Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2009**, *42*, 8003–8005 **8003**
DOI: 10.1021/ma901474b

Side-Chain Polypseudorotaxanes with Heteromacrocyclic Receptors of Cyclodextrins (CDs) and Cucurbit[7]uril (CB7): Their Contrast Lower Critical Solution Temperature Behavior with α-CD, γ-CD, and CB7

Tomoki Ogoshi,* Kazuyuki Masuda, Tada-aki Yamagishi, and Yoshiaki Nakamoto*

Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

Received July 7, 2009
Revised Manuscript Received October 4, 2009

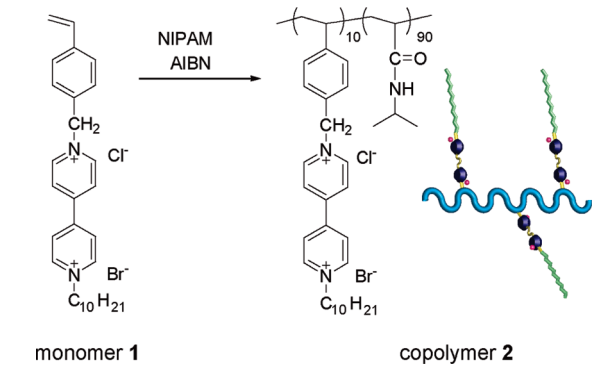
Introduction. Polypseudorotaxanes consisting of cyclic rings and polymeric chain have attracted tremendous interest from researchers because they are widely used as components in functional supramolecular materials.[1] Polypseudorotaxanes are categorized into two types: main- and side-chain type polypseudorotaxanes. For construction of the main- and side-chain type polypseudorotaxanes, cyclodextrins (CDs) have been widely used as ring segments because CDs form host−guest complexes with various hydrophobic molecules.[2] Since cucurbit[*n*]urils (CBs, $n = 5-8$) can form very stable host−guest complexes with positively charged molecules, the main- and side-chain type polypseudorotaxanes based on CBs have been also prepared.[3]

Moreover, combinations of these heteromacrocyclic receptors such as CDs and CBs are a nowadays hot topic and open new direction of supramolecular chemistry because multiple interactions between two or more complex molecules give insights into molecular recognition and self-assembly processes. Based on CDs and CBs, new molecular recognition systems[4] and supramolecular architectures[5] have been reported. Construction of the main-chain type polypseudorotaxane containing heteromacrocyclic receptors of CDs and CBs was reported by Yui, Kim, and co-workers.[6] Here in this Communication, we report novel side-chain type polypseudorotaxanes constituted of heteromacrocyclic receptors of α-CD, γ-CD, and cucurbit[7]uril (CB7). CDs and CB7 form host−guest complexes with hydrophobic decyl and cationic viologen moieties, respectively.[7] Therefore, for the synthesis of the side-chain type polypseudorotaxanes, we synthesized new vinyl monomer **1** carrying the decyl and viologen guest moieties (Scheme 1). Poly(*N*-isopropylacrylamide), which shows lower critical solution temperature (LCST) behavior around 32 °C, was employed as main chain. From radical copolymerization of monomer **1** and *N*-isopropylacrylamide (NIPAM) with 2,2′-azobis(isobutyronitrile) (AIBN), we prepared thermosensitive copolymer **2** (Scheme 1). In this study, we report unexpected contrast LCST behavior of copolymer **2** by formation of the side-chain type polypseudorotaxanes with α-CD, γ-CD, and CB7.

