Macromolecules **2008**, *41*, 6925−6934

Poly(*N*-vinylcarbazole) Star Polymers and Amphiphilic Star Block Copolymers by Xanthate-Mediated Controlled Radical Polymerization

Hideharu Mori,*,[†] Hiroshi Ookuma,[†] and Takeshi Endo*,[‡]

Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan, and Molecular Engineering Institute, Kinki University, Iizuka, Fukuoka 820-8555, Japan

Received June 5, 2008; Revised Manuscript Received July 10, 2008

ABSTRACT: Four-arm poly(*N*-vinylcarbazole), poly(NVC), stars were synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization/macromolecular design via interchange of xanthates (MADIX) using three different xanthate-type tetrafunctional chain transfer agents (CTAs). Two Z-designed CTAs having different R (leaving) groups, in which the Z (stabilizing) groups are linked to the core, and one R-designed CTA were compared. The R-group approach was found to be the most efficient for the controlled synthesis of four-arm poly(NVC) stars having a low polydispersity and controlled molecular weights. Amphiphilic star block copolymers were synthesized by the polymerization of NVC using the poly(acrylic acid) star, which was prepared from the R-designed tetrafunctional CTA. The characteristic assembled structures and optical properties of the amphiphilic star block copolymers in selective solvents were investigated by dynamic light scattering (DLS), UV−vis, and fluorescence spectroscopic methods.

Introduction

The design and synthesis of novel star copolymers having characteristic architectures, such as star block copolymers and heteroarm or miktoarm (mixed) star polymers, are attracting significant attention because of their interesting structures and properties.[1−7] Amphiphilic star block copolymers can form a variety of superstructures as a result of self-organization, and the resulting assembled structures should be governed by the branched architecture, in addition to the chemical nature of the components, their composition, and molecular weight. In order to achieve highly ordered assembly systems and to obtain a better understanding of the relation between the primary branched architectures and assembled structures based on self-organization, it is necessary to produce well-defined amphiphilic star block copolymers. A variety of controlled/living polymerizations were employed for this purpose. As examples, the so-called core-first method using atom transfer radical polymerization has been frequently employed for the synthesis of amphiphilic star block copolymers containing (meth)acrylic acid segments.[8−10] Recently, reversible addition−fragmentation chain transfer (RAFT) polymerization using Z-designed multifunctional chain transfer agents was also used to synthesize well-defined amphiphilic star block copolymers composed of polystyrene and poly(acrylic acid).[11,12] These amphiphilic star block copolymers showed characteristic solution behaviors because of the nature of the poly[(meth)acrylic acid]s as weak polyelectrolytes, in which the degree of ionization is governed by the pH and ionic strength of the aqueous solution.

Among the various controlled radical polymerizations, RAFT polymerization has proven to be extremely versatile with respect to the monomer type and reaction conditions.[13−26] For example, dithiocarbonates (xanthates) are useful for controlling the radical polymerization of *O*-vinyl and *N*-vinyl monomers, such as vinyl acetate[27−30] and *N*-vinylpyrrolidone.[31−33] Recently, we also reported the xanthate-mediated controlled radical polymerization of various *N*-vinyl monomers involving *N*-vinylcarbazole (NVC),[34] *N*-vinylindole derivatives,[35] and *N*-vinylphthalimide.[36] In general, the controlled radical polymerization of the *N*-vinyl and *O*-vinyl monomers was considered difficult, since the generated radical species are highly reactive due to their nonconjugated nature and strong electron-donating pendant groups. When xanthates are employed as reversible chain transfer agents (CTAs), the terminology MADIX (macromolecular design via the interchange of xanthates) is frequently used to describe the process.[37,38] RAFT/MADIX polymerization was also employed for the syntheses of various star polymers based on the poly(vinyl acetate),[39−41] poly(*N*-vinylpyrrolidone),[42] and poly(NVC).[43]

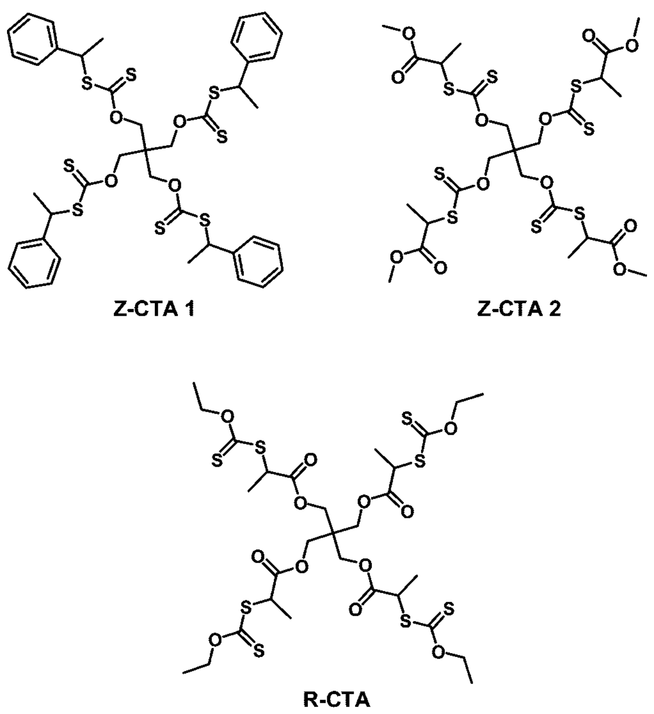
We now present the synthesis of amphiphilic star block copolymers containing poly(NVC) segments and characterization of their solution and optical properties. Polymers with carbazole pendant groups are of considerable scientific and industrial interest due to their attractive features, such as hole-transporting, high charge carrier, and electroluminescent properties.[44] Three-dimensional hierarchical structures formed by self-organization of the amphiphilic star block copolymers may lead to unique electronic and photonic functions, depending upon the ordered structures and stacking of the poly(NVC) segment. In the RAFT/MADIX system, two different approaches can be used for the synthesis of star polymers: the so-called R-group approach (propagation attached to core) and Z-group approach (propagation away from core).[23,40,45−48] Previously, we demonstrated the controlled synthesis of four-arm poly(NVC) stars with a relatively narrow polydispersity ($M_w/M_n = 1.3-1.5$) by the RAFT/MADIX polymerization using a Z-designed tetrafunctional xanthate (Z-CTA 1), in which the stabilizing groups were linked to the core via a nonfragmenting covalent bond (Scheme 1).[43] In general, the Z-group approach avoids the formation of higher-order coupling reaction, as the core will not have any propagating radicals and the propagation takes place in the solution surrounding the core. In the R-group approach, in contrast, the leaving groups are linked to the core, and the core itself becomes a radical by the fragmentation. Possible side products in the R-group approach involve star−star coupled product from radical termination reaction via combination and linear dead polymer as an impurity in the star polymer. Recent deeper investigations indicated that optimizing the

---

* To whom correspondence should be addressed: e-mail h.mori@yz.yamagata-u.ac.jp or tendo@me-henkel.fuk.kindai.ac.jp; Ph +81-238-26-3765; Fax +81-238-26-3749.
[†] Yamagata University.
[‡] Kinki University.

10.1021/ma801266h CCC: $40.75

Scheme 1. Structures of R- and Z-Designed Xanthate-Type Tetrafunctional Chain Transfer Agents (CTAs)


Z-CTA 1

Z-CTA 2

R-CTA

precise chemical nature of the multifunctional CTA involving the structures of the R and Z groups and the suitable choice of the approach are required, depending on the kind of the monomer, to synthesize well-defined star polymers by RAFT polymerizations.[23]

In the present study, we initially compared the R-group and Z-group approaches for the synthesis of the four-arm poly(NVC) stars. A suitable selection of CTA, as the choice of the R and Z groups, depending upon the kind of monomer is one of the key points to achieve well-defined polymers via the RAFT/MADIX process. To find a suitable multifunctional CTA for the controlled synthesis of the poly(NVC) stars, we selected two Z-designed tetrafunctional CTAs having different R groups (Z-CTA 1 and Z-CTA 2) and one R-designed tetrafunctional CTA (R-CTA), as shown in Scheme 1. In the Z-CTA 1, the leaving R group corresponds to $CH(CH_3)Ph$, which yields a secondary radical species upon fragmentation, and the *O*-alkyl core acts as the Z group (or stabilizing group). The leaving R group in Z-CTA 2 corresponds to $CH(CH_3)COOCH_3$, which yields a secondary radical species having a different reactivity. The synthesis of amphiphilic star block copolymers containing poly(NVC) segments was conducted using a suitable tetrafunctional CTA. As shown in Scheme 2, our approach involves the RAFT polymerization of NVC using the poly(acrylic acid), poly(AA), star as a tetrafunctional macro-CTA, resulting in the formation of a well-defined star block copolymer, in which the poly(AA) is located in the core and the poly(NVC) in the shell.

