



Synthesis and characterization of reactive polyhedral oligomeric silsesquioxanes (R-POSS) containing multi-*N*-methylol groups

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ABSTRACT

Novel high-reactive polyhedral oligomeric silsesquioxanes bearing multi-*N*-methylol groups (R-POSS) is synthesized. The chemical structure of R-POSS is characterized by FT-IR, ^1H NMR, ^{29}Si NMR. Nano-structure of R-POSS is observed by field emission scanning electro microscope (FSEM) and AFM. R-POSS monomer imparts a nano-sized inorganic core and organic corner with multi-*N*-methylol groups. R-POSS can readily crosslink to cellulose polymer and improve elastic recovery of cellulose materials. R-POSS as novel POSS reagent may be utilized for preparation of nanocomposite materials and functional biomaterials.

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1. Introduction

In the last years, organic–inorganic hybrids have received considerable interest among the academic community and industries due to their unique structure and excellent properties, such as mechanical, optical, electric, thermal and biocompatible [1–7]. The polyhedral oligomeric silsesquioxane (POSS)-based hybrid materials are important organic–inorganic hybrids. They have attracted considerable attention for dielectric, heat-resistant and radiation-resistant paint and coatings [8–11]. POSS derivatives as functional and reactive reagents play an important role in preparation of hybrid materials. POSS reagents are unique in both their chemical composition and physical nature. The thermally stable silicon–oxygen framework contains an oxygen to silicon ratio of 3/2, which is intermediate between siloxane and silica. POSS compounds have a well-defined structure with a silica-like core in 1–3 nm size surrounded by organic corner groups which enable POSS to react with other functional organic monomers to prepare POSS-based hybrid materials [12–15]. The incorporation of POSS into some polymers has offered the opportunity to develop high-performance functional materials.

A number of attempts have been made to prepare organic–inorganic hybrids containing POSS [16–19]. However, synthesis and research of functional POSS reagents are scarce. Some families of POSS monomers with different organic groups have been developed as precursors to hybrid inorganic–organic polymers. Previous

studies have revealed that functional POSS monomers can generally be obtained by the controlled cleavage of completely condensed polyhedral oligosilsesquioxane in the presence of strong acid or base [20–22]. Corner-capping of the POSS trisilanol can be carried out using a variety of couple reagent. Feher reported synthesis of POSS containing amine- and ester-substituted frameworks in the strong acid condition [23–25]. The POSS containing amine has excellent potential as cores for starburst dendrimers. In order to further develop organic–inorganic hybrid biomaterials, high-reactive and functional POSS monomers also need to be investigated.

In this paper, novel high-reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups (R-POSS) is synthesized. The structure of R-POSS containing multi-*N*-methylol groups is shown in Scheme 1.

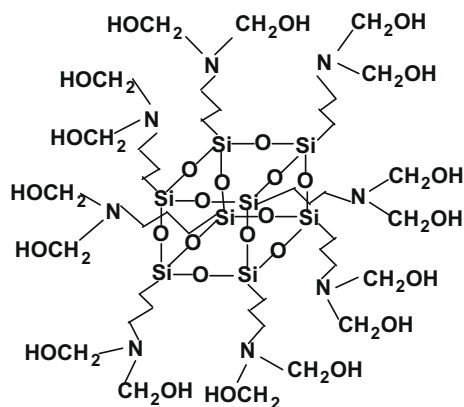
The chemical structure of R-POSS is characterized by FT-IR, ^1H NMR, ^{29}Si NMR. Nano-structure of R-POSS film is observed by FSEM and AFM. Novel high-reactive polyhedral oligomeric silsesquioxanes may be utilized for preparation of Si-containing building blocks and interpenetrating polymer networks (IPN) for nanocomposite materials.

2. Experimental

2.1. Materials

γ -Aminopropyltriethoxysilane (APTES) as a couple reagent was obtained from Hangzhou Dadi Chemical Co., Ltd., Hangzhou, China.

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Scheme 1. Chemical structure of high-reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups.

The formaldehyde and other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Measurements

FT-IR spectra of the samples were measured by an OMNI Sampler of the Nexus-670 FT-IR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI). ^1H NMR and ^{29}Si NMR spectra were recorded on a Bruker AV 400 (Bruker Co., Faellanden, Switzerland), respectively.

