

Synthesis and characterization of poly(*N*-isopropyl acrylamide) gels prepared by using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ -Tegomer H-Si 2111 redox pair

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Summary

Hydrogels have been prepared by free radical solution polymerizations in acetone and acetonitrile of *N*-isopropyl acrylamide (NIPAAM). The redox pair composed of ceric ammonium nitrate ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, Ce(IV)) as a catalyst and $\cdot\text{Si}\cdot$ -dihydroxy poly(dimethylsiloxane) (Tegomer H-Si 2111, H-Si) as an activator and hydrophobic constituent was used to initiate the polymerizations. The equilibrium swelling degrees against the temperature and lower critical solution temperatures (LCSTs) in water were investigated for the gels produced by changing the initial $[\text{Ce}(\text{IV})] / [\text{H-Si}]$ ratios and monomer concentrations in the reaction media. Results showed that type of synthesis-solvent had an important effect on the stability and concentration of Ce(IV)-H-Si complexes, which had been used to synthesize the PNIPAAM gels having hydrophobic Tegomer H-Si end groups.

Introduction

N-alkyl substituted acrylamides, and in particular *N*-isopropyl acrylamide (NIPAAM) gels are known as thermoresponsive crosslinked polymer networks and prepared by free radical polymerization using radical initiators [1-3]. NIPAAM hydrogels exhibit a sharp phase transition from hydrophilic to hydrophobic structure that occurs at its lower critical solution temperature (LCST, T_c). When NIPAAM is copolymerized so as to obtain the right balance of hydrophobic and hydrophilic monomers, its LCST, which is close to the body temperature (32-34°C) as well as poor mechanical properties can be manipulated and, thus these hydrogels may be used in biotechnological applications [4-12]. From starting point of view, siloxane containing NIPAAM copolymer gels can be prepared because polysiloxanes have high chain flexibility, hydrophobicity and biocompatibility.

The free radical polymerization is only one of the synthetic techniques leading to the formation of polysiloxane based linear segmented copolymers. To prepare these type materials, macroinitiators consisting of siloxane oligomers and carrying free radical initiators as end groups are utilized [13-14].

Initiation by a redox process can be another method used to obtain the siloxane-NIPAAM linear and crosslinked copolymers. Redox systems are widely used as

initiators in free-radical polymerizations[15,16]. Polymerization products obtained in the presence of vinyl monomers are the molecules containing the reducing substrates, i. e., activator as the end groups of the polymer chains formed [17-19].

In this study, we attempted to synthesize and characterize NIPAAM gels modified with hydrophobic α,ω -dihydroxy poly(dimethylsiloxane) constituent. For this purpose, Tegomer H-Si 2111 (H-Si, activator) – $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (Ce(IV), catalyst) redox pair was used to initiate the polymerization reactions. The effects of hydrophobic end groups, type of synthesis-solvent, crosslinking density, catalyst and monomer concentrations on the yields, water absorption capacities and LCSTs of the gels obtained were investigated.

Experimental

Materials

N-isopropyl acrylamide (NIPAAM) was used without further purification, as were the catalyst, ceric ammonium nitrate (Ce(IV); BDH Chemicals Ltd.); the activator, α,ω -dihydroxy poly(dimethylsiloxane) (Tegomer H-Si 2111, $M_n = 950 \pm 80$ g/mol; Goldschmidt AG) and the crosslinker, N,N'-methylenebisacrylamide (BIS, Merck). Acetone, acetonitrile (Merck) and distilled deionized water were used as solvents for polymerizations and swelling measurements, respectively.

Synthesis

NIPAAM gels initiated by using hydroxyl ended polysiloxane - Ce(IV) redox pair were prepared by mixing the monomer solutions containing NIPAAM (0.50, 0.70, 0.90 and 2.00 mol/L), BIS (1.25×10^{-2} , 2.50×10^{-2} and 7.50×10^{-2} mol/L) and H-Si (1.50×10^{-2} , 3.00×10^{-2} and 4.50×10^{-2} mol/L) with Ce(IV) solutions (1.50×10^{-2} , 3.00×10^{-2} and 4.50×10^{-2} mol/L) in acetone which is acidified with 0.1 M HNO_3 or in acetonitrile. After polymerizations at 60°C for 4 days, the gelated samples were immersed into the synthesis-solvents for 2 days and distilled-deionized water for 2 days to extract unreacted compounds and soluble portions.

