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Synthesis of Star Polymers Based on Xanthate-Mediated Controlled Radical Polymerization of *N*-Vinylcarbazole

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Summary: Poly(*N*-vinylcarbazole) [poly(NVC)] stars were synthesized by macromolecular design via interchange of xanthate (MADIX)/reversible addition-fragmentation chain transfer (RAFT) polymerization. Four-armed poly(NVC) stars with controlled molecular weights and low polydispersities were obtained using a tetrafunctional xanthate, in which the stabilizing groups are linked to the core. The controlled character of the polymerization was also confirmed by the linear increase in the molecular weight with the conversion. The comparison of the polymerization behaviors using the tetrafunctional xanthate and a monofunctional one suggested that the multifunctional core has a clear effect on the polymerization kinetics, but has no significant influence on the controlled character of the polymerization.

Keywords: N-vinyl carbazole; radical polymerization; reversible addition-fragmentation chain transfer (RAFT); star polymers; xanthate

Introduction

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.[1] Poly (*N*-vinylcarbazole) [poly(NVC)] is the first and the most widely studied polymeric photoconductor. NVC undergoes facile cationic polymerization with almost all cationic initiators to give poly(NVC), and living cationic polymerization of NVC with hydrogen iodide has been also reported.[2] Free radical initiators, such as azo compounds and peroxides, can readily polymerize NVC, and radical polymerization was used in manufacturing the polymer.[1]

Controlled/living radical polymerization has allowed to synthesize various functional polymers with predetermined molecular weights, narrow polydispersity, and controlled architectures by a facile approach. Among various controlled radical polymerization systems, reversible addition-fragmentation chain transfer (RAFT) polymerization has proven to be extremely versatile with respect to monomer type and reaction conditions.[3–6] Although several attempts to synthesize poly(NVC) using controlled/living radical polymerization systems have appeared in the literature, the convincing proof for the controlled character of the homopolymerization of NVC has not been provided. The difficulties in adapting the controlled radical polymerization to NVC may rely on the fact that the NVC propagating radical is relatively unstable and thus highly reactive, which is mainly due to the electron-donating carbazolyl pendant. Recently, we published the first report of the precise synthesis of poly(NVC)s by controlled radical polymerization of NVC using a xanthate-type mediating agent as a chain transfer agent (CTA, Scheme 1).[7] We demonstrated that the ability of the xanthate-type CTA to control the NVC

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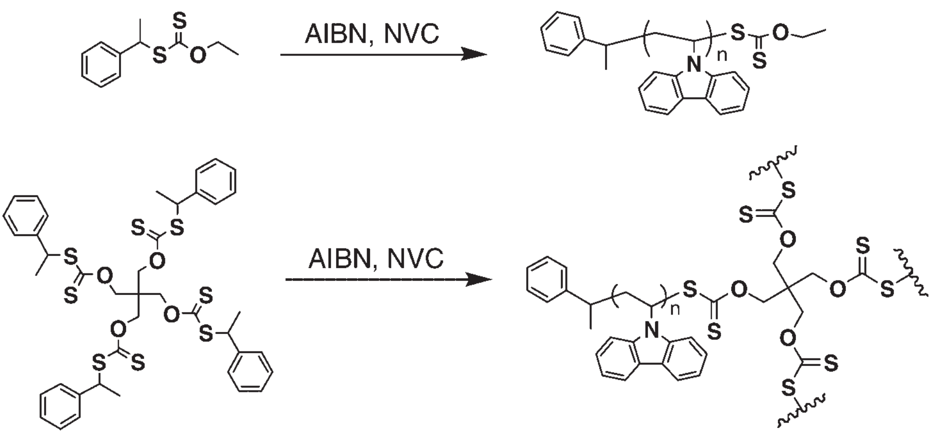

Scheme 1.
Synthesis of linear poly(NVC) and four-armed poly(NVC) star using xanthate-type chain transfer agents.

polymerization is correlated with the electron density on the central carbon atom of the xanthate and preferable fragmentation of a secondary carbon radical, 1-phenylethyl radical, from the intermediate. The electron-donating *O*-alkyl substituent leads to a destabilized intermediate radical center, which allows fragmentation via the release of the leaving group. An increased stability of the CTA through their conjugation also lowers the rate of addition of the propagating radicals to the sulfur atom. These effects may lead to a delicate balance of the forward and reverse rates of addition and fragmentation, together with the rates of reinitiation and propagation.

