

Surface Graft Polymerization of Styrene onto Nano-Sized Silica with a One-Pot Method

Peng LIU,^{*,**,*†} Jun TIAN,^{*} Weimin LIU,^{*} and Qunji XUE^{*}

^{*}State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, Gansu 730000, China

^{**}Chemistry Department, Lanzhou University, Lanzhou, Gansu 730000, China

(Received September 25, 2002; Accepted February 25, 2003)

ABSTRACT: A facile method for free radical graft polymerization of styrene onto the surface of nano-sized silica was developed by using a one-pot method. The initiator (2,2'-azobisisobutyronitrile, AIBN), the coupling agent (vinyl triethoxysilane, VTEOS), styrene and the nano-sized silica were mixed and reacted in toluene medium. The two reactions, the copolymerization of VTEOS and styrene and the coupling reaction of the ethoxyl groups in the side chains of the copolymer and the silanol groups on the surface of the nano-sized silica, were occurred synchronously in the preparing procedure. The effects of the amount of AIBN and VTEOS, the polymerizing temperature and the polymerizing time on the conversion of styrene (*C*), the percentage of grafting (*PG*), the grafting efficiency (*GE*) and the average relative molecular masses (M_n and M_w) of the grafted polystyrene (PS_g) and the non-grafted polystyrene (PS_n) were discussed. IR and XPS showed that the surface of the nano-sized silica had been covered partially by PS and TEM showed that the dispersibility of PS grafted nano-sized silica in organic solvent was improved.

KEY WORDS *In-Situ* Graft Polymerization / Polystyrene / Nano-Sized Silica / One-Pot Method /

Nano-sized silica has attracted increasing attention for its superior properties over conventional micrometer particles.¹ It has been widely used as filler in the manufacture of paints, rubbers, plastics, binders, functional fibers, anti-virus materials, and so on. However, its agglomeration and incompatibility with the organic matrix are impeding problems, which limit its efficient use. It is known that surface modification by grafting of polymers onto nano-sized silica is an effective way to improve its dispersability in an organic polymeric matrix and its compatibility with the polymeric matrix, thus enhancing the properties of the composite materials.^{2,3}

There were a variety of attempts to achieve polymer grafted nano-sized silica composite.⁴ *In-situ* disperse polymerization was one of the most effective methods.⁵ Before the *in-situ* disperse polymerization, initiators or polymerable groups should be introduced onto the surface of the nano-sized silica. Peroxide groups,^{6,7} azo groups^{8–10} and redox initiators¹¹ had been introduced onto the surface of nano-sized silica for the free radical polymerization of styrene and methyl methacrylate. Acylium perchlorate groups¹² had been immobilized onto the surface of the nano-sized silica for the cationic polymerization of styrene, cyclic ethers and lactone. Styrene,^{13–16} methyl methacrylate¹³ and butyl methacrylate¹⁷ had been initiated for the atom transfer radical polymerization (ATRP) on the surface of the nano-sized silica. In our previous work, the nano-sized

silica had been modified with γ -methacryloxypropyl triethoxysilane for the introduction of a polymerable group, methacrylate group. Then the methacrylate group free radical copolymerized with styrene to prepare polystyrene (PS) grafted nano-sized silica *via* a solvent polymerization method.^{18,19} These methods were all time-consuming and troublesome because of the two steps of reactions.

In the present work, the PS grafted nano-sized silica was prepared with a one-pot method. Styrene was copolymerized with coupling agent, vinyl triethoxysilane (VTEOS), in the presence of nano-sized silica, initiated by 2,2'-azobisisobutyronitrile (AIBN). There were two reactions occurred synchronously in the preparing procedure. One was the copolymerization of styrene and VTEOS. The other was the coupling reaction of the VTEOS and the surface silanol groups of nano-sized silica. The proposed method for PS grafted nano-sized silica was simpler than other preparation methods.

EXPERIMENTAL

Materials

Nano-sized silica used, MN1P, was obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area, particle size and silanol group content were $640 \text{ m}^2 \text{ g}^{-1}$, 10 nm and 48%, respectively. It was dried in vacuum at 110°C for 48 h before use.

[†]To whom correspondence should be addressed (E-mail: pliu@lzu.edu).

