

Synthesis and Structural Characterization of a New Polysiloxane with Second-Order Nonlinear Optical Effect

Zhen Li,¹ Jingui Qin,¹ Zhou Yang,² Cheng Ye²

¹Department of Chemistry, Wuhan University, Wuhan 430072, China

²Center for Molecular Science, Organic Solids Laboratory, Institute of Chemistry, The Chinese Academy of Science, Beijing 100080, China

Received 30 April 2003; accepted 8 March 2004

DOI 10.1002/app.20942

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A new polysiloxane (**P2**), with a high density of the indole-based chromophore and carbazolyl side groups, was prepared. Thus a polysiloxane (**P1**), with indole and carbazolyl groups as side chains, was first synthesized through a hydrosilylation reaction, and then the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring gave the multifunctional indole-based chromophore-functionalized polysiloxane (**P2**). Molecular structural characterization for the polymers was determined by

¹H-NMR, IR, and UV-visible spectra, gel permeation chromatography, and differential scanning calorimetry. The polymers were easily soluble in common organic solvents. The poled film of **P2** revealed a resonant d_{33} value of 27 pm/V by second-harmonic generation measurements. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 769–774, 2004

Key words: polysiloxanes; synthesis; second-harmonic generation (SHG); NMR; UV-vis spectroscopy

INTRODUCTION

In the past decade, growing attention has been focused on the development of organic nonlinear optical (NLO) chromophore-containing polymeric materials because of their potential photonics applications and many advantages over single crystals, such as superior chemical flexibility, processability, and low cost.^{1,2} Polysiloxanes are polymers with an inorganic backbone and have many excellent properties such as temperature resistance, resistance to weather, and good electrical properties. Furthermore, polysiloxanes generally possess low glass-transition temperature and can be easily prepared by various methods including hydrosilylation. Because of these advantages, polysiloxanes were applied in various fields, such as the automotive industry, aviation, aerospace, and for medical apparatus.³ Some functional polysiloxanes were synthesized for use as second-order nonlinear optical materials and showed good properties for potential practical applications in the past several years by our research group^{4–6} and by other scientists.^{7,8}

However, studies reporting on the design and synthesis of polysiloxanes with NLO properties are still very scarce.

Recently, our research group developed a novel synthetic strategy to prepare polymers with indole-based chromophore side chains.⁹ This synthetic route is very simple, and the purification of the products very easy. Recently, this new method was further applied to prepare polysiloxanes containing indole-based chromophore side groups with second-order nonlinear optical properties. For this article, a new polysiloxane (**P2**), with a high density of the indole-based chromophore and carbazolyl side groups, was prepared by two steps. Thus a polysiloxane (**P1**) with indole and carbazolyl groups as side chains was to be synthesized first through a hydrosilylation reaction, and then the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring would yield the indole-based chromophore-functionalized polysiloxane (**P2**).

EXPERIMENTAL

Materials and measurements

Toluene was dried over, and distilled from, sodium under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was dried over, and distilled from, K–Na alloy under an atmosphere of dry nitrogen. The *p*-nitrobenzenediazonium fluoroborate was synthesized following a procedure described in the literature.¹⁰ Dicyclopentadienedichloroplatinum was synthesized

Correspondence to: J. Qin (jqin@whu.edu.cn).

Contract grant sponsor: National Science Foundation of China.

Contract grant sponsor: Science Foundation of Hubei Province.

Contract grant sponsor: National Fundamental Key Research Program.

according to the method of Doyle and Jonassen.¹¹ *N*-Allylcarbazole was prepared as reported previously.⁶ *N*-Methylpyrrolidone (NMP) was dried over, and distilled from, CaH₂ under an atmosphere of dry nitrogen. All other reagents were used as received. The hydrosilylation reaction of poly(hydrogen-methylsiloxane) was carried out in a dry nitrogen atmosphere using the Schlenk technique.

¹H-NMR spectroscopy was conducted with a Varian Mercury300 spectrometer (Varian Associates, Palo Alto, CA). FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series (Shimadzu, Kyoto, Japan) in the region of 3000–400 cm⁻¹ on KBr pellets. UV-visible spectra were obtained using a Shimadzu 160A spectrometer in the polymer DMF solution. Molecular weights were determined by gel permeation chromatography (GPC) combined with light scattering (LS) in THF solution.

