Incorporation of pyrimidine fluorophores into poly(methylmethacrylate) polymer structures

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ABSTRACT

Three polymethyl methacrylate based copolymers bearing arylvinylpyrimidine chromophores have been synthesized in four steps. Spectral properties of the copolymers have been studied in solution, powder and thin films and compared with the corresponding free chromophores. The copolymers exhibit strong emission solvatochromism and act as polarity sensors. They also exhibit halochromism: when adding acid, a bathochromic shift is observed in absorption whereas a red-shifted fluorescence is observed with increased intensity for the methoxy-substituted macromolecule.

Résumé

Trois copolymères a base de polyméthacrylate de méthyle portant des chromophores de type arylvinylpyrimidine ont été synthétisés en quatre étapes. Les propriétés spectrales des copolymères ont été étudiées en solution, sous forme de film et de poudre et comparées au chromophore libre correspondant. Les copolymères présentent un fort solvatochromisme d'émission et sont donc susceptibles d'être utilisés comme sonde de polarité. Ils présentent également des propriétés d'halochromisme : en milieu acide, un déplacement bathochrome du spectre d'absorption peut être observé. Dans le cas du copolymère substitué par un groupement méthoxy, un déplacement vers le rouge de la bande d'émission est également observé.

1. Introduction

Over the past decades, there has been a great interest in the synthesis of luminescent pyrimidine derivatives [1,2]. The pyrimidine ring is a highly π-deficient aromatic
heterocycle that can be used as the electron-withdrawing
unit in a push-pull structure for intramolecular charge
transfer (ICT). Such structures generally exhibit high
luminescence properties that can be modulated by the
nature of the electron donating group and/or the nature of
the π-conjugated bridge [3–5]. Some pyrimidine push-pull
derivatives were described as polarity sensors due to their
strong emission solvatochromism [6–12] as well as pH
sensors due to the basic character of the nitrogen atoms of
the heterocycles [9–13]. Some pyrimidine fluorophores
have also found applications for the detection of biomole-
cular species such as proteins and DNA [14–16]. It should
be noted also that 4,6-di(arylvinyl)pyrimidines have
become well established two-photon absorption chromo-
phores [17] that have found applications in
micromachining [18].

However, despite their high emission efficiency in so-
lution, many organic materials are non-luminescent in the
solid state, because of the fluorescence quenching caused
by intermolecular interactions occurring in the condensed
phase. One way to overcome this problem consists of
incorporating the fluorophore into a polymer matrix
[24–26]. When the fluorophores are covalently bounded to
the polymer structure, a better distribution of the dye will
be obtained and self-aggregation will be avoided [27–29].
Moreover, a covalent immobilization of fluorescent sensors
on carrier matrices improves the practical use because it
enables long-term measurements, avoiding leaching and a
possible contamination of the sample under investigation
[30,31].

The aim of the work described here was to synthesize
poly(methylmethacrylate) copolymers doped with (aryl-
vinyl)pyrimidine chromophores. The photophysical
properties, including emission solvatochromism and pH
sensitivity, are reported and compared to the correspond-
ing free chromophores.

2. Experimental

2.1. General methods

All reagents and solvents were purchased from com-
mercial suppliers (Sigma Aldrich, Acros or Alfa Aesar). Dry
THF was obtained by means of the Na-benzophenone
ketyl procedure. Methylmethacrylate stabilized with tert-
butylcatechol was purified by washing with aqueous 2M
NaOH and water, dried over magnesium sulfate, and used
immediately. KtBuO was purified by the procedure
described by Glinka [32] and kept under nitrogen. In air and
moisture–sensitive reactions, all glassware was flame-dried
and cooled under nitrogen. Compounds 4
[33] and 8 [34] were synthesized according to a reported
procedure.

NMR spectra were acquired at room temper-

ture on a Bruker AC-300 spectrometer. Chemical shifts
were recorded with a UVIKON xm SECOMAM spectrom-
eter using standard 1 cm quartz cells. Fluorescence
spectra were recorded using Spex FluoroMax–3 Jobin-
Yvon Horiba apparatus. Measurements were performed at
room temperature with solutions of OD < 0.1 to avoid re-
absorption of the emitted light, and data were corrected
with a blank and from the variations of the detector with
the emitted wavelength.

