New Poly(phenylenevinylene)-Methyl Methacrylate-Based Photonic Crystals

SYLVAIN ACHELLE,[1] ÁLVARO BLANCO,[2] MARTÍN LÓPEZ-GARCÍA,[2] RICCARDO SAPIENZA,[2] MARTA IBISATE,[2] CEFE LÓPEZ,[2] JULIÁN RODRÍGUEZ-LÓPEZ[1]

[1]Facultad de Química, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, 10, Ciudad Real 13071, Spain

[2]Instituto de Ciencia de Materiales de Madrid (CSIC), C/ Sor Juana Inés de la Cruz, 3, Madrid 28049, Spain

Received 4 February 2010; accepted 29 March 2010
DOI: 10.1002/pola.24049

ABSTRACT: Monodisperse colloids have been prepared efficiently by copolymerization of methyl methacrylate and fluorescent first- and second-generation poly(phenylenevinylene) dendrons under surfactant-free emulsion polymerization conditions. The copolymers were characterized by UV–vis and fluorescence spectroscopy and size exclusion chromatography. Transmission electron microscopy revealed that the copolymers were microspheres with smooth surfaces and narrow dispersity. The bead diameter could be varied by changing the monomer/water ratio. The materials could be crystallized to give polymer opal photonic crystals. The emission was not affected by the periodic structure because of the large spectral distance between the emission and the pseudogap position. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2659–2665, 2010

KEYWORDS: colloids; emulsion polymerization; fluorescence; photonic crystals; PPV dendrimers

INTRODUCTION Over the past decade, there has been considerable interest in the synthesis and study of functional and patterned artificial opals.[1] Such materials, which are also called photonic crystals, consist of self-assembled colloidal crystals with diameters ranging from 200 to 900 nm. As a result of their periodic nanostructure, the assemblies are able to reflect light that matches their periodicity [ultraviolet (UV) to infrared (IR) radiation depending on the size of the colloids]. The range of reflected wavelengths is known as a photonic band gap, an energy interval in which photonic states are not present. Artificial opals are commonly formed by silica[2] or polymer[3] beads, with the latter systems having superior optical quality.

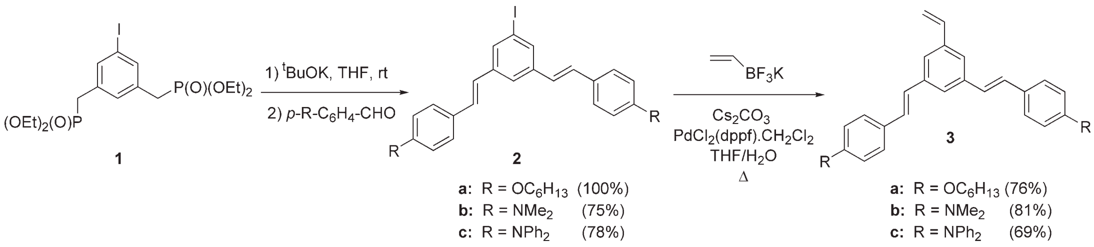
Polymer-based opals can be prepared from various types of polymer colloids (mainly polystyrene or polymethacrylates).[4] To obtain a high-quality polymer opal, it is important to prepare a stable polymer colloid with a spherical geometry and a high monodispersity (polydispersity less than 5%). This process can be carried out by the surfactant-free emulsion polymerization (SFEP) technique.[5]

One of the most important aspects in the study of functional artificial opals concerns the incorporation of fluorescent materials to investigate the influence of the photonic band structure on photoluminescence properties.[6] In particular, opals with fluorescent dyes can show an enhanced stimulated emission that can lead to applications such as in low-threshold lasers.[7] The incorporation of such units can be carried out by infiltrating the opal with fluorescent material from solution[8] or by coating of the preformed spheres.[9] However, self-aggregation of dye molecules at high concentrations often results in almost complete suppression of fluorescence. Another possibility consists of incorporating the fluorophore directly into the matrix, but generally the dye is not covalently bonded to the photonic crystal elements.[10]

Monodisperse dendritic materials have emerged as attractive candidates for photonic applications. Dendritic poly(phenylenevinylene)s (PPVdend), also called stilbenoid dendrimers, represent an important group within this class of molecules. Numerous different studies have been published to date concerning the synthesis and properties of these materials.[11] For example, such compounds have been used successfully as light-emitting materials.[12] Therefore, PPVdend are good candidates to be incorporated into artificial opals as fluorescent dyes.

