Facile Synthesis of Poly(Carbonyl Urea) Oligomer (Pcuo) from Urea and Dipropyl Carbonate (Dprc) Applied as Nitrogen Slow-Release Fertilizer

[1,2]JIANCHAO CHEN, [2]YAQING LIU*, [1]HONGFANG JIU, [2]PEIHUA ZHAO AND [2]FUTIAN ZHU
[1] Department of Chemistry, School of Science, North University of China, Taiyuan 030051, P. R. China
[2] Research Center for Engineering Technology of Polymeric Composites of Shanxi Province, North University of China, Taiyuan 030051, P. R. China.
Lyq@nuc.edu.cn[*]

Summary: A novel slow-release nitrogen fertilizer poly(carbonyl urea)oligomer (PCUO) was prepared by the condensation polymerization of urea and dipropyl carbonate (DPrC) at normal pressure, in which anhydrous potassium carbonate was as a catalyst. The oligomer was characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, which showed that the number average degree of PCUO was 1 to 5. The effects of the molar ratio of urea to DPrC, reaction time as well as the temperature on the yields were investigated and optimized. In addition, the slow-release behaviour of PCUO was evaluated in distilled water and the results showed that the product with good slow-release properties could be expected to have wide potential applications in modern agriculture and horticulture.

Introduction

The consumption of synthetic nitrogen fertilizer in agriculture has increased over the past several decades, and it might continue to rise in order to meet the food demand of the growing global population [1]. Urea as the most conventional nitrogen fertilizer has been applied all over the world for many years due to its high nitrogen content [2]. However, it is so water-soluble that the released nitrogen dosage far exceeds plant uptake in a short time, which reduced the fertilizer use-efficiency. Furthermore, it could also lead to a buildup of the unemployed nitrogen nutrient in the soil, which may cause environment problems and low efficiency because of degradation and volatilization *etc* [3~5]. In recent years, slow-release fertilizer has been considered as an effective mean of improving fertilizer use-efficiency and overcoming the environmental problems associated with the application of traditional water-soluble fertilizers.

To compensate for the shortcomings of urea, many attempts to improve its slow-release properties by the polymerization have been reported [6~8]. Poly(carbonyl urea)oligomer as a novel type of slow-release fertilizer has attracted much attention due to its significant advantages over the earlier reported fertilizer. As is reported, the common methods for synthesizing slow-release fertilizer using physical methods have lots of drawbacks as complex techniques [9~11]. However, triuret as one of the poly(carbonyl urea)oligomer (n=1), can be generated by oxidation reaction or radical reaction [12~13]. Meanwhile, tetrauret, pentauret and hexauret were synthesized from carbonyl diisocyanate and ur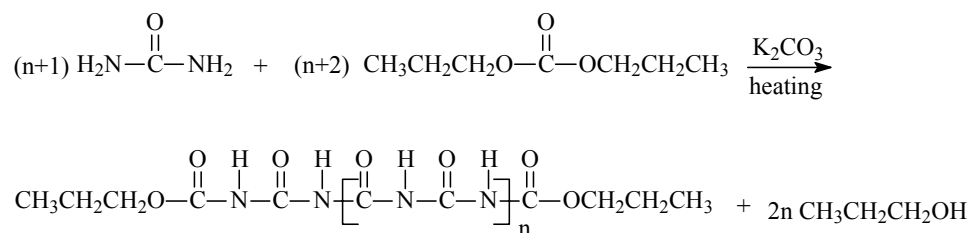ea or ammonia [14]. However, the above-mentioned methods for poly(carbonyl urea)oligomer have some drawbacks: the raw materials (e.g. sulfurisocyanatidic chloride, phosgene) and by-products (e.g. chlorinegas, hydrogen chloride and so forth) were poisonous and corrosive, which would be harmful to environment and human.

In this paper, we report the facile synthesis of a novel slow-release nitrogen fertilizer poly(carbonyl urea) oligomer (PCUO), which was a "designed" molecule synthesized from DPrC and urea at optimized Oconditions. PCUO have good slow-release property depending on the average polymerization degree, and especially, it may be degraded into urea and carbon dioxide by chemical and biological degradation in soils. These were significant advantages over the normal slow-release fertilizer, which generally have polymer matrix residue and heavy metal residue after application in soil. Additionally, we evaluate the releasing behavior of PCUO in detail .

