

# Synthesis and Characterization of Poly(*N*-isopropylacrylamide)s Initiated with Siloxane Oligomer-(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> Redox Pair

Candan Erbil, Hatice Akin, Nurseli Uyanik

*Istanbul Technical University, Chemistry Department, 80626 Maslak, Istanbul, Turkey*

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**ABSTRACT:** Poly(*N*-isopropylacrylamide)s (PNIPAAM)s were synthesized via free-radical polymerization using a ceric ammonium nitrate, Ce(IV)- $\alpha$ - $\omega$ -dihydroxy(polydimethylsiloxane) (Tegomer H-Si 2111, PDMS) redox pair in hexane at 30°C in a nitrogen atmosphere. The dependence of the initiation and termination steps on the [NIPAAM]/[Ce(IV)] and [NIPAAM]/[PDMS] ratios were studied using gravimetry and FTIR, <sup>1</sup>H-NMR, UV-vis, and GFAA spectroscopy techniques. Gravimetric results indicated that, in the case of high concentrations of PDMS, the percentage of the solid portions of the products decreased while the amount of the oligomeric NIPAAM chains increased, that is, as the amount of PDMS in hexane was increased, the number of the short NIPAAM chains having PDMS segments at

the two ends, also increased. UV-vis results showed that the LCST of PNIPAAM initiated with Ce(IV) alone was higher than those of the ones that were synthesized using common initiator systems such as an ammonium persulfate-*N,N,N',N'*-tetramethylethylenediamine redox pair and azobis(isobutyronitrile). Further, it was observed that both siloxane blocks and —NH— groups forming coordination bonds with free Ce(IV) ions and/or metal-ligand complexes had an important effect on the aggregation process of the chains. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1248–1254, 2003

**Key words:** polysiloxanes; stimuli-sensitive polymers; FT-IR

## INTRODUCTION

Stimuli-sensitive polymeric materials are called “intelligent” polymers. Among these temperature- and pH-sensitive polymers are ones that are most frequently studied because those factors are the variables that create a change in typical physiological, biological, and chemical systems.<sup>1–8</sup> The thermosensitive polymers are characterized by their lower critical solution temperatures (LCSTs). Poly(*N*-isopropylacrylamide) (PNIPAAM) is the most intensively studied member of thermosensitive *N*-alkylacrylamide polymers and exhibits a well-defined and reversible LCST in water around 32–34°C, which is close to body temperature.<sup>9–16</sup>

Recently, *N*-alkylacrylamides have been copolymerized with the monomers having hydrophobic or hydrophilic groups to prepare the products with LCST values different from those of their homopolymers.<sup>17–22</sup> For instance, LCSTs and water absorptions of linear and crosslinked PNIPAAM chains that are modified hydrophobically decrease with an increasing hydrophobic content, while the swelling degrees,

LCSTs, and pH sensitivities of its thermosensitive copolymers with ionizable groups in their side chains are higher than those of the homopolymer of NIPAAM.

Polymer chains containing segments with different chemical structures and physicochemical properties can be obtained from utilizing prepolymers with appropriate end groups. The number of end groups per oligomer molecule and their nature help in building block copolymers.

Polysiloxanes have high chain flexibility, thermal stability, hydrophobicity, and biocompatibility but poor thermodynamic compatibility. The most effective way to overcome the difficulties resulting from their thermodynamic incompatibilities is to form copolymer systems and interpenetrating networks of siloxanes. One of the synthetic techniques leading to the formation of siloxane-containing linear or graft copolymers is free-radical polymerization.<sup>23,24</sup> To synthesize polysiloxane-based linear segmented or block copolymers, siloxane macroinitiators carrying free-radical initiators are utilized.<sup>25–27</sup>

Initiation by a redox process is another method used to obtain these types of polymers.<sup>28–30</sup> Redox systems are widely used as initiators in free-radical polymerizations. Compared to other methods, they have the prime advantage of operating at very moderate temperatures. Cerium salts in combination with a hydroxyl or carboxylic group containing a reductant are

Correspondence to: C. Erbil.