The X-ray diffraction pattern (XRD) was measured with a D/max-2550 PC X-ray Diffractometer (Rigaku Corporation, Japan), which used Cu-K target at 40 kV 300 mA, $\lambda = 1.542 \text{ \AA}$.

For FSEM (Field Emission Scanning Electro Microscope) analysis, the samples were sputtered with carbon and then examined

with a S-4800 field emission scanning electron microscope (HIT-ACHI, Cor. Japan).

Atomic force microscope (AFM) image was obtained with SPM Multimode-Nanoscope IIIa (Digital Instruments, USA) at room temperature, in tapping mode.

2.3. Synthesis of octa-aminopropylsilsesquioxane (POSS-NH₂)

Octa-aminopropylsilsesquioxane (POSS-NH₂) was synthesized according to the procedures described in the Refs. [24,25]. The resulting crude product was recrystallized with THF. White microcrystalline powder was obtained.

Yield was 43.76%. IR (KBr, cm^{-1}): 3034 ($-\text{NH}_3$); 2906, 2903 ($-\text{CH}_2-$); 1604, 1047 ($\text{Si}-\text{C}-$); 1145, 1047 ($\text{Si}-\text{O}-\text{Si}-$). ^1H NMR (ppm, D₂O, room temp.) δ : 0.66 (m, $-\text{CH}_2-$, 16H); 1.72 (m, $-\text{SiCH}_2\text{CH}_2-$, 16H); 2.93 (m, $-\text{SiCH}_2-$, 16H); 8.16 (s, $-\text{NH}_3$, 24H). ^{29}Si NMR (ppm, solid state) δ : -57.75 (s, $\text{Si}-\text{C}-$); -66.59 (s, $\text{Si}-\text{O}-$).

2.4. Synthesis of reactive polyhedral oligomeric silsesquioxanes (R-POSS) containing multi-*N*-methylol groups

A 150 ml glass flask equipped with thermometer, magnetic stirrer and distilling head, was charged with 25 g formaldehyde water solution (30% w/w). The pH of formaldehyde solution was adjusted

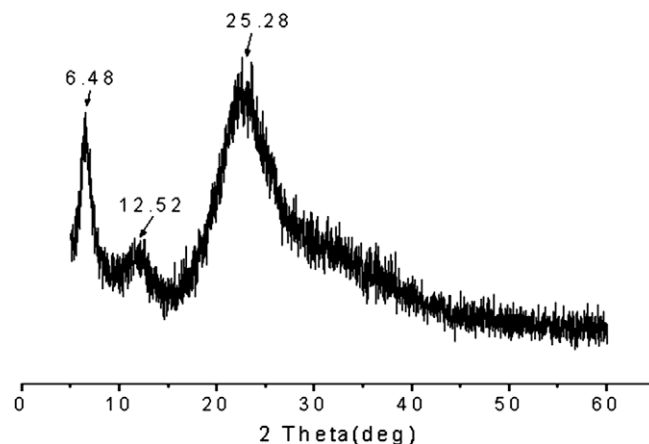
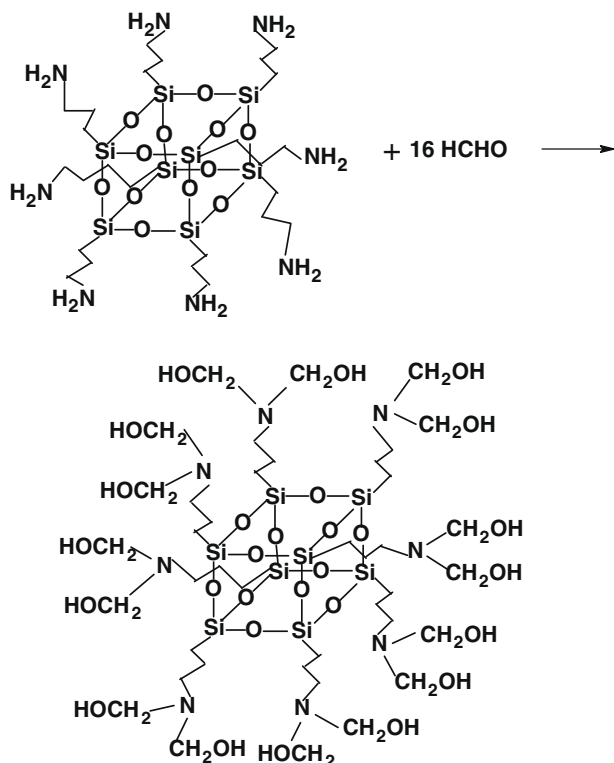


Fig. 1. X-ray diffraction pattern of R-POSS.



