

Effects of Annealing on the Structural Deformation of Polyelectrolyte Complexes based on Two Anionic Polysaccharides

Sang-Gyun Kim[†] and Kew-Ho Lee*

Innovative Graduate School of Energy & Environmental Materials, Chungnam Nat'l University, 220 Gung-dong, Yuseong-gu, Daejeon, Korea

*Nat'l Research Lab. for functional Membranes, Korea Research Institute of Chemical Technology, P.O Box 107, Yuseong-gu, Daejeon, Korea

(Received October 24, 2008, Accepted November 21, 2008)

Abstract: Polyelectrolyte complex based on two anionic polysaccharides, composed of sodium alginate and carrageenan, were prepared by interacting with divalent calcium ions in solution. The effects of annealing on the structural deformation of polyelectrolyte complex and on their characteristics at removing water from a methanol mixture from the point of molecular sieve were investigated and discussed. The result showed that the structural deformation of the annealed polyelectrolyte complex has an effect on the free volume between these polymer chains and the chelate segments such a shrinking of the overall morphology, which act as a molecular sieve in the separation of methanol and water mixtures.

Keywords: polysaccharide, sodium alginate, carrageenan, chelate structure, polyelectrolyte complex, annealing effect

1. Introduction

Polyelectrolyte complex has been focused on as potential practical materials, such as dialysis membranes, ultrafiltration membrane, antistatic materials and biomedical materials, because of their high chemical stability as well as their electrolytic nature [1-5,11]. Generally, polyelectrolyte or polysalt complexes are formed when macromolecules of opposite charge are allowed to interact. Electrostatic interactions constitute the main attractive forces, but hydrogen bonding, ion dipole forces, and hydrophobic interactions frequently play a significant role in determining the ultimate structures. Ionic polymers are important as components of polyelectrolyte complexes, which are prepared simply by mixing cationic polymers and anionic polymers in

aqueous solutions.

Among these polymers, the ionic polysaccharides can be considered as ionic polymers, which are typically anionic polyions. The negatively charged substituents attached to the polymer backbone are most frequently, either carboxylate or sulphate groups. As it were, as shown in Fig. 1, sodium alginate (SA) is a polysaccharide consisting of linear chains of 1,4 linked β -D-mannuronate (M) and α -L-guluronate (G) residues in various proportions and arranged in blocks of the two monomers, while a carrageenan (CG) is composed of 1,3-linked β -D-galactose-4-sulphate residues [6].

We already have announced for polyelectrolyte complexes (PEC), based on an ionic polysaccharide such as sodium alginate and chitosan in previous works, and then, these complexes exhibited the excellent separation performance for the dehydration in most alcohol aqueous solutions except methanol-water mixtures [7]. It could consider that the desorption rate, related to

[†] Author for all correspondences
(e-mail : sanggyun@shinbiro.com)

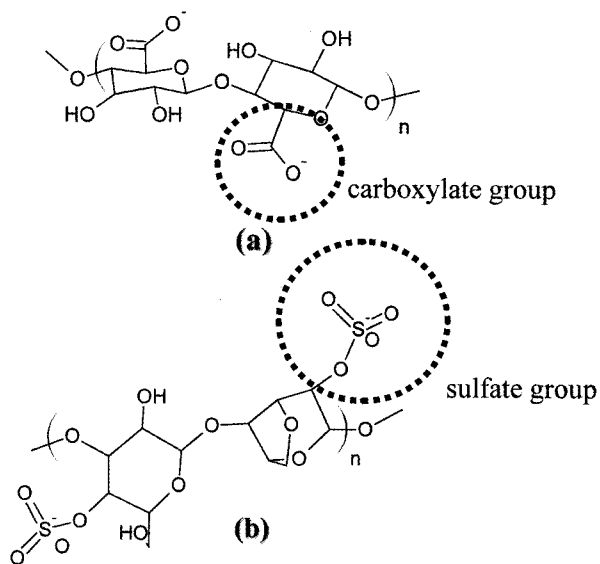


Fig. 1. Repeating structures of, (a) sodium alginate (1,4-linked β -D-mannuronate (a) and α -L-guluronate) and (b) carrageenan (1,3-linked β -D-galactose-4-sulphate residues).

retention time of permeants in membrane, acts as a predominant factor for organic matters of similar physicochemical properties and molecular sizes by using molecular modeling techniques.