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TABLE I  
Summary of Synthesis Conditions Used to Prepare PNIPAAms Initiated with Ce(IV)–Tegomer H-Si Redox Pair

| Sample no. | NIPAAm (mol/L) | Ce(IV) (mol/L × 10 <sup>3</sup> ) | Tegomer (mol/L × 10 <sup>2</sup> ) | Total conversion (%) | Conversion (collapsed portions,%) | Conversion (acetone/hexane portions,%) | Conversion (liquid products,%) |
|------------|----------------|-----------------------------------|------------------------------------|----------------------|-----------------------------------|--|--------------------------------|
| 1          | 0.20           | 1                                 | —                                  | 9.3                  | 9.3                               | —                                      | —                              |
| 2          | 0.20           | 10                                | 1                                  | 27.7                 | —                                 | 27.7                                   | —                              |
| 3          | 0.20           | 1                                 | 1                                  | 21.9                 | —                                 | 21.9                                   | —                              |
| 4          | 0.20           | 0.5                               | 1                                  | 8.1                  | 5.4                               | 2.7                                    | —                              |
| 5          | 0.50           | 1                                 | 1                                  | 28.8                 | 28.8                              | —                                      | —                              |
| 6          | 0.50           | 1                                 | 5                                  | 22.7                 | 9.4                               | 10.8                                   | 2.5                            |
| 7          | 0.50           | 1                                 | 10                                 | 6.2                  | 1.4                               | 0.3                                    | 4.5                            |
| 8          | 0.30           | 1                                 | 10                                 | 37.3                 | 5.1                               | 1.3                                    | 30.9                           |
| 9          | 0.10           | 1                                 | 10                                 | 12.7                 | 0.9                               | 1.5                                    | 10.3                           |

the initiators that are mostly used. Polymerization products obtained in the presence of vinyl monomers have molecules bearing those reducing substrates on the chain ends.<sup>31–33</sup>

In this work, we attempted to synthesize and characterize siloxane-containing NIPAAm polymers. A hydroxyl-terminated siloxane oligomer [ $\alpha$ - $\omega$ hydroxy(polydimethylsiloxane) (PDMS), Tegomer H-Si 2111]–ceric ammonium nitrate [(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> ·  $\cdot$ ], Ce(IV) · ] redox pair was used to initiate the polymerization reactions. The characteristics of the products obtained were investigated by UV-visible (UV-vis), proton-nuclear magnetic resonance (<sup>1</sup>H-NMR), Fourier transform infrared (FTIR), and graphite furnace atomic absorption (GFAA) spectroscopic techniques.

## EXPERIMENTAL

### Materials

The monomer *N*-isopropylacrylamide (NIPAAm), purchased from the Aldrich Chemical Co., was used without further purification, as were the oxidant, ceric ammonium nitrate [Ce(IV); BDH Chemicals Ltd.] and the reductant, PDMS (Tegomer H-Si 2111,  $M_n = 950 \pm 80$  g/mol; Goldschmidt AG). Hexane (Riedel-de Haen AG) and distilled deionized water were used as solvents for polymerizations and cloud-point measurements, respectively.

### Synthesis

Polymerization reactions were performed in hexane containing 2% (v/v) dichloroethane to increase the solubility of NIPAAm (heterogeneous solution polymerization). First, NIPAAm and Tegomer H-Si 2111 were dissolved in it; then, the calculated amount of Ce(IV) salt was added and the mouth of the reaction flask was closed tightly with a rubber cap. The polymerization mixture was stirred with a magnetic stirrer and bubbled with nitrogen through a syringe for 30

min. The polymerizations were carried out at 30°C for 48 h. One NIPAAm homopolymer and eight different PDMS-containing NIPAAm copolymers were synthesized using various [Ce(IV)]/[NIPAAm]/[Tegomer H-Si 2111] ratios.

To purify the PNIPAAms having higher NIPAAm content in the polymerization solution, the solid reaction products were dissolved in water, collapsed by heating, and then washed with hexane and hot water to remove unreacted PDMS and NIPAAm, respectively. The samples prepared using higher siloxane and Ce(IV) contents in the reaction mixtures were separated into two or three portions. The first ones, having a lower siloxane content, were collected by shaking with cold water. These water-soluble products were precipitated by heating to a temperature above the LCST (~40°C) to obtain the NIPAAm chains with a low siloxane content. The second portions were the water-insoluble products, which had been dried in a vacuum oven. They were purified by dissolution in acetone and reprecipitation from hexane. Milky white liquid products (third portions of the samples) were obtained by evaporation of the hexane used for both reprecipitation of the second portions and the preparation of the polymerization solutions. The reaction conditions and conversions are given in Table I.

