

G. 研究発表

2009 年度

1. 論文発表

1)Hidenori Ohashi, Maiko Watanabe,
Taichi Ito,Takanori Tamaki,Takeo
Yamaguchi,

*Journal of Photopolymer Science
and Technology* 2010, in press

“Fabrication of Protein Renaturation
Facilitating Membrane Using Plasma
Graft Pore Filling Technique”

2)Hidenori Kuroki, Hidenori Ohashi
Taichi Ito, Takanori Tamaki ,Takeo
Yamaguchi,

Journal of Membrane Science,
2010, in press

“Isolation and Analysis of Grafted
Polymer onto a Straight Cylindrical
Pore in a Thermal-Responsive
Gating Membrane and Elucidation
of its”

3) Taichi Ito, Yuhei Oshiba,
Hidenori Ohashi, Takanori Tamaki
Takeo Yamaguchi,

Journal of Membrane Science,
2010, 369-375

“Sensitivity enhancement of a
molecular recognition ion gating
membrane in an aqueous ethanol
solution”

2. 学会発表
- 1) 日本膜学会 第31年会
東京理科大学森戸記念館
2009年5月21日-22日
2B-5,P-9
菅原勇貴・大橋秀伯・伊藤大知・
山口猛央
抗体固定PEG修飾金ナノ粒子
を用いた新規抗原認識システムの
開発
- 2) The Fifth Conference of
Aseanian Membrane Society
神戸ポートピアホテル
2009年7月12日-14日
P10-24
大橋秀伯・伊藤大知・山口猛央
Development of a Microscopic Free
Volume Theory for Prediction of
Penetrant Self-diffusivity in
Polymeric Systems
- 3) The Fifth Conference of
Aseanian Membrane Society
神戸ポートピアホテル
2009年7月12日-14日
P1-15
菅原勇貴・黒木秀記・大橋秀伯・
伊藤大知・山口猛央
New Antigen-responsive System
Amplified by Water Shell around
Gold Nanoparticle
- 4) The Fifth Conference of
Aseanian Membrane Society
神戸ポートピアホテル
2009年7月12日-14日
P1-14
黒木秀記・大橋秀伯・伊藤大知・
山口猛央
Novel Biomolecular Recognition
Gating Membrane Using Phase
Transition
- 5) 化学工学会 米沢大会 2009
山形大学工学部(米沢)
2009年8月10日-11日
P117
大柴 雄平・大橋 秀伯・伊藤 大知・
平川 秀彦・山口 哲志・長棟 輝行・
分子認識性ポリマー複合型人工アロ
ステリック酵素の開発
- 6) 化学工学会 第41回秋季大会
広島大学東広島キャンパス
2009年9月16日-18日
AC127
大柴雄平・大橋 秀伯・伊藤 大知・
平川 秀彦・山口 哲志・長棟 輝行・
山口 猛央
分子認識型人工アロステリック酵素
の開発
- 7) 化学工学会 第41回秋季大会
広島大学東広島キャンパス
2009年9月16日-18日
U106
岩元 望・大橋 秀伯・
伊藤 大知・清野 竜太郎・山口 猛央
ミクロな考察に基づいた高分子溶液
系における分子核酸モデルの構築
- 8) 化学工学会 第41回秋季大会
広島大学東広島キャンパス
2009年9月16日-18日,U108
渡辺麻衣子・大橋 秀伯・伊藤 大知・
山口 猛央
タンパク質リフォーディング支援膜
の開発

<p>9)材料化学システム工学討論会 2009 2009年12月6日-7日 23 大橋 秀伯・伊藤 大知・山口 猛央 ミクロな自由体積拡散性予測モデルにおけるパラメータシステムの構築</p>	<p>人エアロスティック酵素の開発のための分子認識ポリマーと遺伝子組み換え酵素の複合化 13)平成21年度つくば学生研究交流会 独立行政法人産業総合研究所つくば中央第5事業所研究第2本間6階会議室 2010年3月12日 16</p>
<p>10)材料化学システム工学討論会 2009 2009年12月6日-7日 P8 大柴 雄平・田巻 孝敬・大橋 秀伯・伊藤 大知・平川 秀彦・山口 哲志・長棟 輝行・山口 猛央 分子認識ポリマーを用いた人工エアロスティック酵素の開発 11)ポストシリコン物質・デバイス創製基盤技術アライアンス 2010年3月10日 A3-6 大橋 秀伯・田巻 孝敬・伊藤 大知・山口 猛央 高分子中の分子拡散性を予測するミクロ自由体積モデルにおけるパラメータシステム構築 12)平成21年度つくば学生研究交流会 独立行政法人産業総合研究所つくば中央第5事業所研究第2本間6階会議室 2010年3月12日 10 大柴 雄平・田巻 孝敬・大橋 秀伯・伊藤 大知・平川 秀彦・山口 哲志・長棟 輝行・山口 猛央</p>	<p>菅原 勇貴・黒木秀記・大橋秀伯・田巻 孝敬・伊藤大知・山口猛央 生体分子認識ゲート膜を用いた高速イムノクロマト法 14)化学工学会第75回年会 鹿児島大学郡元キャンパス 2010年3月18日-20日 A103 黒木秀記・大橋秀伯・田巻 孝敬・伊藤大知・山口猛央 ゲート機能膜における細孔内グラフトポリマー物性と透過流束特性 15)化学工学会第75回年会 鹿児島大学郡元キャンパス 2010年3月18日-20日 N208 渡辺 麻衣子・大橋 秀伯・田巻 孝敬・伊藤大知・山口猛央 タンパク質リフォールディング支援膜の開発および性能評価 16)化学工学会第75回年会 鹿児島大学郡元キャンパス 2010年3月18日-20日 N209 大柴 雄平・田巻 孝敬・大橋 秀伯・伊藤 大知・平川 秀彦・山口 哲志・長棟 輝行・山口 猛央</p>

アロステリック効果を有する分子
認識ポリマー・酵素複合体の開発

17) 日本膜学会 第32回年会
産業技術総合研究所臨海副都心セ
ンター別館

2010年5月13-14日

2C-3

菅原 勇貴・黒木秀記・大橋秀伯・
田巻 孝敬・伊藤大知・山口猛央
生体分子認識ゲート膜における金
ナノ粒子透過性の評価

2008 年度

1. 論文発表

1) Nuttapol Limjeerajarus, Yosuke Nishiyama, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi

Journal of Chemical Engineering of Japan 2009, in press

“Modeling for Modified Model for PEFC MEAs Based on Separation of Structural and Reaction Parameters Reaction Rate on Pt Surface Area and Microstructures of Catalyst Layers”

2) Nobuo Hara, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi,

Journal of Physical Chemistry B, 2009(113)4656-4663

“Rapid proton conduction through unfreezable and bound water in a wholly aromatic pore-filling electrolyte membrane”

3) Nobuo Hara, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi,

Macromolecules, 2008(42)980-986

“Reverse Response of an Ion-recognition Polyampholyte to Specific Ion Signals at Different pHs”

4) Nuttapol Limjeerajarus, Tatsunori Yanagimoto, Toshio Yamamoto, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi,

Journal of Chemical Engineering of Japan, 2009(42)86-94

“Analysis of Oxygen Reduction Reaction Activity of Pt/C Catalysts for Actual PEFC MEAs”

5) Takanori Tamaki, Taichi Ito, Takeo Yamaguchi,

Fuel Cells, 2009(9)37-43

“Modeling of Reaction and Diffusion Processes in a High-Surface-Area Biofuel Cell Electrode Made of Redox Polymer-Grafted Carbon”

6) Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi,

Journal of Chemical Engineering of Japan, 2009(42)86-96

“A New Free Volume Theory Based on Microscopic Concept of Molecular Collisions for Penetrant Self-diffusivity in Polymers”

7) Nuttapol Limjeerajarus, Tatsunori Yanagimoto, Toshio Yamamoto, Taichi Ito, Takeo Yamaguchi,

Journal of Power Sources, 2008(185)217-221

“Quantitative analysis of the amount of oxygen-containing species adsorbed on the Pt surface of a PEMFC MEA electrode using stripping voltammetry”

8) Miyaoi Naoko, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi

Journal of Chemical Engineering of Japan, 2008(41)766-770

“An Analysis of Pore Size Using a Straight-Pore Molecular Recognition Ion Gating Membrane”

2. 学会発表

- 1) 電気化学会 第76回大回
京都大学吉田キャンパス
2009年3月29日-31日
2Q18
藤井啓太郎・大橋秀伯・
伊藤大知・山口猛央
全固体高分子形アルカリ燃料電池用新規芳香族系細孔フィリング膜のOH-伝導特性
- 2) 電気化学会 第76回大回
京都大学吉田キャンパス
2009年3月29日-31日
2Q19
豊田将平・大橋秀伯・伊藤大知・山口猛央
細孔フィリング電解質膜を用いた全固体高分子形アルカリ燃料電池の開発
- 3) 電気化学会 第76回大回
京都大学吉田キャンパス
2009年3月29日-31日
1L04
平出篤志・田巻孝敬・大橋秀伯・伊藤大知・山口猛央
バイオ燃料電池の性能向上のための酵素集積電極の解析及びナノ構造制御
- 4) 電気化学会 第76回大回
京都大学吉田キャンパス
2009年3月29日-31日
2Q17
原 伸生・大橋秀伯・伊藤大知・山口猛央
微細細孔内充填電解質ポリマー中の特異なプロトン伝導機構

- 5) 化学工学会 第74年会
横浜国立大学
2009年3月18日-20日
Q305
平出 篤志・田巻 孝敬・大橋 秀伯・
伊藤 大知・山口 猛央
バイオ燃料電池における酵素集積電極のナノ構造制御
- 6) 化学工学会 第74年会
横浜国立大学
2009年3月18日-20日
L307
藤井 啓太郎・大橋 秀伯・
伊藤 大知・山口 猛央
全固体高分子形アルカリ燃料電池用新規芳香族系細孔フィリング膜のOH-伝導特性
- 7) 化学工学会 第74年会
横浜国立大学
2009年3月18日-20日
L305
豊田 将平・大橋 秀伯・
伊藤 大知・山口 猛央
細孔フィリング電解質膜を用いた全固体高分子形アルカリ燃料電池のシステム設計
- 8) 化学工学会 第74年会
横浜国立大学
2009年3月18日-20日
L306
Limjeearajarus Nuttapol・大橋 秀伯・
伊藤 大知・山口 猛央
A Novel modeling based on secondary pore and microscopic reaction models for PEFCs
- 9) 化学工学会 第74年会

横浜国立大学 2009年3月18日-20日 S116 黒木 秀記・大橋 秀伯・ 伊藤 大知・山口 猛央 架橋ゲート膜型バイオセンサー開 発における細孔内構造制御 10) 化学工学会 第74年会 横浜国立大学 2009年3月18日-20日 I202 原 伸生・大橋 秀伯・ 伊藤 大知・山口 猛央 微細細孔内充填電解質ポリマー中 の特異なプロトン伝導の特性と解 析 11) 化学工学会 第74年会 横浜国立大学 2009年3月18日-20日 I105 大橋 秀伯・伊藤 大知・ 山口 猛央 高分子中の分子拡散性を予測する ミクロ自由体積モデルにおけるパ ラメータシステム検討 12) 高分子材料開発のための俯 瞰的シンポジウム 2009 京都大学桂キャンパス 2009年1月13日-14日 5 伊藤 大知・Yoon Yeo, Christopher B. Highley, Evangelia Bellas, Iain P. Fraser, Robert Langer, Daniel S. Kohane The prevention of peritoneal adhesions by in situ cross-linking	hydrogels of hyaluronic acid and cellulose derivatives 13) 高分子材料開発のための俯瞰的 シンポジウム 2009 京都大学桂キャンパス 2009年1月13日-14日 4 大橋 秀伯・伊藤 大知・山口 猛央 ミクロな自由体積理論を用いた高分子 中の分子拡散性予測：種々の高分子系 への応用 14) ポストシリコン物質・デバイス 創製基盤技術アライアンス平成20年度 成果報告会 北海道大学 2008年12月25日-26日 PG3-12 大橋 秀伯・伊藤 大知・ 山口 猛央 高分子中の分子拡散性を予測する新し いミクロモデルの構築 15) ポストシリコン物質・デバイス 創製基盤技術アライアンス平成20年度 成果報告会 北海道大学 2008年12月25日-26日 PG3-11 大橋 秀伯・伊藤 大知・山口 猛央 分子認識イオンゲート膜の創製とデバ イス応用 16) 2008年度高分子計算機科学研究 会・高分子ナノテクノロジー研究会 合 同討論会 東京工業大学大岡山キャンパス 2008年12月11日-12日 6
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大橋 秀伯・伊藤 大知・山口 猛央
高分子中の分子拡散性を予測する
ミクロな新規自由体積モデルの構築

17) International Symposium on
Engineering Micro-/Nano-Materials
based on Self-Assembling and
Self-Organization, ISEM2008
Returns

The National Museum of Emerging
Science and Innovation (Miraikan),
Japan

Dec. 8-10, 2008

No.8

Hidenori Kuroki, Hidenori Ohashi,
Taichi Ito and Takeo Yamaguchi

Development of Novel Bioresponsive
Gating System using Biorecognition
Crosslinker

18) 膜シンポジウム 2008

大阪大学豊中キャンパス

2008年 11月 14日 -15日

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伊藤 大知・大橋 秀伯・山口 猛央

Nonlinear Self-Excited Oscillation of
a Synthetic Ion Channel-Inspired
Membrane

19) 膜シンポジウム 2008

大阪大学豊中キャンパス

2008年 11月 14日 -15日

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大橋 秀伯・伊藤 大知・山口 猛央

ミクロな自由体積理論を用いた高
分子中の分子拡散性予測：気体・
溶媒から溶質分子まで

20) 日韓高分子若手シンポジウ

ム発表 (JAPAN-KOREA Polymer
Young Scientist Symposium)

Niigata

October 23-25, 2008

F22

Ju-Myeong Lee, Hidenori Ohashi,
Taichi Ito, Takeo Yamaguchi,

Capping Phenomenon on Interface
Between Nanoparticles and Electrolyte
Polymer and Its Application to Polymer
Electrolyte Fuel Cells

21) 日韓高分子若手シンポジウム発
表 (JAPAN-KOREA Polymer Young
Scientist Symposium)

Niigata

October 23-25, 2008

F24

Taichi Ito, Hidenori Ohashi, Takeo
Yamaguchi

Nonlinear Self-Excited Oscillation of a
Synthetic Ion Channel-Inspired Membrane

22) 日韓高分子若手シンポジウム発
表 (JAPAN-KOREA Polymer Young
Scientist Symposium)

Niigata

October 23-25, 2008

F32

Hidenori Ohashi, Taichi Ito, Takeo
Yamaguchi,

Development of A Novel Microscopic
Free Volume Theory for Self-Diffusivity
Prediction in Polymer Matrices