Experimental Section

Materials. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. *N*-Vinylcarbazole (NVC, Tokyo Kasei, 98%) was recrystallized two times from methanol. Acrylic acid (AA, Tokyo Kasei, 99%) was distilled under vacuum before use. 1,4-Dioxane (Kanto Chemical, 99%) was distilled from sodium wire. Note that distilled dioxane was stored under a nitrogen atmosphere in the dark, which was carefully employed for the polymerization, because of the possible effect of peroxide impurities in the solvent.[49] Methanol (dehydrated MeOH, Kanto Chemical, 99.8%) and *N*,*N*-dimethylformamide (dehydrated DMF, Kanto Chemical, 99.5%) were purchased and used as received. The methylation agent, trimethylsilyldiazomethane (2 M solution in diethyl ether), was purchased from Aldrich and used as received. All other materials were used without further purification.

Synthesis of Tetrafunctional Chain Transfer Agents (CTA)s. Three different tetrafunctional CTAs were prepared (Scheme 1) in order to compare the Z-group and R-group approaches and to clarify the effect of the chemical structure of the R groups. The Z-core tetrafunctional CTA (Z-CTA 2) was synthesized by the reaction of the potassium salt of pentaerythritol with carbon disulfide, followed by the reaction with methyl 2-bromopropionate, according to a previously reported method with slight modifications.[40] The synthesis of another Z-core tetrafunctional CTA (Z-CTA 1) was conducted from pentaerythritol using (1-bromoethyl)benzene, according to the literature.[41,43] These Z-designed CTAs were finally purified by column chromatography on silica with hexane/ethyl acetate (8/2 vol %) for Z-CTA 2 and toluene and then hexane/diethyl ether (10/1 vol %) for Z-CTA 1. The R-core tetrafunctional CTA (R-CTA) was synthesized by a two-step procedure according to a previously reported procedure.[40] The first step is the reaction of pentaerythritol with 2-bromopropyl bromide in the presence of pyridine to yield a tetrafunctional bromide precursor. The precursor was then reacted with potassium ethyl xanthogenate to afford the tetrafunctional CTA. The R-CTA was finally purified by column chromatography on silica with hexane/ethyl acetate (7/3 vol %) as the eluent to give a pale yellow viscous oil.

Synthesis of Four-Arm Poly(NVC) Stars. All polymerizations were carried out with AIBN as an initiator in a degassed sealed tube. A representative example for the synthesis of the four-arm poly(NVC) star is as follows: NVC (0.600 g, 3.10 mmol), R-CTA (13.1 mg, 0.0155 mmol), AIBN (2.5 mg, 0.0155 mmol), and 1,4-dioxane (1.8 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 12 h. The transparent solution remained throughout the polymerization without any significant change in its viscosity. The reaction was stopped by rapid cooling with liquid nitrogen, and then the reaction mixture was precipitated in a large excess of hexane and isolated by filtration. The resulting product was finally dried under vacuum at room temperature to yield the four-arm poly(NVC) as a white powder. The polymer had an $M_{n,GPC} = 18\,000$ and $M_w/M_n = 1.14$ according to GPC using polystyrene calibration and $M_{n,GPC\text{-}RALLS} = 33\,300$ according to GPC/RALLS. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in $CDCl_3$ (see Supporting Information), and the integration of one proton of the $CH_2{=}C$ peak at around 5.6 ppm was compared to the intensity of the sum of the aromatic peaks of the polymer and the monomer and vinyl peaks observed at 4.1−8.2 ppm. The conversion determined by this method was >99%. Additionally, the polymer yield was gravimetrically determined from the hexane-insoluble polymer sample (98%, 0.601 g).

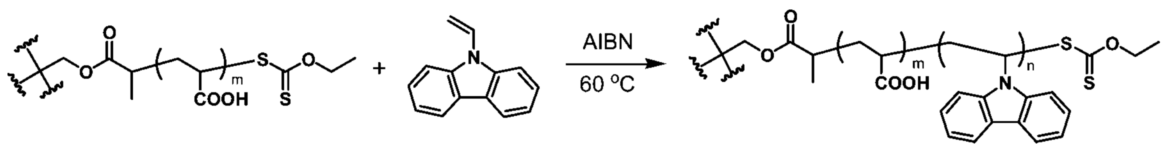
The theoretical number-average molecular weight of the star polymers upon conversion is defined as follows:

$$M_n(\text{theor}) = \frac{[\text{monomer}]_0}{[\text{CTA}]_0} \times M_{\text{monomer}} \times \text{conv} + M_{\text{CTA}} \qquad (1)$$

in which M_{CTA} and M_{monomer} are the molecular weights of the tetrafunctional CTA and the monomer, NVC, and $[\text{monomer}]_0$ and $[\text{CTA}]_0$ are the initial concentrations of the monomer and CTA, respectively. In an ideal RAFT process, the polymer directly derived from the initiators is considered to be minimal.

Arm Cleavage of Poly(NVC) Stars. For the stars prepared by the R-group approach, arm cleavage was achieved via the base-catalyzed transesterification in methanol similar to that adopted for the solvolysis of other star polymers.[50,51] The four-arm star polymer (50 mg) was dissolved in 50 mL of THF. A methanol solution of NaOH (5.0 mg, 5 mL) was added to the star polymer solution at room temperature, and then the mixture was refluxed at 80 °C for

Scheme 2. Synthesis of Amphiphilic Star Block Copolymer



3 h. After the solvent was evaporated, it was precipitated into MeOH to yield the cleaved arms. The molecular weight of the resulting product was analyzed using conventional GPC and GPC/RALLS measurements.

The cleavage of the arms from the star polymers obtained by the Z-group approach was conducted through the dithiocarbonate functionalities using a primary amine.[40] The poly(NVC) star prepared with Z-CTA 1 (50 mg) was dissolved in 0.5 mL of THF. Propylamine (0.1 mL) was added to the star polymer solution at room temperature, and then the mixture was stirred at room temperature for 1 h. The product was precipitated into MeOH to yield the cleaved arms.

Synthesis of Four-Arm Star Block Copolymers. The synthesis of a star block copolymer composed of AA and NVC was conducted using the poly(AA) star as a macro-CTA as follows: AA (2.00 g, 27.8 mmol), R-CTA (0.234 g, 0.278 mmol), AIBN (45.6 mg, 0.278 mmol), and methanol (6.0 mL) were placed in a dry ampule. After the solution was degassed by three freeze−evacuate−thaw cycles, the mixture was stirred at 60 °C for 4 h. After the product was purified by precipitation into diethyl ether, it was dried under vacuum at room temperature to yield the poly(AA) star as a white powder (yield = 90%), which was employed as a macro-CTA. The molecular weight of the poly(AA) star was calculated by comparison of the area of the peak at 1.3−2.6 ppm corresponding to the methine and methylene protons of the main chain to the peak at 3.8−4.3 ppm corresponding to three protons of the end group. The molecular weight determined by this method was $M_{\mathrm{n,NMR}} = 9100$, which was employed for the calculation of the feed ratio in the synthesis of the star block copolymers, as mentioned below. For the GPC measurement, the resulting poly(AA) star was modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane according to a previously reported method.[52,53]The resulting methylated sample had an $M_{\mathrm{n,GPC}}$ of 8400, which corresponds to $M_{\mathrm{n}} = 7200$ in the carboxylic acid form and a polydispersity index ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of 1.16.

