

# Synthesis of Fluorescent Poly(1-vinylimidazole-co-(1-pyrene) methyl 2-methyl-2-propenoate) and Determination of Monomer Reactivity Ratios

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**ABSTRACT:** A new fluorescent copolymer, poly(1-vinylimidazole-co-(1-pyrene) methyl 2-methyl-2-propenoate) (VI-co-PyMMP), has been designed and synthesized by a free-radical copolymerization of VI and PyMMP as well as characterized using ultraviolet (UV), Fourier transform infrared spectroscopy (FTIR),  $^1\text{H}$  NMR, and fluorescence spectroscopies. The monomer reactivity ratios are determined by two methods of Fineman-Ross ( $r_1 = 0.28 \pm 0.04$  for VI,  $r_2 = 1.32 \pm 0.11$  for PyMMP) and Kelen-Tüdös ( $r_1 = 0.23 \pm 0.05$ ,  $r_2 = 1.22 \pm 0.12$ ). Based on the reactivity ratios, the monomer sequence lengths and  $Q$  and  $e$  for PyMMP

monomer are further calculated. The results suggest that the copolymerization of VI and PyMMP is a nonideal copolymerization without an azeotropic point (i.e.,  $r_1 < 1$ ,  $r_2 > 1$  and  $r_1 r_2 < 1$ ) and has a low alternation tendency. The conclusions drawn in this work may not only direct the later synthesis of the copolymers but also enrich the database of free-radical copolymerization. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2867–2873, 2012

**Key words:** radical polymerization; copolymer; fluorescence; monomer reactivity ratios

## INTRODUCTION

Over the past half-century, both homopolymer and copolymer based on 1-vinylimidazole (VI) have persistently evoked great interest to the research community. Because of the unique properties including ion exchange, complexation behavior, catalysis, biological and/or physiological activities, and thermal resistance, the VI-based polymers have been actively used as carrier agent for protein separation,<sup>1</sup> active ingredient of electrolytic enzymes,<sup>2</sup> and materials for the preparation of anion exchange membranes<sup>3</sup> and various electrochemical devices.<sup>4,5</sup> On the other hand, as one of the most common organic fluorescent materials, pyrene and its derivatives possess an excellent quantum yield as high as 0.65 in ethanol at 293 K and a long fluorescent lifetime of 410 ns, thus having been widely used to make dye and its precursors.<sup>6</sup> Once copolymerizing of VI with a vinyl monomer bearing pyrene group, such as (1-pyrene) methyl 2-methyl-2-propenoate (PyMMP),<sup>7,8</sup> the resultant copolymer may acquire fluorescent characteristics.

The fluorescence stemming from pyrene group in combination with the biocompatibility of imidazole group, which is a crucial element of primary biomacromolecules (such as DNA, RNA, and proteins)<sup>9</sup> and has been incorporated into many pharmaceuticals and protein-like copolymers,<sup>9–15</sup> enables the VI-based polymers to develop further potential applications ranging from biosensors/chemsensors<sup>16,17</sup> to probes for sensing processes in polymers.<sup>18</sup>

It is well-known that the properties of polymers are dominantly governed by the structures. With regard to the copolymer materials, if influence of the structures (mainly the average composition and the sequence length distribution) on the properties is well understood, it is of high possibility to synthesize the target copolymers with the expected performance. In general, the average composition and sequence lengths of the copolymers are determined by the monomer feed ratios and reactivity ratios. To some extent, the latter is more important. Additionally, the reactivity of a fixed monomer fluctuates much with the variation of its comonomers, displaying the noticeable kinetic effect. Therefore, the determination of monomer reactivity ratios is of particular significance for the copolymer synthesis: on the experimental side, the reactivity ratios can be further used to estimate the average composition of the copolymers and to distinguish the copolymerization tendency, thereby directing the design of experiment; on the theoretical side, the reactivity ratios for

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new comonomer pairs enrich the database of free-radical copolymerization. With these considerations in mind, a great deal of research has been carried out to determine the monomer reactivity ratios. For example, the researchers have implemented copolymerization of VI with diisopropyl-*p*-vinylbenzyl phosphonate,<sup>5</sup> acrylonitrile,<sup>19</sup> styrene,<sup>20</sup> vinyl acetate,<sup>20</sup> methyl methacrylate,<sup>20</sup> 1-vinylpyrrolidone,<sup>20</sup> 4-amino-styrene,<sup>21</sup> methacrylate,<sup>22</sup> or maleic anhydride<sup>23</sup> and evaluated the monomer reactivity ratios. The methods of Mao-Huglin,<sup>24</sup> Tidwell-Mortimer,<sup>25</sup> Kelen-Tüdös (K-T),<sup>26</sup> Finemann-Ross (F-R),<sup>27</sup> and Mayo-Lewis<sup>28</sup> have been used for determination of the reactivity ratios. Among them, the K-T and F-R methods, a linear least squares method, are used most commonly. For application of these two methods, the monomer conversion should be controlled below 10%.

