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Conformational Transformation of Poly(β-phenetyl-L-aspartate) in Block Copolymer with Polystyrene in 1,1,2,2-Tetrachloroethane

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ABSTRACT: Temperature dependences of conformations of poly(β-phenethyl-L-aspartate) (PA) in block copolymer systems, in which polystyrene (PS) was attached to either N-terminus (PA_n-N-PS_m) or C-terminus (PS_n-C-PA_m) of the PA, respectively, were investigated in 1,1,2,2-tetrachloroethane (TCE) solutions by using ^{1}H NMR spectroscopy. The block copolymers were synthesized by combination of atom transfer radical polymerization and ring-opening polymerization of *N*-carboxy amino acid anhydride. Whereas PA homopolymer (H-PA_n, $n = 68$) with right-handed helical conformation started to transform to left-handed structure at 70 °C, the helical-sense inversion of PA_{68}-N-PS_{38} occurred at a lower temperature, 40 °C. Further transformation from left-handed conformation was not observed for both polymers in the temperature range of 70 °C to 110 °C. On the other hand, ^{1}H NMR spectra of PS_{70}-C-PA_{170} showed coexistence of right- and left-handed helices of PA at 8.2 and 8.8 ppm at 30 °C, respectively. These peaks, however, disappeared above 90 °C, and a new peak at 8.5 ppm was observed. Thus, the introduction of PS chain into PA termini affected conformational stability of PA in a different way, although the transformational behaviors were not influenced by the difference of the chain length of PS segments. [doi:10.1295/polymj.PJ2007020]

KEY WORDS Poly(β-phenethyl-L-aspartate) / Block Copolymer / Helical-Sense Inversion / Chain Terminus / NMR /

Controlling the higher ordered structure of polymers is one of the most important factors for producing functional polymeric materials. In that context, polypeptides have been frequently investigated and utilized because they can assume various higher ordered structures. For example, poly(aspartate ester)s are known to form various conformations including right-handed helix (RH), left-handed helix (LH), β-sheet, and random coil (RC) depending on structure of side-chain groups, temperature, and solvents.[1–13] In particular, RH and LH conformations are interesting because their formation can be reversibly controlled by thermal stimulus.[5–8] The helical-sense inversion has been reported to be caused by difference in the conformational entropy of the side-chain between the two opposite helical structures.[9–13]

In addition to the side-chain groups, chain termini of poly(aspartate ester)s should have a significant effect on their conformations, thus, allowing us to control them. Although a number of reports addressing the effect has been limited so far, Ushiyama *et al.* have demonstrated that attaching helical poly(γ-benzyl-L-glutamate) (BG) segment at the chain terminus of poly(β-phenethyl-L-aspartate) (PA) by block copolymerization have a significant influence on the helical-sense inversion of the PA segment.[14] Thus, it would be intriguing if we can use other polymer segment in place of the BG, because then more detailed analysis will become possible without undesirable overlapping of the signals in instrumental measurements such as CD, IR, X-ray, and NMR.

As a method for such block copolymerizations, a combination of ring-opening polymerization (ROP) of *N*-carboxy amino acid anhydride (NCA)[15] and atom transfer radical polymerization (ATRP)[16] of vinyl monomers has been demonstrated to be quite effective. For example, amino-terminated poly(methyl methacrylate) (PMMA)[17] and polystyrene (PS)[18] prepared via ATRP were used as macroinitiators for ROP of NCA to afford PMMA- or PS–polypeptide block copolymers with well-defined structure, which was given by living character for the two types of the polymerization. Whereas the PMMA or PS segment was attached C-terminus of the polypeptide segments, block copolymers having the conjugation point at polypeptides' N-terminus were also prepared by initiating the ATRP from polypeptide macroinitiators whose N-terminus was capped with halogens.[19–21]

In this paper, the block copolymerization method is applied for PA for the first time and the effect of PS segment at N- and C-termini on conformational transformations of PA in 1,1,2,2-tetrachloroethane (TCE) is estimated from ^{1}H NMR spectra.

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EXPERIMENTAL

Materials

Triethylamine (TEA), tetrahydrofuran (THF), chloroform, and styrene (Nacalai, 98%) were purified by conventional methods before use. 2-Bromoisobutyrylbromide (Aldrich, 98%), *tert*-butylamine (TCI, 98%), CuBr (Wako, 95%), (–)-spartein (TCI, 95%), phthalimide potassium salt (Nacalai, 98%), hydrazine monohydrate (Nacalai, 80%), and anisole (Wako, 95%) were used as received.