The dithiocarbonate-terminated poly(AA) star (0.236 g, 0.0259 mmol), AIBN (4.2 mg, 0.0259 mmol), NVC (0.500 g, 2.59 mmol), and 1,4-dioxane (2.0 mL) were placed in a dry ampule. The solution was degassed by three freeze−evacuate−thaw cycles, and then the ampule was flame-sealed under vacuum. After the solution was stirred at room temperature for 24 h to obtain a homogeneous solution, the polymerization was conducted at 60 °C for 12 h (conversion determined by ^{1}H NMR spectroscopy = 95%). The reaction mixture was precipitated from a THF solution into acetonitrile, followed by reprecipitation from a THF solution into water. The product was finally collected by filtration to give the four-arm amphiphilic block copolymer (0.593 g, yield = 81%), [poly(AA)-*b*-poly(NVC)]$_4$. The comonomer composition was determined using ^{1}H NMR spectroscopy by a comparison of the peak at 12.3 ppm attributed the carboxylic acid proton (COO*H*, 1H) of the AA unit and peaks at 4.1−8.4 ppm that correspond to the aromatic protons (8H) of the NVC unit. The molecular weight determined by this method was $M_{\mathrm{n,NMR}} = 30\,500$, and the value determined by the elemental analysis was $M_{\mathrm{n,EA}} = 25\,600$, which are comparable to the theoretical value ($M_{\mathrm{n,theory}} = 27\,400$) calculated by the monomer conversion, $[\mathrm{NVC}]_0/[\mathrm{poly(AA)\ star\ macro\text{-}CTA}]_0$ in the feed, and the M_{n} of poly(AA) star used as a macro-CTA. The methylation of the poly(AA) segment in the star block copolymer was also conducted by treating the carboxylic acid groups using trimethylsilyldiazomethane to afford the poly(methyl acrylate)-*b*-poly(NVC) star, which was employed for SEC measurement ($M_{\mathrm{n}} = 15\,300$, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.26$ in the methylated form, which corresponds to $M_{\mathrm{n}} = 13\,700$ in the carboxylic acid form).

Instrumentation. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded by a JEOL JNM-ECX400. The UV−vis spectra were recorded using a JASCO V-630BIO UV−vis spectrophotometer. The fluorescence spectra were obtained from a JASCO FP-6100 spectrofluorophotometer. The elemental analysis was carried out using a Perkin-Elmer 2400 Π CHNS/O analyzer.

The number-average molecular weight (M_{n}) and molecular weight distribution ($M_{\mathrm{w}}/M_{\mathrm{n}}$) were estimated by GPC using a system consisting of a Tosoh DP-8020 pump and a Viscotek TDA model-301 triple detector array (RI, viscosity, and RALLS; wavelength = 670 nm). The column set was as follows: four consecutive columns [Tosoh TSK-GELs (exclusion limited molecular weight): GMH$_{\mathrm{XL}}$ (4×10^8), G4000H$_{\mathrm{XL}}$ (4×10^5), G3000H$_{\mathrm{XL}}$ (6×10^4), G2500H$_{\mathrm{XL}}$ (2×10^4), 30 cm each] and a guard column [TSK-guard column H$_{\mathrm{XL}}$-H, 4.0 cm] eluted with THF at the flow rate of 1.0 mL/min. Polystyrene standards were employed for calibration. GPC with a right-angle laser light scattering detector (GPC-RALLS) was also performed to determine the absolute molecular weights. The excess refractive index increment ($\mathrm{d}n/\mathrm{d}c = 0.253$) was measured in THF at 25 °C using a DRM1021 differential refractometer operating at 633 nm.

The characterization of the amphiphilic star block copolymers in various solvents was conducted using dynamic light scattering (DLS). The measurements were performed using an Otsuka Electronics DLS-7000 spectrometer with a He−Ne laser ($\lambda_0 = 632.8$ nm) at 25 °C and a scattering angle of 90°. Micelles consisting of the four-arm amphiphilic polymers were formed by the gradual addition of deionized water (19.5 mL) to the polymer solution (20.0 mg in 0.5 mL of DMF) to afford a mixed solvent (water/DMF = 39/1 vol %). The solution was dialyzed against deionized water (Spectra Pore; MWCO 1000 Da) for 4 days. An inverse polymer micelle was obtained by the gradual addition of 19.5 mL of CHCl$_3$ (spectrophotometric grade) to a 0.5 mL solution of the previously prepared 1.0 mg/mL DMF solution.

Results and Discussion

Preliminary Comparison of Tetrafunctional RAFT Core Molecules. For the synthesis of the well-defined poly(NVC) stars, the suitable selection of a tetrafunctional CTA having effective R and Z groups is crucial. In a previous study, we found that *O*-ethyl-*S*-(1-phenylethyl)dithiocarbonate having a −CH(CH$_3$)Ph moiety as a leaving group was effective as a xanthate-type CTA for the homopolymerization of NVC.[34] Additionally, our recent preliminary investigations with various monofunctional xanthate-type CTAs suggested the effectiveness of the leaving group structures (R = CH(CH$_3$)Ph and CH(CH$_3$)COOCH$_3$ in S═C(OEt)S−R) in the xanthate derivatives for the controlled polymerization of NVC (see Supporting Information, Table S1). On the basis of the results, we selected two Z-designed and one R-designed tetrafunctional CTAs having the secondary R groups, as shown in Scheme 1. We initially studied the effectiveness of these tetrafunctional CTAs for the controlled radical polymerization of NVC to produce well-defined star polymers.

The polymerization of NVC using these tetrafunctional CTAs were conducted with AIBN in 1,4-dioxane at 60 °C at the ratio $[\mathrm{NVC}]_0/[\mathrm{CTA}]_0 = 200$ and $[\mathrm{CTA}]_0/[\mathrm{AIBN}]_0 = 1$. The results are summarized in Table 1. Note that the CTA-to-AIBN ratio corresponds to the xanthate moiety to AIBN ratio of 4 because of the multifunctional nature of the CTAs having a quadruple concentration of the xanthate groups. We conducted the po-

Table 1. Synthesis of Four-Arm Stars by Polymerization of *N*-Vinylcarbazole (NVC) Using Tetrafunctional Chain Transfer Agents (CTAs) and 2,2′-Azobis(isobutyronitrile) (AIBN) as Initiator in 1,4-Dioxane at 60 °C[a]

entry	CTA[b]	time (h)	conv[c] (%)	$M_{n,theory}$[d]	$M_{n,GPC}$[e] (PDI)	$M_{n,RALLS}$[f] (PDI)
1	Z-CTA 1	24	42	17 100	8 200 (1.34)	11 300 (1.34)
2	Z-CTA 2	4	79	31 300	11 900 (1.35)	19 200 (1.38)
3	R-CTA	8	95	37 600	16 800 (1.14)	31 400 (1.16)

[a] $[NVC]_0/[CTA]_0/[AIBN]_0 = 200/1/1$, monomer concentration = 1.0 g/3.0 mL (1.72 mol/L). [b] See Scheme 1. [c] Calculated by ^1H NMR in $CDCl_3$. [d] Theoretical molecular weight ($M_{n,theory}$) = (MW of NVC) × $[NVC]_0/[CTA]_0$ × conv + (MW of CTA). [e] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF with RI detector. [f] Measured by SEC in THF with RALLS detector.

lymerization at a relatively dilute monomer concentration (1.0 g/3.0 mL, which corresponds to 1.72 mol/L) according to our previous result, in which better control of the polymerization of NVC using Z-CTA 1 was attained under the diluted condition.[43] When the polymerizations of NVC were conducted with these Z-designed tetrafunctional CTAs, the transparent solutions were maintained without any significant change in their viscosity during the polymerization. The polymerization with Z-CTA 2 was relatively fast, in which more than a 70% conversion (as determined by ^1H NMR spectroscopy in $CDCl_3$) was reached within 4 h. In contrast, less than a 50% conversion was reached even after 24 h with Z-CTA 1. In the case of the polymerization with R-CTA, an almost full conversion (95%) was reached after 8 h under these conditions. The star polymer obtained with R-CTA showed a narrower polydispersity ($M_w/M_n = 1.14$) compared to those obtained with two Z-designed CTAs ($M_w/M_n = 1.34-1.35$).

In all cases, the molecular weights of the poly(NVC) stars, measured by GPC in THF, were lower than the theoretical values calculated from the monomer/CTA molar ratio and conversion of the monomer. The molecular weights obtained by the conventional GPC using polystyrene calibration are just the apparent ones due to the compact nature of the branched macromolecules and the lack of suitable standards. Note that the same tendency, the significant difference between the $M_{n,SEC}$ and $M_{n,theory}$, was observed for the linear poly(NVC)s (see Supporting Information, Table S1, and our previous publication[34]). The lower $M_{n,SEC}$ measured by polystyrene calibration was also reported for linear poly(NVC) prepared by living cationic polymerization.[54] Therefore, these discrepancies are mainly due to small excluded volume of poly(NVC), in comparison to the polystyrene standards. The star polymers were further characterized by GPC using a right-angle laser light scattering detector (GPC-RALLS) in order to obtain the absolute molecular weights. In all cases, the GPC traces are unimodal with no evidence of high molecular weight species (see Supporting Information, Figure S3). Furthermore, the light scattering and RI detector gave similar curves, but with a slight difference in the elution time range. As can be seen in Table 1, the molecular weights estimated by GPC/RALLS are apparently higher than those obtained by the conventional GPC.