Only a few examples of artificial opals that incorporate dendrimers can be found in the literature, but they are not used as fluorescent dyes.[13] We describe here the preparation of monodisperse colloids from first- and second-generation PPVdend-methyl methacrylate (MMA) copolymers, which can be used to form patterned opals. The optical properties and, in particular, the influence of the photonic band gap on the spontaneous-emission lifetimes of the resulting materials were studied.

Additional Supporting Information may be found in the online version of this article. Correspondence to: J. Rodríguez-López (E-mail: julian.rodriguez@uclm.es)
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 2659–2665 (2010) © 2010 Wiley Periodicals, Inc.



SCHEME 1 Synthesis of first-generation PPV dendrons by HWE and Suzuki reactions.

EXPERIMENTAL

Chemicals

MMA stabilized with *tert*-butylcatechol was purified by washing with aqueous 2*M* NaOH and water, dried over magnesium sulfate, and used immediately. All other commercially available products were obtained from Aldrich or Acros and were used without further purification. Deionized water was obtained from a Milli-Q system.

Synthesis of Dendritic Monomers

Experimental details for the synthesis of dendritic monomers are given in the Supporting Information.

Synthesis of Copolymer Microspheres

The colloid particles were synthesized in a 250-mL flask fitted with an argon inlet, a condenser, and a mechanical stirrer by SFEP in batches from 100 to 150 mL reaction volume. The flask was charged with water and potassium peroxodisulfate (0.01*M*) and was immersed in an oil bath preheated at 90 °C and flushed with argon for 30 min. The internal temperature reached 75 °C. A solution of the dendritic monomer (0.5 mol %) in MMA was added rapidly, and the polymerization started. During the polymerization, the mixture was stirred at 1200 rpm. After 5 h, the flask was opened (oxygen), and the colloids were purified from large agglomerations by filtration through glass wool, followed by repeated centrifugation, wash, and redispersion cycles. The resulting suspensions were almost free of salt and low molecular weight impurities. The suspensions were stored at a concentration of 5–20 wt %.

Colloidal Crystal Fabrication

Copolymer opal photonic crystals were fabricated by the vertical deposition method.[14] Glass substrates previously cleaned with piranha were fixed vertically into the copolymer suspension with a concentration of 0.1 wt % and were maintained for 3–4 days at constant temperature (45 °C).

RESULTS AND DISCUSSION

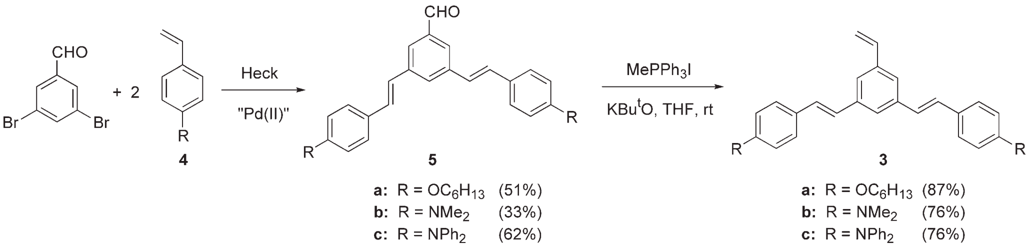
Synthesis of Dendritic Monomers

The starting first-generation PPV dendrons required for the copolymerization with MMA were easily synthesized by two different approaches used previously by some of us in the preparation of PPV dendritic architectures.[11]