Accordingly, we attempted to develop of the effective material for removing water from mixtures with methanol through the morphologic control methods in molecular level, considering the structural characteristics of the zeolite. For this purpose, the PEC, based on two anionic polysaccharides, composed to sodium alginate and carrageenan, inducing divalent calcium ions crosslinking, were prepared and modified their morphology by using the annealing method as a post-treatment.

2. Experimental

2.1. Materials

Sodium alginate (SA) and carrageenan (CG) were purchased from Aldrich, Inc. (USA) Methanol (guaranteed reagent) was supplied by Merck (Darmstadt, Germany). Calcium chloride dihydrate (extrapure grade) was purchased from Junsei Chemical Co. (Tokyo, Japan). Ultra pure deionized water was used. All

chemicals were used without any further purification.

2.2. Polyelectrolyte Complex Preparation

SA and CG was dissolved in deionized water to form a homogeneous solution of 2 wt% polymer. The mixtures of SA/CG solution with weight ratios of 95/05, 90/10, 80/20, respectively, were stirred at room temperature for 12 h. The mixed solutions were cast on a glass plate to give thickness of 80 μ m, and dried them at room temperature for 24 h in a dust free, environmentally controlled chamber. The dried films immersed in 5 wt% CaCl_2 aqueous solution for 12 h, and washed several times with pure water to eliminate any possible residual calcium ions, and dried at room temperature. The annealed polyelectrolyte complex has been prepared by heating the complex membranes in convection oven at 110°C during 4 h.

2.3. Polyelectrolyte Complex Characterization

The chemical structures of the resulting polymers were characterized with a fourier transform infrared spectroscopy (FT-IR) (Digilab FTS-80; Bio-Rad, Richmond, CA). The change of morphology was investigated with a wide-angle X-ray diffractometry (model D/MAX IIB; Rigaku) with a scintillation counter detector using $\text{CuK } \alpha$ -radiation as a source. Angles (2θ) ranged from 2° to 50°. The thermal properties were measured with a thermogravimetric Analysis (Model: 2950). The DSC measurements were made using a Du Pont 9000 thermal analyzer with liquid nitrogen for cooling and with heating rate of 10°C/min. in the temperature range from 30 to 300°C. TGA thermograms were obtained with a Du Pont 951 thermogravimetric analyzer with a heating rate of 10°C/min in the temperature range from 30 to 800°C under a continuous nitrogen flow of 50 mL/min.

3. Results and Discussion

Figs. 4~6 show the results of FT-IR, XRD, and DSC for SA/CG polyelectrolyte blends and SA/CG/ Ca^{2+} ions complexes. In the case of the FT-IR

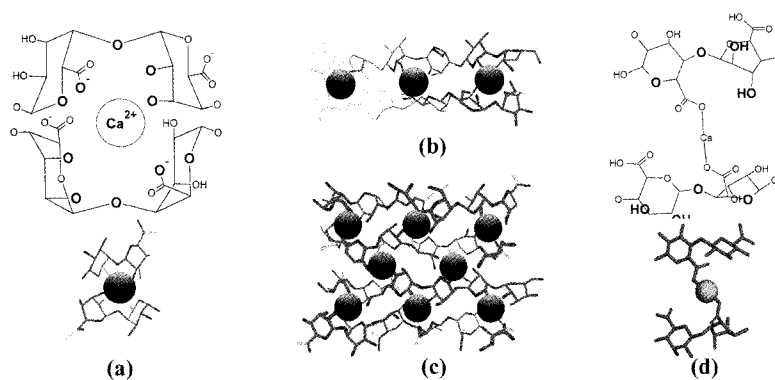


Fig. 2. Schematics representation of chelate formation of sodium alginate by calcium ions (a), egg-box model of low chelation (b), egg-box model of high chelation (c), and ion-pair formation with carboxyl groups (d); green and gray color: carbon, red color: oxygen, black and green color circle: calcium ion.