23) 第57回 高分子討論会
大阪市立大学 杉本キャンパス

2008年 9月 24日 -26日

2I10

黒木 秀記・大橋 秀伯・伊藤 大知・
山口 猛央

生体分子認識ゲート膜における細
孔内グラフトポリマーのナノ構造
制御

24) 化学工学会 第 40 回秋季大
会

東北大学

川内北キャンパス

2008 年 9 月 24 日-26 日

P316

平出 篤志・田巻 孝敬・大橋 秀伯・
伊藤 大知・山口 猛央

新規ナノ構造制御酵素集積型バイ
オ燃料電池の開発

25) 化学工学会 第 40 回秋季大
会

東北大学

川内北キャンパス

2008 年 9 月 24 日-26 日

F202

藤井 啓太郎・山口 猛央・伊藤 大
知・大橋 秀伯

固体高分子形アルカリ燃料電池
用新規芳香族系細孔フィリングア
ニオン交換膜の開発

26) 化学工学会 第 40 回秋季大
会

東北大学

川内北キャンパス

2008 年 9 月 24 日-26 日

F201

豊田 将平・大橋 秀伯・伊藤 大
知・山口 猛央

細孔フィリング電解質膜を用い
た固体高分子形アルカリ燃料電池

の開発

27) Second International Conference on
Polymer blends, Composites, IPNS,
Membranes, Polyelectrolytes and Gels:
Macro to Nano Scales

India

September 22-24,2008

Invited speaker

Hidenori Ohashi, Taichi Ito and Takeo
Yamaguchi

Bio-Inspired Material Development
according to the Notion of "Material
System" and Prediction Tool of Molecular
Diffusivity in Polymeric Systems for
Material Design

28)

National Institute for Interdisciplinary
Science & Technology

National Institute for Interdisciplinary
Science & Technology, India

September 19, 2008

Invited lecture

Hidenori Ohashi, Taichi Ito and Takeo
Yamaguchi

Bio-Inspired Material Development
according to the Notion of "Material
System" and Prediction Tool of Molecular
Diffusivity in Polymeric Systems for
Material Design

29)

化学工学会新潟大会 2008

新潟大学

2008 年 8 月 21 日-22 日

PC110

(ポスター)

黒木秀記・大橋秀伯・伊藤大知・

山口猛央
生体分子認識ゲート膜を用いたバ
イオセンサー開発におけるナノ細
孔構造制御

30)

International Congress on Membranes
and Membrane Process 2008

Sheraton Waikiki Hotel, Honolulu,
Hawaii USA

July 12-18, 2008

75(Poster)

Nobuo Hara, Taichi Ito, Takeo
Yamaguchi

Development, Microstructure and
Properties of Novel Wholly Aromatic
Pore-Filling Electrolyte Membranes
for PEFCs and DMFCs

31)

International Congress on Membranes
and Membrane Process 2008

Sheraton Waikiki Hotel, Honolulu,
Hawaii USA

July 12-18, 2008

56(Poster)

Hidenori Kuroki, Taichi Ito, Takeo
Yamaguchi

Development of Nobel
Biomolecule-Responsive Gating
System using Biomolecular
Recognition Gating Membrane

32)

International Congress on Membranes
and Membrane Process 2008

Sheraton Waikiki Hotel, Honolulu,
Hawaii USA

July 12-18, 2008

Hidenori Ohashi, Taichi Ito, Takeo
Yamaguchi

Development of a Microscopic Free
Volume Theory for Molecular
Self-Diffusivity Prediction in Polymeric
Systems

33)

International Congress on Membranes and
Membrane Process 2008

Sheraton Waikiki Hotel, Honolulu, Hawaii
USA

July 12-18, 2008

Taichi Ito, Takeo Yamaguchi

Fixed-Charge Group-Like Behavior of the
Captured Ion by Crown Ether and Its
Effect on the Response of a Molecular
Recognition Ion Gating Membrane

34) 日本膜学会

第30回年会

東京理科大学 森戸記念館

2008年5月15日-16日

A-1

黒木秀記・伊藤大知・山口猛央

生体分子応答ゲート膜におけるナノ細
孔構造制御

H.知的財産権の出願・登録状況

1. 特許取得

予定2件

2. 実用新案登録

該当なし

3. その他

特記事項なし

別紙4 研究成果の刊行に関する一覧表

書籍

著者氏名	論文タイトル名	書籍全体の編集者名	書籍名	出版社名	出版地	出版年	ページ
伊藤大知 山口猛央	多孔体へのプラズマグラフト重合を用いたバイオ材料システムの開発		多孔体の精密制御と機能・物性評価	サイエンス&テクノロジー	東京都	2008	461-467

雑誌

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
Nobuo Hara, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi	Reverse response of an ion recognition polyampholyte to specific ion signals at different pHs	<i>Macromolecules</i>	42	980-986	2008
Hidenori Ohashi, Maiko Watanabe, Taichi Ito, Takanori Tamaki, Takeo Yamaguchi	Fabrication of Protein Renaturation Facilitating Membrane Using Plasma Graft Pore Filling Technique	<i>Journal of Photopolymer Science and Technology</i>		In press	2010
Hidenori Kuroki, Hidenori Ohashi, Taichi Ito, Takanori Tamaki, Takeo Yamaguchi	Isolation and Analysis of a Grafted Polymer onto a Straight Cylindrical Pore in a Thermal-Responsive Gating Membrane and Elucidation of its	<i>Journal of Membrane Science</i>		In press	2010
Taichi Ito, Yuhei Oshiba, Hidenori Ohashi, Takanori Tamaki, Takeo Yamaguchi	Sensitivity enhancement of a molecular recognition ion gating membrane in an aqueous ethanol solution	<i>Journal of Membrane Science</i>	348	369-375	2010
Miyaoi Naoko, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi	An Analysis of Pore Size Using a Straight-Pore Molecular Recognition Ion Gating Membrane	<i>Journal of Chemical Engineering of Japan</i>	41	766-770	2008

Hidenori Ohashi, <u>Taichi Ito</u> , Takeo Yamaguchi	A New Free Volume Theory Based on Microscopic Concept of Molecular Collisions for Penetrant Self-diffusivity in Polymers	<i>Journal of Chemical Engineering of Japan</i>	42	86-96	2009
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別紙4 研究成果の刊行に関する一覧表

書籍

著者氏名	論文タイトル名	書籍全体の編集者名	書籍名	出版社名	出版地	出版年	ページ
伊藤大知 山口猛央	多孔体へのプラズマグラフト重合を用いたバイオ材料システムの開発		多孔体の精密制御と機能・物性評価	サイエンス&テクノロジー	東京都	2008	461-467

雑誌

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
Nobuo Hara, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi	Reverse response of an ion recognition polyampholyte to specific ion signals at different pHs	<i>Macromolecules</i>	42	980-986	2008
Hidenori Ohashi, Maiko Watanabe, Taichi Ito, Takanori Tamaki, Takeo Yamaguchi	Fabrication of Protein Renaturation Facilitating Membrane Using Plasma Graft Pore Filling Technique	<i>Journal of Photopolymer Science and Technology</i>		In press	2010
Hidenori Kuroki, Hidenori Ohashi, Taichi Ito, Takanori Tamaki, Takeo Yamaguchi	Isolation and Analysis of a Grafted Polymer onto a Straight Cylindrical Pore in a Thermal-Responsive Gating Membrane and Elucidation of its	<i>Journal of Membrane Science</i>		In press	2010
Taichi Ito, Yuhei Oshiba, Hidenori Ohashi, Takanori Tamaki, Takeo Yamaguchi	Sensitivity enhancement of a molecular recognition ion gating membrane in an aqueous ethanol solution	<i>Journal of Membrane Science</i>	348	369-375	2010
Miyaoi Naoko, Hidenori Ohashi, Taichi Ito, Takeo Yamaguchi	An Analysis of Pore Size Using a Straight-Pore Molecular Recognition Ion Gating Membrane	<i>Journal of Chemical Engineering of Japan</i>	41	766-770	2008

