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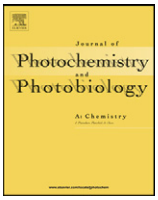

FRET function of polymeric ionic liquid film containing rhodamine moieties for exhibiting emissions by excitation at wide wavelength areas

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ABSTRACT

This paper reports synthesis of an imidazolium-type fluorescent polymeric ionic liquid film containing rhodamine moieties, which shows fluorescence resonance-energy-transfer (FRET) property, resulting in emissions by excitation at wide wavelength areas. First, radical copolymerization of two polymerizable ionic liquid, which had one and two polymerizable groups, respectively, was carried out with AIBN as an initiator to confirm whether a transparent polymeric ionic liquid film could be produced. Then, radical terpolymerization of the two ionic liquids with a rhodamine derivative having a polymerizable group was performed under the similar conditions as that for the above copolymerization to give the fluorescent polymeric ionic liquid film containing rhodamine moieties. The fluorescence spectra of the resulting film exhibited emissions due to the rhodamine group by excitation at wide wavelength areas. This result indicated occurrence of FRET from the polymeric ionic liquid units to the rhodamine moieties in the film because the excitation-wavelength-dependent emissions due to the polymeric ionic liquid were partially overlapped with an absorption peak due to the rhodamine group.

1. Introduction

In recent years, considerable effort has been devoted to developing new fluorescent dye-based materials such as probes as excellent sensors for biomolecules [1]. To develop the novel polymeric fluorescent materials, furthermore, fluorescent dye-containing polymers, exampling polymethacrylate, polyacrylamide, and conjugated polymer bearing covalently linked rhodamine groups, have been synthesized [2]. As appeared in these studies, rhodamines are one of the most common fluorescent dyes for the red region of the visible spectrum and have been widely used in various applications owing to their excellent spectroscopic properties such as large molar extinction coefficient and high fluorescence quantum yields [3].

Besides exhibiting emission excited at the characteristic wavelength of each fluorescent dye, the fluorescent materials in the practical applications are sometimes required to exhibit fluorescent emissions by excitation at wide wavelength areas. For the purpose to develop such dye materials, we have noted a fluorescence resonance-energy-transfer (FRET) technique, which has been used in designed fluorescent materials to obtain a large shift of the excitation wavelength from that the dyes natively show [4]. FRET is an interaction between the electronic excited states of two fluorescent substrates, in which excitation energy is transferred from a donor to an acceptor without emission of a photon [5].

On the other hand, ionic liquids, which are low-melting point salts and form liquids at temperatures below the boiling point of water, have been used as green solvents for environmental protection because of their negligible vapor pressure and excellent thermal stability [6]. Beyond such traditional properties, recently, ionic liquids have increasingly attracted much interesting attention as designer substrates with controllable physical and chemical properties or even specific functions [7], so-called 'Task-Specific Ionic Liquids [8].' As one of unique and specific properties of the ionic liquids, it has been reported that imidazolium-type ionic liquids exhibit excitation-wavelength-dependent fluorescent behavior due to the presence of energetically different associated species [9].

On the basis of the above viewpoints, we successfully provided a unique FRET system using a rhodamine derivative (rhodamine 6G) and an imidazolium-type ionic liquid (1-butyl-3-methylimidazolium chloride, BMIMCl) [10]. In the study, we found that FRET from BMIMCl as a donor to rhodamine 6G as an acceptor occurred in a solution of rhodamine 6G in BMIMCl by excitation at wide wavelength areas because the specific excitation-wavelength-dependent fluorescent emissions of BMIMCl excited at each wavelength were overlapped with an absorption of rhodamine 6G. Consequently, the emissions due to rhodamine 6G were appeared by excitation at the wide wavelength areas in the solution. Furthermore, we prepared the gel material