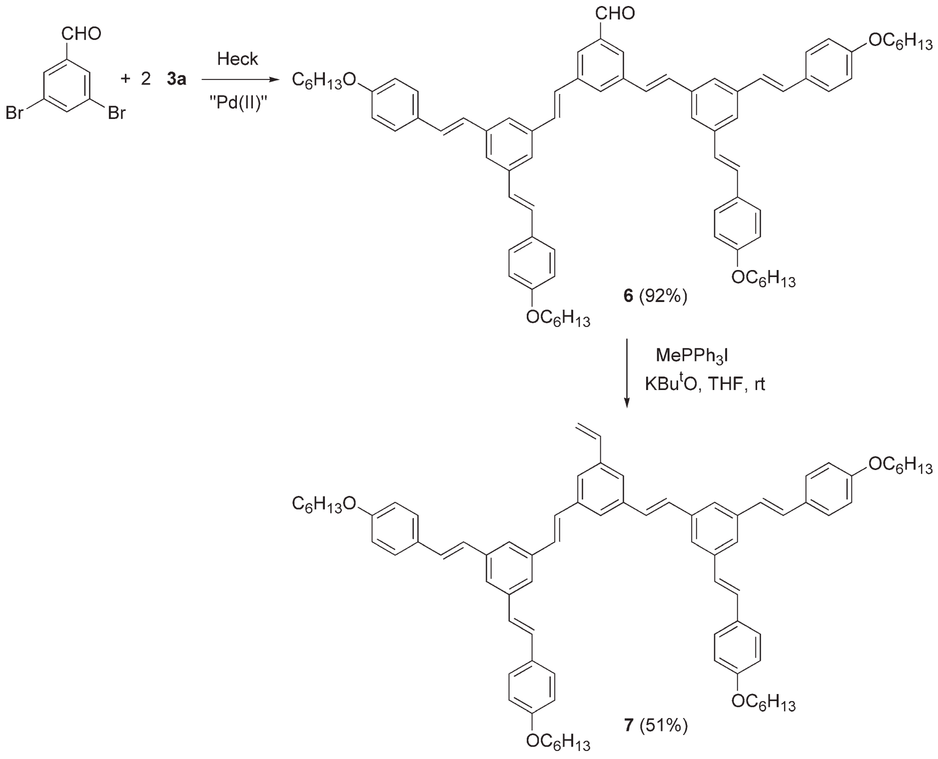
The first reaction sequence involved the Horner-Wadsworth-Emmons reaction of two molecules of the appropriate *para*-substituted benzaldehyde derivative with the readily available diphosphonate **1**[15] to form the first-generation aryl iodides **2a**–**c** (Scheme 1). This step was followed by a Suzuki cross coupling reaction with potassium vinyltrifluoroborate[16] to give the desired products **3a**–**c** in yields ranging from 69 to 81%.

The second method started with the Heck cross coupling reaction[17] of two molecules of the easily accessible *para*-substituted styrene derivatives **4** with 3,5-dibromobenzaldehyde. In this way, the corresponding first-generation PPV dendritic aldehydes **5a**–**c** were obtained in moderate yield. A Wittig reaction with methyltriphenylphosphonium iodide afforded the first-generation dendritic compounds **3a**–**c** in good yield (Scheme 2). Starting from **3a**, and following the aforementioned methodology, the second-generation PPV dendron **7** was also obtained (Scheme 3).

All the dendrons bear a polymerizable styryl group at the focal point and have an all-*trans* stereochemistry for the double bonds, a structure that was unequivocally established on the basis of the coupling constant of the vinylic protons in the ^1H NMR spectra ($J \cong 16$ Hz). Furthermore, the exact molecular weights were measured by matrix-assisted laser desorption ionization (MALDI) time-of-flight mass spectrometry, with all the experimental results in good agreement with the expected molecular weights for the structures. The optical properties are listed in Table 1.



SCHEME 2 Synthesis of first-generation PPV dendrons by Heck and Wittig reactions.



SCHEME 3 Preparation of the second-generation PPV dendron **7**.

Because of the *meta* arrangement of the dendrons, the absorption spectra consisted of a superposition of the absorptions due to the different stilbene chromophores. The introduction of different groups has a negligible influence on the extinction coefficients, although a red shift of the absorption band was observed on increasing the electron-donating strength of the peripheral group. Comparison of the first-generation monomer **3a** and second-generation monomer **7** shows, as one would expect, that the molar extinction coefficient increases with increasing generation, whereas the fluorescence quantum yield remains constant. The dimethylamino derivative **3b** presents a lower quantum yield in comparison with the hexyloxy derivative **3a**. The diphenylamino derivative **3c** exhibits the highest extinction coefficient and quantum yield.

