Controlled Synthesis of Poly(*N*-ethyl-3-vinylcarbazole) and Block Copolymers via RAFT Polymerization

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ABSTRACT: Poly(*N*-ethyl-3-vinylcarbazole), in which the carbazole unit is directly bound to the polymer main chain, has been synthesized by reversible addition−fragmentation chain transfer (RAFT) polymerization. The homopolymers with controlled molecular weights and low polydispersities ($M_w/M_n = 1.15-1.29$) were obtained by the polymerization of *N*-ethyl-3-vinylcarbazole (E3VC) with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator in the presence of benzyl 1-pyrrolecarbodithioate as a chain transfer agent (CTA). Good control of the polymerization was confirmed by the linear first-order kinetic plot, linear increase in the molecular weight with the conversion, and the linear relationship between the molecular weight and the monomer/CTA molar ratio. Successful chain extension from dithiocarbamate-terminated poly(E3VC) was also observed. Well-defined block copolymers with poly(E3VC) segment have been synthesized using the dithiocarbamate-terminated polystyrene as a macro-CTA. The resulting polymers, poly(E3VC) and polystyrene-*b*-poly(E3VC), absorbed light in the range from 300 to 380 nm and exhibited excimer emission at 454 nm with blue fluorescence. These polymers showed thermal stability above 350 °C under nitrogen.

Introduction

Carbazole-based compounds are of considerable scientific and industrial interest due to their attractive features, such as hole-transporting, high charge carrier, and electroluminescent properties. Since the first success of poly(*N*-vinylcarbazole) in electrophotographic applications, numerous studies have been devoted to carbazole-containing polymers.[1] Recent development in this field is connected mostly to the applications in polymeric light-emitting diodes, organic photorefractive materials, and photovoltaic devices. In general, the carbazole-containing polymers can be divided into two groups: polymers containing carbazole moieties in the main chain or side chain. Poly(*N*-vinylcarbazole) belongs to polymers having carbazolyl groups in the side chains. A variety of polymers with pendant carbazolyl groups have been reported, including polyacrylate,[2,3] polymethacrylate,[4−6] and polystyrene[7,8] derivatives. Many factors, such as chemical structures, polymer architectures, conformation, location, and stacking of the carbazole units, play a crucial role in manipulation of the properties and in several practical applications. However, it was difficult to control the molecular weights and their architectures because most of these polymers with pendant carbazolyl groups have been synthesized by conventional radical polymerization. To manipulate unique electronic and photonic functions, it is desirable to establish precise synthetic methods to control molecular weight, polydispersity, topology, composition, and functions.

Controlled/living radical polymerization combines the benefits of the robust nature of conventional radical polymerization with the capability to prepare well-defined macromolecular architectures common to living polymerization techniques. This method has allowed to synthesize various functional polymers with predetermined molecular weights, narrow molecular weight distribution, and controlled architectures, such as graft and block copolymers, by a facile approach. The systems include atom transfer radical polymerization,[9,10] nitroxide-mediated radical polymerization,[11] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[12,13] Several attempts to synthesize polymers with pendant carbazolyl groups using controlled/living radical polymerization systems have appeared in the literature. However, the control of synthesis is still questionable. For example, Fukuda et al. demonstrated that the control of *N*-vinylcarbazole homopolymerization could not be achieved by a typical nitroxide-mediated radical polymerization, whereas the copolymerization with styrene under the same conditions proceeded in a living fashion.[14] Nitroxide-mediated controlled copolymerization of styrene and *N*-vinylcarbazole was also reported by another group, while they demonstrated that the synthesis of the homopolymer, poly(*N*-vinylcarbazole), with controlled molecular weights and narrow polydispersity was still problematic.[15,16] Nowakowska et al. reported that the synthesis of poly(sodium styrenesulfonate-*b*-*N*-vinylcarbazole) by nitroxide-mediated radical polymerization was possible only when the polymerization of *N*-vinylcarbazole was conducted in the presence of acetic anhydride as an accelerator.[17] Unfortunately, there was no detailed information on the homopolymerization of *N*-vinylcarbazole, reaction mechanism, and structure of the block copolymer. Atom transfer radical polymerization (ATRP, $C_{60}Cl_n$/CuCl/2,2′-bipyridine) was also applied for the synthesis of poly(*N*-vinylcarbazole) having narrow polydispersity ($M_w/M_n = 1.33$). However, the actual structure of the product was a starlike architecture with a C_{60} core because of multiple chlorine atoms in one initiator molecule, $C_{60}Cl_n$, and there was no information on each poly(*N*-vinylcarbazole) and their detachments from the surface of C_{60}.[18] They also demonstrated that the attempt to

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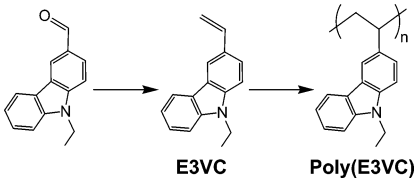
Scheme 1



synthesize the block copolymer, poly(*N*-vinylcarbazole-*b*-styrene), using this ATRP system provided products having bimodal molecular weight distributions.[19] In all cases, as described above, the convincing proof for the controlled character of the homopolymerization of *N*-vinylcarbazole, such as kinetic investigation, evaluation of the end groups, and chain extension experiment, was not provided. In particular, controlled synthesis of block copolymers containing *N*-vinylcarbazole segments remains a concern.

Here, we report the synthesis of poly(*N*-ethyl-3-vinylcarbazole), poly(E3VC), with controlled molecular weights and narrow molecular weight distribution by controlled radical polymerization (Scheme 1). *N*-Ethyl-3-vinylcarbazole (E3VC), which can be regarded as a styrene derivative, was chosen as a carbazole-containing monomer because the carbazole unit is directly bound to the polymer main chain formed after the polymerization. Poly(E3VC) was reported to be synthesized by cationic polymerization with a boron trifluoride initiator,[20,21] while detailed investigation of the polymerization behavior was not given. The direct linkage of the carbazole unit to the polymer main chain is an important feature of this monomer because it may affect not only the polymerization behavior but also electronic and photonic properties. For example, systematic investigations of photophysical properties of various polymethacrylate derivatives suggested that carbazole-containing polymers have no excimer-forming sites, except when the carbazole units are directly connected to the main chain.[6] Characterization of photoinduced discharge property of polyacrylates, in which the carbazole groups are separated from the polymer backbone by alkyl spacers of different lengths, has also shown an interesting effect of the spacer length.[3]

In this study, we employed RAFT polymerization for the synthesis of well-defined poly(E3VC) because the process appears to be the most tolerant of a wide range of monomers, functional groups, and reaction conditions. Additionally, ease of scale-up of the reaction process and no pollution of final product by metal residues make it a promising technique to produce functional polymers for various electrooptical applications. The controlled/living character of the RAFT polymerization of E3VC using a suitable chain transfer agent (CTA) was investigated by performing kinetic measurements and chain extension experiments. We also demonstrated the ability to synthesize block copolymers in a controlled fashion by chain extension from a macro-chain transfer agent (macro-CTA) with an appropriate comonomer.