Results and Discussion. Copolymer **2** was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, elemental analysis, and viscosity measurements. The introduction efficiency of guest moieties calculated by ^{1}H NMR and elemental analysis for nitrogen was found to be 10.0 and 9.6 mol %, respectively. The viscosity-average molecular weight was 27 000. Copolymer **2** should form short block due to the reactivity between styrene and *N*,*N*-dimethylacrylamide.[8]

The host−guest interaction of copolymer **2** with CDs and CB7 was investigated by ^{1}H NMR measurements (Figure 1). In copolymer **2** (Figure 1a, concentration of guest part was 5 mM), peaks at high magnetic field (0.77, 1.54, and 2.00 ppm) and low magnetic field (8.51 and 9.10 ppm) were ascribable to protons from the decyl and viologen moieties, respectively. Upon addition of α-CD (Figure 1b, 5 mM), the proton signal of the methyl group (peak a) shifted to lower magnetic fields and a new proton resonance of the methylene moiety (peak c) appeared at 2.08 ppm. Proton peaks from α-CD moieties also showed shifts by complexation with the guest moieties (Supporting Information). In contrast, resonance bands of the viologen moieties showed no significant

Scheme 1. Synthesis of Thermosensitive Copolymer 2 Carrying Two Guest Moieties at the Side Chain[a]



[a] **NIPAM = *N*-isopropylacrylamide, AIBN = 2,2′-azobis-(isobutyronitrile).**

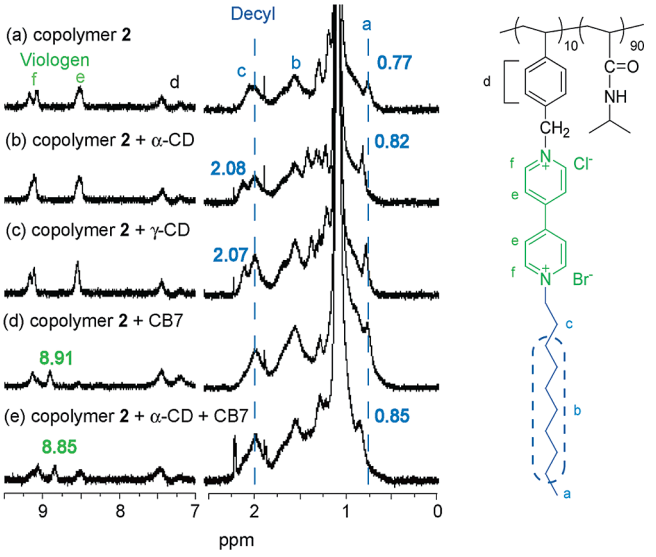


Figure 1. Partial ^{1}H NMR spectra of copolymer **2** (concentration of guest part was 5 mM) (a) without host and with (b) α-CD (5 mM), (c) γ-CD (30 mM), (d) CB7 (5 mM), and (e) α-CD (5 mM) and CB7 (5 mM) in D_2O at 25 °C.

*Corresponding author: Tel +81-76-234-4775; Fax +81-76-234-4800; e-mail ogoshi@t.kanazawa-u.ac.jp (T.O.), nakamoto@t.kanazawa-u.ac.jp (Y.N.).

Published on Web 10/08/2009

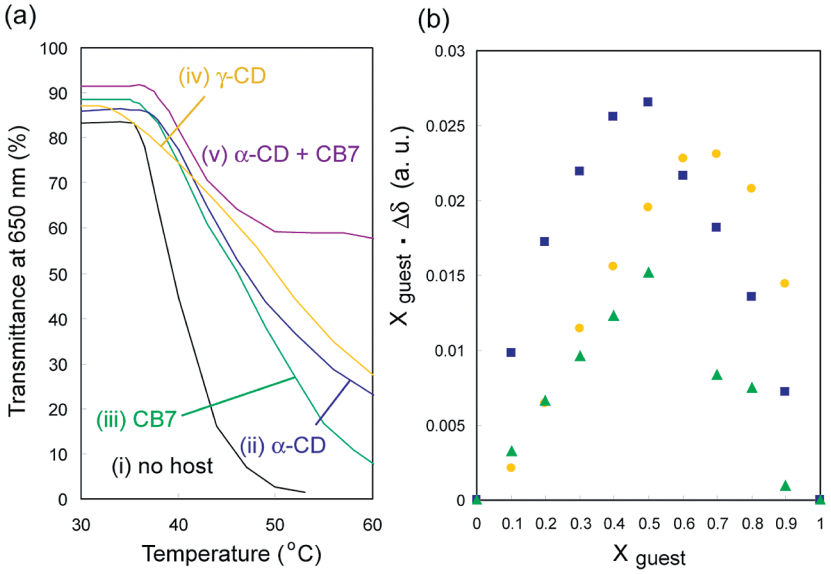
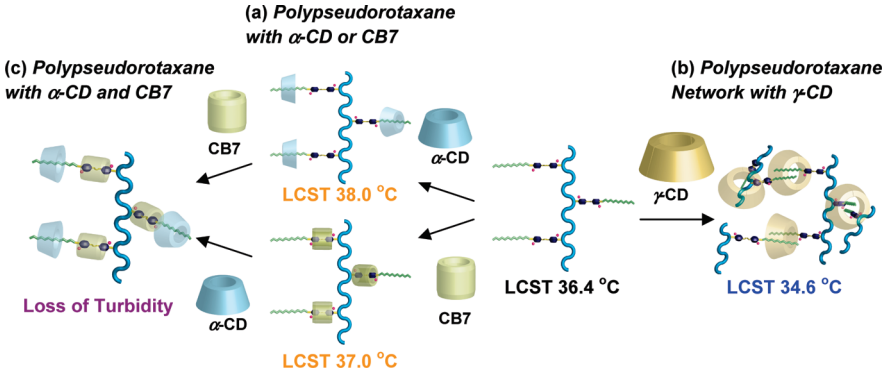


