Colored and Luminous Aliphatic Polyester via One-Pot Intra- and Intermolecular Knoevenagel Reactions

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ABSTRACT: A novel aliphatic polyester containing a malonate group in the main chain was prepared by one-pot reaction of malonyl dichloride with ethylene glycol in the presence of triethylamine. The NMR, IR, and UV−vis studies revealed that the polymer partially underwent intra- and intermolecular Knoevenagel type self-condensation in solution and solid states, respectively, leading to formation of a certain conjugated structure in the polymer chain. The polymer exhibited a very weak, but clear, absorption around 363 nm as well as an absorption at 322 nm due to carbonyl n−π* transition. Furthermore, the polymer exhibited blue/greenish-blue photoluminescence due to ESIPT when excited at wavelengths longer than 350 nm. This polymer is the first example of a colored and photoluminescent aliphatic polyester.

Introduction

Recently, in many fields, the use of degradable polymers has been demanded to minimize polymer waste management caused by nondegradable polymers and, ultimately, to protect our planet's environment.[1] Synthetic aliphatic polyesters are promising for such degradable polymer materials due to their biodegradability, biocompatibility, hydrolytic degradability, and suitable mechanical strength.[2] So far, however, most studies have focused only on their biomedical and agricultural applications. Since aliphatic polyesters intrinsically exhibit neither visible absorption nor luminescence because of the forbidden transition due to the carbonyl group, there have been no applications using these polymers as photonic/electronic device materials. Thus, modulation of their photophysical and electrical properties by means of a simple synthetic method may be an impressive challenge in terms of new development of degradable light-emitting diodes (LEDs) materials.

Some polymers which exhibit excited-state intramolecular proton transfer (ESIPT) have been developed for photo- (PL) and electroluminescent (EL) materials.[3] Malonate compounds also undergo ESIPT because they have both acidic methylene and dicarbonyl groups capable of acting as a proton donor and acceptor, respectively. However, little attention has been paid to the synthesis and photophysical property of aliphatic polyesters containing a malonate group because most aliphatic polyesters have been known as nonluminescent materials.

A condensation reaction can occur between ketone (or aldehyde) and any compound having an acidic methylene group activated by the two directly bonded electron-withdrawing groups such as cyano, nitro, and ester.[4] This reaction, the so-called Knoevenagel condensation, is brought in the presence of organic base to provide an unsaturated compound. Noticeably, malonate ester consists of both ketone and active methylene groups in itself. This means that its dimer and/or polymer could undergo Knoevenagel type self-condensation in the presence of organic base.

On the basis of this idea, we prepared a novel aliphatic polyester containing a malonate group by one-pot reaction of malonyl dichloride with ethylene glycol in the presence of triethylamine. We eventually found that a small fraction of malonate moieties in the polymer turn to a certain conjugated form through intra- and intermolecular Knoevenagel condensations in solution and solid states, respectively. Moreover, the polymer film turned to a partially insoluble gel with conjugated cross-linkages by soaking in the organic base. Unlike conventional aliphatic polyesters, the polymer exhibited such unusual photophysical properties as a visible absorption and blue/greenish-blue photoluminescence based on the ESIPT phenomenon.

Results and Discussion

Initially, we attempted to synthesize a polymer by a bulk condensation of malonyl dichloride and ethylene glycol with degassing the hydrochloride under highly reduced pressure less than 3 mmHg. However, this method was not useful to obtain a high molecular weight polymer due to formation of oligomer only ($M_w < 500$). On the other hand, the condensation reaction in the presence of 2 equiv of triethylamine at room temperature provided a fairly high molecular weight polymer, **1** ($M_w = 3200$, $M_w/M_n = 2.0$ by GPC; eluent THF; polystyrene standard) in 35% yield, as shown in Scheme 1. It means that trapping hydrochloride gas with an organic base is more effective to avoid depolymerization than degassing under reduced pressure.