Scheme 2. Reaction scheme of reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups.

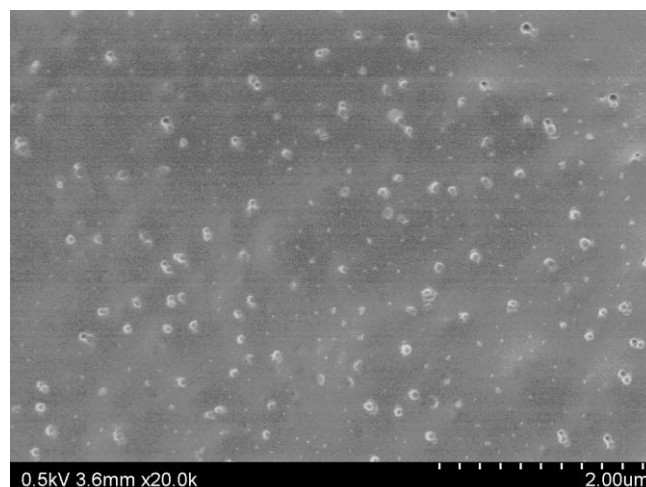


Fig. 2. FSEM of the functional polyhedral oligomeric silsesquioxane (POSS).

to 9.3, and a solution of octa-aminopropylsilsesquioxane (3.5 g POSS-NH₂) was resolved in 20 ml MeOH) was dropped stepwise. The reaction mixture was then refluxed at 90 °C for 16 h. The pH of reaction mixture was keeping 9.3 with 10% (w/w) sodium carbonate in reaction procedure. Then the mixture was distilled under 10 mm Hg vacuums and white powder was obtained. The crude product was recrystallized with MeOH. White powder (R-POSS) was obtained. The obtained polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups is readily soluble in water.

The yield was 83.21%. IR (KBr, cm⁻¹): 3468, 3339 (–OH); 2945, 2739 (–CH₂–); 1602, 1594 (Si–C–); 1134, 1046 (Si–O–Si–). ¹H NMR (ppm, D₂O, room temp.) δ: 0.66 (m, –CH₂–, 16H); 1.62 (m, –SiCH₂CH₂–, 16H); 3.09–2.81 (m, –NCH₂–, 48H); 8.40 (s, –OH, 16H). ²⁹Si NMR (ppm, solid state) δ: –58.34 (s, Si–C–); –67.67 (s, Si–O–).

2.5. Modification of cellulose fabrics with reactive polyhedral oligomeric silsesquioxanes (R-POSS)

R-POSS was diluted with distilled water to certain concentration solution. Citric acid and MgCl₂ as catalysts were used in the crosslinking reaction. The mixtures were sufficiently mixed by stirring at room temperature.

Cellulose fabrics were padded with the R-POSS mixtures to give 80% wet pick-up. The dry temperature and time were 95 °C and 3 min, respectively. After drying, the fabrics were cured for 1 min at 165 °C.

Dry crease recovery angle (CRA) was determined according to ASTM method D-1296-98. Values of CRA in both warp and weft directions were determined. The samples were conditioned at 20 °C and 65% relative humidity for at least 24 h before testing.

