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Synthesis of a Conjugated Star Polymer and Star Block Copolymers Based on the Living Polymerization of Phenylacetylenes with a Rh Catalyst

Keiji Kanki and Toshio Masuda*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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ABSTRACT: The synthesis of a star polymer with poly(phenylacetylene) arms was examined. 1,4-Diethynylbenzene, which has a similar structure to the monomer, was added as linking agent to the living polymerization system of phenylacetylene by $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst. A star polymer was selectively formed, and the linear polymer was virtually completely consumed. The M_n and arm number of a typical star polymer were 145 000 and 25, respectively. Since the arm number of the star polymer increased with increasing concentration of the linking agent and temperature of the linking reaction and with decreasing DP_n of the linear polymer, the arm number could be controlled by these factors. Further, star block copolymers composed of blocks of phenylacetylene and (4-methylphenyl)-acetylene were prepared.

Introduction

Star polymers have different properties and functions than those of linear polymers because of their spherical shapes and more condensed structure.[1] The methods of synthesizing star polymers include (1) living polymerization with multifunctional initiators, (2) coupling reaction of a living linear polymer with multifunctional terminators, and (3) linking reaction of a living linear olefinic polymer with divinyl compounds as linking agents. Though methods 1 and 2 are capable of exactly controlling of the arm number of star polymers, it is rather difficult to synthesize star polymers having a large number of arms by these methods. On the other hand, method 3 readily provides star polymers with many arms, though it cannot strictly control the arm number.[1,2] The syntheses of star polymers by method 3 have been reported by Rempp and co-workers for living anionic polymerization.[2] Kanaoka et al. have reported the application of method 3 to living cationic polymerization.[3] Further, the syntheses of star polymers by method 3 have been examined for living radical polymerization by Baek et al. and Matyjaszewski et al.[4] To our knowledge, however, there have been no syntheses of star polymers comprising substituted acetylene units, which should exhibit unique properties. Even the star polymer based on conjugated polymers is restricted to substituted polythiophene arms as reported by Wang et al.[5]

Group 5 and 6 transition metal catalysts and Rh catalysts polymerize substituted acetylenes.[6] Noyori and co-workers reported that the living polymerization of phenylacetylene (PA) proceeds in the presence of Rh catalysts such as $(Ph_3P)_2Rh(C{\equiv}CC_6H_5)(nbd)/4\text{-}Me_2N\text{-}$pyridine (DMAP)[7] and $[(nbd)Rh(OCH_3)]_2/Ph_3P/DMAP$.[8,9] We accomplished the living polymerization of PA by the $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst[10,11] and $(nbd)Rh(CPh{=}CPh_2)(P(4\text{-}Cl{-}C_6H_4)_3)$ which was isolated from the Rh ternary catalyst.[10,12]

In the present study, a star polymer composed of poly(PA) was synthesized by method 3; i.e., the living polymerization of PA with $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst was carried out, and then linking agents were added. 1,4-Diethynylbenzene (DEB) was effective as the linking agent to selectively give a star poly(PA) [denoted as *star*-poly(PA)], and the number of arms could be roughly controlled by conditions of the linking reaction (Scheme 1). Further, the synthesis of star block copolymers has been achieved.

Scheme 1

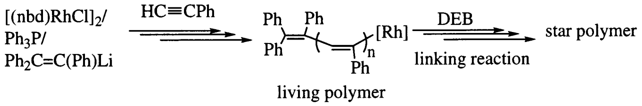
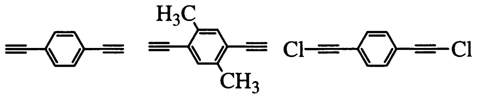


Chart 1



DEB 1 2

Results and Discussion

Effect of Linking Agents. The synthesis of star polymer was examined using several linking agents, i.e., DEB, which has a structure similar to PA, 1,4-diethynyl-2,5-dimethylbenzene (**1**), which has methyl groups at an ortho position of the ethynyl group, and 1,4-bis(chloroethynyl)benzene (**2**), which is an internal diacetylene (Chart 1, Table 1).