Surprisingly, polymer **1** appeared to be a dye in dark orange unlike colorless conventional polyesters. The reason why it exhibits a visible absorption will be fully mentioned with the UV−vis spectra later. At first, the structure of the polymer was characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopic analyses, as shown in Figure 1. In the ^{1}H NMR spectrum, two singlet signals around 4.39 and 3.47 ppm are due to ethylene (*b*) and methylene (*a*) groups, respectively. In the ^{13}C NMR spectrum, three signals due to carbonyl (*a*′),

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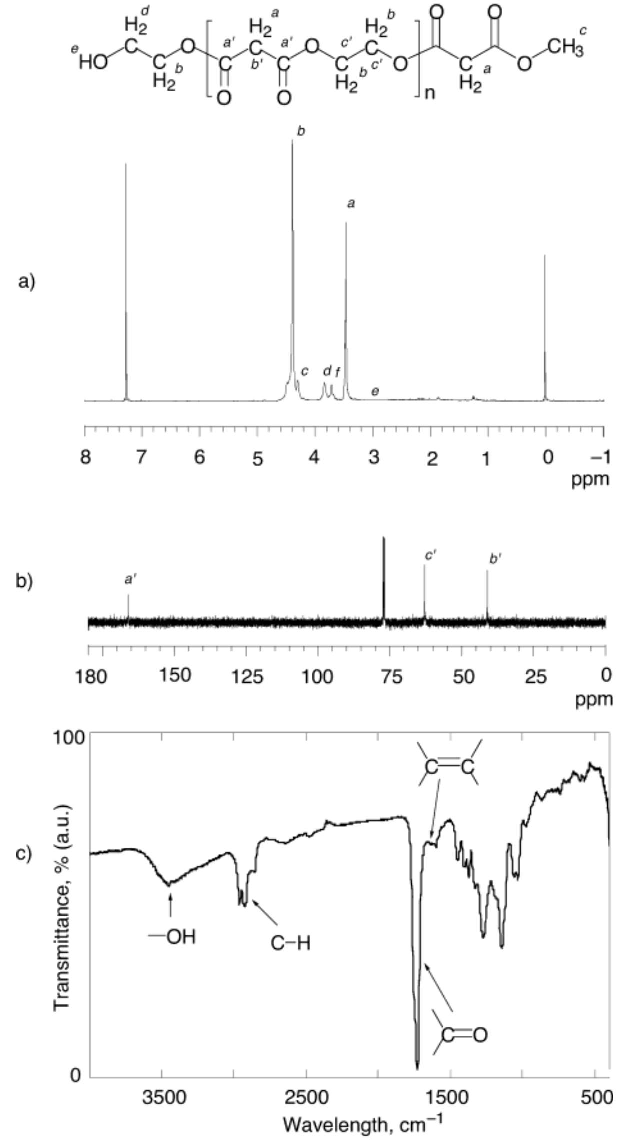
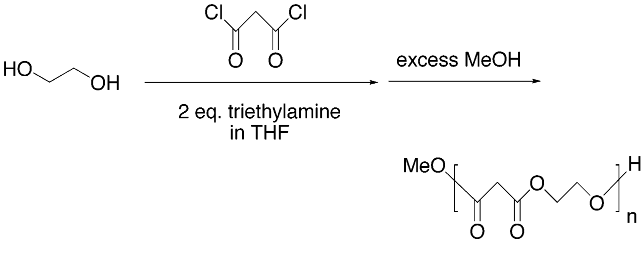


Figure 1. (a) ^{1}H NMR, (b) ^{13}C NMR, and (c) IR spectra of **1** (NMR determined in CDCl$_3$; IR in the film state).

Scheme 1. Synthesis of Polymer 1



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ethylene (c'), and methylene (b') groups are shown at 166.0, 62.8, and 41.0 ppm, respectively. Also, the ^{1}H NMR spectrum proved the existence of end groups: a small singlet signal around 4.30 ppm is characteristic of terminal methoxy protons (c), and a signal at 3.83 ppm is due to a methylene (d) group adjacent to a terminal hydroxyl (e) group. Although the terminal hydroxyl proton peak is very broad and hardly detected, a well-resolved peak could be detected at 3.1 ppm in the oligomer (see Supporting Information). The IR spectrum exhibits an absorption due to the terminal hydroxyl group at 3500 cm^{-1} as well as carbonyl (1750 cm^{-1}) and methylene (2900 cm^{-1}) absorption peaks. These spectra confirm the well-defined structure of the polymer.

