Article

Journal of
Nanoscience and Nanotechnology
Vol. 16, 1085–1089, 2016
www.aspbs.com/jnn

Properties and Applications of Sodium (5-methyl-2-alkyl-1,3-dioxane-5-yl)-Carboxylate Synthesized with Nanosolid Superacid

Lin Yuan, Guo Kai Jia, Zhong Yan Li, Min Zhang, and Xian You Yuan*

Key Laboratory of Comprehensive Utilization of Advantage Plants Resources in Hunan South,
Hunan University of Science and Engineering, Yongzhou 425199, Hunan, P. R. China

A series of novel sodium (5-methyl-2-alkyl-1,3-dioxane-5-yl) carboxylate surfactants were synthesized using nanosolid superacid SO_4^{2-}/Fe_2O_3 as a catalyst and characterized by ^{1}H NMR, IR and elemental analysis. The critical micelle concentration (CMC) of surfactants was determined and the results showed that the CMC values were less than 2.0×10^{-3} mol/L. Other relevant surface properties (Krafft point, emulsion stability, foam ability, degradability) were also evaluated. It was suggested that with respect to emulsion formation, foam stability and the range of application temperature, compared with traditional surfactants, the new surfactants could give better results and showed better properties when used as an emulsifier in emulsion polymerization. In addition, the surfactants were stable under neutral and alkaline conditions, and could form solid under acid condition. The solid will generate the original surfactants for reuse with alkali. Sodium (5-methyl-2-alkyl-1,3-dioxane-5-yl) carboxylate is likely to be a new type of 'environmentally friendly' surfactant.

Keywords: Nanosolid Superacid, Synthesis, Acetal, 1,3-Dioxane, Surfactant.

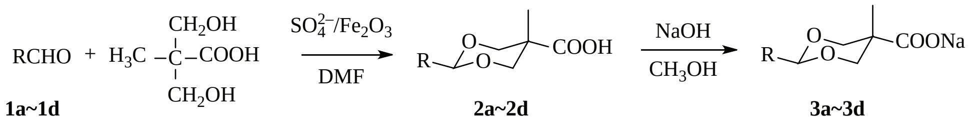
1. INTRODUCTION

Surfactants are a special class of compounds possessing important physicochemical properties. Classical surfactants are composed of two distinct parts, one polar and the other nonpolar, incompatible with eath other. Because of this amphiphilicity, surfactants tend to self-aggregate into micelles (above a certain concentration, known as the critical micelle concentration, CMC). This aggregation forms the basis of many biochemical process and is advantageous in different industrial areas, like cleaning, paint, pharmaceuticals, emulision, oil recover, catalysis, microreactor and cosmetics.[1–3]

Due to environment concerns, the research on novel surfactants has been made widely in recent years. In order to achieve the goal, a wide variety of new surfactants, cyclic acetal (ketal) compounds,[4–6] have been synthesized and their physicochemical behaviors have been investigated. Generally speaking, compared with traditional surfactants, this type of cyclic acetal (ketal) compounds possess unusual physicochemical properties and can be used with higher efficiency in the emulsion polymerization and emulsion of organic reactions.[7–11] The microemulsion could be decomposed under acid condition, and the products could be separated easily from two phases after the reaction in presense of these novel surfactants.[12–15] Recently, we reported the synthesis and properties of acetal sulfonate surfactant containing 1,3-dioxane.[16] In this paper, a new type of segregative and degradable surfactants containing 1,3-dioxane were synthesized by 2,2-dihydroxymethyl propionic acid with short-chain fatty aldehyde, using nanosolid superacid SO_4^{2-}/Fe_2O_3 as a catalyst (Scheme 1). The new surfactants were stable under neutral and alkaline conditions, and would degrade into the raw materials for reuse in acid environment. Moreover, nanomaterials have been widely investigated in last few years,[17–41] and it seems that some nanomaterials work well when used for catalytic application. Based on the above characteristics, these surfactants are promising to be a new type of 'green surfactants'[42–46].