Results and discussion

Synthesis of PCUO

As is shown in Scheme 1, PCUO, the polymerization degree of which is 1 to 5, was prepared by the treatment of urea with DPrC in the present of the catalyst anhydrous potassium carbonate and obtained as a white solid in 65%~85% yields. The polymerization degree of PCUO was not so high due to the low reaction reactivity of urea with DPrC as well as the thermolysis of the product (PCUO). However, the lower polymerization degree of PCUO was appropriate to be used as slow-release fertilizer for a suitable degradation cycle.

$$(n+1)\ H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2\ +\ (n+2)\ CH_3CH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2CH_3\ \xrightarrow[\text{heating}]{K_2CO_3}$$

$$CH_3CH_2CH_2O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\left[\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}\right]_{n}\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2CH_3\ +\ 2n\ CH_3CH_2CH_2OH$$

Scheme 1:   The synthetic route of PCUO.

In addition, the only by-product *n*-propanol is hardly poisonous and has little negative repercussions to the human and the environment, and it could further react with dimethyl carbonate or directly with CO_2 to produce DPrC so as to achieve reaction recycling [15~17]. Consequently, the new synthetic method of the oligomer should be environmentally friendly and much more economical.

Characterization of PCUO (n = 5).

As shown in Fig. 1, FT-IR spectrum gave comparison of pure urea with PCUO. Compared with the FT-IR spectrum of pure urea, that of PCUO exhibited lots of new absorption peaks. For example, the new peak at 1785 cm^{-1} ascribes to the strong stretching frequency of carbonyl group. The new peaks observed at 3423 cm^{-1} corresponds to N-H group in PCUO. Meanwhile, the appearance of the new absorption bands at 1058 cm^{-1} (-CO-O-CH$_2$-, stretching of alkoxyl group), 1462 cm^{-1} (-CH$_2$-, scissor bending vibration of methylene group), 2995 and 1385 cm^{-1} (-CH$_3$, asymmetrical stretching vibration and symmetrical deformation vibration of methyl group) are also observed. These new absorption bands give direct evidence for the formation of PCUO.
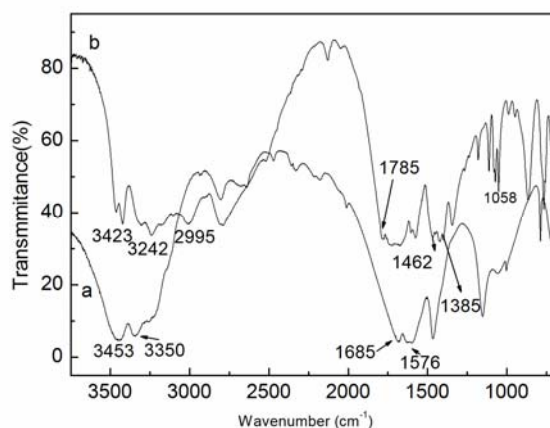
The structure of PCUO was further confirmed by the ^{1}H-NMR spectrum as shown in Fig. 2. It gave three proton signals at δ 6.01-7.05 ppm (5H, a), 8.02-8.33 ppm (1H, b), and 9.61-10.37 ppm (4H, c), which were consistent with those of the reported biuret and triuret [14,18]. Furthermore, it exhibited two characteristic signals at δ 3.58-3.71 ppm and δ 2.85/1.33 ppm assigned to methylene and methyl group, respectively. Consequently, the number average degree of PCUO could be confirmed as five from the the ratio of total integrated H$_c$ signals to integrated H$_b$ signal based on the reported literatures[19~20].

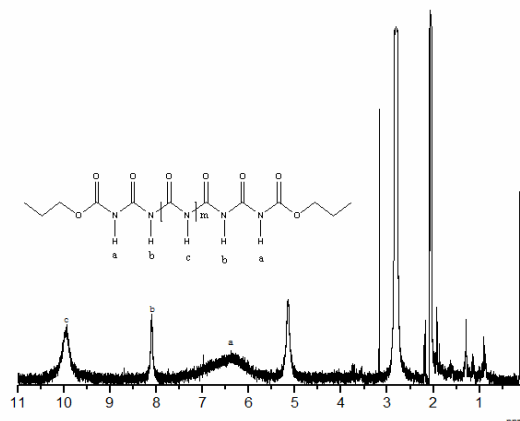Fig. 2:   ^{1}H-NMR spectrum of PCUO.

