Controlled Radical Polymerization of *N*-Isopropylacrylamide Initiated by Photofunctional 2-(*N*,*N*-Diethyldithiocarbamyl)isobutyric Acid Sodium Salt in Aqueous Medium

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ABSTRACT: Photopolymerizations of *N*-isopropylacrylamide (NIPAAm) were carried out in water, initiated by 2-(*N*,*N*-diethyldithiocarbamyl)isobutyric acid sodium salt (DTCA-Na) as water-soluble initiator under UV irradiation. The first-order time-conversion plots showed slowly decreasing slopes indicating a slow decrease of the active radical concentration. The number-average molecular weight (M_n) of the obtained poly(*N*-isopropylacrylamide) (PNIPAAm) increased in direct proportion, roughly, to monomer conversion. Until ca. 60% of conversion, the polydispersity was relatively narrow (ca. 1.6). 1-Vinyl-2-pyrrolidone (VP) could also be polymerized in living fashion with such PNIPAAm precursor as a macroinitiator, because PNIPAAm exhibited dithiocarbamate (DC) groups at terminal ends. It was concluded that the polymerization of NIPAAm proceeded via a controlled radical mechanism in the range ~60% of conversion. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3233–3238, 2004

Key words: NIPAAm; water-soluble initiator; controlled radical polymerization; block copolymer

INTRODUCTION

Recently, the synthesis of polymers via living radical polymerization has gained importance due to its great versatility with a wide range of monomers, the control of the molecular weights, and the low polydispersities of the resulting polymers. In general, these investigations use a polymerization system in which the growing polymer chain end remains in a dynamic equilibrium between active and dormant species as a result of rapid, reversible termination or reversible degenerative chain transfer reaction. The propagation and reversible termination or transfer reaction should be much faster than any irreversible termination. If the initiation is also very fast, the process yields polymers with a narrow molecular weight distribution. The available methods are (i) the well-designed dithiocarbamate (DC)-mediated stable free radical polymerization,[1] (ii) a nitroxide-mediated process,[2–6] (iii) a transition metal complex-mediated atom transfer radical polymerizations (ATRP),[7–12] and (iv) a degenerative transfer reaction with alkyl iodides.[13–15] Moreover, DC compounds have been employed to mediate radical polymerization as reversible addition fragmentation chain transfer (RAFT) agents.[16] The RAFT process follows a different mechanism than that proposed by Otsu. Dithioester compounds control the radical polymerization according to the RAFT process as was proven by Quinn et al.[17]

More recently, we demonstrated that density functional theory calculations provide a reliable and quantitative prediction of the trends in C—S bond dissociation energies for several model DC compounds as photoinitiator.[18] On the basis of this information, we designed the photofunctional initiator, 2-(*N*,*N*-diethyldithiocarbamyl)isobutyric acid (DTCA), to polymerize hydrophilic vinyl monomers. It was concluded from the results for photopolymerization of 2-hydroxyethyl methacrylate (HEMA) initiated by DTCA that the polymerization system proceeded via a living radical mechanism. Moreover, DTCA sodium salt (DTCA-Na) was soluble in water.

We are interested in studying the radical polymerization of hydrophilic vinyl monomers using this initiator in aqueous medium. Poly(*N*-isopropylacrylamide) (PNIPAAm) has been used in many forms including single chains, macroscopic gels, microgels, latexes, thin films, membranes, coatings, and fibers.[19] It is also well known that the PNIPAAm gel phase transition has been observed to be extremely temperature de-

