence spectra of ω-pyrenyl-functionalized PCHD (PY-PCHD-3). A strong fluorescent emission due to the pyrenyl end-group was observed. In these spectra, three peaks at 382, 400, and 422 nm appeared, and the emission maximum was around 382 nm (excitation wavelength: (c) 244 nm, (d) 278 nm, (e) 347 nm). The intensity of fluorescent emission was decreased with increasing excitation wavelength, as shown in Figure 3(c–e). These spectra were shifted to the longer wavelength region, relative to the corresponding peaks of pyrene (379, 395, and 417 nm) measured under the same condition, as for the case of the UV/vis spectrum of ω-pyrenyl-functionalized PCHD [Fig. 2(b)].

CONCLUSIONS

ω-Pyrenyl-functionalized PCHD was successfully synthesized for the first time by the postpolymerization reaction of the PCHDLi/amine system with ClMe-PY. This postpolymerization reaction consisted of two competitive reactions (i.e., the addition reaction of the pyrenyl group, and a hydrogen abstraction reaction (ortho-lithiation) as a side reaction). The degree of nucleophilicity of PCHDLi to control lithiation of the pyrenyl group was a very important factor in the reaction. The PCHDLi/TMEDA and PCHDLi/DABCO systems, with high nucleophilicity of the C—Li bond, resulted in high conversion from PCHDLi/amine to ω-pyrenyl-functionalized PCHD. The UV/vis and fluorescence spectra for ω-pyrenyl-functionalized PCHD were bathochromically shifted relative to that of pyrene. The ω-pyrenyl-functionalized PCHD obtained will be used to reveal the structural, conformational, and dynamic properties of PCHD, its blends, and colloids.

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