Figure 2. (a) Transmittance changes of copolymer **2** (concentration of guest part was 4 mM) (i) without host and with saturating amounts of (ii) α-CD (175 mM), (iii) CB7 (5.5 mM), (iv) γ-CD (90 mM), and (v) α-CD (175 mM) and CB7 (5.5 mM) during heating. (b) Job plots between (i) monomer **1** and α-CD (blue square), (ii) monomer **1** and CB7 (green triangle), and (iii) monomer **1** and γ-CD (yellow circle).

Scheme 2. Schematic Representation of the Side-Chain Polypseudorotaxanes with (a) α-CD or CB7, (b) γ-CD, and (c) α-CD and CB7



shifts. By adding γ-CD (Figure 1c, 30 mM), a new proton resonance of the methylene moiety (peak c) was found at 2.07 ppm, while no peak shifts of the viologen group were observed. These observations indicate that CDs form host−guest complexes with the decyl moieties in copolymer **2**. In contrast, upon addition of CB7 (Figure 1d, 5 mM), a new proton peak from the viologen moieties was observed at 8.91 ppm, while peak shifts were not observed in proton signals from the decyl moieties, strongly suggesting complexation of the viologen moieties with CB7. When both heteromacrocyclic receptors of α-CD (5 mM) and CB7 (5 mM) were added (Figure 1e), lower magnetic field shifts of the peak from methyl proton signal (peak a) in the decyl moiety, peak shifts from α-CD (Supporting Information), and new peak at 8.85 ppm from the viologen moiety were found. From these results, by adding both α-CD and CB7 to copolymer **2** in aqueous solution at the same time, formation of the side-chain type polypseudorotaxane containing heteromacrocyclic receptors of α-CD and CB7 was confirmed.

Figure 2a shows turbidity curves of copolymer **2** in the presence and absence of macrocyclic receptors of CDs and/or CB7. To examine effect of complexation with hosts, excess amounts of hosts (saturating concentrations of hosts) were employed. In the absence of CDs and CB7 (Figure 2a-i), LCST of copolymer **2** was 36.4 °C. Since typical poly(*N*-isopropylacrylamide) shows LCST behavior around 32 °C,[9] introduction of the decyl and viologen moieties at the side chain in copolymer **2** increased LCST. By adding saturating amounts of α-CD to copolymer **2** in aqueous medium (Figure 2a-ii), LCST was observed at 38.0 °C. When saturating amounts of CB7 were added to aqueous copolymer **2** solution (Figure 2a-iii), LCST was found at 37.0 °C. These results indicate that addition of CB7 or α-CD increases LCST. This is because complexation of the receptors of CB7 and α-CD at the side chain in copolymer **2** should inhibit shrinking of the polymer chain (Scheme 2a). On the other hand, by adding saturating amounts of γ-CD (Figure 2a-iv), LCST was decreased (LCST = 34.6 °C). The contrasting LCST changes depending on kinds of macrocyclic receptors were caused by the difference in stoichiometry of host−guest complex. Figure 2b shows Job plots between model compound of monomer **1** with α-CD, γ-CD, and CB7. In case of α-CD or CB7 used as a host (Figure 2b-i,ii), the peak top was observed in molar fraction: $X_{guest} = 0.50$. In contrast, in the case of γ-CD (Figure 2b-iii), the peak top was found in molar fraction $X_{guest} = 0.66$. Therefore, the stoichiometry of α-CD−monomer **1** or CB7−monomer **1** systems is 1:1 whereas that of γ-CD−monomer **1** system is 1:2.[10] Since 1:2 host−guest complexes between γ-CD and decyl moieties in copolymer **2** act as cross-links to form network structure, LCST behavior occurred even at low temperature (Scheme 2b). In addition,