TABLE 1 UV-Vis and Photoluminescence Data for First- and Second-Generation PPV Dendrons and Copolymers in Dichloromethane

Compound[a]	UV–Vis, λ_{max} (nm) (ε, M^{-1} cm^{-1})	PL, λ_{max}, (nm)	Φ_F[b]
3a	327 (36,900)	408	0.33
3b	366 (52,400)	459	0.24
3c	300 (41,100) 378 (67,900)	460	0.70
7	328 (134,000)	421	0.32
CP1a	326	409	0.27
CP1b	370	455	0.15
CP1c	300, 376	458	0.74
CP2	330	422	0.21

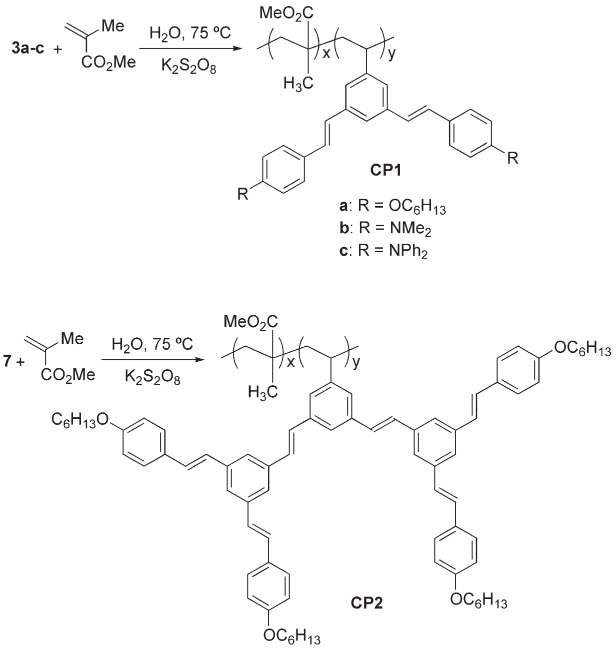
[a] Spectra for PPV dendron **3a–c**, **7** were recorded at $c \cong 1{\cdot}10^{-5}$ to $5{\cdot}10^{-6}$ M. **CP1a–c** and **CP2** were recorded at $c = 10$ g/L.

[b] Fluorescence quantum yield (±10%) obtained using quinine sulfate in 0.1 M H_2SO_4 ($\Phi_f = 0.58$) as standard.[18]

Synthesis and Characterization of Copolymers

Although the homopolymerization of various type of dendrons with either styryl or acrylate groups has been reported widely,[19] only a few examples involving copolymerization have been described.[20] The copolymerization of PPV dendrons with a styryl focal point (**3a–c**, **7**) and MMA (0.5 mol % of dendron) was carried out in water at 75 °C under conventional radical, surfactant-free emulsion conditions (Scheme 4).[21] This method led to monodisperse colloidal suspensions with submicron scale beads (see later) of copolymers **CP1a–c** and **CP2**.

It proved difficult to determine the chemical structures of the copolymers obtained because of the low concentrations of dendritic monomer used. NMR is not a sufficiently sensitive technique, and signals corresponding to the dendron were 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 MMA moiety (1724 cm^{-1}). However, the UV–vis and fluorescence spectra of CH_2Cl_2 solutions of the copolymers showed characteristic bands for PPV dendrons, indicating that the fluorescent dendritic monomer had been incorporated into the chain (Table 1). The photophysical properties of copolymers **CP1a–c** and **CP2** are similar to those of their corresponding monomers, although the fluorescence quantum yields are usually a little lower. The colloid obtained by polymerization under the same conditions of MMA in the presence of a PPV dendron without a polymerizable styryl



SCHEME 4 Copolymerization of PPV dendrons and MMA.

group (i.e., an iodo group at the focal point) did not show any emission band. This finding provides evidence that the dendrons are effectively integrated into the macromolecules and are covalently bonded. The level of incorporation of the dendrons was estimated by UV–vis on the assumption of a similar molar absorptivity for the free dendron and for the linked dendron. The level of functionalization was approximately 0.05% for the first-generation compounds **3a**–**c**, although in the case of the second-generation dendron **7** this percentage was lower—probably due to the low solubility of this compound in MMA. A decrease in the incorporation ratio observed on increasing the generation number in copolymerizations has been observed previously.[20]

Size exclusion chromatography and MALDI analyses also indicated the absence of unreacted dendrons in the purified colloidal beads. The synthesized copolymers showed molecular weights ranging between 39,499 and 74,368 g mol^{-1} and polydispersities ranging between 1.10 and 1.29 (Table 2).

The sphere diameter, which can be varied by changing the monomer/water ratio, was determined by transmission electron microscopy (TEM) (Table 2). All colloids described have a smooth surface and a narrow size distribution (less than 5%) and should, therefore, have the potential to crystallize in an opal structure. Some examples of TEM images are given in Figure 1.