Characterization

Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PS precursors were measured by means of gel permeation chromatography (GPC) on a Jasco–Bowin system (ver. 1.50) equipped with PS calibrated Tosoh TSKgel (G3000H_{HR}, G4000H_{HR}, and G6000H_{HR}) using THF as an eluent. GPC spectra for H-PA$_n$ and PA block copolymers were also detected with TSKgel G4000H_{XL} using chloroform as an eluent.

^{1}H (400 MHz) NMR spectra were recorded on a Brucker Avance 400 spectrometer. 10% of trifluoroacetic acid (TFA)–$CDCl_3$ solutions were measured to determine M_n of PA in H-PA$_n$ and block copolymers on the basis of initiators. For conformational studies of PA segment, TCE-d_2 solutions, in which 2% of PA segments were dissolved and then placed overnight, were measured at various temperatures between 30 and 110 °C under dry nitrogen.

Synthesis of PA$_n$-N-PS$_m$

H-PA$_{68}$ ($M_n = 15000$) was synthesized by a standard ROP of *N*-carboxy-β-phenethyl-L-aspartate anhydride (PLA-NCA) using *tert*-butylamine as an initiator in dry chloroform at room temperature.[15] Then 2-bromoisobutyrylbromide (2.0 mL, 8.6 mmol) was added dropwise to the ice-cooled dry chloroform solution of the H-PA$_{68}$ (2.4 g, 0.19 mmol) and dry TEA (4.2 mL, 17.3 mmol). The reaction was warmed to room temperature, stirred for 12 h, and concentrated by evaporation. PA$_{68}$-Br was reprecipitated from methanol for several times and thoroughly dried.

A mixture of styrene (5.2 g, 50 mmol), PA$_{68}$-Br (1.5 g, 0.10 mmol), CuBr (14 mg, 0.10 mmol), (–)-spartein (47 mg, 0.20 mmol), and anisole (12 g) was divided into two glass tubes, degassed, sealed off under vacuum, and placed at 110 °C for 4 h and 6 h, respectively. The polymeric mixtures were diluted with THF, passed through neutral alumina, and evaporated. Two PA$_{68}$-N-PS$_m$s were reprecipitated from methanol and thoroughly dried. ^{1}H NMR (10% TFA–$CDCl_3$); $\delta = 8.0$ (s, N*H*, 1H), 7.3–7.1 (m, aromatic *H*), 4.8 (s, C$^{\alpha}H$, 1H), 4.3 (m, O–C$^{\varepsilon}H_2$–C$^{\zeta}H_2$, 2H), 2.9 (s, C$^{\beta}H_2$, 2H), 2.8 (t, benzyl CH_2, 2H) for PA segment and 7.3–7.1 (m, aromatic *H*), 6.6 (br, aromatic *H*, 2H), 1.9 (br, CH_2–C*H*, 1H), 1.5 (br, CH_2–CH, 2H) for PS segment, respectively.

