energy (ZPE) were also calculated. The ground states and TSs were determined by the number of imaginary frequencies. The energies of **1**, **3** (η^6-arene = C_6H_6), and TSs **6** were obtained by the single-point calculations of the second-order Møller-Plesset method using the decontracted LANL2DZ basis set with an f-polarization function ($\alpha = 1.235$)[17] for Ru, 6-311 + G(d) for the phenyl groups, and 6-311 ++ G(d,p) for other atoms (RMP2/BS-II). Energies of the other compounds were obtained by single-point calculations of the RMP2 method using the same basis set as BS-II for Ru and 6-311 ++ G(d,p) for remaining atoms (RMP2/BS-III). Relative energies were corrected with unscaled ZPE. NPA[18] was carried out at the B3LYP/BS-I level. The Mulliken bond population was calculated by the restricted Hartree–Fock (RHF/BS-I) procedure using the geometries obtained by B3LYP/BS-I.

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---

[1] a) R. Noyori, S. Hashiguchi, *Acc. Chem. Res.* **1997**, *30*, 97–102; b) M. J. Palmer, M. Wills, *Tetrahedron: Asymmetry* **1999**, *10*, 2045–2061.

[2] a) S. Hashiguchi, A. Fujii, T. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562–7563; b) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521–2522; c) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 297–300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; d) S. Hashiguchi, A. Fujii, K.-J. Haack, K. Matsumura, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 300–303; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 288–290; e) K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1997**, *119*, 8738–8739.

[3] J. Takehara, S. Hashiguchi, A. Fujii, S. Inoue, T. Ikariya, R. Noyori, *Chem. Commun.* **1996**, 233–234.

[4] I. Yamada, R. Noyori, *Org. Lett.* **2000**, *2*, 3425–3427.

[5] a) M. Nishio, M. Hirota, Y. Umezawa in *The CH/π Interaction: Evidence, Nature, and Consequences* (Ed.: A. P. Marchand), Wiley-VCH, Weinheim, **1998**, chap. 2, pp. 11–45; b) Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, M. Nishio, *Tetrahedron* **1999**, *55*, 10047–10056; c) J. H. Williams, *Acc. Chem. Res.* **1993**, *26*, 593–598; d) P. Hobza, H. L. Selzle, E. W. Schlag, *J. Am. Chem. Soc.* **1994**, *116*, 3500–3506; e) S. V. Lindeman, D. Kosynkin, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 13268–13269, and references therein.

[6] R. B. Woodward, R. Hoffmann, *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 781–853.

[7] M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466–1478.

[8] D. A. Alonso, P. Brandt, S. J. M. Nordin, P. G. Andersson, *J. Am. Chem. Soc.* **1999**, *121*, 9580–9588.

[9] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

[10] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[11] M. F. Semmelhack, *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36–51.

[12] The reaction of these substrates catalyzed by [RuH{(*R*,*R*)-NTsCH(C_6H_5)CH(C_6H_5)NH_2}(η^6-C_6H_6)] affords the *R* alcohols with 99, 97, and 96 % *ee*, respectively.[4] The enhanced enantioselectivity is a result of an additional *N*-Ts/η^6-arene nonbonded interaction that destabilizes the *Re*-TS to some extent. Unlike in the reaction catalyzed by **1**, replacement of the C_6H_6 ligand by $C_6(CH_3)_6$ lowers the reaction rate.

[13] a) Y. Kodama, K. Nishihata, M. Nishio, N. Nakagawa, *Tetrahedron Lett.* **1977**, *24*, 2105–2108; b) P. J. Breen, J. A. Warren, E. R. Bernstein, J. I. Seeman, *J. Am. Chem. Soc.* **1987**, *109*, 3453–3455; c) Y. Nakai, K. Inoue, G. Yamamoto, M. Oki, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2923–2931; d) J. E. Anderson, V. Bru-Capdeville, P. A. Kirsch, J. S. Lomas, *J. Chem. Soc. Chem. Commun.* **1994**, 1077–1078.

[14] a) W. E. Silverhorn, *Adv. Organomet. Chem.*, **1975**, *13*, 47–137; b) E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982**, *82*, 499–525.