Polymerization of NVC Mediated with Z-Designed Tetrafunctional RAFT Agents. The effectiveness of the Z-designed tetrafunctional CTAs was compared by performing kinetic investigations. The polymerization of NVC was conducted with AIBN in 1,4-dioxane at 60 °C at the ratio $[NVC]_0/[CTA]_0/[AIBN]_0 = 200/1/1$. Figure 1 shows the variations in the monomer conversion and $\ln([M]_0/[M]_t)$ vs polymerization time. As expected, the polymerization with Z-CTA 2 was relatively fast, in which more than a 90% conversion was reached within 5 h. In contrast, no detectable polymer was obtained in the same time period when the polymerization was conducted with Z-CTA 1. For the polymerization with Z-CTA 1, induction periods of less than 6 h could be observed in the time−conversion plot (conversion = 4% at 6 h). The nonlinear first-order kinetic plot is also observed, suggesting that the radical concentration is not constant in the presence of Z-CTA 1. It is worth mentioning that the significant influence of the R-group structure in the Z-designed CTAs is seen on both the induction period and the polymerization rate, namely inhibition and retardation.

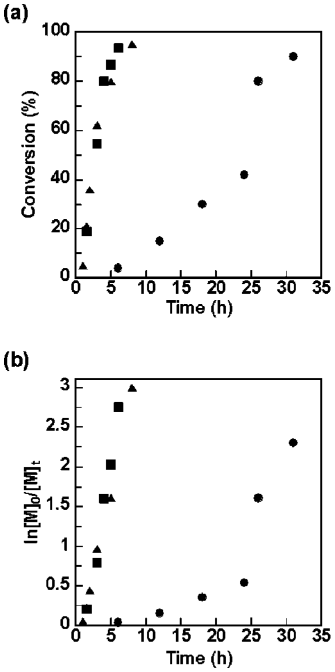


Figure 1. (a) Conversion as a function of polymerization time and (b) first-order kinetic plots for the polymerization of NVC with AIBN in the presence of Z-CTA 1 (circles), Z-CTA 2 (squares), and R-CTA (triangles) at $[NVC]_0/[CTA]_0/[AIBN]_0 = 200/1/1$ in 1,4-dioxane (1.0 g/3.0 mL, which corresponds to 1.72 mol/L) at 60 °C.

An induction period is often observed during the RAFT polymerization, and the reasons for the induction periods with some CTAs are not clearly understood. However, a number of possible explanations have been suggested,[55−59] including slow fragmentation of the initiating leaving group radical, slow reinitiation by the expelled radical, increased stability of the intermediate radical (with and without intermediate radical termination), tendency of the expelled radical to add to the CTA rather than to the monomer, and impurities in the CTA. For the synthesis of star polymers using the Z-group approach, there is an inherent difficulty in reaching a high conversion and high molecular weight material, which is due to the limited accessibility of the propagating polymer radicals to the thiocarbonylthio moiety present at the core.[23] This behavior may lead to a slower polymerization rate with Z-CTA 1 compared to that with the Z-CTA 2.

Figure 2a,b shows the evolution of M_n and M_w/M_n with conversion during the polymerizations of NVC with the Z-designed tetrafunctional CTAs. The linearity of the M_n vs conversion plots are observed in both cases, indicating that the polymerization proceeds in a controlled fashion. A progressive increase in the molar mass with conversion is clearly revealed by the narrow unimodal GPC peaks (Figure 2d,e), suggesting the well-defined nature of the poly(NVC) stars without detectable byproducts formed by unfavorable coupling reactions. Apparently, lower molecular weights of the star polymers compared to their theoretical values are observed, which should be due to the compact nature of the poly(NVC) stars. The polydispersity indices (M_w/M_n) for all samples prepared with

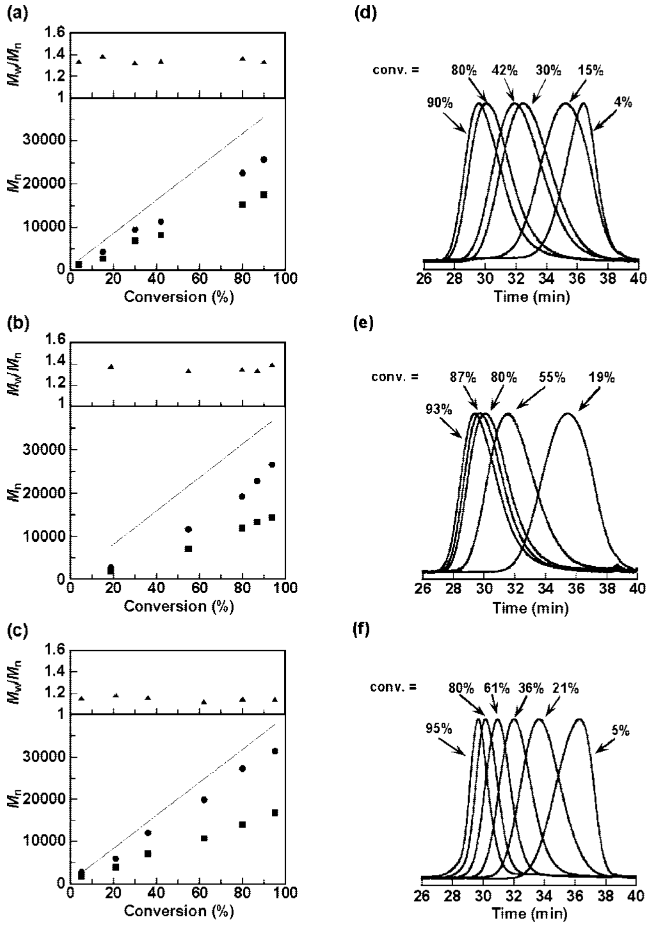


Figure 2. (a, b, c) Number-average molecular weight (GPC/RALLS: circles; GPC/RI: squares) and molecular weight distribution (triangles) as a function of conversion and (d, e, f) evolution of GPC traces with conversion for the polymerizations of NVC with AIBN in the presence of Z-CTA 1 (a, d), Z-CTA 2 (b, e), and R-CTA (c, f) at $[\mathrm{NVC}]_0/[\mathrm{CTA}]_0/[\mathrm{AIBN}]_0 = 200/1/1$ in 1,4-dioxane (1.0 g/3.0 mL, which corresponds to 1.72 mol/L) at 60 °C. Lines in (a)−(c) indicate the theoretical values.

the Z-designed CTAs ranged between 1.32 and 1.40, and these values remained constant, regardless of the conversion and the nature of the CTAs used in this study. These results suggest that the structure of the R group in the Z-designed CTAs has a clear effect on the polymerization kinetics but has no significant influence on the controlled character of the NVC polymerization.

Polymerization of NVC Mediated with R-Designed Tetrafunctional RAFT Agent. A kinetic investigation was also conducted in order to evaluate the effectiveness of the R-designed tetrafunctional CTA to achieve the controlled character of the polymerization. Figure 1 show the variations in the monomer conversion and $\ln([M]_0/[M]_t)$ vs time for the polymerization of NVC with R-CTA. The results of the polymerization with Z-CTA 2, which can be regarded as an analogue of R-CTA, are shown as a comparison, since both CTAs have similar R ($-\mathrm{CH(CH_3)COOCH_2}-$ vs $-\mathrm{CH(CH_3)COOCH_3}$) and Z ($-\mathrm{OCH_2CH_3}$ vs $-\mathrm{OCHH_2CH_2}-$) groups. When the polymerization was conducted with R-CTA, an almost full conversion (95%) was reached after 8 h, as shown in Figure 1a. A linear first-order kinetic plot is seen until the last stage of the polymerization (Figure 1b). The induction period roughly estimated simply by extrapolating the linear part of the curve to the time axis is less than 1 h, which is comparable to that with Z-CTA 2 (see Supporting Information, Figure S4). This is an indication that the induction period and the retardation are independent of the R-group or Z-group approach, while the chemical structure of the leaving group (R group) has a significant effect on both phenomena. As shown in Figure 2c, the number-average molecular weight increases with the conversion, maintaining a low polydispersity. The SEC traces (refractive index) of the poly(NVC) stars obtained at different reaction times are shown in Figure 2f. A progressive increase in the molar mass with conversion and narrow unimodal SEC peaks (M_w/M_n = 1.13−1.16) are clearly seen, as normally observed for a controlled/living polymerization. These results suggest that well-defined four-arm poly(NVC) stars could be synthesized using the R-designed tetrafunctional CTA even at a high conversion (>90%). This behavior is in good agreement with the theoretical guideline, suggesting that well-defined star polymers could be obtained from monomers having high propagation rate coefficients when using the R-group approach polymerization.[23,48] Actually, the R-group approach has been successfully used for the synthesis of well-defined star polymers of vinyl acetate[39,40] and *N*-vinylpyrrolidone,[42] which form relatively unstable (reactive) propagating radical species and thus have relatively large propagation rate coefficients.