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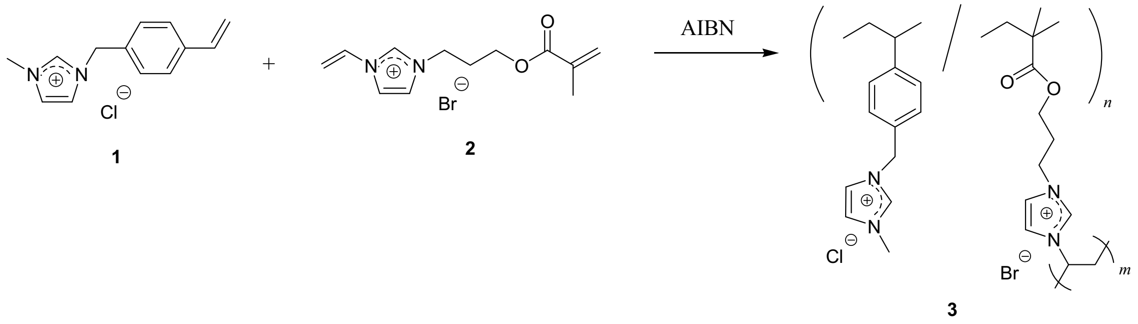


Scheme 1. Synthesis of **3** by radical copolymerization of **1** with **2** initiated with AIBN.

exhibiting the function of such FRET system by means of a gelling procedure of BMIMCl using guar gum of a natural polysaccharide; the gelling system had been reported in our previous studies [11].

In this study, we attempt to incorporate such unique FRET function into a film material, which exhibits emissions due to the fluorescent dye by excitation at wide wavelength areas. For this purpose, a film form of the imidazolium-type ionic liquid, i.e., the polymeric ionic liquid film [12], was first attempted to synthesize by radical polymerization of ionic liquids having polymerizable groups, so-called the polymerizable ionic liquids. Consequently, we found a good polymeric ionic liquid film was obtained by the radical copolymerization of two imidazolium-type polymerizable ionic liquids **1** having a vinylbenzyl polymerizable group and **2** having vinyl and methacrylate polymerizable groups initiated with AIBN. Then, the rhodamine moieties as the fluorescent dye group were incorporated into the film by terpolymerization of the polymerizable ionic liquids with a rhodamine derivative having a polymerizable group. Consequently, we found that FRET from the polymeric ionic liquid units to the rhodamine moieties in the film occurred by excitation at wide wavelength areas to exhibit the emissions due to the rhodamine group at each wavelength.

2. Experimental

2.1. Materials

Polymerizable ionic liquids **1** and **2** were prepared according to the literature procedures [13]. Methanol was purified by distillation. Other reagents were commercially available and used as received.

2.1.1. Preparation of polymeric ionic liquid film 3

The polymerizable ionic liquid **1** (0.400 g, 1.70 mmol) and **2** (0.0511 g, 0.177 mmol) and AIBN (3.00 mg, 0.0182 mmol) were dissolved in methanol (0.40 mL) with stirring. The resulting solution was sandwiched between two glass plates and heated at 65 °C for 30 min. Further heating it at 75 °C for 2 h gave a film, which was then removed from the glass plates. After the resulting film was soaked in ethanol, it was dried under reduced pressure to give a film of **3**.

