Synthesis of Water-Soluble Spiropyran-Modified Poly(acrylic acid) Micelles and Their Optical Behaviors

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In this study, a spiropyran derivative (SPOH) is firstly grafted onto a polymer backbone of a poly(acrylic acid) (PAA) via an esterification process. The synthesized spiropyran-modified poly(acrylic acid) (PAA-SP) polymer is characterized by FTIR and 1H NMR. The synthesized PAA-SP is then dissolved into water to achieve water-soluble micelles. The optical behaviors of PAA-SP micelles are investigated by ultraviolet-visible (UV-Vis) absorption spectra and fluorescence emission spectra under acid/base and light stimuli in aqueous solution. Our experimental results reveal that the as-prepared PAA-SP micelles are water-soluble and show good photochromic and emissive behaviors. Meanwhile, the optical behaviors of the micelles are light-responsive and acid/base-responsive and hence can be tailored via the adjustments of both light and pH value of the solution sample. And our results may be meaningful for practical application of hydrophobic spiropyran derivatives in aquatic environments.

Keywords: Spiropyran, Poly(acrylic acid), Water-soluble micelles, Photochromism, Emission

1. Introduction

In recent years, the stimuli-responsive polymer materials are of great interest for their wide range of applications [1-5]. Among various physical and chemical stimuli, light stimulus has attracted more attention due to its minimal impact on both surroundings and material [6-10]. As a class of light-responsive materials, photochromic compounds undergo reversible transformation with different absorption spectra by light irradiation [11,12]. The photo-responsive polymers based on pyrene [13,14], spiropyran [15,16], and azobenzene [17,18] groups have been extensively investigated. As one of the most typical photochromic compounds, ring-closed hydrophobic spiropyran (SP) can be isomerized to ring-opened hydrophilic merocyanine (MC) via C-O bond cleavage induced by light irradiation (Fig. 1) [19]. Inspired by such switchable characteristic with different remarkable properties, e.g., absorption spectra, dipole moment, dielectric constant, geometrical structure, and coordination property etc., light sensitive polymers containing spiropyran units have been fabricated for specific applications such as bioimaging [20], controlled release [1,21,22], mechanic sensor [23], colorimetric detector [24,25], etc.

![Isomerization process of SP.](image1)

Fig. 1. Isomerization process of SP.

On the other hand, acid/base-responsive polymers in aqueous media have drawn increasing attention [26-28]. As we know, these polymers generally contain functional groups being able to protonate or deprotonate under pH value change with reversible variations in conformation and solubility between the extended and collapsed chain states [29-31]. Poly(acrylic acid) (PAA) is a typical acid/base-responsive polymer because it contains pH-responsive system of carboxylic groups (-COOH). When the pH value is larger than the pKₐ, -COOH
will deprotonate to -COO- and the polymer chains show a fully stretched conformation because of the electrostatic repulsion. In the case of the pH value less than the pKₐ, the polymer chains tend to exhibit a compact structure in aqueous solution due to the protonation of -COOH [29,32-35].

In this study, we report a dual stimuli-responsive polymer synthesized by combination of a light-responsive spiropyran derivative (SPOH) and an acid/base-responsive polymer of poly(acrylic acid) (PAA) via an esterification process. In comparison with the crosslinked water-insoluble nanogels [36], the spiropyran-modified PAA (PAA-SP) we obtained in this study can be dissolved in water to form micellar particles with a core/shell structure, in which the hydrophobic chromophore of spiropyran (SP) stays inside as the core and the hydrophilic -COOH groups stretch outside fully as the shell. Due to light and acid/base-responses the optical behaviors of the polymer can be tailored via the adjustments of both light and the pH value of the solution sample and hence are meaningful for practical application of hydrophobic spiropyran derivatives in aquatic environments. The synthesized PAA-SP is characterized by FTIR and 1H NMR, and the optical behaviors of the micelles are investigated by ultraviolet-visible (UV-Vis) absorption spectra and fluorescence emission spectra under acid/base and light stimuli in aqueous solution.

2. Experimental

2.1. Materials

2,3,3-Trimethyl-3H-indole is synthesized on the basis of a reference [37]. Poly(acrylic acid) (PAA, Mw = 3000, Aladdin) is used without further purification. CH₃CN (AR) is distilled with CaH₂. 4-Dimethylaminopyridine (DMAP, 99%, Aladdin), dicyclohexylcarbodiimide (DCC, 99%, Aladdin), 2-bromoethanol (96%, Aladdin), phenylhydrazine (98%, Aladdin), dimethyl sulfoxide (AR), and others are purchased from Sinopharm Chemical Reagent Co. Deionized water is used for all the experiments.