To address the issues mentioned above, in this work, a new fluorescent copolymer, poly(1-vinylimidazole-*co*-(1-pyrene) methyl 2-methyl-2-propenote) (VI-*co*-PyMMP), has been synthesized by a free-radical copolymerization of VI and PyMMP with azobisisobutyronitrile (AIBN) as an initiator. Chemical structure and fluorescent property of the new copolymer were characterized by UV, FTIR, <sup>1</sup>H NMR, and fluorescence spectroscopies. Because it is the first time to explore the copolymerization of VI and PyMMP, the determination of monomer reactivity ratios makes up another important subject of this research work. After the molar fractions of comonomer units in VI-*co*-PyMMP were calculated according to the elemental analysis data, the monomer reactivity ratios were determined by both K-T and F-R methods. Further, the monomer sequence lengths and *Q* and *e* for PyMMP monomer were also estimated on the basis of the monomer reactivity ratios.

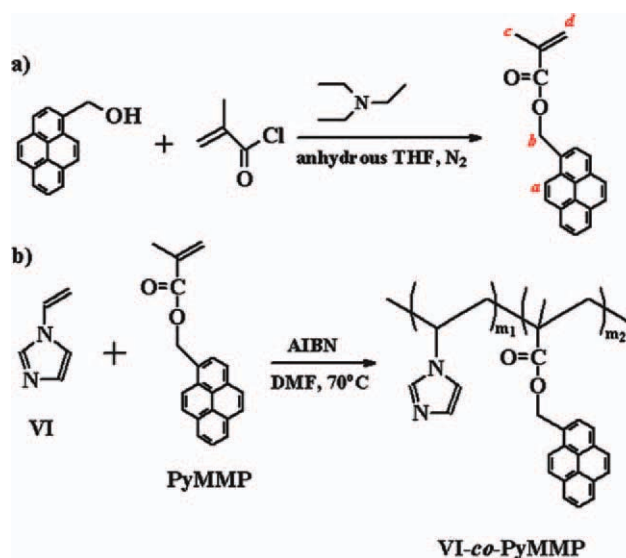
## EXPERIMENTAL

### Materials

1-Pyrenemethanol (98%) and methacryloyl chloride ( $\geq 99\%$ ) were supplied by Aldrich and Fluka, respectively. VI (99%) and AIBN were obtained from Aladdin, China. The AIBN radical initiator was recrystallized twice from methanol solution before use. Dimethylformamide (DMF) and tetrahydrofuran (THF) were distilled and stored in tightly sealed flasks over 5 Å molecular sieves. Other solvents and chemicals were purchased from commercial suppliers (China) and used as-received.

### Synthesis of VI-*co*-PyMMP

As schematized in Figure 1(a), PyMMP was synthesized from 1-pyrenemethanol and methacryloyl chlo-



**Figure 1** Scheme for the synthesis of (a) PyMMP and (b) VI-*co*-PyMMP copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

ride according to a previously reported method<sup>7,8</sup> [<sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 7.94–8.25 (a), 5.85 (b), 1.90 (c), 6.07 and 5.49 (d); FTIR ( $\nu$ , cm<sup>-1</sup>): 1708 (C=O), 1156 (C–O–C), 1630 (C=C)].

VI-*co*-PyMMP copolymer was synthesized by a free-radical copolymerization of VI and PyMMP with AIBN as an initiator in DMF solution [Fig. 1(b)]. VI (710 mg, 7.5 mmol), PyMMP (22 mg,  $7.5 \times 10^{-2}$  mmol), AIBN (15 mg, 2% of the total monomer weight), and DMF (6 mL) were successively added into a 50-mL two-neck flask equipped with a water jacketed condenser. The mixture was then magnetically stirred and heated to 70°C. After the reaction was sustained for 20 h under N<sub>2</sub> atmosphere, the liquid solution was poured into 20 mL ethyl acetate. The precipitated solid was washed by THF (3  $\times$  20 mL) and dried in the vacuum oven at 60° for 12 h. The target product of VI-*co*-PyMMP is a light yellow solid with the yield of 71.1%. Its viscosity-average molecular weight ( $\overline{M}_v$ ) was measured to be 16 kDa by dilute solution viscometry.