pendent.[19] Ganachaud et al.[20] reported the first use of the RAFT process (solvent; benzene or 1,4-dioxane) to polymerize N-(isopropylacrylamide) (NIPAAm). A range of relatively monodisperse polymer samples [polydispersity (M_w/M_n) < 1.4] were obtained with molecular weights ranging from 2×10^3 to 4×10^5. More recently, Schilli et al.[21] have applied the principles of the RAFT method to the polymerization of NIPAAm, which was carried out in the presence of the dithiocarbamates benzyl 1-pyrrolecarbodithioate and cumyl 1-pyrrolecarbodithioate, respectively, as chain transfer agents in 1,4-dioxane. The resulting polymers had polydispersities < 1.3, but the polymerization system was accompanied with disproportionation or transfer. On the other hand, Jewrajka and Mandal[22] have reported the ATRP of acrylamide in water or in glycerol–water medium at 130°C using water-soluble initiators, i.e., 2-chloropropionamide or 2-bromopropionamide and CuX (X = Cl, Br) bipyridine complex as catalyst. However, the polydispersity was high, ca. 1.6–1.7.

For this study, the photopolymerization of hydrophilic monomer NIPAAm was carried out in water, initiated by DTCA-Na as a water-soluble initiator, under UV irradiation. We performed kinetic analysis to understand the radical mechanism of propagation. We also prepared amphiphilic PNIPAAm-block-poly(1-vinyl-2-pyrrolidone) (PVP) by copolymerization of 1-vinyl-2-pyrrolidone (VP) with PNIPAAm precursor as a macroinitiator via living polymerization.

EXPERIMENTAL

Synthesis of initiator DTCA-Na

DTCA was prepared by the reaction of 2-bromoisobutyric acid (Tokyo Kasei Organic Chemicals, Tokyo, Japan) with N,N-diethyldithiocarbamate sodium salt (Kanto Kagaku Chemicals, Tokyo, Japan) in acetone. The synthetic procedure and purification have been given elsewhere.[18] The DTCA-Na was prepared by neutralization of DTCA with an equivalent molar amount of NaOH.

Polymerization of NIPAAm

The NIPAAm (Aldrich) monomer was purified from recrystallization using a toluene–hexane system. Photopolymerizations (P1–P5) of NIPAAm ([NIPAAm]$_0$ = 1.325 mol/L) were carried out in water (15 wt %) initiated by DTCA-Na ([DTCA-Na]$_0$ = 9.80 × 10^{-3} mol/L) as an initiator at 30°C varying the UV irradiation time (250-W high-pressure mercury lamp, Ushio Denki SX-UI 250 HAMQ; absorption wavelength 300–600 nm, UV intensity 42 mW/cm^2, irradiation distance 15 cm). After polymerization, water used as the sol-

vent was evaporated and the polymer was recovered by precipitation from tetrahydrofuran (THF) solution to hexane. The conversion was estimated by gravimetric measurements.

Synthesis of block copolymers

To prove the existence of the DC group at the terminal end of PNIPAAm, we synthesized block copolymers initiated by PNIPAAm precursor as a macroinitiator. Photopolymerization of VP (Tokyo Kasei Organic Chemicals; 2 mL) was carried out in ethanol (10 mL) initiated by PNIPAAm macroinitiator (P1; 0.25 g) at 30°C under 3 h of UV irradiation time. After polymerization, PNIPAAm-block-poly(1-vinyl- 2-pyrrolidone) (PVP) was recovered by precipitation with hexane.

Characterization

The weight-average molecular weight (M_w) of PNIPAAm was calculated by intrinsic viscosity [η]. For PNIPAAm in water, the following Mark–Houwink relation was used:[23]

$$[\eta](mL/g) = 145 \times 10^{-3} M_w^{0.50} \quad \text{at } 20°C \quad (1)$$

The [η] of PNIPAAm was measured with an Ubbelohde viscometer. The number-average molecular weight (M_n) was evaluated from M_w using the molecular weight distribution (M_w/M_n) values of the samples determined by gel permeation chromatography (GPC) traces.