---

*Author to whom correspondence should be addressed.



a. R = C_4H_9; **b.** R = C_5H_{11}; **c.** R = C_6H_{13}; **d.** R = C_7H_{15}

Scheme 1. Synthesis of surfactants **3a**~**3d**.

2. EXPERIMENTAL SECTION

2.1. Instrumentation and Materials

2.1.1. Instruments

The nanosolid superacid SO_4^{2-}/Fe_2O_3 made of an amorphous solid powder was prepared according to the literature.[47, 48] The particle size of the sample is very small (≤50 nm) with large specific surface area ($\geq 145\ m^2 \cdot g^{-1}$) within the scope of nanoparticles. Melting point data were recorded on a XRC-1 microscopic melting point meter, the thermometer without correction. Element analysis was recorded on PE2400 instrument. The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets and a Niconet AVATAR-360 spectrometer. ^1H NMR spectra were recorded in a $CDCl_3$ and D_2O solution with a VARAN UNTTY INOV-400 spectrometer. 2,2-dihydroxy methyl propionic acid (98%, Aladdin) and all of the aldehyde (Aladdin) were purified by distillation before use. Other materials and solvents were commercially available and were used without further purification.

2.1.2. General Procedure for the Synthesis of 5-methyl-2-alkyl-1,3-dioxane-5-Carboxylic Acid (2a–2d)

The method adopted for the synthesis of 5-methyl-2-butyl-1,3-dioxane-5-carboxylic acid (**2a**) can be described as follows. 5.10 g (38.07 mmol) 2,2-dihydroxy methyl propionic acid, 3.61 g (41.89 mmol) *n*-pentanal and 0.12 g nanosolid superacid SO_4^{2-}/Fe_2O_3 were added into a mixture of *N*,*N*-dimethylformamide (10 mL) and cyclohexane (10 mL) and refluxed for 5 h with stirring. After the reaction, sodium bicarbonate 0.06 g (0.70 mmol) was added to the mixture, and stirred at room temperature for half an hour. The solvent was then removed under reduced pressure using a rotary evaporator and a solid precipitated out. The isolated solid was dissolved in cyclohexane and washed with saturated salt water (10 mL × 2) and water (10 mL × 2), the organic layer was dried over anhydrous magnesium sulfate overnight. After removal of the solvent, the crude product was purified by recrystallization from *n*-hexane to afford white crystals.

2a: a white solid; yield 53.6%; m.p. 135.4 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.48–4.50 (t, $J = 5.2$ Hz, 1 H, OCHO), 4.42–4.45 (d, $J = 11.6$ Hz, 2 H, OCH_2C, H_{eq}), 3.45–3.48 (d, $J = 11.6$ Hz, 2 H, OCH_2C, H_{ax}), 1.61–1.65 (m, 2 H, $CH\underline{CH_2}CH_2$), 1.29–1.38 [m, 4 H, $CH_2(\underline{CH_2})_2CH_3$], 1.02 ($s$, 3 H, CCH_3), 0.872–0.906 (t, $J = 6.8$ Hz, 3 H, $\underline{CH_3}CH_2$); IR (KBr) ν: 3001, 2953, 2862, 2644, 2349, 1692, 1460, 1407, 1325, 1258, 1216, 1185, 1125, 1067, 1009, 953, 918, 871, 800, 725, 669, 587 cm^{-1}; Anal. calcd for $C_{10}H_{18}O_4$: C 59.36, H 8.90, Found C 59.42, H 8.87.