The VI-*co*-PyMMP copolymers used for determination of the monomer reactivity ratios were synthesized by using the similar process but the monomer conversion rate was controlled below 10% by appropriately reducing the reaction time. Table I summarizes the synthesis data for these copolymers.

In a systematic work, Bamfor and Schofield have shown that VI homopolymerization kinetics is complicated by a so-called "degradative addition" (addition of propagating radical to the monomer).<sup>29</sup> According to their discussion, this side reaction is significant for the VI polymerization in DMF when the concentration of VI is higher than 8.5 mol L<sup>-1</sup> and occlusion

TABLE I  
Synthesis of VI-co-PyMMP<sup>a</sup>

| Samples | Molar feed ratio of VI to PyMMP | Reaction time (h) | Conversion (%) |
|---------|---------------------------------|-------------------|----------------|
| 1       | 8 : 1                           | 6                 | 9.1            |
| 2       | 5 : 1                           | 6                 | 8.7            |
| 3       | 1 : 1                           | 6                 | 7.5            |
| 4       | 2 : 3                           | 10                | 9.3            |
| 5       | 1 : 4                           | 10                | 4.6            |

<sup>a</sup> All syntheses are conducted under N<sub>2</sub> atmosphere at 70°C. The amount of AIBN is 2% of the total monomer weight. The concentration of DMF solution is 4 mg mL<sup>-1</sup> of PyMMP.

phenomena take place in the polymerization. In our work, however, the VI concentration in DMF is controlled to be no higher than 1.25 mol L<sup>-1</sup>, and the reaction system is always homogeneous in the polymerization. Therefore, the effect of degradative addition on the copolymerization kinetics is negligible. That is to say, the standard Mayo-Lewis treatment is still available in this study.

### Characterization

FTIR spectra were obtained using a VERTEX 70 spectrometer in the attenuated total reflectance mode. <sup>1</sup>H NMR spectra (500 MHz, *6d*-DMSO or CDCl<sub>3</sub>) were recorded on a Bruker AC-500 spectrometer. UV spectra were collected on a TU-1800PC spectrophotometer. Fluorescence measurements were performed on a HITACHI F-4600 spectrofluorometer. Elementary analysis of copolymers was carried out using Elementar Vario EL III; each reported datum is an average of three parallel measurements.

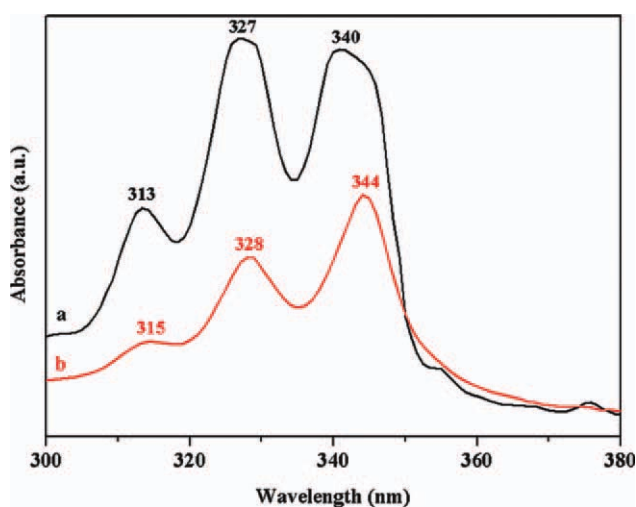


Figure 2 UV spectra of DMF solutions of (a) PyMMP and (b) VI-co-PyMMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

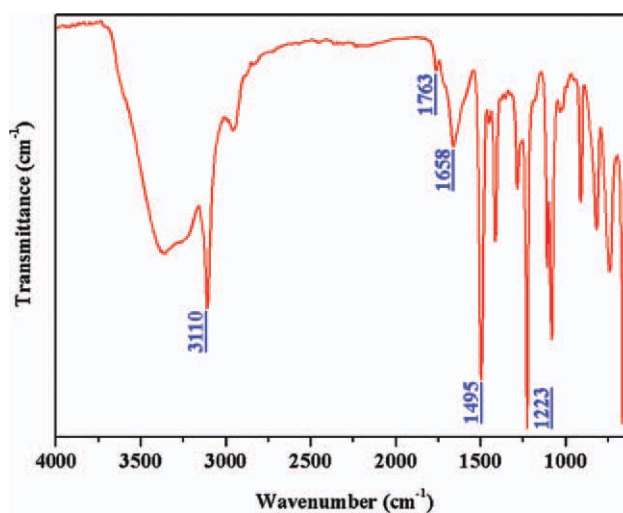


Figure 3 FTIR spectrum of VI-co-PyMMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