Experimental Section

Materials. *N*-Ethylcarbazole-3-carboxaldehyde (Kanto Chemical, 94%), methyltriphenylphosphonium bromide (Kanto Chemical, 98%), and *n*-BuLi (Kanto Chemical, 1.6 M hexane solution) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. THF (Kanto Chemical, 99%) was distilled over sodium wire, and toluene (Kanto Chemical, 99.5%) was distilled before use. Other materials were used without further purification. Synthesis of chain transfer agent (CTA), benzyl 1-pyrrolecarbodithioate, was carried out according to the procedure reported in the literature.[22] The product was finally purified by column chromatography on silica with *n*-hexane as the eluent to afford the corresponding CTA as a yellow oil (^{1}H and ^{13}C NMR spectra; see Supporting Information).

***N*-Ethyl-3-vinylcarbazole.** The monomer was prepared by the Wittig reaction of *N*-ethylcarbazole-3-carboxaldehyde according to a method reported previously with a slight modification (Scheme 1).[20] Methyltriphenylphosphonium bromide (10.27 g, 0.0288 mol) and dry THF (86.5 mL) were placed in a 500 mL three-necked flask. The hexane solution of *n*-BuLi (1.60 M, 18 mL, 0.0288 mol) was added dropwise to the mixture under a nitrogen atmosphere at room temperature and was vigorously stirred for 2 h. Then, *N*-ethylcarbazole-3-carboxaldehyde (5.58 g, 0.025 mol) in dry THF (37.5 mL) was added gradually to the reaction mixture, which was refluxed for 1.5 h. After the reaction mixture was cooled to room temperature, it was dropped into hexane (220 mL). The precipitate, which corresponds to phosphonium oxide, was filtered off, and the filtrate was evaporated under reduced pressure to give a crude product. The crude monomer was purified by recrystallization from ethanol to give white needles (2.63 g, 48%); mp = 69.6 °C (lit.[20] 66−67 °C). ^{1}H NMR ($CDCl_3$): δ 1.43 (t, 3H, CH_3), 4.36 (q, 2H, NCH_2), 5.19, 5.77 (2d, 2H, $-C{=}CH_2$), 6.92 (dd, 1H, $=CH$), 7.23−7.58 (m, 5H, ArH), 8.11−8.12 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$): δ 14.4 (CH_3), 38.2 (NCH_2), 109.2, 109.3, 111.7 ($=CH_2$), 119.3, 119.7, 121.2, 123.8, 123.9, 124.8, 126.5, 129.7 ($=CH$), 138.4, 140.6, 141.2. Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 87.04; H, 6.95; N, 6.28.

General Polymerization Procedure. For a typical polymerization, *N*-ethyl-3-vinylcarbazole (E3VC, 0.80 g, 3.6 mmol), benzyl 1-pyrrolecarbodithioate (8.4 mg, 0.036 mmol), AIBN (3.0 mg, 0.018 mmol), and toluene (1.2 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. The ampule was flame-sealed under vacuum and allowed to stand at 60 °C for 24 h. The characteristic pale yellow color maintained during the polymerization. The reaction was stopped by rapid cooling with liquid nitrogen. The reaction mixture was precipitated in a large excess of methanol and isolated by filtration. The resulting product was finally dried under vacuum at room temperature to yield poly(E3VC) as a pale yellow powder. The polymer had M_n = 13 600 and M_w/M_n = 1.25 according to GPC using polystyrene calibration. For the determination of the monomer conversion, the ^{1}H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in $CDCl_3$, and the integration of the monomer C=C−H peak at around 5.2 ppm was compared with the intensity of the sum of the methylene peaks (NCH_2) of the polymer and the monomer at 3.0−4.5 ppm. Conversion determined by this method was 94%. Additionally, the polymer yield was gravimetrically determined from the methanol-insoluble polymer sample (yield = 93%, 0.74 g). The resulting polymer was soluble in dichloromethane, benzene, dioxane, and DMF while insoluble in acetone, diethyl ether, hexane, and water. ^{1}H NMR ($CDCl_3$): δ 0.6−1.4 (broad s, 3H, CH_3), 1.4−3.0 (broad m, 3H, CH_2-CH), 3.4−4.4 (broad s, 2H, NCH_2), 5.7−8.2 (broad m, 7H, ArH).

The theoretical number-average molecular weight on conversion is defined as follows:

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

where M_{CTA} and $M_{monomer}$ are molecular weights of chain transfer agent and monomer, and $[monomer]_0$ and $[CTA]_0$ are the initial concentrations of monomer and chain transfer agent, respectively.

Chain Extension Using Poly(*N*-ethyl-3-vinylcarbazole) as Macro-CTA. For the chain extension experiments, poly(E3VC) having lower molecular weights was prepared

according to the above procedure. E3VC (0.60 g, 2.7 mmol), CTA (25.3 mg, 0.11 mmol), AIBN (9.0 mg, 0.055 mmol), and toluene (0.9 mL) were placed in an ampule, and then the solution was degassed by three freeze−evacuate−thaw cycles. The ampule was subsequently immersed in an oil bath preheated to 60 °C, and the polymerization mixture was stirred for 2 h before being quenched by rapid cooling with liquid nitrogen. Conversion of the double bonds, as detected by ^{1}H NMR, was 26%. The resulting poly(E3VC) had an M_n (as determined by SEC) of 1800 and a polydispersity index of 1.16. The product was purified by precipitation into methanol and then isolated by filtration. Finally, the resulting poly(E3VC) was freeze-dried from dioxane and dried under vacuum at room temperature.

A representative example of chain extension experiment is as follows: the dithiocarbamate-terminated poly(E3VC) (0.0326 g, 0.018 mmol; M_n = 1800, M_w/M_n = 1.16), E3VC (0.40 g, 1.8 mmol), AIBN (1.5 mg, 0.009 mmol), and toluene (3.0 mL) were placed in a dry ampule, and then the solution was degassed by three freeze−evacuate−thaw cycles. The polymerization was conducted at 60 °C for 24 h. Polymer yield determined from the methanol-insoluble sample was 62%. The resulting poly(E3VC) had an M_n (as determined by SEC) of 12 100 and a polydispersity index of 1.20. Chain extension to prepare poly(E3VC)-*b*-polystyrene was also carried out using the dithiocarbamate-terminated poly(E3VC) in a similar way (see Supporting Information).

Synthesis of Block Copolymers Using Polystyrene as Macro-CTA. Polystyrene employed as macro-CTA was prepared using benzyl 1-pyrrolecarbodithioate as a CTA and AIBN as an initiator. A representative example is as follows: styrene (1.07 g, 10.3 mmol), CTA (22.4 mg, 0.096 mmol), AIBN (7.9 mg, 0.048 mmol), and toluene (1.5 mL) were placed in an ampule, and then the solution was degassed by three freeze−evacuate−thaw cycles. The ampule was subsequently immersed in an oil bath preheated to 60 °C, and the polymerization was conducted for 12 h. The polystyrene had an M_n (as determined by SEC) of 4000 and a polydispersity index of 1.26 with 29% conversion. The product was purified by precipitation into methanol and then isolated by filtration. Finally, the resulting polystyrene was freeze-dried from dioxane and dried under vacuum at room temperature.