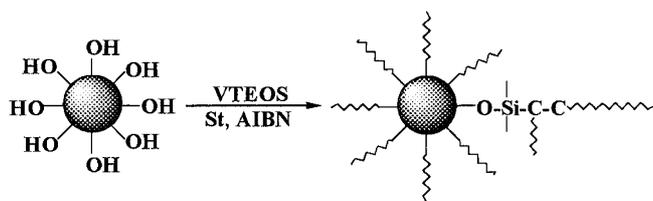


Figure 1. Preparation procedure of the PS-grafted nano-sized silica.

The coupling agent, vinyl triethoxysilane (VTEOS) (Gaizhou Chemical Industrial Co. Ltd., Liaoning, China) was chemical pure grade and used as received. Styrene was washed with dilute alkali solution, dried over barium oxide, and distilled twice under reduced pressure. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN) (Tianjin Chemicals Ltd. Co. Tianjin, China) was re-crystallization in ethanol. Toluene and tetrahydrofuran (THF) were refluxed over sodium and distilled before use. Methanol and hydrofluoric acid (HF) used were all analytical reagent grade.

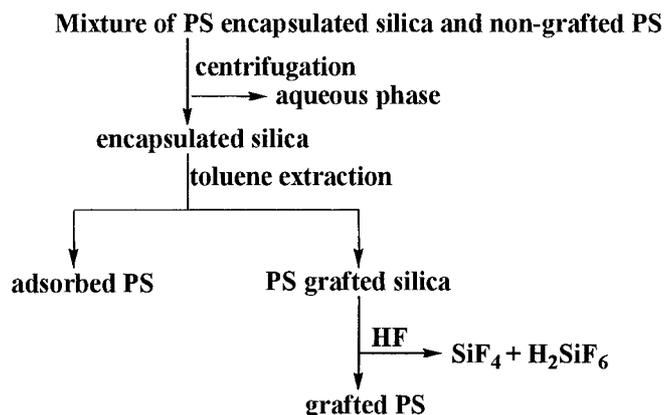
Graft Polymerizing and Coupling Procedure

The polymerization was according with the classical solvent polymerization method.²⁰ The recommended method was as followed: Into a 250 mL flask, 30 mL styrene, 40 mL dried toluene, 1.0 g nano-sized silica, 2.0 g VTEOS and 0.45 g AIBN were charged and the mixture was dispersed with ultrasonic vibrations for 30 min, bubbling with helium. Then the mixture was heated to 70 °C and stirred with a magnetic stirrer for 3 h at the temperature. Helium was bubbling throughout the polymerizing period. After cooling to the room temperature, the reaction mixture was poured into 500 mL methanol and the precipitate was dried *in vacuo* at 40 °C. The preparation procedure of the PS grafted nano-sized silica was showed in Figure 1.

The resulting product was dispersed in toluene with ultra sonic vibration and the dispersion was centrifuged at 1.0×10^4 rpm for 1 h. The ultra fine particles were extracted with THF using Soxhlet apparatus until no PS was eluted in the refluxing solvent. The final product was the PS grafted nano-sized silica.

Characterizations

Elemental analysis (EA) of C and H was performed on Elementar vario EL instrument. Bruker IFS 66 $v s^{-1}$ infrared spectrometer was used for the diffuse reflectance IR analysis. The morphology of the nano-sized silica and PS grafted nano-sized silica were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). The powers were dispersed in toluene in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated



Scheme 1. Treatment of the mixture to separate the PS_g and the PS_n .

carbon film. X-Ray photoelectron spectroscopy (XPS) was accomplished using a PHI-5702 multi-functional X-ray photoelectron spectrometer with pass energy of 29.35 eV and an Mg $K\alpha$ line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference.

The average relative molecular masses of the PS_g and the PS_n were determined by gel permeation chromatography (GPC) with a HP1100 instrument using binary liquid chromatography pump and ultra-violet detector, so as to determine the average relative molecular masses of the samples. THF was used as the eluent at a flow rate of 1 mL min^{-1} . The PS_g was obtained by the following procedure:²¹ The PS grafted nano-sized silica hybrid was immersed with 20% aqueous HF solution and stirred slowly at room temperature for 12 h. Then the organic compound was washed with distilled water until the washing was neutral. The organic compound was extracted with toluene and the solvent was vaporized under vacuum at the room temperature. The sample was treated according to Scheme 1.