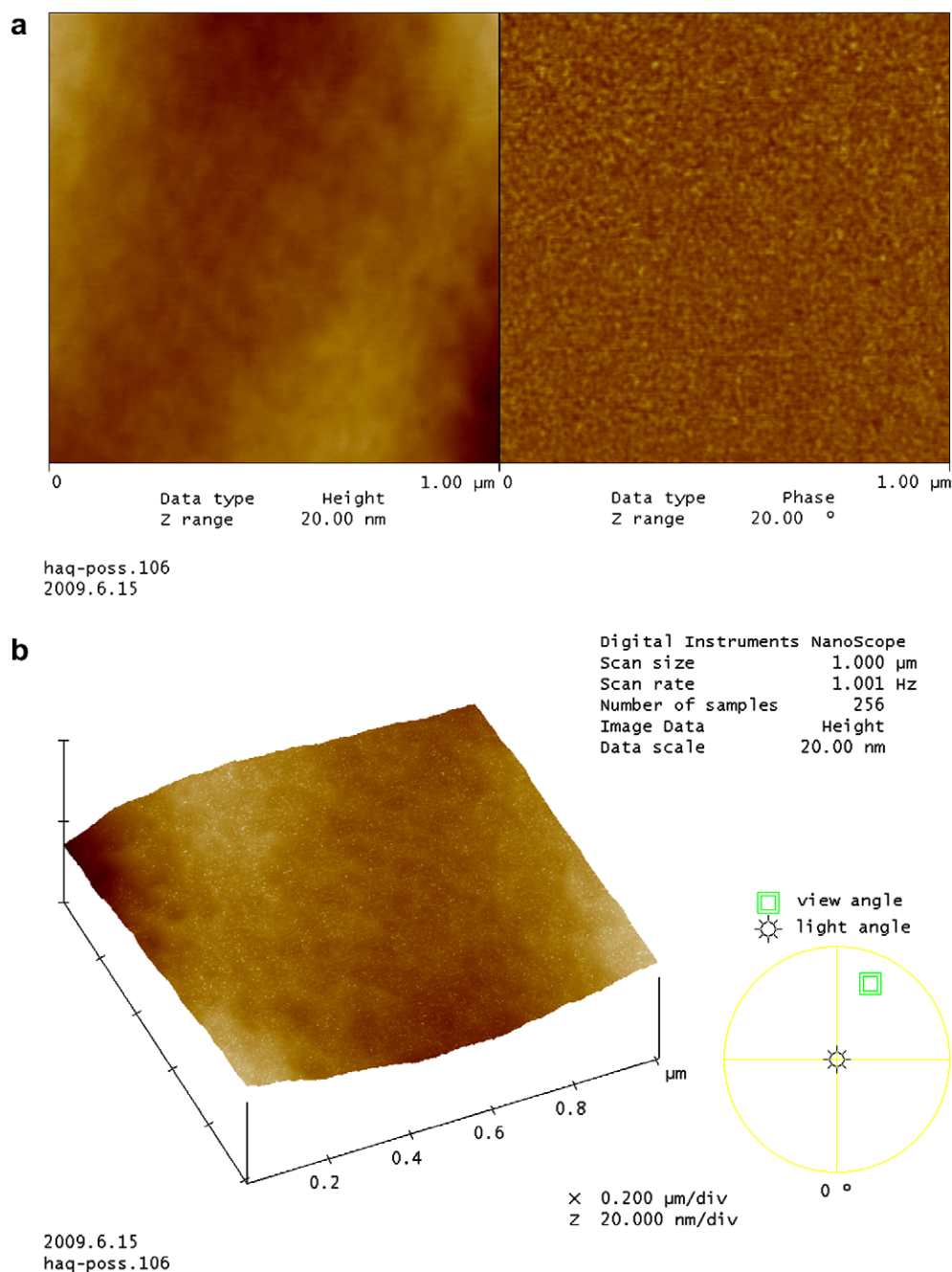


Fig. 3. AFM images of R-POSS (a) flat image; (b) three dimensional image.

3. Results and discussion

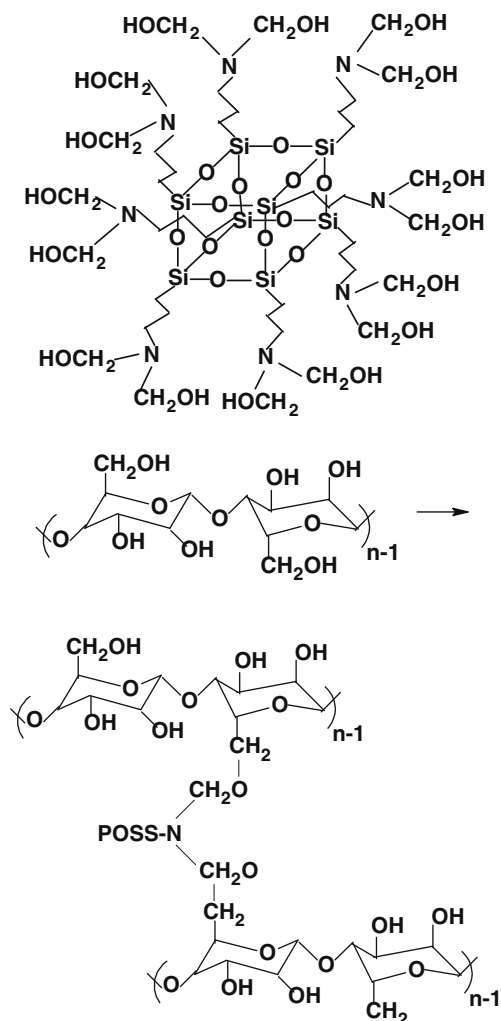
3.1. Synthesis and characterization of reactive polyhedral oligomeric silsesquioxanes (R-POSS)