Here, we report the controlled synthesis of four-armed poly(NVC) star by RAFT/macromolecular design via interchange of xanthate (MADIX) polymerization using a tetrafunctional xanthate. In general, there are two main methods to obtain star polymers: either by linking a given number of linear chains to a central core ("arm-first" method) or by growing branches from an active core ("core-first" method). In RAFT/MADIX system, additionally two different approaches can be applied for the synthesis of star polymers; so-called R-group approach (propagation attached to core) and Z-group approach (propagation away from core).[8,9] In this study, we selected the Z-group approach using a tetrafunctional xanthate, in which the stabilizing groups are linked to the core via a nonfragmenting covalent bond, as shown in Scheme 1.

Experimental Part

Materials

N-Vinylcarbazole (NVC, Tokyo Kasei, 98%) was recrystallized two times from methanol. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. 1,4-Dioxane (Kanto Chemical, 99%) was distilled from sodium wire. Tetrafunctional xanthate-type chain transfer agent (tetrafunctional CTA) was synthesized from pentaerythritol according to previously reported method with slight modification.[10] Monofunctional CTA, *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate, used as a comparison was synthesized by the reaction of potassium *O*-ethyl dithiocarbonate with (1-bromoethyl)benzene.[7,11,12] All other materials were used without further purification.

Instrumentation

The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-ECX400. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by GPC using a system consisting of a Tosoh DP-8020 pump, a Viscotek TDA model-301 triple detector array (RI, Viscosity, and RALLS; wavelength = 670 nm). 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 (dn/dc = 0.253) was measured in THF at 25 °C using a DRM1021 differential refractometer operating at 633 nm.

General Polymerization Procedure

All polymerizations were carried out with AIBN as an initiator in the presence of CTA in a degassed sealed tube.

Results and Discussion

To examine suitable polymerization conditions for the synthesis of well-defined poly(NVC) stars, the polymerization of NVC was studied in the presence of the tetrafunctional CTA using AIBN as an initiator under various conditions. In the tetrafunctional CTA, 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). We initially investigated the polymerizations using different chain transfer agent-to-initiator ratios, $[CTA]_0/[AIBN]_0 = 0.5$, 1.0, and 2.5, since the ratio can frequently be a critical factor in determining the overall success of a RAFT/MADIX polymerization. Note that these CTA-to-AIBN ratios correspond to the xanthate moiety to AIBN ratios of 2, 4, and 10, respectively, because of the multifunctional nature of the CTA having quadruplicate concentration of the xanthate groups. In all cases, the polymerization was conducted in 1,4-dioxane at 60 °C, keeping the monomer-to-chain transfer agent ratio at a constant value of $[NVC]_0/[CTA]_0 = 200$. Under the conditions, the transparent solution maintained without significant change in the viscosity during the polymerization.