### Characterization methods

The chemical structures of the polymers were studied by <sup>1</sup>H-NMR, FTIR, UV-vis, and GFAA spectroscopic techniques. Infrared spectra of the solid products were recorded on a Mattson 1000 FTIR using KBr pellets. The compositions of samples 3, 5, 6, and 8 in Table I were determined by using <sup>1</sup>H-NMR and GFAA spectrophotometers. <sup>1</sup>H-NMR spectra were obtained in chloroform (CHCl<sub>3</sub>)-*d*<sub>6</sub> using a Bruker 200 AC (250 MHz) Model spectrophotometer. The ratio of the peak area of the proton attached to the secondary carbon

TABLE II  
Absorption Bands of Original Groups of Initiator, Activator, and Monomer

| Functional group                                       | Tegomer H-Si 2111 (cm <sup>-1</sup> ) | Metal-ligand complexes (cm <sup>-1</sup> ) | PNIPAAM (cm <sup>-1</sup> ) |
|--|---------------------------------------|--|-----------------------------|
| Si(CH <sub>3</sub> ) <sub>2</sub>                      | 1275–1260<br>880–760                  |  |                             |
| Si–O   | 1100–1000<br>900–600                  |  |                             |
| Ce(NO <sub>3</sub> ) <sub>n</sub> <sup>x(+ or -)</sup> |                                       | 1450–1350<br>650–550                       |                             |
| C=O stretching   |                                       |  | 1690–1650                   |
| N–H bending  |                                       |  | 1570–1530                   |
| CH(CH <sub>3</sub> ) <sub>2</sub>                      |                                       |  | 1385–1370                   |

atom of the isopropyl group of NIPAAM to that of the methyl protons of siloxane of Tegomer H-Si 2111 was used to determine the composition of each PNIPAAM sample having siloxane blocks and/or end groups. A Perkin-Elmer 3030 Zeeman atomic absorption spectrophotometer equipped with an HGA-600 graphite furnace was used for the determination of the Si content of the same samples ( $1 \times 10^{-3}$  g/mL polymer in acetone). The results are summarized in Table II.

Aqueous solutions of the polymers (0.01–0.5 wt %) were prepared and subjected to cloud-point measurements. Optical densities (ODs) were measured at 400 nm on a UV-vis recording spectrophotometer (Shimadzu UV-160 A), equipped with a temperature-controlled cell. The heating rate was controlled at 1°C/min. Cloud points were taken as the initial break points in the resulting OD versus temperature curves.

## RESULTS AND DISCUSSION

The purpose of this work was to prepare hydrophobically modified but still water-soluble PNIPAAM derivatives with a high tendency to aggregate. As to this aim, polymers were prepared by free-radical polymerization of NIPAAM in the presence of a Ce(IV)–hydroxyl-terminated PDMS redox pair. Polymerizations were carried out by varying the initiator [(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>], activator (Tegomer H-Si 2111), and monomer concentrations.

### Conversions and FTIR structural analysis

Both total yields and the ones corresponding to the fractions that are obtained with different procedures together with the synthesis conditions are given in Table I. The results show that the third fractions of the samples increased with increasing activator and decreasing monomer concentrations, in case of a constant initiator concentration (samples 6–9). This means that the milky white liquid portions of the products consist of only oligomeric siloxane chains having short NIPAAM segments because of the high [PDMS]/[NIPAAM] ratios used in the feed composition. On the

