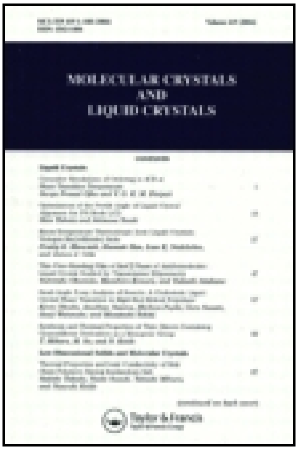

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Optical Properties of Poly(Propylene Carbonate) which Contains $C_{60}(OH)_n$ Structure in the End of Polymer Chain

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Poly(propylene carbonate) which contains $C_{60}(OH)_n$ *structure in the end of polymer chain was synthesized by copolymerization of propylene oxide and* CO_2 *with* $Et_2Zn\text{-}C_{60}(OH)_n$ *catalytic system. Emission and absorption spectra of the product polymer were determined and discussed. An emission band with a few peaks in UV-region were seen in the emission spectrum.*

Keywords: fullerol; fluorescence; aliphatic carbonate; carbon dioxide copolymerization

INTRODUCTION

In these days, fullerenes [1,2] and other carbon/non-carbon materials [1] are widely used in physical, chemical, and also in biological investigations. One of the fullerenes' inconvenient properties, which are obstructive for their applications, is their low solubility [3,4] to water (H_2O) and various organic solvents. Chemical modification is a key to overcome the inconvenience and to utilize them for various applications.

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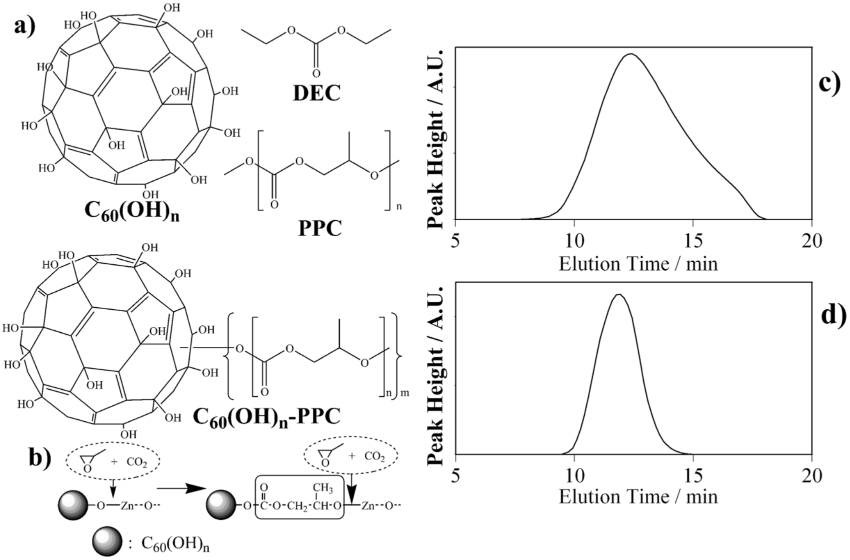


FIGURE 1 (a) Formulae of $C_{60}(OH)_n$, DEC, PPC, and $C_{60}(OH)_n$-PPC, (b) Schematic representation of copolymerization of $C_{60}(OH)_n$-PPC, and GPC chromatograms of the product polymer detected with (c) RI, and d) UV absorbance.

In this study, we reported the optical properties of polyhydroxylated fullerene(s) (called as "fullerenol" or "fullerol," described them as $C_{60}(OH)_n$) [5]), especially as a co-catalyst for copolymerization of propylene oxide (PO) and carbon dioxide (CO_2) to form poly(propylene carbonate) (PPC) using diethylzinc (Et_2Zn), which is known as a highly reactive material and used as a catalyst for copolymerization [6–9]. Only several chemical or biological applications had been investigated for $C_{60}(OH)_n$ [for example, 10–12]. This study is one of the trials for utilizing fullerene derivatives to a new application of fullerene derivatives. Formulae for $C_{60}(OH)_n$, PPC, and other related molecules were shown in Figure 1(a). The schematic representation of copolymerization of PO and CO_2 using $C_{60}(OH)_n$ and Et_2Zn was drawn in Figure 1(b).