Synthesis of PS$_n$-C-PA$_m$

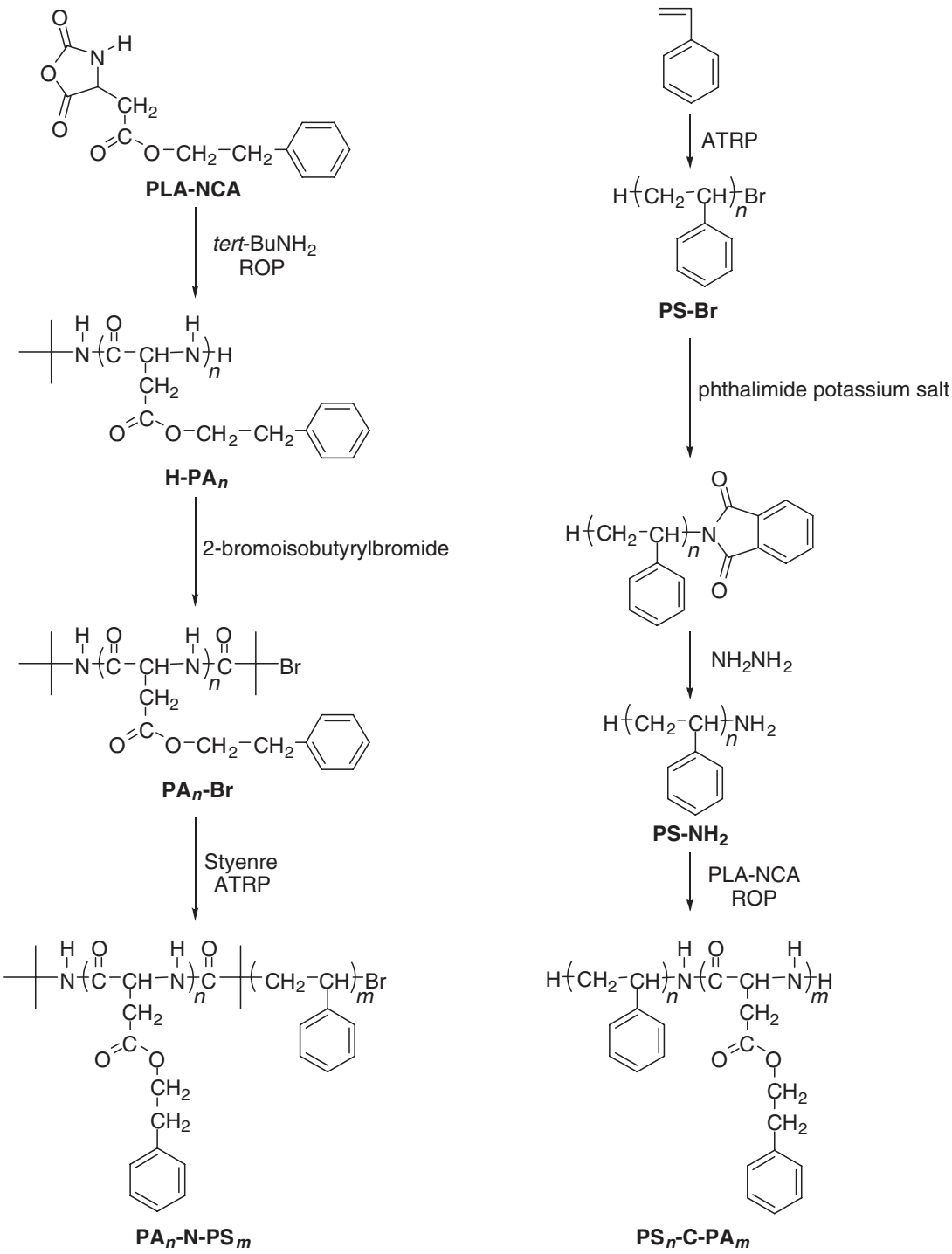
A bromo-terminated PS homopolymer (PS$_{93}$-Br) ($M_n = 9700$, $M_w/M_n = 1.08$) was synthesized by ATRP.[16] A solution of the PS$_{93}$-Br (1.4 g, 0.14 mmol) and phthalimide potassium salt (0.32 g, 1.6 mmol) in dimethylformamide (DMF) (80 mL) was stirred at room temperature for 24 h under dry nitrogen and concentrated. The residue was dissolved in chloroform and washed two times with 5% NaOH aqueous solution and further two times with water. The chloroform solution was dried with $MgSO_4$, filtrated, and concentrated. Obtaining PS$_{93}$-phthalimide was reprecipitated from methanol and thoroughly dried. The PS$_{93}$-phthalimide and large amount of hydrazine monohydrate (60 mL) were dissolved in THF (100 mL), stirred at 45 °C for 24 h, and evaporated in order to precipitate polymer. Residual hydrazine was removed by decantation. The product was dissolved to THF and reprecipitated from methanol. PS$_{93}$-NH_2 was further purified by column chromatography in order to eliminate residual PS$_{93}$-Br and PS$_{93}$-phthalimide and then by reprecipitation for several times. Yield; 370 mg (0.037 mol, 26%).

A mixture of PLA-NCA (1.06 g, 4.02 mmol), the PS$_{93}$-NH_2 (370 mg, 0.037 mmol), and chloroform (80 mL) was charged into a flask and stirred for 36 h. The PS$_{93}$-C-PA$_{55}$ was reprecipitated from diethyl ether for several times in order to remove residual monomer and inactivated macroinitiator PS$_{93}$-NH_2 and thoroughly dried. Yield; 317 mg (0.015 mmol, 22%). ^{1}H NMR (10% TFA–$CDCl_3$); $\delta = 8.0$ (s, N*H*, 1H), 7.3–7.1 (m, aromatic *H*), 4.8 (s, C$^{\alpha}H$, 1H), 4.3 (m, O–C$^{\varepsilon}H_2$–C$^{\zeta}H_2$, 2H), 2.9 (s, C$^{\beta}H_2$, 2H), 2.8 (t, benzyl CH_2, 2H) for PA segment and 7.3–7.1 (m, aromatic *H*), 6.6 (br, aromatic *H*, 2H), 1.9 (br, CH_2–C*H*, 1H), 1.5 (br, CH_2–CH, 2H) for PS segment, respectively.

