기체분리용 고투과선택성 탄소-실리카막

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High-Permeability, High-Selectivity Carbon-Silica Membrane for Gas Separation

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1. Introduction

The molecular sieving carbons (MSCs) are commonly granular, powdery, or fibrous form, which are expected to be utilized as an adsorbent for pressure swing adsorption (PSA) process, one of the gas separation processes and/or a shape-selective catalyst support. On the other hand, MSCs has started to be prepared as a film-type shape (membrane-type) during the past two decades. Since Koresh and Soffer [1] reported the preparation of carbon membrane in 1983, a variety of carbon membranes have obtained from poly(furfuryl alcohol) [2], phenolic resin [3,4] polyimides [5-8], poly(vinylidene chloride)-acrylate terpolymer [9], and polypyrrolone [10].

In these pyrolytic carbon membranes, the effective formation of micropores is a crucial key factor. It has been demonstrated in pyrolytic carbon membranes that such microporosity can be created by channeling molecular debris through a thermosetting polymer matrix during controlled pyrolysis of synthetic and natural hydrocarbon precursors. An early development in pyrolytic carbon membranes for gas separation has found that the pyrolysis conditions such as temperature, heating protocol, and heating atmosphere have a strong influence on the final membrane properties [11]. Up to now, the studies on the pyrolytic carbon membrane have been conducted mostly in terms of only a

few criteria, that is, the pyrolysis conditions and the type of precursors.

Actually, in order to effectively control the molecular size and shape-selective micropores in the pyrolytic carbon membranes, the microstructure of the precursor should be firstly understood in a molecular level. Therefore, central to the present study was finding the possibility of a new class of template carbonization using self-organized polymeric nanostructures materials (SOPNMs) such as block copolymers that consisted of two thermo-stable blocks, only differing the carbon-density in a nanoscale. Although carbon itself is perhaps the most thermo-chemically stable material, carbon is very susceptible to oxidation condition, which is an obvious drawback to the readily and reproducible fabrication of the carbon membrane. Therefore, joining with silicon and/or silicon compounds seems to be a natural choice for the next generation in expanding the membrane material science. Particularly, carbon and silica play an important part in material science due to their relevance in academic field and practical applications. Although the chemical combination of the two materials has been reported in several papers [12-14], most methods are restricted as the pyrolysis followed by hybridization of polymer and silica sol.

In the present study, we report a new approach to the preparation of pyrolytic carbon containing silica phase through the pyrolysis of the polymer containing carbon-rich and silicon-rich phases and to examine the micro-structure of the final materials. To achieve these, we used imide-siloxane block copolymer (PIS) as a precursor of the pyrolytic carbon membrane. The rationales for the choice of PIS are as follows: (i) The structure of PIS is typically composed of rigid and flexible blocks whose phases give rise to micro-phase structures, (ii) two blocks will be expected to conserve the skeleton of the domain during the heat treatment because two blocks are thermally stable, (iii) and imide blocks will be changed into the carbon-rich phase (the role of high selectivity) while siloxane blocks will be changed into carbon-lean phase (the role of high permeability).

2. Experimental Section

Materials. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were obtained from Tokyo Kasei Co., Inc. and used without further purification. α, ω-aminopropyl poly(dimethyl siloxane) (PDMS) was kindly

donated by from Shinetsu Co., Inc. and used after drying in vacuum oven at 90°C. *N*-methylpyrrolidinone (NMP) and tetrahydrofuran (THF) were obtained from Aldrich Chemical Co. Inc. and dried over 5 Å molecular sieves overnight.

Synthesis of Precursor. Imide-siloxane block copolymers (PISs) as precursors were synthesized by two-step polymerization. Powders of PMDA (10mmol) were added dropwise to the THF solution of PDMS (0.2, 1.0, and 2.0mmol, respectively) under a nitrogen atmosphere, and then the solutions of mixtures were stirred for 1h.