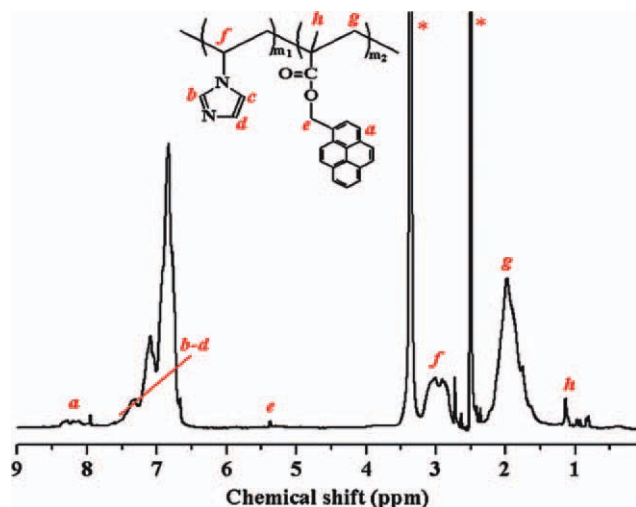
## RESULTS AND DISCUSSION

### Characterization of VI-co-PyMMP

To verify the copolymerization of VI and PyMMP ready to proceed, the regular but rapid UV measurements were conducted in DMF solution. As depicted in Figure 2, the pyrene moiety in PyMMP displays the UV absorption at 313, 327, and 340 nm. After reaction with VI, these characteristic peaks are still presented in the spectrum of purified product but red shifted by 1–4 nm, indicating that the product is not a mixture of PyMMP and homopolymer of VI.<sup>30</sup> As thus, the UV data roughly suggest that the VI-co-PyMMP copolymer has been successfully synthesized.

Both FTIR and <sup>1</sup>H NMR measurements were also carried out on the VI-co-PyMMP copolymer. The FTIR spectrum shown in Figure 3 reveals that the copolymer product includes the characteristic moieties of imidazole ring (=C–H 3110 cm<sup>-1</sup>; C=N 1658 cm<sup>-1</sup>; C–N 1495 cm<sup>-1</sup>) and ester (C=O 1763 cm<sup>-1</sup>; C–O–C 1223 cm<sup>-1</sup>). The broad and strong absorption band centered at 3350 cm<sup>-1</sup> is attributed to a small amount of water absorbed during the measurement, indicating the high hydrophilic trait of the copolymer. Actually, the solubility of VI-co-PyMMP in water at room temperature is measured to be as high as 0.3 mg mL<sup>-1</sup>. Figure 4 gives the <sup>1</sup>H NMR spectrum of the copolymer product. The major peaks are assigned to the protons on imidazole ring (7.56–6.55 ppm), methane protons adjacent to imidazole ring (3.19–2.76 ppm), and methylene protons of backbone (2.24–1.59 ppm). The weak multiplet at 8.46–7.92 ppm is from the pyrene protons. Another two weak peaks at 5.42 and 1.15 ppm are attributed to the methylene protons





**Figure 4**  $^1\text{H}$  NMR spectrum of VI-co-PyMMP. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

adjacent to pyrene and the methyl protons, respectively. No spectral feature is observed between 6.10 and 5.50 ppm, suggesting the absence of the protons corresponding to  $\text{C}=\text{CH}_2$ . These structural data from both FTIR and  $^1\text{H}$  NMR spectra further confirm that the VI-co-PyMMP copolymer has been successfully synthesized by a free-radical copolymerization method.