RESULTS AND DISCUSSION

Synthesis of block copolymers comprising PA and PS

Two types of block copolymers modified at N- and C-termini of PA with PS, PA$_n$-N-PS$_m$ and PS$_n$-C-PA$_m$, respectively, were prepared by a combination of ROP of PLA-NCA and ATRP of styrene (Scheme 1). For the synthesis of PA$_n$-N-PS$_m$s, a terminal amino group of a PA homopolymer (H-PA$_n$, $n = 68$; initiator, *tert*-butylamine) was converted into a bromide group (PA$_{68}$-Br) by the reaction with 2-bromoisobutyrylbro-



Scheme 1. Synthesis of PA_n-N-PS_m and PS_n-C-PA_m.

mide. GPC of the block copolymer obtained from polymerization of styrene with the PA_{68}-Br/CuBr/(–)-spartein system showed one peak in higher molecular weight region with rather broad molecular weight distribution (Figure 1a, $M_w/M_n = 1.91$). This unexpected M_w/M_n value can be accounted for by a ligand exchange of Cu-center between (–)-spartein and the amide group of the PA backbone.[19] In the ^{1}H NMR spectrum measured in a mixture of 10% TFA–$CDCl_3$, along with the peaks deviated from PS segment, the signals for the N*H* and C$^{\alpha}$*H* protons appeared at 8.0 and 4.8 ppm, respectively, indicating the formation of RC in PA (Figure 1b). Weight fraction of each polymer segment was determined from integral ratio of resonances corresponding to aromatic *H* (2H) at 6.6 ppm for the PS segment to C$^{\varepsilon}H_2$ (2H) at 4.3 ppm for the PA segment, resulting in the ratio of 68:38 (mol/mol) PA/PS ($t_p = 4$ h). As expected, block copolymer with higher content of PS segment (68:120 PA/PS) was obtained for $t_p = 6$ h. The M_ns of com-

prising polymer segments in the PA_n-N-PS_ms are summarized in Table I.

For the synthesis of PS_n-C-PA_ms, PS_n-Br prepared by ATRP was converted into PS_n-NH_2 by the reaction of the PS_n-Br with phthalimide potassium salt, followed by treatment with hydrazine (Scheme 1). We used the PS_n-NH_2 as a macroinitiator for ROP of PLA-NCA. Block copolymers were purified by reprecipitation from diethyl ether for elimination of residual monomer and inactivated macroinitiator. GPC charts for PS_{93}-C-PA_{55} showed a unimodal distribution ($M_w/M_n = 1.15$) and larger M_n than that of the PS_{93}-Br (Figure 2). ^{1}H NMR spectra in the mixture of 10% TFA–$CDCl_3$ showed signals and the chemical shifts were identical with those for the PA_n-N-PS_m. These results indicate that PS_{93}-C-PA_{55} was successfully prepared by combination of ATRP and ROP of PLA-NCA. The PS_n-C-PA_ms with various M_ns and weight fractions were also prepared as listed in Table II.

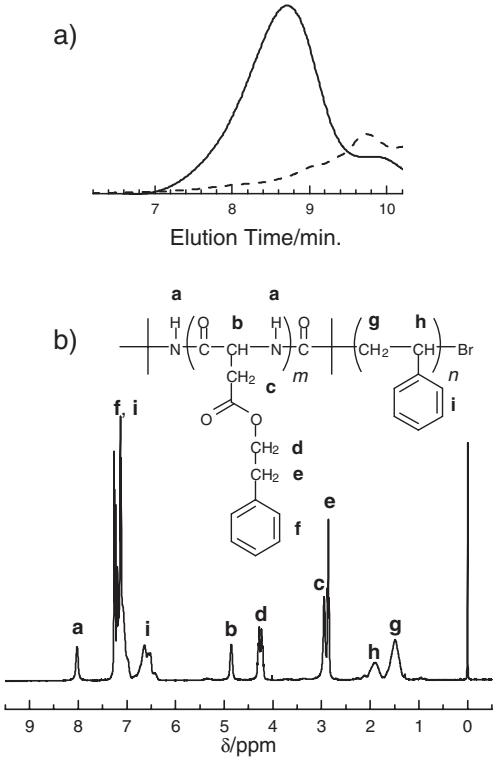


Figure 1. a) GPC charts and b) ^{1}H NMR signals for PA_{68}-N-PS_{38}, respectively. In the GPC charts which were observed with $CHCl_3$ as an eluent, solid and dashed lines denote the block copolymer and the corresponding macroiniriator, respectively. For the ^{1}H NMR, the polymers dissolved in 10% TFA–$CDCl_3$.