Second, the reaction mixtures were added dropwise to NMP solutions of ODA (9.8, 9.0, and 8.0mmol, respectively). The resulting solutions were stirred at room temperature for 6h. Resultantly, homogeneous yellowish siloxane-containing poly(amic acid) (PAA) solutions were then obtained. The solid concentration of PAAs was kept about 10% by weight. The PAA solutions were cast onto a glass plate and then thermally imidized at 100°C for 1h, 200°C for 1h, 300°C for 1h and 350°C for 1h under a vacuum so as to produce strong, flexible, and dense 15-30m films. These films were stored in a desiccator filled with dry silica gel to avoid the influence of humidity until use. The chemical composition of PISs prepared in this study is summarized in Table 1.

Table 1. The sample designation and the composition of PISs prepared in this study

Sample	PMDA (mmol)	ODA (mmol)	PDMS (mmol)	Volume fraction of siloxane moiety
PIS I	10	9.8	0.2	0.06
PIS II	10	9.0	1.0	0.27
PIS III	10	8.0	2.0	0.46

Calculated from group contribution method.

Pyrolysis Method. The pyrolytic carbon membranes obtained in this work were prepared by the pyrolysis of the imide-siloxane copolymers with different compositions. Before starting a pyrolysis trial, the freestanding films of precursors were completely rinsed with deionized water and stored at 80°C under a vacuum oven until any residual solvent and dusts were completely removed. After these pretreatments, the precursor films were then pyrolyzed in a muffle furnace equipped with an automatic temperature controller.

A pyrolysis protocol was followed thoroughly to obtain reproducible gas separation properties of the final carbon membranes. The pyrolysis protocol used in this work was determined by the result from thermal gravimetric

analysis coupled with mass spectroscopy (TGA-MS). Prior to heating the furnace, the precursor films were kept for 1h under an inert purge in order to stabilize the atmosphere and to remove any humidity in a quartz tube.

The heating rate used in the initial stage was 10°C/min from room temperature to 400°C. The heating rate was slowed to 3°C/min until the temperature reached up to 600°C. Then the precursors were kept at 600°C for 2h (PIS-600). From 600°C, the heating rate was again ramped to 3°C/min up to 800°C. The pyrolytic films were held at 800°C for 2h (PIS-800). Finally, from 800°C, the heating rate was increased to 3°C/min until the temperature reached up to 1000°C and the resultant films were held at this temperature for 2h (PIS-1000). The furnace was allowed to cool slowly to room temperature. The final pyrolytic carbon membranes were taken from the quartz tube and then stored in a desiccator filled with dry silica gel to minimize the humidity effect.

3. Results and Discussion

Solid-State ^{29}Si NMR. Before analyzing the final carbonized structures based on imide-siloxane copolymers, it was assumed that the bulk structure of these carbonaceous membranes comprised of the SiO_2-rich phase having sparse carbon clusters (from siloxane blocks) within a continuous carbon-rich matrix (from imide blocks). Thereby, in order to examine the formation of SiO_2 in the pyrolytic carbon matrix, solid-state ^{29}Si NMR was used to evaluate the local environment of the silicon atom in the bulk state of PIS II pyrolyzed at 600 and 800°C, respectively.

Fig. 1. Solid-state ^{29}Si-NMR spectra of PIS and C-SiO₂ membrane

In the solid-state ^{29}Si NMR spectra (Fig. 1), it was found that the transition of D unit [(CH₃)₂$\underline{Si}$O] in precursor to Q units of SiO_2 derivatives after thermal treatment. The ^{29}Si-NMR spectrum of original PIS II (*a*) exhibits only one peak at 20.4 ppm designated as D^2 structure. This D unit disappeared in the spectra of PIS II-600 and PIS II-800.
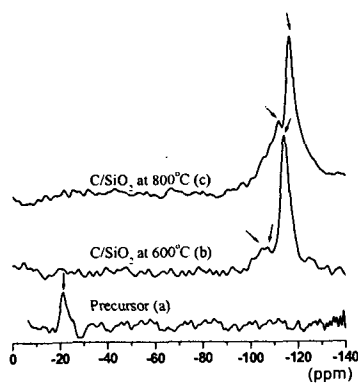
The main signals are observed between 100 and 110 ppm, corresponding respectively to Q^3 units [$\underline{Si}$(OR)$_1$(OSi)$_3$ with R = H or CH$_3$] and Q^4 units [$\underline{Si}$(OSi)$_4$]. The presence of Q^f signal in the bulk state verified the formation of (SiO$_2$)x within pyrolytic carbon matrix.