Table 2. Effect of $[\mathrm{NVC}]_0/[\mathrm{R\text{-}CTA}]_0$ Ratio on MADIX/RAFT Polymerization of NVC with R-Designed Tetrafunctional Chain Transfer Agent (R-CTA) and 2,2′-Azobis(isobutyronitrile) (AIBN) in 1,4-Dioxane at 60 °C for 12 h[a]

entry	$[\mathrm{NVC}]_0$/ $[\mathrm{R\text{-}CTA}]_0$	$M_{n,\mathrm{theory}}$[b]	$M_{n,\mathrm{GPC}}$[c] (PDI)	$M_{n,\mathrm{RALLS}}$[d]	R_g[d] (nm)
1	200	39 100	18 000 (1.14)	33 300	4.0
2	400	77 400	40 300 (1.26)	54 200	5.3
3	600	115 600	61 900 (1.28)	81 400	6.7
4	800	153 900	78 700 (1.38)	102 300	7.8

[a] $[\mathrm{R\text{-}CTA}]_0/[\mathrm{AIBN}]_0 = 1$, monomer concentration = 1.0 g/3.0 mL (1.72 mol/L), conversion >99% in all cases. [b] Theoretical molecular weight ($M_{n,\mathrm{theory}}$) = (MW of NVC) × $[\mathrm{NVC}]_0/[\mathrm{CTA}]_0$ × conv + (MW of CTA). [c] Measured by size-exclusion chromatography (SEC) using polystyrene standards in THF with RI detector. [d] Measured by SEC in THF with RALLS detector.

With a view to preparing poly(NVC) stars over a wide range of molar masses, different degrees of polymerization were targeted. For this purpose, the polymerization of NVC using R-CTA was conducted at different $[\mathrm{NVC}]_0/[\mathrm{R\text{-}CTA}]_0$ ratios between 200 and 800, while the R-CTA/AIBN molar ratio was held constant at 1/1 (the xanthate moiety/AIBN molar ratio = 4). When the polymerizations were conducted in 1,4-dioxane ([M] = 1.0 g/3.0 mL, which corresponds to 1.72 mol/L) at 60 °C for 12 h, the conversions were quantitative in all cases (>99%, as determined by ^{1}H NMR spectroscopy), as shown in Table 2. The number-average molecular weights of the poly(NVC) stars increase with the [M]/[CTA] ratio, and the molecular weight distributions remain relatively narrow (M_w/M_n = 1.14−1.38), indicating the feasibility of controlling the molecular weights. In all cases, the SEC traces are unimodal with no evidence of high molecular weight species, as shown in Figure 3.

In all cases, the experimental molecular weights determined by GPC are apparently lower than the theoretical ones, as can be seen in Table 2. The molecular weights determined by GPC/RALLS are higher than the apparent ones obtained by conventional GPC, as expected. A slight difference between the theoretical values and the experimental values determined by GPC/RALLS is particularly seen at the higher $[\mathrm{NVC}]_0/[\mathrm{R\text{-}CTA}]_0$ ratios. Nevertheless, these results suggest good control of the NVC polymerization using the tetrafunctional R-CTA, leading to the belief that the molecular weight of the poly(NVC) stars can be easily adjusted by the monomer-to-CTA ratio under suitable conditions. The radii of gyration of the star polymers are quite low (R_g < 8 nm, Table 2), and this value slightly increases with the increasing $[\mathrm{NVC}]_0/[\mathrm{R\text{-}CTA}]_0$, which may corresponds to the arm length.

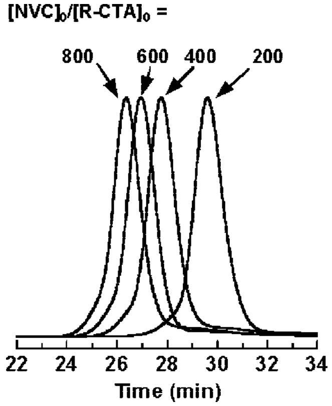


Figure 3. SEC traces of the four-arm poly(NVC)s obtained at different $[NVC]_0/[R\text{-}CTA]_0$ ratios (see Table 2 for detailed conditions).

Table 3. Characterization of Cleaved Arms of Poly(NVC) Stars

			cleaved arms		
entry	method	$M_{n,RALLS}$ of star polymer[a] (M_w/M_n)	$M_{n,theory}$[b]	$M_{n,GPC}$ (M_w/M_n)[c]	$M_{n,RALLS}$[a]
1	Z-CTA 1	22 600 (1.30)	7700	7600 (1.86)	8400
2	Z-CTA 2	22 900 (1.34)	8400	8200 (1.68)	10600
3	R-CTA	31 400 (1.13)	9200	6200 (1.21)	8300

[a] Measured by size-exclusion chromatography (SEC) in THF with RALLS detector. [b] Theoretical molecular weight ($M_{n,theory}$) = (MW of NVC) × $[NVC]_0/[CTA\ moiety]_0$ × conv. [c] Measured by SEC using polystyrene standards in THF with RI detector.

Arm Cleavage of the Poly(NVC) Stars. To determine the exact number and molecular weights of the arms of the stars prepared by the R-group and Z-group approaches, we conducted cleavage of the arms from the tetrafunctional CTAs. We employed three poly(NVC) stars having similar molecular weights ($M_{n,GPC\text{-}RALLS}$ = 22 600−31 400), which were prepared with Z-CTA 1, Z-CTA 2, and R-CTA, respectively. Table 3 summarizes the detailed characterization of the cleaved arms. For the poly(NVC) star polymer prepared by the R-group approach, the ester linkage between the core and arms was hydrolyzed via a base-catalyzed transesterification. As shown in Figure 4c, a clear shift in the GPC trace of the star polymer toward a low molecular weight region is seen, suggesting the effective cleavage of the ester group under these conditions. The GPC trace of the cleaved poly(NVC) arm is apparently broad and consist of two peaks, which suggest some coupling reaction. Nevertheless, the value of the molecular weight distribution is relatively low (M_w/M_n = 1.21). The absolute molecular weight of the cleaved arms determined using the GPC/RALLS measurement is in good agreement with the theoretical value, suggesting that each xanthate moiety linked to the core is involved in the formation of an arm via the chain growth from the core to afford a well-defined four-arm poly(NVC).

For the star polymers prepared with the Z-designed CTAs, the cleavage of the xanthate linkage between the core and arms was conducted by aminolysis using propylamine. As shown in Figure 4a,b, in both cases, the cleaved arms exhibited monomodal GPC traces with tailing in the low molecular weight regions, while there was no high molecular weight byproducts (twice molecular weight of one arm), which may have originated from unfavorable arm−arm coupling. The polydispersities of the cleaved arms (M_w/M_n = 1.68−1.86) are broader than those of the original star polymers (M_w/M_n = 1.30−1.34). The absolute molecular weights of the cleaved arms determined on the basis of the GPC/RALLS measurements are apparently higher than those of the theoretical values, suggesting that the average number of arms is lower than the number of xanthate functional groups present on the core in the Z-group approach.

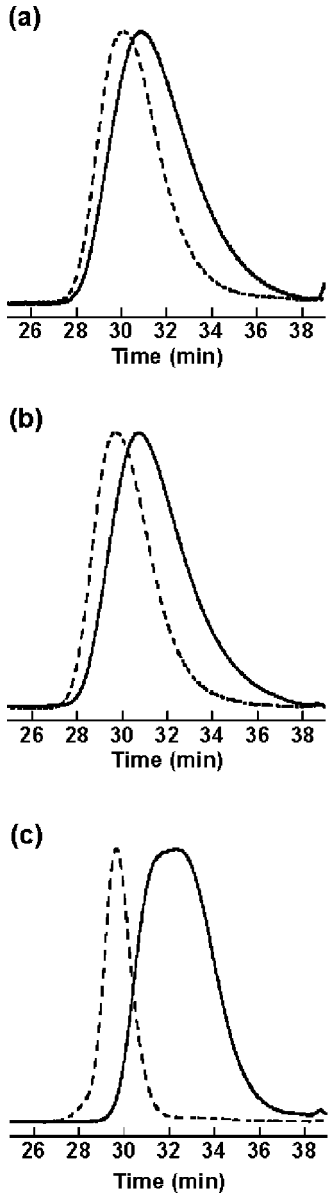


Figure 4. GPC traces of poly(NVC) stars (dotted traces) prepared with (a) Z-CTA 1, (b) Z-CTA 2, and (c) R-CTA and cleaved arms (solid traces).

