

# Morphology and Activity of Nanosized $\text{NdCl}_3$ Catalyst for 1,3-Butadiene Polymerization

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**ABSTRACT:** The binary lanthanide catalyst for 1,3-butadiene was invented for 40 years ago. However, it has not been employed in commercial application due to its poor solubility and low activity. Nanosized neodymium chloride ( $\text{NdCl}_3$ ) was prepared in tetrahydrofuran (THF) medium through dissolution, chelation, and colloidal formation steps. Anhydrous  $\text{NdCl}_3$  was dissolved in THF, and *ca.* 1.5 THF molecules were coordinated. In the colloidal formation step, THF was slowly replaced with the addition of cyclohexane, and pale blue nuclei, nanosize below 200 nm, were formed. The structural studies for  $\text{NdCl}_3 \cdot x\text{THF}$  using X-ray powder diffraction (XRD) and scanning electron microscope (SEM) indicate that high ordered crystallinity is decreased

with reduced particle size from trigonal prismatic to porous sphere structure. Nano  $\text{NdCl}_3$ , obtained as colloidal state in cyclohexane, was activated with  $\text{Al}(\text{iBu})_3$  and  $\text{Al}(\text{iBu})_2\text{H}$  at room temperature and employed for 1,3-butadiene solution polymerization. The nanosized Nd catalysts showed high activity ( $1.0 \sim 1.3 \times 10^5$  g/Nd mol · h), which is comparable to that of the ternary neodymium catalyst  $\text{Nd}(\text{neodecanoate})_3/\text{AlEt}_2\text{Cl}/\text{Al}(\text{iBu})_3$ . The microstructures of polybutadiene, *cis*, *trans*, and vinyl, are about 96.0, 3.5, and 0.5%, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1279–1283, 2005

**Key words:** nanoparticles; catalysts; polybutadiene

## INTRODUCTION

Lanthanide-polybutadiene has high *cis* microstructure (up to 99%) and provides excellent dynamic mechanical properties.<sup>1,2</sup> Since the early discoveries of Shen and coworkers for binary lanthanide-based catalysts [ $\text{LnX}_3/\text{AlR}_3$  ( $X = \text{F}, \text{Cl}, \text{Br}, 1$ )] in the 1960s,<sup>3</sup> many kinds of binary and ternary lanthanide catalysts for diene polymerization have been developed.<sup>4–25</sup> As for binary lanthanide-based catalysts,  $\text{NdCl}_3$ -based catalysts such as  $\text{NdCl}_3 \cdot x\text{THF}$  (where  $x$  is an integer ranging from 1 to 6) and  $\text{NdCl}_3 \cdot y\text{TBP}$  (where  $y$  is an integer ranging from 1 to 6; TBP is tributyl phosphine) are the typical examples.<sup>26–32</sup> The binary system, however, has not been employed in commercial application due to its poor solubility and low activity. Our studies have focused on the preparation of nanosized  $\text{NdCl}_3$  and on its structure to understand the low activity of the binary catalytic system in 1,3-butadiene polymerization.

## EXPERIMENTAL

### Materials

Anhydrous  $\text{NdCl}_3$  and tetrahydrofuran were purchased from Aldrich. 1,3-Butadiene and cyclohexane

were obtained from the Korea Kumho Petrochemical Co..

### Nano $\text{NdCl}_3$ preparation

Anhydrous and tetrahydrofuran (105.9 g) were placed in a 200-mL beaker under in the nitrogen atmosphere and stirred at room temperature for 24 h to form a blue solution. The filtrate solution (14 mL) was taken with a syringe and gradually added to cyclohexane (300 mL). The mixture was vigorously stirred for 4 h and then heated slowly to remove tetrahydrofuran by azeotropic distillation with a Dean–Stark apparatus. Simultaneously, cyclohexane was continuously added as much as the distilled amount. Thus, a colloid suspension existing in cyclohexane was obtained. The residual THF was measured by means of gas chromatography.

### Catalyst activation

Nanocolloidal  $\text{NdCl}_3 \cdot x\text{THF}$  ( $2.8 \times 10^{-5}$  mol, cyclohexane), triisobutyl aluminum (TIBA,  $8.4 \times 10^{-4}$  mol, 1.0M in *n*-heptane), and diisobutyl aluminum hydride (DIBAL,  $2.8 \times 10^{-4}$  mol, 1.0M in *n*-heptane) were added to a 100-mL flask under a nitrogen atmosphere and aged at 20°C for 1 h.