[15] a) K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1199–1200; b) K. Murata, T. Ikariya, R. Noyori, *J. Org. Chem.* **1999**, *64*, 2186–2187; c) J. Mao, D. C. Baker, *Org. Lett.* **1999**, *1*, 841–843.

[16] Related phenomena: a) H. Brunner, *Angew. Chem.* **1983**, *95*, 921–931; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 897–907; b) R. W. Quan, Z. Li, E. N. Jacobsen, *J. Am. Chem. Soc.* **1996**, *118*, 8156–8157; c) J. A. Gladysz, B. J. Boone, *Angew. Chem.* **1997**, *109*, 566–602; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 550–583; d) E. P. Kündig, C. M. Saudan, G. Bernardinelli, *Angew. Chem.* **1999**, *111*, 1298–1301; *Angew. Chem. Int. Ed.* **1999**, *38*, 1220–1223.

[17] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111–114.

[18] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO, version 3.1, Gaussian, Inc., Pittsburgh, PA, **1998**.

Architecture of Polymeric Superstructures: Self-Color Tone Films Constructed by Mesoscopically Ordered Cubic Lattices

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It is well known that submicron-sized colloidal spheres form a body-centered cubic (BCC) or face-centered cubic (FCC) lattice in aqueous solution.[1] Ascher et al.[2] have developed an approach to permanently lock the ordering of a crystalline colloidal array in a hydrogel matrix. We have also constructed polymeric superstructures by the free-radical polymerization of *N*-vinylpyrrolidone (VP) monomer after polypyrrole microspheres had become arranged into a BCC lattice in a solution of the VP monomer.[3] More recently, we demonstrated that core–shell polymer microspheres[4] and highly branched star polymers[5] led to a hierarchical structural transformation of the cubic lattices. That is, these radially branched polymers formed a lattice with a BCC structure near the overlap threshold (*C**, concentration where the coils begin to become densely packed). This structure changed to a FCC lattice in the bulk region of the films. After these branched polymers had formed a cubic lattice in polymerizable vinyl monomer, the polymeric superstructures were locked permanently into an ordered lattice in a solid matrix by means of free-radical polymerization.[6] This technique is one of the best methods for creating nanoscopic polymeric superstructures composed of two or three phase-separated

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microdomains. However, the microspheres, which had relatively large particle diameters, were packed in an irregular arrangement as a result of polymerization-induced phase separation. Herein we report the architecture of films of polymeric superstructures, especially of self-color tone films (developed color films without some kinds of color formers), formed by the locking of a polymer matrix through graft polymerization of photofunctional core–shell polymer microspheres.

The construction of the polymeric superstructures (three phase-separated microdomains) is illustrated in Scheme 1. The well-defined polystyrene-block-poly(4-vinylpyridine) (PS-block-P4VP) diblock copolymers (SV1: $\bar{M}_n = 18.6 \times 10^4$, P4VP block 30 mol% and SV2: $\bar{M}_n = 8.5 \times 10^4$, P4VP block 43 mol%) were prepared by a sequential anionic polymerization technique. The details concerning the synthesis and characterization of diblock copolymers have been given elsewhere.[7] Figure 1 a and 1 b show the transmission electron microscopy (TEM) photographs of SV1 cast from chloroform/toluene (1/3, v/v) and SV2 cast from chloroform/dioxane (6/4, v/v), respectively. The dark portions are the P4VP phases selectively stained with OsO_4. The morphological structures of the SV1 and SV2 specimens showed dispersed P4VP spheres in a PS matrix and alternating P4VP/PS lamellae, respectively. The periodic distance of the lamellae for SV2 was 92 nm (PS lamella: 41 nm; P4VP lamella: 51 nm).