Octa-aminopropylsilsesquioxane (POSS-NH₂) is an interesting and important monomer which derived from the hydrolytic condensation of trifunctional organosilicon compound (γ -aminopropyltriethoxysilane). γ -Aminopropyltriethoxysilane can be hydrolyzed and formed trisilanol compound. Corner-capping of condensed POSS trisilanols is an efficient method for preparing POSS reagents in which only one corner is functionalized with modifiable amino group. POSS-NH₂ can further react with formaldehyde to form high-reactive multi-*N*-methylol compound. The reaction process is shown in Scheme 2.

The X-ray diffraction pattern (XRD) of reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups was measured (shown in Fig. 1).

There are major crystal diffraction peaks at 6.48°, 12.52°, 25.28°. This is typical inorganic POSS crystalline core and consistent with previous reports [15,21,26]. It demonstrates that the center of polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups has inorganic crystalline core.

The nano-morphology of the reactive polyhedral oligomeric silsesquioxane containing multi-active groups was observed by



Scheme 3. Crosslinking reaction of cellulose and R-POSS.

Table 1

Effect of R-POSS concentration on physical properties of modified cellulose with R-POSS.

Samples	R-POSS (% w/w)	Crease recovery angle		Crease recovery angle (W+F, °)
		Weft	Warp	
Control	0	54.6	53.0	107.6
1	0.8	65.3	74.7	140.0
2	1.2	70.4	86.5	156.9
3	2.0	87.2	90.4	177.6
4	3.2	91.0	97.4	188.4

field emission scanning electro microscope and atomic force microscope image. For FSEM and SEM analysis, the sample was dispersed in MeOH with supersonic wave and dropped on a glass plate. The glass plate was dried at 90 °C 1 h. Representative FSEM micrograph of R-POSS is shown in Fig. 2.

It shows that there are a lot of nano-sized POSS-particle cores with high degree of homogeneity. Around the cores, there are some transparent organic mass. Atomic force microscope three dimensional image (AFM) can be used to characterize any changes about the surface morphology of the R-POSS. AFM of R-POSS is shown in Fig. 3. The AFM graphs (flat and three dimensional images) show the topography of the R-POSS with the low distribution profiles of smooth surface. R-POSS can form the film with high degree of homogeneity and purity at a molecular level. FSEM and AFM of R-POSS are in very good agreement.

3.2. Preparation of nanocellulose hybrids

R-POSS has nano-sized cores and high-reactive multi-*N*-methylol groups. The high-reactive multi-*N*-methylol of R-POSS can be used to modify polymer materials and form network structure containing nano-sized particles. The crosslinking reaction of cellulose materials and R-POSS are shown in Scheme 3. In the crosslinking reaction, POSS particles are dispersed in the cellulose host matrix, bonding to the cellulose through covalent bonds.

The cellulose fibers are crosslinked by R-POSS at citric acid 0.1%, MgCl₂ 1.5% condition. The elastic recovery property of nanocellulose is shown in Table 1. It shows that R-POSS as crosslinking agent can readily crosslink to cellulose and significantly improve elastic recovery property of cellulose fabrics. The crease recovery angles both weft and sharp significantly increase. With increasing R-POSS concentration, the crease recovery angles of nanocellulose sharply increase from 107.6 (control sample) to 188.4. It demonstrates that R-POSS possesses high active ability. It can readily crosslink to cellulose and improve elastic recovery of cellulose fabrics. Nanocellulose materials containing POSS as ultrafiltration membranes would be used in separation of toxic heavy metal ions. Application of R-POSS and its composites will be further investigated. So, R-POSS as nano-crosslinking agent has excellent potential application in composites and biomaterials.