At first, PA was polymerized by addition of the monomer ($[M]_0/Rh = 50$) to a toluene solution of $[(nbd)RhCl]_2/Ph_2C{=}C(Ph)Li/Ph_3P$ ternary catalyst ($[P^*]/[Rh] = 1.0$) to give a polymer with $M_n = 5350$ and $M_w/M_n = 1.13$. Then 5 equiv of DEB to the Rh atom was added and allowed to react at 30 °C for 30 min. DEB was completely consumed after 10 min according to GC, and a yellow polymer was obtained in 100% yield. The molecular weight and polydispersity ratio of this polymer were 37 500 and 1.2, respectively, according to GPC analysis, indicating a narrow molecular weight distribution (MWD). GPC showed that 3% of linear poly(PA) remained unreacted. UV−vis spectra of the linear and

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Table 1. Effect of Various Linking Agents on the Synthesis of *Star*-Poly(PA) through Living Polymerization[a,b]

run	linking agent	convn, %	M_n(star)[c]	linear/star[d]
1	DEB	100	37 500	3/97
2	**1**	100	19 700	25/75
3	**2**	98		

[a] Polymerization: in toluene, 30 °C, 30 min; [Rh] = 4.0 mM, [Rh]/[Li]/[P] = 1/2/3, $[M]_0$ = 0.20 M. M_n(arm) = 5350, M_w/M_n(arm) = 1.17. [b] Linking reaction: 30 °C, 30 min; [DEB]/[Rh] = 5. [c] Methanol-insoluble product. Determined by GPC (eluent: THF, PSt standards). [d] The ratio was determined from the GPC curve.

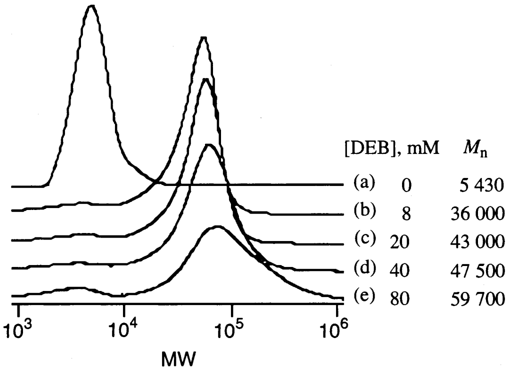

Figure 1. Effect of DEB concentration on the GPC profile of star poly(PA) (polymerized in toluene at 30 °C for 30 min; [Rh] = 4.0 mM, $[M]_0$ = 0.20 M; M_n(arm) = 5430; linking reaction performed at 30 °C for 30 min).

star polymers were measured in THF. *Star*-poly(PA) was reddish-brown and had absorption maxima (ϵ_{max} 3550 M^{-1} cm^{-1}, λ_{max} 325 nm; ϵ_{max} 3060 M^{-1} cm^{-1}, λ_{max} 375 nm), and the cutoff wavelength was ca. 505 nm, which was nearly the same as those of linear poly(PA).

When **1** was used as the linking agent (M_n(arm) = 9380, [**1**]/[Rh] = 5), **1** was completely consumed and *star*-poly(PA) (M_n = 35 000) was obtained, but up to 25% of linear poly(PA) remained. This is likely because (2-methylphenyl)acetylene is less reactive and hardly polymerizes in a living fashion with the present Rh catalyst. Further, no star polymer was obtained when **2** was employed as the linking agent. This is attributable to the inertness of the 1-chloro-2-phenylacetylene monomer to the Rh catalyst. Thus, DEB, whose structure is analogous to PA, is the most favorable.

Effect of the Concentration of Linking Agent. The effect of DEB concentration was examined by changing the ratio of DEB to the active species in the range 2–20 (Figure 1). DEB was completely consumed within 30 min in every case according to GC. When 8 mM DEB (i.e., 2 equiv to active species) was added, *star*-poly(PA) (M_n = 36 000 by GPC) was obtained, and linear polymer was hardly observed in the GPC curve. This indicates that DEB reacts with the living chain end quantitatively, and the second ethynyl group of DEB is also sufficiently reactive. The molecular weight of the star polymer increased somewhat with increasing DEB concentration up to 20 equiv per Rh.