EXPERIMENTAL

Chemicals, Catalyst Preparation, and Polymerization

PO, Et_2Zn and 1,4-dioxane were used after purification. C_{60} was used as supplied. The solvents and reagents used for the optical measurements, such as acetonitrile (ACN), H_2O, methanol (MeOH), and diethyl carbonate (DEC), were used as received. $C_{60}(OH)_n$, a polyhydroxylated fullerene was synthesized according to the previously reported method [5]. The number of OH group (n) as the major component of $C_{60}(OH)_n$ was approximately 13 [13]. For the preparation of catalyst, the mixture of Et_2Zn (0.73 mmol) with 1,4-dioxane (1.9 mL) was added to the stainless autoclave, in which $C_{60}(OH)_n$ (69 mg) had been placed, under nitrogen atmosphere. CO_2 gas (50 atm) was introduced directly from a cylinder at 50 atm. The autoclave was kept at 100°C for 24 hours. After the release of CO_2, the addition of PO (1.0 mL) and the pressurization with fresh CO_2 again was carried out into the autoclave for the copolymerization. The reactor stood for 44 hours in a H_2O bath at 40°C. The reaction product recovered with benzene was washed successively with dilute hydrochloric acid and H_2O. The product was reprecipitated with an excess of MeOH, and subjected to be freeze-dried. The product was analyzed with Gel permeation chromatography (GPC) with THF using a GL-R400M column (Hitachi chemical Co., Ltd.).

Absorption and Luminescence Measurement

All UV-Vis spectra and luminescence spectra were recorded with UV-2001 (Hitachi Co. Ltd.) and F-4500 (Hitachi Co. Ltd.), respectively.

RESULTS AND DISCUSSION

Copolymerization

The copolymer of CO_2 and PO (Mn: 4.9×10^4, Mw/Mn: 5.3, fCO_2: 49) was obtained at the yield of 0.19 g by using Et_2Zn-$C_{60}(OH)_n$ catalytic system. Obtained polymer was white-colored. The main component of MeOH insoluble part, the product polymer was assigned to PPC by IR, ^{1}H-NMR and ^{13}C-NMR (data not shown). GPC chromatograms detected by refractive index (RI) and UV absorption ($\lambda = 250$ nm) were shown in Figure 1(c) and Figure 1(d), respectively. From our previous results (data not shown), aliphatic carbonates were considered to be under the detection limit in UV-curve, as their low absorption coefficient. So the appearance of peaks in UV-curves had been interpreted as the existence of some aromatic molecules. In this case, the UV-curve (Fig. 1(d)) would correspond to the existence of $C_{60}(OH)_n$-connecting to polymer chains. At same time, the rest part of RI-detected chromatogram which is invisible in UV-detection would be considered to be polymer chains without the connection of $C_{60}(OH)_n$, though the ratio of two kinds of the polymer had never known yet. In the case of aromatic molecules aggregating with polymers, UV-detected peaks should appear in low molecular weight region as same as in high molecular weight region. From the lack of peaks in low molecular weight region in UV-curve (Fig. 1(d)), no evidence of aggregation was observed. From ^{1}H-NMR, fCO_2, the content of oxycarbonyl unit in PPC chain was ~50% (it corresponds to $PO:CO_2 \sim 1:1$) similar to other results. At least, we concluded that a part of PPC polymer chains were connected to $C_{60}(OH)_n$ moieties on the ground of these results. We described the product polymer as "$C_{60}(OH)_n$-PPC" as follows. In addition, we had no information about the number of polymer chain(s) connected to one $C_{60}(OH)_n$ molecule.