Infrared spectra of dried samples were recorded on a Mattson 1000 FT-IR spectrometer by using KBr pellets.

Swelling Studies

Small pieces of dry gels were weighed and immersed into the distilled deionized water. During the measurements, the temperature was controlled by circulating thermostatted water through the water-jacket around the cell. After equilibration at one temperature, gel samples were removed from the cell, blotted with dry filter paper, weighed and then reequilibrated at another temperature. The swelling degrees of the gel samples at different temperatures were determined as the ratio $(m_s - m_d) / m_d$, where m_s is the mass of the swollen gel and m_d is the mass of the dry gel.

Results and Discussion

Effect of the presence of a hydrophobic constituent on swelling and phase transition behaviours of the gels

The differences in the phase transition temperatures result from the interactions between the side groups of NIPAAm and hydrophilic or hydrophobic comonomers added to the main structure of the network chains, and water molecules. In the case of NIPAAm homopolymers initiated with Ce(IV) and crosslinked by using a crosslinker having similar chemical structure with the monomer, i.e., N,N'-methylenebisacrylamide, the values of LCSTs were independent of the BIS concentration. Both the results on phase transition temperatures and swelling degrees being related to the BIS contents of homopolymer gels of NIPAAm indicated that crosslinking density had an important effect only on the water absorption capacities of the hydrogels but not LCSTs (Samples 1 and 2). On the other hand, for constant crosslinker concentration (1.25×10^{-2} mol/L), both of them decreased with increasing content of hydrophobic constituent (Samples 6 and 7 in Table I).

Table I. Reaction conditions, yields, swelling degrees and LCSTs for NIPAAm gels prepared in the presence of Ce(IV)-H-Si redox pair

Sample No. (G)	H-Si (mol/L) $\times 10^{-2}$	Total Yield (in %)	Gel Fraction (in %)	Gel/Sol Ratio	Swelling* Degree (in %)	LCST °C
1	-	96	64	2.0	607	33.6
2 ^o	-	80	59	2.8	312	33.6
3	1.50	87	57	1.9	652	33.4
3**	1.50	95	80	5.3	1011	35.8
4 ^o	1.50	79	60	3.2	578	33.2
5***	1.50	83	-	-	-	31.1
6	3.00	85	55	1.8	516	32.1
7	4.50	60	47	3.6	205	31.1

Synthesis-solvent: acetone acidified with 0.1 M HNO₃; * t=25°C

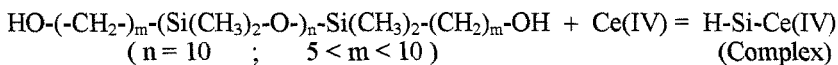
[NIPAAm] = 0.90 mol/L; [BIS] = 1.25×10^{-2} mol/L; °[BIS] = 2.50×10^{-2} mol/L

[Ce(IV)] = 1.50×10^{-2} mol/L; **[Ce(IV)] = 3.00×10^{-2} mol/L; ***uncrosslinked polymer and [Ce(IV)] = 1.50×10^{-2} mol/L

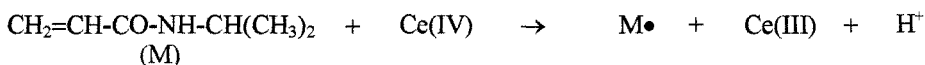
Effects of [Ce(IV)]/[H-Si] ratios on Gel/Sol ratios, LCSTs and Water absorption capacities of NIPAAm gels

The results in Tables 1 and 2 show that NIPAAm gels obtained with lower and higher [Ce(IV)] / [H-Si] ratios (0.50 and 0.33 in acetone and, 2.00 and 3.00 in acetonitrile, respectively) than that of the equal concentration condition of Ce(IV) and H-Si have lower phase transition temperatures. The highest gel/sol ratios obtained with the highest [Ce(IV)] / [H-Si] ratios in acetonitrile correspond to the lowest LCSTs while the lowest [Ce(IV)] / [H-Si] ratios in acetone produce the highest gel/sol ratios and the lowest LCSTs.

