Journal of Inclusion Phenomena and Macrocyclic Chemistry **44:** 303–306, 2002.

Synthesis of Cyclic Poly(Methacrylic Acid) by Template Polymerization of β-Cyclodextrin Monomer

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(Received: 7 May 2002; in final form: 1 October 2002)

Key words: ATRP, β-cyclodextrin, macrocyclic polymer, template polymerization

Abstract

Atom transfer radical polymerization of template monomer synthesized by introduction of methacryloyl groups into secondary hydroxyl groups of β-cyclodextrin [β-CD] was carried out with 1,3-dibromobutane as an initiator. Then, closing of polymerized methacryloyl groups was carried out by reaction of bromine groups at both ends with 1,3-diamino propane [DAP] or 1,4-diamino butane [DAB]. The macrocyclic poly(methacrylic acid) [PMAA] obtained by hydrolysis of products was analyzed by GPC, MALDI-TOF-mass. It was found that template monomer of β-CD was effective for synthesis of macrocyclic oligomers and that DAP was the preferred closing reagent for the methacryloyl groups polymerized in the template monomer.

Introduction

Strict control of the architecture of a polymer is important to develop highly functional materials. Anionic and cationic living polymerizations are well-known as successful techniques for control of the architecture of the polymer [1]. However, preferable monomers for the anionic and cationic polymerization are limited. Recently, controlled/living radical polymerization [2–8], including atom transfer radical polymerization (ATRP [6–8]) has been well investigated. However, even by ATRP, it is difficult to control the architecture of oligomers.

Template polymerization is another approach to control polymerization [9–12]. However, the free radical polymerization was initiated at random in the template and the arrangement of the vinyl groups in the template was insufficient. From a viewpoint of template polymerization, β-CD will be a unique template by introduction of 14 methacryloyl groups into 14 secondary hydroxyl groups. By polymerization of methacryloyl groups in the molecule of template monomer and hydrolysis of polymerized products, PMAA oligomers with 14 of degree of polymerization (DP) will be obtained (Figure 1).

Based on this concept, polymerization of template monomer of β-CD was carried out by free radical polymerization [13], controlled/living radical photo polymerization [13] and ATRP with 1,3-dibromobutane [14]. It was found that the template monomer of β-CD was useful template monomer for synthesis of PMAA oligomers. Especially, controlled/living radical polymerization and ATRP with 1,3-dibromobutane were effective for the template monomer of β-CD.

After ATRP with 1,3-dibromobutane, two bromine groups, which existed at both end of poly(methacryloyl group), were arranged side by side in the template monomer. By reaction of two bromine groups with bi-functional compound, cyclization of the poly(methacryloyl groups) will occur. The purpose of this work is to obtain macrocyclic PMAA oligomers by reaction of diamine compounds with bromine groups in the template monomer after ATRP. In this work, DAP and DAB were chosen as diamine compounds. The reaction of amine and bromine was determined by Volhart's titration.

Experimental

Materials

Template monomer of β-CD was synthesized previously [13]. Average numbers of acetyl groups and methacryloyl groups were 7.0 and 10.9, respectively.

Polymerization of template monomers

ATRP of the template monomer was carried out with 1,3-dibromrobutane, 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA), and CuBr as an initiator, ligand and catalysit, respectively for 3 h at 35 °C [14]. Monomer concentration and solvent were 1.0 wt% and THF, respectively.