### 1,3-Butadiene polymerization

Cyclohexane (50 g), 1,3-butadiene (10 g), and the activated Nd-catalyst ( $2.8 \times 10^{-5}$  Nd mol) were added

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to a 100-mL pressure glass reactor under a nitrogen atmosphere and reacted at 40°C for 2 h. The resulting polybutadiene was stabilized with 2,6-di-*t*-butyl-4-methylphenol and terminated by methanol.

### Characterization

The microstructures of polybutadiene were measured in CS<sub>2</sub> solution by IR spectroscopy (Bio-Rad, FTS 60-A). The particle size of neodymium chloride was measured by using a laser light scattering method with Model 127 from the Molvern Company. The neodymium compounds were characterized by powder X-ray diffraction on a MAC model diffractometer with graphite monochromator and Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). A scanning rate of 0.05/s was applied to record the patterns and data in a  $2\theta$  range of 10–60°. Scanning electron microscopy (SEM) images were collected using a JEOL JSM-5400. Samples were sputter-coated with gold prior to examination. All simulations were carried out with the Cerius<sup>2</sup> molecular modeling environment running on SGI Origin3200 (Accelrys, Cerius<sup>2</sup> version 4.7; Accelrys Inc.; www.accelrys.com). The simulated diffraction patterns and morphologies of NdCl<sub>3</sub> were generated using C<sup>2</sup> Diffraction-Crystal module in Cerius<sup>2</sup> software. The crystal structures used for NdCl<sub>3</sub> were taken from the Cambridge Crystallographic Database. The thermal weight loss of NdCl<sub>3</sub> · *x*THF was determined by thermal gravimetric analysis (TGA) using a Perkin–Elmer 7 series thermal analysis system. A heating rate of 20°C/min was employed.

## RESULTS AND DISCUSSION

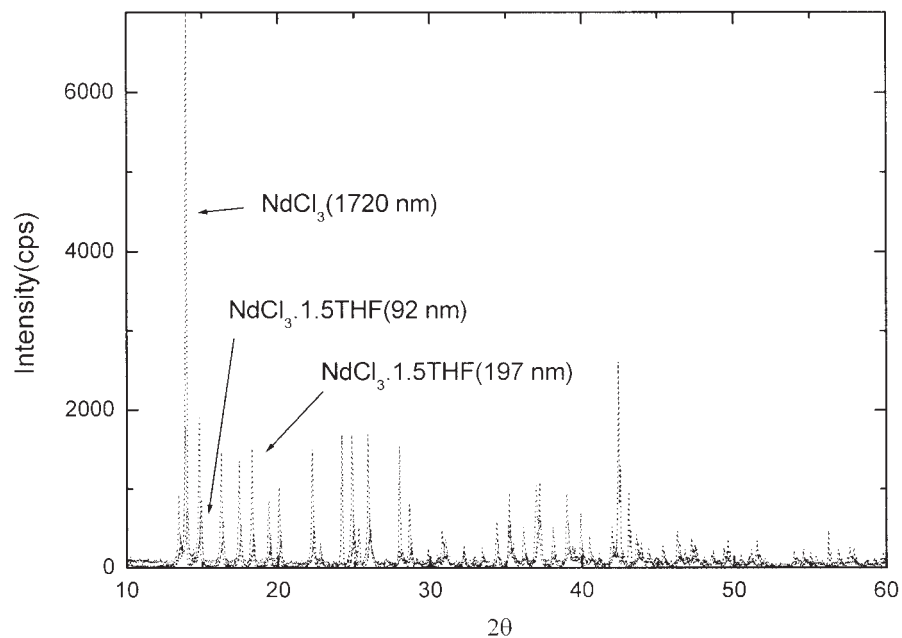
### Preparation of nanosized NdCl<sub>3</sub>

Colloidal and nanosized neodymium catalyst was considered for suitable for solution polymerization with high activity. To make such a neodymium catalyst, NdCl<sub>3</sub> was primarily manipulated with tetrahydrofuran. THF is a very useful compound to make nanoparticle of NdCl<sub>3</sub> because it is a good solvent with an aprotic nature and chelating properties. The nanoparticle of neodymium chloride was prepared in the sequential steps of dissolution, chelation, and colloidal formation. Dissolution and chelation steps took place simultaneously in dissolving NdCl<sub>3</sub> in THF. In this step 1.5 molecules of THF, according to the thermal gravimetric analysis (TGA) result, were coordinated to form NdCl<sub>3</sub> · *x*THF ( $x \sim ca.$  1.5). Colloidal formation was a key step for manipulation of nanosized NdCl<sub>3</sub>, in which THF was slowly replaced by adding cyclohexane that is a solvent for 1,3-butadiene polymerization. Dilute conditions were employed with a large amount of cyclohexane to increase the stability of the particles.<sup>33</sup> Pale blue nuclei form in the