Effect of the Temperature on Linking Reaction. Figure 2 shows the effect of temperature on the linking reaction. Though *star*-poly(PA) was obtained (M_n = 32 100 by GPC) even at 0 °C, 20% of linear poly(PA) remained. This is attributed to the decreased reactivity and mobility of the linear poly(PA) at low temperature. At 60 °C, on the other hand, *star*-poly(PA) with higher molecular weight was obtained (M_n = 46 300 by GPC), but 10% of linear poly(PA) remained. This should be because the linking reaction proceeds so fast that the core becomes appreciably large and hence sterically less reactive toward the remaining linear poly(PA).

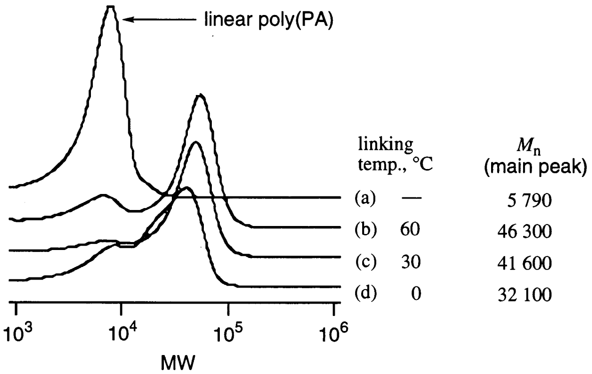

Figure 2. Effect of linking temperature on the GPC profile of star poly(PA) (polymerized in toluene at 30 °C for 30 min; [Rh] = 4.0 mM, $[M]_0$ = 0.20 M; linking reaction performed for 30 min; [DEB] = 20 mM).

Time Profile of Star Polymer Formation. The time dependence of formation of *star*-poly(PA) was examined. The ^{13}C NMR and IR spectra of the star polymer reacted for 5 min are shown in Figure 3. The absorption at 3198 cm^{-1} in the IR spectrum suggests that over 90% of the ethynyl group has been consumed. On the other hand, 17% of the linear polymer remained according to GPC (Figure 4). These results suggest that the first ethynyl group of DEB reacts faster than the second remaining ethynyl group of the DEB for steric reason. Further, no signals of the ethynyl carbons (δ 83.0, 79.1) are seen in the ^{13}C NMR spectrum (Figure 3), which implies that the remaining ethynyl group exists in the vicinity of the core of star polymer and not at the end of linear polymer.

The molecular weight of star polymer increased and the proportion of linear polymer decreased with increasing reaction time. A shoulder of the high molecular weight polymer, probably an intermediate product, finally disappeared. Although a small amount of the ethynyl group remained after 60 min and 24 h, the molecular weight of star polymer hardly changed. This implies that the linking reaction between star polymers is totally suppressed because of the steric hindrance and that the molecular weight of star polymer converges to a certain value.

Multiangle Laser Light Scattering (MALLS) Measurement. The GPC profiles demonstrate that *star*-poly(PA) has been formed practically selectively by using DEB as the linking agent. The molecular weight of star polymers determined by GPC is much smaller than the absolute values because of their rather small hydrodynamic volume.[13] This means that the number of arms evaluated by GPC is not strict. Thus, the molecular weights of a few *star*-poly(PA)s were measured by SEC-MALLS, which gives absolute values (Table 2). The two star polymers that were prepared under standard conditions (different batches), and had about six arms according to GPC, actually possess 23–25 arms on the basis of MALLS. The M_w/M_n ratio of the star polymers (ca. 1.2) determined by MALLS is close to those based on GPC.