Synthesis of *N*-allylindole (3)

Powdered potassium hydroxide (12 g) was stirred with DMF (50 mL) at room temperature for 30 min. The mixture was then stirred with indole (5.0 g, 42.6 mmol) at room temperature for 1 h. Allyl chloride (6 mL, 75 mmol) in DMF (10 mL) was added slowly, and the resultant mixture was stirred continuously at room temperature for 24 h. Then the mixture was poured into water (1 L) and the aqueous mixture was extracted with chloroform. The extract solution was dried with Na₂SO₄, and the solvent was removed at reduced pressure. The liquid residue was fractionally distilled off (0.3 mmHg, 116–118°C) *in vacuo* to give 5.8 g of yellow viscous liquid (86%). ¹H-NMR (CDCl₃) δ = 7.65 (d, 1H), 7.18 (m, 4H), 6.54 (d, 1H), 6.05 (m, H¹), 5.22 (m, 2H), 4.70 (t, 2H).

Synthesis of polysiloxane P1

Poly(hydrogen-methylsiloxane) (0.384 g, 6.4 mmol), *N*-allylindole³ (0.30 g, 2.0 mmol) and toluene (12 mL) were placed in a Schlenk tube with a nitrogen inlet. After the addition of a small amount of dichlorodicyclopentadiene platinum (10⁻⁴ mol/mol SiH), the mixture was agitated at 60°C for 48 h. Then *N*-allylcarbazole (2.0 g, 9.7 mmol) was added, and the resultant mixture was reacted at 60°C for three days. After the reaction, the main parts of the solvent were distilled under vacuum. Some methanol was added to precipitate the white solid. The resultant product was purified by several precipitations from chloroform into methanol. (1.1 g)

Preparation of polysiloxane P2

Polysiloxane P1 (0.26 g) was dissolved in 2 mL of *N*-methylpyrrolidone (NMP), and then *p*-nitroben-

zenediazonium fluoroborate (102 mg) was added under cooling with an ice bath. The color of the solution changed immediately to dark red. After stirring for 8 h at 0°C, excessive anhydrous potassium carbonate was added, after which the mixture was stirred for an additional hour and then filtered. The residue was washed with THF, the filtrate was collected, and THF was removed under reduced pressure. Then some methanol was added dropwise to precipitate the polymer. Reprecipitation from chloroform into methanol gave 0.20 g of red product.

Polymer film preparation

Polysiloxane P2 was dissolved in THF, and the solution (5 wt %) was filtered through syringe filters. Polymer films were spin-coated onto indium-tin-oxide (ITO)-coated glass substrates (which were cleaned by *N,N*-dimethylformide, acetone, distilled water, and THF, respectively, in an ultrasonic bath). Residual solvent was removed by heating the films in a vacuum oven at 40°C for 2 days. The film thickness of the active layer was 0.35 μm measured by a Tencor 500 surface profiler.