A representative example of the synthesis of the block copolymer using polystyrene macro-CTA is as follows: the dithiocarbamate-terminated polystyrene (0.0632 g, 0.016 mmol; M_n = 4000, M_w/M_n = 1.26), E3VC (0.350 g, 1.6 mmol), AIBN (1.3 mg, 0.008 mmol), and toluene (2.6 mL) were placed in a dry ampule. After the solution was degassed by three freeze−evacuate−thaw cycles, the polymerization was conducted at 60 °C for 24 h. Conversion of the double bonds, as detected by ^{1}H NMR, was 65%. The reaction mixture was precipitated in a large excess of methanol and isolated by filtration (polymer yield = 62%). The resulting block copolymer had an M_n (as determined by SEC) of 11 600 and a polydispersity index of 1.19. ^{1}H NMR ($CDCl_3$): δ 0.4−2.8 (broad m, CH_3 and CH_2−CH), 3.2−4.4 (broad s, NCH_2), 5.6−8.2 (broad m, ArH).

Block copolymer composition (styrene/E3VC = 38/62) was determined using ^{1}H NMR spectroscopy by a comparison of peaks associated with the two comonomers. The peak at 3.0−4.4 ppm is attributed the methylene protons (NCH_2, 2H) of the poly(E3VC) segment, whereas the peaks at 0.4−2.8 ppm correspond to the sum of methylene and methine protons in the backbone of both segments (3H for E3VC + 3H for styrene) and methyl protons (NCH_2CH_3, 3H) of the poly(E3VC). Thus, the comonomer composition can be calculated using the eq 2,

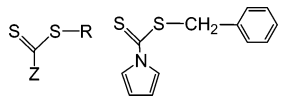
$$\frac{2(x)}{6(x) + 3(1 - x)} = \frac{\text{integral at 3.0−4.4 ppm}}{\text{integral at 0.4−2.8 ppm}} \qquad (2)$$

where x is the fraction of the E3VC and $1 - x$ is the fraction of the styrene in the block copolymer.

Instrumentation. ^{1}H (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were recorded with a JEOL EX-270. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated by size-exclusion chromatography (SEC) using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors at 40 °C. The column set was as follows: three consecutive hydrophilic vinyl polymer-based gel columns [TSK-GELs (bead size, exclusion limited molecular weight): SuperAW5000 (7 μm, 4 × 10^6), SuperAW4000 (6 μm, 4 × 10^5), SuperAW3000 (4 μm, 6 × 10^4), 15 cm each] and a guard column [TSK-guardcolumn Super AW-H, 3.5 cm]. The system was operated at a flow rate of 0.6 mL/min using *N*,*N*-dimethylformamide (DMF) containing 10 mM LiBr as an eluent. Polystyrene standards were employed for calibration. GPC with a multiangle light scattering detector (GPC-MALS) was also performed to determine the true molecular weights of the resulting polymer. The measurement was conducted using a Shodex GPC system 21 with two consecutive columns (Shodex KD-806M × 2, exclusion limited molecular weight = 2 × 10^7, 30 cm each) and DAWN DSP-F (Wyatt Technology Co.) detector equipped with He−Ne laser (632.8 nm). DMF containing 10 mM LiBr was used as an eluent at a flow rate of 1.0 mL/min. Excess refractive index increment (d*n*/d*c*) was measured using a differential refractometer DRM1021 at 25 °C.

The UV−vis spectra were recorded with a JASCO V-550-DS spectrophotometer. Fluorescence spectra were obtained from a JASCO FP-6500 spectrofluorometer. Thermogravimetric analysis (TGA) was performed on a SEIKO SSC/5200 at a heating rate of 10 °C/min under N_2. For differential scanning calorimetry (DSC) measurements, a SEIKO DSC/6200 apparatus was used (heating rate: 20 °C/min; cooling rate: 10 °C/min). Samples were heated from 30 to 300 °C at a rate of 20 °C/min, kept for 1 min, and cooled at a rate of 10 °C/min. The data collection was carried out on the second heating process, and the glass transition temperature (T_g) was taken to be the midpoint—the temperature corresponding to half of the endothermic shift. The calorimeter was calibrated with an indium standard. Elemental analysis was carried out on a Perkin-Elmer 2400II CHNS/O analyzer.

Scheme 2



Results and Discussion

Homopolymerization of *N*-Ethyl-3-vinylcarbazole (E3VC). RAFT involves a reversible addition−fragmentation chain transfer between an active and a dormant species, and the polymerization is performed by adding a suitable chain transfer agent (CTA). It has been demonstrated that successful implementation of the RAFT process requires careful selection of the CTA and reaction conditions, depending upon the monomer.[22−26] The Z group (Scheme 2) stabilizes the intermediate radical and promotes addition to the C=S bond, while the R moiety should be a good homolytic leaving group, and the formed R* radical should be able to reinitiate the polymerization. Here, we selected benzyl 1-pyrrolecarbodithioate as the CTA because it had been used for RAFT polymerization of styrene,[22,27] methyl acrylate,[27] and a nitrogen-containing monomer, *N*-isopropylacrylamide.[28]

Polymerization of *N*-ethyl-3-vinylcarbazole (E3VC) was conducted at 60 °C using benzyl 1-pyrrolecarbodithioate as the CTA and AIBN as an initiator under various conditions. Table 1 summarizes the conditions and the results. When E3VC was polymerized in toluene at $[M]_0/[CTA]_0$ = 50 using a ratio of AIBN to CTA of 1:2, high conversion (>95% determined by ^{1}H NMR) was reached after 24 h, and a polymer was obtained as a powder (entry 2, Table 1). The characteristic pale yellow

Table 1. Polymerization of *N*-Ethyl-3-vinylcarbazole Using AIBN as Initiator and Benzyl 1-Pyrrolecarbodithioate as Chain Transfer Agent at 60 °C

					$M_n \times 10^{-3}$		
entry	$[E3VC]_0:[CTA]_0:[AIBN]_0$[a]	solvent	time (h)	conv[b] (%)	theory	SEC[c]	M_w/M_n[c]
1	100:0:1	toluene	6	83		116.6	2.16
2	100:2:1	toluene	24	96	11.0	7.4	1.29
3	60:2:1	toluene	2.5	28	2.1	1.8	1.19
4	200:2:1	toluene	24	94	21.2	13.6	1.25
5	200:2:1	1,4-dioxane	24	95	21.1	12.4	1.30
6	200:2:1	chlorobenzene	24	98	21.8	11.7	1.36
7	300:2:1	toluene	24	91	30.6	20.0	1.17
8	400:2:1	toluene	24	86	37.6	23.8	1.15

[a] E3VC = *N*-ethyl-3-vinylcarbazole, CTA = benzyl 1-pyrrolecarbodithioate, and AIBN = 2,2′-azobis(isobutyronitrile); monomer concentration = 1.0 g/1.5 mL. [b] Calculated by ^{1}H NMR. [c] Measured by SEC using polystyrene standards in DMF containing 0.01 M LiBr.

color of the solution maintained without significant change in the viscosity during the polymerization. The molecular weight distribution of the resulting poly(E3VC) was narrow (M_w/M_n = 1.29), and the number-average molecular weight was M_n = 7400, as determined by SEC. The observed molecular weight is roughly comparable to the theoretical value (M_n = 11 000), calculated from the monomer/CTA molar ratio and conversion of the monomer using eq 1. In contrast, the polymerization mixture became viscous after 6 h in the case of conventional radical polymerization of E3VC without CTA, yielding a high molecular weight homopolymer with broad molecular weight distribution (M_n = 116 600 and M_w/M_n = 2.16, entry 1). The significant difference in the molecular weights of the polymers obtained in the presence and absence of CTA supports the effectiveness of the reaction conditions to achieve controlled polymerization. Under similar conditions and conversions, a 10-fold lower molecular weight for the polymer obtained in the presence of CTA can ensure that the fraction of dead polymer chains is less than 10%.[29] Apparently, this is a rough guide when one considers the selection of CTA and reaction conditions.