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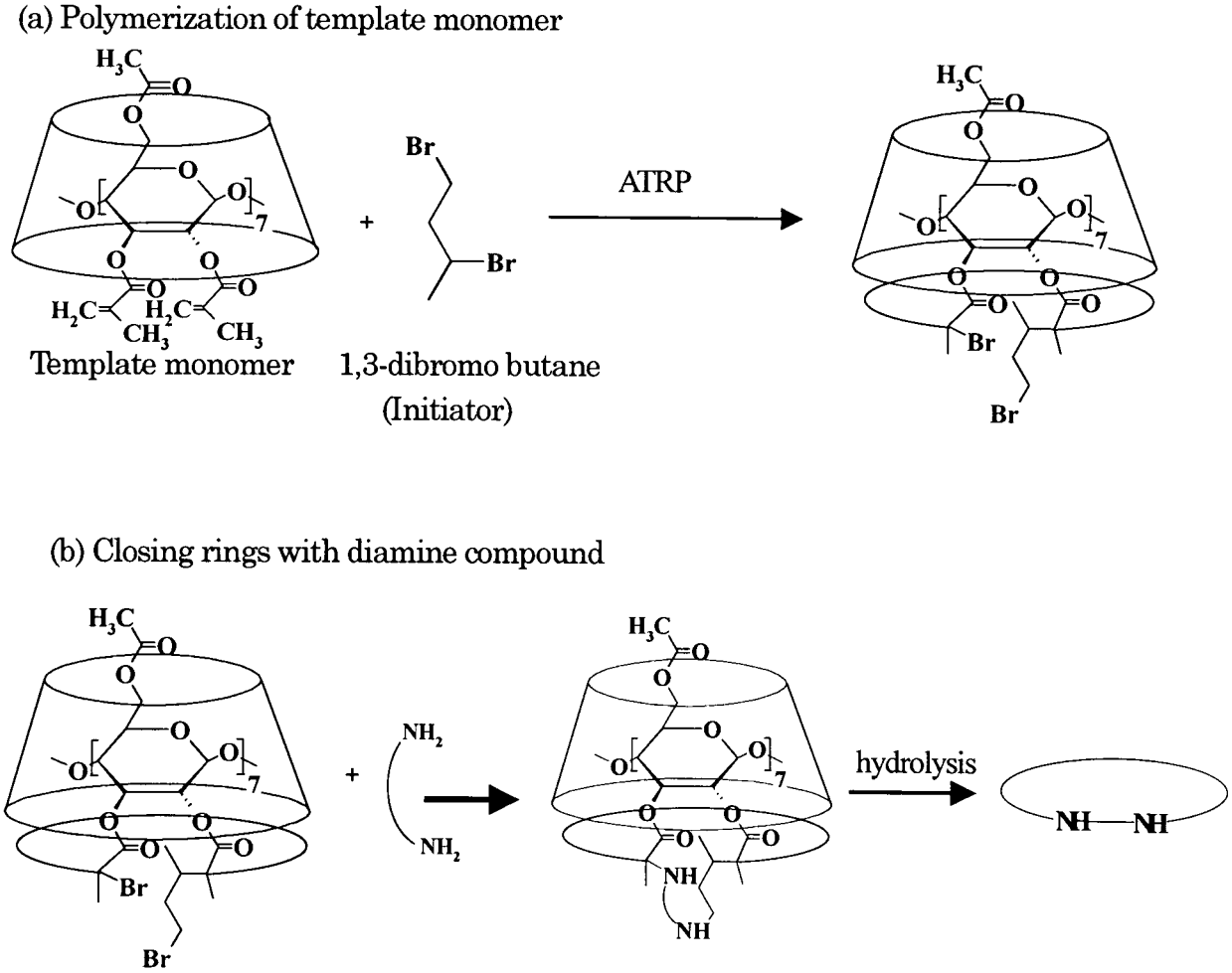

Figure 1. Synthetic concept of macrocyclic polymer with template monomer of β-cyclodextrin.

Cyclization

1.24×10^{-1} M concentration of polymerized product was dissolved in benzene. 1.0 N of aqueous NaOH and DAP or DAB were added to the solution with [NaOH]: [$-NH_2$]: [–Br] = 1 : 1 : 1. The solution was reacted at 40 °C for 7 days.

Hydrolysis of polymerized products

Hydrolysis of the products was carried out as previously reported [14].

Characteristics

Number-average molecular weight, Mn, was measured with GPC (TOSOH, HLPC 8020) fitted with refractive index detector and UV double detection equipment. Eluent was THF for template monomer and polymerized products, and methanol for PMAA. Molecular weight of PMAA was also measured out with matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (Shimazu, Kraros Kompact MALDI 2) at positive state. FT-IR spectra were measured with a Jasco Fourier-transform infrared spectrometer FT/IR-410. Concentration of bromide ion synthesized in the solution by cyclization was measured by Volhart's titration.

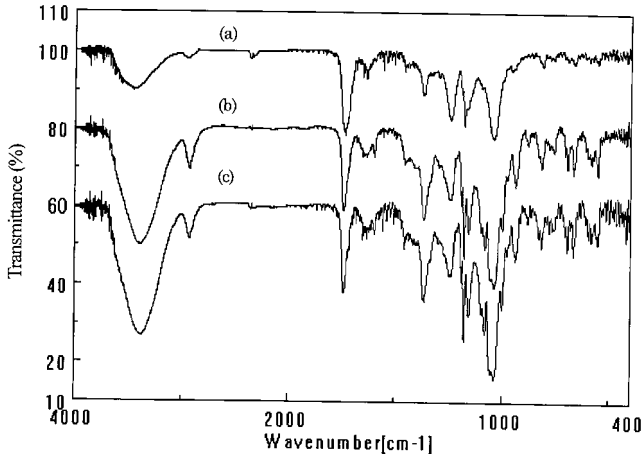

Figure 2. FT-IR spectra before and after closing rings: (a) After reaction with DAP; (b) after reaction with DAB; and (c) before reaction.