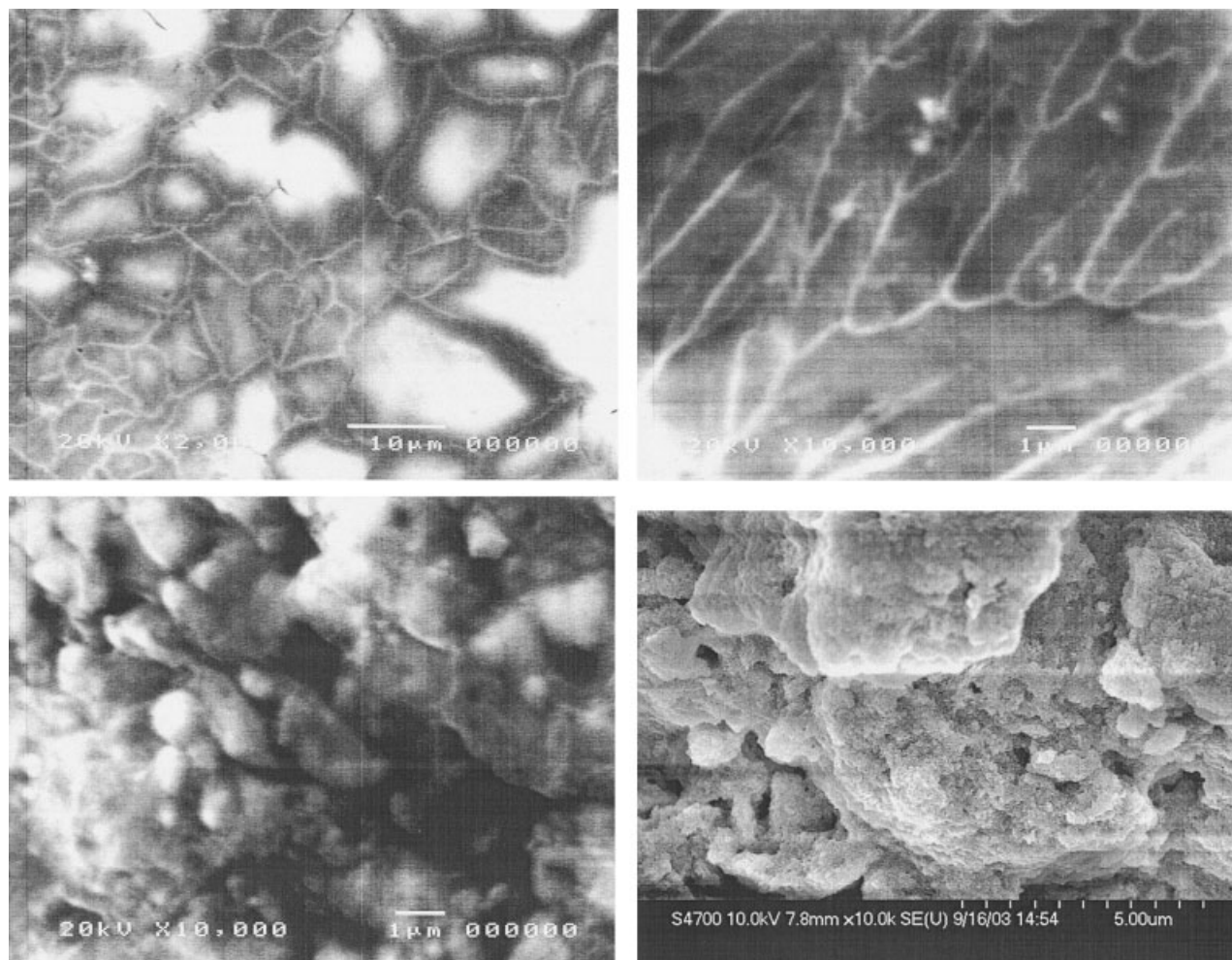
step, conducted by the distillation of THF with a Dean–Stark apparatus until THF remained below 100 ppm (gas chromatography check). Slower distillation (6 h) of THF yielded a smaller particle size of NdCl<sub>3</sub> (97 nm). Once colloidal suspension of NdCl<sub>3</sub> was prepared in cyclohexane, it was apparently transparent and nanosized. The particle size was determined by laser light scattering. NdCl<sub>3</sub> without any treatment shows its particle size to be 1720 nm. In the condition in which no surfactant was used to stabilize the particles, a further reduction of particle size was limited. The introduction of surfactant in the manipulation of particle size was not considered because surfactants inhibit propagation in butadiene polymerization.