Measurement of Grafting Parameters

The grafting parameters were estimated from the weight of the samples before and after grafting. The conversion of styrene (C), the percentage of grafting (PE) and the grafting efficiency (GE) were calculated according to the following relationships:

$$C (\%) = \text{Total PS (g)} / \text{Monomer used (g)} \times 100\%$$

$$PE (\%) = \text{Grafted PS (g)} / \text{Nano-sized silica used (g)} \times 100\%$$

$$GE (\%) = \text{Grafted PS (g)} / \text{Total PS (g)} \times 100\%$$

RESULTS AND DISCUSSION

Effect of the Amount of AIBN

The effect of the amount of AIBN on C , PG , GE , and the average relative molecular masses were was in-

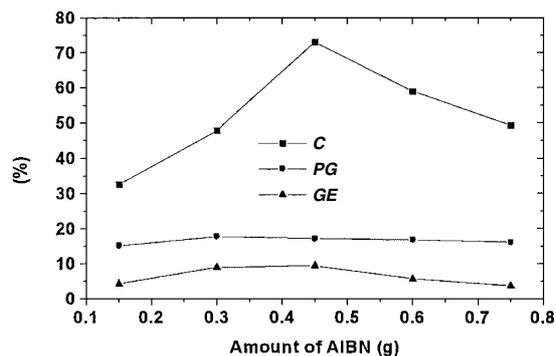


Figure 2. The effects of the amounts of AIBN on the conversion (C), the percentage of grafting (PG) and the grafting efficiency (GE). Styrene, 30 mL; dried toluene, 40 mL; VTEOS, 2.0 g; nano-sized silica, 1.0 g; 70 °C for 3 h.

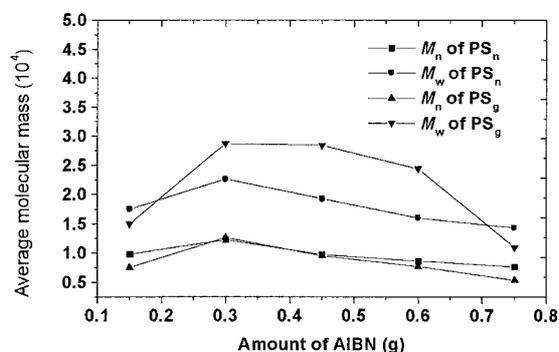


Figure 3. The effect of the amount of AIBN on the average relative molecular masses of the PS_g and the PS_n . Details as Figure 1.

investigated in the range of 0.15 g to 0.75 g. The results were showed in Figures 2 and 3. It was found from Figure 2 that C , PG , and GE achieved the maximum values when 0.45 g AIBN was charged. However, the average relative molecular masses were the maximum when 0.30 g AIBN was charged, as Figure 3. The M_n of the grafted PS was as much as that of the non-grafted PS. But the M_w of the grafted PS was bigger than that of the non-grafted PS markedly. It may be due to the chain-transfer reaction between the copolymers of styrene and VTEOS in the certain microenvironment.

0.45 g AIBN was used in the further experiments as comprise although the average relative molecular masses achieved the maximum when 0.30 g AIBN was charged. The amount of AIBN used was more than the conventional amount (0.15 g)²⁰ probably because of the reaction between the primary radicals resulted from the decomposition of AIBN and the superfluous charges of the nano-sized silica surface,²² VTEOS or the trace impurity in VTEOS. Because of the more initiator used than that in our present work,¹⁸ the average relative molecular masses of the PS_n and the PS_g were all smaller.

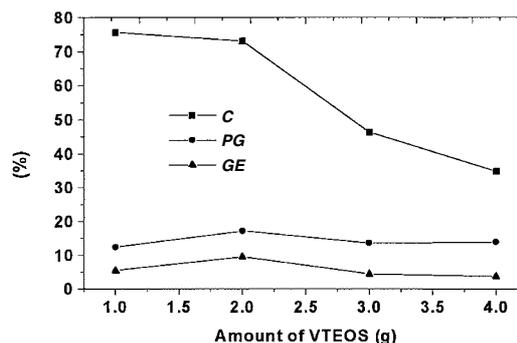


Figure 4. The effect of the amount of VTEOS on the conversion (C), the percentage of grafting (PG) and the grafting efficiency (GE). AIBN, 0.45 g, other details as Figure 1.