The values of M_w/M_n were determined by GPC with a refractive index (RI) detector using the standard polystyrene calibration. The GPC characterization of PNIPAAm in THF involves various problems[24,25] due to irreversible chain aggregation after complete drying of the polymer samples.[20] Nevertheless, Schilli et al.[21] have obtained good results by the addition of 0.25 wt % tetrabutylammonium bromide (TBAB) to the THF solution and using polystyrene gel columns. GPC measurements were carried out with a Tosoh high-speed liquid chromatograph HLC-8120, which was operated with two TSK gel columns, GM-H$_{XL}$ and G2000H$_{XL}$, in series using THF/0.25 wt % TBAB (Tokyo Kasei Organic Chemicals) as the eluent at 38°C.

The composition of PNIPAAm-block-PVP was determined by ^{1}H NMR (500-MHz JEOL GSX-500 NMR spectrometer) in CD$_3$OD.

RESULTS AND DISCUSSION

Photolysis of initiator DTCA-Na (1) leads to the initiating isobutyric acid sodium salt radical with the less active DC radical (see Scheme 1). This isobutyric acid
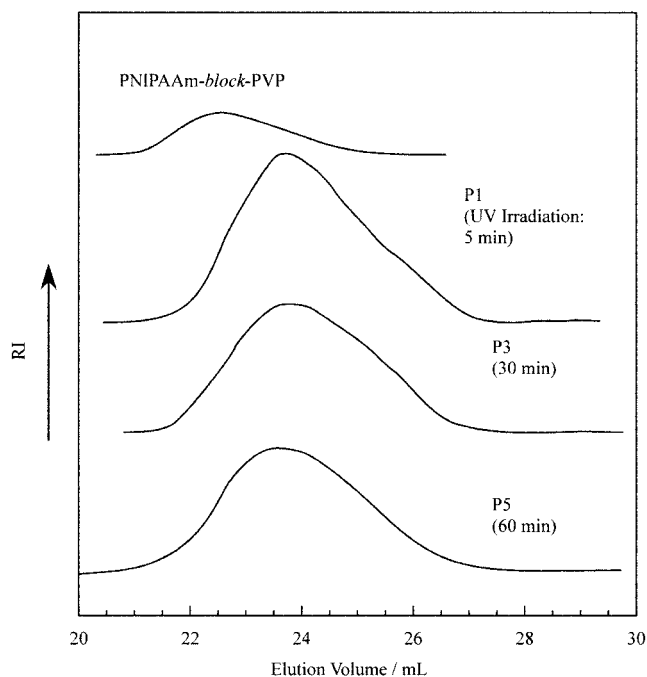
Scheme 1

sodium salt radical can add to the vinyl group of a NIPAAm monomer. Propagating radicals always take the route of equilibrium with DC radicals in the case of no termination or transfer. By repeating these elementary reactions, this polymerization system proceeds to form PNIPAAm (2).

To demonstrate this concept, photopolymerizations of NIPAAm were carried out in 15 wt % aqueous solution of NIPAAm initiated by DTCA-Na varying the irradiation time. Polymerization conditions and results are listed in Table I. Typical GPC profiles of P1 (irradiation time = 5 min), P3 (30 min), and P5 (60 min) are shown in Figure 1. All the GPC curves show a unimodal pattern but have relatively broad polydispersities (M_w/M_n = 1.62–2.08). The molecular weight seems to increase slightly with increasing reaction times. The conversion was estimated by gravimetric measurements for the recovered polymers. The conversion reached ca. 60% even after 5 min of irradiation time, regardless of low monomer concentration (15 wt % aqueous solution). The polymerization rate of NIPAAm was very high due to the polar nature of the monomer. The NMR method may be advantageously used to get conversion data at the very beginning of the polymerization. The accumulation of data below 70% conversion is the subject for a future study. The first-order time-conversion plots (Fig. 2) show slowly

decreasing slopes indicating a slow decrease of the active radical concentration, where $[M]_0$ is the initial concentration of NIPAAm.