In the ^{1}H NMR spectrum, however, a small peak at 3.71 ppm (f) still remains as unassignable, which is absent in the oligomer prepared without using triethylamine (see Supporting Information). Also, the IR spectrum shows an unexpected absorption at 1684 cm^{-1} probably due to the carbon−carbon double bond. This is presumably because, in the presence of the organic base, Knoevenagel condensation occurs between the carbonyl and acidic methylene groups in the polymer chain as a side reaction during the polymerization. Scheme 2a shows the proposed reaction mechanism which has been described in detail by Tietze et al. in recent years.[4c] If this idea were right, the 3.71 ppm peak should be assigned to the methylene proton (f) within such a conjugated ring form, as shown in Scheme 2a.

To gain concrete evidence for the existence of the conjugated form in the polymer chain, we measured UV−vis spectra of the polymer in THF. Figure 2a shows the spectra before and after addition of triethylamine into the THF solution of the polymer. Interestingly, the polymer exhibited a very weak, but clear, absorption around 363 nm as well as an absorption at 322 nm due to carbonyl n−π* transition. Furthermore, after the addition of a drop of triethylamine, the longer wavelength absorption increased and shifted to 398 nm, while the carbonyl absorption decreased. At the same time, peak f in the ^{1}H NMR spectrum slightly increased after the addition of triethylamine (see Supporting Information). Actually, the color of the solution remarkably changed from yellow to orange by the addition of triethylamine. The longer wavelength absorption and the increase of peak f strongly supported the idea that, in the presence of the organic base, the present polymer undergoes Knoevenagel type self-condensation, leading to formation of the conjugated structure in the polymer chain. This well explains the reason why the polymer looks like a dark orange dye. In addition, the polymer was readily decomposed in the presence of piperidine. Presumably, the polymer underwent amidation of the ester group because the base was too strong. Thus, such a tertiary amine as triethylamine is more suitable for an organic base in the polymerization system than primary and secondary amines. The model compound, diethyl malonate, showed no absorption around the longer wavelength of 363 nm. No changes were observed in the UV−vis spectra even after the addition of excess triethylamine. This means that the present polymer undergoes intramolecular Knoevenagel condensation in the solution state.

Figure 2b shows the UV−vis spectra before and after soaking the polymer film in triethylamine; the longer wavelength absorption around 364 nm increased and shifted to 399 nm after the soaking in the amine at room temperature for several hours, whereas the carbonyl absorption decreased. Simultaneously, the 1684 cm^{-1} peak in the IR spectrum increased a little after the amine treatment (see Supporting Information). Also, it should be noted that the film became partially insoluble in a wide range of organic solvents such as THF, chloroform, and acetone after the treatment with triethylamine. This implies that the present polymer undergoes intermolecular Knoevenagel condensation in the solid state as shown in Scheme 2b, leading to formation of the conjugated cross-linkages in the film.