On the basis of these results, we selected the R-designed CTA for our further investigations of the precise synthesis of amphiphilic star block copolymers involving poly(NVC) segments with characteristic optoelectronic properties.

Synthesis of Four-Arm Amphiphilic Star Block Copolymers. For the synthesis of well-defined amphiphilic star block copolymers containing poly(NVC) segments, we selected poly(acrylic acid), poly(AA), as a hydrophilic segment. The R-group approach was employed for the synthesis of well-defined amphiphilic star block copolymers having different compositions of the hydrophilic and hydrophobic segments and their chain lengths. We initially attempted to synthesize a star block copolymer, in which the poly(NVC) is located in the core and the poly(AA) in the shell, by polymerization of AA using the poly(NVC) star as a tetrafunctional macro-CTA. However, our first attempt was unsuccessful. As shown in Figure S5 (see Supporting Information), the SEC chromatogram of the product showed bimodal distributions, which may be attributed to the residue of the starting poly(NVC) star macro-CTA and second-growth polymer, suggesting an insufficient blocking efficiency

Table 4. Synthesis of Star Block Copolymers by the Polymerization of *N*-Vinylcarbazole (NVC) Using 2,2′-Azobis(isobutyronitrile) (AIBN) and Poly(AA) Star as a Macro-CTA in 1,4-Dioxane at 60 °C[a]

entry	$[NVC]_0/[macro\text{-}CTA]_0$	time (h)	conv[b] (%)	$M_{n,theory}$[c]	$M_{n\ SEC}$[d] (PDI)	$M_{n,NMR}$[b] ($M_{n,EA}$)[e]	composition[b] AA:NVC
1	50	12	78	16 600	12 300 (1.22)	15 400 (14 200)	78:22
2	100	4	68	22 300	13 700 (1.26)	23 900 (21 400)	60:40
3	100	12	95	27 400	15 300 (1.26)	30 500 (25 600)	51:49
4	200	12	90	43 900	24 800 (1.33)	48 300 (42 700)	36:64

[a] Poly(AA) star ($M_{n,NMR} = 9100$, $M_w/M_n = 1.16$, DP = 114), $[\text{poly(AA) star macro-CTA}]_0/[AIBN]_0 = 1$, monomer concentration = 1.0 g/4.0 mL (1.29 mol/L, entries 2−4), 1.0 g/8.0 mL (0.65 mol/L, entry 1). [b] Calculated by ^1H NMR in DMSO-d_6. [c] Theoretical molecular weight ($M_{n,theory}$) = (MW of NVC) × $[NVC]_0/[\text{poly(AA) star macro-CTA}]_0$ × conv + (M_n of macro-CTA). [d] Methylated samples were measured by size-exclusion chromatography (SEC) using polystyrene standards in THF. [e] Calculated by elementary analysis.

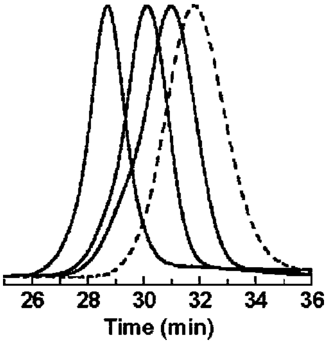


Figure 5. SEC traces of methylated products of poly(AA) star used as a tetrafunctional macro-CTA (dotted trace) and poly(AA-*b*-NVC) stars obtained by the polymerization of NVC at different $[NVC]_0/[macro\text{-}CTA]_0$ ratios (solid traces). See Table 4 for detailed polymerization conditions.

and/or the existence of a certain number of dead chains. This result is consistent with the general tendency of the order of blocking for the synthesis of well-defined block copolymers by the RAFT process.[60,61] In this case, the first xanthate-terminated star polymer (S=C(Z)S−A; A block corresponds to the poly(NVC) star, whereas Z is the O-ethyl group) should have a high transfer constant in the subsequent polymerization of the second monomers to give the B block. This requires that the leaving ability of the propagating poly(NVC) radical ($A^\bullet$) is greater than, or at least comparable to, that of the second poly(AA) radical ($B^\bullet$) under the given reaction conditions. In order to achieve a block copolymer with a low polydispersity, the rapid conversion of the macro-CTA into a block copolymer is also required, by which all of the second blocks can be initiated at approximately the same time.[55,62] In the next stage, therefore, we conducted the polymerization of NVC using the dithiocarbonate-terminated poly(AA) star as a macro-CTA under suitable conditions.

The chain extension of the four-arm star poly(AA) star with NVC results in the formation of a star block copolymer, in which the poly(AA) is located in the core and the poly(NVC) in the shell, as shown in Scheme 2. The reaction conditions, monomer conversions, molecular weights, polydispersities, and block copolymer compositions are summarized in Table 4. In all cases, the polymerization of NVC was carried out with AIBN using the dithiocarbonate-terminated poly(AA) star as a macro-CTA at 60 °C in 1,4-dioxane. The initial CTA-to-initiator ratio ($[macro\text{-}CTA]_0/[AIBN]_0$) was held constant at 1/1, while the monomer to CTA ratio ($[NVC]_0/[macro\text{-}CTA]_0 = 50-200$) was varied in order to control the comonomer content and the molecular weight of the star block copolymers. Figure 5 presents SEC traces of the methylated product of the starting poly(AA) star macro-CTA and the second-growth polymers, which were obtained by the polymerization, followed by methylation of the carboxylic acid groups.[52,53] A shift in the SEC trace toward higher molecular weight regions, with the polydispersity remaining of $M_w/M_n < 1.35$, clearly demonstrates the efficient block formation. There is no significant homopolymer impurity in the block copolymers. These results suggest a sufficient efficiency of the fragmentation from the intermediate radical to the poly(AA) radical combined with an efficient reinitiation, resulting in the rapid conversion of the poly(AA) macro-CTA into the block copolymer under the conditions used in this study.

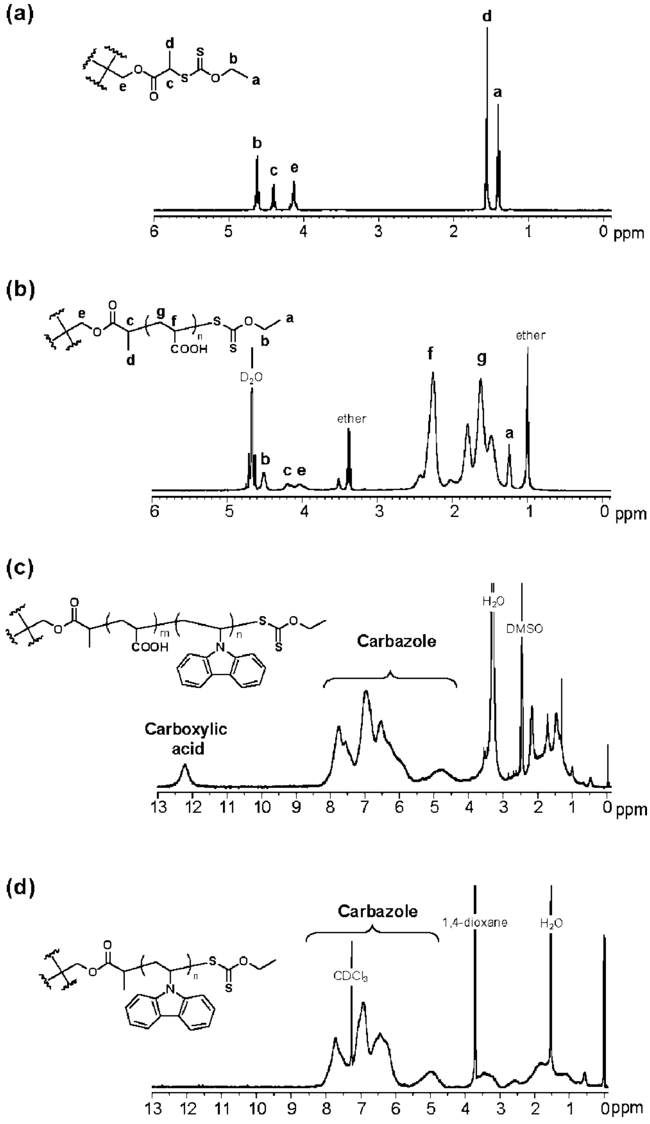


Figure 6. ^1H NMR spectra of (a) R-CTA ($CDCl_3$), (b) poly(AA) star (D_2O), (c) poly(AA-*b*-NVC) star (DMSO-d_6), and (d) poly(NVC) star ($CDCl_3$).