Synthesis and Characterization of Opals

Thin opal films were grown on glass substrates by means of the vertical deposition method from aqueous suspensions of copolymer spheres having different diameters (Table 2). The final thickness can be easily controlled by varying experimental parameters such as concentration, temperature, or humidity.[22] Details on the fabrication and previous optical characterization by means of reflection and transmission spectroscopy can be found elsewhere.[14] Artificial opals self-assemble in an fcc lattice with (111) planes parallel to the substrate, an arrangement that is very convenient for further optical characterization. A scanning electron microscopy (SEM) image of a film obtained from sample S3 (sphere size: 180 nm) is shown in Figure 2. This picture summarizes the average quality of the samples prepared. Polycrystalline structures with a domain size of approximately 5–10μ are caused by polydispersity. Image processing yields a lattice parameter on the surface of 250 nm—a value slightly higher than expected, which indicates a close-packed structure that is not perfect. This situation was also observed in the optical characterization, as discussed later.

Optical characterization was performed using a Fourier transform infrared spectrophotometer attached to an optical microscope. Normal incidence reflectance measurements explore directions perpendicular to (111) planes and are sensitive to sphere stacking (monolayers) and, therefore, gaps occurring in that particular direction (ΓL direction within the first Brillouin zone). The specular reflectance of the opal film obtained from S3 in the visible range is shown in Figure 3. The observed band corresponds to a photonic pseudogap (dependent on the propagation direction within the structure) and its spectral position, λ_B (at normal incidence), can be approximately estimated using the following relation:

TABLE 2 Data for Synthesized Colloidal Beads

Sample	Copolymer	Batch (mL)	Monomer (mL)	M_w[a] (g mol^{-1})	Polydispersity[a]	Sphere Diameter[b] (nm)
S1	**CP1a**	150	4	74,368	1.29	118
S2	**CP1a**	100	8	39,499	1.17	200
S3	**CP1b**	100	8	47,096	1.10	180
S4	**CP1b**	100	6	50,490	1.14	150
S5	**CP1c**	100	7.5	42,614	1.24	234
S6	**CP2**	100	8	43,992	1.24	208

[a] Molecular weight (M_w) and polydispersity were determined by SEC using polystyrene as standard.

[b] Determined by TEM.

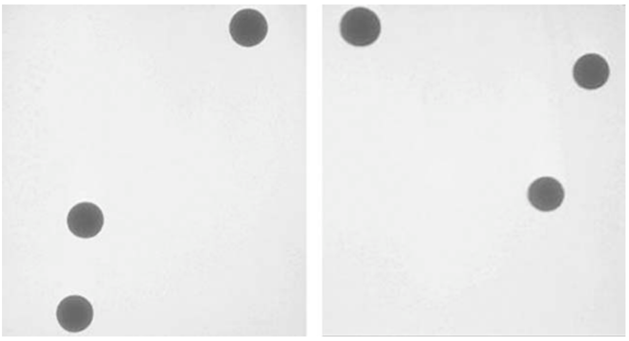


FIGURE 1 TEM images of colloidal samples S2 (left) and S4 (right).

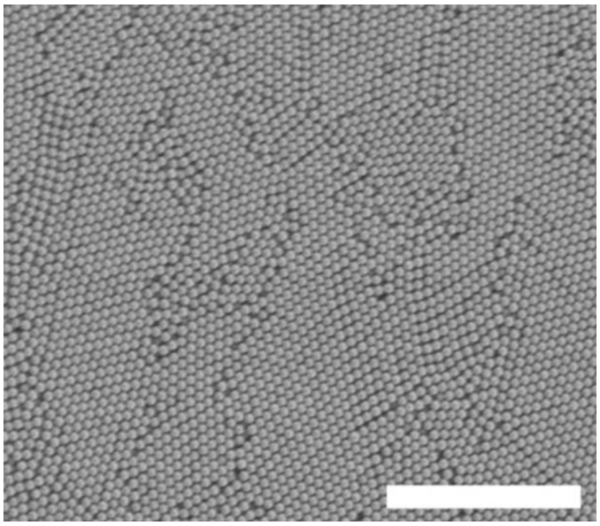


FIGURE 2 SEM image of a freshly prepared film of S3 (sphere diameter: 180 nm). Scale bar is 5μ.