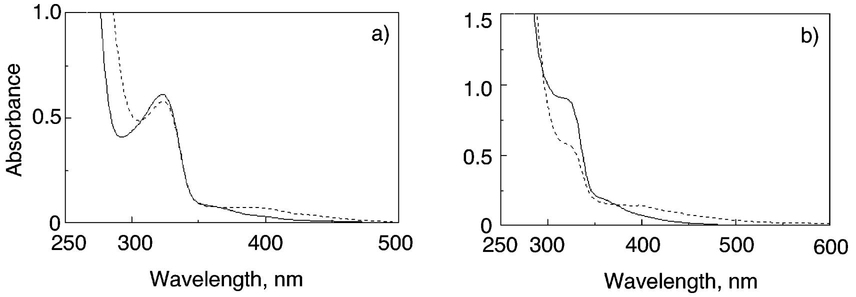
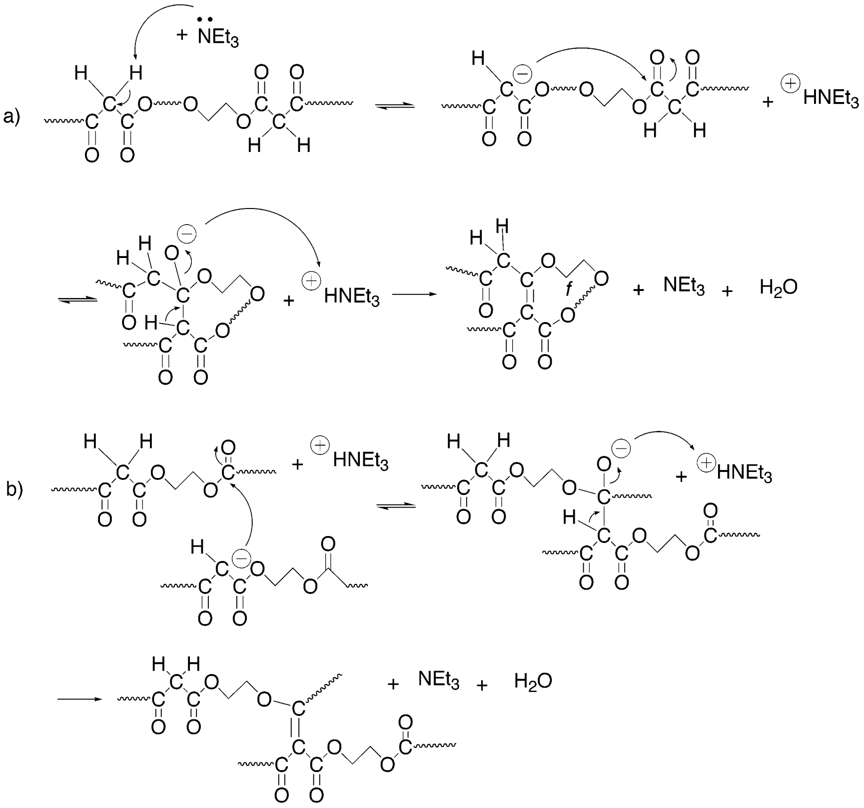


Figure 2. UV–vis spectra of **1** before (—) and after (- - -) triethylamine treatment (a) in solution ([conc] = 2.5 × 10^{-3} M in THF) and (b) in film state.

Scheme 2. Proposed Mechanism of the Knoevenagel Condensation in (a) Solution and (b) Film of 1



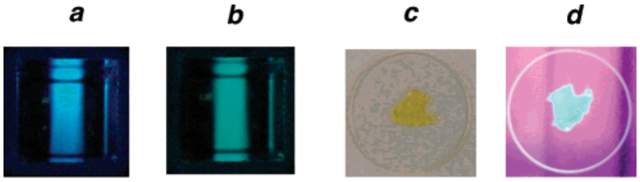


Figure 3. Pictures of **1** in THF (a: excited at 370 nm; b: excited at 420 nm) and solid film (c, d: before and after irradiation >370 nm, respectively).

In previous papers, it has been reported that network aliphatic polyester gels show enhanced resistance to heat and chemicals.[5] As for the present polymer, the incorporation of a cross-linked structure into the polymer chain is of particular interest from the viewpoint of controlling the photophysical property.

Most interestingly, polymer **1** emitted blue/greenish blue light when excited at wavelengths longer than 350 nm in both solution and solid film (see the pictures in Figure 3). Figure 4a shows the luminescence spectra of the polymer in THF. When excited at 370 nm, the polymer exhibited a luminescence band with a maximum peak at 398 nm and shoulders at 454 and 470 nm. On the other hand, when excited at 420 nm, the luminescence maxima appeared at 454 and 470 nm. These spectral features have been recognized as the blue and greenish-blue emissions, respectively, that are clearly seen by the naked eye. When excited at wavelengths shorter than 330 nm, however, this polymer showed little luminescence.