Hidenori Ohashi, <u>Taichi Ito</u> , Takeo Yamaguchi	A New Free Volume Theory Based on Microscopic Concept of Molecular Collisions for Penetrant Self-diffusivity in Polymers	<i>Journal of Chemical Engineering of Japan</i>	42	86-96	2009
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Reverse Response of an Ion-Recognition Polyampholyte to Specific Ion Signals at Different pHs

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ABSTRACT: We synthesized and characterized for the first time an ampholytic ion-recognition linear copolymer of [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), acrylic acid (AA), and benzo[18]crown-6-acrylamide (BCAm). In this copolymer, the MAPTAC unit has a positive charge. The AA unit has a negative charge that depends on the pH. The crown receptor of the BCAM unit forms a complex with specific ions such as Ba²⁺ because of the high complex formation constant which behaved like a fixed positive charge. Thus, the copolymers behaved as an ion-recognition polyampholytes and shrank at a pH equal to the isoelectric point (IEP), which shifted to a higher pH when the BCAM complexed with a cation. At that time, the BCAM also became hydrophilic with water of hydration accompanied by the cation. As a result of the combination of these two effects, we found that the reverse behaviors of swelling and shrinking occurred at different pHs in response to the same ion signal.

Introduction

Biopolymers such as protein, DNAs, and RNAs are known to have various intramolecular interactions, such as electrostatic, hydrophilic, and hydrophobic interactions, as well as hydrogen bonds. These interactions are considered to be among the important factors in determining the structures and functions of biopolymers. Biopolymers also show many functions in response to molecular signals. In the case of proteins, phosphorylation/dephosphorylation usually changes the polymer's function. In the case of DNAs, polymer function is mainly controlled by methylation.

Some synthetic molecular-signal-responsive polymers and hydrogels have also been reported, inspired by the functions of biopolymers. A lectin-loaded cross-linked polymer network of *N*-isopropylacrylamide (NIPAM) showed distinct swelling behavior in response to different saccharides.¹ A temperature-sensitive hydrogel copolymerized via molecular imprinting showed a volume change in response to specific molecules.² An antigen–antibody semi-IPN hydrogel showed reverse swelling behavior in a buffer solution in response to a specific antigen.³ These previous researches utilized the change in cross-linking density or hydration condition induced by molecular signals but did not utilize the electrostatic interaction.

Recently, there has been much interest in polyampholytes because they have many similarities to biopolymers such as proteins.⁴ The polymer chain of polyampholytes contains both cationic and anionic groups, and the balance of positively and negatively charged groups can be controlled by changing the monomer content in the feed solution.^{5,6} The balance of positively and negatively charged groups also changes when these charged groups are sensitive to the pH of the solution. Synthetic polyampholytes have an isoelectric point (IEP) at a specific pH, where the polymer chain is electroneutral and shrinks.⁷ The synthetic polyampholytes also show the antipolyelectrolyte effect, in which the polymer chain is soluble at the IEP because of the electric shielding of the fixed charges due

to a high salt concentration.⁸ However, this electrostatic interaction has not been controlled by molecular signals.

Many synthetic host compounds such as crown ethers⁹ and cryptand complexes^{10,11} have been designed and analyzed in the field of supramolecular chemistry.¹⁰ Benzo[18]crown-6-acrylamide (BCAm), one of the molecular recognition compounds, has a crown ether receptor and traps specific ions such as K⁺ and Ba²⁺.¹² The copolymer of NIPAM and BCAM was synthesized, and the shift in the lower-critical-solution temperature was observed when the BCAM captured specific ions.¹³ Recently, we hypothesized on the basis of our previous researches that captured ions behaved like fixed positive charges when the BCAM formed a complex with a specific ion because of the osmotic pressure generated by the Donnan exclusion-like effect under a specific ion concentration gradient.¹⁴ In addition, we found that the complex of a BCAM and a specific ion retains about 70–80 water molecules and makes the polymer chain more hydrophilic.¹⁵

In this research, we synthesized a linear copolymer of MAPTAC, AA, and BCAM (Figure 1). Its phase-separation behavior in response to pH, ion species, and salt concentration was investigated. The effect of the composition of the copolymers was also studied. MAPTAC has a stable quaternary ammonium base, amide bond, and propyl group, while AA has a pH-sensitive carboxylic acid group.¹⁶ The molecular structure of poly-MAPTAC-*co*-AA-*co*-BCAM contains both positively and negatively charged groups and well-balanced molecular interactions, such as electrostatic, hydrophilic, and hydrophobic interactions, as well as hydrogen bonds. In addition, complex formation between BCAM and ions has the above-mentioned unique physicochemical effects, which are expected to trigger unique phase-separation phenomena of the copolymer.

Experimental Section

Materials. [3-(Methacryloylamino)propyl]trimethylammonium chloride (MAPTAC, 50 wt % aqueous solution) was purchased from Aldrich Co., Ltd.; inhibitor was removed using an adsorption column before polymerization. Acrylic acid was purchased from Wako Chemical Co., Ltd., and purified by distillation. BCAM was synthesized according to reported procedures.¹² 2,2'-Azobis(2-methylpropionamide) dihydrochloride (V-50) was purchased from Wako Chemical Co., Ltd., and used as an initiator. Standard aqueous