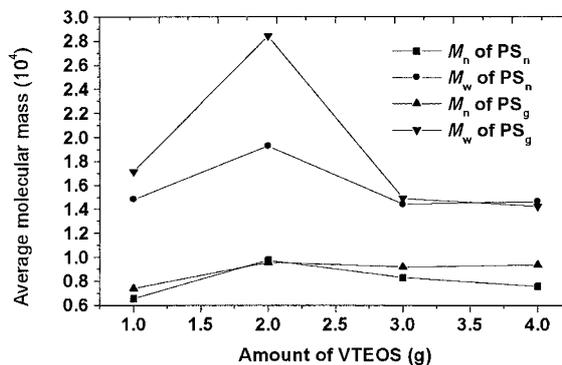


Figure 5. The effect of the amount of VTEOS on the average relative molecular masses of the PS_g and the PS_n . Details as Figure 3.

Effect of the Amount of VTEOS

The more amounts of VTEOS would increase PG and GE of PS. But it might decrease C of styrene because of the poor copolymerizing ability of VTEOS and styrene. So the effect of the amount of VTEOS was investigated as Figures 4 and 5. It was found that C decreased slightly with the amount of VTEOS increasing from 1.0 g to 2.0 g and decreased obviously with the amount of VTEOS increasing from 2.0 g to 3.0 g. PG , GE , and the average relative molecular masses achieved the maximum values when 2.0 g VTEOS was added. So 2.0 g VTEOS was added as coupling agent in the further experiments.

Effect of the Polymerizing Temperature

The higher polymerizing temperature is propitious to the coupling reaction between VTEOS and the surface silanol groups of the nano-sized silica. However, it would result in the faster decomposition of AIBN so as to decrease the conversion of styrene. The effect of the polymerizing temperature on C , PG , GE , and the average relative molecular masses of the PS_g and the PS_n was investigated and the results were showed in Table I. It was found that C , PG , and GE decreased with

Table I. Graft copolymerizing at different temperatures^a

Polymerizing Temperature (°C)	70	80	90
<i>C</i> (%)	73.0	53.7	52.6
<i>PG</i> (%)	17.1	16.3	15.9
<i>GE</i> (%)	9.40	6.93	5.76
M_n of PS _n (10 ⁴)	0.9741	0.5755	0.4713
M_w of PS _n (10 ⁴)	1.929	1.305	1.172
M_n of PS _g (10 ⁴)	0.9558	0.9793	0.7929
M_w of PS _g (10 ⁴)	2.842	1.728	1.594

^aOther reaction conditions: styrene, 30 mL; dried toluene, 40 mL; VTEOS, 2.0 g; AIBN, 0.45 g; nano-sized silica, 1.0 g; 3 h.

Table II. Graft copolymerizing with different times^a

Polymerizing Time (h)	1	3	5
<i>C</i> (%)	59.3	73.0	81.9
<i>PG</i> (%)	15.1	17.1	17.3
<i>GE</i> (%)	7.86	9.40	9.66
M_n of PS _n (10 ⁴)	0.9420	0.9741	0.9802
M_w of PS _n (10 ⁴)	1.896	1.929	1.907
M_n of PS _g (10 ⁴)	0.9543	0.9557	0.9564
M_w of PS _g (10 ⁴)	2.792	2.842	2.837

^aOther reaction conditions: styrene, 30 mL; dried toluene, 40 mL; VTEOS, 2.0 g; AIBN, 0.45 g; nano-sized silica, 1.0 g; 70 °C.

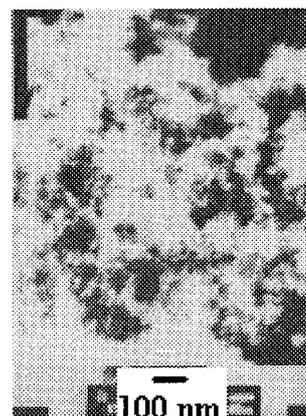
the increase of the polymerizing temperature. With the increase of the copolymerizing temperature, the life of the radicals was shortening. So the average relative molecular masses of the PS_n and the PS_g were decreased. Therefore, 70 °C was used as the polymerizing temperature in the further experiments.

