

# On a Novel Catalytic System Based on Electrospun Nanofibers and M-POSS

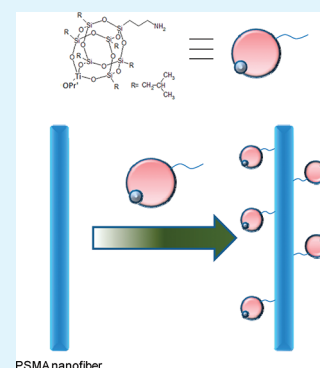
Erika Simona Cozza,<sup>†</sup> Valentina Bruzzo,<sup>†</sup> Fabio Carniato,<sup>‡</sup> Enrico Marsano,<sup>†</sup> and Orietta Monticelli<sup>\*,†</sup>

<sup>†</sup>Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso, 31, 16146 Genova, Italy

<sup>‡</sup>Dipartimento di Scienze e Tecnologie Avanzate and Nano-SISTEMI Interdisciplinary Centre, Università del Piemonte Orientale 'A. Avogadro', Viale Teresa Michel 11, 15121 Alessandria, Italy

## S Supporting Information

**ABSTRACT:** We report on a novel catalytic system based on electrospun polymer nanofibers, which were modified with a metal-containing polyhedral oligomeric silsesquioxanes (M-POSS). In particular, a titanium-based POSS, characterized by an amino group as reactive side, was contacted with poly(styrene-*co*-maleic anhydride) (PSMA) nanofibers, which were dispersed in a solvent capable of solubilizing the above metal silsesquioxane. FTIR measurements evidenced the occurrence of the reaction between the MA group of PSMA and the amino group of POSS molecule. The catalytic activity of the PSMA/Ti-POSS-NH<sub>2</sub> system was proved in the degradation of sulforhodamine B under UV light. The presence of metal center, directly attached to the nanofiber surface, renders the system catalytically active.



**KEYWORDS:** electrospinning, M-POSS, surface functionalization, heterogeneous catalyst

Electrospinning is a simple method capable of producing ultrafine fibers with diameters, ranging from nanometer to micrometer scales.<sup>1</sup> In particular, polymer nanofibers have been studied for a number of applications including composites, filtration, and biomaterials. Among the various exploitations of these materials, recently their use as support of homogeneous<sup>2</sup> and heterogeneous catalysts<sup>3,4</sup> has been proposed. Indeed, immobilization of catalyst on solid supports is of great interest because it can make the handling and recovery of catalysts much easier. Nanostructured supports, such as mesoporous materials and nanoparticles, are widely studied because they provide a high surface to mass ratio;<sup>5,6</sup> among these, polymer nanofibers offer several advantages over other nanostructures. Long and continuous polymer nanofibers can easily be made with an electrospinning process.<sup>7,8</sup> This technique is applicable to a variety of polymer materials. The electrospun polymer nanofibers can be structurally tailored to nonwoven mats, well-aligned arrays, or membranes.<sup>9</sup> The large surface-to-mass ratio of nanofibers provides an advantage of higher loading per mass, and thus higher catalytic activity per mass. Moreover, electrospun nanofibers can be easily recovered from solution and reused.

In particular, as far as Ti-based catalysts are concerned, the object of the present work and generally applied as titanium dioxide (TiO<sub>2</sub>), electrospinning has been used to prepare both neat TiO<sub>2</sub><sup>10–13</sup> nanofibers or rice grain-shaped TiO<sub>2</sub> mesostructures<sup>14</sup> and polymer-containing TiO<sub>2</sub> nanofibers.<sup>2,15–17</sup> Moreover, electrospun nanofibers have been used as support of

titanium dioxide, deposited by several techniques, such as sputter coating,<sup>18</sup> layer by layer,<sup>19</sup> and tip coating.<sup>20</sup>

Indeed, TiO<sub>2</sub> has been extensively studied as a photocatalyst because of its chemical stability and nontoxicity.<sup>21</sup> In recent years, one of the most active areas in photocatalysis is environmental remediation with TiO<sub>2</sub>-based photocatalysts, which turned out to be effective for the degradation of many organic pollutants.<sup>22</sup> Moreover, the photocatalytic activity of TiO<sub>2</sub> was enhanced by doping the nanoparticles with nitrogen,<sup>23</sup> or by using composite systems based, for example, on carbon nanotubes<sup>24</sup> and graphene.<sup>25</sup> However, one the major drawback of the above catalytic system is the difficulty of the photocatalyst recovery by separation of the fine TiO<sub>2</sub> particles from the liquid. As previously mentioned, to solve this problem, many immobilization systems have been tested employing several supports.