Results and discussion

Figure 2 shows FT-IR spectra of before and after cyclization with DAP and DAB. DAP and DAB were introduced in the polymerized template monomer, and a new peak for the amino groups was observed at 1340 cm^{-1} after cyclizations with DAP and DAB.

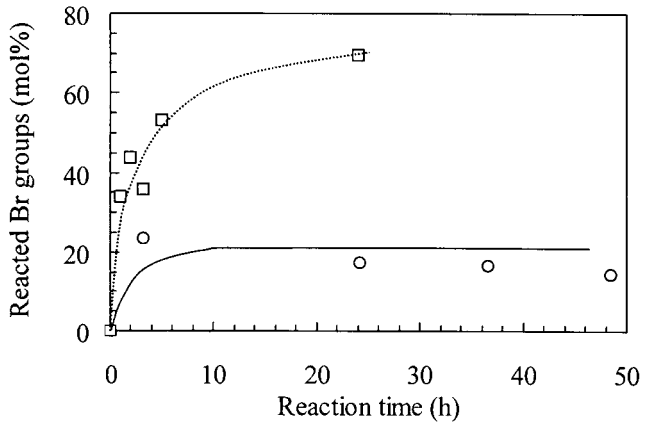

Figure 3. Time conversion of bromine groups reacted with diamine compounds: (□) Reaction with DAP; (○) reaction with DAB.

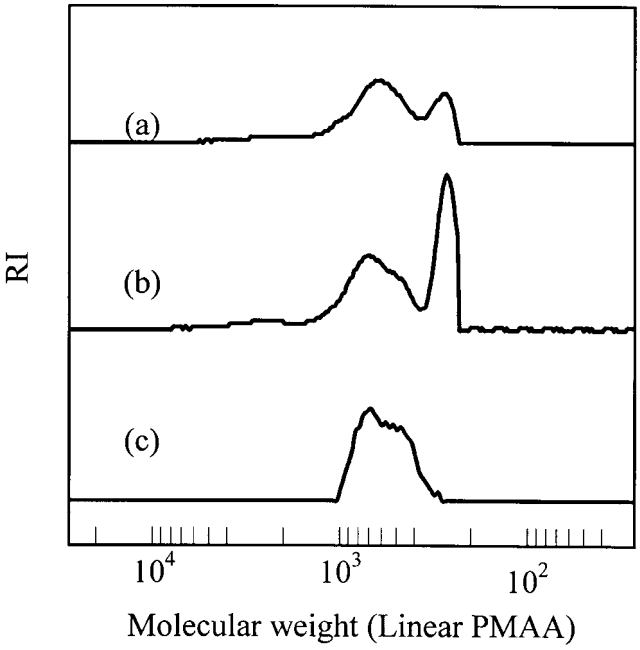

Figure 4. GPC profiles of poly(methacrylic acid) oligomers before and after closing rings measured with methanol: (a) After reaction with DAP; (b) after reaction with DAB; and (c) before reaction.

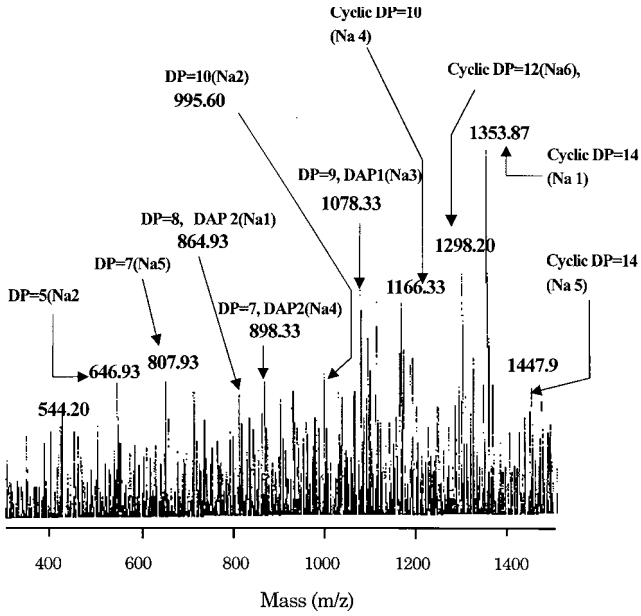

Figure 5. MALDI-TOF-mass spectra of poly(methacrylic acid) oligomer obtained by hydrolysis of reacted product with DAP.

