

Polymerizable ionic liquids: Development to photo functional poly(ionic liquid) materials

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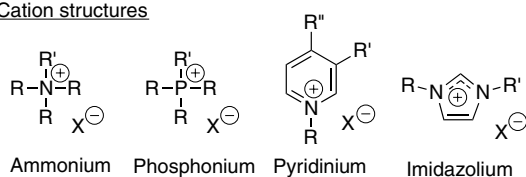
1. Introduction

Ionic liquids (ILs) are regarded as low-melting analogous of classical molten salts, which generally form liquids at temperatures below the boiling point of water.¹⁾ The property is owing to thermodynamically favorable because of the large size and conformational flexibility of the ions. Over the past decade or more, ILs have attracted much attention due to their specific characteristics such as a negligible vapor pressure and excellent thermal stability. Therefore, ILs have been employed as substitutes of volatile organic solvents in a variety of organic reactions, chemical processing, and extracting. The other important advantage of ILs is the diverse structure and chemical composition, which can be constructed by pairing any of a variety of organic cations with a wide range of either organic or inorganic anions (Figure 1). Common IL cations are ammonium, phosphonium, pyridinium, imidazolium, and so on. Accordingly, ILs have exhibited controllable physical and chemical properties and specific functions because of a variety of such ion pairs, and thus, been found for a wide range of applications in practical fields such as catalysis and electrochemistry.²⁾ Beyond the traditional applications of ILs, their interests are also being extended to the researches related to biomolecules such as naturally occurring polysaccharides because of specific affinities of ILs for them.³⁾ Recently, furthermore, specific photo functions of ILs have also been reported. In this article, therefore, the author would like to review his advanced research development on photo functional poly(ionic liquid)s by radical polymerization of polymerizable ILs.

2. Polymerizable ionic liquids and poly(ionic liquid)s

Poly(ionic liquid)s (PILs), also called polymerized ionic liquids or polymeric ionic liquids, refer to polymeric compounds that feature an IL species in each monomer repeating unit, connecting through a polymeric backbone, which are obtained by polymerization of ILs having polymerizable groups (polymerizable ILs).⁴⁾ The major advantages for such polymeric forms of ILs are enhanced stability, improved processability, flexibility, and durability in applications as practical materials. Polymerizable ILs as a source of PILs can be available by incorporating polymerizable groups either at anionic or at cationic site in the IL structure and which gave the corresponding PILs by radical polymerization (Scheme 1). In the former case, polymerizable anions are ionically exchanged with some anions of general ILs to produce the polymerizable ILs. In the latter case, vinyl, (meth)acryloyl, and vinylbenzyl groups have typically been employed as the polymerizable group covalently attached to cationic sites. 1-Vinylimidazole is a commercially available reagent, and thus 1-vinylimidazolium-type polymerizable ILs are facilely prepared by its quarternization with a variety of alkyl halides. The reaction of a commercial available vinylbenzyl chloride (Scheme 2(a)) or bromoalkyl (meth)acrylates, which are prepared from bromoalkanols with (meth)acryloyl chloride (Scheme 2(b)), with 1-alkylimidazoles yields the corresponding imidazolium-type polymerizable ILs.⁵⁾ Furthermore, when the reaction is carried out using 1-vinylimidazole, the polymerizable ILs having two polymerizable groups are obtained. Because this