In this work, a novel titanium-based heterogeneous catalytic system based on polymer nanofibers has been assessed. In particular, for the first time, grafting of the metal center on the nanofiber surface has been attempted through the exploitation of a functionalized metal-containing polyhedral oligomeric silsesquioxanes (POSS), namely a silsesquioxane potentially capable of reacting with the polymer surface. Indeed, the polymer/M-POSS nanofibers should represent not only an easily recoverable catalyst but, with respect to the other

**Received:** December 13, 2011

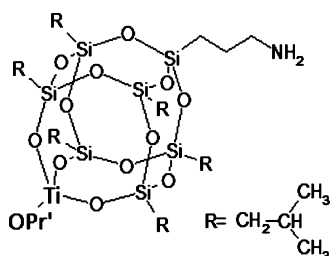
**Accepted:** January 27, 2012

**Published:** January 28, 2012

mentioned catalytic systems, should also hold higher accessible catalytic centers because of the direct grafting of the metal on the polymer surface.

In general, POSS are organic/inorganic molecules, sizing approximately 1 to 3 nm, with general formula  $(\text{RSiO}_{1.5})_n$ , where R is hydrogen or an organic group, such as alkyl, aryl, or any of their derivatives. As far as M-POSS are concerned, they can be prepared from incompletely condensed structures, i.e., open-corner POSS molecules.<sup>26</sup> Indeed, M-POSS, already exploited in the field of both homogeneous and heterogeneous catalysis (e.g., epoxidation<sup>27</sup> and lactide polymerization<sup>28</sup>), turned out to strongly affect thermo-oxidative degradation of polymer nanocomposites.<sup>29,30</sup>

In our work, a titanium-based POSS, characterized by an amino group as reactive side (Figure 1), was contacted with



**Figure 1.** Amino hexaisobutyl titanium POSS (Ti-POSS-NH<sub>2</sub>).

poly(styrene-*co*-maleic anhydride) (PSMA) nanofibers, which were dispersed in a silsesquioxane solvent.

Indeed, this work has been preliminary focused on the study of the influence of the electrospun nanofiber morphology on nanofiber dispersibility in a solvent capable of solubilizing Ti-POSS-NH<sub>2</sub> molecules. In particular, as shown in Figure 2, by keeping constant all the electrospinning parameters (polymer concentration, voltage tension, air flow, distance, etc.) and increasing the relative humidity (Rh) the morphology completely changes; passing Rh from 20 to 50%, the homogeneity of the fibers increases.

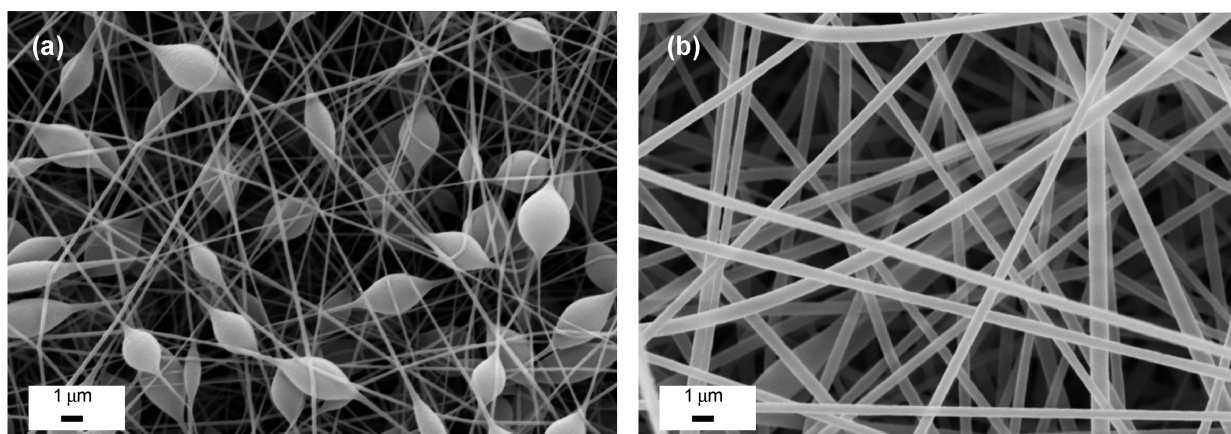
It is worth mentioning that the above parameter, which is generally not studied, was only recently considered by Casper et al.,<sup>31</sup> who concentrated their investigation on the influence of the amount of moisture on the surface morphology of electrospun PS fibers from THF, finding that high level of humidity (above 30%) favored the formation of pores on the