2.1.2. Synthesis of rhodamine derivative **4** having a methacrylate group

Under argon, a mixture of rhodamine B (0.719 g, 1.50 mmol), 1,3-dicyclohexylcarbodiimide (DCC, 0.619 g, 3.00 mmol), 4-dimethylaminopyridine (DMAP, 0.0475 g, 2.96 mmol), and 2-hydroxyethyl methacrylate (HEMA, 0.360 mL, 2.96 mmol) in 1,2-dichloroethane (10 mL) was stirred at room temperature for 32 h. To the mixture, DCC (0.310 g, 1.50 mmol) was additionally supplied and the reaction was further performed for 40 h. After a small amount of hydroquinone as a radical inhibitor was added to the reaction mixture, it was evaporated and dried under reduced pressure. Then, water was added to the resulting residue and the insoluble material was removed by filtration. After the filtrate was concentrated and dried under reduced pressure, the residue was dissolved in a small amount of methanol. The solution was poured into diethyl ether to precipitate the product, which was isolated by decantation and dried under reduced pressure to give **4** (0.701 g, 1.19 mmol) in 79.0% yield based on rhodamine B. ^{1}H NMR ($CDCl_3$) δ 8.30 (d, J = 6.9 Hz), 7.85 (t, J = 6.9 Hz), 7.75 (t, J = 7.1 Hz), 7.35 (d, J = 7.8 Hz) (benzoate, 4H), 7.08 (d, J = 9.2 Hz, 1,8-XanH, 2H), 6.94 (dd, J = 9.6, 2.3 Hz, 2,7-XanH, 2H), 6.83 (d, J = 2.3 Hz, 4,5-XanH, 2H), 6.03 (s, $=CH_2$, (trans to $-CH_3$), 1H), 5.56 (s, $=CH_2$, (cis to $-CH_3$), 1H), 4.31 (dd, J = 5.7, 3.4 Hz, $-OCH_2-$, 2H), 4.19 (dd, J = 5.5, 3.7 Hz, $-OCH_2-$, 2H), 3.66 (q, J = 7.2 Hz, $-CH_2N-$, 8H), 1.90 (s, $=C-CH_3$, 3H), 1.34 (t, J = 7.1 Hz, $-CH_2-CH_3$, 12H).

2.1.3. Preparation of polymeric ionic liquid film **5** containing rhodamine moieties

The two polymerizable ionic liquid **1** (0.402 g, 1.71 mmol) and **2** (0.0501 g, 0.173 mmol), **4** (1.00 mg, 0.00169 mmol), and AIBN

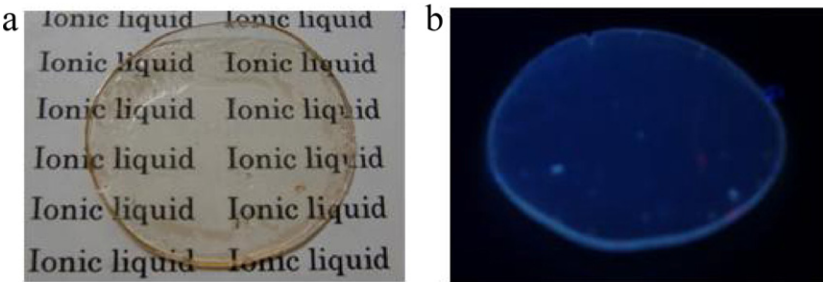
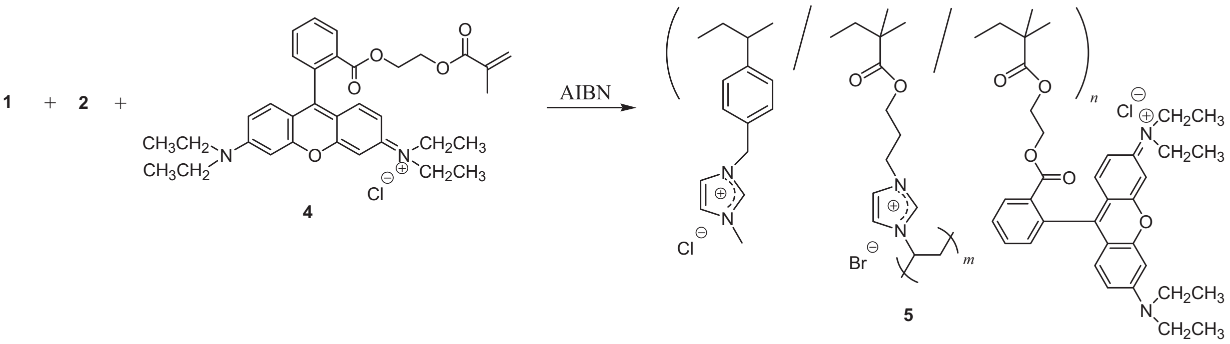


Fig. 1. Photographs of film of **3** (a) and it under UV light irradiation at 365 nm (b).



Scheme 2. Synthesis of **5** by radical terpolymerization of **1**, **2**, with **4** initiated with AIBN.

