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A simple and cost-efficient method for fluorescent microsphere synthesis, which does not require any fluorescent monomers or modification steps to incorporate fluorescent moieties into the polymer particles, is reported. Using rhodamine B and benzophenone as bimolecular initiation system in type II photoinitiated precipitation polymerization, the method enables the preparation of fluorescent microspheres in one step, at room temperature and without the need for a stabilizer or surfactant of any type.

1. Introduction

From flow cytometry to sensor development, fluorescent polymer microspheres have found key applications in materials science.[1] Precipitation polymerization (PP), a surfactant and emulsifier free polymer particle synthesis technique, yields micron size polymer particles with uniform size.[2] A common method to incorporate fluorescence properties into the polymer microspheres is to use fluorescent monomer(s) during the polymerization step in PP. For instance, a pyrene functional styrene monomer is copolymerized with ethylene glycol dimethacrylate in PP to yield fluorescent particles.[3] In another work, fluorescent core-shell particles with *N*-vinylcarbazole unit in the shell were obtained by two stage distillation PP.[4] In another example, coumarin, fluorescein, rhodamine, and cyanine groups were incorporated into polymer nanoparticles by using their monomers in the polymerization mixture.[5] Despite the ease of the method and no requirement for additional functionalization step, fluorescent monomers are usually expensive due to their synthetic procedure. In addition, some of the fluorescent monomers are inevitably lost during polymerization step, not only because the polymerization does not operate with full conversion but also because of the difference in the reactivity of the monomer(s). Alternatively, fluorescent monomers can be prepared in house prior to their use.[1f,6] An innovative photoligation approach for fluorescent particle synthesis in the absence of fluorescent molecules was also developed.[7] The method is based on photocrosslinking of prefunctionalized soluble polymers via nitrile-imine mediated tetrazole-ene cycloaddition (NITEC) reaction to yield fluorescent pyrazoline group and particles in the submicron range (0.25–0.75 μm) were obtained in exceptionally short times for PP. Alternatively, fluorescent molecules can be introduced to the microspheres via click reaction, NITEC photoligation, or by acidification that triggers the aromatization of the ligation points to form naphthalene.[8] The examples above illustrate the need for more effective and/or cost efficient ways to incorporate fluorescent units into the polymer microspheres.

Photoinitiators can be categorized as type I or type II depending on how they generate radicals. Type I photoinitiators are unimolecular photoinitiators, which absorb light to generate radicals through homolytic bond cleavage. On the other hand, type II initiators require a photosensitizer molecule and a suitable hydrogen donor to start polymerization; therefore, they are bimolecular photoinitiating systems unless a special effort is made to attach two components.[9] The photosensitizer molecule is excited upon irradiation and abstracts hydrogen at its excited state from a co-initiator such as amines, thiols, carbazoles, alcohols, and ethers, to form radicals. Recently, we have reported the first combined use of type II photoinitiation with PP for the synthesis of alkyne functional microspheres.[10] The new method, called type II photoinitiated precipitation polymerization (T2PPP), in principle, enables the incorporation of several functionalities into the polymer microspheres in one step simply by changing the co-initiator type, without the requirement for a further modification. Using a similar methodology, more recently, we reported fluorescent hydrogel synthesis without fluorescent monomers for the first time, using rhodamine B (RhB) and benzophenone (BP) as bimolecular photoinitiation system.[11] Both reactions operate at room temperature and they benefit from the inherent characteristics of photopolymerization, in that the temporal and spatial control can be achieved by simply switching on and off the light source.[12]