### Structure of NdCl<sub>3</sub> particles

The structural studies of the neodymium chloride were carried out using X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). For the studies, the colloid of NdCl<sub>3</sub> was precipitated, filtered as powder, and dried in air at room temperature. The XRD patterns of NdCl<sub>3</sub> and NdCl<sub>3</sub> · *x*THF are shown in Figure 1. The intense and sharp diffraction of NdCl<sub>3</sub> indicates its high crystallinity. The four strongest peaks appear at 14.0 ( $hkl = 100$ ), 24.1 (110), 27.9 (200), 42.4 (300) °/ $2\theta$  in the powder pattern, in which neodymium has nine approximately equidistant chlorine neighbors and a tricapped trigonal prismatic structure.<sup>34</sup> Small peaks at 13.9, 14.8, 24.9, and 25.9°/ $2\theta$ , corresponding to those of NdCl<sub>3</sub> hydrates, indicate that it was partly hydrated. In the SEM image of NdCl<sub>3</sub>, dense crystalline plates were observed in Figure 2(a). In the XRD patterns of THF-chelated NdCl<sub>3</sub>, the peak positions and intensity were different from that of NdCl<sub>3</sub>. The four strongest peaks at 13.9 (10–1), 14.8 (101), 24.9 (11–2), and 25.9 (112) °/ $2\theta$  were observed irrespective of the particle size (197, 92 nm). The different positions indicate that THF chelation to NdCl<sub>3</sub> forms a different crystal structure, which would be hydrated NdCl<sub>3</sub> · *x*THF. The lesser intensity suggests a decrease of high ordered crystallinity. The SEM image of NdCl<sub>3</sub> · *x*THF [197 nm, Figure 2(b)] shows a scalelike layer structure. For the smaller NdCl<sub>3</sub> · *x*THF (92 nm), the loss of crystallinity was also observed as indicated by the less intense peak. The result corresponds well to the simulated X-ray powder diffraction pattern, in which the peak intensity at the same positions [42.3 (211), 45.0, 49.6, 51.7, 56.1 (212), 57.8 °/ $2\theta$ ] was decreased as the reduced plate size along the *c*-axis (Figure 3). The SEM image of NdCl<sub>3</sub> · *x*THF [92 nm, Figure 2(c)] shows sphere particles, and the bulk image [Figure 2(d)] represents porous nanoparticles, which would be potentially applicable to the gas polymerization process. The size appearing in SEM images is larger than that



**Figure 1** Powder XRD patterns of  $\text{NdCl}_3$  particles.



**Figure 2** SEM images of  $\text{NdCl}_3$  particles: (a) 1720 nm, (b) 197 nm, (c) 92 nm, and (d) bulk image of 92 nm.

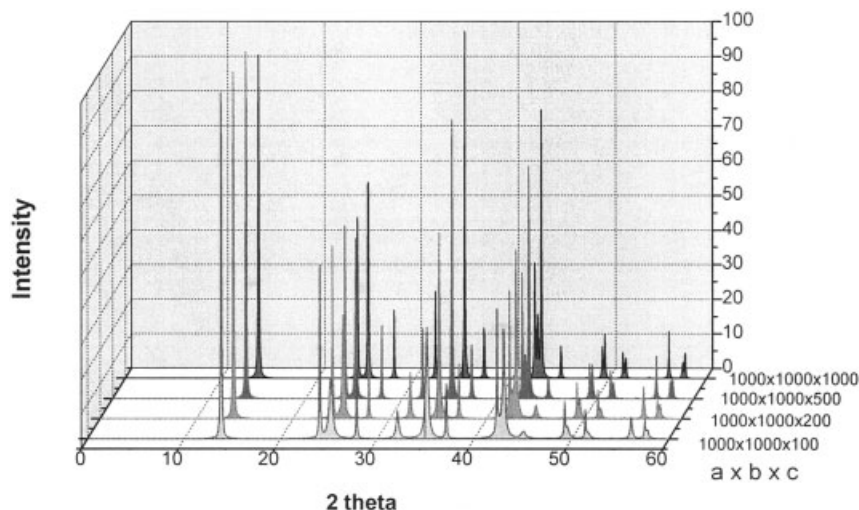


Figure 3 Simulated XRD data of different particle sizes.

observed in colloidal suspension due to aggregation during a drying step.