When the polymerization was carried out at $[E3VC]_0/[CTA]_0/[AIBN]_0$ = 60/2/1, the monomer conversion reached 28% after 2.5 h (entry 3, Table 1), and the resulting polymer possessed low polydispersity with low molecular weight (M_w/M_n = 1.19, M_n = 1800) close to that predicted from eq 1. This is an indication that the system shows a good control even at the beginning stage of the polymerization. Aiming to control the molecular weights, in the next stage the polymerization of E3VC was conducted in toluene at 60 °C for 24 h at different $[M]_0:[CTA]_0$ ratios between 50 and 200, keeping the chain transfer agent-to-initiator ratio at a constant value of $[CTA]_0/[AIBN]_0$ = 2/1. Under the conditions, the conversion determined by ^{1}H NMR was >85% in all cases. Figure 1 shows the relation of molecular weight and polydispersity with $[M]_0:[CTA]_0$ ratio for the polymerization. A linear increase of the number-average molecular weight with the ratio without significant change of the polydispersity (M_w/M_n = 1.15−1.29) indicates a feasibility to control the molecular weights by the ratio. Note that the straight line could be obtained only when the monomer conversions are substantially the same in all cases. Nevertheless, the result suggests that the molecular weights of the poly(E3VC)s can be easily adjusted by the monomer-to-CTA ratio.

The influence of the polymerization solvent and the ratio of CTA to initiator on the polymerization behavior was also investigated in terms of the molecular weights

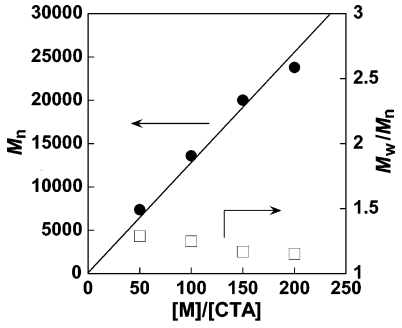


Figure 1. Dependence of number-average molecular weight and molecular weight distribution on $[E3VC]_0:[CTA]_0$ ratio for polymerization of *N*-ethyl-3-vinylcarbazole (E3VC) using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator and benzyl 1-pyrrolecarbodithioate as a chain transfer agent (CTA) in toluene at 60 °C for 24 h. $[CTA]_0/[AIBN]_0$ = 2/1. Monomer concentration = 1.0 g/1.5 mL. Conversion = 86−96%.

Table 2. Effect of Chain Transfer Agent/Initiator Ratio on Polymerization of *N*-Ethyl-3-vinylcarbazole Using AIBN and Benzyl 1-Pyrrolecarbodithioate in Toluene at 60 °C for 24 h[a]

			$M_n \times 10^{-3}$		
entry	$[CTA]_0/[AIBN]_0$	conv[b] (%)	theory	SEC[c]	M_w/M_n[c]
1	2	94	21.2	13.6	1.25
2	3	93	20.8	14.0	1.25
3	5	88	19.8	11.7	1.19
4	10	84	18.8	12.6	1.18

[a] $[E3VC]_0/[CTA]_0$ = 100, E3VC = *N*-ethyl-3-vinylcarbazole, CTA = benzyl 1-pyrrolecarbodithioate, and AIBN = 2,2′-azobis(isobutyronitrile); monomer concentration = 1.0 g/1.5 mL. [b] Calculated by ^{1}H NMR. [c] Measured by SEC using polystyrene standards in DMF containing 0.01 M LiBr.

and the polydispersity of the resulting poly(E3VC). The polymerization in dioxane or chlorobenzene afforded the polymers with slightly broad molecular weight distributions, whereas there was no remarkable effect on the polymerization rate and the molecular weights (entries 5 and 6, Table 1). To evaluate the effect of the CTA/initiator ratio, the polymerization of E3VC was conducted in toluene at 60 °C for 24 h at different $[CTA]_0:[AIBN]_0$ ratios between 2 and 10, keeping the monomer-to-chain transfer agent at a constant value of $[E3VC]_0/[CTA]_0$ = 100/1. As shown in Table 2, the monomer conversion decreased slightly from 94% to 84% as the [CTA]/[I] ratio increased from 2 to 10, suggesting that higher concentrations of initiator resulted in higher rates of polymerization due to an increase in the number of radicals available for propagation. Interestingly, no significant influence on the molecular weights and molecular weight distribution was observed, irrespective

of the concentration ratio of CTA to initiator. In RAFT polymerization, the total number of chains is determined by the number of CTAs that have successfully fragmented and reinitiated polymerization plus the number of initiator-derived chains. In other words, the molecular weights of resulting polymers should be decreased with decreasing $[CTA]_0/[I]_0$ ratio under the same monomer-to-chain transfer agent ratio and monomer conversion. However, the number of polymer chains directly derived from the initiator molecules should be minimal in an ideal RAFT process, and the initial CTA concentration is large enough compared to the number of the initiator-derived chains.[25,30] Further, the reactivity of the CTAs is usually substantially higher than that of monomer, favoring initiation by R• fragments. The consumption of CTA and reversible fragmentation of intermediate to produce reinitiating R• fragment are often referred to as the "preequilibrium". The narrow molecular weight distribution is apparently due to rapid establishment of the preequilibrium, efficient reinitiation from the R• fragment, and attainment of the so-called "main equilibrium" in which the population of dormant chains and/or intermediate radicals is much higher than the total number of propagating chains.[31] In our system at $[E3VC]_0/[CTA]_0 = 100$, the molecular weight obtained at $[CTA]_0/[AIBN]_0 = 10/1$ is almost the same to that at $[CTA]_0/[AIBN]_0 = 2/1$, and the molecular weight distribution remains narrow (M_w/M_n = 1.18−1.25), indicating that the difference in $[AIBN]_0$ had little effect on the total number of the polymer chains. A similar tendency was also reported in another RAFT system,[30] in which no deterioration in the control of the polymerization was observed as $[CTA]_0/[I]_0$ decreased from 8 to 1.5. They demonstrated that the molecular weights determined by GPC with a multiangle light scattering detector are well in agreement with the values calculated from eq 1, regardless of the ratio of CTA to initiator ($[CTA]_0/[I]_0 = 1.5-8$).

As can be seen later, in all cases, the experimental molecular weights are apparently lower than calculated ones, which may be due to the difference in hydrodynamic volume between poly(E3VC) and the linear polystyrene standards used for GPC calibration. Another possible explanation is that the number of living polymer chains is larger than that of CTA due to an initiator-derived chain. To clarify the point, GPC with a multiangle light scattering detector (GPC-MALS) was applied for the determination of the absolute molecular weights of representative samples. The polymers obtained at $[E3VC]_0$:$[CTA]_0$ ratios = 150 and 200 had M_w = 42 200 and M_w/M_n = 1.15 ($M_{n,GPC-MALS}$ = 36 600, as determined by GPC-MALS), compared to $M_{n,calcd}$ = 30 600 and $M_{n,GPC}$ = 20 000 (entry 7, Table 1) and M_w = 49 400 and M_w/M_n = 1.16 ($M_{n,GPC-MALS}$ = 42 700, as determined by GPC-MALS), compared to $M_{n,calcd}$ = 37 600 and $M_{n,GPC}$ = 23 800 (entry 8, Table 1), respectively. There was no significant difference between $M_{n,GPC-MALS}$ and $M_{n,calcd}$, suggesting that the number of living polymer chains is comparable to that of CTA. Nevertheless, it is hard to evaluate the number of the initiator-derived chain existed in this system. Further investigations, such as MALDI-TOF MS investigation, may be required to clarify this point, which will be reported elsewhere.