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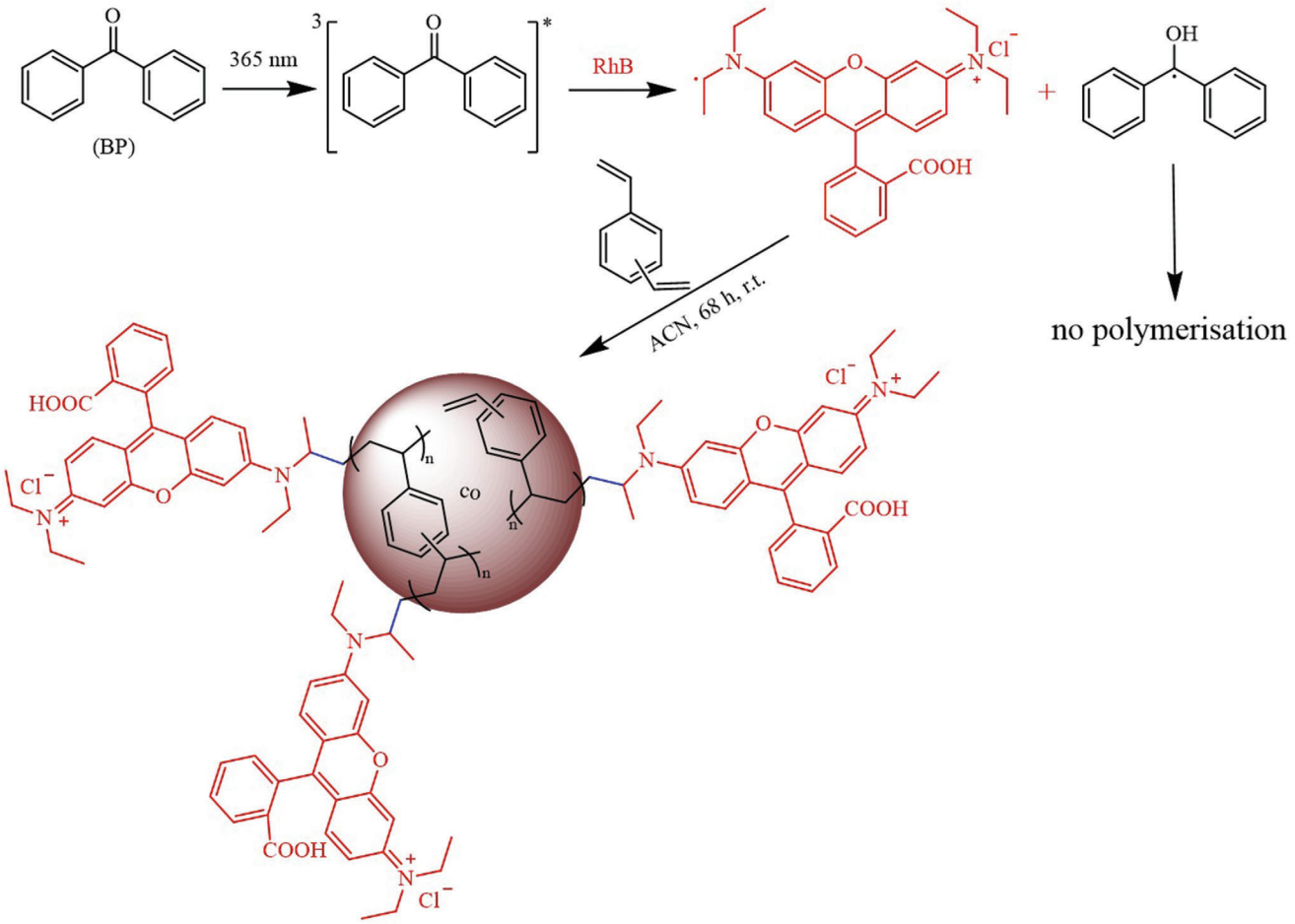

Figure 1. The proposed reaction scheme for fluorescent polyDVB synthesis and expected chemical structure of polymer particles prepared by BP and RhB in PP.

2. Results and Discussion

As a continuation of our previous works on fluorescent polymers and efforts to find easy routes for polymer functionalization, herein, we investigate the possibility of incorporating fluorescent units into highly crosslinked poly(divinylbenzene) (polyDVB) microspheres in one step, without using fluorescent monomer(s) of any type. Using inexpensive and commercially available RhB as hydrogen donor (co-initiator) and BP as photosensitizer molecule in T2PPP, we aim to immobilize rhodamine units into the polymer particles in one step at room temperature by UV irradiation. The proposed reaction scheme is illustrated in **Figure 1**.

Tertiary amines are known for their hydrogen donation ability in type II photopolymerization; therefore, the reaction is expected to occur through the hydrogen abstraction of BP from RhB to generate radical species on carbon adjacent to the tertiary amine group of the RhB moiety. The radical formed on the RhB is likely to start polymerization, since the concurrently formed ketyl radical is known to be unreactive for vinyl polymerization.[13] PP starts with a homogenous mixture of the monomer(s), initiator, and the solvent. As the reaction proceeds, oligomers start to form and precipitate out from the reaction mixture. Particles continue to grow by capturing soluble oligomers via reacting with the unreacted double bonds on the particle surface.[14] T2PPP is of no exception, with only difference being the formation mechanism of radicals that initiate polymerization. When irradiated, BP is excited and it is able to abstract a hydrogen from a suitable donor at its excited state.[15]

Initial reactions were carried out at 2% (by volume) monomer concentration, which is typical for PP, and RhB amount is gradually decreased from 2:1 to 0.1:1 RhB: BP mole ratio, while other reaction parameters including BP to DVB mole ratio (1:100), reaction time (68 h), and total reaction volume (30 mL) were held constant. **Figure 2**a,b shows the photograph of the reaction vessels before (Figure 2a) and after polymerization (Figure 2b). As can be seen, reaction mixtures were transparent at the start of the polymerization. After 68 h of UV irradiation, all samples turned into pink suspensions of polymers in acetonitrile. Figure 2c–f shows the SEM images of the polyDVB particles prepared at different BP to RhB mole ratios. Polydisperse, spherical, and discrete particles were obtained at each initiator concentration and the number average diameter of the particles increased from 0.34 to 1.17 μm, as the RhB:BP mole ratio is raised from 0.1:1 to 0.5:1 (**Table 1**, entries 3–5).