Helical-sense inversion for PA_n-N-PS_m

For characterizing the conformation of polypeptides in solutions, NMR is one of powerful tools; that is,

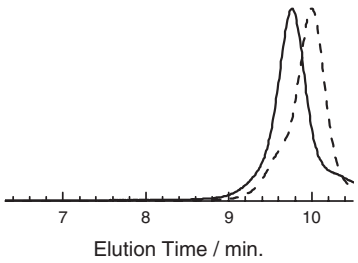


Figure 2. GPC charts for PS_{70}-C-PA_{170} (a solid line) and PS_{70}-Br (a dashed line). Condition for the observation was the same as that in Figure 1.

Table I. Synthesis and characterization of PA_n-N-PS_ms[a]

Macroinitiator	[Styrene]/[PA-Br]	Conc.[b]/wt %	Time[c]/h	$M_{n,PA} \times 10^{-3}$[d]	$M_{n,PS} \times 10^{-3}$[e]	Block Copolymer
PA_{68}-Br	500	33	4.0	15	4.0	PA_{68}-N-PS_{38}
PA_{68}-Br	500	33	6.0	15	12	PA_{68}-N-PS_{120}

[a]Prepared by ATRP of styrene at 110 °C. [b]Concentration of the styrene diluted with anisole. [c]Polymerization time. [d]Molecular weight of PA segment determined by ^{1}H NMR in $CDCl_3$ with addition of 10% of trifluoroacetic acid. [e]Molecular weight of PS segment determined by ^{1}H NMR on the basis of $M_{n,PA}$.

Table II. Synthesis and characterization of PS_n-C-PA_ms[a]

Macroinitiator	[PLA-NCA]/[PS-NH_2]	Time[b]/h	$M_{n,PS} \times 10^{-3}$[c]	$M_{n,PA} \times 10^{-3}$[d]	Block Copolymer
PS_{93}-NH_2	100	72	9.7	12	PS_{93}-C-PA_{55}
PS_{70}-NH_2	100	72	7.3	36	PS_{70}-C-PA_{170}
PS_{38}-NH_2	50	120	4.0	49	PS_{38}-C-PA_{230}
PS_{70}-NH_2	100	170	7.3	98	PS_{70}-C-PA_{450}

[a]Prepared by ring-opening polymerization of PLA-NCA using PS_n-NH_2 as macroinitiators at room temperature. Concentration of the PLA-NCA at 1% diluted with dry chloroform. [b]Polymerization time. [c]Molecular weight of PS segment determined by GPC measurements for PS_n-Br precursors. [d]Molecular weight of PA segment determined by ^{1}H NMR measurement in $CDCl_3$ with addition of 10% of trifluoroacetic acid on the basis of the $M_{n,PS}$.

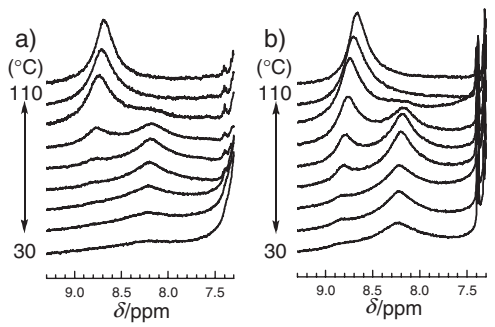


Figure 3. N*H* proton signals in ^{1}H NMR for a) H-PA_{68} and b) PA_{68}-N-PS_{38} in a dilute TCE-d_2 solution observed at various temperatures between 30 and 110 °C in 10 °C intervals, respectively.