Additionally, the molecular structure of PCUO was also estimated by the ^{13}C-NMR spectrum as shown in Fig. 6, which clearly showed four carbon spectrum signals at δ 157.0 ppm (C$_a$), 159.4 ppm (C$_b$), 161.9 ppm (C$_c$) and 162.4 ppm (C$_d$). As a result, these results further confirmed the formation of PCUO.

Effects of Polymerization Degree of PCUO

Influence of Reaction Temperature on Polymerization Degree of PCUO

As shown in Fig. 3, the influence of the reaction temperature on the degree of polymerization was investigated. It clearly shows that the

Fig. 1:   FT-IR spectrum of (a) pure urea and (b) PCUO.

polymerization degree of PCUO increases with the reaction temperature range from 141 ^{0}C to 160 ^{0}C. Especially, the polymer chain grows more rapidly at higher temperature, which was consistent with step-condensation reaction of low molecular. The same phenomenon can be observed in those of the reported poly(carbonate-co-esters) and the other polymers [21-22].
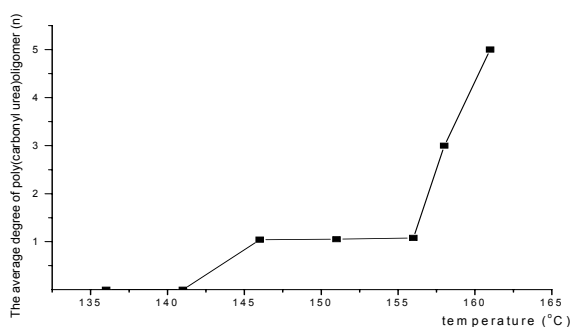

Fig. 3:   Influence of temperature on the average degree of PCUO: n (urea):n (DPrC) = 1.5:1, 8 h, 0.45 g K_2CO_3.

It is well-known that triuret (n = 1) has been confirmed as a controlled release fertilizer on the basis of its low solubility and its structure [23]. Moreover, triuret has a nitrogen release pattern approximating the needs of one-season crops [24] although the release period of triuret may be too limited when applied to the crops of longer growth period. However, the prepared PCUO may much easily meet the nitrogen need of the various crops due to its average degree of polymerization in the range from 1 to 5 in our study.

Influence of Reaction Time on Polymerization Degree of PCUO

Fig. 4, 5 shows the influence of the reaction time on the degree of polymerization under the conditions of n (urea): n (DPrC) = 1.5:1, 161 °C, 0.45 g anhydrous potassium carbonate. It is obvious that the reaction time is an important factor affecting the degree of polymerization. The degree of polymerization increases with an increase of the reaction time until it reaches a maximum at 8 h. However, when the reaction time is larger than 8 h, the number average degree of polymerization slightly decrease with the continue of the reaction. These behaviors may be attributed to the reaction of urea and DPrC as well as the decomposition of urea[18,25], which are complied with Le Chatelier's principle. Further more, the average degree of the oligomer generally increases as reaction time goes on because of further condensation polymerization,

however, the PCUO and urea will decompose in to lower degree of PCUO and ammonia respectively.

Influence of n (urea):n (DPrC) on Polymerization Degree of PCUO

The effect of the molar ratio of urea to DPrC on the average degree of the polymer was displayed in Fig. 5. It is obvious that the polymerization degree of the oligomer increases as the reaction temperature increases from 145 ^{0}C to 160 ^{0}C. The average degree of the oligomer was 4 when n (urea):n (DPrC) = 1.2:1 , whereas that of the oligomer was 5 when n (urea): n (DPrC) = 1.5:1. The results seem to be different from the theoretical calculations, because urea will evaporate and then condense in the flask so that parts of urea can't react with DPrC at the temperature between 156 ^{0}C and 160 ^{0}C. Meanwhile, ammonolysis reaction of DPrC is reversible, so it is economical to obtain slow/controlled released fertilizer by increasing molar weight of urea. In addition, the rest of urea will meet the nitrogen nutrient of the crops at seedling period.
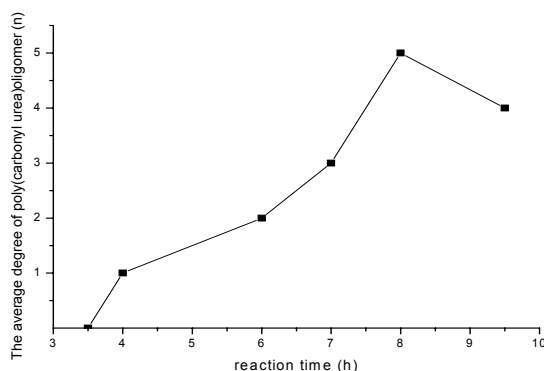