### Fluorescent property of VI-co-PyMMP

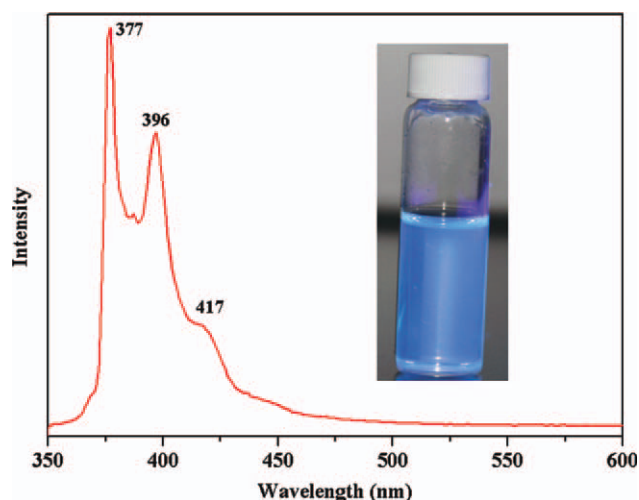
Successful introduction of pyrene units into VI-co-PyMMP endows the copolymer with fluorescent property. As shown in the inset of Figure 5, the clear and colorless VI-co-PyMMP solution ( $5 \times 10^{-6}$  g  $\text{mL}^{-1}$ ) in the mixed solvent of DMF and  $\text{H}_2\text{O}$  (DMF :  $\text{H}_2\text{O}$  = 1 : 1, v/v) emits bright blue fluorescence under 365 nm UV light irradiation. The fluorescent property was further studied by the fluorescence spectroscopy. Once excited at the maximum absorption wavelength of 344 nm, the abovementioned solution shows strong characteristic fluorescence of pyrene with distinct peaks at 377, 396, and 417 nm that correspond to monomer emission of pyrene. No emission band is observed in the region of 450–550 nm which corresponds to excimer emission of pyrene, suggesting the absence of pyrene–pyrene stacking in the sample.<sup>31</sup> In other words, the distribution of PyMMP units in the main chain of copolymer is discrete when the monomer feed ratio of VI to PyMMP is 100 : 1. With quinine sulfate as a standard substance ( $\phi = 0.546$ ),<sup>32</sup> the fluorescence quantum yield of VI-co-PyMMP was measured to be 0.49. In this way, the excellent fluorescent property of pyrene has been perfectly transferred to the VI-co-PyMMP copolymer. The acquired fluorescence together with the biological activity originating

from the imidazole rings provides the copolymer with many promising biotechnological applications such as biosensor and biolabel. A high feasible example of application is to use the copolymer as carrier agent for protein separation as having been demonstrated by using other VI-polymers,<sup>1,14</sup> characterizing that this separation process can be monitored in an online manner by employing a spectrofluorometer or a fluorescence microscope.

### Determination of monomer reactivity ratios

The actual composition of the copolymer was determined by elementary analysis. Table II summarizes the data of elementary analysis and the calculated molar content of VI-unit as a function of the monomer feed ratio. It is noted that, as expected, there is a strong dependence of the VI-unit content on the monomer feed ratio. When the monomer feed ratio of VI to PyMMP is varied from 8 : 1 to 1 : 4, the VI-unit content is changed from 73.3% to 14.7%.

The basic free-radical copolymerization theory tells that the copolymer composition ( $F$ ) is a function of the feeding monomer composition ( $f$ ) at the same copolymerization instant. The  $F$ - $f$  curve can thus be used to roughly describe the monomer behavior during the copolymerization. According to the data in Table II, the  $F$ - $f$  curve of the VI-co-PyMMP copolymers is drawn in Figure 6. As observed in Figure 6, the  $F$ - $f$  curve lies below the diagonal, indicating that the free-radical copolymerization of VI and PyMMP is a nonideal copolymerization without an azeotropic point, i.e.,  $r_1 < 1$  for reactivity ratio of VI,  $r_2 > 1$  for reactivity ratio of PyMMP, and  $r_1 r_2 < 1$ .



**Figure 5** Fluorescence emission spectrum of VI-co-PyMMP in a mixed solvent of DMF and  $\text{H}_2\text{O}$  (DMF :  $\text{H}_2\text{O}$  = 1 : 1, v/v;  $c = 5 \times 10^{-6}$  g  $\text{mL}^{-1}$ ;  $\lambda_{\text{ex}} = 344$  nm). Inset is a digital photograph of the same solution under 365 nm UV light irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE II  
Data of Elementary Analysis and Calculated Molar Content of VI-Unit in the Copolymer as a Function of the Monomer Feed Ratio

| Samples | Molar feed ratio of VI to PyMMP | Data of elementary analysis (wt %) |      |       | Molar content of VI-unit in copolymer |
|---------|---------------------------------|------------------------------------|------|-------|---------------------------------------|
|         |                                 | C                                  | H    | N     |                                       |
| 1       | 8 : 1                           | 60.37                              | 5.74 | 11.12 | 73.3                                  |
| 2       | 5 : 1                           | 66.58                              | 5.81 | 8.77  | 62.3                                  |
| 3       | 1 : 1                           | 70.85                              | 6.19 | 3.88  | 35.8                                  |
| 4       | 2 : 3                           | 81.3                               | 5.71 | 3.78  | 31.7                                  |
| 5       | 1 : 4                           | 74.84                              | 4.99 | 1.38  | 14.7                                  |