The controlled/living character of this process was investigated by performing kinetic investigations. Figure 2a shows the variation of the monomer conversion

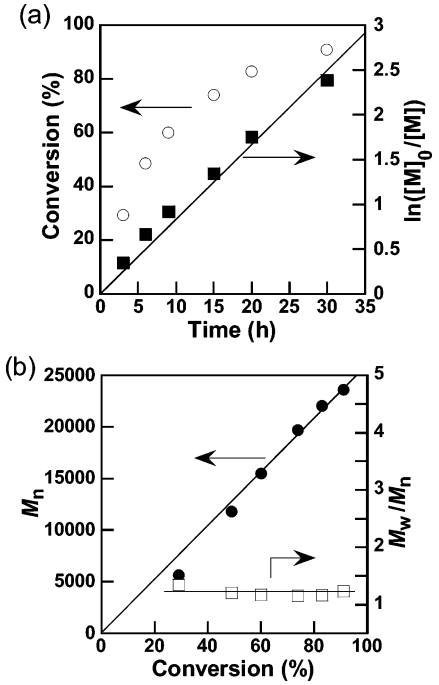


Figure 2. (a) Conversion as a function of polymerization time and first-order kinetic plot and (b) dependence of M_n and M_w/M_n on the monomer conversion for the polymerization of E3VC in toluene at 60 °C: $[E3VC]_0/[CTA]_0/[AIBN]_0 = 400/2/1$, where E3VC = *N*-ethyl-3-vinylcarbazole, CTA = benzyl 1-pyrrolecarbodithioate, and AIBN = 2,2′-azobis(isobutyronitrile). Monomer concentration = 1.0 g/1.5 mL.

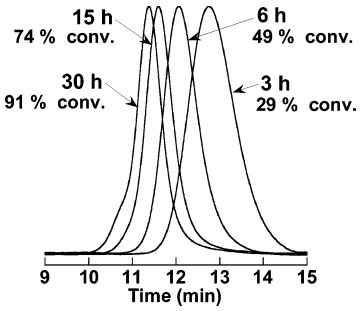


Figure 3. SEC traces of poly(E3VC)s obtained at different polymerization times. See Figure 2 for detailed polymerization conditions.

and $\ln([M]_0/[M]_t)$ vs polymerization time for the polymerization of E3VC at $[E3VC]_0/[CTA]_0/[AIBN]_0 = 400/2/1$. The linear first-order kinetic plot is seen. As shown in Figure 2b, a linear increase of the number-average molecular weight with conversion reveals a constant number of propagating chains throughout the polymerization and the absence of nondegenerative chain transfer reaction. The SEC traces (refractive index) of poly(E3VC)s obtained at different reaction times are shown in Figure 3. A progressive increase of molar mass with conversion with narrow unimodal peaks (M_w/M_n = 1.15−1.34) is clearly seen, as normally evidenced for a controlled/living polymerization. A small shoulder peak at high molecular weight region appears only at high conversion (>80%). This is frequently observed for RAFT polymer obtained at high monomer conversion, which is most probably due to combination of the growing polymer chains at longer reaction times. Nevertheless, the polydispersity remained low (M_w/M_n = 1.23) even at 91% conversion.

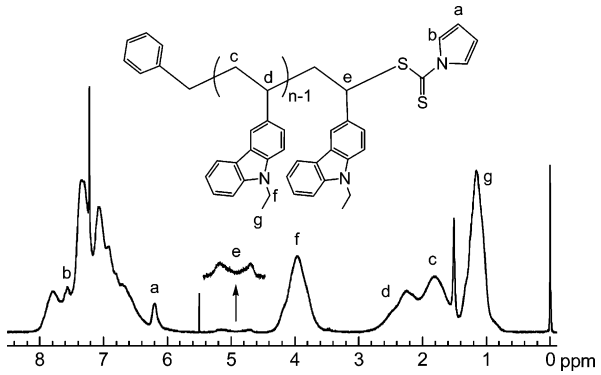


Figure 4. ^{1}H NMR spectrum ($CDCl_3$) of poly(E3VC) ($M_{n,GPC}$ = 1800, M_w/M_n = 1.19, conversion = 28%, sample: entry 3 in Table 1) synthesized by the polymerization of E3VC in toluene 60 °C for 2.5 h: $[E3VC]_0/[CTA]_0/[AIBN]_0$ = 60/2/1, where E3VC = *N*-ethyl-3-vinylcarbazole, CTA = benzyl 1-pyrrolecarbodithioate, and AIBN = 2,2′-azobis(isobutyronitrile). Monomer concentration = 1.0 g/1.5 mL.

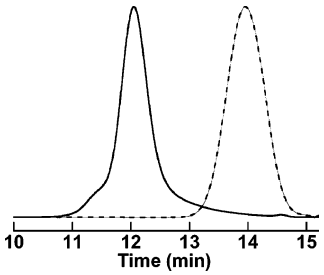


Figure 5. SEC traces of the parent poly(E3VC) macro-CTA (dotted trace, M_n = 1800, M_w/M_n = 1.16, conversion = 26%) obtained at 60 °C at the ratio $[E3VC]_0/[CTA]_0/[AIBN]_0$ = 50/2/1 for 2 h and the chain extended polymer (solid trace, M_n = 12 100, M_w/M_n = 1.20, sample: entry 1 in Table 3) obtained after the polymerization with E3VC at 60 °C at the ratio $[E3VC]_0/[macro\text{-}CTA]_0/[AIBN]_0$ = 200/2/1 for 24 h.

The ^{1}H NMR spectrum of the poly(E3VC) synthesized using benzyl 1-pyrrolecarbodithioate as the CTA is presented in Figure 4 (sample refers to entry 3 in Table 1). The sample obtained after the precipitation was employed to get clear signals. The characteristic peaks at 0.6−1.4 (CH_3), 1.4−3.0 (main chain), 3.4−4.4 (NCH_2), and 5.7−8.2 (aromatic) are clearly observed. In addition to these peaks attributed to the poly(E3VC), the peaks corresponding to the CTA are also visible. A comparison of this spectrum with that of the CTA (see Supporting Information) and dithiocarbamate-terminated polystyrene shown later (Figure 6a) enabled the different protons of end groups to be assigned. The signals at 6.2 and 7.6 ppm are characteristic of pyrrolecarbodithioate moiety. The broad peaks at 4.6−5.4 ppm are assigned to methine terminus of the polymer chains. The relative peak intensity of the methine peaks (one proton) to the pyrrole signal observed at 6.2 ppm (two protons) is roughly 2, suggesting that the pyrrolecarbodithioate moiety is attached to the methine terminus of the polymer chains.

