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Architecture of hybrid structures on star polymers formed by polymerization-induced phase separation

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Polyisoprene (PI) star polymers with many arms formed a body-centred cubic (BCC) structure near the overlap threshold (C^*) in solution. After the PI stars (arm number n above about 90) revealed a superlattice of BCC structure in vinyl monomers (methyl methacrylate, styrene and t-butyl acrylate), the hybrid structures were constructed by locking the ordered superlattice into a solid matrix by means of free radical polymerization of the vinyl monomers. The morphologies of the polymerization-induced phase separation depended strongly on the arm number, propagation rate of the vinyl monomers, and the addition of chain transfer or cross-linking agents. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: star polymer; superlattice; hybrid structure)

INTRODUCTION

We have demonstrated previously that core-shell polymer microspheres led to a hierarchical structural transformation of cubic lattices[1,2]. That is to say, these microspheres formed a lattice with a body-centred cubic (BCC) structure near the overlap threshold (C^*) in solution. In the bulk of the film, this structure changed to a face-centred cubic (FCC) lattice.

Subsequently, we reported the architecture of a polymeric superstructure film formed by locking the cubic lattice of the core-shell microspheres in poly(methyl methacrylate) (PMMA)[3]. In short, after these microspheres formed a cubic lattice such as a BCC structure in methyl methacrylate (MMA) monomer, the polymeric superstructures were constructed by locking a permanently ordered lattice into a solid matrix by means of the free radical polymerization of MMA. These films were constructed with three-phase separated microdomains having different refractive indices, i.e. core, shell and continuous matrix portions. Therefore, these polymeric superstructures can possibly be applied in non-linear optical materials such as optical filters and controlled wavelength rejection filters, etc.

Such structures of core-shell microspheres are somewhat similar to those of star-shaped polymers. Daoud and Cotton[4] have studied the conformations and dimensions of star polymers using the thermal blob model. According to theoretical results[5], the central cores of star polymers do not interpenetrate with each other even beyond C^* in polymer concentration. Thus, stars with many arms are expected to form a crystalline array near C^*. In fact, Willner et al.[6,7] investigated the ordering phenomena of stars around the C^* by means of small-angle neutron scattering (SANS). They showed that the ordering was very weak for 8- and 18-arm polymers but became stronger with increasing arm number. More recently, we have prepared polyisoprene (PI) stars with many arms by the microgelation of PI anions with divinylbenzene (DVB) in a selective solvent such as n-heptane. It was indicated from small-angle X-ray scattering (SAXS) that PI stars (arm number n above about 90) formed a BCC structure near C^* and this structure changed to a mixed lattice of BCC and FCC structures on increasing the polymer concentration[8]. Therefore star polymers with many arms are expected to construct polymeric superstructures by molecular design of locking as well as core-shell microspheres.

In this article, PI stars ($91 \leq n \leq 237$) revealed a superlattice of BCC structure in vinyl monomers such as MMA, t-butyl acrylate and styrene near C^*. Subsequently, hybrid structures were constructed by locking a permanently ordered lattice in a solid matrix by means of free radical polymerization under various conditions.

EXPERIMENTAL

Synthesis and characterization of star and block copolymers

PI stars were prepared by cross-linking PI anions with a small amount of DVB in n-heptane. Details concerning the synthesis and characterization have been given previously[8]. *Table 1* lists the characteristics of PI stars.

Poly(isoprene(I)–b–MMA) diblock copolymer as a compatibilizer was synthesized by the usual sequential anionic addition polymerization using n-butyllithium as the initiator in a toluene/tetrahydrofuran (THF) mixture at −78°C. The terminal ends of the PI anions were capped with 1,1-diphenylethylene. The number-average molecular weight ($\bar{M}_n$) of the PI precursor was determined by gel permeation chromatography (g.p.c.; Tosho high-speed liquid chromatograph HLC-8020) using PI standard samples with THF as the eluent at 38°C, a TSK gel GMH_{XL} column and a flow rate of 1.0 ml min^{-1}. The total molecular weight of the diblock copolymer was determined

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Table 1 Characteristics of PI stars