$$\lambda_{\mathrm{B}} = 2 \cdot \sqrt{\frac{2}{3}} \cdot D \cdot n_{\mathrm{eff}} \quad (1)$$

where D is the sphere diameter, and n_{eff} is the average refractive index of the structure. The latter value was calculated taking into account the components of the structure and their filling fraction as follows:

$$n_{\mathrm{eff}} = (n_{\mathrm{p}}^2 \cdot 0.74 + 0.26)^{1/2} \quad (2)$$

n_{p} being the polymer refractive index (taken as 1.59) and taking into account the fcc filling fraction of 0.74. From this formula, the estimated sphere diameter corresponding to a peak spectral value of 578 nm is 242 nm, which is consistent with the value obtained by SEM analysis. Rapid oscillations observed in the low energy range of the spectrum are Fabry-Perot modes due to sample thickness. These oscillations can also be used to calculate the total thickness of the structure, which in this particular case is 50 monolayers (12μ).[23]

Emission measurements were carried out on the bulk material, and opals fabricated with the different spheres are shown in Table 2. The equipment used for the measurements was a Hamamatsu streak camera coupled to an 80 MHz repetition rate UV laser ($\lambda = 355$ nm) pulsed at 12 ps. The spectral range available with this equipment covers the visible and ultraviolet spectrum (355–800 nm). At the same time, decay time measurements were performed. The temporal range between 70 ps and 2 ns is available. The first measurements were made without any photonic structure over the emitter, and the results show that lifetimes of the molecule are approximately 200–300 picoseconds depending on the sample. It is important to note that decay times are multiexponential, as one would expect for organic emitters.[24] As a result, it is necessary to ignore the first 50 ps decays because of fast electronic transitions to obtain the real decay time. The decay time was obtained by adjusting the value in the first approximation to a monoexponential decay. This fitting seems to work well despite the fact that different processes are involved in the emission of the dendrimer. The measurements for a freshly prepared opal from sample S4 (copolymer **CP1b**) are shown in Figure 4. Notice that the increase in the emission lifetime in nanostructured dendrimers (from 300 to 500–600 ps) is probably due to a barely change in the chemical environment rather than any photonic effect, which in any case should take place within the photonic band gap region, approximately 500–600 nm, where the decay time curve is almost flat (approximately 575 ps).

It is well known that photonic crystals can produce changes in the local density of states that might inhibit or enhance emission for any emitter inside the lattice such as quantum dots[25] or organic emitters. In this case, it would be expected that some change in emission would occur for the opals fabricated with the samples in Table 2 because of the periodicity of the media. However, it can be observed that the emission maxima of the opals (approximately 450 nm) and the pseudogap of the photonic crystals (around 590 nm) are

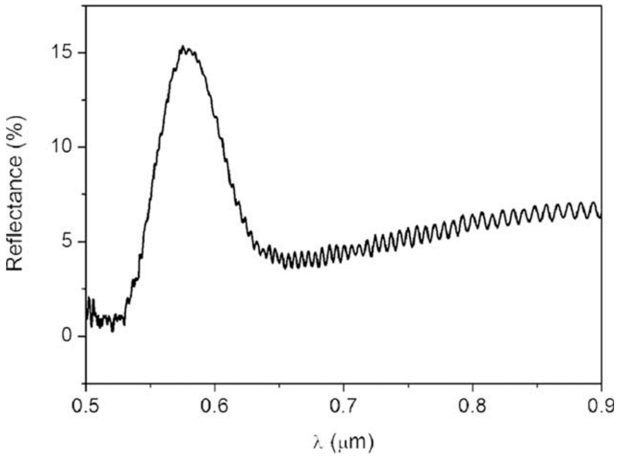


FIGURE 3 Optical reflectance of the opal film obtained from sample S3. The observed peak corresponds to the first photonic pseudogap (Bragg Peak). Fabry-Perot oscillations from 0.65 to 0.9μ can also be observed.