In principle, this NMR technique could be used to determine the molecular weight of the polymer chains by comparing the integrals of peaks for the chain-end protons to those of the main-chain protons. However, this spectroscopic method is only valid for the poly(E3VC) having low molecular weights because of the overlap of the peaks from the pyrrole group with the broad peaks of the carbazole units at 6.0−8.0 ppm. For example, the molecular weight of poly(E3VC) calculated

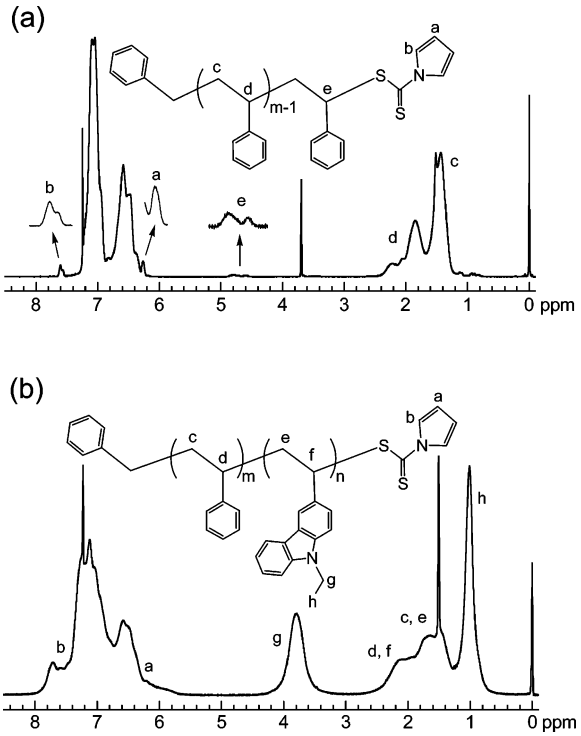


Figure 6. ^{1}H NMR spectra ($CDCl_3$) of the (a) dithiocarbamate-terminated polystyrene ($M_{n,GPC}$ = 4000, M_w/M_n = 1.26, conversion = 29%) obtained by the polymerization in toluene at the ratio $[styrene]_0/[CTA]_0/[AIBN]_0$ = 200/2/1 at 60 °C for 12 h and (b) the block copolymer, polystyrene-*b*-poly(E3VC) ($M_{n,GPC}$ = 20 000, M_w/M_n = 1.32, conversion = 79%, sample; entry 3 in Table 3), obtained after the polymerization with E3VC at 60 °C at the ratio $[E3VC]_0/[macro\text{-}CTA]_0/[AIBN]_0$ = 400/2/1 for 48 h.

by comparison of the area of the peak at 3.5−4.4 ppm corresponding to the methylene protons adjacent to a nitrogen atom in the carbazole repeating units to the peak at 6.2 ppm corresponding to two protons of the end group is M_n = 1900, which is in agreement with the value (M_n = 1800) obtained from GPC using polystyrene standards and the theoretical value (M_n = 2100) calculated using eq 1. For the determination of the molecular weight, the terminal methine proton signal observed at 4.6−5.4 ppm, which does not overlap with any other signal, was also employed instead of the pyrrole protons signal. The molecular weight calculated from the methine peak exhibits a slightly higher value (M_n = 2700), which may be due to low signal-to-noise ratio of the peak.

Chain Extension. An important criterion of controlled/living character of the polymerization is the successful extension of a chain from a preformed polymer chain as a macro-CTA. To investigate this point, the dithiocarbamate-terminated poly(E3VC) prepared independently by the polymerization using benzyl 1-pyrrolecarbodithioate was employed as a macro-CTA for chain extension experiments. We used a low-molecular-weight poly(E3VC) (M_n = 1800, M_w/M_n = 1.16) and dilute monomer concentration (1.0 g/7.5 mL) to achieve a homogeneous reaction system without significant increase of the solution viscosity during the polymerization. The initiator:macro-CTA molar ratio was maintained at 1:2. After the chain extension, the resulting products were analyzed by SEC and compared to the original macro-CTA. The results are shown in Table 3 and Figure 5. Note that the formation of the dithiocar-

Table 3. Polymerization of *N*-Ethyl-3-vinylcarbazole Using Macro-CTA in Toluene at 60 °C[a]

entry	macro-CTA[b]	[E3VC]/[macro-CTA]	time (h)	conv[c] (%)	$M_n \times 10^{-3}$ calcd[d]	$M_n \times 10^{-3}$ obsd[e]	$M_n \times 10^{-3}$ SEC[f]	M_w/M_n[f]
1	P(E3VC)	100	24	*g*	15.6		12.1	1.20
2	PSt	100	24	65	18.4	17.1[h]	11.6	1.19
3	PSt	200	48	79	39.0	32.9[i]	20.0	1.32

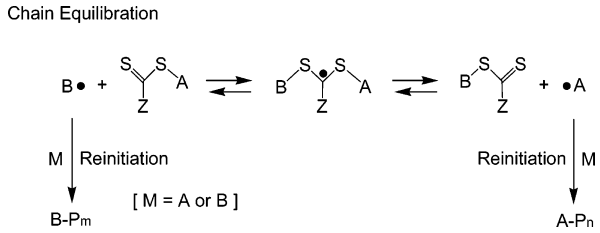
[a] $[\text{Macro-CTA}]_0/[\text{AIBN}]_0 = 2$, monomer concentration = 1.0 g/7.5 mL. [b] P(E3VC): poly(*N*-ethyl-3-vinylcarbazole) ($M_n = 1800$, $M_w/M_n = 1.16$, PSt: polystyrene ($M_n = 4000$, $M_w/M_n = 1.26$). [c] Calculated by ^{1}H NMR. [d] Calculated by the conversion and the molecular weight of the PSt macro-CTA. [e] Evaluated by M_n value of the polystyrene macro-CTA and composition of block copolymers determined by ^{1}H NMR. [f] Measured by SEC using polystyrene standards in DMF containing 0.01 M LiBr. [g] Polymer yield = 62% (methanol-insoluble part). [h] Calculated and observed compositions of the block copolymer (St/E3VC): 36/64 and 38/62. [i] Calculated and observed compositions of the block copolymer (St/E3VC): 19/81 and 22/78.

bamate-terminated poly(E3VC) is independent of the ratio of CTA-derived chain/AIBN-derived chain, even if the initiator-derived chains are existed in the system. The CTA-derived initiator may produce the polymer with chain transfer agent fragments at the polymer chain ends (α-chain end with the benzyl group and the ω-chain end with the pyrrolecarbodithioate group), whereas AIBN-derived initiator may produce the polymer with an initiator fragment at the α-chain end and the pyrrolecarbodithioate group at the ω-chain end. When the chain extension was performed at 60 °C at the ratio $[\text{E3VC}]_0/[\text{macro-CTA}]_0/[\text{AIBN}]_0 = 200/2/1$, the polymer yield was 62% after 24 h, and the polymer was recovered by precipitation in methanol. Near-quantitative efficiency (percentage of macro-CTA converted to extended polymer) was confirmed by the clear shift in the SEC traces for the macro-CTA and the corresponding polymer. The extended polymer exhibited low polydispersity ($M_w/M_n = 1.20$). These results suggest that most of the chain ends of the poly(E3VC) are functionalized with dithiocarbamate end groups, which can be used as a macro-CTA for further chain extension reactions.