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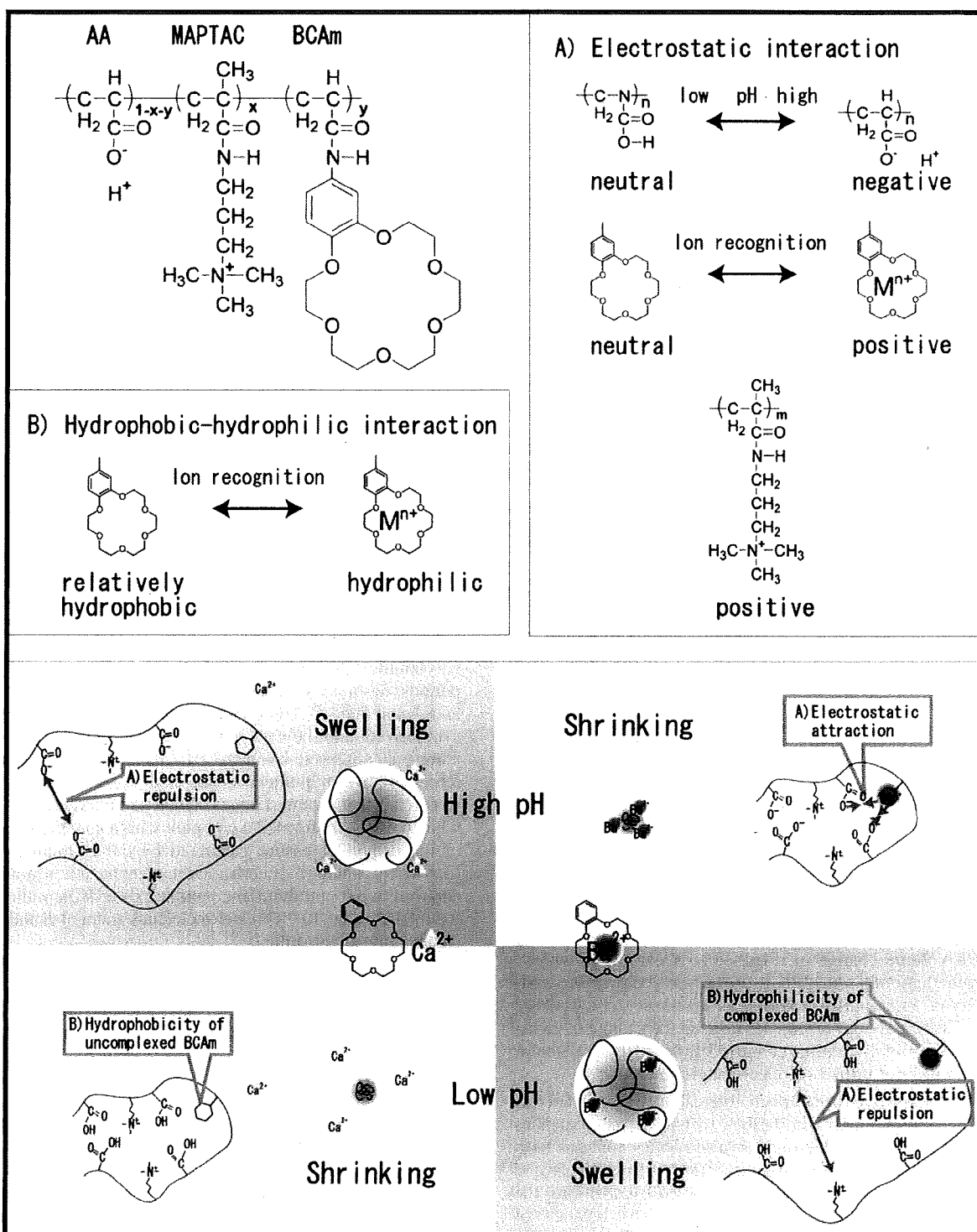


Figure 1. Chemical structure, intramolecular interactions, and concept of molecular-recognition response of poly-MAPTAC-co-AA-co-BCAm.

solutions of hydrochloric acid and sodium hydroxide were purchased from Wako Chemical Co., Ltd., and used for IEP measurements and turbidimetric titrations.

Preparation of the Linear Copolymer. Poly-MAPTAC-co-AA-co-BCAm was synthesized by free-radical copolymerization. The molar copolymerization ratios were controlled according to Table 1. Aqueous solutions of MAPTAC, AA, and BCAm were prepared from degassed RO water. The ratio of initiator was fixed at 0.5 mol % for all monomers, and the weight percentage of monomers was fixed at 15 wt %. The aqueous solution was kept at 50 °C for 48 h under N_2 after initiating polymerization by visible light for 12 min. The copolymer was dissolved in RO water, purified by

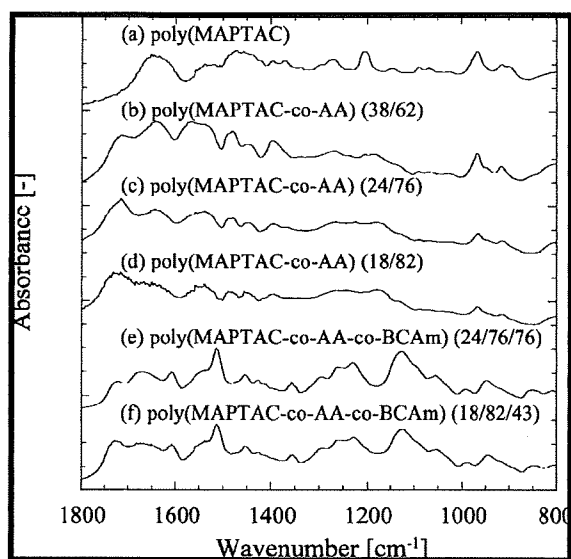
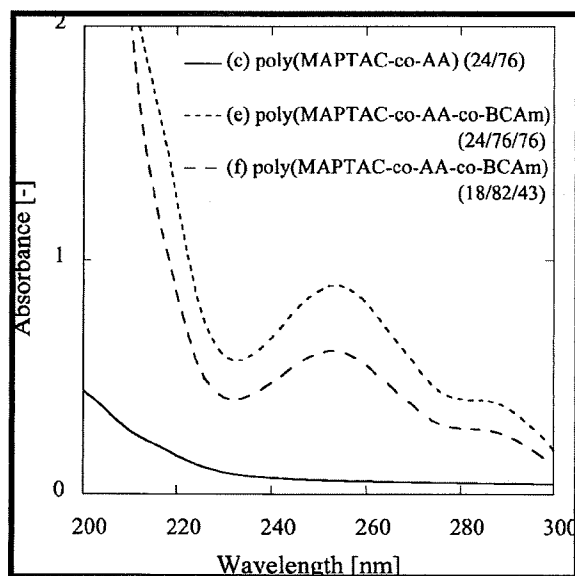
dialysis—using a dialysis membrane for which the molecular weight cutoff was about 12 000—and dried under vacuum. Chloride ions contained in the aqueous monomer solution of MAPTAC were also removed by dialysis after polymerization.

Characterization. The synthesized linear copolymers were characterized by FT-IR, elemental analysis, and UV-vis spectroscopy. The FT-IR spectrum of the linear copolymer was measured using the KBr disk technique with an MGNA 550 (Nicolet). Elemental analysis was performed on a 2400II (Perkin-Elmer). The UV-vis spectrum of the linear copolymer was measured using a U-3310 (Hitachi). The absorption intensities in the UV-vis spectrum were measured using an aqueous solution of copolymers.

Table 1. Molar Compositions of the Monomer Solutions and Copolymers, with MAPTAC, AA, and BCAM Content as 100 mol %^a

[mol %]	composition of monomer solutions			copolymerization ratio		
	MAPTAC	AA	BCAM	MAPTAC	AA	BCAM
(a)	100			100		
(b)	38	62		39	61	
(c)	24	76		25	75	
(d)	18	82		18	82	
(e)	14	43	43	12	39	49
	(24)	(76)	(76)	(23)	(77)	(96)
(f)	12	57	30	9	65	26
	(18)	(82)	(42)	(12)	(88)	(35)

^a Compositions with MAPTAC and AA content as 100 mol % are shown in parentheses.

**Figure 2.** FT-IR spectra of poly(MAPTAC), poly(MAPTAC-co-AA), and poly(MAPTAC-co-AA-co-BCAM).**Figure 3.** UV spectra of poly(MAPTAC-co-AA) and poly(MAPTAC-co-AA-co-BCAM).

Turbidimetric Measurement. Copolymer solutions change turbidity when copolymer chains shrink, and this behavior was measured spectrophotometrically as the optical density at 650 nm. Turbidimetric titration of the linear copolymer solution was performed in 0.2 wt % copolymer concentration at 25 °C. The pH

was first changed to about pH 2 by adding 0.01 M HCl aqueous solution, and it was then changed to pH 12 by adding 0.01 M NaOH aqueous solution in 10 μ L aliquots. Each time, the pH was measured using a pH meter HM21P (TOD-DKK), and the optical density was measured. Measurements were carried out a few minutes after titration to obtain a stable optical density value. The turbidimetric titration of the linear copolymer solution was also carried out with various concentrations of CaCl₂, SrCl₂, and BaCl₂. Turbidity changes were also measured by adding 0.1 M aqueous solution of CaCl₂, SrCl₂, and BaCl₂ in 10 μ L aliquots in both acid and base conditions and by alternately adding 0.1 M aqueous solution of BaCl₂ and [18]crown-6.

