Synthesis of Well-Defined Alternating Copolymers by RAFT Copolymerization of *N*-Vinylnaphthalimide

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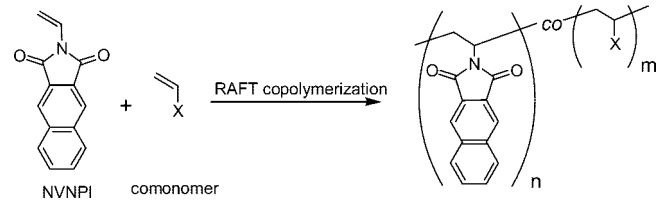
ABSTRACT: A novel nonconjugated *N*-vinyl monomer, *N*-vinylnaphthalimide (NVNPI), was copolymerized with various comonomers via reversible addition-fragmentation chain transfer process. Two different chain transfer agents (CTAs), *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 1) and benzyl 1-pyrrolecarbodithioate (CTA 2), were compared for these copolymerizations with 2,2′-azobis(isobutyronitrile) as an initiator. The structures of the resulting copolymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, suggesting the sufficient incorporation of NVNPI, when methyl acrylate and *N*-isopropylacrylamide (NIPAAm) were used as comonomers. The copolymerization of NVNPI and NIPAAm using CTA 2 afforded well-defined copolymers with a predominantly alternating structure, controlled molecular weights (M_n = 2000−10700), and low molecular mass distributions (M_w/M_n = 1.21−1.29). Characteristic optical properties of the naphthalimide-containing copolymer were investigated by UV−vis and fluorescence spectroscopic methods.

Introduction

Naphthalenic imides are an important and a versatile class of heterocyclic compounds that have been applied in a large variety of areas. For example, 2,3-naphthalimide and 1,8-naphthalimide were used as fluorescent compounds in the biological fields, such as probes for monitoring peptide binding to histocompatibility complex proteins,[1] selective opioid peptides,[2] and environment-sensitive fluorescent probe for peptide−peptide interactions.[3] A variety of 1,8-naphthalimide and bisnaphthalimide derivatives have good anticancer activity, and clinical trials of these compounds have already been reported.[4−9] In addition to their wide variety of medical and biological applications, much attention has been paid to the photochemistry of naphthalimide derivatives.[10−12] Naphthalimide derivatives have been also used to form complexes with various compounds, such as Zn(II),[13] cyclodextrins,[14−16] Hg^{2+} ion,[17] and $H_2PO_4^-$ anion.[18] Luminescence studies of these complexes have been conducted extensively. The most recent applications of naphthalimide derivatives have been oriented toward the fields of organic electronic and optoelectronic applications involving organic light-emitting diodes.[19,20] During recent years, increasing attention has been paid to dendrimers with peripheral naphthalimide groups due to unique electronic and photophysical properties of their complexes with rare earth ions, such as Eu^{3+}.[21,22]

A variety of polymers containing naphthalimide moieties in the main and side chains has been synthesized. For example, sulfonated poly(arylene-*co*-naphthalimide)s[23] and poly(arylene ether)s with naphthalimide moieties[24] were synthesized as aromatic-type polymers, which exhibited characteristic thermal, mechanical, and electrical properties. Synthesis of naphthalimide-containing copolymers of styrene,[25−27] vinylcarbazole,[28] and methyl methacrylate[26] were reported by several groups. However, the content of the naphthalimide moiety was limited, and detailed information about the polymer structure was not provided, even if their photochemical and luminescent properties were investigated intensively. To manipulate unique electronic and photonic functions of these naphthalimide-containing polymers, it is desirable to control various factors, including the chemical structure, content and location of the naphthalimide moiety, molecular weight and molecular weight distribution, sequence and conformation, and polymer architecture.

Scheme 1. RAFT Copolymerization of *N*-Vinylnaphthalimide with Various Comonomers



We now report the synthesis of novel naphthalimide-containing copolymers with controlled molecular weights and narrow polydispersity by copolymerization of a novel nonconjugated *N*-vinyl monomer, *N*-vinylnaphthalimide (NVNPI), via reversible addition-fragmentation chain transfer (RAFT) process (Scheme 1). Controlled/living radical polymerization has allowed synthesizing various functional polymers with predetermined structural parameters involving chain length, polydispersity, functionality composition, and architecture.[29−32] The method can also offer an opportunity to control comonomer sequence distribution (block, random, periodic or gradient distribution), which plays a key role in determining various polymer properties. However, controlled radical polymerization of *N*-vinyl and *O*-vinyl monomers had been difficult until recent years, since the generated radical species are highly reactive due to their nonconjugated nature and strong electron donating pendant groups. Recently, we published a series of reports on the xanthate-mediated controlled radical polymerization of *N*-vinyl monomers, which involve *N*-vinylcarbazole,[33,34] *N*-vinylindole,[35] and *N*-vinylphthalimide.[36] Dithiocarbonates (xanthates) are also useful for controlling the radical polymerization of *O*-vinyl and *N*-vinyl monomers, such as vinyl acetate[37−38] and *N*-vinylpyrrolidone.[39,40] The RAFT process is generally accomplished by performing a radical polymerization in the presence of the thiocarbonylthio compound, such as dithioesters,

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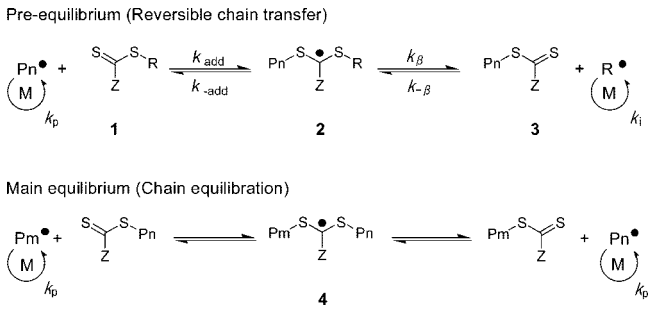
Scheme 2. Basic Reaction Steps of the RAFT Process



dithiocarbamates, trithiocarbonates, and xanthates, which all act as reversible chain transfer agents (CTAs).[32,41−44] When xanthates are employed, the terminology MADIX (macromolecular design via the interchange of xanthates) is frequently used to describe the process.[42,43] Both MADIX and RAFT processes are based upon the generally accepted RAFT mechanism between an active and a dormant species, as shown Scheme 2.