The true values of the monomer reactivity ratios were determined in this work by either F-R method [eq. (1)] or K-T method [eq. (2)]:

$$\frac{R(\rho - 1)}{\rho} = r_1 \frac{R^2}{\rho} - r_2 \quad (1)$$

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \quad (2)$$

where  $R$  is the molar feed ratio of VI to PyMMP and  $\rho$  is the molar ratio of VI-unit to PyMMP-unit in the copolymer and determined using the data of elementary analysis,  $\eta = \frac{R(\rho-1)/\rho}{R^2/\rho+\alpha}$ ,  $\alpha = \sqrt{(R^2/\rho)_{\max}(R^2/\rho)_{\min}}$ , and  $\xi = \frac{R^2/\rho}{R^2/\rho+\alpha}$ . With  $R$  and  $\rho$  as the starting data, the relative parameters are calculated and summarized in Table III. By linear fitting of the F-R plot of  $R(\rho - 1)/\rho$  versus  $R^2/\rho$  and the K-T plot of  $\eta$  versus  $\xi$  (Fig. 7), the monomer reactivity ratios are determined to be  $r_1 = 0.26$  and  $r_2 = 1.28$  for the F-R method and  $r_1 = 0.24$  and  $r_2 = 1.20$  for the K-T method, respectively. To examine the reproducibility of the determination, two more sets of experiments were carried out in parallel. The average values based on these three replicate experiments are  $r_1 = 0.28 \pm 0.04$  and  $r_2 = 1.32 \pm 0.11$  for the F-R method and  $r_1 = 0.23 \pm 0.05$  and  $r_2 = 1.22 \pm 0.12$  for the K-T method, respectively. It is interesting to note that the reactivity ratios determined by two methods are very close, suggesting high agreement between the used models. The  $r_1 < 1$  and  $r_2 > 1$  implies that both VI and PyMMP monomers can be added onto the active  $\sim$ VI $\cdot$  macroradical but the addition of PyMMP is predominant and that the VI moiety is surrounded by the PyMMP units in the early stage (steady state) of the copolymerization. In other words, PyMMP is incorporated faster in the initial stage, and the copolymer is rich in the PyMMP-unit. Once PyMMP is depleted, more VI monomer is added or directly forms the homopolymer. It is thus reasonable to conclude that this composition drift will become significant when the content of PyMMP is very low. Actually, the above-discussed product that was synthesized from the recipe of

VI : PyMMP = 100 : 1 displays only 87% of the fluorescence emission of PyMMP under the same molar concentration. Although the weakened fluorescence may be attributed to several factors, the compositional heterogeneity (the product includes a portion of VI-homopolymer) is believed to play an important role.

Besides the elementary analysis, the  $^1\text{H}$  NMR spectroscopy was also used to evaluate the composition of VI-co-PyMMP copolymer. The calculation was performed using the following equation [eq. (3)]:

$$\rho = 3A_1/A_2 \quad (3)$$

where  $A_1$  and  $A_2$  are the intensities of protons on imidazole ring and pyrene protons, respectively, determined from the imidazole ring and pyrene peak areas in the  $^1\text{H}$  NMR spectrum. The reactivity ratios are hereby determined to be  $r_1 = 0.29 \pm 0.02$  and  $r_2 = 1.29 \pm 0.14$  for the F-R method and  $r_1 = 0.27 \pm 0.05$  and  $r_2 = 1.26 \pm 0.09$  for the K-T method, respectively, which are fairly consistent with the values based on the elementary analysis method.

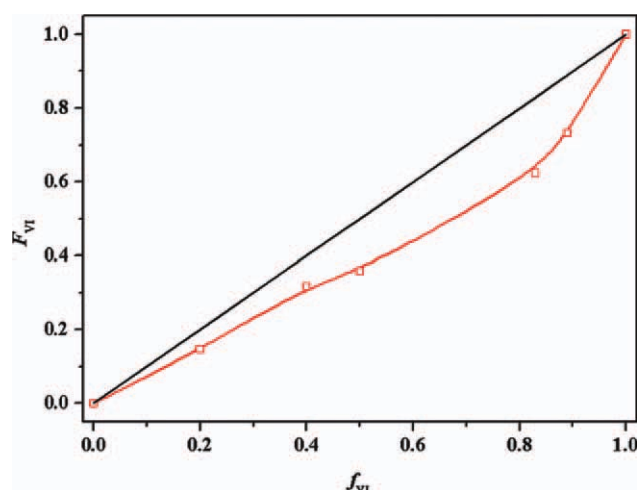


Figure 6  $F$ - $f$  curve of the VI-co-PyMMP copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE III  
Parameters for F-R and K-T Equations