Cation structures



Anion structures

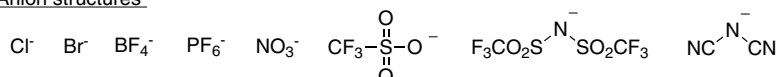
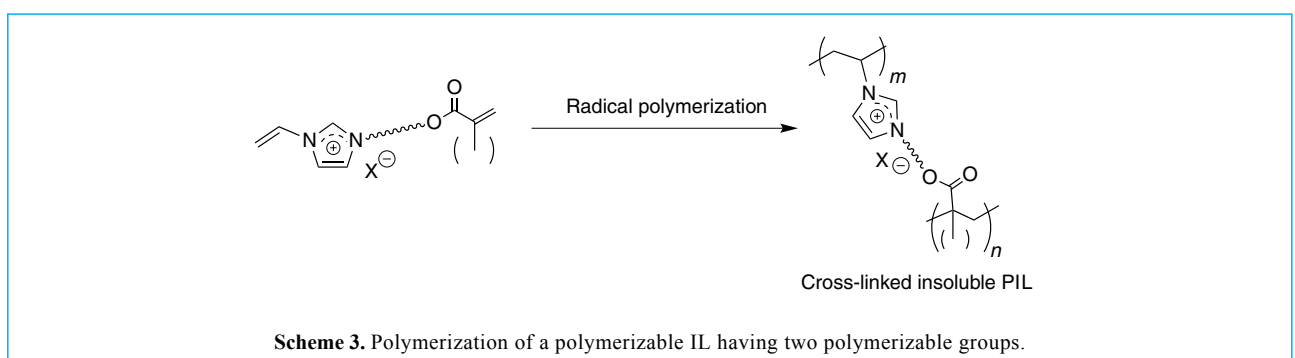
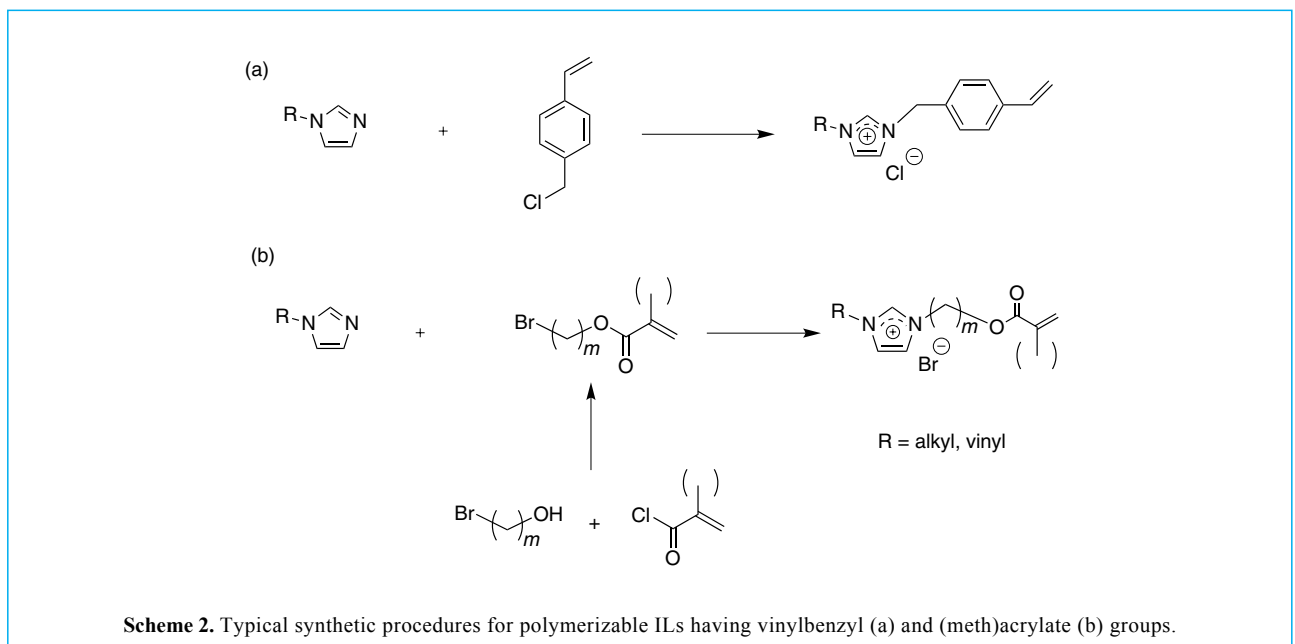
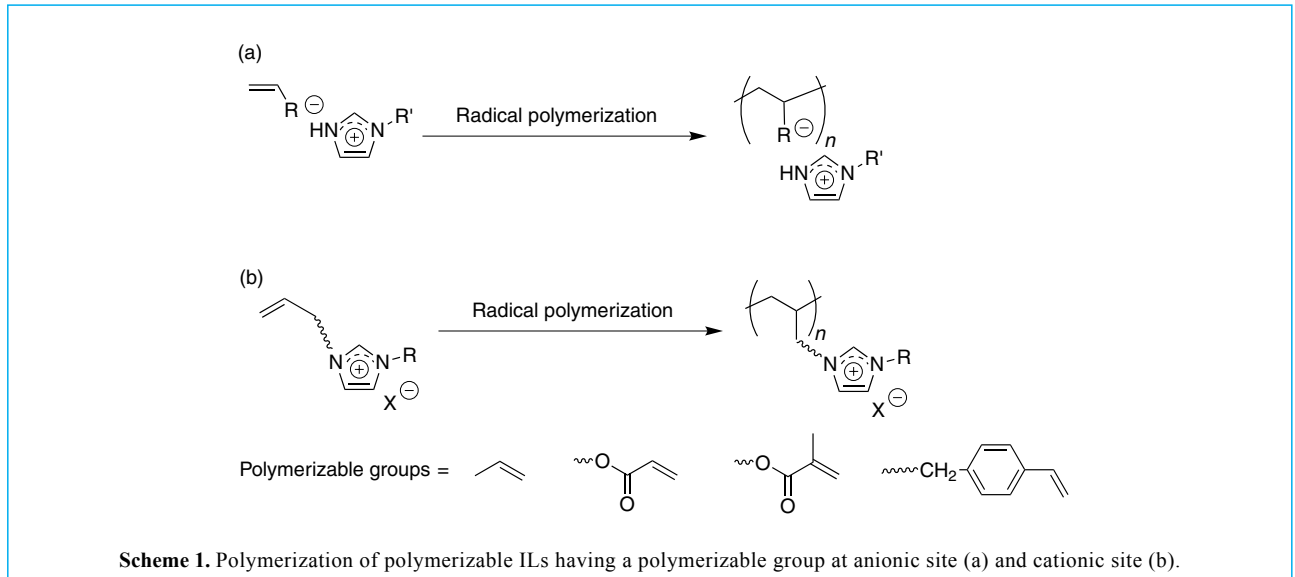