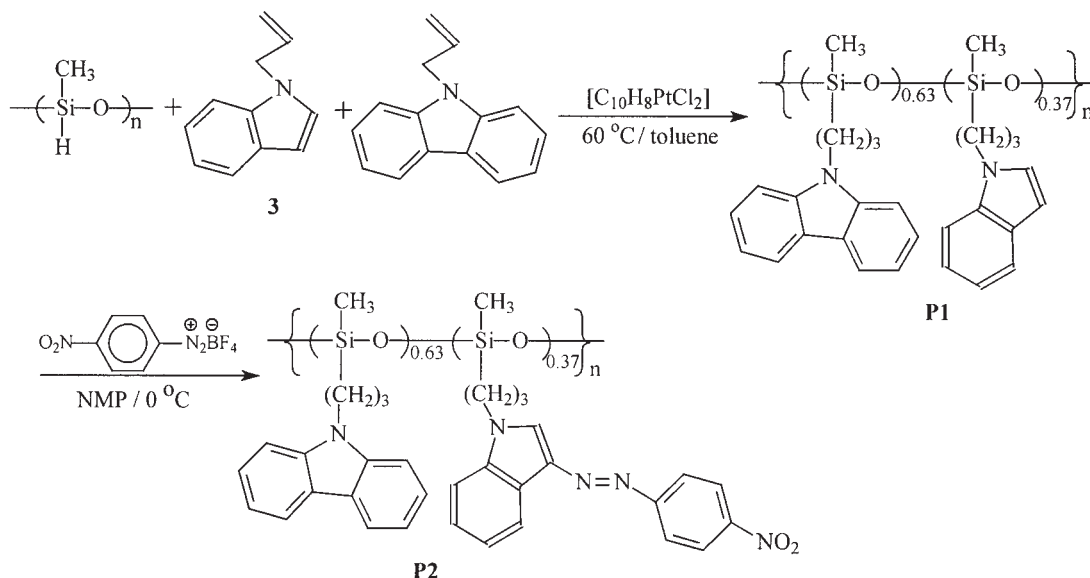
Characterization of poled films

The second-order optical nonlinearity of polysiloxane P2 was determined by *in situ* second-harmonic generation (SHG) experiments using a closed temperature-controlled oven with optical windows and three needle electrodes. The film, which was kept at 45° to the incident beam, was poled inside the oven, and the SHG intensity was monitored simultaneously. Poling conditions were as follows: temperature, 85°C; voltage, 8.5 kV at the needle point; gap distance, 0.8 cm. SHG measurements were carried out with a Nd : YAG laser operating with a 10-Hz repetition rate and an 8-ns pulse width at 1064 nm. A Y-cut quartz crystal served as the reference.

RESULTS AND DISCUSSION

Polymer synthesis

Polysiloxane P1 was prepared by a hydrosilylation reaction of poly(hydrogen-methylsiloxane) with the terminal double bonds of the allyl chains of *N*-allylindole and *N*-allylcarbazole. Its structure is shown in Scheme 1. If there were some unreacted Si—H bonds in the product, polysiloxane P1 would crosslink during the period of storage and become insoluble. Thus in the synthetic procedure, some *N*-allylindole was added to the reaction mixture to react with Si—H bonds first, then excess *N*-allylcarbazole was added, which reacted completely with the remaining Si—H bonds because the reacting period was sufficiently



Scheme 1

long. Figure 1 shows the IR spectra of polysiloxanes **P1** and **P2**. There is no absorption at 2155 cm^{-1} that could be attributed to Si—H stretching, indicating that the Si—H has been completely replaced. The same situation happens in $^1\text{H-NMR}$ where the Si—H peak (at about δ 4.6 ppm) was absent in polysiloxanes **P1** and **P2**. Dichlorodicyclopentadiene platinum was chosen as the catalyst because it was soluble in toluene and its catalytic activity remains high during the period of the reaction.

P2 was synthesized by a post-azo coupling reaction, which was recently used as a convenient method to introduce azo chromophores into the side chains of EO polymers. This method was first used by Katz et al.¹² to functionalize a copolymer of methyl methacrylate and methacrylate ester of *N*-ethyl-*N*-(hydroxyethyl) aniline in acetic acid. Because an acid medium was not a favorite solvent medium for most polymers, S. K. Tripathy et al.¹³ improved this method by using a polar organic solvent such as dimethylformamide or dimethylacetamide. In our previous studies, we could easily synthesize DR-1 containing polyphosphazene by the azo-coupling reaction in NMP with high yield.¹⁴ Recently, we also successfully applied the post-azo coupling reaction to prepare the indole azo chromophore, with a satisfactory result.⁹ Here, this method was extended further to synthesize polysiloxane with a high loading of indole azo chromophores. The overall synthesis of polysiloxane **P2** was carried out in only two steps. The synthetic route was very simple, and the purification of the products was very easy.

At the very beginning of this research, we were concerned that the *p*-nitrobenzenediazonium fluoroborate might attack the carbazolyl ring to form azo

carbazolyl moieties. If this were the case, then the structure of the resultant product would be very complicated. To seek an answer to this question, a comparison experiment was conducted (Scheme 2): another polysiloxane (**P3**), was dissolved in NMP and reacted with *p*-nitrobenzenediazonium fluoroborate. The reacting conditions were the same as described in the preparative procedure of **P2**. However, there was no absorption assigned to the azo carbazolyl chromophore in the UV-vis spectroscopy of the resultant solid, and no absorption of the nitro groups appeared in the IR spectroscopy. On the contrary, the UV-vis, IR, and NMR spectra were essentially the same as those of **P3**. These results demonstrated that the azo salts did not attack the carbazolyl ring in the side chain of **P3** under these reacting conditions. Therefore, in the preparative procedure of **P2**, the *p*-nitrobenzenediazonium fluoroborate would attack only the indole groups, and the structure of **P2** was just as shown in Scheme 1.