2b: a white solid; yield 64.0%; m.p.135.3 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.51–4.53 (t, $J = 4.8$ Hz, 1 H, OCHO), 4.44–4.47 (d, $J = 11.2$ Hz, 2 H, OCH_2C, H_{eq}), 3.49–3.52 (d, $J = 11.2$ Hz, OCH_2C, H_{ax}), 1.63–1.69 (m, 2 H, $CH\underline{CH_2}CH_2$), 1.37–1.43 (m, 2 H, $CH_2\underline{CH_2}CH_3$), 1.30–1.31 [m, 4 H, $CH_2(\underline{CH_2})_2CH_2$], 1.05 ($s$, 3 H, CCH_3), 0.89–0.92 (t, $J = 6.8$ Hz, 3 H, CH_3CH_2); IR (KBr) ν: 2950, 2924, 2858, 2653, 1691, 1461, 1406, 1327, 1256, 1161, 1127, 1070, 1020, 946, 915, 805, 722, 670, 588, 476 cm^{-1}; Anal. calcd for $C_{11}H_{20}O_4$: C 61.03, H 9.25, Found C 61.11, H 9.17.

2c: a white solid; yield 64.7%; m.p. 134.4 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.49–4.52 (t, $J = 5.2$ Hz, 1 H, OCHO), 4.38–4.41 (d, $J = 11.2$ Hz, 2 H, OCH_2C, H_{eq}), 3.48–3.51 (d, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.61–1.66 (m, 2 H, $CH\underline{CH_2}CH_2$), 1.34–1.38 (m, 2 H, $CH_3\underline{CH_2}CH_2$), 1.26 [m, 6 H, $CH_2(\underline{CH_2})_3CH_2$], 1.029 ($s$, 3 H, CCH_3), 0.85–0.87 (t, $J = 6.8$ Hz, 3 H, CH_3CH_2); IR (KBr) ν: 2921, 2856, 2653, 1692, 1460, 1407, 1325, 1256, 1161, 1127, 1071, 945, 851, 801, 725, 670, 585 cm^{-1}; Anal. calcd for $C_{12}H_{22}O_4$: C 62.55, H 9.56, Found C 62.48, H 9.63.

2d: a white solid; yield 57.2%; m.p. 134.0 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 4.48–4.51 (t, $J = 4.8$ Hz, 1 H, OCHO), 4.40–4.43 (d, $J = 11.2$ Hz, 2 H, OCH_2C, H_{eq}), 3.46–3.49 (d, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.61–1.66 (m, 2 H, $CH\underline{CH_2}CH_2$), 1.37 (m, 2 H, $CH_2\underline{CH_2}CH_3$), 1.26 [m, 8 H, $CH_2(\underline{CH_2})_4CH_2$], 1.02 ($s$, 3 H, CCH_3), 0.85–0.89 (t, $J = 6.8$ Hz, 3 H, CH_3CH_2); IR (KBr) ν: 2920, 2853, 2650, 1691, 1462, 1404, 1327, 1258, 1161, 1128, 1074, 1033, 1008, 947, 917, 877, 808, 720, 670, 590 cm^{-1}; Anal. calcd for $C_{13}H_{24}O_4$: C 63.87, H 9.83, Found C 63.82, H 9.89.

2.1.3. General Procedure for the Synthesis of 5-methyl-2-alkyl-1,3-dioxane-5-carboxylic Acid Sodium Salt (3a–3d)

The method adopted for the synthesis of 5-methyl-2-butyl-1,3-dioxane-5-carboxylic acid sodium salt (**3a**) is described. 5.00 g (24.7 mmol) 5-methyl-2-butyl-1,3-dioxane-5-carboxylic acid (**2a**) and 1.00 g (25 mmol) sodium hydroxide were added into anhydrous methanol (30 mL) and refluxed for 8 h. After removal of the solvent, the crude product was purified by recrystallization from isopropyl alcohol to afford a white block solid.

3a: a white solid; yield 82.23%; ^{1}H NMR (D_2O, 400 MHz) δ: 4.63–4.65 (*t*, $J = 4.4$ Hz, 1 H, OCHO), 4.37 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{eq}), 3.50 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.56 (*m*, 2 H, $CH_2\underline{CH_2}CH$), 1.30 [*m*, 4 H, $CH_2\underline{(CH_2)}_2CH_3$], 0.86 [*m*, 6 H, $\underline{CH_3}CH_2$, $C\underline{CH_3}$]; IR (KBr) ν: 2957, 2858, 1593, 1465, 1410, 1366, 1295, 1195, 1145, 1106, 1000, 950, 910, 881, 840, 790, 669, 579 cm^{-1}; Anal. calcd for $C_{10}H_{17}O_4Na$: C 53.53, H 7.58, Found C 53.47, H 7.65.