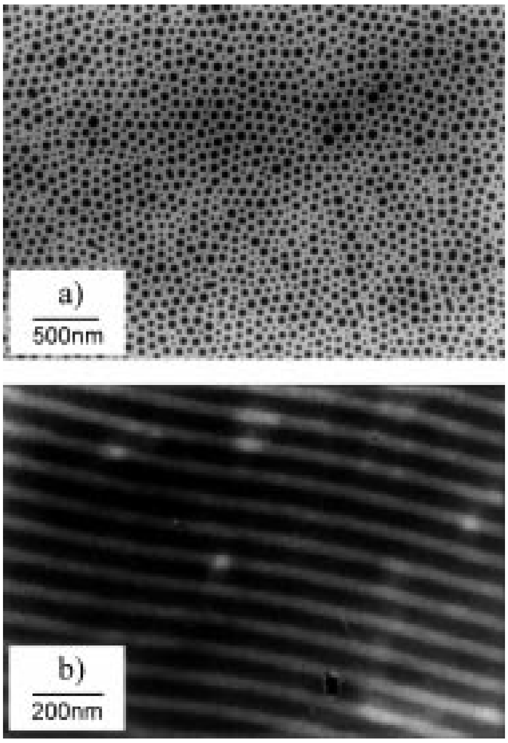
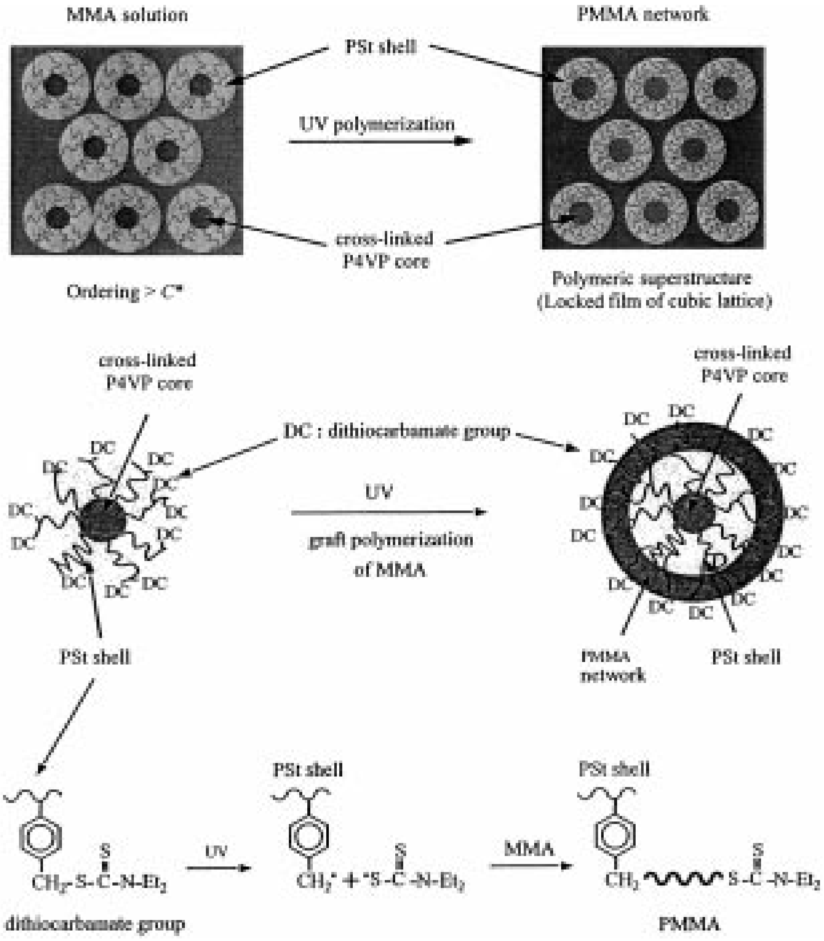


Figure 1. TEM photographs of PS-block-P4VP diblock copolymer films: a) SV1 cast from chloroform/toluene (1/3, v/v); b) SV2 cast from chloroform/dioxane (6/4, v/v).



Scheme 1. Illustration of the polymeric superstructures and the reaction scheme locking the nanoscopic cubic lattices.

The core–shell polymer microspheres (SV-M) were synthesized by cross-linking the segregated chains in the spherical microdomains of P4VP with 1,4-dibromobutane (DBB) vapor at room temperature. The details concerning the synthesis and characterization of such microspheres have been given previously.[8] Characteristics of the SV1-M microsphere are listed in Table 1. The cross-link density of the P4VP cores was 19.4 mol%. A TEM photograph of SV1-M microspheres cast from benzene showed the same texture as the SV1 diblock copolymer. The average diameter (D_c) of the cross-linked P4VP cores, which had a narrow size distribution, was estimated to be 60.4 nm from a survey of 300 samples picked from the photographs obtained. It was shown previously by small-angle X-ray scattering (SAXS) measurements that the P4VP cores were packed in a FCC arrangement in a bulk film.[4] The hydrodynamic diameter ($D_H = 190$ nm) of the microspheres was determined by means of dynamic light scattering (DLS) measurements. The C^*[9] value of SV1-M in benzene was calculated from the D_H value and total molecular weight of the microsphere to be 6.52 wt%.