2.2. Synthesis of SPOH

SPOH (2-(3',3'-dimethyl-6-nitro-3H-spiro [chromene-2,2'-indol]-1'-yl)ethanol) is synthesized according to the reference [15], and the process is shown in Fig. 2. The synthesis of 2,3,3-trimethylindole is reported in reference [38]. A solution of 2,3,3-trimethyl-3H-indole (2.38 g, 15 mmol) and 2-bromoethanol (2.286 g, 18 mmol) in CH₃CN (20.00 mL) is heated for 24 h under reflux and N₂. After cooling down to 25 °C, the solvent is distilled off under reduced pressure. The residue is suspended in hexane (10.00 mL) and the mixture is sonicated and filtered. The resulting solid is crystallized from CHCl₃ (20.00 mL). Then the solid (2.29 g, 8 mmol) and KOH (0.684 g, 12 mmol) in water (20.00 mL) is stirred at 25 °C for 10 min. It is extracted with Et₂O (3×30.00 mL). The organic phase is concentrated under reduced pressure to afford a yellow oil. Then the yellow oil (1.025 g, 5 mmol) and 2-hydroxy-5-nitrobenzaldehyde (1.245 g, 7.5 mmol) in EtOH (15.00 mL) are heated for 3 h under reflux and N₂. After cooling down to 20 °C, the mixture is filtered. The resulting solid was washed with cold EtOH (10.00 mL) and dried to afford SPOH (1.45 g, 82% yield) as a purple solid powder. FTIR spectrum of SPOH (Fig. 3) (Sample/KBr = 1%, the assignments of the peaks, cm⁻¹): Ar-H, 3081; -CH₃, 2962, 2869, 1460, 1379; -CH₂-, 2922, 1337; -C = C-, 1647, 953, 920; Ar-C, 1608, 1574, 1481; -C-O-C-, 1088; 1,2,4-substituted aromatic ring, 836, 807; 1,2-substituted aromatic ring, 746; -OH, 3322. 1H NMR spectrum (Fig. 4) (CDCl₃, δ, ppm): 8.01 (m, 2H), 7.20 (td, 1H, J = 7.6 and 1.2 Hz), 7.10 (d, 1H, J = 7.5 Hz), 6.90 (dd, 2H), 6.76 (d, 1H, J = 8.8 Hz), 6.67 (d, 1H, J = 8.10 Hz), 5.88 (d, 1H, J = 10.2 Hz), 3.80 (s, 1H), 3.72 (m, 2H), 3.41 (m, 2H), 1.29 (s, 3H), 1.18 (s, 3H), 1.56 (H₂O).
2.3. Synthesis of PAA-SP

PAA-SP is synthesized according to the reference [39]. The synthesis process of PAA-SP is shown in Fig. 5. The experiment is carried out at a molar ratio of SPOH/DCC/DMAP of 1/1.1/0.1. Solvent of DMSO (5 mL), SPOH, DMAP are added to a dried flack. The reaction mixture is stirred for 10 min at 0 °C. DCC is dissolved in DMSO (5 mL), and then the solution is dropped into the above mixture slowly. The reaction mixture is stirred for 1 h at 0 °C. The mixture is then stirred for 48 h at 25 °C. After that, the reaction is stopped by exposing to air. The mixture is filtered, and the solvent is distilled off under reduced pressure. The remaining liquid is precipitated with anhydrous methanol. The resulting solid is filtered and dried in vacuum for 24 h to obtain a solid powder. Several feed ratios on PAA: SPOH (1:1, 1:3, 1:5, and 1:10) are tried and PAA-SP polymers are finally obtained. The 1H NMR spectra of PAA-SP5 (Fig. 6) (D$_2$O, ppm): 8.12 – 7.92 (m, 6H), 7.76 (s, 3H), 7.18 (d, $J$ = 28.4 Hz, 3H), 7.03 (s, 3H), 4.71 (s, 3H), 4.20 – 4.06 (m, 6H), 3.04 – 2.99 (m, 6H), 2.79 (d, $J$ = 18.7 Hz, 1H), 2.64 (s, 1H), 1.25 – 1.14 (m, 41H), 1.10 (t, $J$ = 7.1 Hz, 8H), 0.99 (t, $J$ = 7.1 Hz, 3H), 0.84 (t, $J$ = 7.4 Hz, 3H), 4.71 (D$_2$O).