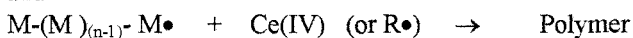
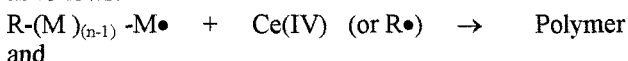
The first step in the polymerization is a redox reaction between Ce(IV) and α,ω -dihydroxy poly(dimethylsiloxane) and the following scheme can be suggested for the initiation of PNIPAAm chains:



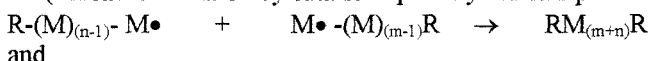
Another route to produce primary radicals from the NIPAAM molecules in this reaction conditions is a reaction between Ce(IV) ions and monomer molecules (M):



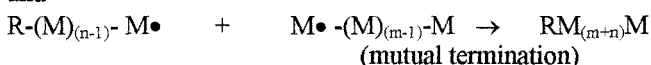
The activated poly(dimethylsiloxane) and/or NIPAAM molecule (R• and M•, respectively), having an unpaired valance electron, can combine with NIPAAM or BIS molecules. If the solutions include only NIPAAM monomer, the chains will be straight. The termination of the activated chains in those systems may be represented as follows:



(Linear termination by catalyst or primary radicals produced from activator)



and



But the presence of BIS in our reaction media leads to the formation of crosslinks between chains. As a result, PNIPAAM grows into a complex web including reducing agent and metal ion terminated chain ends.

Table 2. Reaction conditions, yields, swelling degrees and LCSTs for NIPAAMgels prepared in the presence of Ce(IV)-H-Si redox pair

Sample No. (G)	Ce(IV) (mol/L) $\times 10^{-2}$	H-Si (mol/L) $\times 10^{-2}$	Total Yield (in %)	Gel Fraction (in %)	Gel/Sol Ratio	Swelling* Degree (in %)	LCST °C
8	1.50	-	75	50	2.0	282	33.5
9	1.50	1.50	53	33	1.7	436	33.2
10	1.50	3.00	78	50	1.8	328	34.2
11	1.50	4.50	69	54	3.6	322	32.6
12	3.00	-	93	75	4.2	720	33.3
13*	3.00	1.50	63	-	-	-	31.7
14	3.00	1.50	98	82	5.1	640	31.5
15	4.50	1.50	99	98	98.0	577	31.1
16	3.00	3.00	93	58	1.7	635	33.0
17	3.00	4.50	80	60	3.0	511	32.8

Synthesis-solvent: acetonitrile; * $t=25^\circ\text{C}$; [NIPAAM] = 0.90 mol/L; [BIS] = 1.25×10^{-2} mol/L; *Sample 13 is uncrosslinked polymer.

High total yields and gel/sol ratios of the Samples 1, 2, 8 and 12 in Tables 1 and 2 prove that Ce(IV) salts are affected to initiate polymer chains, even if in the absence of any reducing agent. This means that the PNIPAAM chains can be initiated easily