Measurement of Optical Properties

Absorption and emission spectra of $C_{60}(OH)_n$, $C_{60}(OH)_n$-PPC, PPC, and DEC were determined and shown in Figure 2(a) and (b). In Figure 2(a), small peaks were appeared in the region of 200~300 nm, for $C_{60}(OH)_n$, $C_{60}(OH)_n$-PPC, and PPC, respectively, but these peaks were too obscure to be assigned their origins [14,15]. Their emission spectra remarkably changed with alternating excitation wavelength. As an example, normalized (at $\lambda_{max.}$) emission spectra with excitation at 350 nm were represented in Figure 2(b). The sharp peak appeared for each spectrum around 400 nm was Raman scattering. Spectra for PPC and DEC showed only scattering and any significant peak could

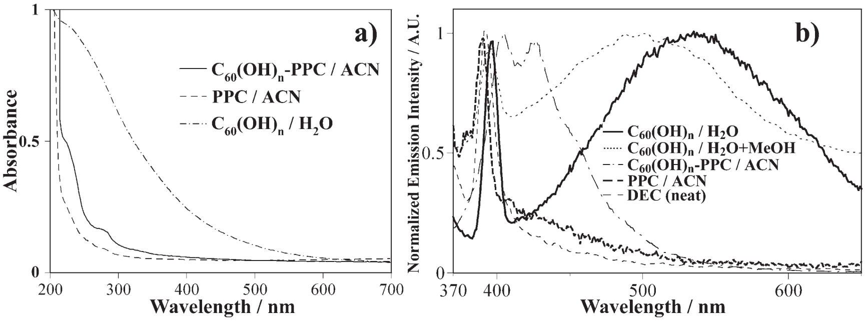
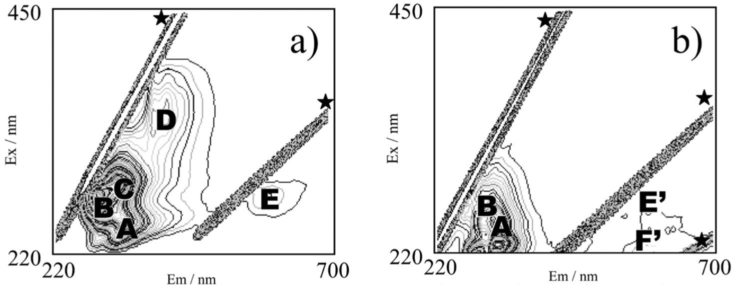
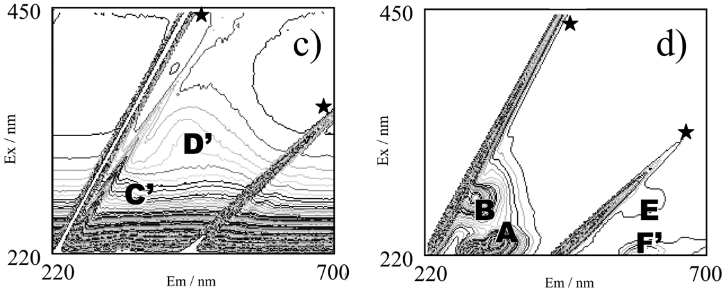


FIGURE 2 (a) Absorption spectra of $C_{60}(OH)_n/H_2O$ (—), and C_{60}(OH)n-PPC/ACN (—) and PPC/ACN (—), and (b) normalized emission spectra of $C_{60}(OH)_n/H_2O$ (—), $C_{60}(OH)_n/H_2O$ + MeOH (—), C60(OH)n-PPC/ACN (—), PPC/ACN (—) and DEC (—), excited at 350 nm.