other hand, it was observed that both the total yields and the amounts of the solid products increased with increasing initiator (samples 3–5) and monomer (samples 2 and 5) concentration, for the constant and lowest concentration of the activator ( $1 \times 10^{-2}$  mol/L). Two solid fractions were obtained from the resulting polymers, after reprecipitation procedures proceeded in water (by heating to 50°C, to collapse the NIPAAM oligomers or polymers) or acetone/hexane (solvent/nonsolvent) pair. From the inverse relation between [NIPAAM]/[Ce(IV)] (20, 200, 400, and 500 for samples 2–5, respectively) and acetone–hexane fraction/collapsed portion ratios (27.7/0, 21.9/0, 2.7/5.4, and 0/28.8, in %), it can be concluded that the portions that collapsed easily in hot water have PNIPAAM chains with a low siloxane content and a high molecular weight, and they are being initiated and/or terminated mainly by Ce(IV). On the other hand, it was assumed that the chain structures of the resulting products which were not separated by heating in hot water but dissolved in acetone and precipitated in hexane contained more siloxane units per chain.

NIPAAM polymerizations in hexane were heterogeneous. As to the results of heterogeneous polymerizations in the literature, termination can occur in both the liquid and the precipitated phases. Before precipitation, oligomeric short chains are terminated by either metal ions and primary radicals or oligomeric radicals.<sup>34–36</sup> For this study, it can be said that oligo-NIPAAM chains are terminated in the liquid phase by the primary radicals produced by Tegomer H-Si 2111. This is due to the excess activator acting as a good solvent for oligomeric NIPAAM chains (unimolecular termination). For lower [Tegomer H-Si]/[NIPAAM] ratios, the initiation and propagation steps of NIPAAM polymerization proceed in the liquid phase and the products with a high molecular weight and low siloxane content are produced in the heterogeneous phase by mutual termination of the NIPAAM chains. In other words, after precipitation, termination takes place mainly between macroradicals ended with Ce(IV) ions or the activator.

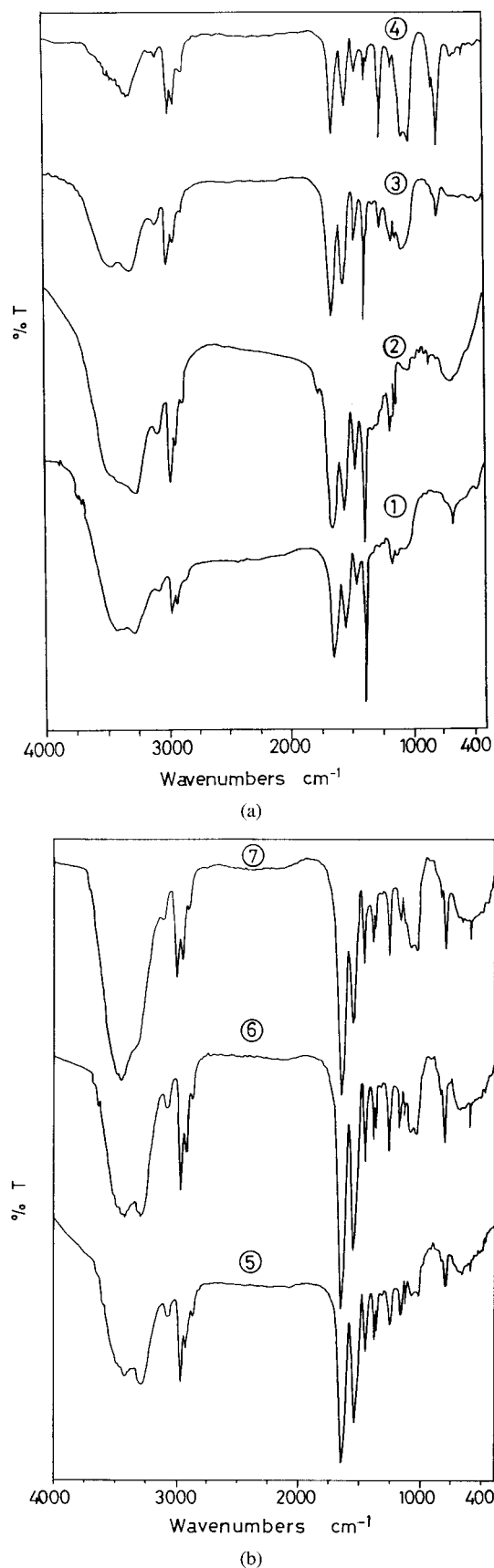
The FTIR spectra of the solid portions of NIPAAM polymers initiated with  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  (sample 1) and the Ce(IV)–Tegomer H–Si 2111 redox pair and the characteristic absorption bands of siloxane units, Ce–ligand complexes, and PNIPAAM are shown in Figure 1(a,b) and given in Table II, respectively. The appearance of the absorption bands characteristic of  $\text{Ce}(\text{NO}_3)_n^{x(+\text{or}-)}$  complexes ( $550\text{--}650$  and  $1350\text{--}1450\text{ cm}^{-1}$ ) together with the specific peaks of PNIPAAM ( $-\text{C}=\text{O}$  stretching for secondary amides at  $1660\text{ cm}^{-1}$ ,  $-\text{NH}$  bending at  $1540\text{ cm}^{-1}$ , and isopropyl group at  $1385$  and  $1370\text{ cm}^{-1}$ ) indicates the presence of both metal ion and nitrate groups in sample 1. This means that Ce(IV) ions and metal–ligand complexes play an important role in the initiation and termination processes in our polymerization conditions.