Figure 3 shows the plot of M_n or M_w/M_n against conversion, where the dotted line indicates the calculated values ($M_{n,calcd}$) assuming that one molecule of the initiator generates one polymer chain. A straight line for M_n versus conversion seems to be plotted from the origin; however, this is only speculation since there are no data below 70% conversion. Moreover, the M_n values are higher than the calculated values. Such deviations may be caused by not only apparent values of M_w, due to the viscosity measurements, but also low initiator efficiency. The polydispersity indices increase gradually with increasing conversion. Until ca. 60% of conversion, the polydispersity was relatively narrow (ca. 1.6), due to combination of growing chains, which is typical for controlled polymerizations with exchange between active and dormant species. However, this system seems to be accompanied by disproportionation or transfer at high conversion (judging from unimodal distribution but broad polydispersities). These speculations are supported by NMR analysis of PNIPAAm. The ^{1}H NMR spectrum of PNIPAAm P1 is shown in Figure 4(a). Characteristic signals are observed at δ 1.13 ppm (e; —*CH₃*), 3.98 ppm (d; >*CH*—), and 7.61 ppm (c; —*NH*—). The

TABLE I
Polymerization Conditions and Characteristic Results of PNIPAAm[a]

Exp. no.	Irradiation time (min)	Conversion[b] (%)	$[\eta]^c$ (mL/g)	$10^{-4} M_w{}^d$	$M_w/M_n{}^e$	$10^{-4} M_n{}^f$
P1	5	69.4	35.60	6.02	1.62	3.72
P2	15	73.8	38.37	7.00	1.80	3.87
P3	30	78.0	40.48	7.79	1.84	4.23
P4	45	86.6	44.12	9.25	2.00	4.63
P5	60	90.7	41.58	8.22	2.08	4.11

[a] Photopolymerizations of NIPAAm ($[NIPAAm]_0$ = 1.325 mol/L) were carried out in water (15 wt % solution) initiated by DTCA-Na ($[DTCA-Na]_0$ = 9.08 × 10^{-3} mol/L) at 30°C under UV irradiation.
[b] Determined by gravimetric measurements.
[c] Measured in water at 20°C.
[d] Calculated by Mark–Houwink relation.
[e] Determined by GPC distributions.
[f] Calculated from M_w using M_w/M_n.

Figure 1 GPC profiles of P1, P3, and P5 as a function of irradiation times, and GPC of PNIPAAm-*block*-PVP block copolymer in THF/0.25 wt % TBAB as eluent at 38°C.

integration ratio of e:d:c was 6:1:1. This means that no extraction of active amide hydrogen of NIPAAm occurred until ca. 60% of conversion. The degree of polymerization (DP$_n$) of P1 was estimated to be 329.
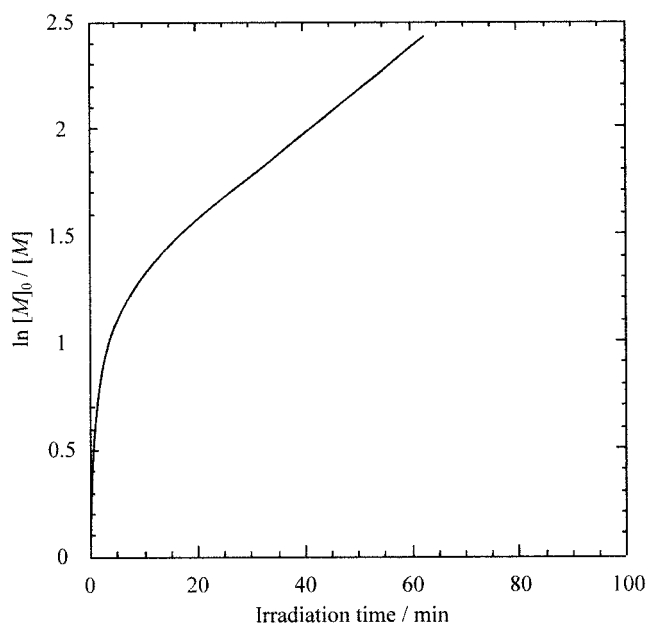
Therefore, the charateristic signals of the terminal DC group were not observed in this spectrum. However, this integration ratio of e:d:c changed to 6:1:0.3 in the NMR spectrum of PNIPAAm P4 (irradiation time = 45 min, conversion = 86.6%). This result indicates that the extraction of active amide hydrogen of PNIPAAm occurred by transfer of propagating radicals during polymerization due to a small amount of residual NIPAAm monomer.