2.2. Synthesis

2.2.1. Synthesis of 4-[4-(4,6-dimethyl-pyrimidin-2-yl)-
benzaldehyde (2)

A stirred mixture of 2-Chloro-4,6-dimethyl-pyrimidine
1 (284 mg, 2.0 mmol), 4-formylphenylboronic acid
(450 mg, 3.0 mmol) and Pd(PPh3)4 (115 mg, 0.1 mmol) in
degassed aqueous 2 M sodium carbonate (3.0 mmol, 1.5 mL)/ethanol (1.5 mL)/toluene (15 mL) was heated under
reflux for 48 h under a nitrogen atmosphere. The reaction
mixture was cooled and filtered, and EtAcO/water 1/1
(20 mL) was added. The organic layer was separated and
the aqueous layer was extracted with additional EtAcO
(2 × 10 mL). The combined organic extracts were dried over
MgSO4 and the solvents evaporated under reduced pres-
sure. The crude product was purified by column chroma-
tography (SiO2, petroleum ether/ EtAcO, 7/3). Pale yellow
solid. Yield: 65% (275 mg) Mp: 89–90 °C. 1H NMR
(300 MHz, CDCl3): δ 2.55 (s, 6H), 6.97 (s, 1H), 7.96 (d, 2H,
J = 8.5 Hz), 8.60 (d, 2H), 8.56 (d, 2H); 13C NMR (CDCl3): δ 129.8 (CH), 137.4 (C), 143.6 (C), 162.8 (C), 167.0 (C), 192.2
(CH). HRMS (ESI/ASAP, TOF) m/z calculated for
C13H12N2O Na+ [M+H]+ 235.0842, found 235.0844.

2.2.2. Synthesis of 4,6-dimethyl-2-(4-vinyl-phenyl)-
pyrimidine (3)

Potassium tert-butoxide (241 mg, 2.16 mmol) was added to
a solution of methyltriphenylphosphonium iodide
(654 mg, 1.62 mmol) in dry THF (20 mL), and the reaction
mixture was stirred at room temperature for 15 min. The
aldehyde 2 (229 mg, 1.08 mmol) was added and the reac-
tion mixture was stirred at room temperature for 90 min.
The reaction was hydrolyzed with water (20 mL), and the
THF was removed under vacuum. The aqueous layer was
extracted with CH2Cl2 (3 × 20 mL), and the combined
organic layers were dried (MgSO4) and evaporated. The
crude product was purified by column chromatography
(SiO2, CH2Cl2). Colorless oil that crystallizes slowly. Yield: 68% (154 mg) Mp: 56–57 °C. 1H NMR (300 MHz, CDCl3):
δ 2.52 (s, 6H), 5.31 (d, 1H, J = 11.4 Hz), 5.85 (d, 1H,
J = 17.7 Hz), 6.77 (dd, 2H, J1 = 17.7 Hz, J2 = 11.4 Hz), 6.90
(s, 1H), 7.50 (d, 2H, J = 8.5 Hz), 8.40 (d, 2H, J = 8.5 Hz). 13C NMR
and JMOD (75 MHz, CDCl3): δ 24.1 (CH3), 114.7 (C), 117.9

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copolymer structures, Comptes Rendus Chimie (2016), http://dx.doi.org/10.1016/j.crci.2015.07.014
(CH), 126.3 (CH), 128.4 (CH), 136.6 (CH), 137.5 (C), 139.4 (C), 163.8 (C), 166.7 (C). HRMS (ESI/ASAP, TOF) m/z calculated for C_{14}H_{15}N_{2} [M+H]^+ 211.1235, found 211.1236.