| Samples | R    | $\rho$ | Parameters for F-R |                    | Parameters for K-T    |        |       |
|---------|------|--------|--------------------|--------------------|-----------------------|--------|-------|
|         |      |        | $R^2/\rho$         | $R(\rho - 1)/\rho$ | $R^2/\rho + \alpha^a$ | $\eta$ | $\xi$ |
| 1       | 8    | 2.75   | 23.27              | 5.09               | 26.20                 | 0.19   | 0.89  |
| 2       | 5    | 1.65   | 15.15              | 1.97               | 18.08                 | 0.11   | 0.84  |
| 3       | 1    | 0.56   | 1.79               | -0.79              | 4.72                  | -0.17  | 0.38  |
| 4       | 0.67 | 0.46   | 0.98               | -0.79              | 3.91                  | -0.20  | 0.25  |
| 5       | 0.25 | 0.17   | 0.37               | -1.22              | 3.30                  | -0.37  | 0.11  |

<sup>a</sup>  $\alpha = \sqrt{(R^2/\rho)_{\max}(R^2/\rho)_{\min}} = 2.93$ ,  $\rho$  is the molar ratio of VI-unit to PyMMP-unit in the copolymer and determined using the data of elementary analysis.

### Evaluation of sequence lengths and $Q$ and $e$ for PyMMP monomer

$$\mu_1 = 1 + r_1\rho \quad (4)$$

$$\mu_2 = 1 + r_2/\rho \quad (5)$$

$$P_{21} = 1/(1 + r_2/R) \quad (6)$$

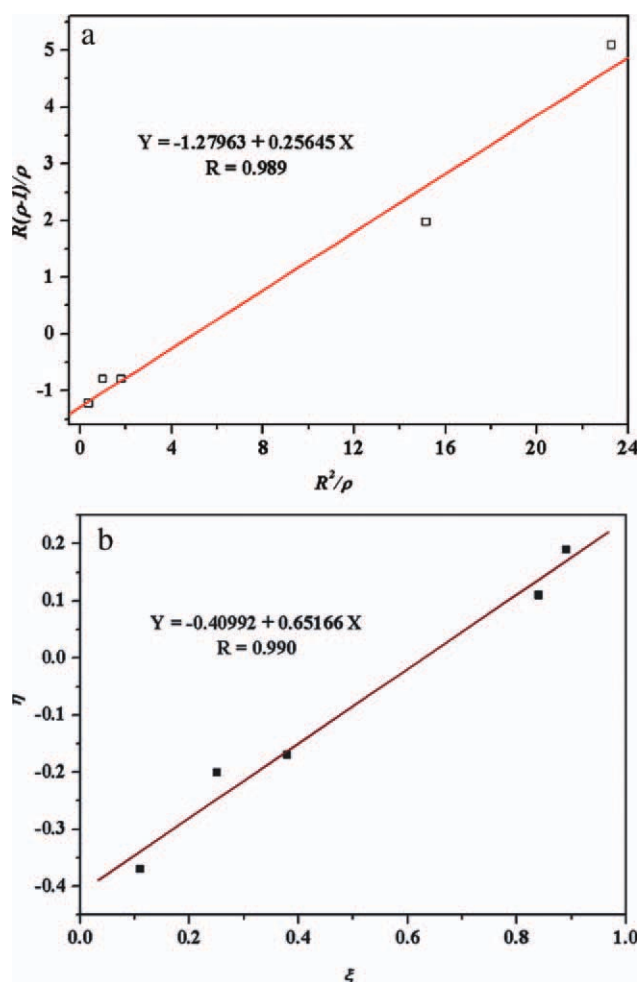


Figure 7 Linear behavior of (a) F-R plot of  $R(\rho - 1)/\rho$  versus  $R^2/\rho$  and (b) K-T plot of  $\eta$  versus  $\xi$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

With the monomer reactivity ratios in hand, the sequence lengths of VI-unit ( $\mu_1$ ) and PyMMP-unit ( $\mu_2$ ) were evaluated using the famous Pyun equations [eqs. (4) and (5)]<sup>33</sup> and summarized in Table IV. Moreover, the probability to form the heterodiad  $M_2M_1\cdot$  radical ( $P_{21}$ ), another important parameter, in the copolymerization was calculated using eq. (6).<sup>33</sup> The obtained data of  $P_{21}$ , along with  $P_{12}$ , are also summarized in Table IV. These data may facilitate the later calculation of the sequence length distribution. For example, the probability of the addition of  $\sim xM_2\sim$  onto  $M_2M_1\cdot$  can be estimated using the equation of  $P_{22}^{x-1}(1 - P_{22})$  where  $P_{22}$  is equal to  $1 - P_{21}$ .