Figure 1. Typical cation and anion structures of ionic liquids.

type of ILs can be converted to insoluble and stable PILs with cross-linked structure by radical polymerization (Scheme 3), they have a highly potential as the source of the components in

the practical materials. Furthermore, anionic exchange reaction of the polymerizable ILs with the corresponding salts can introduce the prospective anions.



3. Development of photo functional poly(ionic liquid) materials

One of the major driving forces for the preparation of PILs is to demonstrate their potential as electrolytes in batteries and fuel cells.⁶⁾ For example, Ohno et al. reported that radical polymerization of imidazolium-type polymerizable ILs gave highly ion conductive flexible films.⁷⁾ Recently, the author has reported the preparation of cellulose-PIL composite materials by radical polymerization of appropriate polymerizable ILs.⁸⁾ Because the author found in this approach that some polymerizable ILs exhibited ability to partially disrupt crystalline structure of cellulose by swelling, cellulose was first immersed in the ILs for swelling and then their in-situ polymerization in the system was performed to obtain the target composite materials. This approach was also applied to other polysaccharides to produce the corresponding composite materials.⁹⁾

As one of other unique and specific properties of ILs, it has been reported that imidazolium-type ILs show excitation-wavelength-dependent fluorescent behavior owing to the presence of energetically different associated species.¹⁰⁾ The author thus has considered that such ILs have a potential as components to contribute to developing new fluorescent photo functional materials. To provide the practical IL material exhibiting unique fluorescent property, first, an attempt was made to obtain a transparent imidazolium-type PIL film by radical copolymerization of two polymerizable ILs, that is, 1-methyl-3-(4-vinylbenzyl)imidazolium chloride (**1**) and 1-(3-methacryloyloxy)propyl-3-vinylimidazolium bromide (**2**) (Figure 2(a)); the former gives PIL with polystyrene-type backbone and the latter acts as cross-linking agent due to the presence of two polymerizable groups.¹¹⁾ These polymerizable ILs were synthesized by quarternization of 1-methylimidazole or 1-vinylimidazole with the corresponding haloalkyl derivatives according to Scheme 2. For the preparation of film form of PIL (**3**), a solution of **1** and **2** (10:1), and a radical initiator, AIBN, in methanol was sandwiched between two glass plates, and then, the system was heated at 65 °C for 30 min and subsequently at 75 °C for 2 h to simultaneously occur the polymerization and evaporation of methanol. The resulting cross-linked PIL (**3**) had

the film form with transparent appearance and exhibited blue emission by UV light irradiation at 365 nm as shown in Figure 2(b) and (c), respectively. The resulting film showed excitation-wavelength-dependent fluorescent behavior (Figure 2(d)) similar as that of the general imidazolium-type ILs such as a well-known ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl).