2.2.3. Synthesis of copolymer CP

A stirred mixture of methyl methacrylate (2.24 g, 22.4 mmol), styrene derivative 3 (237 mg, 1.12 mmol) and benzoyl peroxide with 25% water (364 mg, 1.13 mmol) in toluene (55 mL) was heated under reflux for 15 h under a nitrogen atmosphere. The reaction mixture was cooled and toluene was evaporated. The crude copolymer was crystallized 2 times from CH_{2}Cl_{2}/n-heptane. White solid Yield: 58% (1.43 g).

2.2.4. Synthesis of copolymers CP1–CP3

A mixture of CP (600 mg) and the corresponding aldehyde (0.67 mmol, 2 mmol in case of imidine derivative (1 mmol) and the appropriate aldehyde (0.67 mmol, 2.5 equiv.) was dissolved in THF (30 mL). The mixture was extracted with CH_{2}Cl_{2}, dried over MgSO_{4} and the solvent removed under vacuum. The crude product crystallized 2 times from CH_{2}Cl_{2}/n-heptane. White solid Yield: 76% (410 mg) CP2; yellow solid yield 66% (380 mg) CP3: cream solid yield: 74% (483 mg).

2.2.5. General procedure for the Knoevenagel condensation reaction

A stirred mixture of the corresponding methylpyrimidine derivative (1 mmol) and the appropriate aldehyde (1 mmol, 2 mmol in case of 9) in aqueous sodium hydroxide (5 M, 10 mL) containing Aliquat 336 (44 mg, 0.1 mmol) was heated under reflux for 2 h. The mixture was cooled. The filtrate was filtered off, washed with water and purified by crystallization and/or column chromatography.

2.2.6. 4-[2-(4-N,N-Dimethylamino-phenyl)-vinyl]-2-phenylpyrimidine (5)

Purified by crystallization from CH_{2}Cl_{2}/n-heptane. Yellow solid. Yield: 62% (188 mg). Mp: 136–137 °C. ^{1}H NMR (300 MHz, CDCl_{3}): δ 3.05 (s, 6H), 6.74 (d, 2H, J = 8.7 Hz), 6.95 (d, 1H, J = 15.9 Hz), 7.14 (d, 1H, J = 5.1 Hz), −7.58−7.51 (m, 5H), 7.96 (d, 1H, J = 15.9 Hz), 8.55−8.52 (m, 2H), 8.69 (d, 1H, J = 5.1 Hz), 13^C NMR and JMOD (75 MHz, CDCl_{3}): δ 40.2 (CH_{2}), 112.1 (CH), 116.0 (CH), 121.3 (CH), 123.8 (C), 128.2 (CH), 128.5 (CH), 129.2 (CH), 130.4 (CH), 137.5 (CH), 138.2 (C), 151.2 (C), 157.2 (CH), 163.3 (C), 164.3 (C), HRMS (ESI/ASAP, TOF) m/z calculated for C_{20}H_{20}N_{2} [M+H]^+ 302.1652, found 302.1652.

2.2.7. 4-[2-(4,N,N-Diphenylamino-phenyl)-vinyl]-2-phenylpyrimidine (6)

Purified by column chromatography (SiO_{2}, petroleum ether/EtAcO, 7:3). Non-crystalline yellow solid. Yield: 62% (265 mg). ^{1}H NMR (300 MHz, CDCl_{3}): δ 7.02 (d, 1H, J = 15.9 Hz), 7.13−7.08 (m, 4H), 7.19−7.11 (m, 5H), 7.35−7.28 (m, 4H), 7.55−7.50 (m, 5H), 7.97 (d, 1H, J = 15.9 Hz), 8.57−8.54 (m, 2H), 8.69 (d, 1H, J = 5.1 Hz) ^{13}C NMR and JMOD (75 MHz, CDCl_{3}): δ 116.0 (CH), 122.3 (CH), 123.7 (CH), 123.9 (CH), 125.1 (CH), 128.2 (CH), 128.5 (CH), 128.7 (CH), 129.2 (C), 129.4 (CH), 130.5 (CH), 136.6 (CH), 138.0 (C), 141.7 (C), 149.0 (C), 157.4 (CH), 162.7 (C), 164.4 (C). HRMS (ESI/ASAP, TOF) m/z calculated for C_{30}H_{31}N_{4} [M+H]^+ 424.1965, found 426.1970.