surface of the fibers. Moreover, in a previous work of ours, the effect of Rh on the morphology of PVDF-based nanofiber was assessed.<sup>32</sup>

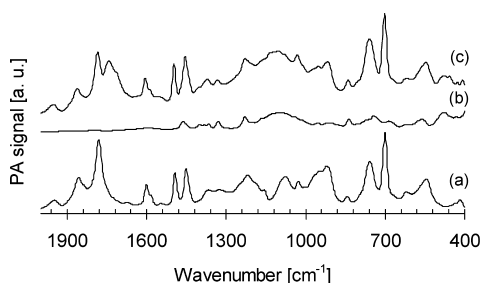
Moreover, recently, Tripatanasuwan et al.<sup>33</sup> studied the effects of the relative humidity on the evaporation rate and solidification of the charged jet during electrospinning of poly(ethylene oxide) from aqueous solution. It was reported that increasing the relative humidity, the nanofibers diameter decreased, thus demonstrating that the vapor concentration of the solvent is a parameter capable to control the fiber morphology. In our case, there is no water present in the polymer solution, so the humidity does not act directly on the solvent concentration in the chamber but it is probably responsible for the polymer precipitation. Indeed, a higher relative humidity might facilitate the polymer precipitation in the ejected solution and, as a consequence, decreases the elongation time of the charged jet. Therefore, at low relative humidity the process of polymer precipitation is not induced and a slower solidification occurs; that is, the charged jet undergoes a more prolonged elongation, thus promoting the formation of thinner nanofibers. Conversely, at high relative humidity, the polymer precipitation is promoted and, consequently, the faster solidification leads the nanofiber average diameter to increase as well as their dimensional homogeneity to improve. Clearly, the surface reaction between the PSMA nanofiber and the solubilized POSS requires the electrospun membrane dispersion in the solvent, namely, the disentanglement of the electrospun mats, which consists of intricate single nanofibers. The dispersion has been found to be related to the nanofiber morphology and in particular, the presence of beads turns out to facilitate the electrospun mat disentanglement. Indeed, the defective nanofibers (Figure 2a) are well-dispersed in MeOH.

To study the kind of interactions and/or reactions occurring between Ti-POSS-NH<sub>2</sub> and the polymer surface, we have analyzed neat PSMA nanofibers, the amino type Ti-POSS, and the modified nanofibers by FT-IR measurements.

In Figure 3, IR spectra of PSMA, Ti-POSS-NH<sub>2</sub>, and the nanofibers contacted with the above metal-POSS are reported. The neat POSS shows a strong Si–O–Si stretching absorption band at ca. 1100 cm<sup>-1</sup>, which is the typical absorption peak of the silsesquioxane inorganic framework.<sup>26</sup> PSMA holds two characteristic absorption peaks at 1772 and 1850 cm<sup>-1</sup> due to symmetric and antisymmetric stretching vibrations of the anhydride carbonyl group as well as a peak at 1213 cm<sup>-1</sup>



**Figure 2.** SEM micrograph of: (a) PSMA nanofibers prepared by applying a Rh of 20%; (b) PSMA nanofibers prepared by applying a Rh of 50%.