Effect of the DP$_n$ of Linear Poly(PA). The effect of DP$_n$ of linear living poly(PA), which is converted into the arm of star polymer, was examined by changing it

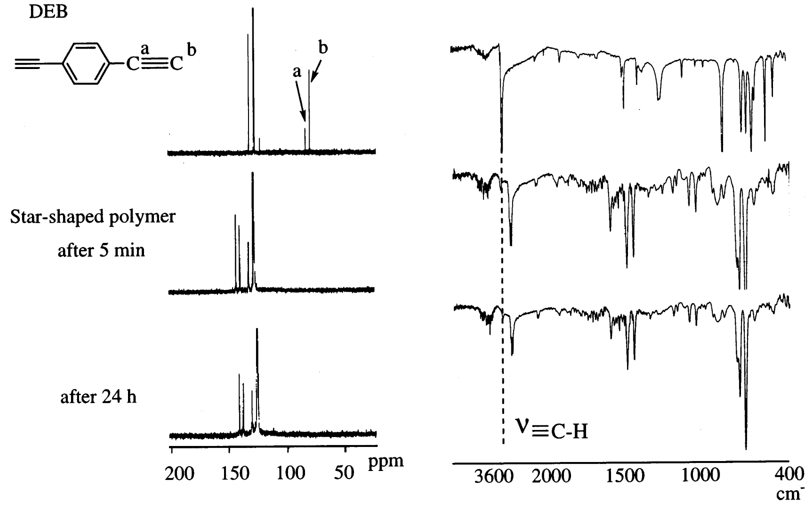

Figure 3. ^{13}C NMR (in C_6D_6) and IR (KBr pellet) spectra of DEB and *star*-poly(PA) (polymerized in toluene at 30 °C for 30 min; [Rh] = 4.0 mM, $[M]_0$ = 0.20 M; linking reaction performed at 30 °C; [DEB] = 20 mM).

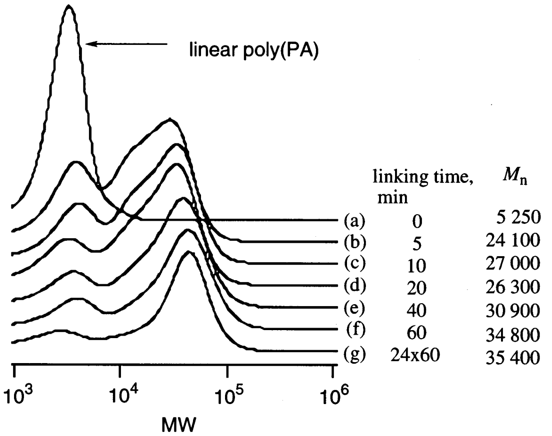

Figure 4. Effect of linking time on the GPC profile of star poly(PA) (polymerized in toluene at 30 °C for 30 min; [Rh] = 4.0 mM, $[M]_0$ = 0.20 M; linking reaction performed at 30 °C; [DEB] = 20 mM).

Table 2. M_n and M_w/M_n of *Star*-Poly(PA) Measured by GPC and MALLS

	GPC			MALLS		
run	M_n	M_w/M_n	f^a	M_n	M_w/M_n	f^a
1^b	37 500	1.17	6.5	145 000	1.21	22.9
2^c	34 800	1.21	6.3	136 000	1.27	21.3
3^d	56 600	1.06	5.2	185 000	1.22	16.4
4^e	95 600	1.10	4.5	246 000	1.10	10.5

[a] f is the number of arms per molecule. f = (weight fraction of PA) × M_n(star)/M_n(arm). [b] Figure 5a, M_n(arm, GPC) = 5250, M_n(arm, MALLS) = 5570. [c] Figure 3f, M_n(arm, GPC) = 5270, M_n(arm, MALLS) = 5610. [d] Figure 5b, M_n(arm, GPC) = 10 300, M_n(arm, MALLS) = 10 700. [e] Figure 5c, M_n(arm, GPC) = 21 600, M_n(arm, MALLS) = 22 900.

in the range 50−200 (Figure 5, Table 2). Though more linear poly(PA) remained with increasing DP_n, the yields of star polymer were higher than 88%. In the case of a star polymer with longer arms (Table 2, runs 2 and 3) as well, the arm number based on MALLS is larger than that based on GPC, showing the same tendency. The number of arms tended to decrease with increasing DP_n. This may be because the core of the star polymer is more difficult to approach by a linear poly(PA) with a longer main chain.