2.2.8. 4-[2-(6-Methoxy-naphthalen-2-yl)-vinyl]-2-phenylpyrimidine (7)

Purified by column chromatography (SiO_{2}, petroleum ether/EtAcO, 1:1), pale yellow solid. Yield: 89% (300 mg). Mp: 142−143 °C. ^{1}H NMR (300 MHz, CDCl_{3}): δ 3.96 (s, 3H), 7.24−7.17 (m, 4H), 7.56−7.54 (m, 4H), 7.82−7.79 (m, 3H), 7.98 (s, 1H), 8.18 (d, 1H, J = 15.9 Hz), 8.59−8.56 (m, 2H), 8.77 (d, 1H, J = 5.1 Hz), ^{13}C NMR and JMOD (75 MHz, CDCl_{3}): δ 55.4 (CH_{3}), 106.0 (CH), 116.3 (CH), 119.3 (CH), 124.3 (CH), 125.4 (CH), 127.4 (CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 128.9 (C), 129.5 (CH), 130.6 (CH), 131.2 (C), 135.2 (C), 137.1 (CH), 138.0 (C), 157.4 (C), 158.5 (C), 162.6 (C), 164.4 (C). HRMS (ESI/ASAP, TOF) m/z calculated for C_{23}H_{19}N_{2}O [M+H]^+ 339.1492, found 339.1490.

2.2.9. 4,6-Bis-[2-(4-N,N-dimethylamino-phenyl)-vinyl]-2-phenylpyrimidine (9)

Purified by crystallization from CH_{2}Cl_{2}/n-heptane. Yellow solid. Yield: 86% (384 mg). Mp: 197−198 °C. ^{1}H NMR (300 MHz, CDCl_{3}): δ 2.96 (s, 12H), 6.65 (d, 4H, J = 8.7 Hz), 6.87 (d, 2H, J = 15.9 Hz), 7.02 (s, 1H), 7.49−7.42 (m, 7H), 7.88 (d, 1H, J = 15.9 Hz), 8.55−8.52 (m, 2H), ^{13}C NMR and JMOD (75 MHz, CDCl_{3}): δ 40.2 (CH_{2}), 112.1 (CH), 113.0 (CH), 122.0 (CH), 124.3 (C), 128.3 (CH), 128.4 (CH), 129.0 (CH), 130.1 (CH), 136.5 (CH), 138.8 (C), 151.0 (C), 163.4 (CH), 164.0 (C). HRMS (ESI/ASAP, TOF) m/z calculated for C_{35}H_{33}N_{4} [M+H]^+ 447.2548, found 447.2552.

3. Results and discussion

The copolymers CP1−CP3 were obtained in 4 steps from commercially available 2-chloro-4,6-dimethylpyrimidine 1 (Scheme 1). The first step consists of a Suzuki cross-coupling reaction with 4-formylphenylboronic acid. The aldehyde 2, obtained with a 65% yield, is then involved in a Wittig reaction with methyltriphenylphosphonium iodide to obtain the styrene derivative 3 with a 68% yield. A copolymerization of methyl methacrylate with 10 w% of 3 is then carried out to yield copolymer CP. The last step consists of the functionalization of pyrimidine fragments by the Knoevenagel condensation reaction with a series of aldehydes.