Results and Discussion

Characterization of Copolymers. Figure 2 shows the FT-IR spectra of the copolymers. Copolymerization of MAPTAC, AA, and BCAM was determined by FT-IR measurements. The peaks are 1650 cm⁻¹ from the amide bond of MAPTAC, 1720 cm⁻¹ from the carboxyl group of AA, and 1133 cm⁻¹ from the ether group of BCAM. Figure 3 shows the UV spectra of copolymers of BCAM, which had an absorbance peak at 255 nm. The copolymerization ratio of BCAM was estimated from the following proportional relationship between the absorbance at 255 nm and concentration of poly-BCAM:

$$C_{\text{BCAM}} = 1.21 \times 10^{-4} a \text{ mol/L} \quad (1)$$

where a is the absorbance at 255 nm and C_{BCAM} is the concentration of poly-BCAM.¹⁷ The copolymerization ratio of MAPTAC to AA was determined by the weight ratio of carbon and nitrogen atoms obtained from elemental analysis. The total molar copolymerization ratios MAPTAC:AA:BCAM determined from these measurements are shown in Table 1. These molar copolymerization ratios are in close agreement with those used in the synthesis. The molar copolymerization ratios are shown for MAPTAC, AA, and BCAM content as 100 mol %.

pH Dependence of Poly(MAPTAC), Poly(MAPTAC-co-AA), and Poly(MAPTAC-co-AA-co-BCAM). In general, a polyampholyte shrinks at a pH equal to the IEP, where the positive and negative charges balance and the solution of linear copolymer becomes turbid.^{5,18} The monomer of MAPTAC is a chloride ion salt, and poly(MAPTAC) acts as a positive charge whose amount is not affected by pH (Figure 1). AA is a weak acid, and it acts as a negative charge whose magnitude is affected by the degree of dissociation. Thus, the balance of positive and negative charges changes depending on the pH of the solution. The amount of negative charge is low because of the low degree of dissociation of AA at pHs below the IEP, while negative and positive charges balance when the pH equals the IEP, and negative charges exceed positive charges at pHs above the IEP. Since the dissociation degree α of weak acid relates to pH by the following equation

$$\text{pH} = \text{p}K_a + \log\left(\frac{\alpha}{1 - \alpha}\right) \quad (2)$$

the pH of the IEP where the ratio of the positive and the negative charges inside the linear polymer balance can be estimated. Using $\text{p}K_a = 4.25$ previously reported for poly(acrylic acid),¹⁹ the pH of the IEP was calculated as 4.5, 3.9, 3.7, 3.9, and 3.7 for copolymer (b), (c), (d), (e), and (f) respectively, for (e) and (f) without considering the effect of the copolymerized BCAM.

Figure 4 shows the pH dependencies for the turbidimetric titrations of the 0.2 wt % aqueous copolymer solutions of poly(MAPTAC), poly(MAPTAC-co-AA), and poly(MAPTAC-co-AA-co-BCAM). The absorbance of the aqueous polymer solution of (a) poly(MAPTAC) is low over the entire pH range. This is because poly(MAPTAC) contains only positive charges

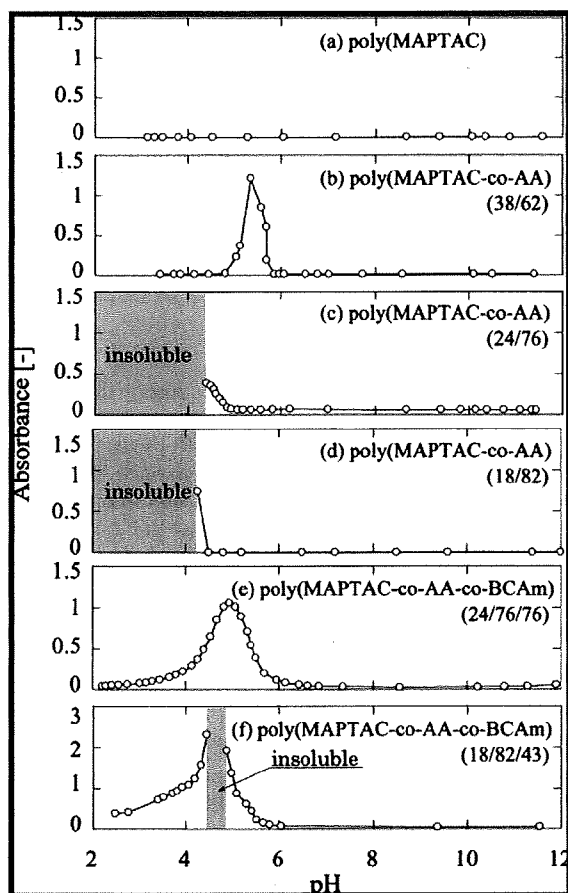


Figure 4. pH dependence of poly(MAPTAC-*co*-AA) and poly(MAPTAC-*co*-AA-*co*-BCAm).

inside the polymer chain and is always swollen by electrostatic repulsion. The absorbance of copolymers of poly(MAPTAC-*co*-AA) varied according to the pH of the solution. A 0.2 wt % aqueous solution of copolymer (b) turned turbid at about pH 5.4; copolymers (c) and (d) turned turbid and resulted in precipitation below pH 4.4 and 4.2, respectively. Copolymers (e) and (f) have the same ratio of MAPTAC to AA as copolymers (c) and (d) and contain BCAM with 43 and 30 mol %, respectively. The 0.2 wt % aqueous solution of copolymer (e) turned turbid at about pH 5.0; copolymer (f) turned turbid and resulted in precipitation at about pH 4.6. However, these values of pH were higher than the pH of the IEP estimated by the calculation; their trends were almost the same according to the monomer compositions. Therefore, behavior as a polyampholyte was confirmed for the aqueous solution of both poly(MAPTAC-*co*-AA) and poly(MAPTAC-*co*-AA-*co*-BCAm). Their differences are expected to be due to the different value of pK_a from the reported value with different component of the copolymerization.

Thus, a solution of copolymer (b) turned turbid when the pH equaled the IEP. Solutions of copolymers (c) and (d) turned turbid and resulted in precipitation because the copolymer of high AA content could reach the IEP with low degree of dissociation and also because of the hydrogen bond between dissociated AA²⁰ and the relatively hydrophobic uncomplexed BCAM. The pH of the IEP of copolymers (e) and (f) were measured to be about 0.5 higher than those of copolymers (c) and (d). Copolymers (e) and (f) were more soluble than (c) and (d), probably because the difference of the value of pK_a and the ratio of hydrogen bonds was decreased by copolymerization with BCAM.