Photofunctional core–shell microspheres (SV1-MP) were prepared as follows. The PS shell of the parent microspheres was chloro-

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Table 1. Characteristics of core – shell microsphere SV1-M.

Code	$\bar{D}_c$ [nm][a]	$10^{-7}M_r$[b]	CD [mol %][c]	f[d]	$\bar{D}_H$ [nm][e]	C^* [wt %][f]
SV1-M	60.4	26.9	19.4	1448	190	6.52

[a] Diameter of the P4VP cores as determined from the TEM photographs. [b] Total molecular weight of the microspheres were determined by static light scattering (SLS) measurements. [c] Cross-link density of the P4VP domains as determined by Volhard titration. [d] Branch number (aggregation number of diblock copolymers) as estimated from the M_r value of the microsphere and the M_n value of the branched block. [e] Hydrodynamic diameter of the microsphere as determined by dynamic light scattering (DLS) measurements in benzene. [f] Overlap threshold in benzene solution calculated from the D_H value.

methylated with chloromethyl methyl ether in the presence of a stannic chloride catalyst.[10] It is well known that the reaction of a chloromethyl group with diethyldithiocarbamic acid sodium salt quantitatively forms a dithiocarbamate (DC) group.[11] These microspheres (6 g) were treated with diethyldithiocarbamic acid sodium salt (1 g) in *N*,*N*-dimethylformamide/water (3/4, v/v) at room temperature for 8 h in a brown flask. The density of chloromethyl groups on the PS shell was determined to be 15 mol % by ^{1}H NMR spectroscopy ($CDCl_3$) from the integrated peak ratios at $\delta = 4.5$ (methylene protons of the *p*-chloromethyl groups) and $\delta = 6.5 – 7.4$ (aromatic protons of the PS shell). ^{1}H NMR spectroscopic analysis of the characteristic peak of the *N*-substituted methyl protons of DC groups at $\delta = 3.5$ showed that the photofunctional DC groups were introduced quantitatively to the PS shell portion under the reaction conditions used. Figure 2 a shows a TEM photograph of SV1-MP cast from a 1.0 wt % benzene solution. This specimen corresponds to the restructured film from the core – shell microspheres. This photograph shows that dark cross-linked P4VP cores with a narrow size distribution are dispersed in a PS matrix.

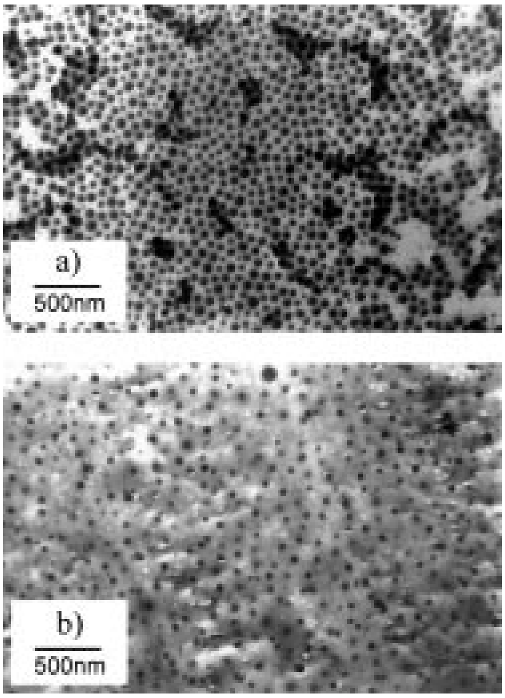

Figure 2. TEM photographs of a photofunctional core – shell polymer microsphere SV1-MP cast from 1.0 wt % benzene solution (a), and locking film MP-L (b).