2.4. Characterization and measurements

FTIR spectra are accomplished by Bruker Tensor 27 spectrometer. The 1H NMR spectra are recorded on a 400 MHz spectrometer (Bruker Advance 400) in D$_2$O with tetramethylsilane (TMS) as an internal standard. The fluorescence (FL) spectra are obtained using a Fluorolog 3-P spectrofluorometer (Jobin Yvon). The UV-Vis absorption spectra are recorded with a U-3010 spectrophotometer (Hitachi).

3. Results and discussion

3.1. Synthesis of PAA-SP and its characterization

In this study the synthesis of PAA-SP is performed by directly grafting SPOH onto the backbone of PAA via an esterification process. The FTIR spectra of PAA, SPOH, and PAA-SP are shown in Fig. 7.
As seen from Fig. 7, broad and strong carboxyl absorption peaks are observed at 3500~3000 cm\(^{-1}\) for both PAA and PAA-SP. This suggests that not all the carboxyl groups but only some of them are consumed during the esterification process. Further analysis of the spectra for PAA-SP can find some typical absorption peaks as below: (1) carbonyl (C=O) peak from ester group at 1735 cm\(^{-1}\); (2) vibrational peaks from benzene ring at 1610, 1577, and 1480 cm\(^{-1}\); (3) C-N peak at 1335 cm\(^{-1}\); (4) nitro peak from SP units at 1274 cm\(^{-1}\). The appearances of these peaks suggest that SPOH has been successfully grafted on the backbone of PAA via the esterification process.

The amount of SPOH grafted onto each PAA molecule, as expected, might have effect on its optical behaviors of PAA-SP to some extent. Thus, four kinds of PAA-SP polymers, namely PAA-SP\(_1\), PAA-SP\(_3\), PAA-SP\(_5\), and PAA-SP\(_{10}\), are synthesized with different raw material feed ratios, as given in Table 1.

Table 1. Synthesis of PAA-SP with different raw material feed ratios.

| PAA | SPOH | Feed ratio | DCC | DMAP | PAA-SP\(_x\) |
|-----|------|------------|-----|------|-------------|
| 1   | 1    | 1:1        | 1.1 | 0.1  | PAA-SP\(_1\) |
| 1   | 3    | 1:3        | 3.3 | 0.33 | PAA-SP\(_3\) |
| 1   | 5    | 1:5        | 5.5 | 0.55 | PAA-SP\(_5\) |
| 1   | 10   | 1:10       | 11  | 1.1  | PAA-SP\(_{10}\) |

The fluorescence measurements suggest that the emission ability of the polymer powders is related to the content of the grafted SP units. As seen from Fig. 8(a), PAA-SP powder with lower content of the SP units dramatically shows stronger emission. The four kinds of the polymer powders as well as SPOH and PAA are dissolved in water to achieve colloidal samples. The UV-Vis results in Fig. 8(b) suggest that both the pure SPOH and PAA-SP\(_{10}\) have poor solubility in water, as revealed by the large absorbances at 700 nm [40]. PAA-SP\(_1\), PAA-SP\(_3\), and PAA-SP\(_5\), however, dissolve quite well in water with very low absorbances at 700 nm. In particular, PAA-SP\(_3\) shows good chromism and moderate emission (see curves in Figs. 8(b) and 8(c) and photographs in Figs. 8(d) and 8(e)). The Tyndall experimental results in Fig. 8(f) suggest that PAA-SP polymer has formed particles in water with visible light path. As we know, PAA contains a large number of hydrophilic carboxyl groups (-COOH) on its chain and can dissolve well in water. The molecule of SPOH, however, is quite nonpolar and hydrophobic.
and practically insoluble in water. After grafting SPOH onto the backbone of PAA, the obtained PAA-SP is amphiphilic. After dissolved in water, micelles of PAA-SP can be achieved with a micellar structure of the hydrophobic SPOH core inside and hydrophilic carboxyl shell outside. Taking into consideration of chromism and emission performances as well as its solubility in water, it is clear that PAA-SP5 is most favorable and desirable and will be used hereafter for further research in this study. $^1$H NMR results show that for each PAA chain (chain units of ~ 40) the amount of the grafted SP units is 3.