The molar amounts of reacted bromine groups were quantitatively measured by Volhart's titration. Figure 3 shows time molar conversion of bromine group in the polymerized template monomer. With any cyclization reagents, the molar conversion of bromine group was saturated at 24 h. The saturated molar conversion of bromine group with DAP was 60 mol%. On the other hand, The saturated molar conversion of bromine group with DAB was ca. 20 mol%. Bromine groups in the template monomer were a primary and a tertiary bromine group. The primary amine preferably reacts with primary bromine group rather than with tertiary bromine group. Theoretically, the cyclization is composed of two steps as follows: First, one amino group in DAP or DAB reacts with primary bromine group in the template monomer. Second, cyclization occurs by reaction of another amino group in DAP or DAB with tertiary bromine group in the template. The lower conversion of DAB than 50 mol% suggests that the cyclization did not occur. Increasing of reaction temperature did not effect on the conversions of the bromine groups. Thus, the low conversion of DAB was not due to the conditions of reaction but the structure of DAB.

Figure 4 is GPC profiles of PMAA obtained by hydrolysis of products before and after cyclization. After cyclization with DAP, the Mn of PMAA measured by GPC was decreased from 830 to 580. Theoretically, the Mn ratio of macrocyclic polymer to linear polymer measured by GPC is 0.8. The decreasing of Mn determined by GPC after cyclization with DAP indicates that the cyclization of PMAA was carried out with DAP. For DAB, the shift of GPC peak to lower molecular weight was insufficient. Thus, DAB was not an appropriate cyclization reagent for β-CD template monomer. This agreed well with the low conversion of bromine groups with DAB. Thus, it is probable that the distance between amine groups in DAB does not fit the distance between bromine groups in the polymerized template monomer.

By MALDI-TOF-mass analysis of PMAA with DAP, Figure 5, macrocyclic PMAA with DP = 12 was confirmed at m/z = 1298.2. However, not only macrocyclic PMAA but also linear PMAA reacted with DAB was observed. Further investigation is required to find ways to increase conversion with cyclization.

Conclusions

Cyclization of poly(methacryloyl group) in template monomer of β-CD with DAP and DAB was investigated. Both DAP and DAB were introduced in polymerized template monomer. It was possible to cyclize poly(methacryloyl group) with DAP. However, the cyclization did not occur with DAB. It was due to the fact that the distance

between amino groups of DAP was appropriate to the bromine groups in the template monomer polymerized with 1,3-dibromobutane.

Acknowledgements

The authors greatly acknowledge the financial and experimental support of LC-Mass measurements by the “Mukai Science and Technology Foundation” and Dr. H. Asanuma, Research Center for Advanced Science and Technology, The University of Tokyo.

References

1. M. Swarc: *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience Publishers, New York (1968).
2. T. Otsu and M. Yoshida: *Makromol. Chem. Rapid Commun.* **3**, 127 (1982).
3. V.B. Golubev, M. Yu. Zaremski, S.M. Mel’nikov, A.V. Olenin and V.A. Kabanov: *Vysokmol. Soed., Seriya A*. **36**, 320 (1994).
4. A.R. Kannurpatti, S. Lu, G.M. Bunker and C.N. Bowman: *Macromolecules* **29**, 7310 (1996).
5. T. Otsu: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 2121 (2000).
6. V. Percec, B. Barboiu, T.K. Bera, M. van der Sluis, R.B. Grubbs and J.M.J. Fréchet: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 4776 (2000).
7. K. Tokuchi, T. Ando, M. Kamigaito and M. Sawamoto: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 4735 (2000).
8. K.A. Davis, B. Charleux and K. Matyjaszewski: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 2274 (2000).
9. R. Jantas: *J. Polym. Sci.*, Part A, *Polym. Chem.* **28**, 1973 (1990).
10. H.L. Frisch and Q. Xu: *Macromolecules* **25**, 5145 (1992).
11. K. Tajima, G. Ogawa and T. Aida: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 4821 (2000).
12. M. Yoshida, Y. Hatate, K. Uezu, M. Goto and S. Furuwaki: *J. Polym. Sci.*, Part A, *Polym. Chem.* **38**, 689 (2000).
13. R. Saito, H. Kobayashi and Y. Okuno: *J. Polym. Sci.*, Part A, *Polym. Chem.* **39**, 3539 (2001).
14. R. Saito and H. Kobayashi: *Macromolecules* **35**, 7207–7213.