**Figure 3.** FTIR spectra of: (a) PSMA electrospun nanofibers, (b) Ti-POSS-NH<sub>2</sub>, and (c) treated PSMA electrospun nanofibers.

attributed to the stretching vibration C–O–C of maleic anhydride units.<sup>34</sup> In the spectrum of the nanofibers treated with Ti-POSS-NH<sub>2</sub>, together with the peaks characteristics of the neat polymer matrix, new bands at ca. 1100 and 1740 cm<sup>-1</sup> appear together with a shoulder at 1710 cm<sup>-1</sup>. The former band, as previously reported, is due to Si–O–Si stretching vibration and gives evidence of the presence of POSS on the polymer surface, whereas the ones at higher wavenumbers at 1740 cm<sup>-1</sup> and the shoulder at 1710 cm<sup>-1</sup>, can be assigned to the carbonyl group stretching vibration of a carboxylic acid and of an amide, respectively.<sup>35</sup> It is worth underlining that the intensity of these peaks do not disappear in the samples after extraction of unbound POSS, evidencing the occurrence of a grafting reaction between the silsesquioxane molecules and the polymer. Thus, as illustrated in Figure 4, these results prove the occurrence of the reaction between the MA group of PSMA and the amino group of POSS molecules.

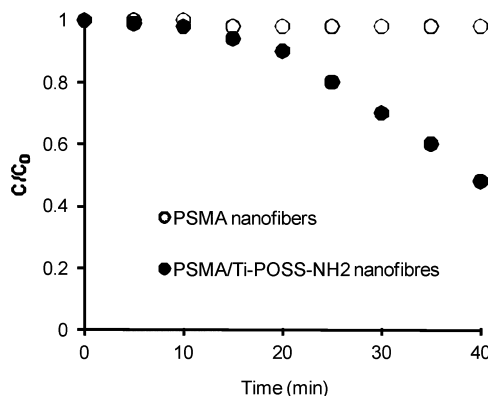
Indeed, as previously reported in the case of the preparation of hybrid systems based on PSMA and an amino-functionalized POSS via melt blending<sup>36</sup> or vapor-phase grafting,<sup>37</sup> the temperatures applied (above 140 °C) allowed the subsequent condensation reaction with the formation of a cyclic imide linkage. Conversely, as demonstrated by FT-IR analysis, the mild conditions used to modify PSMA nanofibers, turn out to promote only the first step of the reaction between the MA and the amino group.

Is important to underline that the morphology of the nanofibers does not change after the contact with Ti-POSS-NH<sub>2</sub>, while SEM-EDS and XPS analysis demonstrates a homogeneous Si distribution on the fiber surface (atomic

percentage of ca. 10%). Clearly, these results confirm the occurrence of the silsesquioxane surface grafting on the nanofiber surface.

The degradation of sulforhodamine B (sB) was investigated to determine the photocatalytic activity of the electrospun nanofibers.

Figure 5 shows the plots of decrease in sB concentration with UV exposure time in presence of PSMA/Ti-POSS-NH<sub>2</sub>