To prove the living nature of NIPAAm polymerization, it is convenient to perform the postpolymerization of PNIPAAm precursor with NIPAAm or the synthesis of block copolymer of PNIPAAm precursor with other monomers. In this work, we carried out the block copolymer synthesis by photopolymerization of VP with PNIPAAm precursor P1 (M_n = 3.72 × 10^4, M_w/M_n = 1.62) as a macroinitiator. Figure 1 shows the GPC profile of the copolymerization product (PNIPAAm-*block*-PVP). The polymerization of VP occurred, and the GPC curve of copolymerization product shifted to the high molecular weight side, keeping a unimodal distribution. It should be noted that the elution count of the low molecular weight side for the copolymerization product did not overlap that for PNIPAAm precursor. These results indicate that PNIPAAm macroinitiator had a DC group at the terminal end and that PNIPAAm-*block*-PVP was formed by the chain extension through the sequential radical copolymerization. The NMR spectrum also supports the formation of block copolymer [see Fig. 4(b)]. In addition to the characteristic signals of the PNIPAAm
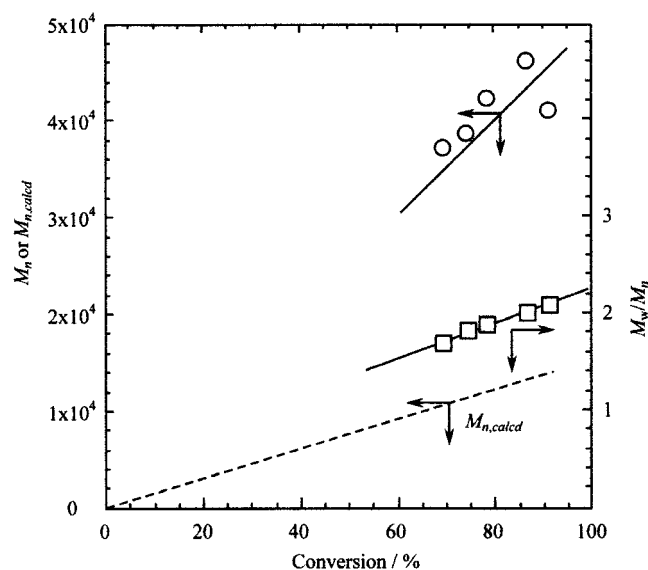

Figure 2 First-order time-conversion plot for photopolymerization of NIPAAm in aqueous solution at 30°C under UV irradiation: [NIPAAm]$_0$ = 1.325 mol/L, [DTCA-Na]$_0$ = 9.80 × 10^{-3} mol/L.