This is in parallel with the results obtained for photoinitiated PP using AIBN as the single component photoinitiator, since

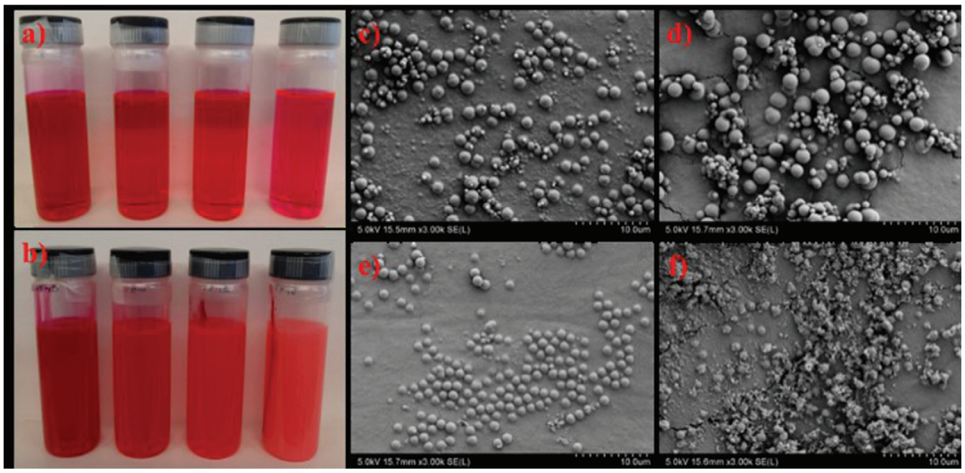

Figure 2. Photographs of the reaction vessels (from left to right, particles are prepared at 1:1, 1:0.5, 1:0.3, and 1:0.1 BP to RhB mole ratios) a) before and b) after polymerization. SEM images of the polyDVB particles prepared at c) 1:1, d) 1:0.5, e) 1:0.3, and f) 1:0.1 BP to RhB mol ratios, respectively.

Table 1. Reaction yield and particle size characteristics of the polymers prepared by using RhB and BP as photoinitiation system at different RhB and monomer concentrations.

Entry	RhB : BP [by mole]	Reaction set-up	Monomer conc. [vol%]	D_n [a] [μm]	D_w [b] [μm]	U [c]	Yield [%] [d]
1	2:1	RS	2	–	–	–	Not isolated
2	1:1	RS	2	0.99	1.52	1.533	2%, >1%
3	0.5:1	RS	2	1.17	1.96	1.674	1%, 1%
4	0.3:1	RS	2	1.13	1.30	1.158	2%, 1%
5	0.1:1	RS	2	0.34	1.12	3.274	2%, 1%
6	0.1:1	RS	3	0.27	1.13	4.219	3%
7	0.1:1	RS	4	0.56	0.91	1.639	3%
8	0.1:1	RS	5	0.42	1.19	2.817	3%
9	-	LPR	4	1.27	1.33	1.045	11%
10	0.1:1	LPR	4	1.24	1.60	1.297	3%
11	0.1:1	LPR	4	1.58	1.73	1.095	3%

[a] Number average diameter; [b] weight average diameter; [c] polydispersity index; [d] determined gravimetrically (RS, rotary shaker; LPR, low profile roller).

RhB is a component of bimolecular initiator system.[16] Surprisingly, when the RhB:BP mole ratio is further raised to 1:1, the average size of the obtained particles slightly decreased to 0.99 μm. This might be due to the fact that RhB has also absorbance in the 365 nm region, which may become more predominant at elevated concentrations, resulting in the inefficient absorption of UV light by BP. For almost every sample, polydisperse particles (PDI > 1.2) were obtained, probably due to the rotary shaker used for polymerization. In PP, reactions are often carried out at a very slow stirring rate using a magnetic stirrer or on a low profile roller at a low rolling rate to prevent the aggregation of the particles and similar results can be obtained at two different reaction set-up.[8c,17]

Table 1 summarizes the particle size and size distributions obtained by SEM images and reaction yield under different polymerization conditions. Reactions are carried out for 68 h to improve the yield of polymerization; however, the yield of the particle synthesis was equal to or lower than 3% in each case. For samples prepared at 1:1, 0.5:1, 0.3:1, and 0.1:1 RhB: BP mole ratios, reactions were repeated and similar yields were observed (Table 1, entries 2–5). Although, it is difficult to comment on such low yields, it is still observed that the yield of polymerization decreases from ≈3% to ≈1.5%, as the RhB:BP mole ratio increases from 0.1:1 to 1:1 and as the mole ratio is further raised to 2:1, no product could be isolated after filtration (Table 1, entry 1). This trend might be due to the fact that RhB has also absorbance in the 365 nm region, albeit to a lesser extent, which may have blocked the UV light that would have been otherwise absorbed by BP, as discussed above. As the reaction proceeds, insoluble particles starts to form and precipitate out from the solution, resulting in a pink suspension of crosslinked polymers that makes the penetration of light through the reaction vessel harder, which may have also contributed to the low polymerization yield. Therefore, the reaction yield can possibly be improved by using thinner but longer reaction tubes, which have higher surface area to volume ratios.