It is known that some compounds having a cyclic hydrogen bond, e.g., acetylacetone, malonaldehyde, and salicylideneaniline, undergo ESIPT.[6] Furthermore, if their photoinduced tautomers in the course of ESIPT are radiatively relaxed to a metastable ground state, photoluminescence with a large Stokes shift occurs.[7] 3-Hydroxychromones are the representative examples for the phototautomeric luminescent compounds and show two-color (blue and yellowish-green) luminescence due to a tautomer and a perturbed tautomer.[7b,c] Because the present polymer has both acidic methylene and carbonyl groups acting as a proton donor and acceptor, respectively, ESIPT should occur in the polymer chain. However, ESIPT within the malonate moiety of the polymer cannot cause photoluminescence, as shown in Scheme 3a, because the keto–enol tautomerization of

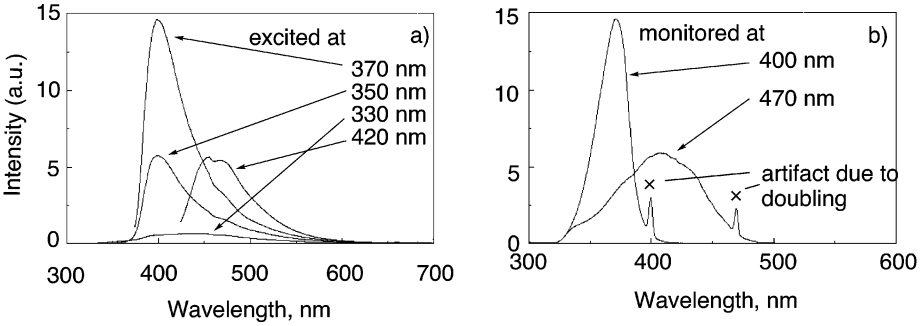


Figure 4. (a) Luminescence and (b) excitation spectra of **1** in solution ([conc] = 2.5 × 10^{-3} M in THF).

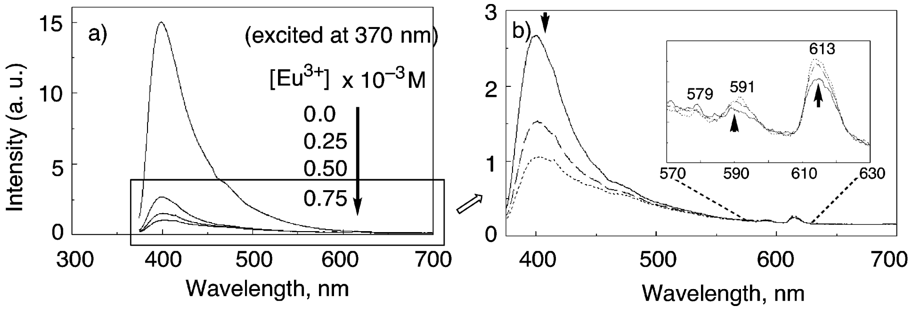
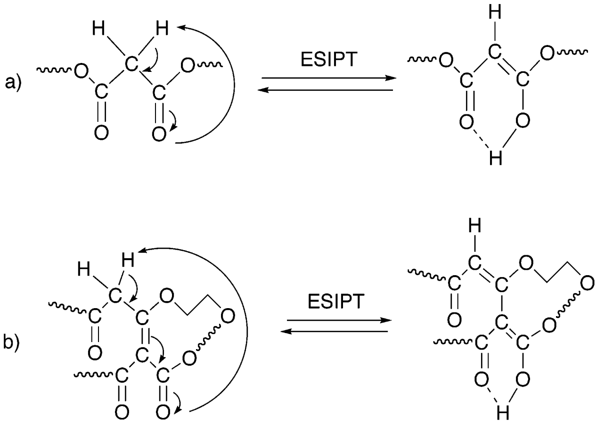


Figure 5. (a) Variation in luminescence spectra of **1** upon addition of europium triflate. (b) Enlarged spectra after the addition of the europium ion ([conc] = 2.5 × 10^{-3} M in acetone).

Scheme 3. Proposed (a) nonradiative and (b) Radiative Keto ↔ Enol Tautomerization in 1



diethyl malonate cannot be adjusted to the radiative process as similar to its analogues such as acetylacetone and malonaldehyde. Thus, it is reasonable to think that the luminescence of the present polymer is ascribed to the ESIPT between the acidic methylene group adjacent to the conjugated form and carbonyl group within the conjugated form, as shown in Scheme 3b.