In this contribution, we also present the synthesis of well-defined alternating copolymers by RAFT copolymerization of the nonconjugated *N*-vinyl monomer, NVNPI, using a suitable CTA. Although the synthesis of well-defined alternating copolymers using controlled radical polymerization has attracted significant research interest, limited examples were reported in the literature.[45−49] Most of studies employed a combination of a strong electron-accepting monomer, such as maleic anhydride, with an electron-donating monomer, and Lewis acid was frequently employed to enhance the tendency toward alternating. We found that RAFT copolymerization of NVNPI with a monosubstituted acryalmide, *N*-isopropylacrylamide (NIPAAm), using the dithiocarbamate-type CTA (CTA 2) afforded copolymers having the predominantly alternating structure, predetermined molecular weights, and low polydispersity.

Experimental Section

Materials. 2,3-Dicarboxynaphthalimide (Tokyo Kasei Kogyo, 98%), sodium tetrachloropalladate(II) (Na_2PdCl_4, Aldrich, 98%), and vinyl acetate (Tokyo Kasei Kogyo, 98%) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from ethanol. *N*-Isopropylacrylamide (NIPAAm, Tokyo Kasei Kogyo, 98%) was purified by recrystallization from *n*-hexane/$CHCl_3$ (5/1 vol %). Methyl acrylate (MA, Tokyo Kasei Kogyo, 98%) and *N,N*-dimethylacrylamide (DMAAm, Aldrich, 99%) were distilled under vacuo. *N,N*-Dimethylformamide (dehydrated DMF, Kanto Chemical, 99.5%) and other chemicals were used without purification.

Synthesis of *N*-Vinylnaphthalimide (NVNPI). NVNPI was prepared by the reaction of 2,3-dicarboxynaphthalimide with a large excess of vinyl acetate, according to a method used for the synthesis of *N*-vinylphthalimide, which can be regarded as an *N*-vinyl analogue, with slight modifications.[50] Na_2PdCl_4 (0.17 g, 0.58 mmol) was added to a stirred solution of 2,3-dicarboxynaphthalimide (3.0 g, 15.2 mmol) in vinyl acetate (20 g, 0.23 mol) and 1,4-dioxane (100 mL) under a nitrogen atmosphere, and the mixture was heated under reflux for 24 h. After cooling, activated charcoal (50 mg) and dichloromethane (200 mL) were added and the mixture was stirred for 10 min. It was then diluted with 1,4-dioxane (50 mL) and dichloromethane (50 mL), the solid was removed by filtration, and the organic solvent in the filtrate was removed by the evaporation. The crude product was recrystallized twice from diethyl ether to afford 2.5 g (11.2 mmol) of NVNPI in the form of gray solid. Yield = 74%, mp = 201.4 °C. ^{1}H NMR ($CDCl_3$): δ 5.1 (d, 1H, CH_2), 6.2 (d, 1H, CH_2), 6.9 (dd, 1H, CH), 7.7 (2H, Ar), 8.0 (2H, Ar), 8.3 (2H, Ar). ^{13}C NMR ($CDCl_3$): δ 105 ($\underline{C}H_2$=CH-), 124 (Ar), 125 (CH_2=$\underline{C}$H-), 127 (Ar), 129 (Ar), 130 (Ar), 135 (Ar), 166 (C=O) ppm. Anal. Calcd for $C_{14}H_9NO_2$: C, 75.33; H, 4.06; N, 6.27. Found: C, 75.27; H, 3.82; N, 6.25. The ^{1}H and ^{13}C NMR spectra of the monomer are shown in Figure S1 (see Supporting Information).

Synthesis of Chain Transfer Agents (CTAs). Syntheses of *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate (CTA 1)[51] and benzyl 1-pyrrolecarbodithioate (CTA 2)[52,53] were conducted according to the procedures reported previously. These CTAs were finally purified by column chromatography on silica with *n*-hexane/ethyl acetate (10/1 vol %) for CTA 1 and *n*-hexane for CTA 2 as the eluent. The elemental analyses of the CTAs gave calculated purities of >99% for CTA 1 and CTA 2.