Figure 3a shows the picture under 365 nm UV irradiation of the particles prepared at different RhB concentrations. For this purpose, each polymer sample (≈1 mg) was suspended in 3 mL acetone and ultrasonicated for ≈2 min. As can be seen, all samples exhibited fluorescence when irradiated at 365 nm. Figure 3b shows the picture of the particle suspensions after leaving overnight (20 h) to settle. As can be seen, a clear and transparent acetone layer is observed after the settlement of the pink particles, indicating that the leakage of RhB is negligible, if not zero. The leakage of fluorescent units from the particles was also studied by fluorescent spectroscopy. For this purpose, 6 mL (1 mg mL^{-1}) of particle suspension in acetone is prepared, transferred into a 15 mL centrifuge tube, and was shaken on rotary shaker at 650 rpm. After 42 h of shaking, almost no peak was observed in fluorescence spectrum of the liquid phase (Figure S1-3, Supporting Information).

Figure 4 (right) shows the fluorescence emission spectra of the same polymer samples (Figure 3a) within the 550–700 nm range. When excited at 540 nm, all polymer suspensions

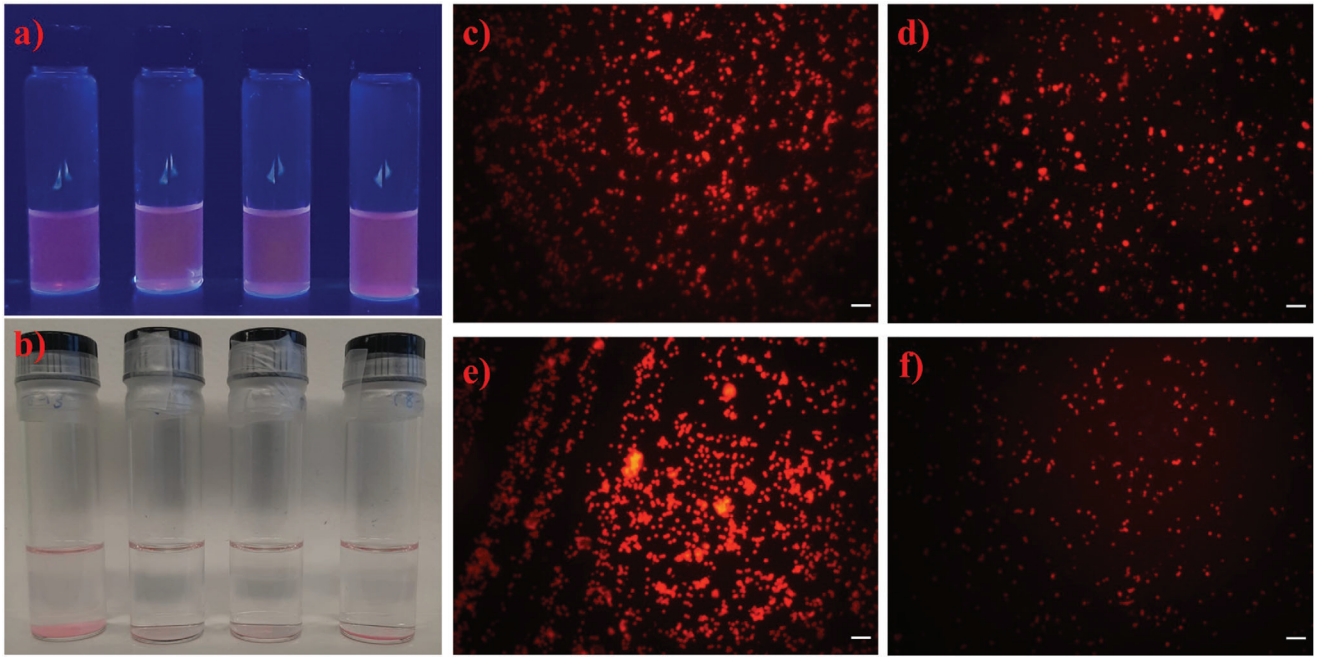

Figure 3. Picture of the particles prepared with different BP to RhB mole ratios (from left to right 1:0.1, 1:0.3, 1:0.5, 1:1 BP: RhB) under 365 nm of UV irradiation when dispersed in a) acetone and b) the picture of the particles taken in the daylight after waiting 20 h for their settlement. Fluorescent microscopy images of polyDVB particles prepared by c) 1:1, d) 1:0.5, e) 1:0.3, and f) 1:0.1 BP to RhB mole ratios, respectively (scale bar corresponds to 10 microns).