The intensities of the peaks at  $\sim 1400$  and  $600\text{ cm}^{-1}$  belonging to the nitrate group and metal–ligand complexes in the FTIR spectra of samples 2–7 decrease with increasing  $[\text{NIPAAM}]/[\text{Ce(IV)}]$  (samples 2–4,  $[\text{Tegomer H-Si}] = 1 \times 10^{-2}\text{ mol L}^{-1}$ ) and  $[\text{NIPAAM}]/[\text{Tegomer H-Si}]$  (samples 7–5,  $[\text{Ce(IV)}] = 1 \times 10^{-3}\text{ mol L}^{-1}$ ) ratios, respectively. The FTIR spectra of these polymers also show the characteristic bands due to the  $\text{Si}(\text{CH}_3)_2$  and  $\text{Si-O}$  of the siloxane units at a broad region of  $1300\text{--}600\text{ cm}^{-1}$ . The intensities of the peaks in this region increase in the reverse order with the bands attributed to metal–ligand complexes. So, we can say that initiation occurs mainly on cerium ions and the propagating chains ended with siloxane units are influenced by the mutual termination step of PNIPAAMs obtained in the case of lower  $[\text{NIPAAM}]/[\text{Ce(IV)}]$  ratios. For lower  $[\text{NIPAAM}]/[\text{PDMS}]$  ratios, the chains are initiated by primary radicals produced from the activator, and free Ce(IV) ions and metal complexes having different numbers of nitrate ions along with PDMS radicals also have an influence upon the termination mechanism.

#### Si content and molecular weight determinations of solid products

The silicone contents of samples 3 (acetone/hexane portion), 5, 6, and 8 (collapsed portions in hot water) in Table I were determined using  $^1\text{H-NMR}$  and GFAA spectroscopic techniques. The results obtained are given in Table III and Figure 2.

The peaks appearing at  $0.06\text{--}0.08$  and  $0.53\text{--}0.55$  ppm and resulting from  $-\text{Si}(\text{CH}_3)_2-\text{O}-$  and  $-\text{Si}-\text{CH}_2-$  groups, respectively, together with signals at  $4.15\text{--}4.16$  and  $7.02\text{--}7.10$  ppm [ $-\text{CO}-\text{NH}-\text{CH}-(\text{CH}_3)_2$ ] indicate the incorporation of PDMS into NIPAAM polymers.  $^1\text{H-NMR}$  was used to determine the siloxane contents in mol percent by calculating the peak areas of the isopropyl protons in NIPAAM ( $4.15\text{--}4.16$  ppm) and dimethylsiloxy protons in siloxane segments ( $0.06\text{--}0.08$  ppm). Further, Si contents obtained