The ^1H NMR spectrum of the star block copolymer, $[\text{poly(AA)-}b\text{-poly(NVC)}]_4$, is shown in Figure 6. The peaks corresponding to poly(AA) and poly(NVC) are clearly observed in the spectrum measured in DMSO-d_6. Integration of the appropriate peaks gave a composition of AA and NVC, which was in good agreement with the composition determined by elemental analysis. The molecular weights of the star block copolymers evaluated from

Table 5. DLS Measurement of Amphiphilic Star Block Copolymers at 25 °C in THF, Chloroform, and Water[a]

entry	sample	THF D_h (nm)	chloroform D_h (nm)	water D_h (nm)
1	poly(AA$_{29}$-*b*-NVC$_8$)$_4$	24.3	20.6	31.9
2	poly(AA$_{29}$-*b*-NVC$_{19}$)$_4$	8.6	17.0	22.3
3	poly(AA$_{29}$-*b*-NVC$_{28}$)$_4$	8.7	17.9	62.2
4	poly(AA$_{29}$-*b*-NVC$_{51}$)$_4$	9.6	21.1	

[a] Concentration: 5.0 mg/mL (THF), 1.0 mg/mL (chloroform, water).

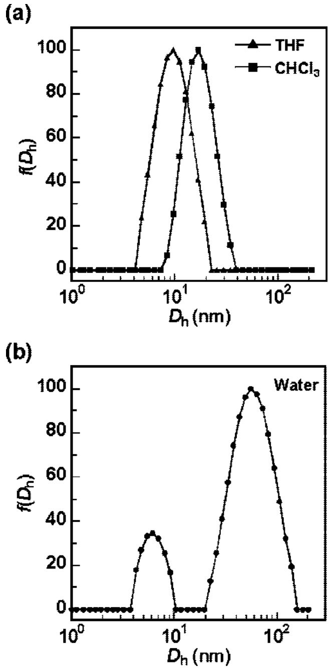


Figure 7. Hydrodynamic diameter distributions, *f*(D_h), of the micelles prepared from poly(AA$_{29}$-*b*-NVC$_{28}$)$_4$ in (a) THF (triangles) and chloroform (squares) and (b) water solution.

the composition and the molecular weight of the poly(AA) star macro-CTA are comparable to the theoretical values evaluated from the monomer conversion, [NVC]$_0$/[macro-CTA]$_0$ feed ratio, and the molecular weight of the macro-CTA. As shown in Table 4, the composition of each segment and molecular weights of the resulting star block copolymers could be adjusted by the [NVC]$_0$/[macro-CTA]$_0$ ratio in the feed and polymerization conditions. These results clearly demonstrate that the chain extension from the poly(AA) star macro-CTA to NVC can be well controlled and provides star block copolymers with as-designed chain structures and a narrow molecular weight distribution.

Solution and Optical Properties of Four-Arm Amphiphilic Star Block Copolymers. The solution properties of the amphiphilic star block copolymers were characterized using dynamic light scattering (DLS) at 90°. Table 5 shows the hydrodynamic diameter (D_h) of the amphiphilic stars in different solvents: THF, CHCl$_3$, and water. Initially, we conducted DLS measurements of the amphiphilic stars in THF solution, which is a good solvent for both components. The solution with a relatively high concentration (5.0 mg/mL) was employed to achieve a sufficient signal intensity. The hydrodynamic diameter distribution of a representative sample in THF is shown in Figure 7a. The diameters are small (8.6−9.6 nm), which are roughly consistent with unimolecular star micelles, and the size slightly increases with the degree of the polymerization of the NVC units, except for the sample having a low NVC content. This may be due to the lower solubility of the poly(AA) segment in THF, which may lead to the formation of aggregated structures. When these amphiphilic stars were dissolved in CHCl$_3$, which is a good solvent only for poly(NVC) segment, the size dramatically increases (17.0−21.1 nm). Since the size is independent of the chain length of the poly(NVC) segment in the amphiphilic stars, this behavior may be due to the fact that the unimolecular micelles coagulate to form larger aggregates.

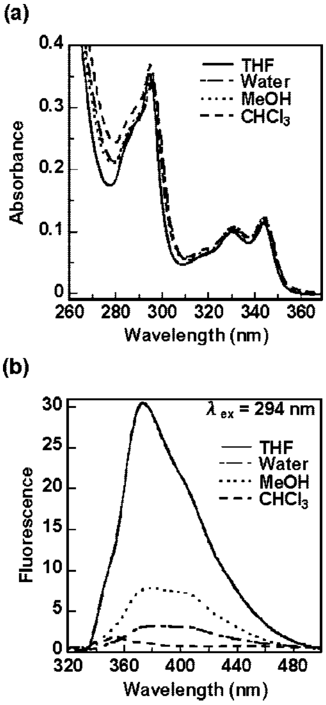


Figure 8. (a) Absorption (4.0×10^{-5} carbazole unit mol L^{-1}) and fluorescence (4.0×10^{-6} carbazole unit mol L^{-1}) spectra of poly(AA$_{29}$-*b*-NVC$_{28}$)$_4$ stars in THF, water, MeOH, and CHCl$_3$.

A DLS measurement was also performed to study the solution properties of the amphiphilic star in water, which is a good solvent only for the poly(AA) segment. A concentrated solution of the amphiphilic stars in DMF, which is a good solvent for both segments, was gradually dispersed in water through the slow addition of water. As shown in Figure 7b, the hydrodynamic diameter distribution at a scattering angle of 90° in water shows a bimodal distribution of $D_h = 11.5$ and 88 nm. A similar bimodal distribution was also observed in the sample prepared by dialysis (see Supporting Information). At the highest number of NVC units per arm (entry 4 in Table 5), precipitation took place during the sample preparation.

The optical properties of the amphiphilic stars were characterized in different solvents. Figure 8a depicts the absorbance spectra of a representative sample, the poly(AA$_{29}$-*b*-NVC$_{28}$)$_4$ star, measured in different solvents, i.e., THF, water, MeOH, and CHCl$_3$. All the amphiphilic stars absorb light in the range from 300 to 380 nm and exhibit absorption peaks at 294, 330, and 343 nm. These peak positions and intensities are independent of the nature of the solvent. The absorption peak of the star block copolymer overlaps with that of the poly(NVC) homopolymer. These results suggest a negligible effect of the ordered structure induced by a selective solvent on the absorbance.

The fluorescence spectra of the amphiphilic star in different solvents are shown in Figure 8b. The emission excited at 294 nm is observed between 330 and 480 nm in THF. In addition to the broad peak, two peaks are detected around 370 and 420 nm. The carbazole chromophore is known to give a partial-overlap (second) and a full-overlap (normal) excimer emission at 370 and 420 nm, respectively.[63−65] A drastic decrease in the peak intensities was observed in the other three solvents without any significant difference in the peak positions. In particular, only low intensities of these peaks are detected in $CHCl_3$, in which the poly(NVC) segment should well extend in the selective solvent. The same tendency was also observed in the fluorescence spectra excited at 343 nm (see Figure S7, Supporting Information). On the basis of these absorbance and fluorescence spectra, it is reasonable to consider that the carbazole groups in the amphiphilic star are too close in the selective solvent to drastically increase the local concentration of the carbazole group, resulting in the extinction. In other words, the amphiphilic stars having poly(NVC) segments possess specific conformation, like micelles and inverse micelles, which affects the characteristic optoelectronic properties. Further studies on the relationship between the optoelectronic properties and the micelle formation of the amphiphilic star block copolymers and linear block copolymers having different compositions and chain lengths are now in progress, which will be separately reported.

Conclusion

This work presented the controlled syntheses of the four-arm poly(NVC) stars and amphiphilic star block copolymers by xanthate-mediated radical polymerization using the tetrafunctional CTAs. The R-group approach was found to be the most efficient for the syntheses of the four-arm poly(NVC) stars having a low polydispersity and controlled molecular weights. A comparison of the polymerization behaviors using two Z-designed tetrafunctional xanthates suggested that the structure of the leaving group (R-group) had a clear effect on the polymerization kinetics involving an induction period and the retardation but had no significant influence on the controlled character of the polymerization. In contrast, the controlled character was affected by the R-group or Z-group approach, and the polymerization kinetics was independent of the difference in the approach. The polymerization of NVC using the poly(AA) star afforded the four-arm star block copolymers with amphiphilic arms, in which the length of the poly(AA) core was kept constant while the poly(NVC) block length in the shell was varied. We believe that this paper represents the first report on controlled synthesis of the amphiphilic star block copolymers containing the poly(NVC) segments, which show characteristic assembled structures and optical properties in selective solvents.