Effect of the Polymerizing Time

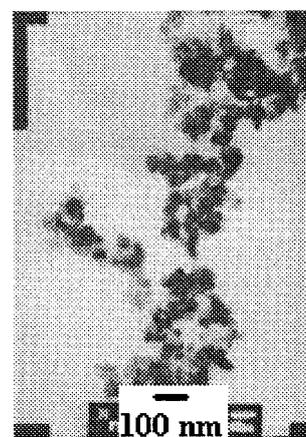
It was well known that *C* increased with the elongation of the polymerizing time in the free radical polymerization. It was expected that *PG* and *GE* would increase with the increase of the polymerizing time. The results (Table II) showed that *C*, *PG*, and *GE* had bigger increases with the polymerizing time increased from 1 h to 3 h than that from 3 h to 5 h. It was also found that the average relative molecular masses of the PS_g and PS_n had not changed with the elongation of the polymerizing time. So 3 h was selected as the polymerizing time.

Characterizations

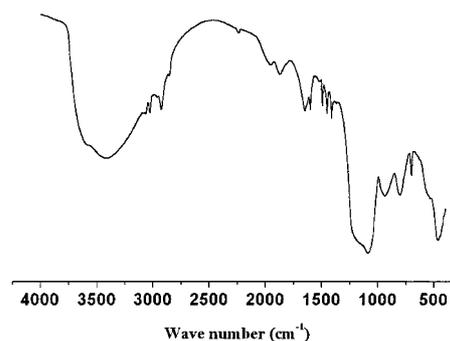
When the nano-sized silica, VTEOS, St, and AIBN were dispersed in toluene with ultra sonic vibration, VTEOS might be fabricated onto the surface of the nano-sized silica (both non-covalently adsorbed and covalently bonded modes) and it would change the surface property of the nano-sized silica. It improved the dispersibility of the nano-sized silica in the mixture of styrene and toluene. The diameter of the PS grafted



(a) nano-sized silica



(b) PS grafted nano-sized silica

Figure 6. TEM images of (a) nano-sized silica and (b) PS grafted nano-sized silica.**Figure 7.** The diffuse reflectance IR of the PS grafted nano-sized silica.

nano-sized silica was larger than that of the nano-sized silica without modification because of its agglomerations (both soft and hard) in the stocking stage (Figure 6). The soft agglomeration could be broken into pieces but the hard agglomeration could not. VTEOS non-covalently adsorbed would be changed into covalently bonded to the surface of the nano-sized silica in the period of heating. The presence of the silanol groups in the FT-IR spectra (Figure 7) showed that the

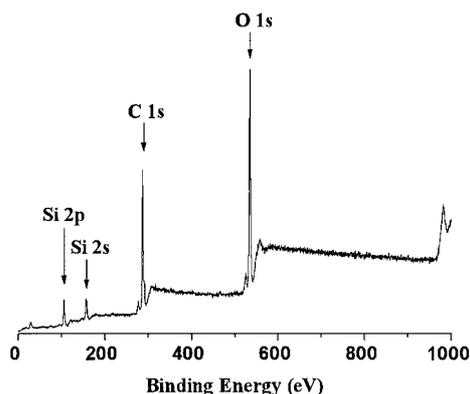


Figure 8. XPS survey of the PS grafted nano-sized silica.

silanol groups had not reacted with VTEOS completely in the period of ultra sonic vibration. The residual silanol groups could not react with VTEOS because of the big space hindrance of the copolymer of VTEOS and styrene. The styrene C–C vibrations can be assigned to 1458 and 1496 cm^{-1} , which were not present in the pure nano-sized silica IR spectrum. The cleaved PS IR spectrum is very analogous to the pure PS spectrum in which 3061 and 3028 cm^{-1} are assigned to PS aromatic C–H stretching vibrations. The peaks at 2925 and 2852 cm^{-1} belong to the aliphatic C–H stretch. The XPS results showed the presence of the relevant C peak, 52.41% element content of the surface layer of the PS grafted nano-sized silica, representing the presence of the PS on the surface of the nano-sized silica (Figure 8). It is interesting to note the presence of relevant Si peaks even with the PS grafted nano-sized silica, indicating the exposure of bare SiO_x surfaces or sufficient XPS penetration depth on the surfaces. This is consistent with the low *PG* as determined by EA, where the particles are composed of nonuniformly grafted nano-sized silica and its aggregates.