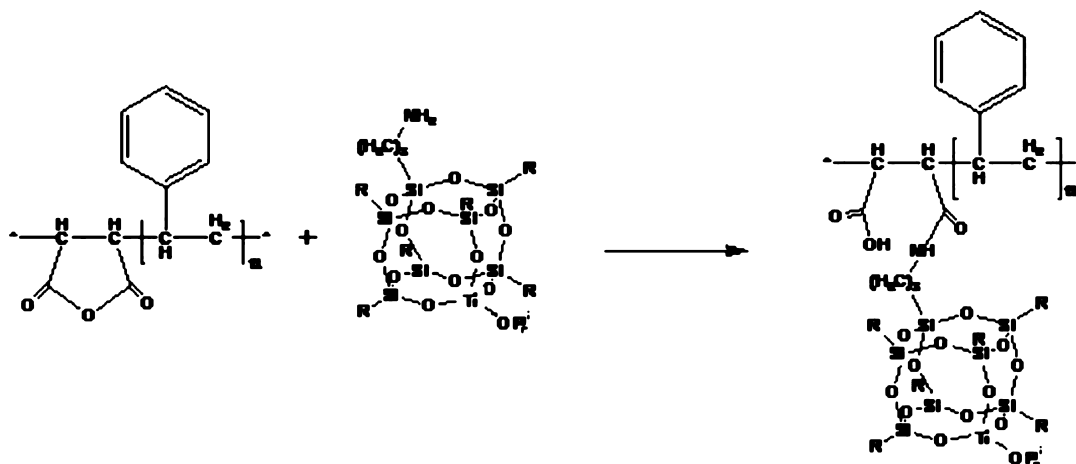


**Figure 5.** Decrease in sB concentration with UV irradiation time (in presence of electrospun webs).

nanofibers, compared to pure PSMA nanofibers. Indeed, in the case of the solutions containing the treated nanofibers, the concentration of sB decrease rapidly after 20 min of exposure and after 40 min about 50% of the above reagent is degraded. Conversely, the concentration of sB for the neat PSMA nanofiber-based solution remains the same. It is important to point out that a following catalytic test demonstrated that the activity of the catalytic system is completely maintained.

Although the results are only preliminary, and a more detailed investigation, mainly on the reaction mechanism and on the catalyst durability, needs to be accomplished, they demonstrate that the nanofiber/M-POSS system, characterized by highly available catalytic centers, shows a relevant photocatalytic activity.

In conclusion, a novel catalytic heterogeneous system, characterized by the presence of metal centers directly attached to the surface of electrospun nanofibers, has been assessed



**Figure 4.** PSMA electrospun nanofiber surface and Ti-POSS-NH<sub>2</sub> reaction scheme.

through the exploitation of a functionalized M-POSS capable of reacting with the polymer matrix. Indeed, the surface reaction has been successfully applied to the grafting of a titanium amino-functionalized POSS on PSMA nanofibers.

Moreover, the work demonstrates the photocatalytic activity of the nanofiber/M-POSS system for degradation of the organic dye sulforhodamine B. Clearly, the easy separation of the nanofibers after the reaction makes the developed heterogeneous catalyst a promising system for a practical exploitation.

Besides the catalytic activity, thanks to the presence of the siliceous POSS structure, other peculiar properties of the nanofiber/M-POSS system can be envisaged.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +39 010 3536196. Fax: +39 010 3538733. E-mail: [orietta.monticelli@unige.it](mailto:orietta.monticelli@unige.it).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to the Italian Ministry of Education and University through the 2008 PRIN Project (Grant 20089B75ML\_001).