RAFT Copolymerization. All copolymerizations were carried out with AIBN as an initiator in a degassed sealed tube. A representative example is as follows: NVNPI (0.22 g, 1.0 mmol), NIPAAm (0.11 g, 1.0 mmol), CTA 2 (4.7 mg, 0.020 mmol), AIBN (1.6 mg, 0.010 mmol), and DMF (1.0 mL) were placed in a dry glass ampule equipped with a magnetic stirring bar, and then the solution was degassed by three freeze−evacuate−thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 24 h. At room temperature, NVNPI was hardly dissolved in DMF, while a homogeneous pale yellow solution was obtained at 60 °C. The characteristic pale yellow color remained during the polymerization without any precipitation. The reaction was stopped by rapid cooling with liquid nitrogen. The polymer obtained was purified by reprecipitation from a DMF solution into a large excess of diethyl ether, and the resulting product was dried at room temperature under vacuum: yield = 94% (0.31 g). The resulting product was soluble in DMF, MeOH, tetrahydrofuran (THF), chloroform ($CHCl_3$), and dichloromethane (CH_2Cl_2) and insoluble in *n*-hexane and water. ^{1}H NMR ($CDCl_3$): δ 0.1−3.0 (11H, CH_2 in the polymer main chain of both components, CH in the main chain of NIPAAm unit, and CH_3 in the NIPAAm residue), 3.0−4.5 (2H, CH in the main chain of NVNPI unit and NCH in the NIPAAm), 5.0−6.5 (1H, NH in the NIPAAm), 6.7−8.2 (6H, aromatic protons). ^{13}C NMR ($CDCl_3$): δ 32−39 (-CH_3 in the NIPAAm unit), 47−53 (CH_2CH in the main chain and NCH in the NIPAAm unit), 124 (Ar), 127 (Ar), 129 (Ar), 130 (Ar), 135 (Ar), 167 (C=O in the NVNPI unit), 172 (C=O in the NIPAAm unit) ppm. The ^{1}H NMR and ^{13}C NMR spectra of the copolymer, poly(NVNPI-*co*-NIPAAm), are shown in Figure 2a and Figure S2 (see Supporting Information).

The theoretical number-average molecular weight is defined as follows,

$$M_n(\text{theor}) = \frac{([M1]_0 + [M2]_0)}{[CTA]_0} \times M_{\text{monomer}} \times \text{yield} + M_{CTA} \quad (1)$$

where M_{CTA} is the molecular weight of chain transfer agent, and $[M1]_0$, and $[M2]_0$, and $[CTA]_0$ are the initial concentrations of monomers and chain transfer agent, respectively. M_{monomer} is the mean molecular weight of a structural unit, which is a function of composition and, therefore, conversion of each monomer in copolymerizations. In a copolymerization of two monomers, M_{monomer} is given by eq 2[54]

$$M_{\text{monomer}} = A_1F_1 + A_2F_2 \quad (2)$$

where A_1 and A_2 are the molecular weights of M1 and M2, respectively, and F_1 and F_2 are the mole fraction of M1 and M2 in the copolymer, respectively.

For the determination of reactivity ratios, low conversion samples over a range of feed compositions were prepared under the same conditions.

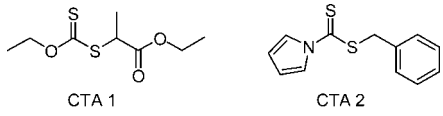
Instrumentation. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL EX-400. The number-average molecular weight (M_n) and molecular mass distribution (M_w/M_n) were estimated by size-exclusion chromatography (SEC) using a system consisting of a Tosoh HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column set was as follows: [Tosoh TSK-GELs (exclusion limited molecular weight): α-*M* (>1 × 10^7), α-4000 (4 × 10^5), α-3000 (9 × 10^4), α-2500 (5 × 10^3), 30 cm each] and a guard column [TSK-guard column α, 4.0 cm] eluted with DMF (10 mM LiBr) at a flow rate

Table 1. RAFT Copolymerization of *N*-Vinylnaphthalimide (NVNPI) with Comonomers Using 2,2′-Azobis(isobutyronitrile) (AIBN) in *N*,*N*-Dimethylformamide (DMF) at 60 °C for 24 h[a]

run	comonomer[b]	CTA[c]	yield[d] (%)	M_n[e] (theory)	M_n[f] (SEC)	M_w/M_n[f]	composition[g] NVNPI/comonomer
1	NIPAAm		98		7700	1.80	49/51
2	NIPAAm	CTA 1	>99	16700	13000	1.99	48/52
3	NIPAAm	CTA 2	94	16000	10700	1.22	50/50
4	DMAAm		>99		75000[h]	3.46[h]	8/92[h]
5	DMAAm	CTA 1	>99	16200	35500[h]	1.62[h]	10/90[h]
6	DMAAm	CTA 2	>99	16200	24700[h]	1.57[h]	8/92[h]
7	MA		89		7700	1.77	43/57
8	MA	CTA 1	91	12900	5200	1.85	39/61
9	MA	CTA 2	98	15800	7400	1.73	53/47
10	St		<1				

[a] $[NVNPI]_0/[comonomer]_0/[CTA]_0/[I]_0 = 100/100/2/1$, $[NVNPI + comonomer]_0 = 1.0$ mol/L. [b] NIPAAm = *N*-isopropylacrylamide, DMAAm = *N*,*N*-dimethylacrylamide, MA = methyl acrylate, and St = styrene. [c] CTA 1 = *O*-ethyl-*S*-(1-ethoxycarbonyl) ethyldithiocarbonate, CTA 2 = benzyl 1-pyrrolecarbodithioate, see Scheme 3. [d] Diethyl ether-insoluble part. [e] The theoretical molecular weight ($M_{n,theory}$) was calculated using eqs 1 and 2. [f] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). [g] Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [h] $CDCl_3$ or DMF-soluble part.

Scheme 3. Structures of CTAs Used in this Study



of 1.0 mL/min. The UV−vis spectra were recorded with a JASCO V-630 BIO spectrophotometer. The fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorometer. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer.