The author found that the fluorescence resonance-energy-transfer (FRET)¹²⁾ from BMIMCl as a donor to rhodamine 6G, a representative red fluorescent dye, as an acceptor occurred by excitation at wide wavelength areas in a solution of rhodamine 6G in BMIMCl because the aforementioned specific excitation-wavelength-dependent fluorescent emissions of BMIMCl, excited at each wavelength, were overlapped with an absorption of rhodamine 6G.¹³⁾ Consequently, the emissions due to rhodamine 6G appeared by excitation at the wide wavelength areas in the solution. On the basis of this result, the author has designed the PIL films which exhibit multicolor emissions depending on combinations of the three primary colors.¹⁴⁾ Besides rhodamine for red emission, for this purpose, the following two fluorescent dyes, that is, 7-(diethylamino)-coumarin-3-carboxylic acid (DEAC) and pyranine were employed for green and blue emissions, respectively. To incorporate these dye moieties in the PIL film, the polymerizable rhodamine, DEAC, and pyranine (**4–6**) having a methacrylate group were synthesized as follows. The direct condensation of rhodamine B with 2-hydroxyethyl methacrylate using a condensing agent gave the polymerizable rhodamine derivative **4** (Scheme 4). The polymerizable DEAC derivative **5** was synthesized from DEAC chloride and 2-hydroxyethyl-methacrylate according to the literature procedure (Scheme 5).¹⁵⁾ The reaction of pyranine with methacryloyl chloride gave the polymerizable pyranine derivative **6** (Scheme 6).

Then, radical copolymerization of **1**, **2**, with **4**, **5**, or **6** was carried out to produce the PIL films **7**, **8**, and **9** carrying respective dye moieties (Figure 3(a)). The fluorescence spectra of the resulting films exhibited the respective dye emissions by excitation at wide wavelength areas (260–400 nm). Because fluorescent emissions of the aforementioned PIL film **3** were partially overlapped with absorptions of the films **7–9**, the emissions of these films excited at 260–400 nm were owing

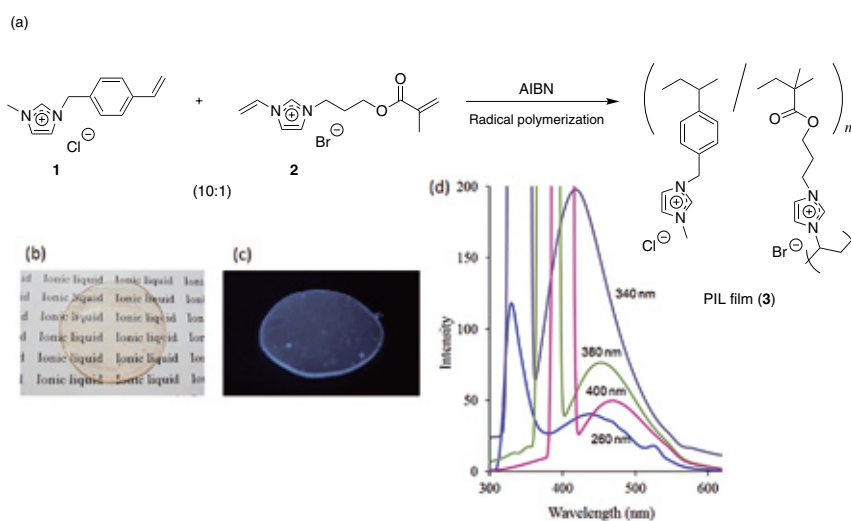


Figure 2. Radical copolymerization of **1** with **2** by AIBN to produce PIL film **3** (a), Photographs of PIL film **3** (b), it under UV light irradiation at 365 nm (c), and fluorescence spectra of PIL film **3** by excitation at 260–400 nm (d).

to either direct excitation of the dye moieties or FRET from the units 1 and 2 to the dye moieties. Actually, these films 7–9

showed the red, green, and blue emissions by light irradiation at 365 nm, respectively (Figure 3(b)).