(3.00 mg, 0.0182 mmol) were dissolved in methanol (0.40 mL) with stirring. The resulting solution was sandwiched between two glass plates and heated at 65 °C for 30 min. Further heating it at 75 °C for 2 h gave a film, which was then removed from the glass plates. After the resulting film was soaked in ethanol, it was dried under reduced pressure to give a film of **5**.

2.2. Measurements

^{1}H NMR spectra were recorded on a JEOL ECX400 spectrometer. UV–vis and fluorescence spectra were recorded on a Jasco V-650Q1 and FP-6300Q3, respectively.

3. Results and discussion

*3.1. Preparation of film of polymeric ionic liquid **3***

To synthesize a cross-linked polymeric ionic liquid for the formation of a film, we employed the two imidazolium-type polymerizable ionic liquids **1** and **2**; the former has a vinylbenzyl polymerizable group and the latter contains vinyl and methacrylate polymerizable groups. Because **2** has the two polymerizable groups, radical copolymerization of **1** with **2** gives the cross-linked polymeric ionic liquid **3** (Scheme 1). For the preparation of the film form of **3**, a solution of **1** and **2** (10:1), and AIBN as a radical initiator (1 mol% for **1** + **2**) was sandwiched between two glass plates. Then, the system was heated at 65 °C for 30 min and subsequently at 75 °C for 2 h to occur the copolymerization with simultaneously evaporating methanol. The resulting material was removed from the glass plates, washed with ethanol to remove the unreacted **1** and **2**, and dried under reduced pressure to give a transparent film of **3** (Fig. 1a).

The UV–vis spectrum of the film (Fig. 2a) showed small absorptions at 280–550 nm, which were probably related to the fluorescent emissions of the imidazolium-type ionic liquids, besides large absorptions at the wavelengths below 280 nm. The fluorescence spectra of the film (Fig. 2b) exhibited excitation-wavelength-dependence fluorescent emission maxima at around 430–530 nm by excitation at 260–480 nm in addition to scattering peaks of excitation lights. As shown in a picture (Fig. 1b), the film exhibited blue fluorescent emission by UV light irradiation at 365 nm. The fluorescent behavior of the film was similar as that of the general imidazolium-type ionic liquid such as BMIMCl, indicating a possibility for occurrence of FRET from the polymeric ionic liquid units to the rhodamine group if it would be incorporated into the film.

*3.1.1. Preparation and fluorescent behavior of film of polymeric ionic liquid **5** containing rhodamine moieties*

The rhodamine derivative **4** having a polymerizable group was synthesized by the esterification of rhodamine B with HEMA using DCC/DMAP as a condensing agent in 1,2-dichloroethane. The structure of the product was confirmed by the ^{1}H NMR spectrum as described in the experimental section. The radical terpolymerization of **1**, **2**, with **4** was performed by the similar procedure as that for **3** (Scheme 2). The molar ratio of **4** to **1** + **2** was optimized to