long tailings of the curves were observed with α-CD, γ-CD, and CB7 (Figure 2a-ii-iv). Hosts formed the complexes with copolymer **2** were bulky; thus, the hosts should inhibit shrinking of the polymer chain.

When α-CD and CB7 were added to the aqueous copolymer **2** solution, loss of turbidity was detected (Figure 2a-v). The aqueous copolymer **2** solution with α-CD and CB7 at 50 °C was translucent (the transmittance at 650 nm = 59.3%) whereas the aqueous copolymer **2** solution at 50 °C was turbid (the transmittance at 650 nm = 2.6%). By adding both α-CD and CB7 at the same time, formation of the side-chain type polypseudorotaxane containing heteromacrocyclic receptors of α-CD and CB7 took place. α-CD and CB7 on the side chain of copolymer **2** were bulky; thus, aggregation of the polymer chains at elevated temperature should be efficiently inhibited (Scheme 2c).

Conclusions. We successfully synthesized the side-chain type polypseudorotaxanes consisted of heteromacrocyclic receptors of α-CD, γ-CD, and CB7. To the best of our knowledge, construction of the side-chain type polypseudorotaxanes containing heteromacrocycles has been little known, while successful synthesis of side-chain type polypseudorotaxanes and polyrotaxanes containing CDs was demonstrated by Ritter and co-workers.[2a−2c] LCST of copolymer **2** with α-CD or CB7 was increased, while that with γ-CD was decreased. Moreover, formation of the polypseudorotaxane with α-CD and CB7 lowered turbidity. LCST behavior of the side-chain type polypseudorotaxanes depended on the kinds and/or combinations of macrocyclic receptors used as ring segments.

Acknowledgment. We thank Prof. Shigeyoshi Kanoh and Dr. Katsuhiro Maeda (Kanazawa University) for variable temperature UV−vis absorption measurements. This work was supported by a Grant-in-Aid (KIBAN C-20550120 and WAKATE B-21750140) from the ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental section, NMR spectra of monomer **1** and copolymer **2**, ^{1}H NMR spectra of α-CD with copolymer **2**, α-CD with CB7 and copolymer **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Review: (a) Wenz, G.; Han, B. H.; Müller, A. *Chem. Rev.* **2006**, *106*, 782–817. (b) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456–464. (c) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H. J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630.

(2) (a) Ritter, H.; Sadowski, O.; Tepper, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 3171–3173. (b) Koopmans, C.; Ritter, H. *J. Am. Chem. Soc.* **2007**, *129*, 3502–3503. (c) Krestschmann, O.; Choi, S. W.; Miyauchi, M.; Tomatsu, I.; Harada, A.; Ritter, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 4361–4365. (d) Harada, A. *Adv. Polym. Sci.* **1997**, *133*, 141–191. (e) Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325–327. (f) Ogoshi, T.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 4878–4879. (g) Zhang, Z. X.; Liu, X.; Xu, F. J.; Loh, X. J.; Kang, E. T.; Neoh, K. G.; Li, J. *Macromolecules* **2008**, *41*, 5967–5970. (h) Yang, C.; Yang, J.; Ni, X.; Li, J. *Macromolecules* **2009**, *42*, 3856–3859. (i) Yang, C.; Li, J. *J. Phys. Chem. B* **2009**, *113*, 682–690. (j) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485–487. (k) Ito, K. *Polym. J.* **2007**, *39*, 489–499. (l) Arai, T.; Hayashi, M.; Takagi, N.; Takata, T. *Macromolecules* **2009**, *42*, 1881–1887. (m) Kihara, N.; Hinoue, K.; Takata, T. *Macromolecules* **2005**, *38*, 223–226.