It proved to be difficult to determine the chemical structures of the copolymers CP1−3. Because of the low concentrations of the pyrimidine monomer used (<10 w%), NMR is not a sufficiently sensitive technique, and the signal corresponding to the pyrimidine fragments was not easily observed. IR spectra did not provide any information about the structure, and the only characteristic peak observed was that corresponding to the ester function of the methyl methacrylate moiety (1732 cm\(^{-1}\)). UV−vis and fluorescence spectra of dichloromethane solutions of the copolymers permit to indicate the presence of arylvinylpyrimidine chromophores (Table 1). Surprisingly, whereas it is generally difficult to isolate the monocoondensation products from 4,6-dimethylpyrimidine [9], comparison of absorption spectra of the copolymers CP1−3
with those of the corresponding 4-arylpyrimidine [11] and 4,6-diarylpyrimidine derivatives [9] seems to indicate that only the monocondensation products of dimethylpyrimidine fragments are observed in our case. To confirm our hypothesis, and to verify that the phenyl ring in position 2 of the pyrimidine does not modify the photophysical properties of the pyrimidine dyes, the chromophores 5–7 were synthesized from 2-phenylpyrimidine derivatives 4 and 8 by Knoevenagel condensation of the corresponding aldehyde in boiling aqueous 5M NaOH solution in the presence Aliquat 336 as the charge transfer catalyst [35] (Schemes 2–3).

The photophysical data of the compounds 5–7 and 9 indicated the negligible influence of the phenyl substituent of the pyrimidine ring on the absorption spectra confirming the structure proposed for the copolymer CP1–3. The weight percentage of chromophore fragments was estimated by UV–vis on the assumption of a similar molar absorptivity for the free dye and the linked dye (Table 2). The w% of chromophores was comprised to be between 2.5 and 7.1 for macromolecule CP1–3.

Size exclusion chromatography analyses were also performed to determine the molecular weights and polydispersities of CP1–3. The synthesized copolymers showed relatively low molecular weights ranging from 2007 to 2996 g·mol⁻¹ and polydispersities ranging between 1.53 and 1.79 (Table 2).

CP1–3 was dissolved in 1,1,2-trichloroethane at concentrations of 170 g·L⁻¹, 280 g·L⁻¹ and 190 g·L⁻¹, respectively. The solutions were then spin-coated on silicon wafers at a speed of 2000 rpm for 10 s. The resulting films were subsequently baked at 100 °C for 20 min yielding film thicknesses of 500–800 nm (measured with a Veeco Dek-tak 150+ Surface Profiler).

The fluorescence properties of the copolymers CP1–3 were examined in dichloromethane solution, as well as in powder and thin film states (Table 1). In the case of CP2 and CP3, the macromolecules in dichloromethane solution show similar emission spectra compared to the corresponding free chromophores (respectively 6 and 7). In the case of dimethylaminophenyl substituted copolymer CP1, a red shift of the emission spectra is observed in comparison with free chromophore 5. The copolymers exhibit fluorescence quantum yield in the same range compared to the

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>UV–Vis in CH₂Cl₂ λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>PL in CH₂Cl₂ λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>PL powder λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>PL thin film λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
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<tbody>
<tr>
<td>CP1</td>
<td>394</td>
<td>552 (0.14)</td>
<td>518</td>
<td>503</td>
</tr>
<tr>
<td>CP2</td>
<td>402</td>
<td>522 (0.55)</td>
<td>518</td>
<td>499</td>
</tr>
<tr>
<td>CP3</td>
<td>360</td>
<td>450 (0.11)</td>
<td>466</td>
<td>456</td>
</tr>
<tr>
<td>5</td>
<td>398 (30.4)</td>
<td>493 (0.086)</td>
<td>536</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>404 (27.2)</td>
<td>528 (0.75)</td>
<td>527</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>351 (31.4)</td>
<td>448 (0.068)</td>
<td>465</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>428 (44.9)</td>
<td>534 (0.58)</td>
<td>530</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>398 (30.4)</td>
<td>493 (0.086)</td>
<td>536</td>
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corresponding free chromophores. The highest quantum yield (0.55) is obtained, as expected, for diphenylamino substituted copolymer CP2. The copolymers CP1-3 are also luminescent either in powder and thin film states. For each copolymer, the emission wavelength maxima are slightly blue-shifted in the thin film state compared to those observed in the powder state and in dichloromethane solution (except for CP3).