Acknowledgment. This work has been supported by Tokuyama Science Foundation. The authors acknowledge Professor Seigou Kawaguchi for help with DLS measurements.

Supporting Information Available: Figures showing the ^1H NMR spectrum of a representative crude poly(NVC) star, GPC traces of poly(NVC)s prepared by the polymerizations of NVC with different monofunctional CTAs (Table S1), comparison of light scattering (RALLS) and RI detector response of the GPC traces of poly(NVC) stars, comparison of the polymerization kinetics with Z-CTA 2 and R-CTA, GPC traces of the products obtained by chain extension of four-arm poly(NVC) star with AA, and vice versa, hydrodynamic diameter distributions of the micelles prepared from poly(AA_{29}-*b*-NVC_{28})$_4$ in water before and after the dialysis, and fluorescence spectra excited at 343 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111–182.

(2) Riess, G. *Prog. Polym. Sci.* **2003**, *28*, 1107–1170.

(3) Mori, H.; Müller, A. H. E. *Prog. Polym. Sci.* **2003**, *28*, 1403–1439.

(4) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A. *Prog. Polym. Sci.* **2005**, *30*, 725–782.

(5) Bernaerts, K. V.; Du Prez, F. E. *Prog. Polym. Sci.* **2006**, *31*, 671–722.

(6) Yagci, Y.; Tasdelen, M. A. *Prog. Polym. Sci.* **2006**, *31*, 1133–1170.

(7) Taton, D.; Gnanou, Y.; Matmour, R.; Angot, S.; Hou, S.; Francis, R.; Lepoittevin, B.; Moinard, D.; Babin, J. *Polym. Int.* **2006**, *55*, 1138–1145.

(8) Heise, A.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647–8648.

(9) Burguiere, C.; Pascual, S.; Bui, C.; Vairon, J.-P.; Charleux, B.; Davis, K. A.; Matyjaszewski, K.; Betremieux, I. *Macromolecules* **2001**, *34*, 4439–4450.

(10) Fang, Z.; Kennedy, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3662–3678.

(11) Whittaker, M. R.; Monteiro, M. J. *Langmuir* **2006**, *22*, 9746–9752.

(12) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *Langmuir* **2007**, *23*, 7887–7890.

(13) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562.

(14) Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 365–375.

(15) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410.

(16) McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312–325.

(17) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347–5393.

(18) Favier, A.; Charreyre, M.-T. *Macromol. Rapid Commun.* **2006**, *27*, 653–692.

(19) Moad, G.; Rizzardo, E.; Thang, S. *Aust. J. Chem.* **2006**, *59* (10), 669–692.

(20) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283–351.

(21) Barner-Kowollik, C.; Buback, M.; Charleux, B.; Coote, M. L.; Drache, M.; Fukuda, T.; Goto, A.; Klumperman, B.; Lowe, A. B.; Mcleary, J. B.; Moad, G.; Monteiro, M. J.; Sanderson, R. D.; Tonge, M. P.; Vana, P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5809–5831.

(22) Coote, M. L.; Krenske, E.; Izgorodina, E. I. *Macromol. Rapid Commun.* **2006**, *27*, 473–497.

(23) Barner, L.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2007**, *28*, 539–559.

(24) Goto, A.; Fukuda, T. *Prog. Polym. Sci.* **2004**, *29*, 329–385.

(25) Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079–1131.

(26) Barner-Kowollik, C., *Handbook of RAFT Polymerization*; Wiley-VCH: Weinheim, 2008.

(27) Stenzel, M. H.; Cummins, L.; Roberts, G. E.; Davis, T. R.; Vana, P.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2003**, *204*, 1160–1168.

(28) Coote, M. L.; Radom, L. *Macromolecules* **2004**, *37*, 590–596.

(29) Charmot, D.; Corpart, P.; Adam, H.; Zard, S. Z.; Biadatti, T.; Bouhadir, G. *Macromol. Symp.* **2000**, *150*, 23–32.

(30) Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. *Macromol. Rapid Commun.* **2000**, *21*, 1035–1039.

(31) Pound, G.; Aguesse, F.; McLeary, J. B.; Lange, R. F. M.; Klumperman, B. *Macromolecules* **2007**, *40*, 8861–8871.

(32) Wan, D. C.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules* **2005**, *38*, 10397–10405.

(33) Devasia, R.; Bindu, R. L.; Borsali, R.; Mougin, N.; Gnanou, Y. *Macromol. Symp.* **2005**, *229*, 8–17.

(34) Mori, H.; Ookuma, H.; Nakano, S.; Endo, T. *Macromol. Chem. Phys.* **2006**, *207*, 1005–1017.

(35) Maki, Y.; Mori, H.; Endo, T. *Macromolecules* **2007**, *40*, 6119−6130.

(36) Maki, Y.; Mori, H.; Endo, T. *Macromol. Chem. Phys.* **2007**, *208*, 2589–2599.

(37) Taton, D.; Wilczewska, A.-Z.; Destarac, M. *Macromol. Rapid Commun.* **2001**, *22*, 1497–1503.

(38) Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. *Macromol. Rapid Commun.* **2002**, *23*, 1049–1054.

(39) Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Chem. Commun. (Cambridge, U.K.)* **2004**, 1546–1547.

(40) Bernard, J.; Favier, A.; Zhang, L.; Nilasaroya, A.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Macromolecules* **2005**, *38*, 5475–5484.

(41) Boschmann, D.; Vana, P. *Polym. Bull.* **2005**, *53*, 231–242.

(42) Nguyen, U. T. L.; Eagles, K.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4372–4383.

(43) Mori, H.; Ookuma, H.; Endo, T. *Macromol. Symp.* **2007**, *249−250*, 406–411.

(44) Grazulevicius, J. V.; Strohriegl, P.; Pielichowski, J.; Pielichowski, K. *Prog. Polym. Sci.* **2003**, *28* (9), 1297–1401.

(45) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505–1513.

(46) Dureault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. *Macromolecules* **2004**, *37*, 5513–5519.
(47) Boschmann, D.; Vana, P. *Macromolecules* **2007**, *40*, 2683–2693.
(48) Chaffey-Millar, H.; Stenzel, M. H.; Davis, T. P.; Coote, M. L.; Barner-Kowollik, C. *Macromolecules* **2006**, *39*, 6406–6419.
(49) Vana, P.; Albertin, L.; Barner, L.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4032–4037.
(50) Muthukrishnan, S.; Plamper, F.; Mori, H.; Müller, A. H. E. *Macromolecules* **2005**, *38*, 10631–10642.
(51) Xue, L.; Agarwal, U. S.; Zhang, M.; Staal, B. B. P.; Müller, A. H. E.; Bailly, C. M. E.; Lemstra, P. J. *Macromolecules* **2005**, *38*, 2093–2100.
(52) Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2003**, *36*, 8260–8267.
(53) Mori, H.; Matsuyama, M.; Sutoh, K.; Endo, T. *Macromolecules* **2006**, *39*, 4351–4360.
(54) Sawamoto, M.; Fujimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916–920.
(55) Vana, P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11*, 823–835.
(56) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300–8306.
(57) Plummer, R.; Goh, Y.-K.; Whittaker, A. K.; Monteiro, M. J. *Macromolecules* **2005**, *38*, 5352–5355.
(58) Coote, M. L. *Macromolecules* **2004**, *37*, 5023–5031.
(59) McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2005**, *38*, 3151–3161.
(60) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071–2074.
(61) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243–245.
(62) Vasilieva, Y. A.; Thomas, D. B.; Scales, C. W.; McCormick, C. L. *Macromolecules* **2004**, *37*, 2728–2737.
(63) De Schryver, F. C.; Vandendriessche, J.; Toppet, S.; Demeyer, K.; Boens, N. *Macromolecules* **1982**, *15*, 406–408.
(64) Tsuchida, A.; Nagata, A.; Yamamoto, M.; Fukui, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1285–1289.
(65) Vandendriessche, J.; Palmans, P.; Toppet, S.; Boens, N.; De Schryver, F. C.; Masuhara, H. *J. Am. Chem. Soc.* **1984**, *106*, 8057–8064.

MA801266H