N*H* proton signals are particularly useful to estimate their helical sense in PA.[13,14] Figure 3a shows the N*H* proton signals for H-PA_{68}, which was used for the synthesis of PA_{68}-N-PS_ms, at various temperature from 30 to 110 °C in 10 °C intervals. At 30 °C, a signal was observed at 8.2 ppm, indicating the formation of RH, and it became sharper above 40 °C. At 70 °C, another signal at 8.8 ppm assignable to LH appeared and became sharper with further increasing temperature, whereas the RH signal became weaker and then disappeared above 100 °C. Any signals at 7.8 ppm which are expected for RC were not observed in whole temperature region. The signals were completely reversible on heating and cooling cycles. The behaviors of the thermally reversible helical-sense inversion of H-PA_{68} were in good agreement with that reported in the literature.[13]

For PA_{68}-N-PS_{38} (Figure 3b), PA segment took RH but some residues form LH at 30 °C, as evidenced by the observation of a weak signal at 8.8 ppm (LH). Again, the formation of RC was not observed. The content of LH increased with increasing temperature, and above 100 °C all of the PA segments took LH in a manner similar to H-PA_{68}. Figure 4 shows temperature dependence of the ratio for the LH to total N*H* peak area ($r_{LH} = P_{LH}/(P_{LH} + P_{RH})$) for H-$PA_{68}$, PA_{68}-N-PS_{38}, and PA_{68}-N-PS_{120}. The difference between the PA_{68}-N-PS_ms and the H-PA_{68} became significant at 40 °C where the r_{LH} of the PA_{68}-N-PS_{38} was 0.12, while that of the H-PA_{68} remained 0. The r_{LH} of the PA_{68}-N-PS_{38} gently increased with elevating temperature, and then curves of the r_{LH} of PA_{68}-N-PS_{38} and H-PA_{68} overlapped one another in the temperature range of 70 to 110 °C, suggesting that no significant influence of PS segments on conformation of PA was operative in this temperature range. Figure 4 also shows that transformational behavior was not influenced by chain length of PS segment in these M_n range. The overall changes of the r_{LH}s for these polymers were completely reversible on heating and cooling cycles, indicating that the helical-sense inversion was governed by a thermodynamic equilibrium.

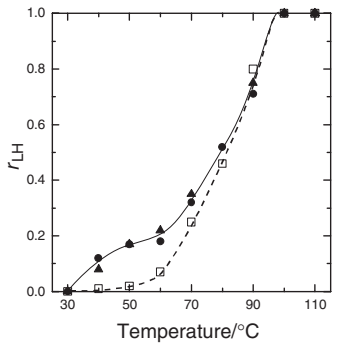


Figure 4. Temperature dependence of LH ratio to total integral of N*H* protons (r_{LH}) for H-PA_{68} (open squares), PA_{68}-N-PS_{38} (filled circles), and PA_{68}-N-PS_{120} (filled triangles), respectively.

The most plausible explanation of the decrease of transformational temperature from RH to LH for PA_{68}-N-PS_{38} is that the RH formation was perturbed by the large chain mobility due to high solubility of PS segment in TCE. However, the gentle slope of the r_{LH} curve up to 60 °C implies that the perturbation occurred in a limited from N-terminus attaching PS. It appears that the counterbalance between the perturbation by the PS segment on N-terminus and the inherent RH formation of PA in C-terminal side is responsible for the decrease of transformation temperature. As described earlier, from the fact that the RC was not observed, it is safe to say that the RC does not contribute to transformation from RH to LH or *vice versa*. These mechanisms of the helical-sense inversions for the H-PA_{68} and the PA_{68}-N-PS_{38} are schematically illustrated in Figure 5.

Conformational transformation for PS_n-C-PA_m

Figure 6a shows temperature dependence of N*H* proton signal for PS_{70}-C-PA_{170}. At 30 °C, both LH and RH signals were observed with $r_{LH} = 0.24$, together with a weak shoulder of RC signal at 8.0 ppm. While main-chain C$^{\alpha}H$ and side-chain C$^{\varepsilon}H_2$ proton signals for H-PA_n and PA_n-N-PS_m are difficult

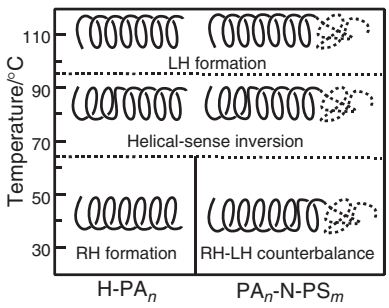


Figure 5. A schematic phase diagram of thermally induced conformational transformations for H-PA_n and PA_n-N-PS_m.