Figure 1 shows the variations of the monomer conversion and $\ln([M]_0/[M]_t)$ versus polymerization time. When NVC was polymerized at $[NVC]_0/[CTA]_0/[AIBN]_0 = 100/0.5/1$, almost full conversion (>90%, as determined by ^{1}H NMR spectroscopy in $CDCl_3$) was obtained at 60 °C after 20 h. The polymerization rate decreases apparently with increasing the $[CTA]_0/[AIBN]_0$ ratio. In all cases, induction periods of less than 10 h could be observed in the time-conversion plots. The non-linear first-order kinetic plots are also observed, suggesting that the radical

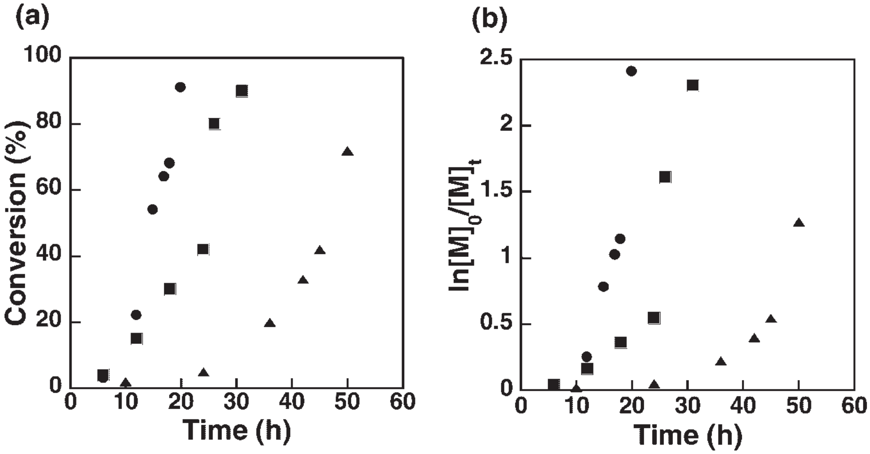

Figure 1.
(a) Conversion as a function of polymerization time and (b) first-order kinetic plot for the polymerization of NVC with AIBN in the presence of the tetrafunctional CTA (see Scheme 1) at $[NVC]_0/[CTA]_0 = 200$ in 1,4-dioxane (1.0 g/3.0 mL) at 60 °C. $[CTA]_0/[AIBN]_0 = 0.5$ (circles), 1.0 (squares), and 2.5 (triangles).

concentrations are not constant. It is worth mentioning that there was no significant influence of the $[CTA]_0$:$[AIBN]_0$ ratio on the induction period, whereas the polymerization rate, namely retardation, was apparently affected by the ratio. Similar tendency was also observed in our previous study on the synthesis of poly(NVC) homopolymer mediated by the corresponding monofunctional xanthate, *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate.[7] An induction period is often observed in 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,[13–17] 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 monomer, and impurities in the CTA.

Figure 2 shows the evolution of experimental molecular weight and polydispersity with monomer conversion. A linear increase of the M_n with conversion is clearly seen, as normally evidenced for a controlled/living polymerization. Each GPC trace (refractive index) of poly(NVC)s obtained at different reaction times exhibits a monomodal distribution, and no peak corresponding to star-star coupling is visible even at the last stage of the polymerization (conversion >80%). Hence, good control of the polymerization of NVC using the tetrafunctional CTA was confirmed by the formation of relatively narrow polydispersity products and the linear increase in the molecular weight with the conversion. These results are consistent with the inherent property of the Z-group approach, in which the leaving group radical reinitiates the polymerization away from the core and the chain equilibration takes place at the core site, resulting in the absence of star-star coupled byproduct.

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 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. The star polymers were further characterized by GPC with a right-angle laser light scattering detector (GPC-RALLS) in order to