Results and Discussion

Monomer Synthesis and Free Radical Polymerization of NVNPI. The synthesis of *N*-vinylnaphthalimide (NVNPI) was conducted by the reaction of 2,3-dicarboxynaphthalimide with a large excess of vinyl acetate in the presence of Na_2PdCl_4. The method was used for the synthesis of an *N*-vinyl analogue, *N*-vinylphthalimide, which was reported by Baret et al.[50] The monomer (NVNPI) was soluble in many organic solvents, such as THF, $CHCl_3$, DMF, DMSO, and a large excess of diethyl ether, and exhibited a greenish blue fluorescence upon 365 nm (see Supporting Information, Figure S7). Because there was no report on radical polymerization of NVNPI, we initially attempted to conduct free radical homopolymerization of NVNPI with AIBN in DMF at 60 °C for 24 h. Although a reasonable polymer yield (62%) was attained under the conditions, the resulting poly(NVNPI) was insoluble in any organic solvents (see Supporting Information, Table S1).

RAFT Copolymerizations of NVNPI with Various Comonomers. To obtain soluble copolymers with NVNPI, we conducted copolymerization with selected vinyl monomers, methyl acrylate (MA), *N*,*N*-dimethylacrylamide (DMAAm), and *N*-isopropylacrylamide (NIPAAm). In all cases, the copolymerizations were conducted with AIBN as an initiator at a constant molar ratio of two monomers in the feed ($[NVNPI]_0/[comonomer]_0$) in DMF at 60 °C for 24 h. The results are summarized in Table 1. When free radical copolymerization was conducted at $[NVNPI]_0/[NIPAAm]_0/[AIBN]_0 = 100/100/1$, the polymerization proceeded homogeneously and the copolymer was obtained as a white powder after the precipitation into diethyl ether. Almost quantitative polymer yield (yield = 98%) was achieved after 24 h, and the resulting copolymer had a M_n = 7700 and $M_w/M_n = 1.80$, according to SEC in DMF (10 mM LiBr) using polystyrene calibration. Residual monomers could be removed by the precipitation, because both monomers, NVNPI and NIPAAm, were soluble in a large excess of diethyl ether. The resulting poly(NVNPI-*co*-NIPAAm) was soluble in THF, $CHCl_3$, DMF, and DMSO, and insoluble in *n*-hexane, diethyl ether, and H_2O.

In the next stage, the copolymerization of NVNPI and NIPAAm was investigated in the presence of CTA 1 or CTA 2 at a constant comonomer ratio ($[NVNPI]_0/[NIPAAm]_0 = 50:50$), keeping the chain transfer agent-to-initiator ratio at a constant value of $[CTA]_0/[AIBN]_0 = 2/1$. We previously demonstrated that controlled radical polymerization of *N*-vinyl monomers, *N*-vinylcarbazole,[33,34] *N*-vinylindole derivatives,[35] and *N*-vinylphthalimide[36] was attained using xanthate-type CTAs. Both CTA 1 and CTA 2 were employed as RAFT agents for the well-controlled polymerization of *N*-vinylphthalimide.[36] The xanthate-type CTA 1 was employed as a RAFT agent for the polymerization of vinyl acetate,[55] and a methoxy derivative of CTA 1 was used for the polymerization of acrylic acid and acrylamide.[56] In contrast, the dithiocarbamate-type CTA 2, which has the nonbonded electron pair of the nitrogen included as part of an aromatic system, was efficient as the CTA for RAFT polymerizations of NIPAAm,[57] styrene,[53,58] and methyl acrylate.[58] When the copolymerization was conducted with CTA 2 in DMF at 60 °C, the characteristic pale yellow solution remained during the polymerization. The polymer yield (94%) was slightly lower than that obtained by free radical copolymerization under the same conditions. As can be seen in Figure 1a and Table 1, the resulting poly(NVNPI-*co*-NIPAAm) obtained with CTA 2 showed symmetrical unimodal SEC peak with a relatively narrow molecular mass distribution ($M_w/M_n = 1.22$). The number average molecular weight, measured by SEC in DMF (10 mM LiBr), was 10700, which was slightly lower than the theoretical value ($M_n = 16000$) calculated from eqs 1 and 2. Note that the molecular weights obtained by conventional SEC are just apparent ones because of the use of polystyrene calibration. Figure 2a shows ^{1}H NMR spectrum of poly(NVNPI-*co*-NIPAAm) obtained by RAFT copolymerization in the presence of CTA 2. The characteristic broad peaks at 6.7−8.2 ppm (aromatic protons), 5.0−6.5 ppm (N−H proton of the NIPAAm), and 3.0−4.8 ppm (NCH in the NIPAAm residue and CH in the main chain of NVNPI unit) are clearly seen. The comonomer composition was determined using ^{1}H NMR spectroscopy by a comparison of the peak at 5.0−6.5 ppm attributed to N−H group (1H) of the NIPAAm unit and peaks at 6.7−8.2 ppm corresponding to the aromatic protons (6H) of the NVNPI unit. Integration of the peaks gave a composition of 50% NVNPI and 50% NIPAAm in the copolymer obtained by the copolymerization with CTA 2. Comparison of the peak at 5.0−6.5 ppm (NH proton of NIPAAm) and the peak at 3.0−4.8 ppm (NCH proton of the NIPAAm and main chain CH proton of NVNPI) showed the same comonomer composition. The copolymerization of NVNPI in the presence

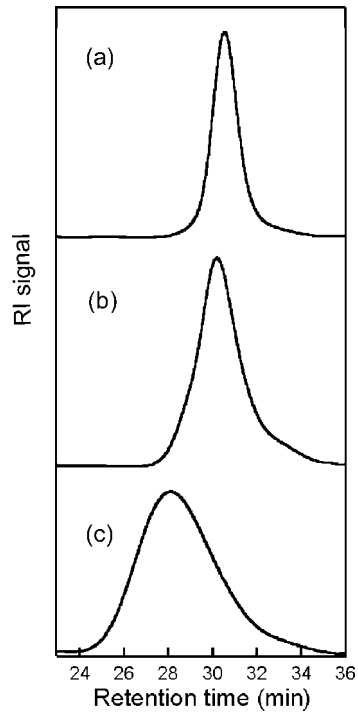


Figure 1. Size exclusion chromatography (SEC) traces of (a) poly(NVNPI-*co*-NIPAAm) (M_n = 10700, M_w/M_n = 1.22), (b) poly(NVNPI-*co*-DMAAm) (M_n = 24700, M_w/M_n = 1.57), and (c) poly(NVNPI-*co*-MA) (M_n = 7400, M_w/M_n = 1.73) prepared by the copolymerizations with CTA 2 (see Table 1 for detailed polymerization conditions).