with Ce(IV) because the reaction conditions in this work, i.e., high temperature and catalyst content promote the efficiency of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ alone. Further, the appearance of the characteristic absorption bands of $\text{Ce}(\text{NO}_3)_n^{x(+or-)}$ complexes ($550-650$ and $1350-1450\text{ cm}^{-1}$) together with the specific peaks of PNIPAAm ($-\text{C}=\text{O}$ stretching for secondary amides at 1660 cm^{-1} and $-\text{NH}$ bending at 1540 cm^{-1}) supports the presence of metal ion and nitrate groups bound to the chains (Figure 1). On the other hand, the FTIR spectra of the gels initiated with Ce(IV)- α,ω -dihydroxy poly(dimethylsiloxane) redox pair show the characteristic bands due to $\text{Si}(\text{CH}_3)_2$ ($1275-1260$ and $880-760\text{ cm}^{-1}$) and Si-O groups ($1110-1000$ and $900-600\text{ cm}^{-1}$) of siloxane units along with the bands attributed to nitrate ions and cerium- plus cerous-ligand complexes ($1400-600\text{ cm}^{-1}$). For low concentration of Ce(IV), the intensities of the peaks resulted from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and its various complexes decrease with increasing concentration of hydrophobic constituent (Figure 1) while the absorption bands corresponding to both catalyst and activator increase with decreasing order of $[\text{Ce}(\text{IV})] / [\text{H-Si}]$ ratios in the case of high Ce(IV) concentration (Figure 2). Our experimental findings support the reaction scheme presented above and indicate that it is dependent on experimental conditions.

From comparison of swelling degrees at 25°C in water of the gels in Table 1 with the ones in Table 2, it was observed that PNIPAAm gels modified hydrophobically swell more than those of the ones synthesized by using Ce(IV) alone, for the synthesis conditions containing the lowest concentrations of Ce(IV) salt and α,ω -dihydroxy poly(dimethylsiloxane) in the reaction media. It can be concluded that for low concentration of hydrophobe ($1.50 \times 10^{-2}\text{ mol/L}$), the hydrophobic attraction of siloxane groups is not enough to overcome the hydrophobic hydration of PNIPAAm chains at 25°C , the presence of these hydrophobic and bulky groups at the ends of the chains prevents to come together the chains and therefore, the swelling degrees of the NIPAAm gels containing siloxane groups are higher than those of the ones obtained by using Ce(IV) alone.

The effects of temperature and $[\text{Ce}(\text{IV})] / [\text{H-Si}]$ ratios on the swelling degrees, i.e., water absorption capacities for the NIPAAm gels in deionized water are shown in Tables 1 and 2 and, Figure 3. As to these experimental results, the number of PNIPAAm chains bearing H-Si end groups and therefore the strength of the hydrophobic interactions increases when the amount of the activator in the reaction media is increased. The higher the temperature and the lower the $[\text{Ce}(\text{IV})] / [\text{H-Si}]$ ratio mean the lower the swelling degree and the lower the gel transition temperature.

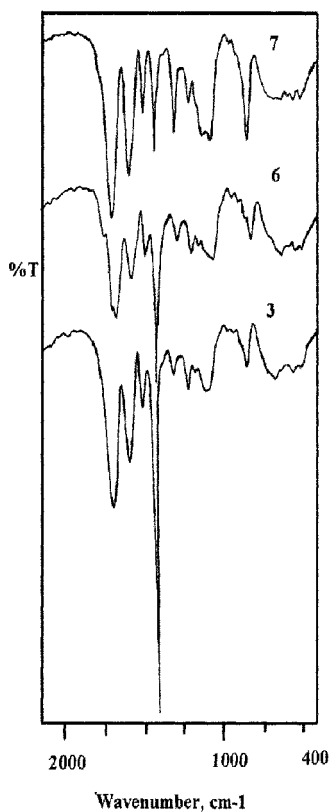


Fig.1. FTIR spectra of G-3, -6 and -7

Effects of types and concentrations of solvents and reagents on the efficiency of gelation process and thermosensitive properties of NIPAAM gel

The experimental results including the effects of monomer concentration, solvent type and, the intermolecular interactions between the reagents in Tables 1-3 can be explained by considering the following:

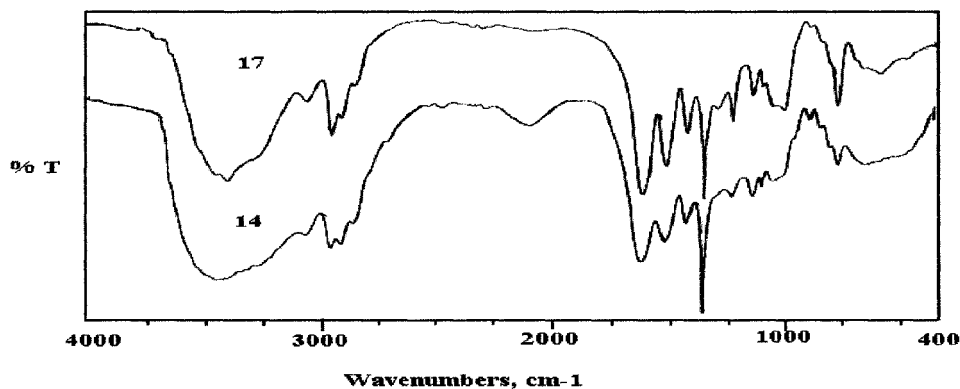


Figure 2. FTIR spectra of samples G-14 and G-17 identified in Table 2.

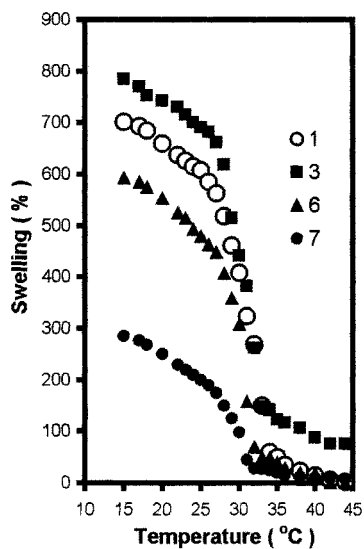


Figure 3. Swelling curves of samples G-1, G-3, G-6 and G-7 in Table 1.

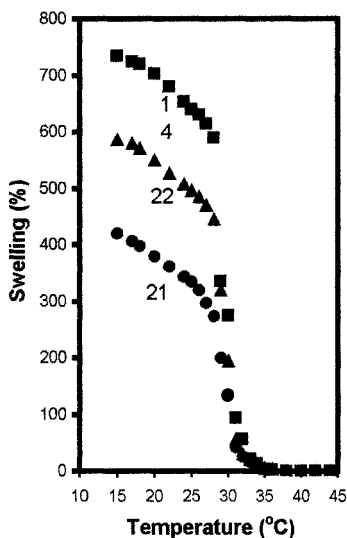


Figure 4. Swelling curves of samples G-14, G-21 and G-22 in Table 3.

The total yields of gelation processes in acetonitrile are lower than those of the ones in acetone acidified with 0.1 M HNO_3 , for $[\text{Ce(IV)}] = 1.50 \times 10^{-2}$ mol/L (Table 2). When this concentration is increased to 2 or 3 times for the lowest hydrophobe concentration (1.50×10^{-2} mol/L), both total yields and gel fractions, and thermosensitive properties

of the products obtained in acetonitrile increase. However, increasing in the catalyst content of the reaction mixtures in acetone affects only yields but not LCSTs of the gels (Table 1). On the other hand, in the case of higher concentrations of hydrophobe the LCSTs of the gel fractions produced by the lower Ce(IV) concentration in acetone are lower than those of the corresponded ones in acetonitrile.

As to this experimental findings, it can be discussed that the type of solvent used during the syntheses, together with Ce(IV) and H-Si concentrations has an important effect on both swelling degrees and LCSTs of the gels. For example, 1.50×10^{-2} mol/L of Ce(IV) for higher concentrations of H-Si is enough to produce siloxane modified NIPAAM gels in acetone while in the case of acetonitrile the products having mainly siloxane terminated chain ends can be obtained by only higher Ce(IV) concentrations for 1.50×10^{-2} mol/L of H-Si.