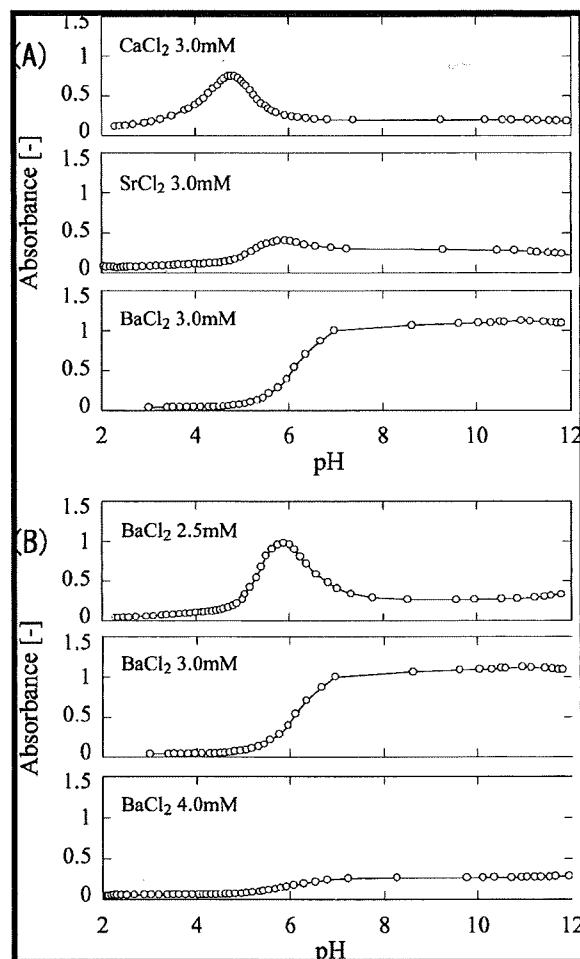


Figure 5. pH dependence of the copolymer used in Figure 4e, poly(MAPTAC-*co*-AA-*co*-BCAm) (24/76/76), with salt. (A) Different ion species of CaCl₂, SrCl₂, and BaCl₂. (B) Concentration dependence of BaCl₂.

The concentration of the Na⁺ ion after turbidimetric titration was about 10 mM. The peak of the turbidity of the IEP was observed at the same pH reproducibly by multicycle measurement of the titration; however, the peak height slightly decreased because of the increase of the concentration of the added salt, which is called the anti-polyelectrolyte effect.

Different Ion Species Changed the IEP Shift. The result for copolymer (e) will be explained after the next two sections. Figure 5A shows the pH dependence for the turbidimetric titrations of 0.2 wt % aqueous polymer solution of poly(MAPTAC-*co*-AA-*co*-BCAm) in the presence of various salts. The concentration of the salts CaCl₂, SrCl₂, and BaCl₂ was controlled to 3.0 mM at the beginning of the titration. BCAM forms complexes with various ions, and the complex formation constants increase in the order Ca²⁺, Sr²⁺, Ba²⁺.²¹ The balance of charges inside the polymer chain is also estimated from the complex formation constant K and eq 2 by considering the complexed divalent ions into positive charges. Using $\log K = 1.1$ and 1.6 for Sr²⁺ and Ba²⁺, respectively, which were previously reported for poly-NIPAM-*co*-BCAm,¹⁷ the pH of the IEP shifted higher by 0.1 and 0.5 in the presence of 3.0 mM ions.

An aqueous solution of copolymer in the presence of 3.0 mM Ca²⁺ ions turned turbid at about pH 4.9. The pH at the IEP did not shift from that of the same titration without Ca²⁺ ions because the complex formation constant of BCAM and Ca²⁺ ion is low, and the positive charges were not introduced inside

the polymer chain. The copolymer also became soluble, and the absorbance decreased because of the anti-polyelectrolyte effect in the presence of CaCl_2 salt. An aqueous solution of the copolymer in the presence of 3.0 mM Sr^{2+} ions turned turbid at about pH 5.9. The pH at the IEP shifted by about 1.0 compared with that of the same titration without Sr^{2+} ions. This was because BCAM and Sr^{2+} ions formed complexes and positive charges were introduced inside the copolymer chain. The solution of the copolymer also became soluble, and the absorbance decreased because of the hydrophilic change of complexed BCAM and the antipolyelectrolyte effect. An aqueous solution of copolymer in the presence of 3.0 mM Ba^{2+} ion turned turbid at a pH of about 6.0. This is because the complex formation constant of BCAM and Ba^{2+} ion is high. The total positive charges of MAPTAC and those introduced inside the copolymer chains are in balance with the negative charges of dissociated AA, and the polymer chain remained at the IEP in the higher pH range. Although the observed shift range of the pH is wider than the calculated values, their trends are well consistent with the order of the complex formation constant. Their differences are expected to be due to the difference of the values of complex formation constant, which are widely different according to the copolymerization systems and other effects such as hydrophilic change of complexed BCAM.

Figure 5B shows the pH dependence for the turbidimetric titrations of 0.2 wt % of aqueous polymer solution of poly-(MAPTAC-co-AA-co-BCAM) in the presence of various concentrations of BaCl_2 , namely 2.5, 3.0, and 4.0 mM. An aqueous solution of the copolymer in the presence of 2.5 mM Ba^{2+} ion turned turbid at about pH 5.9 by complexation of BCAM and Ba^{2+} ions. An aqueous solution of the copolymer in the presence of 4.0 mM Ba^{2+} ions became slightly turbid above a pH of about 6.0. The number of total positive charges on MAPTAC and those introduced inside the copolymer chains exceeds the number of negative charges on the dissociated AA. The polymer chain did not reach the IEP, and the solution turned slightly turbid. The anti-polyelectrolyte effect with high salt concentration and hydrophilic change of complexed BCAM were also reasons for the low absorbance.

From these results, positive charges were introduced into the polymer chain by complex formation of BCAM and cations depending on the complex formation constant and the concentration of the cation. The behaviors of swelling and shrinking of polymer chains and the amount of positive charge inside the polymer chains were controlled by the species and the concentration of the ion.

Ion Recognition Changed by an Anti-polyelectrolyte Effect.

Figure 6A shows the turbidimetric measurements of 0.2 wt % aqueous copolymer solutions upon gradually adding 0.1 M solutions of various salts at pH 5.0, where the copolymer was at the IEP without salt. The polymer initially shrank at the IEP and gradually changed to swelling by the addition of salt solution. The absorbance decreased in the order of Ba^{2+} , Sr^{2+} , Ca^{2+} , which is the order of the complex formation constants. This is because of the IEP shift to higher pH by complex formation of BCAM and the cation, and there is also the influence of the anti-polyelectrolyte effect.

Figure 6B shows the turbidimetric measurements of 0.2 wt % copolymer solution upon gradually adding 0.1 M solution of various salts at pH 11.6. The copolymer was initially swollen and gradually changed to shrinking by the addition of salt solution. The absorbance increased in the order Ba^{2+} , Sr^{2+} , Ca^{2+} , which is the order of the complex formation constants. The carboxylic groups of AA are all dissociated at pH 11.6, and negative charges are initially in excess. Positive charges are introduced into the copolymer chain by complex formation between BCAM and the cation. The polymer chain started to