3b: a white solid; yield 85.4%; ^{1}H NMR (D_2O, 400 MHz) δ: 4.63–4.65 (*t*, $J = 4.8$ Hz, 1 H, OCHO), 4.36–4.39 (*d*, $J = 10.8$ Hz, 2 H, OCH_2C, H_{eq}), 3.49–3.51 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.53–1.57 (*m*, 2 H, $CH_2\underline{CH_2}CH$), 1.27–1.33 [*m*, 6 H, $CH(\underline{CH_2})_3CH_3$], 0.84–0.88 [*m*, 6 H, $\underline{CH_3}CH_2$, $C\underline{CH_3}$]; IR (KBr) ν: 2928, 2855, 1587, 1464, 1409, 1365, 1296, 1147, 1107, 1013, 907, 839, 725, 671, 578, 469 cm^{-1}; Anal. calcd for $C_{11}H_{19}O_4Na$: C 55.39, H 7.97, Found C 55.43, H 7.91.

3c: a white solid; yield 83.8%; ^{1}H NMR (D_2O, 400 MHz) δ: 4.62–4.65 (*t*, $J = 4.8$ Hz, 1 H, OCHO), 4.36–4.39 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{eq}), 3.48–3.51 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.55–1.56 (*m*, 2 H, $CH_2\underline{CH_2}CH$), 1.26–1.28 [*m*, 8 H, $CH(\underline{CH_2})_4CH_3$], 0.86 [*m*, 6 H, $\underline{CH_3}CH_2$, CCH_3]; IR (KBr) ν: 2958, 2926, 2855, 2780, 2662, 1593, 1463, 1411, 1367, 1295, 1143, 1021, 935, 908, 844, 794, 725, 667, 578, 509 cm^{-1}; Anal. calcd for $C_{12}H_{21}O_4Na$: C 57.09, H 8.32, Found C 57.04, H 8.41.

3d: a white solid; yield 82.8%; ^{1}H NMR (D_2O, 400 MHz) δ: 4.62–4.65 (*t*, $J = 5.2$ Hz, 1 H, OCHO), 4.36–4.39 (*d*, $J = 10.8$ Hz, 2 H, OCH_2C, H_{eq}), 3.48–3.51 (*d*, $J = 11.2$ Hz, 2 H, OCH_2C, H_{ax}), 1.53–1.56 (*m*, 2 H, $CH_2\underline{CH_2}CH$), 1.26 [*m*, 10 H, $CH_2\text{–}\underline{(CH_2)}_5\text{–}CH_3$], 0.83–0.86 [*m*, 6 H, $\underline{CH_3}CH_2$, $C\underline{CH_3}$]; IR (KBr) ν: 2954, 2924, 2855, 1598, 1464, 1410, 1366, 1296, 1142, 1104, 1077, 1022, 993, 941, 911, 838, 725, 669, 579 cm^{-1}; Anal. calcd for $C_{13}H_{23}O_4Na$: C 58.59, H 8.64, Found C 58.55, H 8.73.

2.2. Methods

2.2.1. Critical Micelle Concentration (CMC)

The CMCs of surfactants were determined by conductivity measurements. A series of concentration of surfantants **3a**∼**3d** solution were prepared from 0.00005 mol/L to 0.0100 mol/L with water in 50 mL volumetric flasks, then were kept in thermostated water bath at 25 °C for 10 min. The conductivity of the solution was measured using a conductivity cell (type DDS-11A). Each solution was measured three times and the final averaged values were used to draw a κ-C curve. The concentration corresponding to the breakpoint of the specific conductivity versus concentration was taken as the CMC.[1]