ESCA. In many phase-separated copolymeric systems, the thermodynamic driving force for minimizing the total free energy of the system as well as bulk composition, block length, processing condition and block sequence distribution results in preferential surface segregation of the lower surface energy constituent [15-17]. Particularly, polysiloxanes are generally used as a surface modifier through blending or copolymerization with other polymers, due to the free rotatability and polarizability of
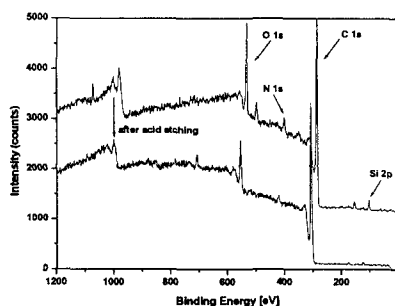

Fig. 2. ESCA analysis of C-SiO$_2$ membrane before and after HF acid treatment

the Si-O bond [18]. Consequently, -Si-O-Si- chain is able to align itself accordingly, resulting in rich in-depth distribution of surface in copolymers and blends. Thereby we focused on the characteristic property of siloxane-based copolymers, and assumed the SiO$_2$-rich surface in the present carbon matrix after pyrolysis.

In order to examine this assumption on the surface of the present pyrolytic carbon membrane, hydrogen fluoride (HF) acid etching was conducted to remove, most perhaps, SiO$_2$ phase on the pyrolytic film surface. Here ESCA was used to reveal the surface composition of the carbon films before and after the acid treatment.

Full scanning ESCA spectra of the carbon films before and after the acid etching was compared as shown in Fig. 2. Signals from four detectable elements (carbon, oxygen, nitrogen, and silicon) were recorded at 284.2 eV (C$_{1s}$), 543.1 eV (O$_{1s}$), 409.9 eV (N$_{1s}$), and 103.0 eV (Si$_{2p}$), respectively. After acid treatment, the Si$_{2p}$ peak became rarely detectable in comparison with one before the acid treatment. Generally, Si$_{2p}$ spectrum can be fitted with two components in silicon compounds: Si(I) at 101.5 eV and Si(II) at about 103.0 eV. It is well-known that Si(I) and Si(II) are attributed to PDMS and SiO$_2$, respectively [19]. We do not observe Si(I) spectrum corresponding to the

existence of dimethylsiloxane after the pyrolysis. These ESCA spectra confirm that the present carbon matrix has SiO_2-rich structure on the surface similar to the in-depth structure revealed in siloxane containing copolymers.

FE-SEM. While observing the surface morphology on both sides of carbon film after HF treatment at room temperature by FE-SEM, very interesting features were found. The surface of only one side (air-polymer interphase) (Fig. 3) in carbon film was observed with well-distributed carbon spheres with grained shape in the form of discrete bright spots. The spheres had nearly a constant size of about 200-220 nm in diameter. A separate energy dispersive X-ray spectrometry (EDX) analysis confirmed that these spheres of carbon grains formed after the removal of the SiO_2 rich phase surface.
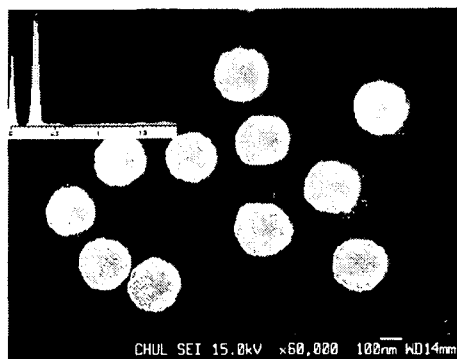

CHUL SEI 15.0kV ×60,000 100nm WD14mm

Fig. 3. FE-SEM images of $C-SiO_2$ top surface after HF treatment

Molecular Probe Study. In order to evaluate the molecular sieving capability of $C-SiO_2$ membranes, molecular probe studies were carried out to measure the pure component gas permeability through the $C-SiO_2$ membranes using nitrogen (N_2, 3.64 Å), oxygen (O_2, 3.46 Å), helium (He, 2.60 Å), and carbon dioxide (CO_2, 3.36 Å).