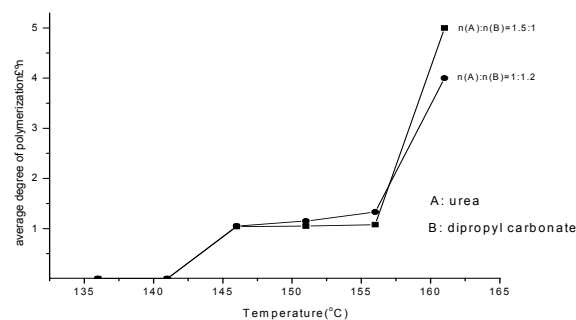Fig. 4:   Influence of reaction time on the average degree of PCUO : n (urea):n (DPrC) = 1.5:1, 161 ^{0}C, 0.45 g K_2CO_3.

Fig.5:   Influence of n (urea): n (DPrC) on the average degree: polymerization time = 8 h, 0.45 g K_2CO_3.

3

Slow Released Properties of PCUO

Further study on the slow-release behavior was carried out in distilled water and Fig. 6 represents the nitrogen slow-release behavior of PCUO (n=2). It is well-known that urea is easily dissolved in water, so it would quickly dissolve in the soil solution after being applied to the soil and the nutrient would be quickly exhausted. As shown in Fig. 7, the nitrogen in PCUO (n=2) possesses excellent slow-release property: the nitrogen in PCUO (n=2) released 12, 40, 65, and 75 % within 5, 15, 25, and 35 days, respectively. The nitrogen release does not exceed 8 % at 2.5 days and is not above 75 % before 35 days. These results indicate that PCUO (n=2) we prepared may be used as slow-release fertilizer without further treatment [26-28]. In addition, the nitrogen slow-release period can be prolonged by increasing the size of PCUO (n=2) particles as we need. The results of the present work indicated that PCUO would find good application in agriculture and horticulture than traditional nitrogen fertilizer.
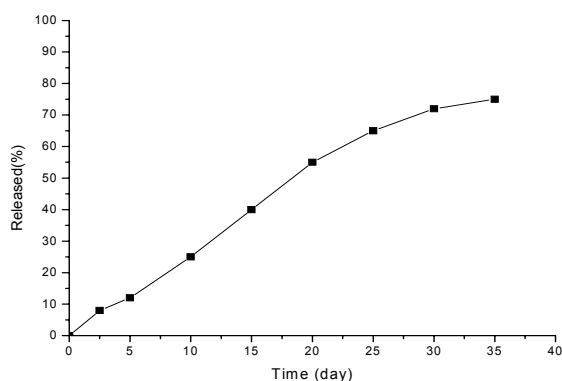

Fig. 6: Slow-release behavior of nitrogen from PCUO (n=2) in distilled water.

Experimental

Materials

Urea, dipropyl carbonate (DPrC), anhydrous potassium carbonate and methanol were commercially purchased from Shandong, Shanghai, Tianjin and Tianjin chemical plant, respectively. Those four raw materials were all of analytical reagent grade and used without further purification.

Preparation of PCUO

A typical procedure of the polymerization was as follows: a certain amount of DPrC (1.0 mol) and anhydrous potassium carbonate (0.45 g) was placed into a 500 ml round-bottom flask equipped with a heating mantle, condensationpipe, magnetic stirrer (or a mechanical stirrer) and thermometer. Urea (1.5 mol) was added to the above mixture solution at 50 ^{0}C. After stirring for additional 10 min, the mixture was gradually heated to 160 ^{o}C. The resulting solution was then stirred for 8 h. After polymerization, the crude product was filtered by vacuum, and washed with methanol three times. After purification, the product (PCUO) was dried in oven at 100 ^{0}C to a constant weight and obtained as a white solid in 65 %.