2.2.2. Emulsion Stability

The emulsion stability of surfactants was measured as the time of separation of the aqueous phase from the emulsion layer. Emulsions were prepared by mixing 20 mL of aqueous surfactant solutions (2 wt%) and 20 mL of benzene at room temperature.[49]

2.2.3. Krafft Temperature

20 mL of surfactant solution (1 wt%), taken in 25 mL graduated cylinders, was placed in a refrigerator, so that solid surfactant-hydrate crystals appeared. The crylinder was then taken out and the temperature was increased until a clear solution was obtained. The temperature at which the solution became clear was taken as the Krafft temperature (K_T).[50]

2.2.4. Foaming Ability

The foaming ability was obtained under vigorous shaking of aqueous surfactant solutions (0.1 wt%) contained in a 50 mL glass-stopper graduated cylinder at room temperature for 5 s, and the height of foam at the moment and the height of foam 30 s later were recorded timely. The ratio between them (the rest height of foam vs. the initial height) was taken as the foaming ability of the surfactant.[51]

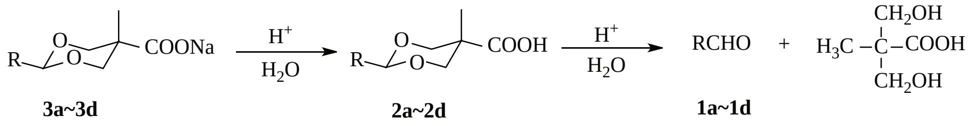
2.2.5. Degradability

Surfactants **3a**∼**3d** can be degraded into biodegradable raw material moleculars, aldehydes and 2,2-dihydroxymethyl propionic acid, through adding dilute HCl with heating. The degradation process is given in Scheme 2.

3. RESULTS AND DISCUSSION

3.1. CMC

All the four studied surfactants showed sharp breaks in the concentration isotherms (Fig. 1) which were used to determine the CMC (Table I). It is clear that the values of



a. R = C_4H_9; **b.** R = C_5H_{11}; **c.** R = C_6H_{13}; **d.** R = C_7H_{15}

Scheme 2. Degradation process of surfactants **3a**∼**3d**.

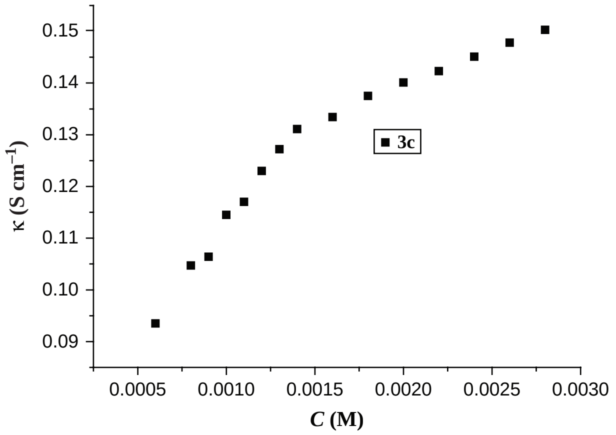


Figure 1. Plot of specific conductance of aqueous **3c** surfactant solutions as a function of the concentration (C).

CMCs of surfactants **3a**~**3d**, given in Table I, are all less than 2.0×10^{-3} mol/L.

3.2. Emulsion Stability

The stability of benzene-in-water emulsion in the presence of these four surfactants was investigated. The emulsions were stabilized by adding an emulsifier or surfactant. Here, in the present case, the stability of the emulsion increases with the increase in length of the hydrophobic tail of the surfactant. In the presence of **3a**, it takes 32 min for separation of the aqueous layer from the emulsion whereas for **3b**, **3c** and **3d** the times taken were 60 min, 174 min and 384 min, respectively. Thus, the emulsion stability increases with the increase in the hydrophobic tail length.