One of the main objectives of this study is to study the changes in properties of the precursor composed of carbon-rich (PMDA-ODA) and SiO_2-rich (PMDA-PDMS) domain during the pyrolysis. The pyrolysis conditions such as the pyrolysis temperature, the heating rate, and the pyrolysis atmosphere, are important factors in determining the microstructure and gas permeation properties of pyrolytic carbon membranes.

In the present work, it has been observed that the pyrolysis temperature has a marked influence on permeation characteristics of $C-SiO_2$ membranes. Table 2 illustrated the He, O_2, N_2 and CO_2 permeability at 25°C for $C-SiO_2$ membrane prepared at different pyrolysis temperature (600, 800, and 1000°C), respectively. All the gas permeabilities increased with the increase of pyrolysis temperature up to 800°C. The gas permeabilities through $C-SiO_2$ membrane are a maximum value at 800°C. However, as the pyrolysis temperature increases

up to 1000°C, the resulting C-SiO$_2$ membranes are less permeable than ones pyrolyzed below 800°C. In the case of C-SiO$_2$ membrane derived from PIS III, the pyrolysis of the polymeric precursor at 1000°C leads to an oxygen permeability of only 2 Barrer in comparison with 68 Barrer at 800°C.

Table 2. Gas permeation results of C-SiO$_2$ membranes at 25°C

Sample	Pyrolysis Temperature (°C)	Permeability [Barrer]				Selectivity to N$_2$		
		He	O$_2$	CO$_2$	N$_2$	O$_2$/N$_2$	CO$_2$/N$_2$	He/N$_2$
PIS I	600	315	7.6	21	0.33	23	62	955
	800	442	27	89	1.47	18.4	61	304
	1000	121	4.5	12	0.19	24	64	643
PIS II	600	1258	30	84	1.35	22.2	62	1033
	800	1393	68	204	3.68	18.5	56	341
	1000	133	2	7.4	0.10	20	74	1330
PIS III	600	610	111	386	18	6.2	21	34
	800	981	168	765	16.8	10	46	58
	1000	207	9.5	36	0.63	15	57	56

The O$_2$ permeabilities and the selectivities of O$_2$/N$_2$ of C-SiO$_2$ membrane prepared at 800°C are represented as a function of initial siloxane content in a precursor matrix in Fig. 4. Note that the O$_2$ permeabilities of C-SiO$_2$ membranes tend to increase with the volume fraction of initial siloxane moiety in original imide-siloxane copolymer matrix, but the O$_2$/N$_2$ selectivities decrease from 19 to 10. It is worthwhile mentioning the gas permeation properties of the polymeric precursor used before pyrolysis, because the microstructure of polymer is closely related with its gas transport behavior. Our previous works on the gas permeation behavior of precursors reported on the transport behavior of rigid-flexible block copolymer membranes such as poly(amideimide siloxane) and poly(imide siloxane) [20,21]. For the polyimides where a siloxane moiety was introduced, the oxygen permeability increased from 1 Barrer to 100 Barrer but the selectivity of O$_2$/N$_2$ selectivity decreased from 10 to 2.5 with an increase in the siloxane content. Interestingly, it was observed that the oxygen permeability drastically increased at around 0.2-0.3 volume fraction of siloxane in a copolymer matrix. The percolation concept meaning the formation of effective shortest path around this composition was introduced and applied to explain this behavior. Indeed, the structure of poly(imide siloxane) could be explained by a two phase model with a partial mixed interphase. Unlike block

copolymers with well-ordered microphase separated structure, the poly(imide siloxane) is segmented block copolymers where the geometric disorder, that is, random segment size distribution, forces the mixing of the hard (rigid) and soft (flexible) segments. Thus, this randomly ordered two-phase system is very similar to percolating system that two components with different characteristics are randomly mixed. Furthermore, a partial mixed interface between two phases might easily lead to connected phases with a gradual addition of one phase. From

Fig. 4. O_2 permeability and O_2/N_2 selectivity of C-SiO_2 membrane prepared by the pyrolysis at 800°C as a function of the volume fraction of siloxane moiety in the precursor

these results, it was assumed that the carbonization of these block copolymers with two characteristic domains should lead to the changes of gas permeation properties. Also, the effect of heterophase such as SiO_2 phase on the gas separation properties of pyrolytic carbon membranes should be seriously considered.