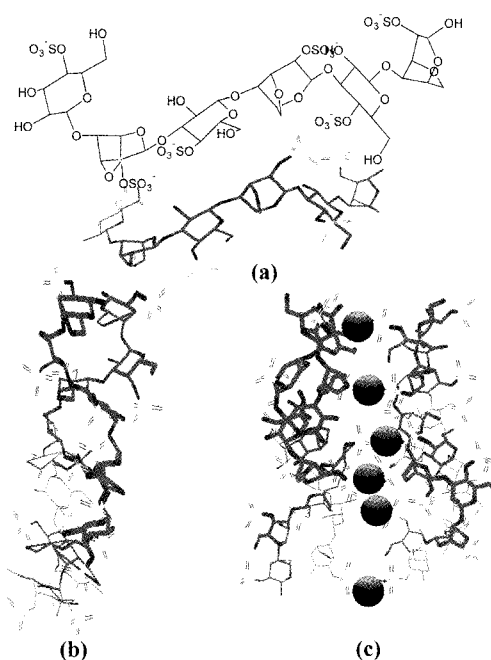


Fig. 3. Schematics representation of the helical structure of carrageenan (a), domain model of double helix type (b), and domain model by cations (c); green color: carbon, red color: oxygen, yellow color: sulfur, black color circle: cation.

analysis, to investigate the influence on the structural deformation of the resulting membranes, the hydrogen bonding interactions in the polyelectrolyte complex focused our interest in the range of $3,200\sim 3,000\text{ cm}^{-1}$ in all spectra, because the calcium ions can occupy interstices in these structures as shown in Figs. 2 and 3 [8,9].

Generally, as can be seen in Figs. 2 and 3, the interaction of sodium alginate can be explained in

terms of three modes of chain association; (a) ion-pair formation with carboxyl groups of mannuronate and isolated guluronate (G) residues; (b) specific site-binding to contiguous G residues; and (c) intermolecular cooperative “egg-box” binding between poly-I-G chain sequence. CG is characterized by cation-mediated helix-helix aggregation based on the formation of either single or double helices of a limited number of chains. In result, as shown in Fig. 4, the hydrogen-

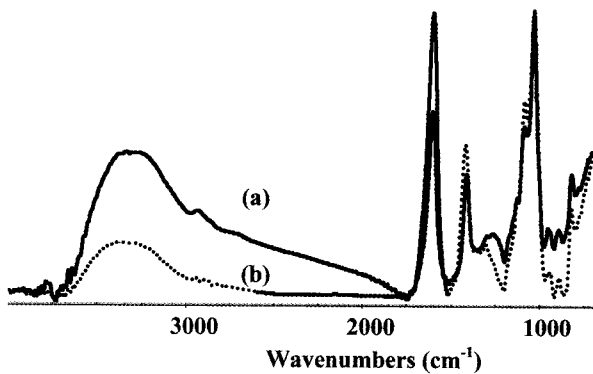


Fig. 4. FT-IR analysis results of polyelectrolyte blend (a) and complex (b).

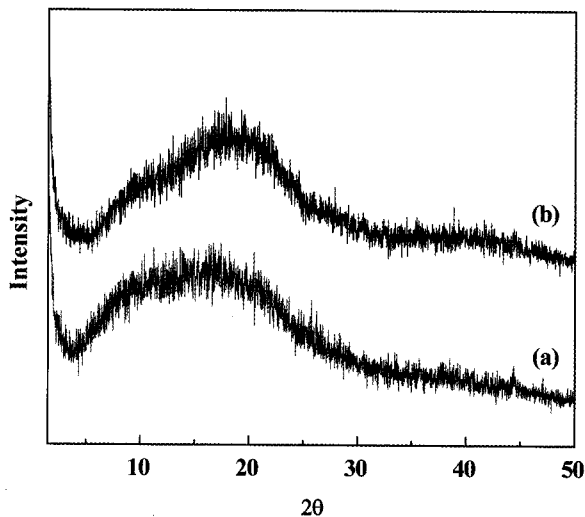


Fig. 5. XRD pattern results of polyelectrolyte blend (a) and complex (b).

bonded peak of the polyelectrolyte complex at 3,200~3,000 cm^{-1} decreased and shifted to upper wave number compared with the spectra of the polyelectrolyte blend, respectively.