**Figure 1** (a,b) FTIR spectra of samples 1–7 (identified in Table I).

TABLE III  
Si Contents and Molecular Weights of the Products

| Sample no. | Tegomer H-Si <sup>a</sup><br>(in mol %) | Atomic no.<br>of Si <sup>b</sup> (%) | Si content <sup>c</sup><br>(in wt %) | Molecular<br>weight |
|------------|---|--------------------------------------|--------------------------------------|---------------------|
| 3          | 12.3 ± 1.0                              | 1.35 ± 0.1                           | 0.7                                  | 5400 ± 400          |
| 5          | 9.6 ± 0.8                               | 1.06 ± 0.1                           | 0.2                                  | 15,000 ± 1000       |
| 6          | 5.3 ± 0.5                               | 0.60 ± 0.1                           | 0.9                                  | 1800 ± 200          |
| 8          | 12.8 ± 1.1                              | 1.41 ± 0.1                           | 0.6                                  | 6600 ± 600          |

<sup>a</sup> Found by <sup>1</sup>H-NMR technique.

<sup>b</sup> Calculated by using total atomic no. of Si per Tegomer H-Si 2111.

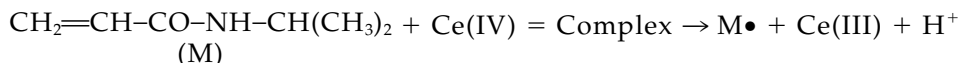
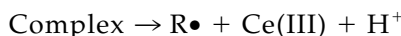
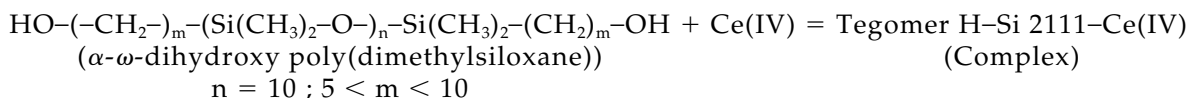
<sup>c</sup> Found by GFAAS technique.

from GFAAS (in ppm) were used to calculate the weight percent and atomic number of Si in the same samples. From these spectroscopic techniques, the molecular weights of the products were calculated.

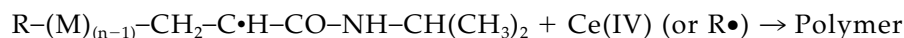
The results summarized in Table III are in agreement with the ones obtained by gravimetric and FTIR analyses. As to the molecular weights of the products, it can be said that [NIPAAM]/[Tegomer H-Si] ratios in the feeds have an important effect on each stage during the heterogeneous polymerization process in this work. Total amounts and molecular weights of the solid products increase with increasing monomer/activator ratios in the reaction mixtures. In other words, as the mol percent of the hydrophobic constit-

uent in the feed solution increases, the molecular weights of the polymers decrease, except for sample 8, having the highest liquid product percent in total conversion. This exception indicates that a great part of the activator is consumed to terminate the radical chains being produced in the liquid phase and, therefore, the molecular weight of the solid product is higher than those of the ones obtained with higher [NIPAAM]/[PDMS] ratios.

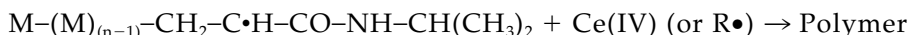
From the spectroscopic results in conjunction with the gravimetric ones, the following reaction scheme is suggested for the formation of NIPAAM polymers initiated with the Ce(IV)-hydroxyl-terminated PDMS redox pair:



(Initiation by free Ce(IV), Ce(NO<sub>3</sub>)<sub>n</sub><sup>x(- or +)</sup> complexes and Ce(IV)-hydroxyl terminated siloxane oligomer)



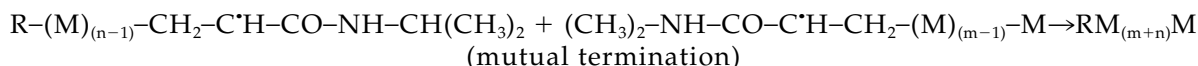
and



(Linear termination by free Ce(IV), Ce(NO<sub>3</sub>)<sub>n</sub><sup>x(- or +)</sup> complexes or primary radicals produced from activator)