(3) (a) Reczek, J. J.; Kennedy, A. A.; Halbert, B. T.; Urbach, A. R. *J. Am. Chem. Soc.* **2009**, *131*, 2408–2415. (b) Tan, Y.; Choi, S. W.; Lee, J. W.; Ko, Y. H.; Kim, K. *Macromolecules* **2002**, *35*, 7161–7165. (c) Liu, Y.; Ke, C. F.; Zhang, H. Y.; Wu, W. J.; Shi, J. *J. Org. Chem.* **2007**, *72*, 280–283.

(4) (a) Yang, C.; Mori, T.; Origane, Y.; Ko, Y. H.; Selvapalam, N.; Kim, K.; Inoue, Y. *J. Am. Chem. Soc.* **2008**, *130*, 8574–8575. (b) Yang, C.; Ko, Y. H.; Selvapalam, N.; Origane, Y.; Mori, T.; Wada, T.; Kim, K.; Inoue, Y. *Org. Lett.* **2007**, *9*, 4789–4792. (c) Zou, D.; Andersson, S.; Zhang, R.; Sun, S.; Åkermark, B.; Sun, L. *Chem. Commun.* **2007**, 4734–4736. (d) Zou, D.; Andersson, S.; Zhang, R.; Sun, S.; Åkermark, B.; Sun, L. *J. Org. Chem.* **2008**, *73*, 3775–3783.

(5) (a) Rekharsky, M. V.; Yamamura, H.; Kawai, M.; Osaka, I.; Aeakawa, R.; Sato, A.; Ko, Y. H.; Selvapalam, N.; Kim, K.; Inoue, Y. *Org. Lett.* **2006**, *8*, 815–818. (b) Chakrabarti, S.; Mukhopadhyay, P.; Lin, S.; Isaacs, L. *Org. Lett.* **2007**, *9*, 2349–2352. (c) Leclercq, L.; Noujeim, N.; Sanon, S. H.; Schmitzer, A. R. *J. Phys. Chem. B* **2008**, *112*, 14176–14184. (d) Liu, Y.; Li, X. Y.; Zhang, H. Y.; Li, C. J.; Ding, F. *J. Org. Chem.* **2007**, *72*, 3640–3645.

(6) Ooya, T.; Inoue, D.; Choi, H. S.; Kobayashi, Y.; Loethen, S.; Thompson, D. H.; Ko, Y. H.; Kim, K.; Yui, N. *Org. Lett.* **2006**, *8*, 3159–3162.

(7) (a) Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875–1918. (b) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H. J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621–630. (c) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844–4870.

(8) Saini, G.; Leoni, A.; Franco, S. *Makromol. Chem.* **1971**, *146*, 165–171.

(9) (a) Hamcerencu, M.; Desbrieres, J.; Popa, M.; Riess, G. *Biomacromolecules* **2009**, *10*, 1911–1922. (b) Qian, J.; Wu, F. *Chem. Mater.* **2007**, *19*, 5839–5841. (c) Lutz, J. F.; Akdemir, Ö.; Hoth, A. *J. Am. Chem. Soc.* **2006**, *128*, 13046–13047. (d) Pasparakis, G.; Cockayne, A.; Alexander, C. *J. Am. Chem. Soc.* **2007**, *129*, 11014–11015.

(10) Qu, X. K.; Zhu, L. Y.; Li, L.; Wei, X. L.; Liu, F.; Sun, D. Z. *J. Solution Chem.* **2007**, *36*, 643−650. Formation of 1:2 host−guest complex between γ-CD and alkylammonium salt was reported.