3.3. Krafft Temperature

The Krafft Temperature (K_T) is the minimum temperature at which surfactants from micelles. Below K_T, micelles do not form and surfactants remain in crystalline form, even in aqueous solution. The values of the Krafft Temperature (K_T) for surfactants **3a**~**3d** are given in Table I, and all of them were taken as less than 0 °C.

3.4. Foaming Ability

The foam ability data for the four surfactants are list in Table II. It is clear that the initial height of foam produced by surfactants increases with the increase in the tail length. Due to the high hydrophobicity, **3d** produces a greater height and more stable foams than the others.

Table I. CMC, emulsifiability and krafft temperature of surfactants **3a**~**3d**.

Surfactant	**3a**	**3b**	**3c**	**3d**
10^3 CMC (mol/L)	0.8	1.6	1.6	1.6
Emulsifiability (min)	32	60	174	384
Krafft temperature	< 0 °C	< 0 °C	< 0 °C	< 0 °C

Table II. Foam ability and emulsion stability of surfactants **3a**~**3d**.

Surfactants	Foam height (mL) (0 s)	Foam height (mL) (after 30 s)	Foam stability (%)
3a	6.27	0.41	6.49
3b	6.45	0.44	6.82
3c	6.68	0.51	7.63
3d	6.86	0.62	9.04

Table III. Degradability of surfactants **3a**–**3d** in 2 N HCl at 50 °C.

Surfactants	**3a**	**3b**	**3c**	**3d**
Surfactant quality (g)	0.1	0.1	0.1	0.1
Time (h)	0.35	1.41	2.56	5.74
Decomposition (%)	100	100	100	100

3.5. Degradability

Surfactants **3a**~**3d** are a type of single carboxylic acid sodium salt with 1,3-dioxane ring, and are water-soluble and stable under neutral and alkaline conditions, and turn into segregative solid precipitation under acid condition so that the system can eliminate the undesirable bubbles and emulsifying phenomenon. The precipitation can be processed with alkali to generate the original surfactants to reuse and can also be easily degraded into biodegradable raw material molecules through adding dilute acid with heating. The degradability of **3a–3d** in 2 N HCl at 50 °C was examined and the results are shown in Table III. From Table III, it is clear that the degradation time of **3a–3d** increases as the alkyl chain length increases under the same conditions.

4. CONCLUSIONS

The sodium (5-methyl-2-alkyl-1,3-dioxane-5-yl)-carboxylate containing 1,3-dioxane ring is a new type of surfactants synthesized using nanosolid superacid SO_4^{2-}/Fe_2O_3 as a catalyst. CMC, Krafft point, emulsion stability, foam ability and degradability of surfactants were determined and the results showed that the CMC values were less than 2.0×10^{-3} mol/L, emulsion formation, foam stability and the range of application temperature, compared with traditional surfactants, the new surfactants give better results and show better properties as the emulsifier in emulsion polymerization. In addition, the surfactants are stable under neutral and alkaline conditions, and can form solid in acid condition. The solid will generate to the original surfactants for reuse with alkali. Based on the above conclusions, sodium (5-methyl-2-alkyl-1,3-dioxane-5-yl) carboxylate is likely to be a new type of 'environmentally friendly' surfactant.

Acknowledgments: This work was financially supported by the Opening Project of Key Laboratory of Comprehensive Utilization of Advantage Plants Resources in Hunan South (XNZW14C01), the Scientific

Research Fund of Hunan Provincial Education Department (14A058), the Construct Program of the Key Discipline in Hunan Province (2011–76).