Synthesis of Star Polymers with Block Copolymer Arms. At first, the synthesis of a star polymer with the block copolymer arms composed of PA and 4-MePA in which 4-MePA is located near the core was examined; this polymer is denoted as *star*-[poly(PA)-*block*-poly(4-MePA)-core]. This star block copolymer was synthesized by polymerizing PA at first with the Rh catalyst in a living fashion (30 °C, 30 min) and then adding equivalent 4-MePA (30 °C, 30 min). Then DEB was added to the formed poly(PA)-*block*-poly(4-MePA). GPC demonstrated that a star block copolymer was selectively formed and no linear polymer remained. In the same way, *star*-[poly(4-MePA)-*block*-poly(PA)-core] was synthesized by polymerizing 4-MePA at first. The molecular weights of the block copolymers, which were finally converted into the arms of star polymers, and the formed star block copolymers are shown in Table 3. Whereas the molecular weights of the linear block copolymers are similar, the molecular weight of the star polymer having the 4-MePA block inside was lower than that of the other star block copolymer. This suggests that the 4-MePA propagating end is more sterically hindered than that of PA in the linking reaction.

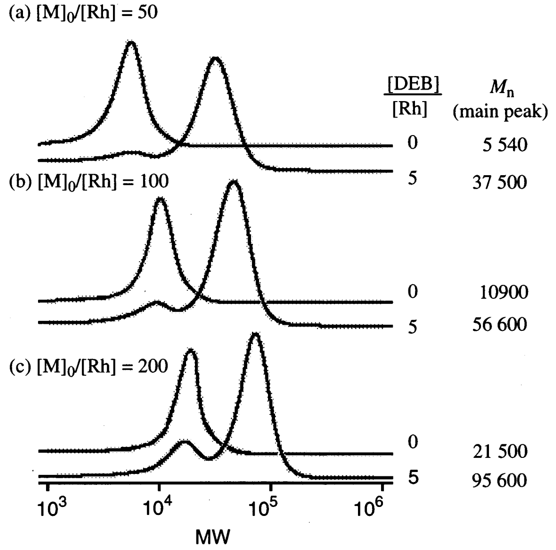

Figure 5. Effect of the DP_n of living poly(PA) on the GPC profile of star poly(PA) (polymerized in toluene at 30 °C for 30 min; [Rh] = 4.0 mM; linking reaction performed at 30 °C for 30 min; [DEB] = 20 mM).

The ^{1}H NMR spectra of the star block copolymers are shown in Figure 6. The compositions of PA and 4-MePA

Table 3. M_n and Composition of Linear Block Copolymers and Star Block Copolymers[a,b]

	$M_n/10^3$ [c]	f [d]	composition, PA:4-MePA[e]
poly(PA)-*block*-poly(4-MePA)	5.3		49:51
poly(4-MePA)-*block*-poly(PA)	5.2		52:48
star-[poly(PA)-*block*-poly(4-MePA)-core]	100.9	18.3	60:40
star-[poly(4-MePA)-*block*-poly(PA)-core]	133.3	24.6	46:54

[a] Polymerization: in toluene, 30 °C, 30 min; [Rh] = 4.0 mM, [Rh]/[Li]/[P] = 1/2/3, $[M]_{0,PA} = [M]_{0,4-MePA} = 0.10$ M. [b] Linking reaction: 30 °C, 30 min; [DEB]/[Rh] = 5. [c] Determined by MALLS. [d] f is the number of arms per molecule. [e] Estimated from the ratio of the methyl (δ 2.08) to olefinic proton (δ 6.17−6.23) in ^{1}H NMR.