Slow-Release Behavior of PCUO

To further study the release behavior of PCUO, the following experiment was carried out: 5 g PCUO sample (n=2, bellow 50 mesh) was immersed in 100 mL distilled water in a glass beaker properly covered at 25   . A quantity of 5.0 mL of solution was taken out to estimate for the contents of nitrogen after a certain interva, and then the same volume of fresh water was replenished. The nitrogen content was estimated by the Kjeldahl method. The above tests were carried out in triplicate, and the average value was taken as the result.

Characterizations

^{1}H-NMR spectrum was recorded using tetramethylsilane as an internal standard in CD$_3$COCD$_3$ on a Bruker Avance   500 MHz spectrometer. ^{13}C-NMR spectrum was recorded using tetramethylsilane as an internal standard in DMSO-d_6 on a Bruker Avance   150 MHz spectrometer. The infrared spectrum was obtained on a shimadzu Fourier-transform infrared spectroscope (FT-IR) 8400S spectrophotometer using KBr tabletting methods to identify the chemical structure of the sample.

Conclusion

Poly(carbonyl urea)oligomer (PCUO) was synthesized by the simple condension polymerization of urea and DPrC. Its structure is confirmed by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra. The effect of reaction conditions on the degree of polymerization was investigated in detail. The results showed that the average degree of polymerization strongly depends on the reaction temperature, the time, and the molar ratio of urea to DPrC. The number average degree of PLUO can be easily controlled , which was helpful to obtain special nitrogen fertilizer for different crops. In addition, further studies on slow-released property of PCUO are in progress in our laboratory.
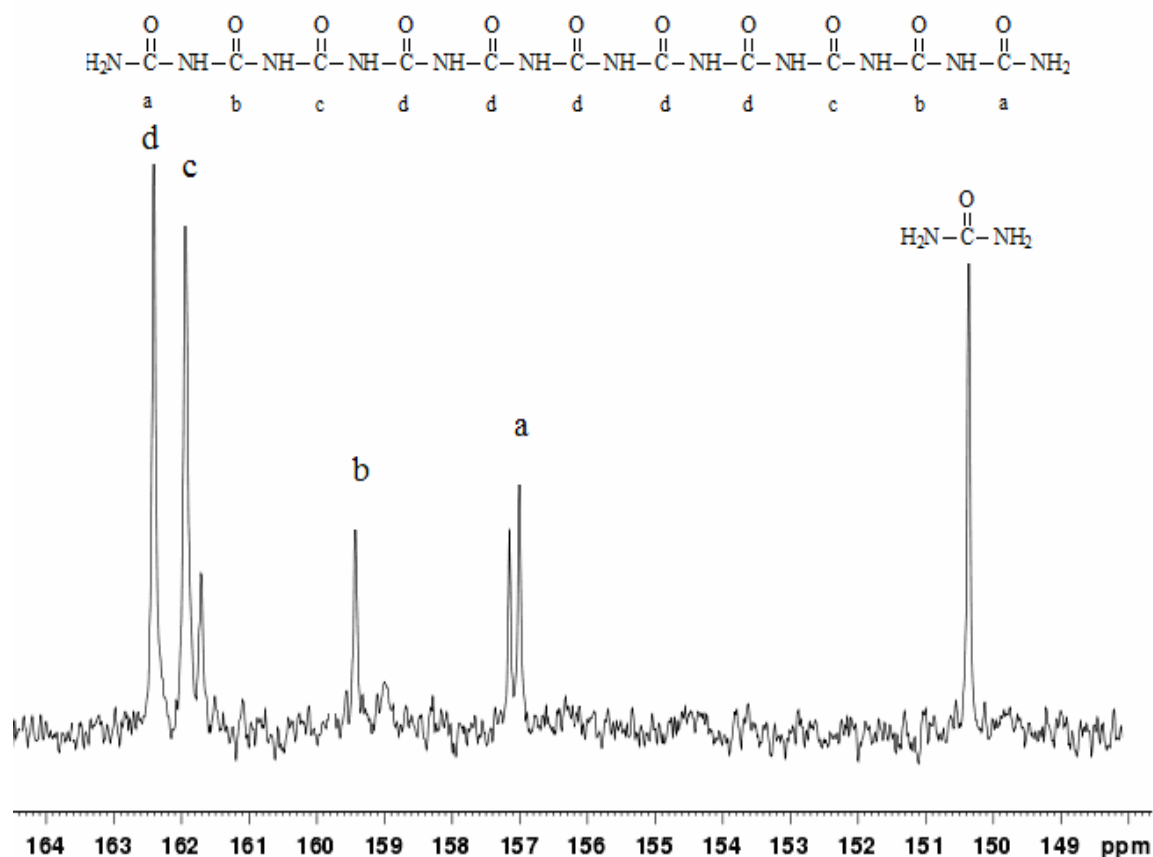
Fig. 7: ^{13}C-NMR spectrum of PCUO.