As a part of our program to create novel macromolecular architectures with controlled chain length, composition, and functionality, obtaining block copolymers of E3VC and styrene is of importance. Chain extension from poly(E3VC) macro-CTA to conventional monomer was attempted to synthesize a block copolymer. In particular, three-dimensional hierarchical structures formed by self-organization of block copolymers may lead to unique electronic and photonic functions, depending upon the ordered structures and property of the poly(E3VC) segment. The dithiocarbamate-terminated poly(E3VC) was employed as a macro-CTA for block copolymerization with styrene. The polymerization was carried out at 60 °C at the ratio $[\text{styrene}]_0/[\text{macro-CTA}]_0 = 300/1$, and the polymer yield was 50% after 72 h. SEC chromatograms of the starting poly(E3VC) macro-CTA and the second-growth polymer showed that the molecular weight shifted clearly to the higher range (see Supporting Information). However, the polydispersity of the resulting block copolymer was relatively high ($M_w/M_n > 1.5$), and some tailing was detected, suggesting insufficient blocking efficiency and/or the existence of a small number of dead chains. Note that a partial inactivation of the poly(E3VC) chains during the homopolymerization and/or purification process can be neglected on the basis of the successful chain extension of E3VC from the dithiocarbamate-terminated poly(E3VC).

In RAFT polymerization process, a delicate balance of the forward and reverse rates of addition and fragmentation, together with the rates of reinitiation and propagation, is required to achieve control. For the synthesis of AB block copolymer with low polydispersity and high blocking efficiency via RAFT process, the first dithioester-terminated polymer (Scheme 3, S═C(Z)S−A; A block corresponds to poly(E3VC), whereas Z is a pyrrole group in this system) should have a high transfer constant in the subsequent polymerization of second monomers to give B block.[32,33] This requires that the leaving ability of propagating poly(E3VC) radical (A•) is greater than, or at least comparable to, that of the second polystyrene radical (B•) under the reaction conditions. On the basis of the resonance effect, the poly(E3VC) radical should be more stable compared to polystyrene radical, suggesting that the fragmentation from the intermediate radical occurs preferentially toward the poly(E3VC)-propagating radical. For the preparation of block copolymers with narrow molecular weight distributions via the RAFT process, the rapid conversion of macro-CTA to block copolymer is also required, by which all of the second blocks can be initiated at approximately the same time.[30,34] Hence, the insufficient blocking efficiency may be due to the poor reinitiation of stable poly(E3VC) radical to styrene.

Scheme 3



Synthesis of Block Copolymers from Polystyrene Macro-CTA. The right choice of the first block is crucial for the synthesis of well-defined block copolymers by RAFT process. At the same time, a good control of polymerization of the first block is essential. Prior to the synthesis of the block copolymer, hence, the polymerization of styrene mediated using benzyl 1-pyrrolecarbodithioate as CTA was investigated under the similar conditions employed in the polymerization of E3VC. When the polymerization of styrene was conducted in toluene at $[\text{M}]_0/[\text{CTA}]_0/[\text{AIBN}]_0 = 200/2/1$, 29% conversion was reached at 60 °C for 12 h. Under these conditions, well-defined dithiocarbamate-terminated polystyrene ($M_n = 4000$, $M_w/M_n = 1.26$) was obtained, which was employed as a macro-CTA for the block formation. Figure 6a shows the ^{1}H NMR spectrum of the polystyrene macro-CTA. The signals at 6.2 and 7.6 ppm attributed to the pyrrolecarbodithioate moiety are clearly observed, indicating the presence of the dithiocarbamate group in the polystyrene chain end. The molecular weight determined by ^{1}H NMR ($M_{n,NMR} = 5000$) was comparable to that evaluated by GPC, suggesting the controlled synthesis of the polystyrene macro-CTA. The

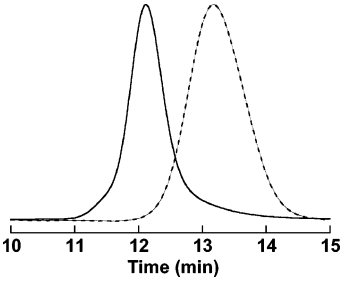


Figure 7. SEC traces of the parent polystyrene macro-CTA (dotted trace, $M_{n,GPC}$ = 4000, M_w/M_n = 1.26) and the block copolymer, polystyrene-*b*-poly(E3VC), obtained after the polymerization with E3VC at 60 °C at the ratio $[E3VC]_0/[macro\text{-}CTA]_0/[AIBN]_0$ = 200/2/1 for 24 h (solid trace, $M_{n,GPC}$ = 11 600, M_w/M_n = 1.19, sample; entry 2 in Table 3).

chain extension was conducted using the polystyrene macro-CTA, and comparison of SEC chromatograms of the starting macro-CTA and the second-growth polymer showed that the extension was successful (see Supporting Information). These results suggest that the dithiocarbamate group is situated predominantly at the chain end of polystyrene and underwent subsequent addition with the corresponding monomer.

The synthesis of a diblock copolymer of styrene and E3VC was performed by the polymerization of E3VC using the dithiocarbamate-terminated polystyrene as a macro-CTA. The initial CTA-to-initiator ratio ($[macro\text{-}CTA]_0/[AIBN]_0$) was held constant at 2/1, while the monomer to CTA ratio ($[E3VC]_0/[macro\text{-}CTA]_0$) was varied in order to assess control of the comonomer content and the molecular weight. The results are summarized in Table 3. Figure 7 presents the SEC traces of the dithiocarbamate-terminated polystyrene and the extended block polymers, polystyrene-*b*-poly(E3VC), obtained at $[E3VC]_0/[macro\text{-}CTA]_0$ = 100. A shift of the SEC trace toward a higher molecular weight region, with polydispersity remaining below 1.20, clearly demonstrates efficient block formation. There is no significant homopolymer impurity in the block copolymer. These results suggest sufficient efficiency of the fragmentation form intermediate radical to the polystyrene radical (B•) combined with efficient reinitiation, resulting in rapid conversion of the polystyrene macro-CTA to the block copolymer under the conditions used in this study. This also indicates that the dithiocarbamate-terminated polystyrene used as a macro-CTA can more easily cross-propagate and polymerize E3VC (the second block) than the reverse chain extension reaction from poly(E3VC) to styrene. Note that no detectable number of AIBN-derived chains is seen in this system, as confirmed by the GPC profile of the block copolymer with no significant peak at the low molecular weight region.

The ^{1}H NMR spectrum of the block polymer, polystyrene-*b*-poly(E3VC), is shown in Figure 6b. The peaks corresponding to polystyrene and poly(E3VC) are clearly observed. Integration of the appropriate peaks gives a composition of 22% styrene and 78% E3VC. This is in agreement with the theoretical composition, 19% styrene and 81% E3VC, calculated from the conversion determined by ^{1}H NMR and the molecular weight of the polystyrene macro-CTA evaluated by SEC. The block copolymer derived from the polystyrene macro-CTA had a theoretical M_n of 39 000, which is in agreement with the value (M_n = 32 900) evaluated by the composition and M_n of the polystyrene macro-CTA. On the other hand, M_ns of the block copolymers evaluated directly from SEC measurements are apparently lower than the calculated ones and the values obtained by the combination of ^{1}H NMR and SEC. These results suggest that the deviation of the molecular weights of the poly(E3VC) from the calculated values shown in Table 1 is mainly due to the difference in hydrodynamic volume between poly(E3VC) and the linear polystyrene. As shown in Table 3, the composition of each segment could be adjusted by the $[E3VC]_0/[macro\text{-}CTA]_0$ ratio in the feed. These results clearly demonstrate that the chain extension from the polystyrene macro-CTA to E3VC can be well controlled and provides block copolymers with as-designed chain structures and narrow molecular weight distribution.