Figure 3 Plots of number-average molecular weight (M_n) or molecular weight distribution (M_w/M_n) against conversion for photopolymerization of NIPAAm in aqueous solution at 30°C under UV irradiation: [NIPAAm]$_0$ = 1.325 mol/L, [DTCA-Na]$_0$ = 9.80 × 10^{-3} mol/L; the dotted line indicates the calculated values of M_n ($M_{n,calcd}$).
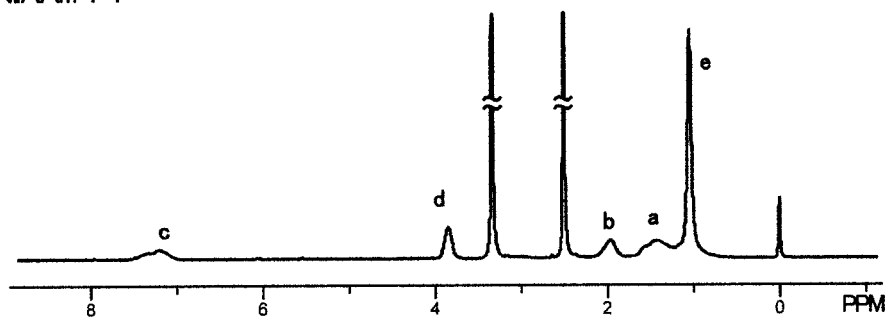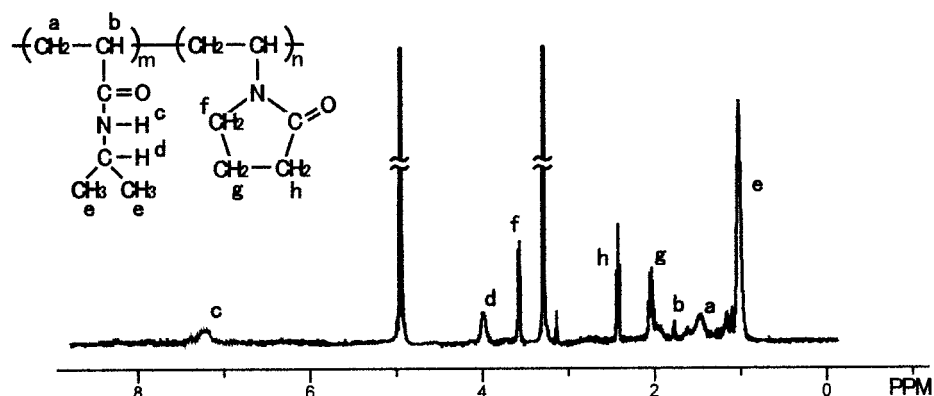
Figure 4 ^{1}H NMR spectra of PNIPAAm macroinitiator P1 (a: M_n = 3.72 × 10^4, M_w/M_n = 1.62) and PNIPAAm-*block*-PVP block copolymer (b) in CD$_3$OD.

block, this displays the expected resonances for —N—CH_2—CH_2— protons (f; 3.56 ppm) and —CH_2—CH_2— protons (g and h; 2.12 and 2.75 ppm) of PVP block. We determined the composition of block copolymer using the signals of e and f. The integration ratio of e:f was 90.5:13.6. The composition of PNIPAAm block was then estimated to be 68.9 mol %, i.e., 100(e/6)/[(e/6) + (f/2)]. Note also that the integration ratio of e:d:c was 6:1:0.3. So, some level of extraction of active amide hydrogen of the PNIPAAm block by propagating PVP radicals seems to occur during block formation. In the architecture of amphiphilic block copolymers, it is better to employ NIPAAm monomer as the comonomer for block extension at the second addition step. DTCA-Na as water-soluble initiator can be expected to be usable for the controlled radical polymerization of hydrophilic vinyl monomers such as methacrylic acid, etc. The results obtained will be reported in the near future.

CONCLUSIONS

We have explored the approach to living radical polymerization of NIPAAm in aqueous medium using photoinitiator DTCA-Na as shown in Scheme 1. The polymerization rate of NIPAAm was very high due to the polar nature of the monomer. The first-order time-conversion plots showed slowly decreasing slopes indicating a slow decrease of the active radical concentration. The M_n of the obtained PNIPAAm increased in direct proportion roughly to monomer conversion. The polydispersity indices were relatively narrow (ca. 1.6) until ca. 60% of conversion, and the polymerization seemed to proceed with controlled radical mechanism. However, this system was accompanied by disproportionation or transfer at high conversion, due to the extraction of active amide hydrogen of PNIPAAm. These speculations were supported by NMR analysis of PNIPAAm precursors. PNIPAAm-*block*-PVA amphiphilic block copolymers could be prepared by

radical copolymerization of VP with PNIPAAm precursor as the macroinitiator.

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