3.2. Acid/base responses of PAA-SP5 micelles

As we know, PAA is a polymer typically responsive to acid and base. In an acid, PAA chain tends to shrink while in a base it fully stretches out due to the formation of -COO-. So, in this section acid/base responses of PAA-SP5 are investigated, and the results are shown in Fig. 9. As seen from Fig. 9, PAA-SP5 micelles in water are chromic and emissive enough and these optical performances significantly vary with the pH value of the solution. In particular, a strong absorption peak appears at 550 nm in a neutral condition while both in an acid and base they are very low. This corresponds to the ring-opening isomerism of spiropyran to merocyanine (SP to MC) that generally occurs in a neutral condition [41,42]. The absorption at 400 nm, however, is absolutely different from that at 550 nm. With the increase of the pH value, the absorption peak at 400 nm firstly decreases to reach a minimum level at pH=7 followed by a rapid increase. The strong absorptions at 400 nm in acidic or base conditions in Figs. 9(a) and 9(b) can be attributed to acid/base-induced ring-opening isomerism of SP. In an acid, the ring-closed SP isomerizes to the protonated ring-opened merocyanine (MC-H) while in a base it isomerizes to the hydroxylated ring-opened merocyanine (MC-OH). Both MC-H and MC-OH have absorption peaks around 400 nm. It is clear that the absorbance at 400 nm of the micelles depends on the content of MC-H or MC-OH revealed by the pH value of the solution.

The emission dependence on the pH value of PAA-SP5 is shown in Figs. 9(c) and 9(d). A strong emission peak appears at 565 nm. It continually decreases with the increase of pH value, giving a monotone decline tendency against pH value of the solution. Thus, the formed MC-H emits well in an acid but for MC-OH in a base its emission is very

Fig. 9. UV-Vis absorption ((a), (b)) and emission ((c), (d)) behaviors of PAA-SP5 micelles in water with different pH values. The concentration of PAA-SP5 is 0.01 mg/mL. All the measurements are conducted at room temperature.
It is necessary to investigate the optical behaviors of other is SP that is a light-responsive material. Thus, parts: one is PAA responding to pH value and the other is SPOH that is a light-responsive material. As we know, PAA is responsive to the pH value of the solution due to the present of large amount of -COOH on its chains. In an acid/base solution, however, tend to stretch out fully due to the deprotonation of the -COOH into -COO-. As a result, solvent-induced fluorescence quenching occurs hardly, and strong emission can be observed. The molecular chains of PAA-SP5 in water, as expected, might act an important role. As we know, PAA is responsive to the pH value of the solution due to the present of large amount of -COOH on its chains. In an acid/base solution, however, tend to stretch out fully due to the deprotonation of the -COOH into -COO-. As a result, the formed micelles are not compact enough and poor emission is observed due to solvent-induced fluorescence quenching. In brief, the results in Fig. 9 suggest that PAA-SP5 micelles are chromic and emissive in acid/base solution and its ability can be adjusted by varying the pH value of the solution.

3.3. Light response of PAA-SP5 micelles

PAA-SP synthesized in this study consists of two parts: one is PAA responding to pH value and the other is SP that is a light-responsive material. Thus, it is necessary to investigate the optical behaviors of PAA-SP5 micelles when light is applied. PAA-SP5 solution sample in an acid is employed since in this case its emission is strong (see Fig. 9(d)). The sample is continuously irradiated with a UV light (365 nm) to achieve its coloration process. The discoloration process is conducted with a LED white light. The results are shown in Fig. 10. As seen from Fig. 10, PAA-SP5 micelles are photochromic under light irradiation. The coloration and discoloration of the micelles mainly occur around 425 nm. The absorbances at 550 nm vary very little. The derived photochromic kinetic constants from Fig. 10(d) are: \( K_{\text{coloration}} = 7.89 \times 10^{-4} \text{ s}^{-1} \) and \( K_{\text{discoloration}} = 6.08 \times 10^{-3} \text{ s}^{-1} \). Thus, the discoloration process is faster than the coloration process. The emissions of PAA-SP5 micelles also vary with the light irradiation. The fluorescence intensities of PAA-SP5 micelles increase with the UV and decrease with the LED white light, as shown in Fig. 11. The kinetic results in Fig. 11(d) suggest again that the discoloration process is faster than the coloration process.