As shown in Fig. 4, the O_2 permeability increased at around 0.3 volume fraction of a siloxane moiety in a precursor, indicating that the characteristic skeleton of two phases might be considerably conserved even after the pyrolysis. Indeed, the rigid imide domain composed of the aromatic backbone and the flexible siloxane domain conducted a role as organic molecular sieve and percolator, respectively. After the transition from the organic to the inorganic phase by the heat treatment, the imide and siloxane domains are gradually changed into carbon rich phase with the crosslinked voids of amorphous regions with the interlayer spacing of the graphite-like or highly ordered microcrystalline, and SiO_2 rich phase with sparse carbon clusters.

Fig. 5 illustrates a hypothetical model of the major structural transitions during the heat treatment of the different domains-imide domain and siloxane domain. During the pyrolysis, the imide domain may preferably change into carbon-rich domain building carbon clusters and carbon network while the siloxane domain may change into carbon-lean domain with partial carbon
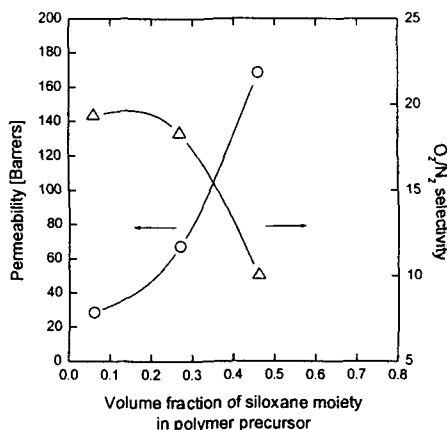
clusters. The domains with no graphite like-carbon network provide the broad pathway to the permeant and simultaneously the domains with high carbon network contribute to the diffusional selectivity. This model may be verified by the observation of the gas permeation behavior in the membrane before and after the pyrolysis. Consequently, this implies that the microphase control of a precursor is a key to prepare the highly-permselective pyrolytic carbon-type membranes.

The diffusion coefficients and diffusion selectivity of O_2 and N_2 are summarized in Table 3. The diffusion selectivities of C-SiO$_2$ membranes are usually higher than those of usual polymeric membranes. The high selectivity of C-SiO$_2$ membrane is attributed mainly by

Fig. 5. A proposed model of the present C-SiO$_2$ membrane inferred from bulk and surface analysis and molecular probe studies

the increase of diffusion selectivity. Generally, non-porous polymers and molecular sieving matrices such as carbon molecular sieves and zeolites transport gas molecules by a similar sorption-diffusion mechanism. The permeability of a penetrant through a membrane is measured as a steady-state flux, normalized by partial pressure difference and membrane thickness. Permeability of component A can be expressed as the product of a kinetic factor, the diffusion coefficient (D_A), and a thermodynamic factor, the sorption coefficient (S_A):

$$P_A = D_A \times S_A \tag{1}$$

The ideal permselectivity, A/B, characterizes the overall ability of a membrane to separate penetrants A and B. This is an inherent property of the material and its molecular geometry. The permselectivity can be factored into a diffusion-selectivity and a sorption-selectivity term as follows.
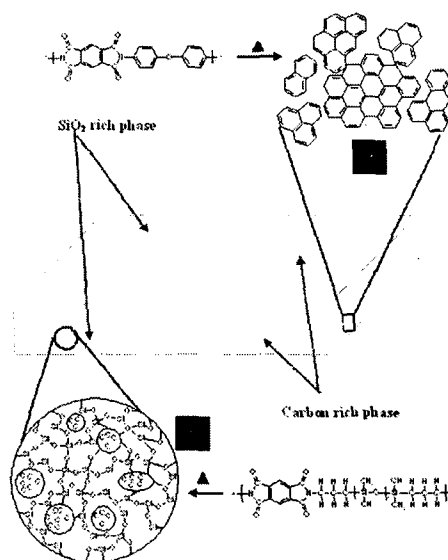
$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \frac{S_A}{S_B}$$

(2)

Table 3. O_2 and N_2 diffusion coefficients ($cm^2s^{-1} \times 10^{-9}$) and diffusion selectivity of C-SiO$_2$ membrane