4. Conclusions

R-POSS is novel functional and high-reactive polyhedral oligomeric silsesquioxane. The R-POSS containing multi-*N*-methylol reagent is successfully synthesized and characterized. The R-POSS is attractive staring macromolecule for new reinforcement materials. It has excellent potential as nano-sized cores for starburst dendrimers. R-POSS can readily crosslink to cellulose and improve elastic recovery of the cellulose materials. This work provides a novel crosslinking POSS reagent for designing functional nanomaterials and organic–inorganic hybrids.

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References

- [1] M. Hasan, A. Ahmad, B. Hameed, Chem. Eng. J. 136 (2008) 164–172.
- [2] G. Wu, Y. Chen, D. Xu, J. Liu, W. Sun, Z. Shen, J. Organomet. Chem. 694 (2009) 1571–1574.
- [3] K. Xie, A. Hou, Y. Zhang, Int. J. Nonlinear Sci. Numer. Simul. 10 (2009) 759–765.
- [4] H. Liu, S. Kondo, R. Tanaka, H. Oku, M. Unno, J. Organomet. Chem. 693 (2008) 1301–1308.
- [5] J. Choi, J. Harcup, A.F. Yee, Q. Zhu, R.M. Laine, J. Am. Chem. Soc. 123 (2001) 11420–11430.
- [6] K. Kataoka, Y. Nagao, T. Nukui, I. Akiyama, K. Tsuru, S. Hayakawa, et al., Biomaterials 26 (2005) 2509–2516.
- [7] A. Hou, M. Zhou, X. Wang, Carbohydr. Polym. 75 (2009) 328–332.
- [8] C. Ramirez, M. Rico, A. Torres, L. Barral, J. Lopez, B. Montero, Eur. Polym. J. 44 (2008) 3035–3045.
- [9] K. Zeng, Y. Liu, S. Zhang, Eur. Polym. J. 44 (2008) 3946–3956.
- [10] A. Hou, X. Wang, Y. Yu, Carbohydr. Polym. 77 (2009) 201–205.
- [11] A. Fina, D. Tabuani, A. Frache, G. Camino, Polymer 46 (2005) 7855–7866.
- [12] S. Duo, M. Li, M. Zhu, Y. Zhou, Mater. Chem. Phys. 112 (2008) 1093–1098.
- [13] K. Xie, Y. Yu, Y. Shi, Carbohydr. Polym. 78 (2009) 799–805.
- [14] T. Ohno, S. Tagawa, H. Itoh, H. Suzuki, T. Matsuda, Mater. Chem. Phys. 113 (2009) 119–123.
- [15] L. Ricco, S. Russo, O. Monticelli, A. Bordo, F. Bellucci, Polymer 46 (2005) 6810–6819.
- [16] Y. Zhao, D.A. Schiraldi, Polymer 46 (2005) 11640–11647.
- [17] T. Seckin, S. Koytepe, A.H. Ibrahim, Mater. Chem. Phys. 112 (2008) 1040–1046.
- [18] K. Xie, Y. Zhang, Y. Yu, Carbohydr. Polym. 77 (2009) 858–862.
- [19] Z. Zhou, L. Cui, Y. Zhang, N. Yin, Eur. Polym. J. 44 (2008) 3057–3066.
- [20] F.J. Feher, D. Soulivong, A.G. Eklund, Chem. Commun. (1998) 399–400.
- [21] W. Nie, G. Li, Y. Li, H. Xu, Chin. Chem. Lett. 20 (2009) 738–742.
- [22] B. Janowski, K. Pielichowski, J. Organomet. Chem. 693 (2008) 905–907.
- [23] F.J. Feher, D. Soulivong, F. Nguyen, Chem. Commun. (1998) 1279–1280.
- [24] F.J. Feher, R. Terroba, J.W. Ziller, Chem. Commun. (1999) 2309–2310.
- [25] F.J. Feher, K.D. Wyndham, Chem. Commun. (1998) 323–324.
- [26] B.X. Fu, B.S. Hsiao, S. Pagola, P. Stephens, H. White, M. Rafailovich, J. Sokolov, P.T. Mather, H.G. Jeon, S. Philips, J. Lichtenhan, J. Schwab, Polymer 42 (2001) 599–611.