As shown in Figure 4b, when the monitor wavelength is fixed at 400 and 470 nm, the polymer showed excitation bands with maxima at 370 and 410 nm, respectively. This means that the polymer can provide plural luminescent photoexcited species in the course of ESIPT.

Figure 5a shows the variation in luminescence spectra of the polymer **1** upon addition of europium cation. The luminescence intensity significantly decreased by the addition of the initial 10 mol % europium triflate. It is well-known that dicarbonyl compounds such as malonate ester readily form complexes with cationic lanthanides such as Eu^{3+}.[8] This leads to the idea that the luminescence quenching is probably due to formation of Eu^{3+} complex with dicarbonyl group in the polymer chain. In other words, ESIPT should not occur because the dicarbonyl group complexed with the metal ion cannot act as a proton acceptor. This strongly supports the idea that the luminescence of the present polymer may originate from ESIPT within the polymer chain.

Figure 5b shows the enlarged spectra after the addition of europium ion. Interestingly, the polymer newly exhibited three narrow emission bands at 579, 591, and 614 nm due to the f−f transition of europium ion although the intensity was quite weak. In general, lanthanide ions complexed with π-conjugated β-diketonate are excited via intramolecular energy transfer from the triplet excited states of the ligands.[9] Thus, the present polymer could be expected to serve as a polymer matrix available for intramolecular ligand-to-metal energy transfer.[10]

Conclusion

We successfully synthesized and characterized a novel aliphatic polyester containing a malonate group in the main chain. In the presence of triethylamine, this polymer partially underwent intra- and intermolecular Knoevenagel reactions in solution and solid states, respectively, leading to formation of a certain conjugated structure in the polymer chain. Especially, the polymer film readily turned to a gel by soaking in the organic base at room temperature. This polymer showed blue/greenish-blue photoluminescence due to ESIPT as well as a visible absorption. To our knowledge, this polymer is the first example of a colored and photoluminescent aliphatic polyester. Biodegradability and hydrolytic degradability could be expected for this polymer. Thus, the present polymer is potentially useful for degradable LED materials and biocompatible optical sensors. Such experiments concerning its degradability are currently underway in our laboratory.

Experimental Section

Synthesis of Polymer 1. A 200 mL round-bottomed flask was equipped with a three-way stopcock, a dropping funnel, and a magnetic stirring bar and flushed with dry nitrogen. Ethylene glycol (2.20 g, 35.5 mmol), triethylamine (6.79 g, 67.2 mmol), and dry THF (40 mL) were placed in the flask at 0 °C. At the same temperature, a solution of malonyl dichloride (5.0 g, 35.5 mmol) in THF (7 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 48 h. After removal of insoluble salt by filtration, THF was evaporated, and then the residue was poured into a large excess of methanol and diethyl ether to precipitate oily gummy polymer in 35% yield. IR (film): 3500, 2900, 1750, 1684 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 4.39 (s, 4H, OCH_2CH_2O), 3.47 ppm (s, 2H, CO-(CH_2)CO). ^{13}C NMR ($CDCl_3$, δ): 166.0 (*C*O), 62.8 (OCH_2CH_2O), 41.0 ppm (CO(CH_2)CO). Anal. Calcd for $(C_5H_6O_4)_n$: C, 46.16; H, 4.65. Found: C, 46.38; H, 4.95.

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were measured in $CDCl_3$ solution at 25 °C on a JEOL EX-400 spectrometer. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers were evaluated using gel permeation chromatography (Shimadzu A10 instruments, Shodex KF806M as a column, and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. IR, UV−vis, and fluorescence spectra were measured on HORIBA FT-730, JASCO UV-550, and JASCO FP-6500 spectrophotometers, respectively. Film sample for UV−vis measurement was prepared from the solvent-casting method ([conc] = 0.15 g/mL in acetone).

Supporting Information Available: ^{1}H NMR/IR spectra after the addition of triethylamine and ^{1}H NMR spectrum of the oligomer. This material is available free of charge via the Internet at http://pub.acs.org.

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