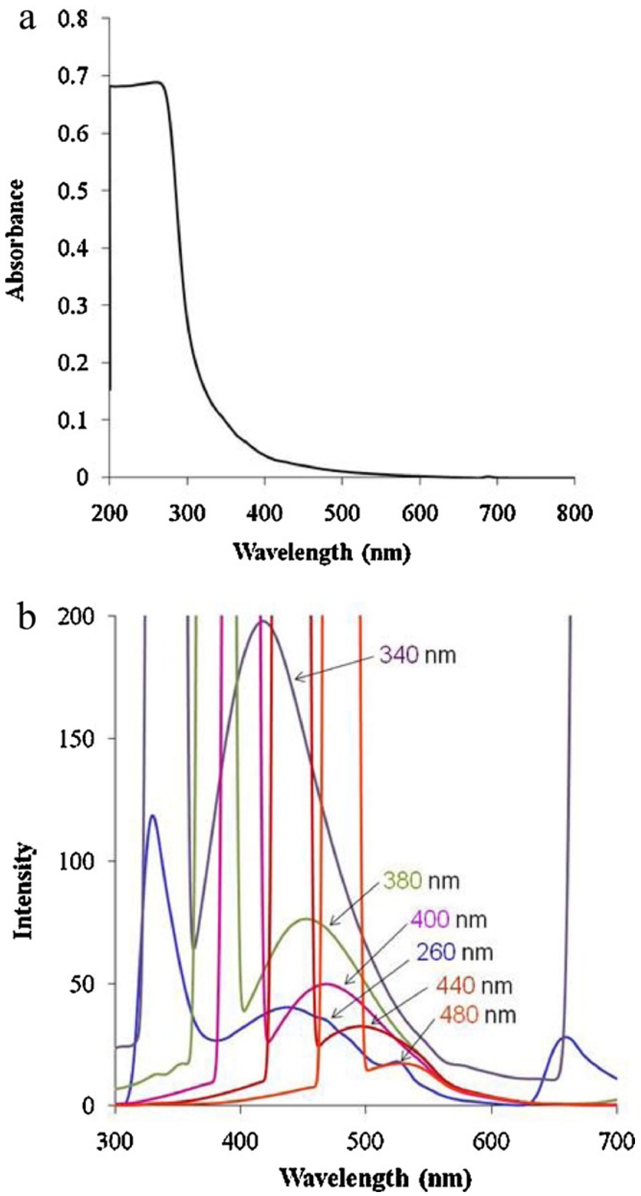


Fig. 2. UV–vis spectrum (a) and fluorescence spectra excited at 340–480 nm (b) of film of **3**.

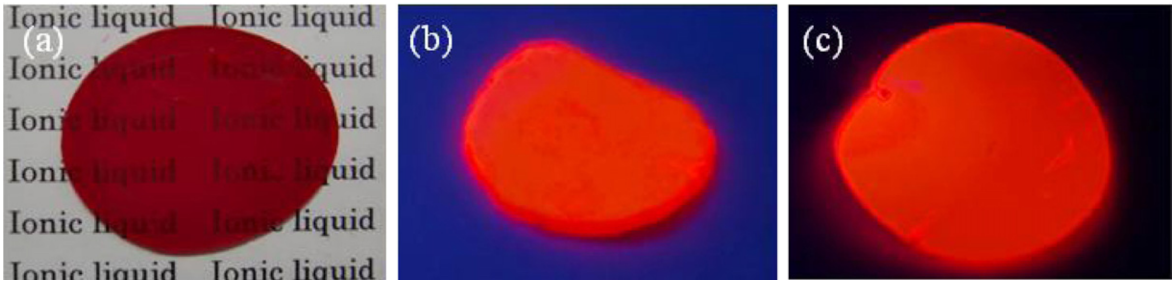


Fig. 3. Photographs of film of **5** (a) and it under UV–vis light irradiations at 254 and 365 nm ((b)–(c)).

be 1 mol% for the following photochemical examinations on the basis of the results for the terpolymerization in various feed ratios of the monomers. After the resulting film was soaked and washed with ethanol for the purification, the ethanol fractions were characterized by the ^{1}H NMR analysis. Consequently, the rhodamine monomer **4** was hardly present in the solution, indicating that the monomer **4** used was quantitatively copolymerized and incorporated in the polymeric ionic liquid **5**. The resulting film was also transparency as shown in Fig. 3a, but showed red color attributed to the rhodamine moieties.