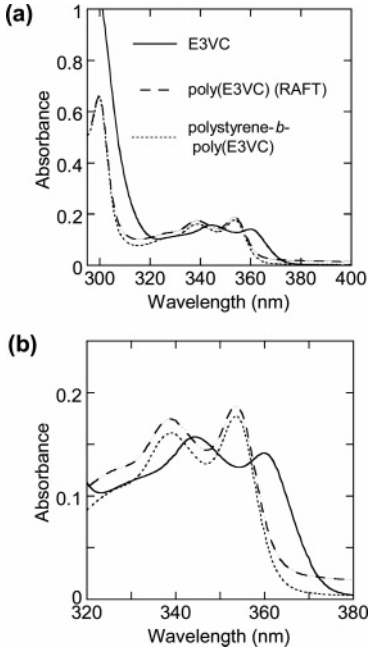


Figure 8. (a) Absorption spectra of E3VC, poly(E3VC) obtained by RAFT polymerization in the presence of CTA (sample: entry 4 in Table 1), and polystyrene-*b*-poly(E3VC) (sample: entry 3 in Table 3) measured in $CHCl_3$ at a concentration of 4.5×10^{-5} carbazole units mol L^{-1}. (b) Magnification of the 320−380 nm range.

Polymer Properties. The resulting polymers were characterized in terms of their optical and thermal properties and compared to a typical carbazole-containing polymer, poly(*N*-vinylcarbazole), which was prepared independently by a conventional radical polymerization with AIBN (see Supporting Information). Figure 8 depicts the absorbance spectra of E3VC, poly(E3VC)s, and polystyrene-*b*-poly(E3VC) measured in $CHCl_3$. Both the monomer and the polymers absorb light in the range from 300 to 380 nm. All of these polymers exhibit absorption peaks at 339 and 354 nm, which appear at shorter wavelengths compared to those of the monomer (λ = 345 and 360 nm). The difference may be related to the disappearance of interaction between the electron-donating carbazolyl chromophore and the electron-accepting carbon−carbon double bound existed in the monomer and/or a specific conformation of poly(E3VC), such as π-stacked structure. No significant difference was seen in the poly(E3VC)s obtained in the presence and absence of the CTA (see Supporting Information), suggesting a negligible effect of the terminal benzyl and dithiocarbamate groups on the absor-

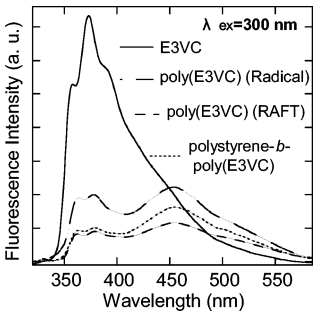


Figure 9. Fluorescence spectra of E3VC, poly(E3VC)s obtained in the absence and presence of CTA (samples: entries 1 and 4 in Table 1), and polystyrene-*b*-poly(E3VC) (sample: entry 3 in Table 3) measured in $CHCl_3$ at a concentration of 4.5×10^{-6} carbazole units mol L^{-1}.

bance. The absorption peak of the block copolymer overlaps with that of the homopolymers.

The fluorescence spectra of the monomer and the polymers are shown in Figure 9. The emission of poly(E3VC)s excited at 300 nm is observed at 363 and 379 nm. In addition to these peaks, a broad peak is observed around 454 nm, which is invisible in the spectrum of the monomer. The carbazole chromophore is known to give a partial-overlap (second) and a full-overlap (normal) excimer emission at 370 and 420 nm, respectively,[35−37] whereas the peak observed at 355 nm corresponds to the monomeric carbazole chromophore. The excimer band with a maximum at 454 nm is red-shifted compared with that (λ_{max} = 444 nm, lit.[4] 430 nm in methylene chloride) of poly(*N*-vinylcarbazole) measured under the same conditions. There is no significant difference in the peak position of the excimer band between the poly(E3VC)s obtained in the presence and absence of the CTA and polystyrene-*b*-poly(E3VC). Actually, the poly(E3VC)s and the block copolymer exhibited a blue fluorescence upon excitation at 365 nm (see photographs in Supporting Information). From these absorbance and fluorescence spectra, it is reasonable to consider that the side-chain carbazole groups in poly(E3VC) are close enough to produce electronic interaction in solution, and poly(E3VC) possesses a specific conformation, such as π-stacked structure, like poly(*N*-vinylcarbazole).

The thermal properties of the resulting polymers were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements. The glass transition temperature (T_g) of poly(E3VC) was found to be 182 °C, which is slightly lower than that of poly(*N*-vinylcarbazole) (T_g = 207 °C, lit.[1] 227 °C for infinitive molecular weight sample). The temperatures for 5% weight loss of poly(E3VC) and polystyrene-*b*-poly(E3VC) under a nitrogen atmosphere were 380 and 383 °C, respectively, which are slightly higher than that of poly(*N*-vinylcarbazole) (T_{dec} = 373 °C). The polymers lost about 50% their weights around 400−450 °C. These TGA measurements indicated that the resulting polymers exhibited a high thermal stability.

Conclusions

This work presents the synthesis of well-defined polymers with pendant carbazolyl groups by RAFT polymerization of *N*-ethyl-3-vinylcarbazole (E3VC) using benzyl 1-pyrrolecarbodithioate as CTA. The controlled/living character of the polymerization was confirmed by the formation of the narrow polydispersity products, the linear first-order kinetic plot, linear increase in the molecular weight with the conversion, feasibility to control molecular weight based on the ratio of monomer consumed to the amount of CTA used, and the ability to extend the chains by the second addition of monomer. Blocking order was found to be important, with differences in fragmentation/reinitiation efficiency for the synthesis of well-defined block copolymers containing poly(E3VC) segment. The dithiocarbamate end-capped polystyrene has been employed as a macro-CTA for the synthesis of block copolymer, polystyrene-*b*-poly(E3VC), having low polydispersity and controlled comonomer composition. Characteristic optical and thermal properties of poly(E3VC) and the block copolymers containing the poly(E3VC) segment were evaluated, which are comparable to a typical carbazole-containing polymer, poly(*N*-vinylcarbazole). These polymers having well-defined architectures can provide viable tailored materials with unique electronic and photonic properties for various applications, such as polymeric light-emitting materials and organic photorefractive materials. Further studies on this carbazole-containing polymers for such application will be reported separately. This work substantially broadens and extends the scope of carbazole-containing polymers, in which precise control of the molecular weight, polydispersity, topology, composition, and functions can be achieved using the controlled radical polymerization technique.

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Supporting Information Available: Figures showing ^1H and ^{13}C NMR spectra of benzyl 1-pyrrolecarbodithioate, SEC traces of the parent poly(E3VC) macro-CTA and poly(E3VC)-*b*-polystyrene, SEC traces of the parent polystyrene macro-CTA and the chain extended polymer, experimental procedure for the synthesis of poly(NVC), absorption spectra of poly(E3VC)s obtained by the polymerization in the presence and absence of CTA, and appearance of samples illuminated with visible and UV (λ_{ex} = 365 nm) light. This material is available free of charge via the Internet at http://pubs.acs.org.

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