### Catalytic activity

To make the active Nd catalyst, the colloidal neodymium chloride was mixed with  $\text{Al}(\text{iBu})_3$  and  $\text{Al}(\text{iBu})_2\text{H}$  at room temperature for 1 h in runs 1–3. Active Nd–C bond forms through alkylation to initiate 1,3-butadiene polymerization. The polymerization results are summarized in Table I. As for a large size of  $\text{NdCl}_3$  (1720 nm, run 1), precipitation took place during polymerization, and a low activity was observed. Molecular weight and microstructure analyses could not be conducted due to poor solubility of the polybutadiene as reported.<sup>3</sup> The low activities of  $\text{NdCl}_3$  are explained due to its large particle size, in which only neodymium atoms located at the surface can participate in the polymerization reaction as active species. In the microstructure of polybutadiene, *cis*, *trans*, and vinyl contents are about 96.0, 3.5, and 0.5%, in runs 2 and 3. GPC studies indicate a weight-average molecular weight ( $M_w$ ) of over 2,000,000 and polydispersity ( $M_w/M_n$ ) of over 4.0. The nanosized Nd catalysts show high activity ( $1.0 \sim 1.3 \times 10^5$  g/Nd mol · h),

which is comparable to that of the ternary neodymium catalyst,  $\text{Nd}(\text{neodecanoate})_3/\text{AlEt}_2\text{Cl}/\text{Al}(\text{iBu})_3$  in run 4.<sup>2</sup> This result represents  $\text{NdCl}_3$ , whose particle size below 200 nm is suitable to the solution polymerization process without aggregation. Less *cis* configuration (96%) of the binary catalyst in runs 2 and 3 is due to the chelated THF, which would hinder the coordination of the penultimate bond of chain end to neodymium.<sup>35,36</sup>

### CONCLUSIONS

Nanosized  $\text{NdCl}_3 \cdot x\text{THF}$  ( $x \sim \text{ca. } 1.5$ ) was prepared through dissolution, chelation and colloidal formation. The  $\text{NdCl}_3$  exists as the state of colloid in a nonpolar medium and is also a suitable catalyst for solution polymerization of 1,3-butadiene. The structure of  $\text{NdCl}_3$  turns to a porous sphere structure from the trigonal prismatic plate as the decrease of particle size and chelation of THF. The nanosized  $\text{NdCl}_3$  shows high efficiency ( $1.3 \times 10^5$  g/Nd mol · h) in 1,3-butadiene polymerization as a binary catalyst with alkyl aluminum. The catalytic activity is increased 15 times by reducing particle diameter and is comparable to that of a ternary neodymium catalyst.

TABLE I  
1,3-Butadiene Polymerization Using  $\text{NdCl}_3$ -based Catalyst

Nd catalyst	Particle size (nm)	Activity (g/Nd mol · h)	Microstructure			$M_w$ ( $\times 10^3$ )	MWD
			<i>cis</i> (%)	<i>trans</i> (%)	vinyl (%)		
1	$\text{NdCl}_3$	$0.9 \times 10^4$	—	—	—	—	—
2	$\text{NdCl}_3 \cdot x\text{THF}$	$1.0 \times 10^5$	96.0	3.5	0.5	2,535	4.39
3	$\text{NdCl}_3 \cdot x\text{THF}$	$1.3 \times 10^5$	96.1	3.5	0.4	1,925	4.21
4 <sup>a</sup>	$\text{NdV3}$	$4.3 \times 10^5$	97.7	1.9	0.4	933	4.31

<sup>a</sup>  $\text{NdV3}(\text{Nd}(\text{neodecanoate})_3)$ ,  $1.4 \times 10^{-4}$  mol, Nd/Cl/DIBAL/TIBA (1/3/15/40), 1 h.