The other side, SA/CG blend exhibits an S=O stretching peak in the sulfate group of CG at 1,232 cm^{-1} , $-\text{COO}^-$ anti-symmetric stretching and in-plane -OH bending peaks in carboxyl groups of SA at 1603 and 1,411 cm^{-1} , and OH stretching or H-bonded -OH stretching peaks in between SA and CG at 3,100~3,600 cm^{-1} . According to the above result, it considered that the chelate formation in between anionic groups of these polysaccharides such as carboxylate and sulfate and calcium ions would be interfered in the intermo-

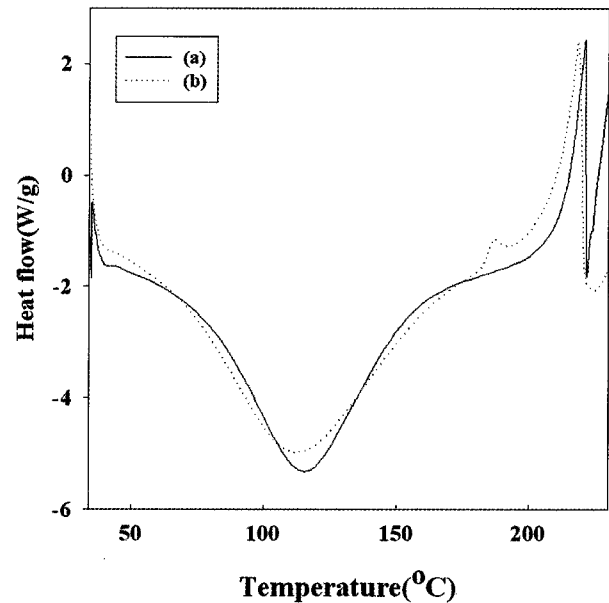


Fig. 6. DSC curve results of polyelectrolyte blend (a) and complex (b).

lecular H-bonding interaction between SA and CG.

To observe the morphology change during the chelate formation with calcium ions involving the intermolecular H-bonding interaction in details, X-ray diffraction patterns of the resulting polymers were studied. Generally, SA is an anionic polysaccharide with amorphous morphology, while CG has crystalline because of a domain structure involving intermolecular double helix formation of a limited number of chains. First, the polyelectrolyte blend exhibited an amorphous characteristic on the whole due to the collapse of crystal structure of CG by intermolecular H-bonding interaction between these polysaccharides, as shown in Fig. 5(a). However, the XRD patterns of polyelectrolyte complex was observed a few sharp peaks regarded as a crystalline at near $2\theta=10^\circ$ and 16° as well as a shifting to upper in the amorphous regions of 17° and the change of d-spacing from 5.4 to 4.9 Å, which was considered to be due to the chelate formation with calcium ions in the G-blocks of SA and the ionic crosslinking in between CG sulfate groups or between anionic groups including CG sulfate and SA carboxylate. Furthermore, as can be seen from Fig. 6, the exothermic peaks of the polyelectrolyte complex

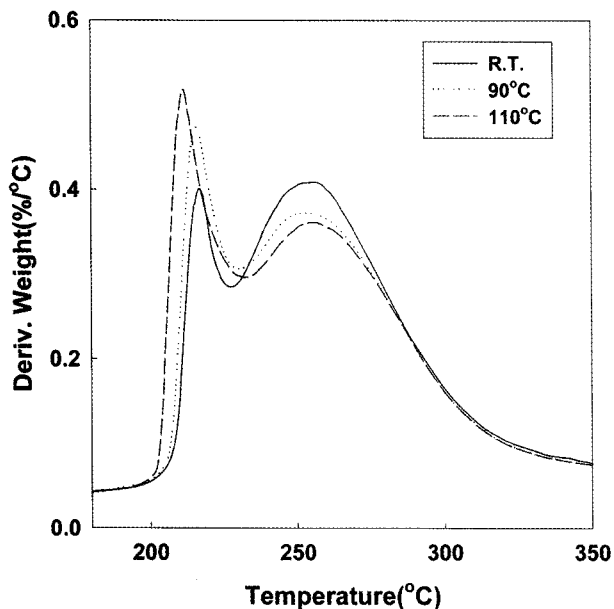


Fig. 7. DTG results of the annealed polyelectrolyte complex as a function of the annealing temperature.

regarded as a crystalline melting at 186°C could be evidence of the above-mentioned specific interactions.

On the other hand, when the polyelectrolyte complex are treated thermally by a annealing method at 110°C , the thermal decomposition patterns of the resulting polymers exhibited an increase in the exothermic peak patterns at approximately 210°C and a reduction of peak at 300°C as shown in Fig. 7. As it were, the weight loss in the first stage at 170 to 231°C increased from 7 to 12% as the annealing temperature increased, in opposition to decreasing patterns from 32.7 to 28.5% in the weight loss of the second stage between 217 and 415°C . Thus behavior might be due to the deformation of the chelate form by means of the dehydration of water molecules around calcium ions as shown in Fig. 8 [10], as well as the transformation of CG morphology involving a thermal-induced change related to the order-disorder transition.