References

1. J. Y. Jiang, Z. H. Hu and W. J. Sun, *Agriculture Ecosystems and Environment*, **135**, 216 (2010).
2. X. Yan, J. Y. Jin and P. He, *Agricultural Sciences in China*, **7**, 469 (2008).
3. A. K. Bajpai and A. Giri, *Reactive and Functional Polymers*, **53**, 125 (2002).
4. M. Guo, M. Liu, Z. Hu, F. Zhan, L. Wu, *Journal of Applied Polymer Science*, **96**, 2132 (2005).
5. P. G. Susana, F. P. Manuel and V. S. Matilde, *Industrial and Engineering Chemistry Research*, **46**, 3304 (2007).
6. J. T. Hays and W. B. Hewson, *Journal of Agricultural and Food Chemistry*, **21**, 498 (1973).
7. M. M. Fan and P. B. Zhang, *Energy and Fuels*, **21**, 633 (2007).
8. E. R. Austln, R. G. Howard and T. J. Bradford, *Industrial and Engineering Chemistry Research*, **24**, 425 (1985).
9. A. I. Ahmed and Y. J. Baba, *Industrial and Engineering Chemistry Research*, **44**, 2288 (2005).
10. R. Liang and M. Z. Liu, *Journal of Agricultural and Food Chemistry*, **54**, 1392 (2006).
11. R. Liang and M. Z. Liu, *Industrial and Engineering Chemistry Research*, **45**, 8610 (2006).
12. S. P. Palii, C. S. Contreras and J. D. Steill, *Archives of Biochemistry and Biophysics*, **498**, 23 (2010).
13. K. M. Robinson, J. T. Morre and J. S. Beckman, *Archieves of Biochemistry and Biophysics*, **423**, 213 (2004).
14. B. Frank, Ph. D. Thesis, *Synthese, Charakterisierung und Untersuchung von*

schwerlöslichen Harnstoffderivaten als Grundlage für Düngemittel, Freie Universität Berlin in Berlin **(1999)**.

15. M. M. Fan and P. B. Zhang, *Energy and Fuels*, **21**, 633 (2007).
16. M. S. Honda, S. Kuno and N. Begum, *Applied Catalysis* A*: General*, **384**, 165 (2010).
17. X. Y. Li, Y. H. Zhang and B. Xue, *Journal of Molecular Catalysis* A*: Chemical*, **287**, 9 (2008).
18. G. Janna, H. Gerhard, M. K. Thomas and J. J. Weigand, *Combustion and Flame*, **139**, 358 (2004).
19. C. Cristiana, O. Astrid, S. B. Gudmund, S. P. Berit, P. Sergio and B. E. Christensen, *Journal of Chromatography* A, **1026,** 271 (2004).
20. M. Zatloukal, F. Rybnikár and P. Sáha, *European Polymer Journal,* **38**, 1925 (2002).
21. Z. Z. Jiang, C. Liu, W. C. Xie and R. A. Gross, *Macromolecules*, **40**, 7934 (2007).
22. Z. Z. Jiang, C. Liu and R. A. Gross, *Macromolecules*, **41**, 4671 (2008).
23. W. H. Smith, H. G. Underwood and J. T. Hays, *Journal of Agricultural and Food Chemistry*, **19**, 816 (1971).
24. J. T. Hays and W. B. Hewson, *Journal of Agricultural and Food Chemistry*, **21**, 498 (1973).
25. L. Andreas, A. Bengt and O. Louise, *Chemical Engineering Journal*, **150**, 544 (2009).
26. M. E. Trenkel, Slow- and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture, International Fertilizer Industry Association-Paris, p. 15, (2010).
27. H. Demiralay, M. Akdogan and M. Ciris, *Journal of the Chemical Society of Pakistan*, **33**, 733 (2011).
28. R. J. Singh, *Journal of the Chemical Society of Pakistan*, **33**, 485 (2011).