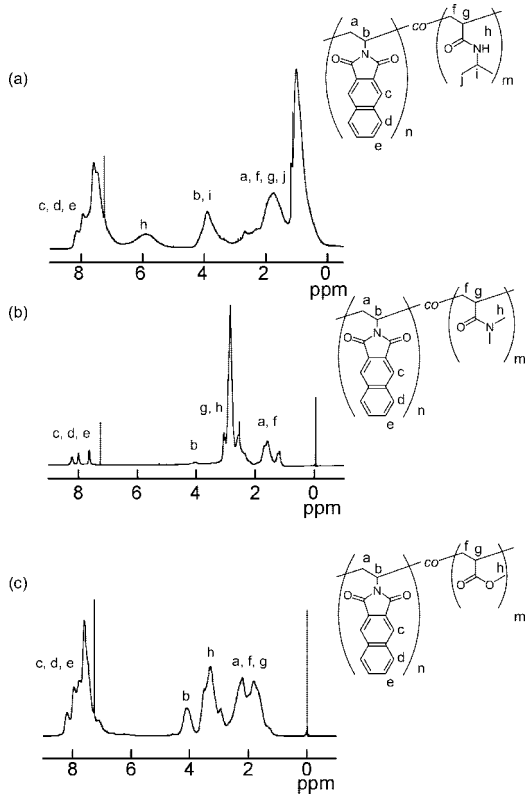


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of (a) poly(NVNPI-*co*-NIPAAm) (M_n = 10700, M_w/M_n = 1.22), (b) poly(NVNPI-*co*-DMAAm) (M_n = 24700, M_w/M_n = 1.57), and (c) poly(NVNPI-*co*-MA) (M_n = 7400, M_w/M_n = 1.73).

of CTA 1 under the same conditions afforded a copolymer having broader molecular weight distribution (M_w/M_n = 1.99; see Supporting Information). These results suggest that the dithiocarbamate-type CTA 2 is efficient for RAFT copolymerization of NVNPI and NIPAAm, while the xanthate-type CTA 1 is ineffective to achieve controlled character of the copolymerization. The behavior is consistent with the general tendency, in which the transfer constants decrease in the series where Z is alkyl ≈ alkylthio ≈ pyrrole ≫ alkoxy.[59] In other words, the transfer constant of the xanthate-type CTA 1 is considered to be too low, especially for RAFT polymerization of the conjugated NIPAAm, resulting in poor control of the copolymerization. Nevertheless, the comonomer compositions were almost consistent with the feed ratio, independent of the nature of CTA, which is due to the quantitative polymer yields (>94%).

The copolymerizations of NVNPI were also conducted with other comonomers, MA and DMAAm, using CTA 1 and CTA 2 under the same conditions. In the cases of the copolymerizations with DMAAm, the polymer yields were quantitative (99%), regardless of the nature of CTA. The NVNPI composition determined using ^{1}H NMR spectroscopy in $CDCl_3$ by a comparison of the peak at 7.4−8.3 ppm attributed to the aromatic protons (6H) of NVNPI unit and the peak at 2.0−3.8 ppm corresponding to the methyl and methine protons (7H) of DMAAm unit were less than 10% composition of NVNPI unit. The structures of the resulting copolymers were also evaluated by ^{13}C NMR spectroscopy, suggesting the preferable incorporation of DMAAm unit (see Supporting Information). The results may be due to the fact that a part of the resulting product (roughly 30 wt %) was swollen in $CDCl_3$, which was hard to be dissolved completely. The comonomer composition determined by ^{1}H NMR is attributed to that of the soluble part having high DMAAm content (>90%). In contrast, the swollen part may be composed of the copolymers having lower DMAAm contents, in which the motions of NVNPI-rich parts are restricted in $CDCl_3$. The comonomer composition was also evaluated by ^{1}H NMR spectroscopy in DMSO-d_6 (see Supporting Information). The swollen part was still existed in DMSO-d_6, and the integrations for both components were comparable to those measured in $CDCl_3$. The SEC measurement of the copolymer was conducted in DMF (10 mM LiBr). As can be seen in Table 1 and Figure 1b, DMF-soluble parts of the copolymers showed broader polydispersities (M_w/M_n = 1.57−1.62). The number-average molecular weights measured by a SEC in DMF (10 mM LiBr) were 35500 (CTA 1) and 24700 (CTA 2), respectively, which are apparently higher than the theoretical value (M_n = 16200).