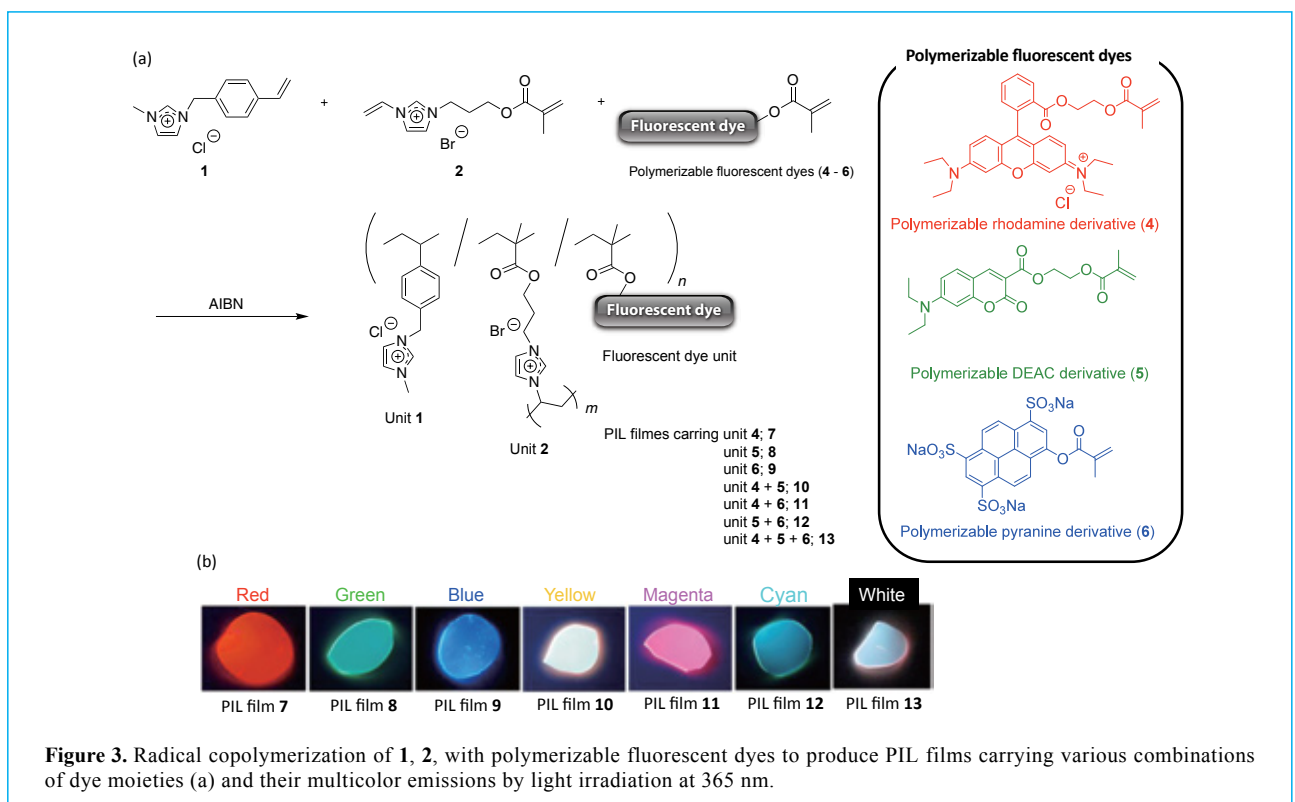
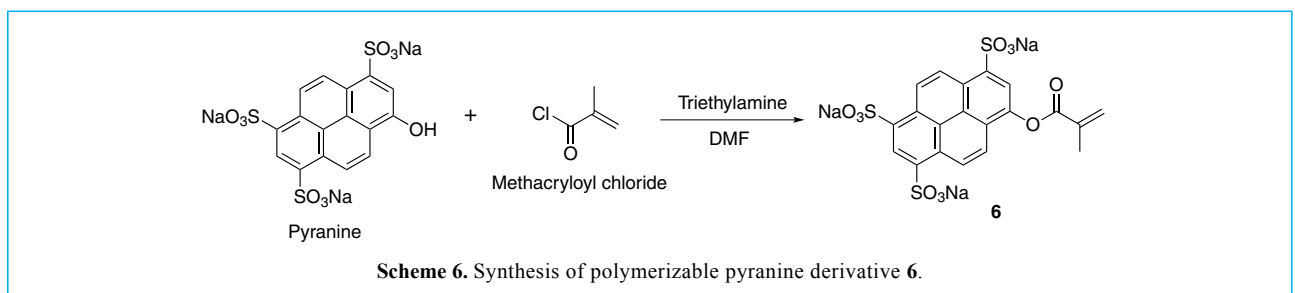
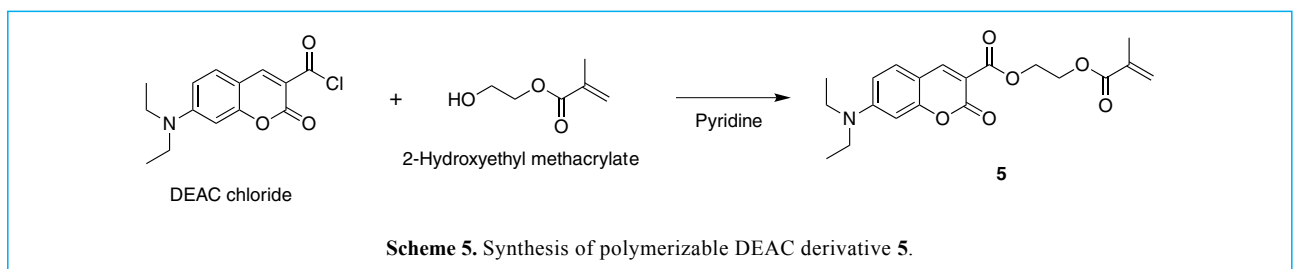
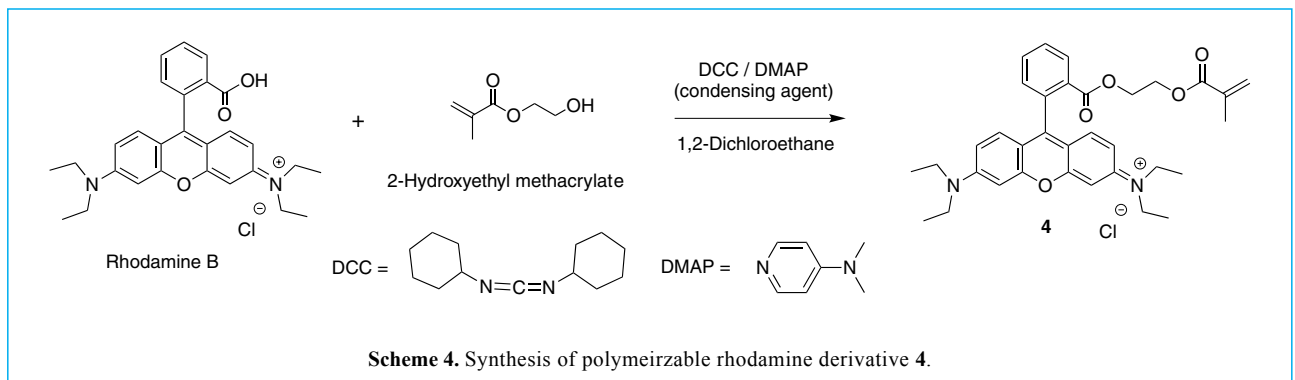