not be found for them. $C_{60}(OH)_n$ showed a broad emission band in visible region. Each of the peak wavelength was different for each solvent. In $H_2O + MeOH$, the peak wavelength was shorter than that in H_2O. It would due to the solvent polarity. It is a feature of aromatic hydroxide, though the structure of aromatic conjugated part of $C_{60}(OH)_n$ is not clear yet and hydroxide moieties are distant from aromatic conjugates by Sp3-carbon. Even the hydroxides are not in conjugate, the characteristics of the emission have those of aromatic hydroxide, not the characteristics of aromatic-substituted aliphatic alcohol moieties. $C_{60}(OH)_n$-PPC showed a distinct emission band in the range of 400 ~ 450 nm. Though it was evidently different from that of $C_{60}(OH)_n$, this feature was similar to be a typical aromatic hydroxides which has a distant pKa^* from pKa to be deprotonated in the photo-excited state, such as naphthols, though $C_{60}(OH)_n$ is not a kind of aromatic hydroxide [for example, 16,17]. So it was not strange if the emission band of $C_{60}(OH)_n$-PPC had some characteristics of aromatic hydrocarbons, contrary to those of $C_{60}(OH)_n$ which has some aromatic hydroxide anion emission. With MeOH addition, the emission maximum of $C_{60}(OH)_n$ was ~35 nm blue-shifted. $C_{60}(OH)_n$ emission in each case was longer than the emission maximum of in $C_{60}(OH)_n$-PPC/ACN, and it would be due to the exclusion of the solvent molecules by PPC polymer chains, which has low polarity than ACN. As their emission properties were very complicated, we introduced the “contour mapping” images (depicted in Fig. 3). On the observed emission bands were alphabetically marked as A, B, C, D, and E for $C_{60}(OH)_n$-PPC in Figure 3(a). Similar bands for other molecules were also marked as A, B, C, D, E, E’, and F’ in Figure 3(b)–(d). E’ and F’ looked little different from E and F in Figure 3(a). Other bands were looked much similar to those in Figure 3(a). The peak that marked with D was not seen for PPC and DEC. So we considered D as to be an emission band of $C_{60}(OH)_n$ moiety. Band D of $C_{60}(OH)_n$-PPC was located in shorter wavelength than that of $C_{60}(OH)_n$ in H_2O (the emission band was very broad and located around 520 nm; data not shown). Though bands C and D was not seen in the contour map of $C_{60}(OH)_n$ in H_2O (data not shown), C and D appeared with the addition of small portion of MeOH (shown in Fig. 3(c)). Those appearances would indicate that the less polar environment was created in the neighbor of $C_{60}(OH)_n$ moieties. Of course it is just a speculation, bands C and D for $C_{60}(OH)_n$-PPC could be considered to be originated from $C_{60}(OH)_n$ connecting to PPC, regarding this result. With detailed experiment for the change in emission wavelength of $C_{60}(OH)_n$ moieties, it would be possible to use $C_{60}(OH)_n$ derivatives as a new kinds of chemical sensors or other optical devices in future.



$C_{60}(OH)_n$-PPC / ACN   Poly(propylene carbonate) / ACN



$C_{60}(OH)_n$ / H_2O + MeOH   Diethyl carbonate

FIGURE 3 Contour maps (2D images) of emission spectra of (a) $C_{60}(OH)_n$-PPC/ACN, (b) PPC/ACN, (c) C60(OH)n/H_2O + MeOH and (d) DEC. (Marked with ★ were not the emission band of samples. Their origins were the excitation light or solvent Raman scattering.)

CONCLUSION

These results suggest a new application of fullerene derivatives as a co-catalyst with organozinc compounds and a possibility to utilize $C_{60}(OH)_n$ derivatives as new optical devices. PPC connecting to $C_{60}(OH)_n$ and PPC without $C_{60}(OH)_n$ could be determined in GPC. Optical measurements were practiced and the difference in emission bands of $C_{60}(OH)_n$, $C_{60}(OH)_n$-PPC and related molecules were displayed.

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