The RAFT copolymerization of NVNPI and MA under the same conditions afforded copolymers with relatively broad polydispersities (M_w/M_n = 1.73−1.85). In all cases, the copolymerizations proceeded homogeneously without any microscopic precipitation, which were apparently different from the homopolymerization of NVNPI. The comonomer composition determined from the peak at 7.0−8.3 ppm attributed to the aromatic protons (6H) of NVNPI unit compared with the peak at 3.0−3.8 ppm corresponding to the methyl protons (3H) of MA unit, was slightly affected by the nature of CTA. However, the addition of CTA 1 or CTA 2 had no significant effect on the polymer yield, molecular weights, and molecular weight distributions of the resulting copolymers, as can be seen in Table 1. The results may be related to the difference in the reactivity between the nonconjugated NVNPI and the conjugated acrylate. Another possible explanation is that the role of CTA is affected by the hydrogen-bond formation between C═O (ester) and NH (amide) fragments during chain growth reactions. Nevertheless, the solubility of the product was improved by the introduction of MA, similarly to the case of the copolymerization with NIPAAm. Both copolymers having the composition of NVNPI/comonomer = roughly 50/50 were soluble in DMSO, DMF, $CHCl_3$, and CH_2Cl_2, while insoluble in *n*-hexane, diethyl ether,

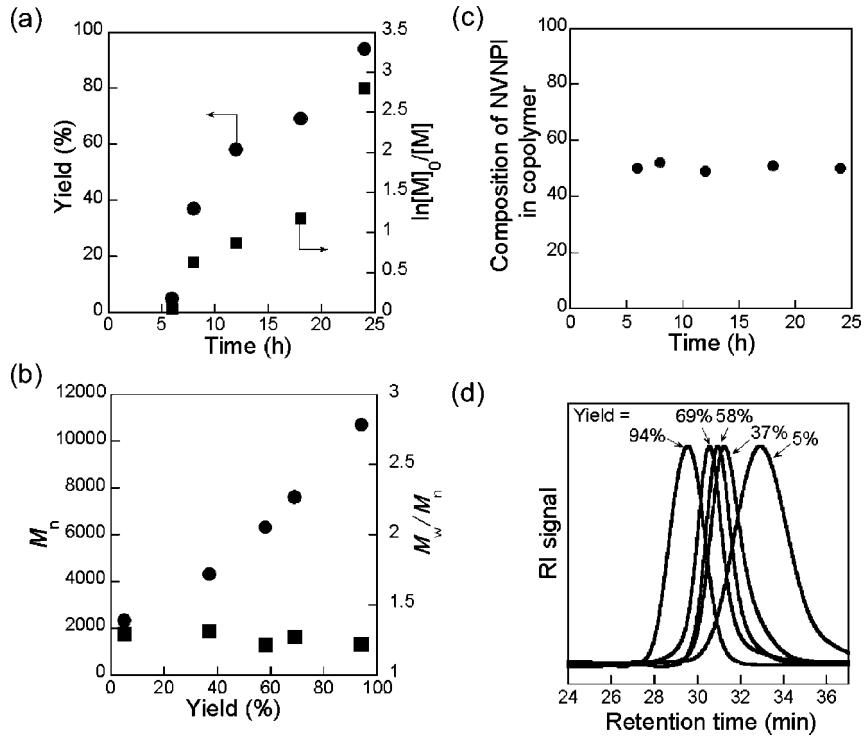


Figure 3. (a) Time-polymer yield (circles) and first order kinetics plots (squares) for the copolymerization at $[NVNPI]_0/[NIPAAm]_0/[CTA\ 2]_0/[AIBN]_0 = 100/100/2/1$. (b) Number-average molecular weight and polydispersity as a function of yield. (c) Composition plot of mole fraction of NVNPI for the time conversion in copolymerization. (d) Evolution of SEC traces with polymer yield.

and H_2O, regardless of the comonomer structure. Poly(NVNPI-*co*-NIPAAm) was soluble in polar solvents, such as methanol, while poly(NVNPI-*co*-MA) was insoluble in those solvents.

We also conducted the copolymerization of the nonconjugated NVNPI with a typical conjugated monomer, styrene. However, the attempt was unsuccessful; the copolymerization of NVNPI and styrene under the same conditions gave no polymer (see Supporting Information). This behavior may be due to the low reactivity of nonconjugated *N*-vinyl monomer, NVNPI. Similar tendency was observed in free radical copolymerization of styrene with an analogue of NVNPI, *N*-vinylphthalimide, in which predominant polymerization of styrene itself occurred with slight incorporation of *N*-vinylphthalimide unit.[60] Recently, Dincer et al. reported a characteristic tendency of radical copolymerization of NIPAAm with maleic anhydride, in which relatively high reactivity of NIPAAm growing radical was explained by hydrogen-bond formation between C═O (anhydride) and NH (amide) fragments during chain growth reactions.[61] On the basis of the results, we expect that the presence of the carbonyl group in MA, DMAAm, and NIPAAm leads to the interaction between NVNPI and the comonomers, resulting in the formation of the corresponding copolymers, while styrene has no specific interaction with NVNPI to afford negligible amount of copolymer. The different behavior in the copolymerization of NVNPI with styrene ($Q = 1.0$, $e = -0.8$), compared with other conjugated monomers (MA; $Q = 0.45$, $e = 0.64$,[62] DMAAm; $Q = 0.41$, $e = -0.26$ may be related to the polarity of the polymerizable double bonds. Although there was no report on the Q and e values of NVNPI, the monomer may have a electron-donating property, on the basis of the reported value of *N*-vinylphthalimide ($Q = 0.36$, $e = -1.52$),[63] which is an analogue of NVNPI having similar *N*-vinyl structure. In contrast, various Q and e values were reported on NIPAAm: $Q = 0.26$, $e = -0.26$ with maleic anhydride and $Q = 0.70$, $e = -0.26$[64] with methacrylic acid. Further discussion will be continued in the next section.