Structural characterization

In Figure 1, the absorption in the range of $1100\text{--}1000\text{ cm}^{-1}$ was attributed to the intense stretching vibration of Si—O—Si bonds, and the absorptions for the Si—CH₃ bonds were at 1265 and 843 cm^{-1} . The apparently strongly enhanced absorption band, appearing at 1328 cm^{-1} , is attributed to the absorption of the nitro unit. This confirmed that the *p*-nitrobenzenediazonium fluoroborate had reacted with the indole ring and that the nitro units were introduced into the polymer side chains. The $^1\text{H-NMR}$ spectra of **P1** and **P2** are shown in Figure 2. For **P1**, the component concentrations could be calculated from the $^1\text{H-NMR}$ peak in-

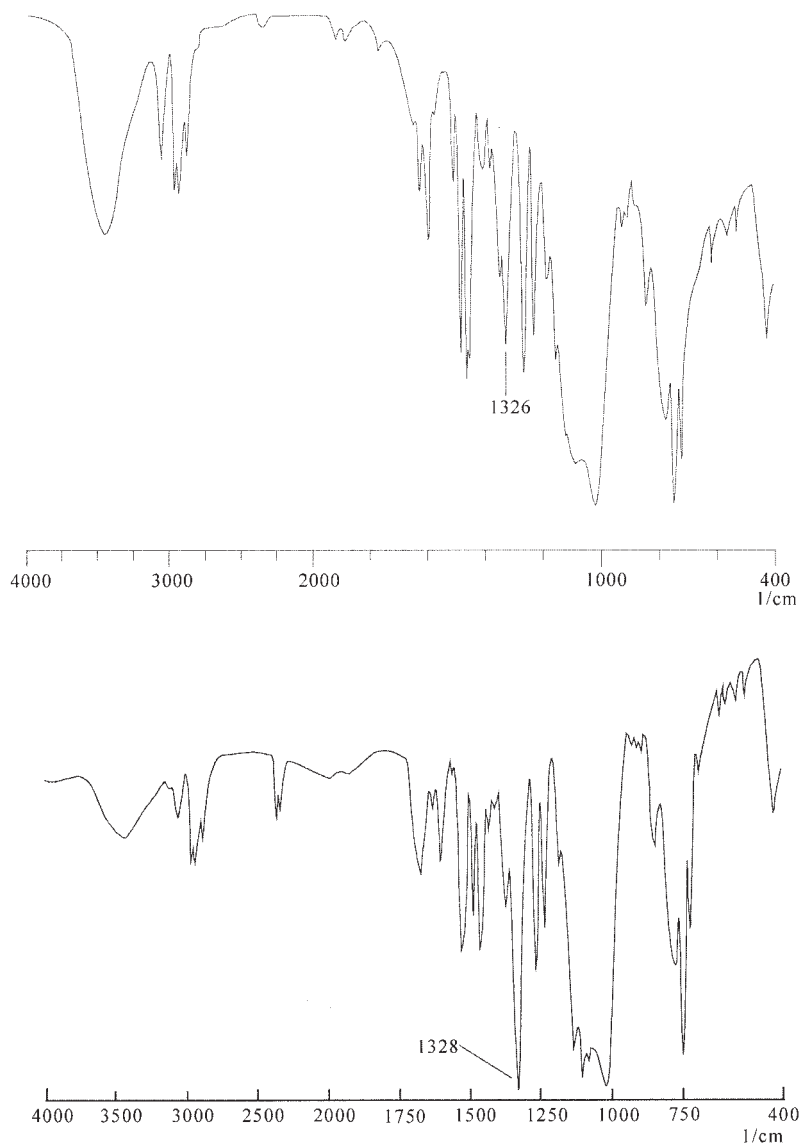
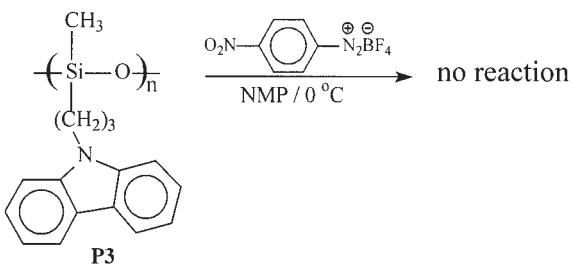