This observation sufficiently is able to reflect from XRD pattern results of these polymers in Fig. 9. The reason is because the crystallinity at about $2\theta=10^{\circ}$ increased and the crystal region of 16° shifted gradually to 15° . Accordingly, it can be considered that the weight loss for the decomposition in the first and

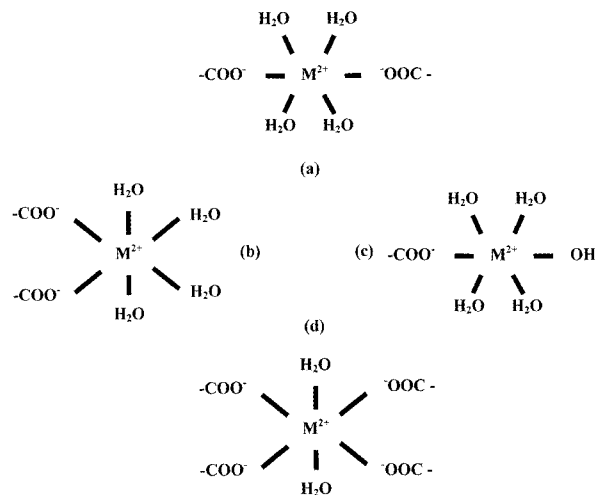


Fig. 8. Schematic representation for the possible chelate structures related to six-coordinate of divalent metal ions; (a) cross-chain di-salt, (b) in-chain di-salt, (c) pendant half-salt, (d) cross-chain tetra-salt.

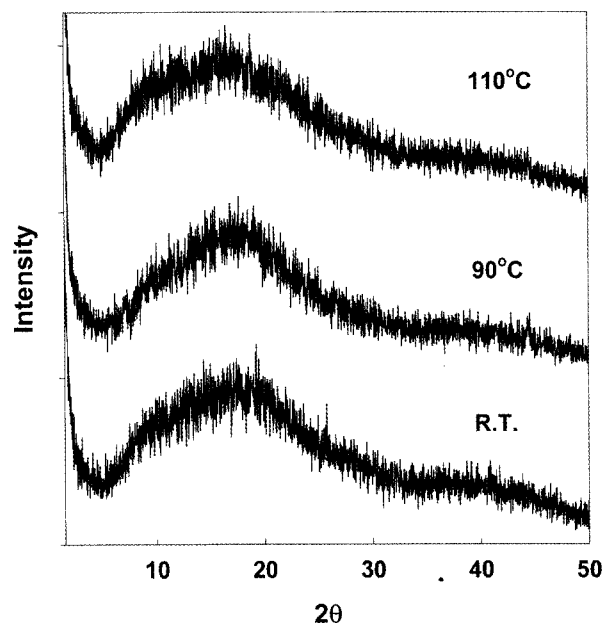


Fig. 9. XRD pattern results of the annealed polyelectrolyte complex as a function of the annealing temperature.

second stage is obviously related to the morphology transformation of the resulting polymer induced by a deformation of chelate segments as well as a rearrangement of these polysaccharide chains during the annealing process, and the alternation in structural viewpoint may results in denser structure and lower free volume in the internal than the pure complex