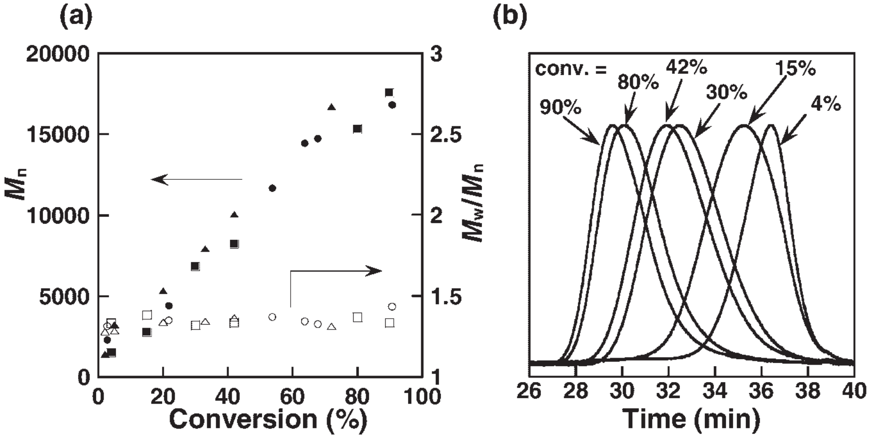

Figure 2.
(a) Number-average molecular weight and polydispersity as a function of conversion at $[CTA]_0/[AIBN]_0 = 0.5$ (circles), 1.0 (squares), and 2.5 (triangles), respectively. See Figure 1 for detailed polymerization conditions. (b) Evolution of GPC traces with conversion for the polymerization of NVC in the presence of the tetrafunctional CTA at $[NVC]_0/[CTA]_0/[AIBN]_0 = 200/1/1$.

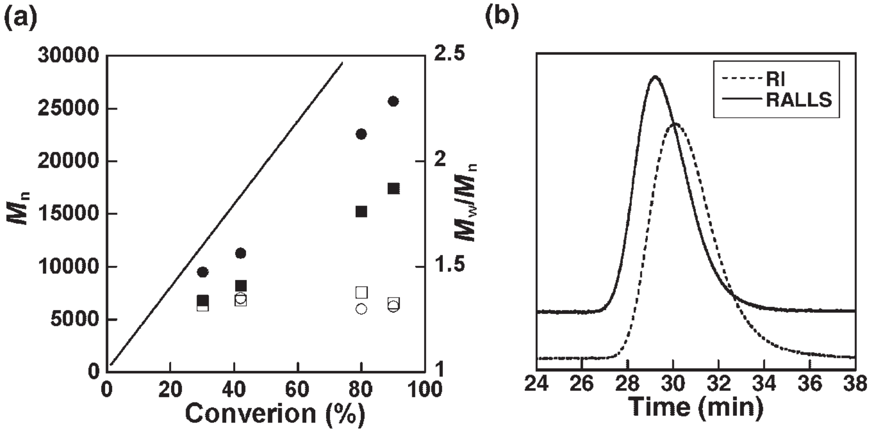

Figure 3.

(a) Number-average molecular weights and polydispersities, estimated by GPC/RALLS (circles) and conventional GPC (squares), as a function of conversion for the polymerization with the tetrafunctional CTA at $[NVC]_0/[CTA]_0/[AIBN]_0 = 200/1/1$. (b) Comparison of light scattering and RI detector responses of the GPC trace for a representative poly(NVC) star (conversion = 80%, $M_{n,GPC\text{-}RALLS} = 22600$, $M_w/M_n = 1.30$, as determined by GPC/RALLS, compared to $M_{n,GPC} = 15300$, $M_w/M_n = 1.38$).

obtain the absolute molecular weights. As shown in Figure 3, the molecular weights estimated by GPC/RALLS are apparently higher than those obtained by conventional GPC. A progressive increase in the molar mass with conversion is clearly revealed by the narrow unimodal GPC-RALLS peaks, suggesting well-defined nature of the poly(NVC) stars without detectable byproducts formed by unfavorable coupling reactions.