RAFT Copolymerization of NVNPI with NIPAAm. The controlled/living character of the copolymerization of NVNPI with NIPAAm was studied by performing kinetic investigations with CTA 2 in DMF at 60 °C. When the copolymerization was conducted at $[NVNPI]_0/[NIPAAm]_0/[CTA\ 2]_0/[AIBN]_0 = 100/100/2/1$, relatively high polymer yield (>95%) was reached after 24 h. Figure 3a shows the variations in the polymer yield and $\ln([M]_0/[M]_t)$ versus polymerization time for the copolymerization. An approximately linear relationship between $\ln([M]_0/[M])$ and polymerization time is seen until 18 h, indicating that the number of active species remains constant during the RAFT copolymerization. At the last stage of the copolymerization, the polymerization rate increases apparently, which may be due to autoacceleration (gel-effect) at higher polymer yields. The first-order kinetic plot is considered to be linear only if the kinetics is first-order with respect to the monomer and the concentration of active species remains constant. Because there is no reason to suspect a higher order dependence of the polymerization rate on monomer conversion, the increased polymerization rate can be also explained by the increase in the radical concentration at the last stage of the polymerization. At the initial stage of the polymerization, an induction period is seen in the pseudo-first-order kinetics plot, and the period roughly estimated simply by extrapolating the linear part of the curve to the time axis is about 5 h. An induction period is often observed in RAFT polymerizations of various monosubstituted acrylamide[65] and *N*-vinyl monomers.[34,35] Nevertheless, the number-average molecular weights, M_n, increase linearly with the polymer yield (Figure 3b). The SEC traces (refractive index) of the copolymers obtained at different reaction times are shown in Figure 3d. A progressive increase in the molar mass with the yield with low unimodal SEC peaks ($M_w/M_n < 1.31$) are clearly seen. The result of the copolymerization kinetics together with the linear evolution of molecular weight versus polymer yield suggest that the copolymerization of NVNPI and NIPAAm initiated by

Table 2. RAFT Copolymerization of *N*-Vinylnaphthalimide (NVNPI) with *N*-Isopropylacrylamide (NIPAAm) Using 2,2-azobis(isobutyronitrile) (AIBN) and Benzyl 1-Pyrrolecarbodithioate (CTA 2) in *N*,*N*-Dimethylformamide (DMF) at 60 °C[a]

run	feed ratio NVNPI/NIPAAm	time (h)	yield[b] (%)	M_n[c] (theory)	M_n[d] (SEC)	M_w/M_n[d]	composition[e] NVNPI/NIPAAm
1	90:10	7	3	750	2000	1.22	53/47
2	75:25	7	5	1100	2100	1.21	50/50
3	50:50	6	5	1100	2300	1.29	50/50
4	25:75	5	5	1100	2500	1.26	50/50
5	10:90	4	6	1200	2300	1.26	48/52

[a] $[NVNPI + NIPAAm]_0/[CTA]_0/[I]_0 = 200/2/1$, $[NVNPI + NIPAAm]_0 = 1.0$ mol/L. [b] Diethyl ether-insoluble part. [c] The theoretical molecular weight ($M_{n,theory}$) was calculated using eqs 1 and 2. [d] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured by size-exclusion chromatography (SEC) using polystyrene standards in DMF (10 mM LiBr). [e] Determined by ^{1}H NMR spectroscopy in $CDCl_3$.

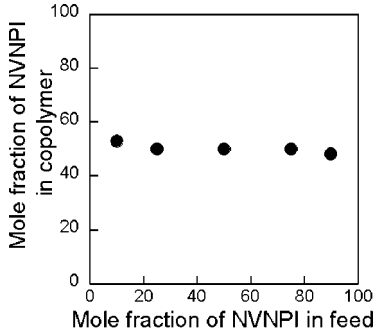


Figure 4. Composition plot of mole fraction of NVNPI in feed and mole fraction of NVNPI in copolymer.

AIBN in the presence of CTA 2 is controllable and of a controlled/living polymerization nature.

The molar fraction of NVNPI in the copolymers obtained at different polymerization times was measured by ^{1}H NMR spectroscopy. Comonomer composition is an important factor in copolymerizations, because it can be employed to obtain information about the chemoselectivity of active species consuming monomer during the copolymerization. One of the most attractive features of controlled radical polymerization is the fact that all polymer chains should have a similar composition, since all chains start growing at approximately the same time. The tendency is significantly different from that of conventional free radical copolymerization, in which the chains obtained at the beginning of the polymerization have a different composition from those formed at the last stage, as the initiation can start throughout the polymerization. As can be seen in Figure 3c, the comonomer composition in the copolymer obtained at equimolar comonomer feed via RAFT process is always close to 1:1, even at different polymer yields. This finding suggests no significant drift in the compositions of the copolymers at these conversions.

To clarify that the copolymer possesses an alternating structure, the copolymerization of NVNPI with NIPAAm was conducted at different feed ratios, which were varied over the entire composition range. The low conversion samples were prepared at designed feed compositions by adjusting polymerization time. Table 2 summarizes initial feed ratios, the composition, molecular weight, and polydispersity of the resulting copolymers. The relationship between the comonomer feed and the composition of the copolymers obtained at low polymer yield (<6%) is shown in Figure 4. The result indicates that the copolymers possess a predominantly alternating structure in a large range of the comonomer feeds. As can be seen in Table 2, the molecular weights of the copolymers are comparable to the theoretical values and polydispersity indexes are less than 1.29, regardless of the comonomer ratio in the feed. Fineman-Ross method was employed to calculate the r_1 and r_2 values, designating NVNPI as M_1 and NIPAAm as M_2. For the copolymerization with CTA 2 in DMF at 60 °C, $r_1 = 0.015 \pm 0.03$ and $r_2 = 0.037 \pm 0.05$ were calculated, indicating predominant alternating tendency.