The locking of the cubic lattice was performed as follows: a solution of SV1-MP microspheres (7 wt %) in methyl methacrylate (MMA; addition of ethylene glycol dimethacrylate as a cross-linker; 50 vol % for monomer) was sandwiched between two glass plates. Graft copolymerization of the photofunctional microspheres was carried out by UV irradiation (250-W high-pressure mercury lamp) in a nitrogen atmosphere at 20 °C for 5 h. SAXS measurements showed that the microspheres formed a lattice with a BCC structure near the C^* value of the MMA solution.[4] We obtained not only a transparent film but also a blue film (MP-L) by this procedure. An ultrathin film (80-nm thick) was prepared by cutting with a microtome (Reinhert – Nissei, Ultracut N) and stained with OsO_4 to obtain a two-dimensional picture of the packing structure of the microsphere in the composite films. Figure 2 b shows a TEM photograph of the film specimen of MP-L after locking treatment. The dark portions correspond to cross-linked cores of P4VP stained with OsO_4. The white portions correspond to the PS and poly(methyl methacrylate) (PMMA) network. This texture indicates that cross-linked cores of P4VP are locked in a state of molecular dispersion in a PMMA network, but that the two-dimensional long-range order is not perfectly maintained. The photofunctional microspheres in this system undergo graft polymerization radially to form three-component copolymers. Therefore, it seems that the microspheres are hard to move during network formation. The polymeric superstructure prepared by locking is composed of three phase-separated microdomains, namely, a cross-linked P4VP core, a PS shell, and the PMMA network. Each step of the preparation of polymeric superstructures is shown in Figure 3. Figures 3 a and 3 b show the photographs of a solution of microspheres in MMA (before locking treatment) and the locking transparent film MP-L, respectively. The solution of microspheres in MMA shows an emulsion tinged with blue. After locking treatment, polymeric superstructure MP-L exhibits a self-blue color tone.

Similar optical behavior was also observed in the diblock copolymer film SV2 which exhibits a lamellar morphology.[12] We cross-linked the segregated chains in the P4VP lamellar layers of the SV2 film with DBB vapor ($CD = 18$ mol %) and obtained a transparent film tinged with yellow. This cross-linked film was insoluble in organic solvents such as benzene and chloroform. We have discovered also that the swollen film exhibits various interference colors (the periodic distance of the lamellae is more than 100 nm; Figure 3 c in benzene). It was mentioned earlier that the periodic distance of the lamellae was 92 nm in the solid state. The cross-linked P4VP phases were converted into hydrophilic phases by quaternization, which resulted in the PS lamellar layers swelling in benzene.

Polymeric superstructure films such as an ordered alloy diffract light and closely follows the Bragg diffraction equation [Eq. (1)]:

$$m\lambda = 2nd\sin\theta \qquad (1)$$

where m is the order of diffraction, λ is the wavelength of incident light, n is the refractive index of the alloy, d is the

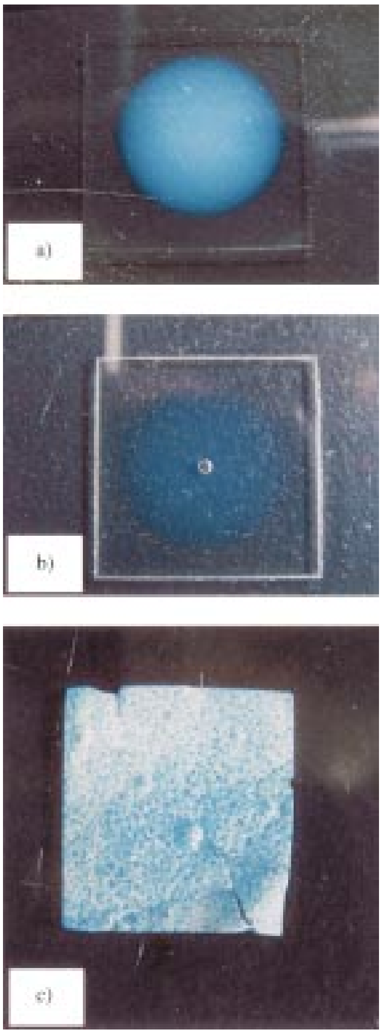

Figure 3. TEM photographs of a) a solution of the microspheres in MMA; b) locking film MP-L; c) a swollen film of cross-linked SV2 which exhibits a lamellar morphology in benzene.