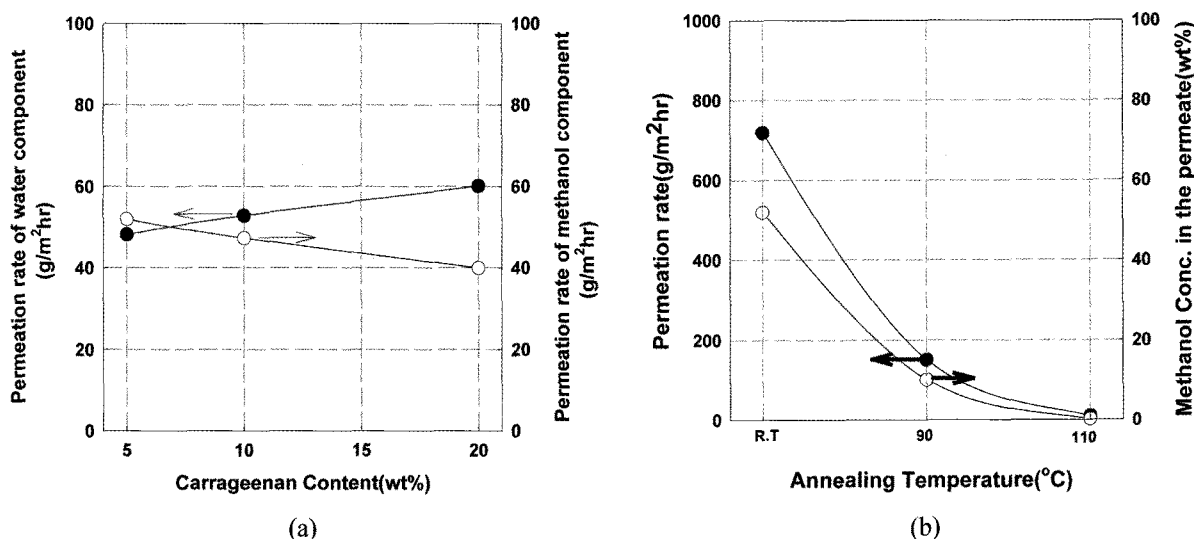


Fig. 10. Permeation rates and methanol concentrations in the permeate on the annealed polyelectrolyte complex for the separation of 80/20 wt% methanol/water mixtures at 50°C.

structure.

Finally, to estimate the effect of the annealing on the structural deformation of the polyelectrolyte complex, the separation of 80/20 wt% methanol and water mixtures was carried out and shown in Fig. 10. In the case of the pure complex, the permselectivity for separating methanol-water mixtures is generally very low, though the permeation rates are high as a whole. On the other hand, the annealed complex reduces greatly the permeation rates and the methanol concentrations in the permeate at the same time, and that the water components almost penetrate through the resulting membrane to the permeate side. From the above-mentioned results, it was concluded that the structural deformation of the annealed polyelectrolyte complex has an effect on the free volume between these polymer chains and the chelate segments such a shrinking of the overall morphology, which act as a molecular sieve in the separation of methanol and water mixtures.

4. Conclusions

In this work, by complexing two anionic polysaccharide blends, composed of sodium alginate and carra-

geenan, with divalent calcium ions, the polyelectrolyte complex was prepared and discussed the effects of annealing on the structural deformation of the polyelectrolyte complex. The results showed that the annealed polyelectrolyte complex exhibited the change of crystallinity in the lateral, due to a rearrangement of two polysaccharide chains, which was explained as a deformation of the chelate structure and the intramolecular or intermolecular interaction between the polysaccharides. Finally, we also assumed that the effect of annealing for the complex membranes acts as a molecular sieving, modulated by shrinking a free volume between the polymer chains in structural viewpoint.

Acknowledgments

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Knowledge Economy (MKE), and a grant from the Basic Research Program of the Korea Research Institute of Chemical technology.

References

1. U. Sander and H. Janssen, *J. Membr. Sci.*, **61**, 113

- (1991).
2. B. Will and R. N. Lichtenthaler, *J. Membr. Sci.*, **68**, 119 (1992).
 3. M. S. Schehlmann, E. Wiedemann, and R. N. Lichtenthaler, *J. Membr. Sci.*, **107**, 277 (1995).
 4. M. M. Yoshikawa, T. Wian, S. Kuno, and T. Kitao, Proceedings of the 6th International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., p. 178 (1992).
 5. K. M. Devaine, A. J. Meier, and C. S. Slater, Proceedings of the 7th International Conference on Pervaporation Processes in the Chemical Industry, Bakish Materials Corp., p. 218 (1995).
 6. M. Yalpani, Polysaccharides, Chapter 2, Elsevier Science Publishers B. V., Amsterdam, Netherlands (1988).
 7. S. G. Kim, K. S. Lee, and K. H. Lee, *J. Appl. Polym. Sci.*, **103**, 2634 (2007).
 8. E. R. Morris, D. A. Rees, D. Thom, and J. Boyd, *J. Carbohydr. Res.*, **66**, 145 (1978).
 9. E. R. Morris, *Brit. Polym. J.*, **18**, 14 (1986).
 10. A. D. Wilson and S. Crisp, *Brit. Polym. J.*, **7**, 279 (1975).
 11. J. H. Kim, S. B. Lee, and X. Feng, *Korean Membrane J.*, **8**, 36 (2006).