## ■ REFERENCES

- (1) Bhardwaj, N.; Kundu, S. C. *Biotechnol. Adv.* **2010**, *28*, 325.
- (2) Stasiak, M.; Röben, C.; Rosenberger, N.; Schleth, F.; Studer, A.; Greiner, A.; Wendorff, J. H. *Polymer* **2007**, *48*, 5208.
- (3) Zhang, C.; Yang, Q.; Zhan, N.; Sun, L.; Wang, H.; Song, Y.; Li, Y. *Colloids Surf., A* **2010**, *362*, 58.
- (4) Nair, S.; Kim, J.; Crawford, B.; Kim, S. H. *Biomacromolecules* **2007**, *8*, 1266.
- (5) Alexeev, O. S.; Gates, B. C. *Ind. Eng. Chem. Res.* **2003**, *42*, 1571.
- (6) Blaser, H. U.; Indolese, A.; Schnyder, A.; Steiner, H.; Studer, M. J. *Mol. Catal. A: Chem.* **2001**, *173*, 3.
- (7) Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
- (8) Li, D.; Wang, Y.; Xia, Y. *Adv. Mater.* **2004**, *16*, 1151.
- (9) Herricks, T. E.; Kim, S.-H.; Kim, J.; Li, D.; Kwak, J. H.; Grate, J. W.; Kim, S. H.; Xia, Y. *J. Mater. Chem.* **2005**, *15*, 3241.
- (10) Yang, D.; Liu, H.; Zheng, Z.; Yuan, Y.; Zhao, J.; Waclawik, E. R.; Ke, X.; Zhu, H. *J. Am. Chem. Soc.* **2009**, *131*, 17885.
- (11) Madhugiri, S.; Sun, B.; Smirniotis, P. G.; Ferraris, J. P.; Balkus, K. J. Jr. *Micropor. Mesopor. Mat.* **2004**, *69*, 77.
- (12) Alves, A. K.; Berutti, F. A.; Clemens, F. J.; Graule, T.; Bergmann, C. P. *Mater. Res. Bull.* **2009**, *44*, 312.
- (13) Francis, L.; Nair, A. S.; Jose, R.; Ramakrishna, S.; Thavasi, V.; Marsano, E. *Energy* **2011**, *36*, 627.
- (14) Nair, A. S.; Shengyuan, Y.; Peininga, Z.; Ramakrishna, S. *Chem. Commun.* **2010**, *46*, 7421.
- (15) Im, J. S.; Kim, M. I.; Lee, Y.-S. *Mater. Lett.* **2008**, *62*, 3652.
- (16) Praharn, C.; Klinsukhon, W.; Roungpaisan, N. *Mater. Lett.* **2011**, *65*, 2498.
- (17) Francis, L.; Marsano, E.; Vijila, C.; Barhate, R. S.; Vijay, V. K.; Ramakrishna, S.; Thavasi, V. *J. Nanosci. Nanotechnol.* **2011**, *11*, 1154.
- (18) Wei, Q. F.; Huang, F. L.; Hou, D. Y.; Wang, Y. Y. *Appl. Surf. Sci.* **2006**, *252*, 7874.
- (19) Ding, B.; Kim, J.; Kimura, E.; Shiratori, S. *Nanotechnology* **2004**, *15*, 913.
- (20) Neuberta, S.; Pliszka, D.; Thavasia, V.; Wintermantel, E.; Ramakrishna, S. *Mater. Sci. Eng., B* **2011**, *176*, 640.
- (21) Thompson, T. L.; Yates, J. T. *Chem. Rev.* **2006**, *106*, 4428.
- (22) Li, J.; Ma, W.; Chen, C.; Zhao, J.; Zhu, H.; Gao, X. *J. Mol. Catal. A: Chem.* **2007**, *261*, 131.
- (23) Burda, C.; Lou, Y.; Chen, X.; Samia, A. C. S.; Stout, J.; Gole, J. L. *Nano Lett.* **2003**, *3*, 1049.
- (24) Yao, Y.; Li, G.; Ciston, S.; Lueptow, R. M.; Gray, K. A. *Environ. Sci. Technol.* **2008**, *42*, 4952.
- (25) Zhou, K.; Zhu, Y.; Yang, X.; Jiang, X.; Li, C. *New J. Chem.* **2011**, *35*, 353.
- (26) Pescarmona, P. P.; Maschmeyer, T. *Aust. J. Chem.* **2002**, *54*, 583.
- (27) Wang, Y. M.; Magusin, P. C. M. M.; van Santen, R. A.; Abbenhuis, H. C. L. *J. Catal.* **2007**, *251*, 453.
- (28) Monticelli, O.; Cavallo, D.; Bocchini, S.; Frache, A.; Carniato, F.; Tonelotto, A. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4794.
- (29) Monticelli, O.; Zunino, E.; Carniato, F.; Boccaleri, E.; Marchese, L.; Chincarini, A. *Polym. Adv. Technol.* **2010**, *21*, 848.
- (30) Hoyos, M.; Fina, A.; Carniato, F.; Prato, M.; Monticelli, O. *Polym. Degrad. Stab.* **2011**, *96*, 1793.
- (31) Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. *Macromolecules* **2003**, *37*, 573.
- (32) Cozza, E. S.; Monticelli, O.; Cavalleri, O.; Marsano, E. *Polym. Adv. Technol.* **2011**, DOI: 10.1002/pat2037, in press.
- (33) Tripatanasuwan, S.; Zhong, Z.; Reneker, D. H. *Polymer* **2007**, *48*, 5742.
- (34) Wang, S.; Wang, M.; Lei, Yong; Zhang, L. *J. Mater. Sci. Lett.* **1999**, *18*, 2009.
- (35) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: New York, 1991.
- (36) Monticelli, O.; Fina, A.; Ullah, A.; Waghmare, W. *Macromolecules* **2009**, *42*, 6614.
- (37) Monticelli, O.; Fina, A.; Cozza, E. S.; Prato, M.; Bruzzo, V. J. *Mater. Chem.* **2011**, *21*, 18049.