CONCLUSION

A one-pot method was developed to prepare the PS grafted nano-sized silica *via* free radical copolymerization of styrene and VTEOS in the presence of nano-sized silica, initiated by AIBN. Although the space hindrance of the copolymer of VTEOS and styrene would decrease the percentage of grafting and the grafting efficiency, a conversion of 73.0%, a percentage of grafting of 17.1% and a grafting efficiency of 9.40% were achieved in the optimized polymerizing condition. With the approximate values of the percentage of grafting and the grafting efficiency compared with those in the previous works, a higher conversion could be achieved by using the pro-

posed method. The proposed method was simpler and more convenient than the methods reported. The higher percentage of grafting and average relative molecular masses could be achieved by using coupling agent which has a proper copolymerizing ability with styrene.

Acknowledgment. The authors gratefully acknowledge the supports of the K. C. Wong Education Foundation, Hong Kong, and the DSFC of Lanzhou University.

REFERENCES

- H. S. Nalwa, Ed., "Handbook of nanostructured materials and nanotechnology", Academic Press, Inc., San Diego, CA, 2000.
- E. Bourgeat-Lami, P. Espiard, A. Guyot, C. Gauthier, L. David, and G. Vigier, *Angew. Makromol. Chem.*, **242**, 105 (1996).
- S. Hayashi, Y. Takeuchi, M. Eguchi, T. Iida, and N. Tsubokawa, *J. Appl. Polym. Sci.*, **71**, 1491 (1999).
- Y. Gu, *Chem. Ind. Eng. Prog.*, **(1)**, 33 (1994).
- P. Liu, J. Tian, W. M. Liu, and Q. J. Xue, *Chem. Bull.*, **66**, 73 (2003).
- N. Tsubokawa and H. Ishida, *J. Polym. Sci. Part A: Polym. Chem.*, **30**, 2241 (1992).
- N. Tsubokawa and H. Ishida, *Polym. J.*, **24**, 809 (1992).
- N. Tsubokawa, A. Kogure, K. Maruyama, Y. Sone, and M. Shimomura, *Polym. J.*, **22**, 827 (1990).
- O. Prucker and J. Ruhe, *Macromolecules*, **31**, 592 (1998).
- O. Prucker and J. Ruhe, *Macromolecules*, **31**, 602 (1998).
- N. Tsubokawa, K. Maruyama, Y. Sone, and M. Shimomura, *Polym. J.*, **21**, 475 (1989).
- N. Tsubokawa and A. Kogure, *Polym. J.*, **25**, 83 (1993).
- T. Von Werne and T. E. Patten, *J. Am. Chem. Soc.*, **123**, 7497 (2001).
- T. Von Werne and T. E. Patten, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **40(2)**, 354 (1999).
- T. Von Werne, I. M. Suehiro, and S. Farmer, *Polym. Mater. Sci. Eng.*, **82**, 294 (2000).
- T. Von Werne and T. E. Patten, *J. Am. Chem. Soc.*, **121**, 7409 (1999).
- G. Carrot, S. Diamanti, M. Manuszak, B. Charleux, and J. P. Vairon, *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 4294 (2001).
- P. Liu, J. Tian, W. M. Liu, and Q. J. Xue, *Chin. Syn. Rubb. Ind.*, **25**, 261 (2002).
- P. Liu, J. Tian, W. M. Liu and Q. J. Xue, *Mater. Res. Innovations*, in press.
- Department of Polymer Sciences and Institute of Polymer Sciences of Fudan University, Ed., "Polymeric Experimental Technology", Publishing House of Fudan University, Shanghai, 1996.
- K. Suzuki, T. Yumura, Y. Tanaka, T. Serizawa, and M. Akashi, *Chem. Lett.*, 1380 (2000).
- R. D. Wu, X. L. Tong, Y. L. Shen, and R. L. Wang, *Chin. Plast.*, **16**, 55 (2002).