3.4. Solubility and recyclability of PAA-SP5 in water

The research goal of this study is to achieve water-soluble micelles of PAA-SP5 with responses to both acid/base and light. So, the solubility of the as-prepared polymer of PAA-SP5 is investigated in this section and the results are shown in Fig. 12.
Fig. 12. UV-Vis (a) and emission (b) behaviors of PAA-SP$_5$ micelles in water with different concentrations of PAA-SP in mg/mL (pH=2). The photographs from the colloidal samples are also recorded in (c) and (d) with a digital camera to show color change and emission. The red laser in (e) is employed to check if there is a Tyndall effect or not.

As seen from Fig. 12(a), a continuous increase of the absorption of the micelles is definitely observed against the concentration for PAA-SP$_5$ micelles. Similar result on emission is obtained for the micelles in Fig. 12(b). The photographs given in Figs. 12(c) and 12(d) visually show such photochromic and emissive tendencies. In order to study the micellization behavior of PAA-SP$_5$ in water, a red laser beam is employed to illuminate the solution samples. It should be noted that the brightness of the laser light path in the Tyndall experiment is more sensitive to the size of the particles than to the concentration of the solution sample. As seen from Fig. 12(e), the brightness of the red laser light path visually increases against the concentration of the solution samples. This means the formation of the micelles with larger size as the increase of the concentration of PAA-SP$_5$. In fact, a concentration of PAA-SP$_3$ as high as 5 mg/mL has been achieved in our experiment but absent in this figure since it is out of range of UV-Vis measurement. The reversibility of PAA-SP$_3$ micelles in water is investigated by applying a UV/Vis irradiation for several cycles. The results in Fig. 13 reveals good reversibility of the micelles both on UV-Vis absorption and fluorescence intensity. This suggests that PAA-SP$_3$

Fig. 13. Reversibility of PAA-SP$_3$ micelles in water upon UV/Vis irradiation cycle. For the coloration process, the solution sample is irradiated with a 365 nm UV lamp for 5 min. In the case of the discoloration process, the sample is kept under a LED white light for 1 min.

micelles are light-responsive and have good reversibility on light irradiation.

4. Conclusion

In this study, the synthesis of PAA-SP is performed by directly grafting a spiropyran derivative of SPOH onto the backbone of PAA via an esterification process. PAA-SP is then dissolved in water to achieve water-soluble micelles. SPOH is a light-responsive material with good photochromic and emissive performances but it does not dissolve in water. PAA is an acid/base-responsive polymer with good water-solubility but does not responds to light. The obtained PAA-SP micelles are water-soluble with good photochromic and emissive behaviors. Meanwhile, the optical behaviors of the micelles are acid/base-responsive and hence can be tailored via the adjustment of the pH value of the solution sample. Thus, our results may be meaningful for practical application of spiropyran derivatives in aquatic environments.
Acknowledgment

This work is financially supported by the Natural Science Foundation of Shandong Province of China (ZR2018MB011).