References and Notes

1. S. Noori, A. Z. Naqvi, W. H. Kram, and U. D. Kabir, *J. Surfact. Deterg.* 17, 409 (**2014**).
2. M. J. Rosen, Surfactants and Interfacial Phenomena, 3rd edn., Wiley, New York (**2004**).
3. K. R. Lange, Surfactants: A Practical Handbook, Hanser Publishers, Munich (**1999**).
4. J. S. Sun, X. W. Han, and B.Yu, *Org. Lett.* 7, 1935 (**2005**).
5. S. Kaihara, S. Matsumura, and J. P. Fisher, *Macromolecules* 40, 7625 (**2007**).
6. L. Yuan, G. C. Ou, J. H. Shi, M. Zhang, and X. Y. Yuan, *Chin. J. Org. Chem.* 33, 1817 (**2013**).
7. X. Y. Zhang, X. Y. Yuan, G. C. Ou, L. Yuan, and M. Zhang, *J. Bionanosci.* 8, 141 (**2014**).
8. M. Ratanajanchai, D. Tanwilai, and P. Sunintaboon, *J. Colloid Interf. Sci*. 25, 409 (**2013**).
9. S. C. Thickett and P. B. Zetterlund, *Macro Lett.* 2, 630 (**2013**).
10. M. Wang, Z. J. Ma, D. Zhu, D. Y. Zhang, and W. Yin, *J. Appl. Polym. Sci.* 128, 4224 (**2013**).
11. J. X. Xu, X. H. Wang, Y. Y. Zhang, W. Q. Zhang, and P. C. Sun, *J. Polym. Sci.* 50, 2484 (**2012**).
12. J. X. Xu, X. H. Wang, Y. Y. Zhang, W. Q. Zhang, and P. C. Sun, *J. Polym. Sci.* 51, 1147 (**2013**).
13. Q. Zhang, G. Q. Yu, W. J. Wang, B. G. Li, and S. P. Zhu, *Macromol. Papid Commun.* 33, 916 (**2012**).
14. Q. Zhang, G. Q. Yu, W. J. Wang, B. G. Li, and S. P. Zhu, *Langmuir* 28, 5940 (**2012**).
15. B. Bogdan, A. W. Kazimiera, S. Adam, and S. Ludwik, *J. Colloid Interf. Sci.* 240, 552 (**2001**).
16. X. Y. Yuan, N. F. Yang, H. A. Luo, and Y. J. Liu, *Chin. J. Org. Chem.* 25, 1049 (**2005**).
17. P. A. Joshi, S. R. Bonde, S. C. Gaikwad, A. K. Gade, K. Abd-Elsalam, and M. K. Rai, *J. Bionanosci.* 7, 378 (**2013**).
18. B. W. Boote, H. Byun, and J. H. Kim, *J. Nanosci. Nanotechnol.* 14, 1563 (**2014**).
19. M. Saravanan, V. Jacob, J. Arockiaraj, and P. Prakash, *J. Bionanosci.* 8, 21 (**2014**).
20. Y. Deng, W. Wang, L. Zhang, Z. Lu, S. Li, and L. Xu. *J. Biomed. Nanotechnol.* 9, 318 (**2013**).
21. R. Devi, A. Phukan, E. Saikia, and B. Chetia, *J. Bionanosci.* 8, 28 (**2014**).
22. Y. Deng, M. Wang, L. Jiang, C. Ma, Z. Xi, X. Li, and N. He, *J. Biomed. Nanotechnol.* 9, 1123 (**2013**).
23. L. Xu, Z. Tang, J. Zhang, J. Du, N. Li, and P. Jiang, *J. Bionanosci.* 7, 575 (**2013**).
24. S. Li, H. Liu, Y. Deng, L. Lin, and N. He, *J. Biomed. Nanotechnol.* 9, 1254 (**2013**).
25. Y. Deng, W. Wang, C. Ma, and Z. Li, *J. Biomed. Nanotechnol.* 9, 1378 (**2013**).
26. P. Jayaraman, S. Doss, H. Sridevi, K. Mathivanan, and P. Arumugam, *J. Bionanosci.* 7, 432 (**2013**).
27. N. He, F. Wang, C. Ma, C. Li, X. Zeng, Y. Deng, L. Zhang, and Z. Li, *J. Biomed. Nanotechnol.* 9, 267 (**2013**).