**References**

1. Gargani, L.; Giuliani, G. P.; Mistrali, F.; Bruzzone, M. *Angew Makromol Chem* 1976, 50, 101.
2. Kwag, G.; Kim, A.; Lee, S.; Jang, Y.; Kim, P.; Baik, H.; Yoon, D.-I.; Jeong, H. Y.; Lee, J.-G.; Lee, H. *Rubber Chem Technol* 2002, 75, 907.
3. Shen, Z.; Gung, C.; Chung, C.; Ouyang, C. *Sci Sinica* 1964, 13, 1339.
4. Hsieh, H. L.; Yeh, H. C. *Rubber Chem Technol* 1985, 58, 117.
5. Throckmorton, M. C. *Kautsch Gummi Kunstst* 1969, 22, 293.
6. Nickaf, J. B.; Burford, R. P.; Chaplin, R. P. *J. Polym Sci* 1995, 33, 1125.
7. Shen, Z.; Wang, F.; Hu, Z.; Yu, F.; Qian, B. *J Polym Sci Polym Chem Ed* 1980, 18, 3345.
8. Oehme, A.; Gebauer, U.; Gehrke, K. *J Mol Cat* 1993, 82, 83.
9. Marina, N. G.; Monakov, Y. B.; Sabirov, Z. M.; Tolstikov, G. A. *Polym Sci* 1991, 33, 387.
10. Oehme, A.; Gebauer, U.; Gehrke, K.; Lechner, M. D. *Kautsch Gummi Kunst* 1997, 50, 82.
11. Shen, Z. *Inorg Chim Acta* 1987, 140, 7.
12. Mazzei, A. *Makromol Chem Suppl* 1981, 4, 61.
13. Carbonaro, A.; Gordini, S.; Cucinella, S. *Eur Patent* 127 236, 1984.
14. Pedretti, U.; Lugli, G.; Poggio, S.; Mazzei, A. *Brit Patent* 2002 003, 1978.
15. Sylvester, G.; Witte, J.; Marwede, G., *Eur Patent* 7 027, 1979.
16. Biagini, P.; Gabriele, L.; Garbassi, F.; Andreussi, P. *Eur Patent* 667 351, 1995.
17. Pettijohn, T. M.; Hsieh, H. L. *U.S. Patent* 5 391 659, 1995.
18. Balducci, A.; Porri, L.; Choubine, N. *U.S. Patent* 6 121 429, 2000.
19. Sone, T.; Takashima, A.; Nonaka, K.; Hattori, I. *U.S. Patent* 6 130 299, 2000.
20. Lynch, T. J. *U.S. Patent* 6 177 603, 2001.
21. Kwag, G. *Macromolecules* 2002, 35, 4875.
22. Quirk, R. P.; Kells, A. *Polym Int* 2000, 49, 751.
23. Kobayashi, E.; Kaita, S.; Aoshima, S.; Furkawa, J. *J Polym Sci Polym Chem* 1998, 36, 2283.
24. Kobayashi, E.; Kaita, S.; Aoshima, S.; Furkawa, J. *J Polym Sci Polym Chem* 1994, 32, 1195.
25. Hattori, I.; Tsutsumi, F.; Sakakibara, M.; Makino, K. *J Elast Plast* 1991, 131.
26. Rossmannith, K. *Monatsch Chem* 1969, 100, 1484.
27. Jihua, Y.; Jingyu, H.; Shufen, F.; Enli, P.; Demin, X.; Chongqi, Z.; Jun, O. *Sci Sinica* 1980, 23, 734.
28. Yang, J.-H.; Tsutsui, M.; Chen, Z.; Bergbreiter, D. E. *Macromolecules* 1982, 15, 230.
29. Iovu, H.; Hubca, G.; Simonescu, E.; Badea, E.; Hurst, J. *Eur Polym J* 1997, 33, 811.
30. Iovu, H.; Hubca, G.; Racoti, D.; Hurst, J. *Eur Polym J* 1999, 35, 335.
31. Srinivasa, G. S.; Jain, R. C.; Upadhyay, V. K. *J Appl Polym Sci* 1999, 71, 595.
32. Kozlov, V. G.; Sigaeva, N. N.; Nefedjev, K. V.; Saveleva, I. G.; Marina, N. G.; Monakov, Y. B. *J Polym Sci Part A* 1994, 32, 1237.
33. Morrison, I. D.; Ross, S. *Colloidal Dispersion: Suspensions, Emulsions, and Foams*; Wiley-Interscience: New York, 2002; p 66.
34. Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984; pp. 421–423, ed. 5.
35. Ricci, G.; Boffa, G.; Porri, L. *Macromol Chem Rapid Commun* 1986, 7, 355.
36. Porri, L.; Gallazzi, M. C.; Destri, S.; Bolognesi, A. *Macromol Chem Rapid Commun* 1983, 4, 485.