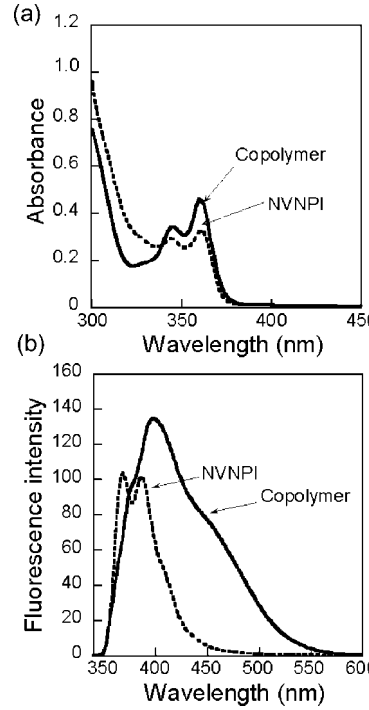


Figure 5. (a) Absorption spectra of NVNPI (dotted trace) and copolymer (solid trace, NVNPI/NIPAAm = 50/50, $M_n = 10700$, $M_w/M_n = 1.22$) in CH_2Cl_2 (concn = 4.6×10^{-5} NVNPI unit mol/L). (b) Fluorescence spectra of NVNPI (dotted trace) and copolymer (solid trace) in CH_2Cl_2 (concn = 9.2×10^{-7} NVNPI unit mol/L, $\lambda_{ex} = 340$ nm).

Similar alternating copolymer was obtained by conventional free radical copolymerization of NIPAAm with *N*-vinylpyrrolidone, in which intermolecular interactions through hydrogen-bonding between NIPAAm and *N*-vinylpyrrolidone play a key role to afford alternating tendency.[64] They claimed that the alternating tendency is due to the formation of hydrogen-bonded complexes between amide and pyrrolidone ring carbonyl groups (-NH···O=C-), and N→O=C coordination between highly polar ternary amide of pyrrolidone ring and NIPAAm carbonyl group. The tendency to polymerize in an alternative fashion was also reported in copolymerization of *N*-vinylformamide with acrylamide-based monomers.[66] Another example is the alternating copolymerization of NIPAAm with maleic anhydride,[61] which is due to the hydrogen-bond formation between C=O and NH groups. In our system, similar hydrogen-bonded complexes (-NH···O=C-) and N→O=C coordination should be acted as driving force to afford alternative structure. Further, the electron poor/electron rich characteristic may favor a cross addition polymerization mechanism, even if the tendency is less than the frequently observed alternating copolymers with maleic anhydrides. In our system, NIPAAm is an electron-accepting type monomer due to strong electron withdrawing nature of the amide group. In contrast, NVNPI is expected to be an electron-donating type monomer, because of the lone pair of electrons

on the nitrogen atom adjacent to vinyl groups. In addition to these electronic effects, another structural feature of NVNPI may induce alternating tendency. The naphthalimide-containing monomer, NVNPI, is inherently bulky, which leads to steric repulsions, resulting in the favorable cross addition with NIPAAm. Further detailed investigation on the mechanism is underway, which will be reported separately.

Optical Properties of NVNPI and Copolymers. The naphthalimide-containing NVNPI and the resulting copolymer, poly(NVNPI-*co*-NIPAAm), were characterized in terms of their optical properties. Figure 5a depicts the absorbance spectra of NVNPI and the copolymer measured in CH_2Cl_2. Both the monomer and the copolymer absorb light in the range from 330 to 380 nm and exhibit absorption peaks at 345 and 367 nm. No significant difference in the peak positions was observed between the monomer and copolymer. The fluorescence spectra of the NVNPI and copolymer are shown in Figure 5b. The emission of NVNPI excited at 340 nm is in the range from 350 to 500 nm, and two excimer bands with maxima at 375 and 393 nm are clearly detected. In contrast, a broad peak between 350 and 570 nm is visible, with a maximum at 415 nm in the copolymer. The difference may be related to the disappearance of interaction between the electron-donating naphthalimide chromophore and the electron-accepting carbon−carbon double bond exited in the NVNPI and/or a specific conformation of the copolymer, such as π-stacked structure and so-called self-quenching effects.[67]

Conclusion

In this study, controlled radical copolymerization of the naphthalimide-containing monomer, NVNPI, with a monosubstituted acrylamide, NIPAAm, has been successfully carried out using the dithiocarbamate-type CTA (CTA 2). The resulting copolymer, poly(NVNPI-*co*-NIPAAm), possessed a designed molecular weight with low polydispersity. Good control of the copolymerization was also confirmed by the linear increase in the molecular weight with the yield. The reactivity ratios were determined by Fineman-Ross method, indicating random copolymerization with a strong alternating tendency. We believe that this paper represents the first example on controlled alternating copolymerization of the nonconjugated *N*-vinyl monomer, NVNPI, with a conjugated monosubstituted acrylamide. The RAFT copolymerizations of NVNPI with MA afforded the copolymers having good solubility in many organic solvents, and the resulting copolymers had broader molecular weight distributions. The naphthalimide-containing monomer, NVNPI, and the copolymer showed characteristic optical properties.

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Supporting Information Available: Homopolymerization of NVNPI, table summarizing the data for solubility of NVNPI, the homopolymer, and the copolymers, figures showing ^{1}H and ^{13}C NMR spectra of the monomer ($CDCl_3$), ^{13}C NMR spectra of the copolymers ($CDCl_3$), ^{1}H NMR spectra of the copolymers (DMSO-d_6), SEC traces of poly(NVNPI-*co*-NIPAAm)s prepared using different CTAs, and appearance of samples illuminated under UV lights. This material is available free of charge via the Internet at http://pubs.acs.org.

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