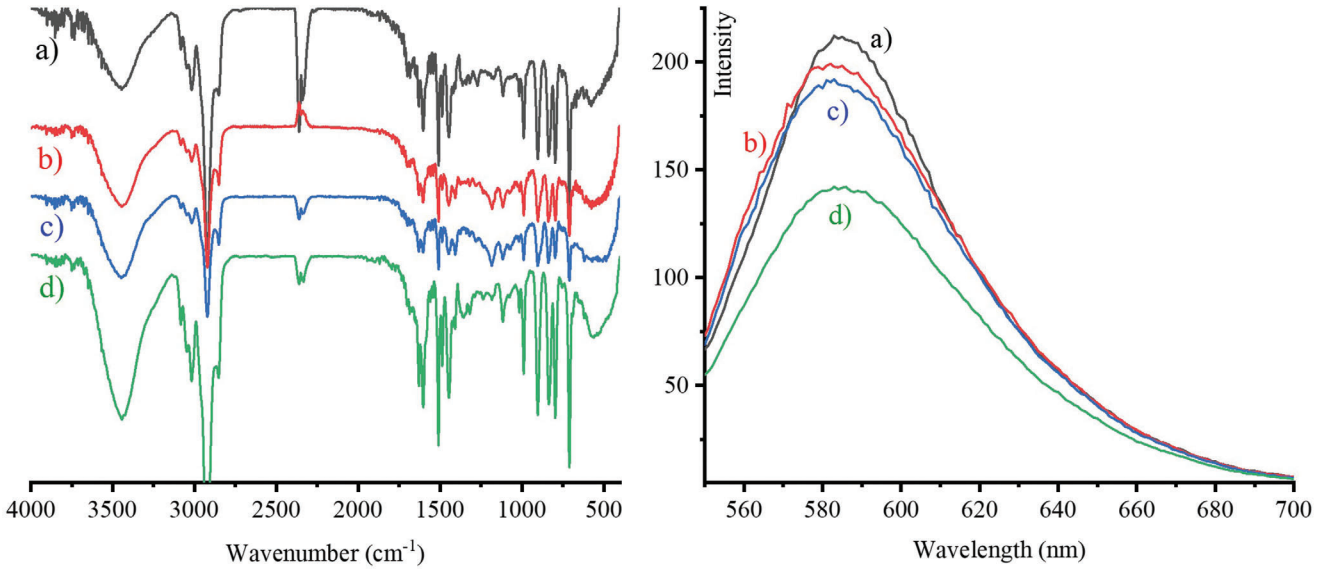

Figure 4. FTIR spectra (left) and fluorescence spectra (right) of the particles prepared at a) 1:1, b) 1:05, c) 1:0.3, and d) 1:0.1 BP to RhB mole ratios.

exhibited a broad emission spectra centered at around 590 nm, arising from the presence of fluorescent units, confirming that all the polymers are fluorescent.

Figure 3c–f shows fluorescent microscopy images of polyDVB particles prepared at different RhB concentrations. As can be seen, fluorescent particles are obtained for each batch and the fluorescence is derived from the individual particles. Dark/black areas between the particles can clearly be identified and do not contribute to the overall fluorescence. Figure 4 (left) shows the FTIR spectra of the particles prepared at different BP to RhB mole ratios (for raw data, please see Supporting Information). In addition to characteristic peaks resulting from polyDVB (aromatic C–H stretches at around: 3016, 3047, and 3084 cm^{-1}, alkyl C–H stretch: 2923 cm^{-1}, aromatic C–C stretches: 1605 , 1508 , 1487 cm^{-1}, C–H bends: 710–1000 cm^{-1}, unsaturated C=C stretch:1630 cm^{-1}), all spectra showed peaks that correspond to