and



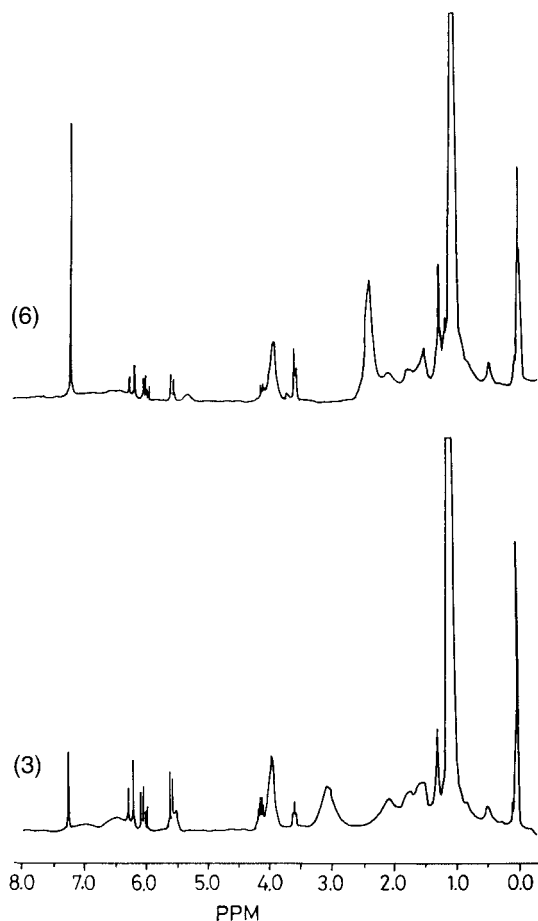


Figure 2  $^1\text{H-NMR}$  of samples 3 and 6 in Table I.

In the monomeric unit, there are free-electron pairs bearing nitrogen groups, which can form coordination bonds with transition metals. Therefore, the mechanism of the ceric salt-initiated step in the NIPAAM polymerization system can be explained by a radical mechanism based upon the formation of Ce(IV)-coordinated NIPAAM. In the case of redox polymerization, PDMS-ended NIPAAM chains can be produced by both Ce(IV)-NIPAAM complexes and free Ce(IV) ions.<sup>37</sup>

#### Thermosensitive properties of siloxane-ended PNIPAAMs

The transition temperatures, that is, the LCSTs of the solid products in the aqueous solutions, were studied to determine the effect of siloxane end groups on the thermal behavior of PNIPAAMs. These LCSTs were traced by monitoring the absorbance values of a 400-nm light in a 1-cm sample cell at different temperatures. OD changes for the sample 6 aqueous solutions at various temperatures and all other results related to the cloud-point measurements are shown in Figure 3 and given in Table IV, respectively.

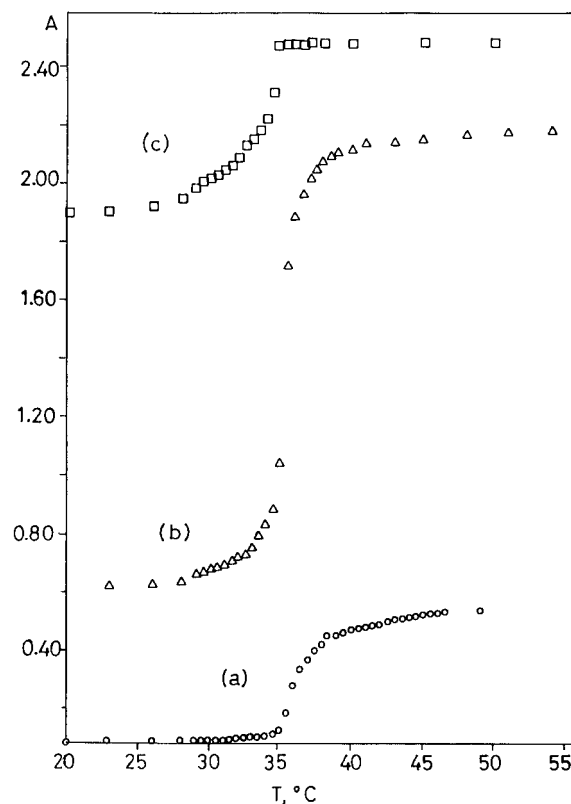


Figure 3 Phase-transition diagrams of (a) 0.01 wt %, (b) 0.1 wt %, and (c) 0.5 wt %; aqueous solutions of sample 6.