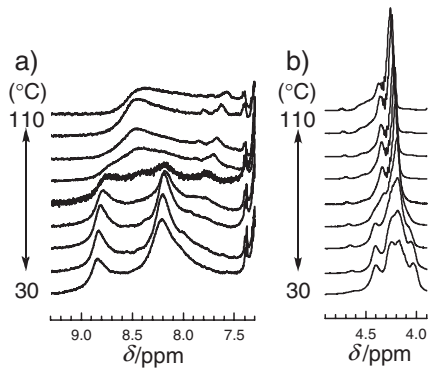


Figure 6. a) N*H* and b) $C^{\alpha}H$ and $C^{\varepsilon}H_2$ proton signals in ^{1}H NMR for PS_{70}-C-PA_{170} in a dilute TCE-d_2 solution observed at various temperatures between 30 and 110 °C in 10 °C intervals, respectively.

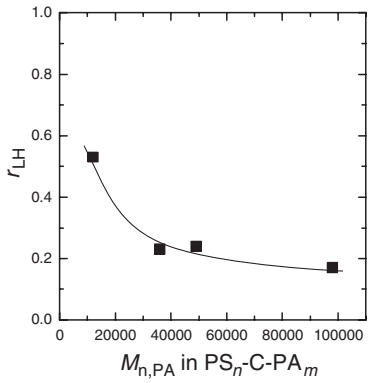


Figure 7. $M_{n,PA}$ dependence of r_{LH} for PS_n-C-PA_ms in a dilute $CDCl_3$ solution.

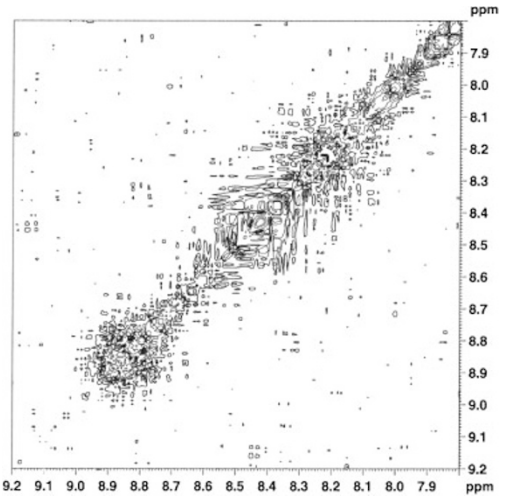


Figure 8. A 2D COSY spectrum for N*H* proton of PS_{70}-C-PA_{170} in a dilute TCE-d_2 solution observed at room temperature.

to be assigned because of their broadness and overlapping each other, characteristic signals of the main-chain $C^{\alpha}H$ proton were observed for the PS_{70}-C-PA_{170} as shown in Figure 6b. The peaks observed at 4.25, 4.40, and 4.65 ppm can be assigned to RH, LH and RC, respectively. Side-chain $C^{\varepsilon}H_2$ protons also showed signals at 4.05 and 4.20 ppm. For the PS_{70}-C-PA_{170}, the r_{LH} value of 0.24 was maintained up to 50 °C, indicating that RH and LH of the block copolymer were rather insensitive to the change of the temperature. However, with further increased of temperature, a very broad signal at 8.5 ppm and weak one at 7.7 ppm appeared, accompanied by disappearance of both the RH and LH signals. The main-chain $C^{\alpha}H$ protons assigned to RH and LH, naturally, disappeared, and new signals were observed at 4.35 and 4.55 ppm. Furthermore, side-chain $C^{\varepsilon}H_2$ protons also were affected by the temperature elevation, i.e., the increase of signal intensity at 4.25 ppm, indicating the formation of more proliferated side-chain conformations.[9–13] Again the signals were completely reversible on heating and cooling cycles.

In the temperature range of 30 to 50 °C, similar coexistence of RH and LH was observed for other PS_n-C-PA_ms listed in Table II. The results indicate that the attachment of PS segment at C-terminus brought about enhancement of the formation of LH. Figure 7 shows the dependence of r_{LH} on molecular weight of PA segment ($M_{n,PA}$) for the PS_n-C-PA_ms. The value became smaller with increasing $M_{n,PA}$, and reached 0.17 at $M_{n,PA} = 98000$, whereas it can be seen that the relative content of LH was not influenced by chain length of PS segment in these M_n range. The result implies that the formation of LH induced by PS segment occurred in a limited from C-terminus. Furthermore, PA conformation would not be exchanged between RH and LH in this temperature region, because 2D-exchange spectra observed at room temperature did not show any cross signals of the two N*H*s for RH and LH (Figure 8).