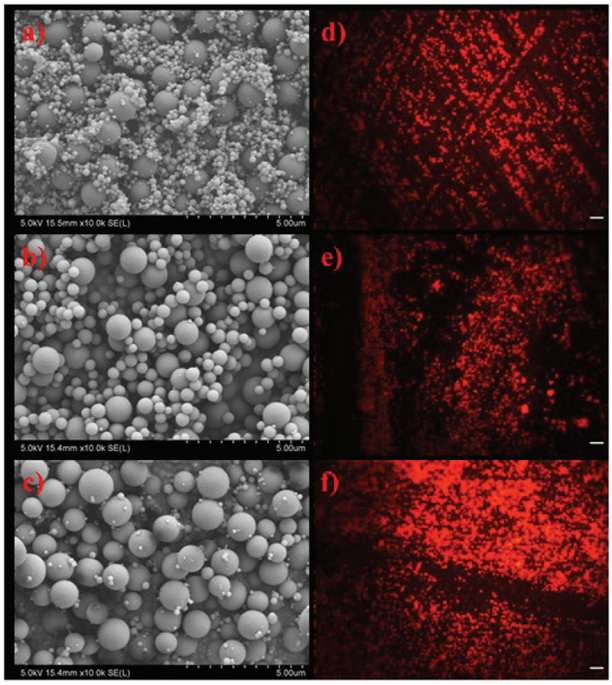

Figure 5. SEM images of the polyDVB particles prepared at a) 3%, b) 4%, and c) %5 monomer concentrations (by volume) at 1:0.1 BP to RhB mole ratio and d–f) their corresponding fluorescent microscopy images (scale bar corresponds to 10 microns).

RhB (O–H stretching vibration arising from the carboxylic acid of RhB, which is centered at around 3445 cm^{-1} and peaks between 1400 and 1600 cm^{-1}, which are also observed in the literature).[18] As the RhB concentration in the feed is raised, the intensity of the broad peak centered at around 3445 cm^{-1} increased, however, no clear trend was observed between each spectrum.

Monomer concentration is known to have an influence on particles synthesized by PP and particle size generally increases as the monomer concentration is raised.[2b,19] Therefore, we investigated the effect of monomer concentration on the particle size and yield of polymerization. **Figure 5**a–c shows the SEM images of the particles obtained at different monomer concentrations and Table 1 summarizes the results obtained from SEM analysis. As the monomer concentration is raised from 2% to 4% (by volume), the number-average diameter of the particles increased from 0.34 to 0.56 µm. As the monomer concentration is further raised to 5%, the number-average diameter of the particles slightly decreases to 0.42 µm. Although, particles bigger than 0.60 µm are also observed, secondary nucleation started at this monomer concentration, and resulted in the decrease in the average diameter of the particles. It is important to note that, though not monodisperse, still discrete, and spherical particles were obtained at 5% (by volume) monomer concentration, which is in parallel with the results obtained from previous studies on photoinitiated PP.[16] Therefore, the amount of isolated product can be increased by simply increasing the monomer concentration in the feed, despite the low yield of polymerization. Fluorescence microscopy images of the particles prepared at different monomer concentrations further confirm that the discrete and fluorescent particles can be obtained even at high monomer concentrations such as 5% (Figure 5d,e).

Initial reactions were carried out on a rotary shaker. Although the rotary shaker is operated at its minimum speed, the reaction mixture was shaken fast enough to create waves on the top; therefore, it was suspected that the high polydispersity of the particles might be due to the rotary shaker used for polymerization. Accordingly, to investigate the influence of reaction set-up used for polymerization on the reaction yield and particle properties, and to further test the reproducibility of our results, we carried out two separate reactions at identical reaction composition, using the conditions for Table 1, entry 7; however, this time on a low profile roller. 27 and 33 mg of product were obtained in each case and it corresponds to 2.5% and 3.0 % yield, respectively, which is similar to the result we obtained using rotary shaker. On the other hand, the SEM images of the samples (**Figure 6**b,c) revealed that the particles synthesized on a low profile roller were more uniform compared to the particles synthesized on the rotary shaker, confirming the requirement for slow agitation to obtain uniform particles in PP (Table 1, entries 10–11).

To compare the performance of the developed strategy with the traditional fluorescent microsphere synthesis, we synthesized fluorescent polyDVB particles using AIBN as initiator and rhodamine based acrylate monomer as the fluorescent monomer, separately (Figure 6a). The yield of reaction was 11%, which was slightly higher than our method. This might be attributed to the slow kinetics of bimolecular photoinitiation, since compared to type I photoinitiators, the rate of initiation of type II photoinitiators is slower.[9a] Uniformity and the average diameter of the particles (1.27 µm) were similar to the particles synthesized by our method (Table 1, entry 9).

After being successful at fluorescent particle synthesis using RhB and BP in PP conditions, we then aimed to investigate the rate of increase in particle size at the initial stage of polymerization. PP, an emulsifier or surfactant-free particle synthesis method, enables the synthesis of narrow or monodisperse particles in micron range (common examples include the synthesis of particles in 1–5 µm range). As the polymerization starts, a suspension of polymer particles forms at the early stage of the polymerization, which causes the inefficient penetration of light through the reaction mixture. As a consequence, compared to thermally initiated PP, the speed of monomer to polymer conversion is generally slower for photoinitiated PP. Dynamic light scattering (DLS) was used to monitor the increase in particle size at the very early stage of polymerization (from $t = 0$ to $t = 6$ h), since at this stage, nano-size particles cannot be isolated efficiently but still could be analyzed by DLS. For this purpose, the reaction was interrupted shortly and measurements were taken at every 1 h. **Figure 7** shows the size of the particles between $t = 0$ and $t = 6$ h, when polymerization is carried out at 1:0.3 BP:RhB mole ratio.