References

1. F. Liu and M. W. Urban, *Prog. Polym. Sci.*, 35 (2010) 3.
2. M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stammt, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, *Nat. Mater.*, 9 (2010) 101.
3. D. Roy, J. N. Cambre, and B. S. Sumerlin, *Prog. Polym. Sci.*, 35 (2010) 278.
4. S. Shao, J. J. Shi, I. Murtaza, P. P. Xu, Y. W. He, S. Ghosh, X. S. Zhu, I. F. Perepichka, and H. Meng, *Polym. Chem.*, 8 (2017) 769.
5. M. L. Wei, Y. F. Gao, X. Li, and M. J. Serpe, *Polym. Chem.*, 8 (2017) 127.
6. N. Fomina, J. Sankaranarayanan, and A. Almutairi, *Adv. Drug Deliv. Rev.*, 64 (2012) 1005.
7. Y. Huang, R. J. Dong, X. Y. Zhu, and D. Y. Yan, *Soft Matter*, 10 (2014) 6121.
8. Y. H. Wu, H. M. Hu, J. M. Hu, T. Liu, G. Y. Zhang, and S. Y. Liu, *Langmuir*, 29 (2013) 3711.
9. G. Pasparakis, T. Manouras, P. Argitis, and M. Vamvakaki, *Macromol. Rapid Commun.*, 33 (2012) 183.
10. S. Sugiuara, A. Szilagyi, K. Sumaru, K. Hattori, T. Takagi, G. Filipcei, M. Zrinyi, and T. Kanamori, *Lab Chip*, 9 (2009) 196.
11. V. I. Minkin, *Theor. Exp. Chem.*, 31 (1995) 140.
12. M. Irie, *Chem. Rev.*, 100 (2000) 1683.
13. J. F. Gohy and Y. Zhao, *Chem. Soc. Rev.*, 42 (2013) 7117.
14. J. Q. Jiang, X. Tong, and Y. Zhao, *J. Am. Chem. Soc.*, 127 (2005) 8290.
15. F. M. Raymo and S. Giordani, *J. Am. Chem. Soc.*, 123 (2001) 4651.
16. V. I. Minkin, *Chem. Rev.*, 104 (2004) 2751.
17. F. D. Jochum and P. Theato, *Chem. Commun.*, 46 (2010) 6717.
18. H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.*, 41 (2012) 1809.
19. G. Berkovic, V. Krongauz, and V. Weiss, *Chem. Rev.*, 100 (2000) 1741.
20. L. Zhu, W. Wu, M. Zhu, J. J. Han, J. K. Hurst, and A. D. Li, *J. Am. Chem. Soc.*, 129 (2007) 3524.
21. R. Tong, H. D. Hemmati, R. Langer, and D. S. Kohane, *J. Am. Chem. Soc.*, 134 (2012) 8848.
22. Q. Jin, G. Liu, and J. Ji, *J. Polym. Sci., Part A: Polym. Chem.*, 48 (2010) 2855.
23. D. A. Davis, A. Hamilton, J. L. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, and S. R. White, *Nature*, 459 (2009) 68.
24. K. H. Fries, J. D. Driskell, G. R. Sheppard, and J. Locklin, *Langmuir*, 27 (2011) 12253.
25. Y. J. Oh, J. A. Nam, A. Al-Nahain, S. Lee, I. In, and S. Y. Park, *Macromol. Rapid Commun.*, 33 (2012) 1958.
26. B. S. Kim, H. F. Gao, A. A. Argun, K. Matyjaszewski, and P. T. Hammond, *Macromolecules*, 42 (2009) 368.
27. L. E. Bromberg and E. S. Ron, *Adv. Drug Delivery Rev.*, 31 (1998) 197.
28. J. Rodriguez-Hernandez and S. Lecommandoux, *J. Am. Chem. Soc.*, 127 (2005) 2026.
29. X. Y. Jiang, G. L. Lu, C. Feng, Y. J. Li, and X. Y. Huang, *Polym. Chem.*, 4 (2013) 3876.
30. S. Dai, P. Ravi, and K. C. Tam, *Soft Matter*, 4 (2008) 435.
31. H. I. Lee, J. R. Boyce, A. Nese, S. S. Sheiko, and K. Matyjaszewski, *Polymer*, 49 (2008) 5490.
32. C. M. Schilli, M. F. Zhang, E. Rizzardo, S. H. Thang, Y. K. Chong, K. Edwards, G. Karlsson, and A. H. E. Muller, *Macromolecules*, 37 (2004) 7861.
33. J. J. Li, Y. N. Zhou, and Z. H. Luo, *Soft Matter*, 8 (2012) 11051.
34. H. I. Lee, J. Pietrasik, S. S. Sheiko, and K. Matyjaszewski, *Prog. Polym. Sci.*, 35 (2010) 24.
35. Y. Zhao, Y. W. Luo, B. G. Li, and S. P. Zhu, *Langmuir*, 27 (2011) 11306.
36. S. Chen, Q. Bian, P. J. Wang, X. W. Zheng, L. Lv, Z. M. Dang, and G. J. Wang, *Polym. Chem.*, 8 (2017) 6150.
37. M. V. Reddington, *Bioconjugate Chem.*, 18 (2007) 2178.
38. J. L. Fan, L. A. Lee, X. J. Peng, X. Qiang, and Q. Wang, WO2013075285-A1 (2013).
39. Y. N. Xue, J. T. Tian, W. G. Tian, P. Z. Gong, J. H. Dai, and X. Wang, *J. Phys. Chem. C*, 119 (2015) 20762.
40. W. Mi, W. G. Tian, J. T. Tian, J. Q. Jia, X. Y. Liu, J. H. Dai, and X. Wang, *Colloids Surf. A: Physicochem. Eng.*, 417 (2013) 179.
41. W. K. Fong, N. Malic, R. A. Evans, A. Hawley, B. J. Boyd, and T. L. Hanley, *Biointerphases*, 7 (2012) 1.
42. R. Klajn, *Chem. Soc. Rev.*, 43 (2014) 1448.