As described above, RC signals at 8.0 (N*H*) and 4.60 ppm ($C^{\alpha}H$) were observed over the temperature range examined, accompanied by the shift to upfield and downfield with increasing temperature, respectively, although both RH and LH were subjected to thermally induced transformation. Taking into considerations of the presence of RC and disappearance of both RH and LH at elevated temperatures, the residues that form RC seemed to exist in the connection part of PA with PS segment.

The conformation corresponding to the major signal at 8.5 ppm has not been clarified at the present time. One can expect that very fast conformational exchange of RH and LH took place above 70 °C. However, the argument requires that the existence of RH in significant amounts even at further elevated temperature, in spite of the fact that RH stability is reduced by attached PS segment. Recently the formation of flexible-rod conformation has been proposed in lyotropic

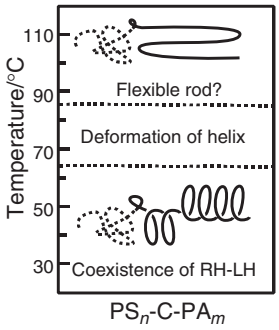


Figure 9. A schematic phase diagram of thermally induced conformational transformations for PS$_n$-C-PA$_m$.

liquid crystalline state of PA homopolymer in the presence of small amount of TFA.[13] Although the flexible-rod conformation has been unfamiliar thus far, we tentatively propose that the peak observed at 8.5 ppm at elevated temperatures is ascribed to the formation of β-strand like conformation of PS$_n$-C-PA$_m$s (Figure 9). If formation of such conformation is involved, the precipitate of the block copolymers is expected to form due to intra- and/or intermolecular interactions. In fact, other work in progress by us includes demonstration that a star-shaped polymer comprising PA, where C-terminus of PA is attached to the core, is precipitated from TCE above the flexible-rod forming temperature.[22] For PS$_n$-C-PA$_m$s, however, any precipitations were not observed in the temperature range of 90 to 110 °C, suggesting that intermolecular hydrogen bonds might be negligibly weak even if the PA segment took the β-strand like conformation.

PS segment in PS$_n$-C-PA$_m$s induced unusual conformational behavior of PA, while inversion temperature of helical sense was lowered in PA$_n$-N-PS$_m$s. The results showed that the conformational free energy in C-terminal side of PA would not be the same as that in N-terminal side. Although the reason remains unclear, one possible explanation is that helix capping[23] contributes to the difference between N- and C-termini. For α-helical polypeptides and proteins, because the first four NH groups and the last four CO groups of helix necessarily lack intrahelical hydrogen bonds, polar side chains at the positions near the terminal ends of the helices are often able to form hydrogen bonds to these unfulfilled groups.[23] Accordingly, it is assumable that the conformational free energy at N-terminus of PA is altered by the helix capping with side-chain ester CO groups which can satisfy the uncompensated main-chain amide NH groups.

SUMMARY

Block copolymers comprising poly(β-phenethyl-L-aspartate) (PA) and polystyrene (PS) where the PS was attached to N- and C-terminus of the PA in PA$_n$-N-PS$_m$ and PS$_n$-C-PA$_m$, respectively, were prepared by combination of ATRP and ROP of *N*-carboxy amino acid anhydride. Conformational transformations of the PA in the block copolymer systems were studied in dilute 1,1,2,2-tetrachloroethane solutions at various temperatures. In the case of PA$_{68}$-N-PS$_m$s, the PS segment played a role to enhance the transformation from right-handed helical structure (RH) to left-handed one (LH) in the temperature range of 40 to 60 °C, but at elevated temperatures the formation of LH seemed to be governed by inherent properties of PA. On the other hand, PS$_n$-C-PA$_m$ showed different behaviors. PS$_n$-C-PA$_m$ took both RH and LH formed at 30 °C. Interestingly, no further helical-sense inversion was induced by temperature changes between 30 and 50 °C, and then the helices were transformed into another conformation, which is tentatively assumed to be flexible-rod structure, at elevated temperatures. Thus, the modification of N- and C-terminus of PA brought about the formation of LH structure at relatively low temperatures. In addition, for the latter polymer extraordinary conformation was formed at elevated temperatures. The results indicate that each chain terminus of PA has different conformational free energy.

As can be seen in these PA block copolymer systems, block copolymerization with various polymer segments will lead control of conformational behavior in poly(aspartate ester)s as well as structure of side-chain groups, temperature, and solvents.

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