As can be seen, the size of the particles rapidly grows within the first 3 h, reaches to 300 nm in size, and then the rate of particle growth slows down. This phenomenon can be explained by the efficient absorption of light at the early stages of polymerization (between $t = 0$ and $t = 3$ h) due to the solution being transparent. As the oligomers start to form, particles start to precipitate out from the solution and form a pink suspension of particles that prevents the efficient penetration of light through the reaction vessel as discussed above, resulting in the decrease in the

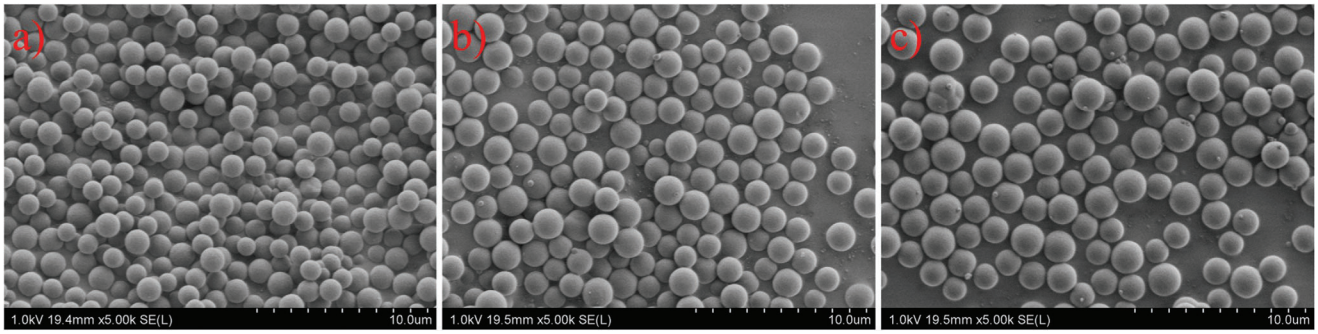

Figure 6. SEM images of the fluorescent microspheres prepared by conventional method using AIBN and a) RhB-monomer and by RhB and b,c) BP as bimolecular initiation system using a low profile roller for polymerization at identical reaction composition.

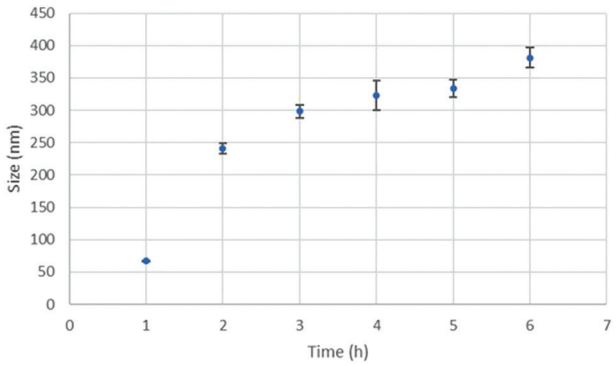

Figure 7. Particle size measurements obtained by DLS at the early stage (between 0 and 6 h) of polymerization.

particle growth speed. When polymerization was further carried out for an additional 3 h, the particle size reached ≈380 nm. After this stage, DLS measurements were no longer accurate, likely due to the increase in the concentration of particles, since laser penetration for the measurement had diminished and also due to the rapid precipitation of the particles.

3. Conclusion

In this work, we reported the synthesis of micron size fluorescent particles in one step, without using fluorescent monomers or modification steps to install fluorescent moieties into the polymer microspheres, for the first time. Using BP and RhB as bimolecular photoinitiation system in T2PPP, though not monodisperse, spherical fluorescent polymer particles are obtained at room temperature by UV irradiation. Despite the relatively low yield of the particle synthesis, the method developed here is still expected to be attractive for researchers working on fluorescent microsphere synthesis. This is not only due to the low price of the starting materials and the simplicity of the overall process, but also due to the fact that the method enables the synthesis of spherical particles even at high monomer concentrations, meaning the amount of isolated product can simply be increased by increasing the monomer concentration in the feed. Furthermore, the use of thinner glass tubes to carry out the reaction is expected to increase the yield of reaction, since the yield of photopolymerization strongly depend on the irradiation efficiency of the reaction. Studies in this line are now in progress.