Figure 3. Radical copolymerization of 1, 2, with polymerizable fluorescent dyes to produce PIL films carrying various combinations of dye moieties (a) and their multicolor emissions by light irradiation at 365 nm.

By means of possible combinations among the above red, green, and blue dyes, the PIL films exhibiting tunable color emissions were synthesized. Three combinations of the polymerizable dyes (4+5, 4+6, 5+6) were copolymerized with 1 and 2 by AIBN to give the PIL films 10-12 (Figure 3(a)). The fluorescence spectra of the resulting films showed two kinds of emissions due to the incorporated dye moieties by excitation at 260–400 nm. These results indicated that the respective dyes in the films were individually emitted by the direct excitation or FRET. The PIL film 13 carrying three dye moieties was also prepared by copolymerization of the three polymerizable dyes with 1 and 2. The fluorescence spectra of the obtained film showed three kinds of emissions due to each dye by excitation at 260–400 nm. The above PIL films having plural dye moieties exhibited yellow, magenta, cyan, and white fluorescent emissions by excitation at a sole wavelength according to the combinations of the dyes (Figure 3(b)).

4. Conclusions

In this article, the author reviewed the preparation of functional PILs by the radical polymerization of polymerizable ILs. The prospective polymerizable ILs were synthesized by simple reaction steps. Specifically, their radical polymerization efficiently gave PILs, which showed the unique and specific photo functions as same as those of the general ILs. New polymerizable ILs will be designed and synthesized in the future for the production of the further high performance PIL materials by the polymerization.

Acknowledgement

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Introduction of the author :

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Jun-ichi Kadokawa was born in Matsuyama in 1964. He studied applied chemistry and materials chemistry at Tohoku University, where he received his Ph.D. in 1992. He then joined Yamagata University as a Research Associate. From 1996 to 1997, he worked as a visiting scientist at the Max-Planck-Institute for Polymer Research in Germany. In 1999, he became an Associate Professor at Yamagata University and moved to Tohoku University in 2002. He was appointed as a Professor of Kagoshima University in 2004. His research interests focus on new functional polymeric materials using ionic liquids. He received the Award for Encouragement of Research in Polymer Science (1997) and the Cellulose Society of Japan Award (2009).