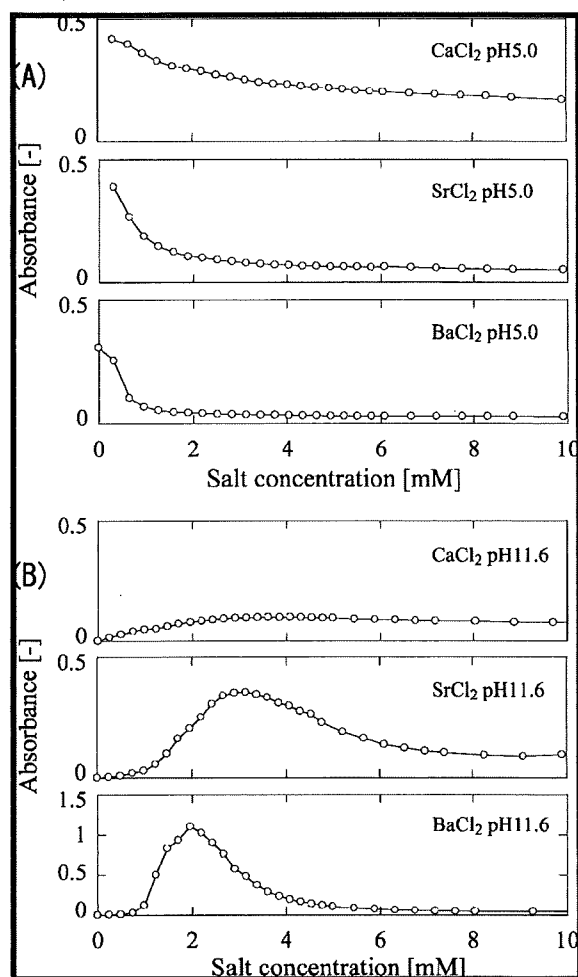


Figure 6. Salt concentration dependence of the copolymer (e) (poly-MAPTAC-co-AA-co-BCAM) (24/76/76). (A) Different ion species of CaCl_2 , SrCl_2 , and BaCl_2 . (B) Concentration dependence of CaCl_2 , SrCl_2 , and BaCl_2 .

shrink at the point where the positive charges balanced the negative charges. When the number of positive charges exceeded the number of negative charges, the polymer chain started swelling again. We also deduce from these results that the number of positive charges inside the polymer chain was controlled by the species and the concentration of ions, and the antipolyelectrolyte effect crucially affected the behavior.

There is another expected effect of adding divalent ions, which dissociated carboxylic groups can be cross-linked by divalent ions above the pH of the IEP. It is understood mainly by electrostatic interaction on their charge size ratio measured in terms of ionic radii.²² Thus, the interaction of added divalent ions decreases in the order of Ca^{2+} , Sr^{2+} , and Ba^{2+} . This interaction is expected to exist in the copolymer chain when divalent ion is added into the solution. However, from the Figure 6B, the copolymer chain shrank more in the order of high complex forming constant with BCAM, not in the order of the strength of the cross-link of the divalent ion. From this result, the effect of complex forming of BCAM with Ba^{2+} is thought to be stronger than the effect of the cross-link of the divalent ion. Therefore, we speculate that the effect of the cross-link by divalent ions is not obvious because the electrostatic interaction between the dissociated AA and the complexed BCAM is thought to be dominant in this copolymer system.

Reverse Response of Poly(MAPTAC-co-AA-co-BCAM) to Specific Ions at Different pHs. Parts A and B of Figure 7 show the alternate salt addition of BaCl_2 and [18]crown-6 to

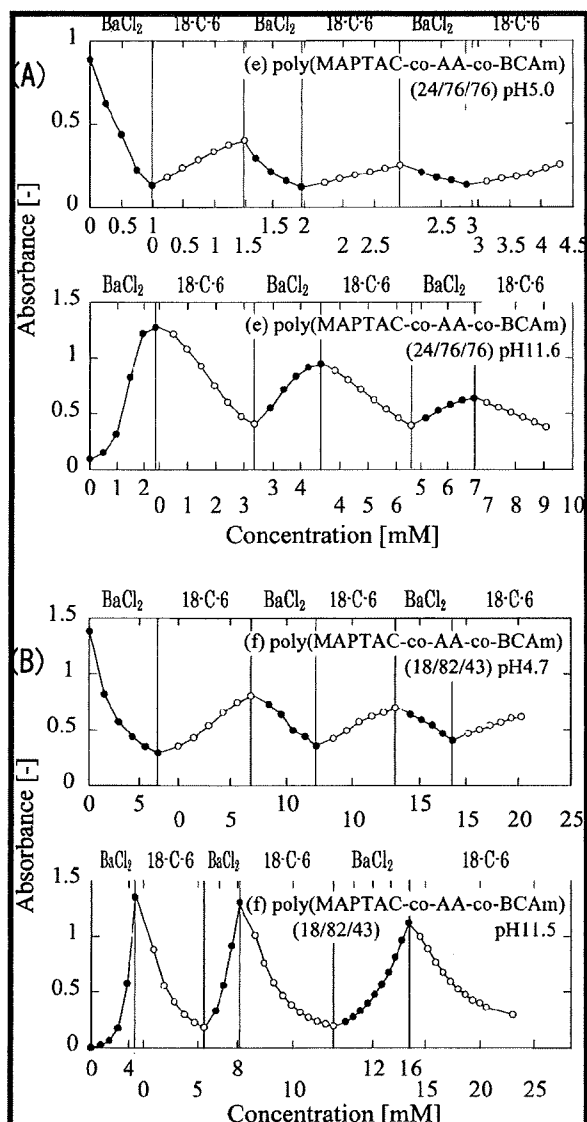


Figure 7. Turbidity change of the aqueous solutions of copolymers (e) and (f) by alternately adding BaCl_2 and [18]crown-6 aqueous solutions.

0.2 wt % aqueous copolymer solutions of (e) and (f), respectively. Turbidity was measured both at the IEPs and higher pHs of alkaline conditions. [18]Crown-6 can remove Ba^{2+} ions from the polymer chain because the complex formation constant of [18]crown-6 is higher than that of BCAM. Therefore, Ba^{2+} ions can be alternately introduced into the polymer chain by adding a 0.1 M aqueous solution of Ba^{2+} and [18]crown-6.

In this measurement, the behavior of swelling and shrinking was observed for both copolymers (e) and (f). The copolymer initially shrank when the pH was at the IEP and then changed to swelling by adding Ba^{2+} ions. The copolymer began shrinking again by adding [18]crown-6, and this behavior was observed alternately. The copolymer initially swelled in alkaline conditions then changed to shrinking by adding Ba^{2+} ions. The copolymer changed to swelling again by adding [18]crown-6, and this behavior was also observed alternately. The absorbance of the copolymer solution in the shrinking condition gradually decreased because of the anti-polyelectrolyte effect caused by the increase in the concentration of salt and [18]crown-6. The response of the absorbance change to salt concentration of copolymer (e) was more sensitive than for copolymer (f). This

is because copolymer (e) has a higher molar composition of BCAM than copolymer (f).

Thus, we demonstrated the alternate swelling and shrinking behavior of an aqueous solution of poly(MAPTAC-co-AA-co-BCAM) by alternately adding a 0.1 M aqueous solution of Ba^{2+} and [18]crown-6. The behaviors of swelling and shrinking in response to the same ion addition were completely opposite under acidic and alkaline conditions.

Conclusions

We synthesized and characterized for the first time an ion-recognition polyampholyte. The copolymers of poly(MAPTAC-co-AA-co-BCAM) showed the behavior of polyampholytes and shrank when the pH equaled the IEP, which was shifted by the ion signal recognized by BCAM, which can form a complex with specific ions depending on the complex formation constant and the concentration of the ions. The intramolecular interactions, mainly electrostatic interactions, were controlled by ion recognition of BCAM and the pH of the solution, which led to the swelling and shrinking behaviors of the copolymer in response to both pH and ion recognition. We found that the reverse behaviors of swelling and shrinking occurred at a different pHs in response to the same ion signal. These phenomena are complicated and interesting, especially in terms of similarity to biopolymers, which respond to the same signal in different ways depending on changes in the external environment such as pH and temperature. The concept of macromolecular design in the present research is expected to be utilized in fields such as separation technology, biomaterials, and drug-delivery systems in the future.

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