4. Experimental Section

Materials: DVB-80 (technical grade, Aldrich) consisting of 80% DVB isomers was purified by passing through a basic alumina column to remove inhibitor. Rhodamine B (RhB, Aldrich, 99%), benzophenone (BP, 99%, Rhone Poulenc), acryloxyethyl thiocarbamoyl rhodamine B (RhB-monomer, Polysciences), azobisisobutyronitrile (AIBN, 98%, Aldrich), acetonitrile (ACN, 99%, Aldrich), and technical grade acetone (Aldrich) were used as received.

Instrumentation: FTIR spectra were obtained on a Bruker Tensor 27 Spectrometer on pressed KBr pellets. Spectra were obtained at regular time intervals in the region of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Dynamic light scattering (DLS): Hydrodynamic diameter (dh) measurements were recorded using a Cordouan Vasco Kin Size analyzer with in situ head. The laser was set at 20% in power, the wavelength was 632 nm and scattering angle 170°. Fluorescence spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer (Agilent, France). Scanning electron microscopy (SEM) images were acquired using a Hitachi SU-70, Schottky gun type, sputter coating: target gold; time 100 s (thickness ≈ 10–15 nm); on a Cressington 108 auto Sputter Coater with a Rotary-Planetary-Tilting (RPT) Stage (The samples on Table 1, entries 9–11 are not coated). Image analyses of the SEM micrographs were performed using Image J47 software, on a population of 200 microspheres, expect for the sample on Table 1, entry 10, where 175 counts were made (particles used for the size measurement in SEM images and individual sizes of the particles used in calculations can be found in the Supporting information). The following equations were used to determine the particle sizing characteristics:

$$U = \frac{D_w}{D_n}; D_n = \sum_{i=1}^{k} (n_i D_i) / \sum_{i=1}^{k} (n_i); D_w = \sum_{i=1}^{k} (n_i D_i^4) / \sum_{i=1}^{k} (n_i D_i^3) \quad (1)$$

where U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, N is the total number of the measured particles, and D_i is the particle diameter of the microspheres.[10,16] Polymers were isolated by filtration using a hydrophilic polyvinylidiene fluoride (PVDF) membrane filter discs with 0.22 µm pore size (Durapore, Sigma).

Experimental: A typical procedure for the synthesis of fluorescent poly-DVB particles via RhB and BP photoinitiation system in PP was as follows (**Table 1**, entry 7): To a borosilicate Kimax tube, were added DVB-80 (1.2 mL, 1.1 mg, 8.42 mmol), RhB (4.0 mg, 8.4 µmol), BP (15.3 mg, 84 µmol), and ACN (28.8 mL). The mixture was then ultrasonicated for few seconds until a clear solution was obtained and it was purged with nitrogen gas for 10 min. Next, the reaction vessel was sealed under nitrogen. The sealed tube was put horizontally onto a rotary shaker

(Heidolph) operating at 150 rpm and irradiated from a UV light source (VL-215.L 2 × 15 W—365 nm tube UV lamb, Fischer Bioblock Scientific), which is placed ≈3 cm above the reaction tube, for 68 h. The product was isolated from the reaction media by vacuum filtration on a membrane filter having 0.22 µm pore size, and washed with acetone (≈250 mL). Finally, the product was dried overnight in a preheated oven (65 °C) to constant mass (33 mg, yield: 3%). Figure S1-1a, Supporting Information shows the photograph of the reaction set-up used for polymerisation. Control experiments (Table 1, entries 9–11) were carried out on a low profile roller operating at 12 rpm using the same UV source and by placing it ≈3 cm above the roller (Figure S1-1b, Supporting Information). For "traditional" fluorescent particle synthesis (Table 1, entry 9), RhB and BP were omitted from the procedure and replaced with RhB-monomer (5.4 mg, 8.3 µmol) and AIBN (13.8 mg, 84 µmol).

RhB Leaching Experiments: Fluorescent polyDVB particles (Table 1, entry 10) (6 mg) were put into a centrifuge tube (15 mL) and dispersed in acetone (6 mL) by ultrasonication for 5 min. Particles were then separated from the liquid phase by centrifuge (10 mins at 8000 rpm) and re-dispersed in acetone (6 mL). The suspension of particles was then put onto a rotary shaker operating at 650 rpm for and the liquid phase was separated from the particles by centrifuge (10 mins at 8000 rpm). The liquid phase was then filtrated through a filter disc (Agilent, PTFE, 0.45 µm) and the emission spectrum was analyzed by fluorescence spectrophotometer within the 550–700 nm range, at 540 nm excitation wavelength. The measurements were taken at the beginning (after ultrasonication) and after 18 h, 42 h, and 66 h of shaking (Figure S1-3, Supporting Information). At the end of each measurement, the liquid phase is separated from the particles completely and fresh acetone was added (6 mL). Vortex mixer was used to re-disperse the particles in acetone each time for ≈20 s.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

benzophenone, fluorescent microspheres, poly(divinylbenzene), precipitation polymerization, rhodamine B, type II photoinitation, type II photoinitiated precipitation polymerization

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