Figure 1 IR spectra of polysiloxanes P1 and P2.

tegration of one-proton resonances of the indole group at 6.22 ppm and the total integration of the other proton resonances of the indole and carbazolyl moieties in the range of 6.60–8.20 ppm. After the azo-coupling reaction, some resonance peaks, appearing in



Scheme 2

the downfield, which were attributed to the *p*-nitro phenyl moieties, also confirmed that the azo-coupling reaction was successful and the azo chromophore really formed. Because the peak at 6.22 ppm, assigned to the 3 position of the indole group, disappeared completely, it was considered that all of the indole groups in P1 reacted with *p*-nitrobenzenediazonium fluoroborate to yield the corresponding azo chromophores. Therefore, P2 should take the structure shown in Scheme 1.

P1 and P2 have good solubility in common organic solvents, such as toluene, CHCl₃, THF, DMSO, and DMF, for example. Figure 3 shows the UV-vis spectra of P1 and P2. After the post-azo coupling reaction, a new strong absorption maximum, of the π - π^* transition of indole-based chromophore, appeared at about 410 nm, with a cutoff at about 560 nm.

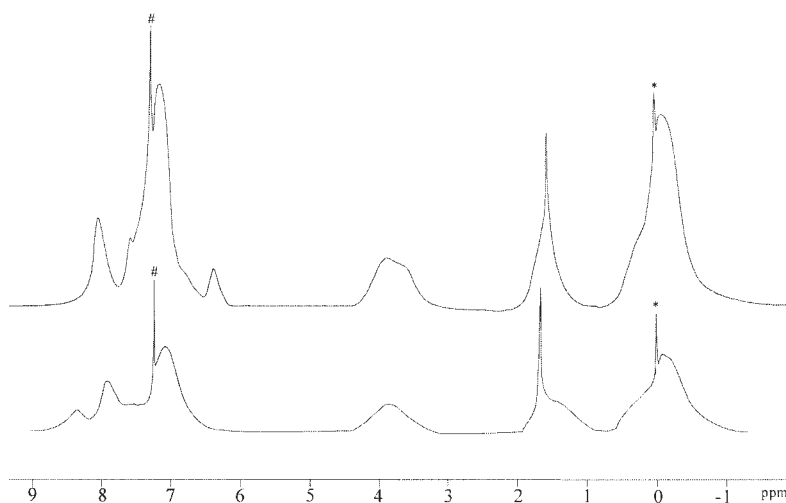


Figure 2 $^1\text{H-NMR}$ spectra of polysiloxanes **P1** and **P2**.

The molecular weights of the polymers were determined by GPC experiments using THF as solvent. The M_n and M_w of **P2** were 5.4×10^3 and 2.8×10^4 , respectively. There was no glass-transition temperature detected from the DSC curve of **P2**.

Nonlinear optical property

To evaluate the NLO activity of the poled polymer films, thin films of polysiloxane **P2** were prepared for SHG measurement. Calculation of the d_{33} value for the poled **P2** is based on the following equation¹⁵:

$$\frac{d_{33,s}}{d_{11,q}} = \sqrt{\frac{I_s}{I_q} \frac{l_{c,q}}{l_s}} F$$

where the $d_{11,q}$ is the d_{11} of the quartz crystals, which is 0.45 pm/V; I_s and I_q are the SHG intensities of the sample and the quartz, respectively; $l_{c,q}$ is the coherent length of the quartz; l_s is the thickness of the polymeric film; and F is the correction factor of the apparatus,

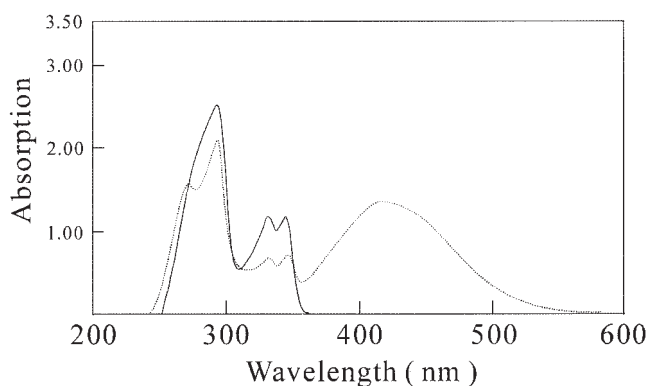


Figure 3 UV-vis spectra of polysiloxanes **P1** (—) and **P2** (- - -).