Precursor		600°C	800°C	1000°C
PIS I	O_2	1.38	5.82	1.09
	N_2	0.14	0.36	0.11
	O_2/N_2	10	15.5	9.9
PIS II	O_2	4.55	9.48	0.89
	N_2	0.50	0.65	0.10
	O_2/N_2	9.1	14.6	8.9
PIS III	O_2	48.60	10.65	0.62
	N_2	15.00	1.03	0.07
	O_2/N_2	3.2	10.3	8.3

Generally, the sorption selectivity term for the O_2/N_2 pair lies in the range of 1-2 in almost all glassy polymers, and between 0.7 and 2 for molecular sieving materials like zeolites 4A and a carbon molecular sieve. Therefore, it is the diffusion selectivity in these C-SiO$_2$ membranes in the present study that is responsible for the remarkable differences in their separation properties.

4. Conclusions

In the present study, a novel carbon implanted SiO$_2$ (C-SiO$_2$) can be readily prepared by pyrolyzing the precursor that combines two building blocks with different carbon density in a nanoscale. The C-SiO$_2$ membranes prepared by the new template carbonization form an asymmetric morphology where the top surface consists of a SiO$_2$-rich phase in a continuous carbon matrix while the bottom surface is mainly a carbon-rich phase. Molecular probe study using small penetrant molecules revealed that C-SiO$_2$ membranes separated small molecules very efficiently by molecular sieving mechanism. The O_2/N_2 selectivity versus O_2 permeability for the C-SiO$_2$ membranes was, to our best knowledge, the highest values in comparison with other gas separation carbon membranes.

References

(1) Koresh, J.; Soffer, A. *Sep. Sci. Technol.* **1983**, *18*, 723.

(2) Cheng, Y. D.; Yang, R. T. *Ind. Eng. Chem. Res.* **1994**, *33*, 3146.

(3) Wang, S.; Zeng, M.; Wang, Z. *Sep. Sci. Technol.* **1996**, *31*, 2299.

(4) Katsaros, F. K. et al. *Microporous Mater.* **1997**, *8*, 171.

(5) Hatori, H.; Yamada, Y.; Shiraishi, M.; Nakata, H.; Yoshitomi, S. *Carbon* **1992**, *30*, 305.

(6) Jones, C. W.; Koros, W. J. *Carbon* **1994**, *32*, 1419.

(7) Suda, H.; Haraya, K. *J. Chem. Soc. Chem. Commun.* **1995**, 1179.

(8) Hayashi, J.; Yamamoto, M.; Kusakabe, K.; Morooka, S. *Ind. Eng. Chem. Res.* **1995**, *34*, 4364.

(9) Rao, M. B.; Sicar, S. J. *J. Membr. Sci.* **1996**, *110*, 109.

(10) Fuertes, A. B.; Centeno, T. A. *J. Membr. Sci.* **1998**, *144*, 105.

(11) Suda, H.; Haraya, K. *J. Phys. Chem. B* **1997**, *101*, 3988.

(12) Rodriguez-Mirasol, J.; Cordero, T.; Radovic, L. R.; Rodriguez, J. J. *Chem. Mater.* **1998**, *10*, 550.

(13) Kyotani, T.; Nagai, T.; Inoue, S.; Tomita, A. *Chem. Mater.* **1997**, *9*, 609.

(14) Muller, H. et al. *Adv. Mater.* **2000**, *12*, 1671.

(15) Zachariasen, W. H. *Theory of X-ray Diffraction in Crystals*; John Wiley & Sons, Inc.; New York, 1945; p. 85.

(16) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons   Carbon Fibre, Glass, and Char*; Cambridge University Press; New York, 1976; p.60.

(17) Zhao, J.; Rojstaczer, S.R.; Chen, J.; Xu, M.; Gardella, Jr., J.A. *Macromolecules* **1999**, *32*, 455.

(18) Chen, X.; Gardella, Jr., J.A.; Ho, T.; Wynne, K.J. *Macromolecules* **1995**, *28*, 1635.

(19) Li, L.; Chan, C.M.; Weng, L.T. *Macromolecules* **1997**, *30*, 3698.

(20) Park, H.B.; Ha, S.Y.; Lee, Y.M. *J. Membr. Sci.* **2000**, *177*, 143.

(21) Ha, S.Y.; Park, H.B.; Lee, Y.M. *Macromolecules* **1999**, *32*, 2394.