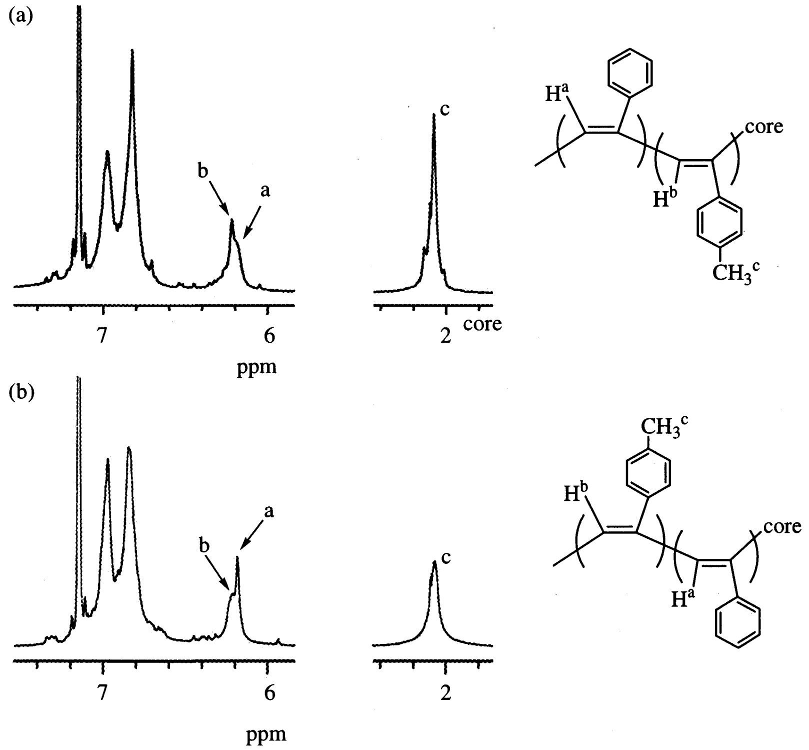

Figure 6. ^{1}H NMR spectra of (a) *star*-[poly(4-MePA)-*block*-poly(PA)-core] and (b) *star*-[poly(PA)-*block*-poly(4-MePA)-core] (in C_6D_6).

were estimated from the ratios of the methyl (δ, 2.08) and olefinic proton (δ, 6.17−6.23) (Table 3). The PA/4-MePA ratios of the linear block copolymers were about 1:1 according to the feed ratio irrespective of the order of monomer additions. On the other hand, the apparent PA/4-MePA ratios of *star*-[poly(PA)-*block*-poly(4-MePA)-core] and *star*-[poly(4-MePA)-*block*-poly(PA)-core] were 60:40 and 46:54, respectively, indicating that the proportions of the internal block decrease. This can be explained by the lower mobility of the internal block and the corresponding large variations of the relaxation times in NMR, which confirms the formation star polymers.

Experimental Section

Materials. PA (Aldrich; purity 98%) was distilled twice from CaH_2 at reduced pressure. Toluene (Wako) was distilled twice from CaH_2. $[(nbd)RhCl]_2$ (Aldrich) was used as received. $Ph_2C{=}C(Ph)Li$ was synthesized by the reaction of $Ph_2C{=}C(Ph)Br$ (TCI, Japan; purity 98%) with Li (Aldrich; purity 99%) in ether according to a literature method[10] and used as ether solution. (4-Methylphenyl)acetylene (4-MePA) was synthesized by a literature method.[14]

1,4-Diethynylbenzene (DEB) and 1,4-diethynyl-2,5-dimethylbenzene (**1**) as linking agents were synthesized according to literature methods[14] and purified by flash column chromatography (Nakalai Tesque Co., silica gel 60; eluent: hexane). 1,4-Bis(chloroethynyl)benzene (**2**) was prepared by modifying a literature method:[15] DEB (40 mmol) was added to *n*-BuLi (52 mL, 1.6 M in hexane) in THF (30 mL) dropwise at −50 °C, and the solution was stirred for 2 h. *p*-Tosyl chloride (Wako, 90 mmol) in THF (20 mL) was added to the solution dropwise at −50 °C. This solution was extracted with hexane, the organic phase was washed with water twice, and hexane was evaporated. The crude product was purified by flash chromatography (Nakalai Tesque Co., silica gel 60; eluent: hexane) to give **2**; yield 53%. ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ 122.3 (Ar), 131.8 (Ar), 70.2 (Ar≡C), 68.9 (≡CCl).