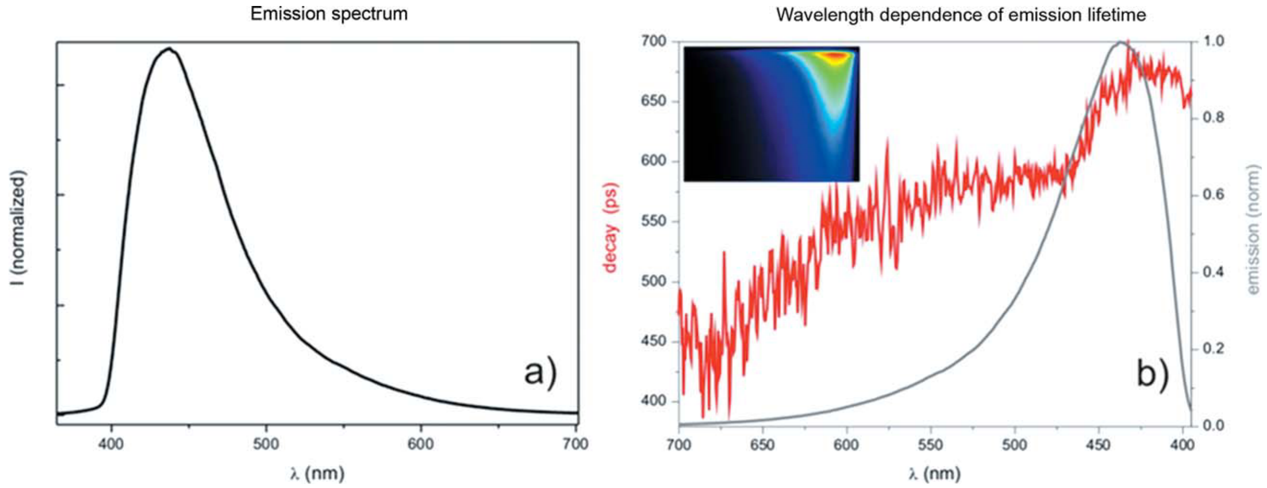


FIGURE 4 (a) Emission spectrum of a freshly prepared opal from sample S4 (copolymer **CP1b**). (b) Wavelength dependence of the emission lifetime for the same sample.

separated by more than 140 nm. Therefore, because emission does not take place in the pseudogap spectral region, the crystal does not seem to have any effect on the photonic crystal emission intensity or lifetime.

CONCLUSIONS

In this article, we have described the copolymerization of highly fluorescent first- and second-generation PPV dendrons with MMA by SFEP. The copolymers are obtained as monodisperse colloidal suspensions of microspheres with smooth surfaces. The fluorescent dendrons are chemically bonded to the polymer main chain, and their emission properties are preserved. Artificial photonic crystals were synthesized using these copolymers; however, the emission is not affected by the opal structure because of the difference between the pseudogaps of the opals and the emission wavelength. Investigations are currently underway aimed at obtaining photonic crystals with a periodicity that matches the emission band of the dendrons.

This work was funded by the Ministerio de Ciencia e Innovación, Spain—projects CSD2006-0019 (Nanolight.es), MAT2006-09062, and CTQ2006-08871 (co-funded by FEDER, European Union) and the Junta de Comunidades de Castilla-La Mancha—project PCI08-0033.

REFERENCES AND NOTES

1 (a) Lange, B.; Fleischhaker, F.; Zentel, R. Macromol Rapid Commun 2007, 28, 1291–1311; (b) López, C. Adv Mater 2003, 15, 1679–1704.

2 Míguez, H.; López, C.; Meseguer, F.; Blanco, A.; Vázquez, L.; Mayoral, R.; Ocaña, M.; Fornés, V.; Mifsud, A. Appl Phys Lett 1997, 71, 1148–1150.

3 (a) Edrington, A. C.; Urbas, A. M.; DeRege, P.; Chen, C. X.; Swager, T. M.; Hadjichristidis, N.; Xenidou, M.; Fetters, L. J.; Joannopoulos, J. D.; Fink, Y.; Thomas, E. L. Adv Mater 2001, 13, 421–425; (b) Lange, B.; Metz, N.; Tahir, M. N.; Fleischhaker, F.; Theato, P.; Schröder, H.-C.; Müller, W. E. G.; Tremel, W.; Zentel, R. Macromol Rapid Commun 2007, 28, 1987–1994; (c) Texter, J. CR Chim 2003, 6, 1425–1433.

4 Egen, M.; Zentel, R. Chem Mater 2002, 14, 2176–2183.

5 (a) Goodwin, J. W.; Hearn, J.; Ho, C. C.; Ottewill, R. H. Colloid Polym Sci 1974, 252, 464–471; (b) Egen, M.; Zentel, R. Macromol Chem Phys 2004, 205, 1479–1488; (c) Mouaziz, H.; Larsson, A.; Sherrington, D. C. Macromolecules 2004, 37, 1319–1323.