and equals 1.2 when $l_{c,q} \gg l_s$. The d_{33} value of **P2** was calculated to be 27 pm/V at 1064 nm fundamental wavelength, a relatively high value. Generally, a photorefractive (PR) effect can occur in materials that simultaneously possess electro-optical activity and photoconductivity.^{1,2} Here, in **P2**, every unit contains one carbazolyl or indole azo chromophore group, and thus the carbazolyl and indole groups are close enough in space because of the high density and the good flexibility of the polysiloxane backbone. The charge carrier can transport between these two moieties because they are good charge-transporting agents,^{1,16,17} which ensure the photoconductivity of **P2**. Given that **P2** has demonstrated a second-order nonlinear optical property, it is thus expected that **P2** could show a PR effect. We will study the PR properties of **P2** in the near future.

CONCLUSION

A new polysiloxane (**P2**), with a high density of the indole-based chromophore, was prepared by a two-step method. First, a polysiloxane (**P1**), with indole and carbazole as side chains, was synthesized through a hydrosilylation reaction, and then the post-azo coupling of *p*-nitrobenzenediazonium fluoroborate toward the indole ring afforded an indole-based chromophore-functionalized polysiloxane (**P2**). This synthetic route is very simple, and the purification of the products is very easy. The polymers exhibited excellent solubility in common organic solvents, such as toluene, CHCl_3 , THF, DMSO, and DMF. The poled film of **P2** revealed a resonant d_{33} value of 27 pm/V by second-harmonic generation (SHG) measurements.

The authors are grateful for the financial support provided by the National Science Foundation of China, the Science

Foundation of Hubei Province, and the National Fundamental Key Research Program.

References

1. Moerner, W. E.; Jepsen, A. G.; Thompson, C. L. *Annu Rev Mater Sci* 1997, 32, 585.
2. Marder, S. R.; Kippelen, B.; Jen, A. K. Y.; Peyghambarian, N. *Nature* 1997, 388, 845.
3. Zhou, N.; Zhang, Z.; Xu, C.; Xie, Z. *Chin Chem Lett* 2000, 11, 511.
4. Li, J.; Ren, P.; Zhan, C.; Qin, J. *Polym Int* 1999, 48, 491.
5. Li, J.; Li, Z.; Zhan, C.; Qin, J.; Li, Y. *Synth Met* 1999, 101, 127.
6. Li, J.; Li, Z.; Zhan, C.; Qin, J.; Kippelen, B.; Peyghambarian, N.; Marder, S. R. *Proc SPIE* 1998, 3554, 229.
7. Belfield, K. D.; Chinna, C.; Najjar, O. *Macromolecules* 1998, 31, 2918.
8. Wu, S.; Zeng, F.; Li, F.; et al. *J Polym Sci* 1999, 37, 3854.
9. Li, Z.; Qin, J.; Li, S.; Ye, C.; Luo, J.; Cao, Y. *Macromolecules* 2002, 35, 9232.
10. Starkey, E. B.; Smith, L. I.; Ungnade, H. E. *Org Synth Coll Vol* 1943, 2, 225.
11. Doyle, J. R.; Jonassen, H. B. *J Am Chem Soc* 1956, 78, 3965.
12. Schilling, M. L.; Katz, H. E.; Cox, D. I. *J Org Chem* 1988, 53, 5538.
13. Wang, X.; Kumar, J.; Tripathy, S. K.; Li, L.; Chen, J. I.; Marturkakul, S. *Macromolecules* 1997, 30, 219.
14. Li, Z.; Qin, J.; Tang, H.; Liu, Y. *J Appl Polym Sci* 2003, 89, 2989.
15. Willand, C. S.; Willams, D. J.; Bunsenges, B. *Phys Chem* 1987, 91, 1304.
16. Moerner, W. E.; Silence, S. M. *Chem Rev* 1994, 94, 127.
17. Moon, H.; Hwang, J.; Kim, N.; Park, S. Y. *Macromolecules* 2000, 33, 5116.