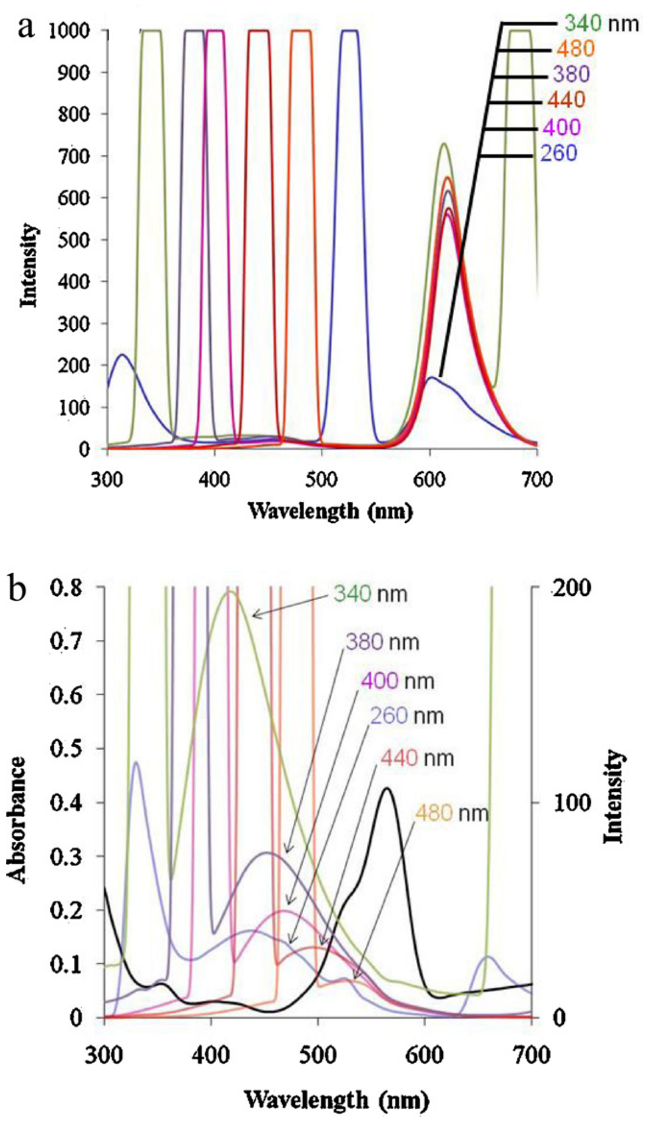


Fig. 4. Fluorescence spectra of film of **5** excited at 260–340 nm (a) and superimposed UV-spectrum of film of **5** on fluorescence spectra of film of **3** excited at 340–480 nm (b).

When the fluorescence spectra of the film were measured by excitation at 260–480 nm, emissions at ca. 620 nm due to the rhodamine group in addition to scattering peaks of excitation lights were observed in all the spectra (Fig. 4a). On the other hand, fluorescent emissions at around 430–550 nm due to the units **1** and **2**, which had already been shown in Fig. 2b, did not appear. These results suggested occurrence of FRET from the units **1** and **2** to the rhodamine group in the film. In deed, all the fluorescent emissions (colored lines) of the film of **3** excited at various wavelengths were partially overlapped with an absorption peak (black line) of the film of **5** at wavelength areas of around 450–600 nm as shown in Fig. 4b. Furthermore, the connection of the rhodamine group with the units **1** and **2** by covalent linkages in a polymeric chain results in their short distance to probably contribute to the occurrence of the efficient FRET in the film. Actually, the film of **5** showed the red fluorescent emissions by the UV–vis light irradiations at 254 and 365 nm (Fig. 3b–c).

4. Conclusion

In this paper, we reported the synthesis of the film of the polymeric ionic liquid film **5** containing the rhodamine moieties and its FRET function for exhibiting the rhodamine emissions by excitation at wide wavelength areas. The radical copolymerization of the two polymerizable ionic liquids **1** and **2** gave the transparent film of **3**. The resulting film exhibited the specific excitation-wavelength-dependent fluorescent behavior as the imidazolium-type ionic liquids had shown. Then, the radical terpolymerization of **1**, **2**, with the rhodamine derivative **4** having a polymerizable group was performed to give the film of **5** containing the rhodamine moieties. The fluorescence spectra of the film exhibited the emissions due to the rhodamine group at ca. 620 nm by excitation at 260–480 nm, whereas the fluorescent emissions due to the units **1** and **2** did not appear. These data indicated occurrence of FRET from the units **1** and **2** to the rhodamine group in the film because all the fluorescent emissions of the film of **3** excited at various wavelengths were partially overlapped with an absorption peak of the film of **5** at wavelength areas of around 450–600 nm.

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