In order to clarify the effect of the multifunctional CTA on the control of the polymerization of NVC, we compared RAFT polymerizations with the monofunctional CTA, *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate, and the tetrafunctional CTA (Scheme 1) under the same conditions. The polymerization was carried out with AIBN at the ratio $[NVC]_0/[CTA]_0 = 200$ and $[\text{xanthate moiety}]_0/[AIBN]_0 = 2$. The pseudo-first-order kinetic plots are shown in

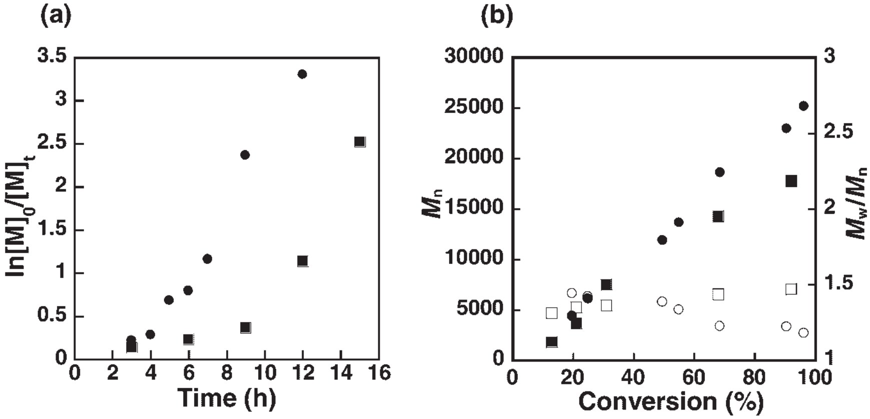

Figure 4.

(a) First-order kinetic plots and (b) number-average molecular weights and polydispersities as a function of conversion for the polymerizations of NVC at 60 °C with AIBN in the presence of the tetrafunctional CTA (squares) and the corresponding monofunctional xanthate (circles) in 1,4-dioxane (1.0 g/1.5 mL) at the ratio $[NVC]_0/[CTA]_0 = 200$ and $[\text{xanthate moiety}]_0/[AIBN]_0 = 2$.

Figure 4a. As expected, the polymerization with the monofunctional CTA was relatively fast, in which more than 90% conversion was reached within 10 h. In contrast, less than 40% conversion could be reached in the same time period when the polymerization was conducted with the tetrafunctional CTA. For the synthesis of star polymers using Z-group approach, there is an inherent difficulty to reach high conversion and high molecular weight material, which is due to the limited accessibility of the propagating polymer radicals to the thiocarbonylthio moiety existed at the core. The behavior may lead to slower polymerization rate with the tetrafunctional CTA, compared to that with the monofunctional one.

Figure 4b shows the evolution of M_n and M_w/M_n with conversion during the polymerizations of NVC with the mono- and tetrafunctional CTAs. The linearity of the M_n versus conversion plots are observed in both cases, indicating that the polymerization proceeds in a controlled fashion. Slightly lower molecular weights of the star polymers compared to their linear analogues are observed, and the difference is more pronounced at higher molecular weight region. This may be due to the compact nature of the poly(NVC) stars. The polydispersity indices (M_w/M_n) for all samples prepared with the tetrafunctional CTA ranged between 1.31 and 1.47, and the value remained constant, regardless of the conversion. The tendency is slightly different from the polymerization with the monofunctional CTA, in which the polydispersity decreased gradually with increasing the conversion, reaching a final value of less than 1.22 at >90%. These results suggest that the multifunctional xanthate used as CTA has a clear effect on the polymerization kinetics, but has no significant influence on the control of the polymerization of NVC.

Conclusions

The tetrafunctional xanthate, in which the stabilizing groups are linked to the core, was used to obtain four-armed poly(NVC) stars with narrow polydispersity by RAFT/MADIX polymerization. To the best of our knowledge, this is the first report of the controlled synthesis of poly(NVC) star using xanthate-mediated controlled radical polymerization. This work substantially broadens and extends the scope of carbazole-containing polymers, in which precise control of the molecular weight, polydispersity, and topology can be achieved using xanthate-mediated controlled radical polymerization technique. Further studies on the properties of the poly(NVC) stars obtained in this study, such as photoconductivity and electroluminescence, will be reported.

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