In previous studies, we have described the important emission solvatochromism of push-pull pyrimidine chromophores: a bathochromic shift of the emission band is observed with increasing solvent polarity as predicted by using the Dimroth-Reichardt polarity parameter (ET(30)) whereas the absorption wavelength is not significantly shifted. Copolymers CP2 and CP3 exhibit the same characteristics. In the case of CP1, a positive emission solvatochromism is observed from Toluene (ET(30) = 33.9) to Acetone (ET(30) = 40.7). A decrease of emission maxima is observed for a more polar solvent (MeCN and DMSO); this might be explained by an encapsulation of the chromophore fragments into the polymer structure which is not observed in the case of CP2 and CP3 that bear more voluminous dye units.

In previous studies, we also demonstrated the ability of arylvinylpyrimidines to act as colorimetric and luminescent pH sensors due to the basic character of the nitrogen atoms of the pyrimidine ring. This is also the case of CP1–CP3. A dichloromethane solution of the copolymers CP1–CP3 underwent a significant color change upon protonation due to an increased charge transfer from the donors to the pyrimidinium moiety (Table 4). This color change is fully reversible by neutralization with a base such as Et3N. The changes observed in the UV–Vis spectra of CP1 are illustrated in Fig. 2. The increase in the concentration of TFA led to the progressive attenuation of the absorption band for the neutral forms and the appearance of a new, more intense red-shifted band corresponding to the protonated species. As far as the fluorescence response is concerned, in the case of amino substituted chromophores, the emission is partially (CP1) or totally (CP2) quenched. However, in the case of methoxy-substituted chromophores, the highest quantum yield (0.55) is obtained, as expected, for diphenylamino substituted copolymer CP2. The copolymers CP1-3 are also luminescent either in powder and thin film states. For each copolymer, the emission wavelength maxima are slightly blue-shifted in the thin film state compared to those observed in the powder state and in dichloromethane solution (except for CP3).

Table 2
Data for synthesized copolymers.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mw (g mol⁻¹)</th>
<th>Polydispersity</th>
<th>Weight % of chromophore</th>
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<tr>
<td>CP1</td>
<td>2034</td>
<td>1.61</td>
<td>5.4</td>
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<tr>
<td>CP2</td>
<td>2007</td>
<td>1.53</td>
<td>2.5</td>
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<tr>
<td>CP3</td>
<td>2996</td>
<td>1.79</td>
<td>7.1</td>
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</tbody>
</table>

a Molecular weight (Mw) and polydispersity were determined by SEC using polystyrene as the standard.
b Determined by UV–Vis measurement.

Table 3
Emission solvatochromism of copolymers CP1–CP3 in aprotic solvents.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>λabs (nm)</th>
<th>λem (nm)</th>
<th>(Φf)</th>
<th>λabs (nm)</th>
<th>λem (nm)</th>
<th>(Φf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>394</td>
<td>525</td>
<td>0.14</td>
<td>515</td>
<td>603</td>
<td>0.063</td>
</tr>
<tr>
<td>CP2</td>
<td>402</td>
<td>522</td>
<td>0.55</td>
<td>515</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CP3</td>
<td>360</td>
<td>450</td>
<td>0.11</td>
<td>435</td>
<td>565</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Fig. 1. Normalized emission of copolymer CP2 in various solvents.

Table 4
Optical properties of copolymers CP1–CP3 with and without the addition of TFA.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>CH₂Cl₂</th>
<th>TFA 10⁻³ M in CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λabs (nm)</td>
<td>λem (nm) (Φf)</td>
</tr>
<tr>
<td>CP1</td>
<td>394</td>
<td>525 (0.14)</td>
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<tr>
<td>CP2</td>
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<td>CP3</td>
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chromophores (CP3), an increase of the luminescence intensity is observed upon protonation (Fig. 3). The emission is also red-shifted due to an increase in the charge transfer into the chromophore fragments (see Fig. 4).

To conclude, we have efficiently synthesized a series of polymethyl methacrylate based copolymers bearing aryl-vinylpyrimidine chromophores. The macromolecules display similar photophysical properties in solution compared to the free chromophores. The thin film of these copolymers was obtained and also exhibits strong luminescence. Due to their sensibility to polarity and pH, these materials have potential for sensing applications. Investigations in this direction are currently being carried out in our laboratories.

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