Polymerization. PA was polymerized under dry nitrogen in a Schlenk tube equipped with a three-way stopcock. A typical procedure of the synthesis of poly(PA) is as follows: A catalyst solution was prepared by adding an ether solution of $Ph_2C{=}C(Ph)Li$ (0.80 mL, 40 μmol) to a solution of $[(nbd)RhCl]_2$ (4.6 mg, 10 μmol) and Ph_3P (15.8 mg, 60 μmol) in toluene (2.2 mL). To the catalyst solution, a toluene solution (2.0 mL) of PA (1.0 mmol) was added immediately. Polymerization was carried out at 30 °C for 30 min and then quenched with acetic acid (1.0 mL). The monomer conversion was determined by GC using bromobenzene as an internal standard (Shimadzu GC-14B; CBP10-M25-025 capillary column; injection and column temperatures were 200 and 100 °C, respectively); conversion 100%. The formed polymer was precipitated in a large amount of methanol, filtered, dried in vacuo, and weighed. Yield 102.1 mg (100%); $M_n = 5350$ (GPC), $M_w/M_n = 1.17$ (GPC).

Synthesis of star polymer was carried out by addition of a linking agent after confirmation of complete monomer consumption in the living polymerization of PA; i.e., after PA (1.0

mmol) was polymerized as mentioned above, a toluene solution (2.0 mL) of DEB (0.10 mmol) as a linking agent was added to a solution of living poly(PA). The mixture was kept at 30 °C for 10 min. The formed polymer was precipitated in a large amount of methanol, filtered, dried in vacuo, and weighed. Conversion of DEB 100%, yield 105.8 mg (100%); $M_n = 37\,500$ (GPC), $M_w/M_n = 1.2$ (GPC).

Synthesis of poly(PA)-*block*-poly(4-MePA) is as follows: After PA (0.50 mmol) was polymerized as mentioned above, a toluene solution (2.0 mM) of 4-MePA (0.50 mmol) was added to the solution of living poly(PA). The mixture was kept at 30 °C for 30 min. The polymerization was quenched with acetic acid (1.0 mL). The conversion of 4-MePA was determined by GC; conversion 100%. The formed polymer was precipitated in a large amount of methanol, filtered, dried in vacuo, and weighed. Yield 95.8 mg (87%); $M_n = 5100$ (GPC), $M_w/M_n = 1.15$ (GPC). To synthesize *star*-[poly(PA)-*block*-poly(4-MePA)-core], a toluene solution (2.0 mL) of DEB (0.10 mmol) was added to the block copolymerization system, and the reaction was continued at 30 °C for another 30 min. Then the reaction system was worked up as described above. Yield 111.3 mg (92%); $M_n = 36\,900$ (GPC), $M_w/M_n = 1.22$ (GPC).

Characterization. The molecular weights of polymers were evaluated by GPC at 40 °C at a flow rate of 1.0 mL/min; eluent THF, polystyrene gel columns Shodex KF-805L × 3, polystyrene calibration; RI detector. The IR, UV−vis, and NMR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer, a Shimadzu UV-2200 spectrophotometer, and a JEOL EX-400 (400 MHz) spectrometer, respectively. The MALLS analysis was performed in $CHCl_3$ at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, $\lambda = 690$ nm). The refractive index increment (dn/dc) was measured in $CHCl_3$ at 25 °C on a Photal DRM-1020 refractmeter ($\lambda = 633$ nm). The dn/dc value was 0.272 mL/g for the star polymer.

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Supporting Information Available: Figure showing GPC profiles of (a) poly(4-MePA)-*block*-poly(PA), (b) *star*-[poly(4-MePA)-*block*-poly(PA)-core], (c) poly(PA)-*block*-poly(4-MePA), and (d) *star*-[poly(PA)-*block*-poly(4-MePA)-core] prepared in the present study. This material is available free of charge via the Internet at http://pubs.acs.org.

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