The phase-transition temperatures of PNIPAAMs obtained with different synthesis conditions appeared near 35°C for dilute solutions (0.01 and 0.1 wt %). In the case of the more concentrated solutions (0.5 wt %), the LCSTs of the same samples having both siloxane and cerium end groups were lower than that of PNIPAAM synthesized by  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  alone.

As to the results obtained in this part, inter- and intramolecular interactions and microstructures of the chains, being related to the hydrophobicity of

TABLE IV  
Phase Transition Temperatures and Initial Absorbance Values of Aqueous PNIPAAM Solutions at Various Concentrations

| Sample no. | c (in %) | OD (initial value) | T (°C)     |
|------------|----------|--------------------|------------|
| 1          | 0.1      | 0.021              | 35.1 ± 0.2 |
|            | 0.5      | 0.121              | 34.0 ± 0.2 |
| 3          | 0.1      | 0.309              | 35.7 ± 0.2 |
|            | 0.5      | 1.539              | 32.0 ± 0.2 |
| 5          | 0.1      | 0.554              | 35.4 ± 0.2 |
|            | 0.5      | 1.814              | 33.0 ± 0.2 |
| 6          | 0.01     | 0.080              | 36.2 ± 0.2 |
|            | 0.1      | 0.608              | 35.2 ± 0.2 |
|            | 0.5      | 1.907              | 33.2 ± 0.2 |
| 8          | 0.01     | 0.034              | 36.8 ± 0.2 |
|            | 0.1      | 0.435              | 36.4 ± 0.2 |
|            | 0.5      | 1.564              | 35.1 ± 0.2 |

Tegomer H-Si 2111 and the presence of metal atoms and metal-ligand complexes, respectively, are the key in the change of the LCSTs of the polymers. At low concentrations of aqueous solutions, hydrophobic repulsion of the siloxane end groups prevents both intra- and intermolecular interactions and, so, the aqueous solutions of the polymers are colloidally stable, even above the LCST of the PNIPAAM chains ( $\sim 34^\circ\text{C}$ ). As the amount of the hydrophobic component and the concentration of the solutions are increased, however, the strength of the hydrophobic interactions between the isopropyl groups overcome the repulsive forces resulting from the end groups and/or blocks and coagulation occurs before the temperature of the solutions is increased to about  $35^\circ\text{C}$ . Further, it is assumed that the presence of polymer-metal complexes along with siloxane end groups have an important effect on the aggregation process of the chains because of the higher LCST of the PNIPAAM initiated with ceric salt as compared to the ones prepared using various initiators.<sup>1,13</sup>

### CONCLUSIONS

PDMS-segmented PNIPAAMs were prepared by free-radical polymerization of NIPAAM in the presence of the Ce(IV)—Tegomer H-Si 2111 redox pair. The polymer samples were separated into three fractions: (i) PNIPAAM chains which were initiated and/or terminated by the free radicals generated from Ce(IV)—monomer complexes (water soluble portions), (ii) mainly PDMS ended polymers, which were isolated by precipitation from acetone solutions into hexane, and (iii) PDMS-terminated oligomers formed in the liquid phase. As to the compositions confirmed by FTIR, GFAAS, and  $^1\text{H-NMR}$  analysis, the [NIPAAM]/[Ce(IV)] and [NIPAAM]/[PDMS] ratios are the most important experimental parameters affecting yields, molecular weights, and structures of the products obtained. In the aqueous solutions of hydrophobically modified polymers, there usually exists a concentration below which the polymers do not aggregate but form colloidally stable particles. The results of the cloud-point measurements in this work also show that the LCSTs in concentrated aqueous solutions ( $5\text{ g L}^{-1}$ ) are lower than those of diluted ones ( $0.1$  and  $1\text{ g L}^{-1}$ ), presumably as a consequence of the presence of the hydrophobic terminal PDMS group and NIPAAM-metal complexes. When the polymer concentration exceeds  $5\text{ g L}^{-1}$ , the increase in the hydrophobic forces between isopropyl groups causes the collapse of macromolecular coils. Thus, colloidally stable and hydrophobically modified PNIPAAMs carrying PDMS

chains either at one or two chain ends exhibit macroscopic phase separation.

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