6 (a) Lodahl, P.; van Driel, A. F.; Nikolaev, I. S.; Irman, A.; Overgaag, K.; Vanmaekelbergh, D.; Vos, W. L. Nature 2004, 430, 654–657; (b) Blanco, A.; López, C.; Mayoral, R.; Míguez, H.; Meseguer, F.; Mifsud, A.; Herrero, J. Appl Phys Lett 1998, 73, 1781–1783; (c) Noda, S.; Fujita, M.; Asano, T. Nat Photonics 2007, 1, 449–458.

7 (a) Kopp, V. I.; Fan, B.; Vithana, H. K. M.; Genack, A. Z. Opt Lett 1998, 23, 1707–1709; (b) Loncar, M.; Yoshie, T.; Scherer, A.; Gogna, P.; Qiu, Y. Appl Phys Lett 2002, 81, 2680–2682.

8 Romanov, S. G.; Maka, T.; Sotomayor Torres, C. M.; Müller, M.; Zentel, R. Appl Phys Lett 1999, 75, 1057–1059.

9 (a) Kim, K.; Webster, S.; Levi, N.; Carroll, D. L.; Pinto, M. R.; Schanze, K. S. Langmuir 2005, 21, 5207–5211; (b) Han, M. G.; Foulger, S. H. Chem Commun 2004, 2154–2155.

10 (a) Fleischhaker, F.; Zentel, R. Chem Mater 2005, 17, 1346–1351; (b) Onodera, T.; Nakamura, M.; Takaya, Y.; Masuhara, A.; Wakayama, Y.; Nemoto, N.; Nakanishi, H.; Oikawa, H. J Phys Chem C 2009, 113, 11647–11651.

11 García-Martínez, J. C.; Díez-Barra, E.; Rodríguez-López, J. Curr Org Synth 2008, 5, 267–290.

12 (a) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. Adv Mater 2007, 19, 1675–1688; (b) Lo, S.-C.; Burn, P. L. Chem Rev 2007, 107, 1097–1116.

13 (a) Li, M.; Wang, J.; Feng, L.; Wang, B.; Jia, X.; Jiang, L.; Song, Y.; Zhu, D. Colloids Surf A 2006, 290, 233–238; (b) Jin, F.; Li, C.-F.; Dong, X.-Z.; Chen, W.-Q.; Duan, X.-M. Appl Phys Lett 2006, 89, 241101.

14 Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. Chem Mater 1999, 11, 2132–2140.

15 Díez-Barra, E.; García-Martínez, J. C.; Rodríguez-López, J. J Org Chem 2003, 68, 832–838.

16 Molander, G. A.; Rodríguez Rivero, M. Org Lett 2002, 4, 107–109.

17 Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. Macromolecules 1999, 32, 5985–5993.

18 Melhuish, W. H. J Phys Chem 1961, 65, 229–235.

19 (a) Frauenrath, H. Prog Polym Sci 2005, 30, 325–384; (b) Al-Hellani, R.; Schlüter, A. D. Macromolecules, 2006, 39, 8943–8951; (c) Zhang, A.; Okrasa, L.; Pakula, T.; Schlüter, A. D. J Am Chem Soc 2004, 126, 6658–6666.

20 (a) Hawker, C. J.; Fréchet, J. M. J. Polymer, 1992, 33, 1507–1511; (b) Xiong, X.; Chen, Y.; Feng, S.; Wang, W. Macromolecules 2007, 40, 9084–9093.

21 Zhao, C.-S.; Liu, X.-L.; Yang, M.; Fang, J.-Y.; Zhang, J.-J.; Liu, F.–Q. Dyes Pigments 2009, 82, 134–141.

22 Zhang, J.; Sun, Z.; Yang, B. Curr Opin Colloid Int 2009, 14, 103–114.

23 The total thickness *t*, which can be estimated from Fabry-Perot oscillations, is proportional to the total number of layers N according to $t = N \cdot d_{111}$, where d_{111} is the space between (111) planes, sqrt(2/3)·*D*, being *D* the sphere diameter.

24 Makhal, A.; Kumar, P.; Lemmens, P.; Pal, S. K. J Fluoresc 2010, 20, 283–290.

25 Lodahl, P.; van Driel, A. F.; Nikolaev, I. S.; Irman, A.; Overgaag, K.; Vanmaekelbergh, D.; Vos, W. L. Nature 2004, 430, 654–657.