28. C. Xu and K. Chung, *Sci. China Chem.* 56, 831 (**2013**).
29. D. Li, L. Yang, J. Shi, E. Hou, and C. Zuo, *J. Bionanosci.* 7, 465 (**2013**).
30. H. Jiang, X. Zeng, Z. Xi, M. Liu, C. Li, Z. Li, L. Jin, Z. Wang, Y. Deng, and N. He, *J. Biomed. Nanotechnol.* 9, 674 (**2013**).
31. S. Dasari, K. A. Suresh, M. Rajesh, C. S. S. Reddy, C. S. Hemalatha, R. Wudayagiri, and L. Valluru, *J. Bionanosci.* 7, 237 (**2013**).
32. S. J. Newati, V. M. Singh, S. Sachdeva, and R. A. Khan, *J. Bionanosci.* 7, 260 (**2013**).
33. X. Ji, T. Wang, L. Guo, J. Xiao, Z. Li, L. Zhang, Y. Deng, and N. He, *J. Biomed. Nanotechnol.* 9, 417 (**2013**).
34. D. Wang, S. Tian, L. Pei, L. Ge, and U. Halmuart, *J. Bionanosci.* 7, 317 (**2013**).
35. Y. Tang, J. Zou, C. Ma, Z. Ali, Z. Li, X. Li, N. Ma, X. Mou, Y. Deng, L. Zhang, K. Li, G. Lu, H. Yang, and N. He, *Theranostics* 3, 85 (**2013**).
36. L. Y. Yang, C. Y. Chang, J. J. Hsu, and K. S. Yao, *J. Bionanosci.* 7, 181 (**2013**).
37. S. Li, H. Liu, Y. Jia, Y. Deng, L. Zhang, Z. Lu, and N. He, *Theranostics* 2, 967 (**2012**).
38. W. Liang and W. Wu, *Sci. China Chem.* 56, 1267 (**2013**).
39. W. Wang, Y. Deng, X. He, L. Xu, and Z. Li, *J. Nanosci. Nanotechnol.* 12, 7301 (**2012**).
40. W. Wang, Y. Deng, L. Xu, and X. He, *J. Biomed. Nanotechnol.* 9, 736 (**2013**).
41. W. Wang, Y. Deng, L. Zhang, J. Fu, Z. Lu, and L. Xu, *J. Nanosci. Nanotechnol.* 12, 7206 (**2012**).
42. I. Bogdan, P. Svitlana, S. Ruslan, T. Takaaki, S. Etsuro, N. Takashi, H. Itaru, and Z. Yaroslav, *J. Nanosci. Nanotechnol.* 12, 8913 (**2012**).
43. M. Zhang and L. M. Dai, *Nano Energy* 1, 514 (**2012**).
44. A. Farouk, S. Sharaf, and M. M. Abd El-Hady, *J. Biological Macromolecules* 61, 230 (**2013**).
45. E. Hanan, A. S. Noha, O. Amina, and I. Medhat, *Nanosci.* 11, 214 (**2014**).
46. M. D. Sandeep, S. K. Meghana, K. B. Kishor, D. C. Pravin, V. B. Ashok, K. N. Basavaraj, and A. S. Saurabh, *J. Bionanosci.* 8, 81 (**2014**).
47. S. H. Zhao, F. J. Shu, Y. M. Li, C. M. Liu, W. W. Shan, Y. T. Cui, and L. Yang, *J. Nanosci. Nanotechnol.* 12, 2607 (**2012**).
48. J. Lin, H. B. Pan, and S. F. Shen, *Spectroscopy and Spectral Analysis* 5, 616 (**2000**).
49. Y. P. An, B. Cui, Y. T. Wang, W. P. Jin, X. P. Geng, X. X. Yan, and B. Li, *Food Hydrocolloid.* 40, 1 (**2014**).
50. S. J. Dong, Y. L. Li, Y. B. Song, and L. F. Zhi, *J. Sufact. Deterg.* 16, 523 (**2013**).
51. M. S. Manono, K. C. Corin, and J. G. Wiese, *Miner. Eng.* 40, 42 (**2013**).

Received: 31 August 2014. Accepted: 3 October 2014.