As suggested by the data in Table IV, increasing of the VI content in the feeding comonomers from  $R = 0.25$  to 8 results in the slight increase of the sequence length of VI-unit ( $\mu_1$ ) from 1.04 to 1.72, but the significant decrease of the sequence length of PyMMP-unit ( $\mu_2$ ) from 6.88 to 1.47. In the meanwhile,  $P_{12}$  decreases from 0.94 to 0.32 and  $P_{21}$  from 0.76 to 0.09. These data clearly suggest that the VI-co-PyMMP copolymers have a weak tendency toward alternation, and the sequence lengths besides the compositions of the copolymers are also strongly dependent on the monomer feed ratios. This implies that it is of high feasibility to synthesize the copolymer with a relatively definitive structure and the

TABLE IV  
The Sequence Lengths of VI-Unit ( $\mu_1$ ) and PyMMP-Unit ( $\mu_2$ ) as well as the Probability of Heterodiad Linkages ( $P_{ij}$ ) as a Function of the Monomer Feed Ratio<sup>a</sup>

| Samples | R    | Sequence length |         | $P_{ij}$ |          |
|---------|------|-----------------|---------|----------|----------|
|         |      | $\mu_1$         | $\mu_2$ | $P_{12}$ | $P_{21}$ |
| 1       | 8    | 1.72            | 1.47    | 0.32     | 0.09     |
| 2       | 5    | 1.43            | 1.78    | 0.43     | 0.14     |
| 3       | 1    | 1.15            | 2.79    | 0.79     | 0.44     |
| 4       | 0.67 | 1.12            | 3.17    | 0.85     | 0.54     |
| 5       | 0.25 | 1.04            | 6.88    | 0.94     | 0.76     |

<sup>a</sup>  $r_1 = 0.26$ ,  $r_2 = 1.28$ , and the values of  $\rho$  in Table III are used here for calculation of  $\mu_1$ ,  $\mu_2$ , and  $P_{ij}$ .

expected performance by controlling the monomer feed ratio.

$$r_1 = \frac{Q_2}{Q_1} \exp[-e_1(e_1 - e_2)] \quad (7)$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)] \quad (8)$$

Moreover, based on the reactivity ratios,  $Q$  and  $e$  of comonomers can also be computed by using the Alfrey-Price model expressed as eqs. (7) and (8).<sup>34</sup> Substituting the values of  $Q_1 = 0.11$  and  $e_1 = -0.68$  for VI<sup>35</sup> into eqs. (7) and (8) gives  $Q_2 = 0.21$  and  $e_2 = 0.37$  for PyMMP. Almost no difference in  $Q$  between VI and PyMMP suggests that it is relatively easy to implement the copolymerization, whereas the small difference in  $e$  implies a lower tendency for alternative copolymerization.

### CONCLUSIONS

A new copolymer of VI-co-PyMMP has been designed and synthesized by a free-radical copolymerization of VI and PyMMP. Its chemical structure was identified by UV, FTIR, and <sup>1</sup>H NMR spectroscopies. The fluorescence measurements showed that the excellent fluorescent property of pyrene has been perfectly transferred to the copolymer with a quantum yield of 0.49 in a mixed solvent of DMF and H<sub>2</sub>O (DMF : H<sub>2</sub>O = 1 : 1, v/v). For achieving a deep understanding of the copolymerization, the monomer reactivity ratios were determined by two methods of F-R ( $r_1 = 0.28 \pm 0.04$ ,  $r_2 = 1.32 \pm 0.11$ ) and K-T ( $r_1 = 0.23 \pm 0.05$ ,  $r_2 = 1.22 \pm 0.12$ ) using the elemental analysis results. Subsequently, the monomer sequence lengths were calculated on the basis of reactivity ratios. The results suggest that there is a strong dependence of the sequence lengths on the monomer feed ratios. Finally,  $Q$  and  $e$  of PyMMP were also calculated and the values are 0.21 and 0.37, respectively. It is certain that the determination of these basic parameters enriches the database of free-radical copolymerization, providing the directions for the later synthesis of the similar copolymers. In practice, the fluorescent copolymer achieved in this work may extend the application fields of VI-polymers to the biotechnology. For example, the copolymer may be used for making biosensors and biolabels. Moreover, the ability of imidazoles to complex with metals can further endow the copolymer with other functionality. In a demonstration, we have complexed the Fe<sup>3+</sup> species onto the imidazole rings in the copolymer and the resultant product thereby shows the bifunctional properties, i.e., fluorescent and magnetic properties. The bifunctional material may find the promising applications in targeted therapy and targeted deliv-

ery of drug and/or biomolecules.<sup>16</sup> These interesting results will be reported in the near future.

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