interplanar spacing, and θ is the glancing angle between the incident light and the diffracting crystal planes. n is defined by Equation (2):

$$n = n_A\phi_A + n_B\phi_B + n_C\phi_C \qquad (2)$$

where ϕ is the volume fraction of each component and subscripts A, B, and C indicate the three phase-separated components, namely, the P4VP core, PS shell, and PMMA matrix, respectively. The Bragg spacing d_1 is related to the cell edge a_c of the cubic lattice and the nearest neighbor distance (D_S) of the spheres [Eqs. (3), (4)]:

$$D_S = (\sqrt{3}/2)a_c = \left(\sqrt{3/2}\right)d_1 \quad \text{for BCC} \qquad (3)$$

$$D_S = (1/\sqrt{2})a_c = \left(\sqrt{3/2}\right)d_1 \quad \text{for FCC} \qquad (4)$$

The interplanar spacings of superstructures can be controlled by changing the monomer concentration and the type of cubic lattices. The work here demonstrates a method for preparing polymeric superstructures composed of nanoscopic cubic lattices. These materials can be used for light modulation in tunable diffracting and transmitting optical devices. We are investigating the diffraction behavior of the polymeric superstructure films with a near-IR spectrophotometer.

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[1] R. Kesavamoothy, S. Tandon, S. Xu, S. Lagannathan, S. A. Asher, *J. Colloid Interface Sci.* **1992**, *153*, 188–198; D. J. W. Aastuen, N. A. Clark, L. K. Cotter, B. Ackerson, *Phys. Rev. Lett.* **1986**, *57*, 1733–1736; P. A. Hitner, Y. S. Papir, M. Krieger, *J. Phys. Chem.* **1971**, *75*, 1881–1886; Y. Monovoukas, A. P. Gast, *J. Colloid Interface Sci.* **1989**, *128*, 533–548; A. Kose, T. Osaki, Y. Kobayashi, K. Tokano, S. Hachisu, *J. Colloid Interface Sci.* **1973**, *44*, 330–338
[2] S. A. Asher, J. Holtz, L. Liu, Z. Wu, *J. Am. Chem. Soc.* **1994**, *116*, 4997–4998.
[3] K. Ishizu, K. Honda, *Polymer* **1997**, *38*, 689–693.
[4] K. Ishizu, *Prog. Polym. Sci.* **1998**, *23*, 1383–1408.
[5] K. Ishizu, T. Ono, S. Uchida, *J. Colloid Interface Sci.* **1997**, *192*, 189–193.
[6] K. Ishizu, T. Ikemoto, A. Ichimura, *Polymer* **1998**, *39*, 449–454; K. Ishizu, A. Ichimura, T. Ono, *Polymer* **1998**, *39*, 2579–2582.
[7] K. Ishizu, T. Fukutomi, *J. Polym. Sci. Polym. Chem. Ed.* **1988**, *26*, 281–286.
[8] K. Ishizu, *J. Colloid Interface Sci.* **1993**, *156*, 299–304.
[9] W. W. Glassley, *Adv. Polym. Sci.* **1974**, *16*, 1–179.
[10] G. D. Jones, *Ind. Eng. Chem.* **1952**, *44*, 2686–2692.
[11] M. Ookawara, T. Yamashina, K. Ishiyama, E. Imoto, *Kogyo Kagaku Zasshi* **1963**, *66*, 1383–1389.
[12] K. Ishizu, T. Hosokawa, K. Tsubaki, *Eur. Polym. J.* **2000**, *36*, 1333–1338.

Incorporation of Peptide Isosteres into Enantioselective Peptide-Based Catalysts as Mechanistic Probes[**]

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The discovery of small-molecule mimics of enzymes has been a longstanding objective at the interface of bioorganic chemistry and organic synthesis.[1] We have been studying small peptide catalysts within this context because they offer great opportunities for structural variation (i.e., diversity).[2, 3] Furthermore, they offer a direct analogy to enzymes because such catalysts are composed entirely of the same fundamental building blocks, amino acid subunits. As such, we have been interested in determining the mechanistic basis for the enantioselectivities that such catalysts afford.[4, 5]

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