This means that in the case of low Ce(IV) and high siloxane concentrations, the performance of Ce(IV)-H-Si complexes in acetone is better than the ones in acetonitrile. It can be related to the solubility differences of hydrophobic constituent in these solvents. As to the results discussed, acetone is a good solvent of Tegomer H-Si 2111 and therefore the number of both primary radicals and NIPAAM chains containing siloxane groups increases with increasing concentration of activator. Further, the results discussed in terms of catalyst concentration show that the inhibition effect of the reaction between Ce(IV) and acetonitrile decreases the number of radicals produced from Ce(IV) ions in the solutions and therefore the yields are lower than acetone. This problem is solved by increasing the concentration of Ce(IV) solution. The experimental results in this work also indicate that the yields of gel fractions decrease with decreasing intermolecular interactions between NIPAAM-BIS and NIPAAM-Ce(IV) pairs in the presence of hydrophobic constituent. The comparison of the data relating to the crosslinked products (Samples 1 and 3 in Table 1; Samples 8 and 9 in Table 2) with the ones for linear polymers (Samples 5 and 13 in Tables 1 and 2, respectively.) shows that in the absence of BIS in the reaction media, the thermosensitive properties of the products obtained increases. In another words, BIS and Tegomer H-Si 2111 affect the reactivities of each other.

Table 3. Reaction conditions, yields, swelling degrees and LCSTs for NIPAAM gels prepared in the presence of Ce(IV)-H-Si redox pair

Sample No. (G)	NIPAAM (mol/L)	Total Yield (in %)	Gel Fraction (in %)	Gel/Sol Ratio	Swelling* Degree (in %)	LCST °C
Acetone acidified with 0.1 M HNO ₃ **						
18	0.50	75	37	2.0	520	33.8
6	0.90	85	55	1.8	516	32.1
19	1.50	86	56	1.9	583	31.9
20	2.00	81	6	0.08	707	33.0
Acetonitrile***						
21	0.50	97	79	4.4	334	31.4
22	0.70	84	62	2.8	496	31.4
14	0.9	98	82	5.1	640	31.5
14 ^f	0.9	96	72	3.0	600	31.4

* $t=25^{\circ}\text{C}$; [BIS] = 1.25×10^{-2} mol/L; ** [Ce(IV)] = 1.50×10^{-2} mol/L;

[H-Si] = 3.00×10^{-2} mol/L; *** [Ce(IV)] = 3.00×10^{-2} mol/L; [H-Si] = 1.50×10^{-2} mol/L

From the results presented above it is apparent that the thermosensitive properties and swelling degrees of PNIPAAm gels prepared by using Ce(IV)-H-Si redox pair can be controlled by the polymerization conditions such as the concentrations of BIS, H-Si and Ce(IV), and type of synthesis-solvent. The effect of monomer concentration on phase transitions and swelling behaviours was chosen as another experimental parameter. Table 3 represents swelling equilibria and LCSTs in water for PNIPAAm gels prepared with five different monomer concentrations. To discuss the effect of monomer concentration, two series of gels were prepared: in one series experiments were carried out at high catalyst concentration and $[Ce(IV)] / [H-Si]$ ratio in acetonitrile (Figure 4), while in the other series the ones were carried out at low catalyst concentration and $[Ce(IV)] / [H-Si]$ ratio in acetone. All results in Table 3 and Figure 4 show that for the gels obtained with 0.50-2.00 mol/L NIPAAm solutions in acetonitrile and acetone, monomer concentration influences water absorption capacities of the samples, but not thermosensitive properties.

Conclusion

Some important features of the reactions carried out the conditions indicated above and the products obtained are the following: (a) due to the hydrophobic nature of the activator used, the equilibrium swelling degrees and LCSTs of PNIPAAm gels were found to be smaller than the gels in Tegomer H-Si 2111 free solutions. (b) different gel / sol ratios and total yields obtained for varying reaction conditions was evidence of a reaction mechanism that could be controlled by the types of synthesis-solvent as well as the catalyst and activator concentrations. (c) due to the differences in the reactivity between the other reagents and NIPAAm in acetone and acetonitrile, swelling of the gels can be controlled not only by crosslinker amount but also by the activator and catalyst concentrations.

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