Code	Molecular weight		Arm number	R_G^c	R_H^d	C^{*e}
	Arm[a] ($10^{-4}\ \bar{M}_n$)	Star[b] ($10^{-6}\ \bar{M}_w$)	(number per molecule)	(nm)	(nm)	(wt.%)
$(\mathrm{SI27})_{91}$	2.7	2.79	91	29.2	22.2	10.1
$(\mathrm{SI42})_{111}$	4.2	5.00	111	41.3	33.0	5.5
$(\mathrm{SI67})_{116}$	6.7	7.97	116	55.7	48.0	2.9
$(\mathrm{SI08})_{237}$	0.8	2.09	237	19.1	18.1	14.1

[a] Determined by g.p.c. using PI standard samples

[b] Determined by static light scattering (s.l.s.; Photal TMLS-6000HL) with the Berry mode in cyclohexane

[c] The radius of gyration (R_G) was determined by s.l.s.

[d] The hydrodynamic radius (R_H) was determined by dynamic light scattering (d.l.s.; scattering angle, 90°) in 0.1 wt.% cyclohexane ($\eta = 0.898$ cp; $n_D = 1.4262$) at 23°C

[e] The overlap threshold (C^*) was calculated from the equation $C^* = 3M_w/(4\pi N_A R_H^3)$, where M_w and N_A are the molecular weight of a PI star and the Avogadro number, respectively

Table 2 Characteristics of the poly(I–b–MMA) diblock copolymer

Code	$10^{-3}\ \bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]	PI block (wt.%)[c]
IM1	6.8	1.02	72

[a] Determined by universal calibration on a gel permeation chromatograph

[b] Determined by g.p.c.[c] Determined by ^{1}H n.m.r. in $CDCl_3$

Table 3 Physical values for the vinyl monomers and the corresponding polymers

Monomer	k_p^a	Polymer	
	($l\ mol^{-1}\ s^{-1}$)	δ ($cal\ cm^{-3})^{1/2b}$	T_g (K)
Styrene	139	9.1	373
MMA	322	9.08	378
t-Butyl acrylate	2100	8.5	316

[a] 40°C

[b] Polyisoprene (PI): $\delta = 8.2\ (cal\ cm^{-3})^{1/2}$

by combining the g.p.c. data with viscometric data (universal calibration[9]: log[η]M *versus* elution volume). The PI content in the block copolymer was determined by ^{1}H n.m.r. spectroscopy on a 500 Hz JEOL GSX-500 spectrometer in $CDCl_3$. The results are listed in *Table 2*.

Locking of superlattice

The locking of the superlattice was carried out by the following two methods. (1) A prescribed vinyl monomer solution of the star polymers was poured into the sample bottle which was fitted with a stopper. Free radical polymerization of the vinyl monomers was carried out in the presence of 2,2-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Ind. Ltd.; 3 wt.% of the monomer) under a nitrogen atmosphere at 40°C for 10 h. (2) A prescribed vinyl monomer solution of the star polymers was poured into a Petri dish. Photopolymerization was carried out in the presence of benzoyl peroxide (BPO; 3 wt.% of the monomer) under irradiation with a u.v. beam in a nitrogen atmosphere at 20°C (25 W high-pressure mercury lamp, Ushio Denki UI 250D; irradiation distance, 30 cm). In these polymerization-induced phase separations, we studied the effects of different kinds of vinyl monomers (MMA, styrene and *t*-butyl acrylate (BA)) and the addition of a chain transfer agent (tetrabromomethane, CBr_4) or a cross-linking agent (ethylene glycol dimethacrylate (EGDM) and DVB (Tokyo Kasei Ltd.; around 55%; meta to para isomer ratio of 2)).

Morphological observations

For the two-dimensional observation of the packing structure of the PI stars in the bulk, an ultrathin film 80 nm thick was prepared by cutting with a microtome (Reinhert-Nissei Co., Ultracut N) and was stained with osmium tetroxide (OsO_4). The morphological results were obtained on a JEOL 100CX transmission electron microscope operated at 100 kV.

RESULTS AND DISCUSSION

Table 3 lists the rate constants of propagation (k_p) of vinyl monomers (styrene, MMA and BA), and the cohesive energy density (δ) and glass transition temperature (T_g) of the corresponding polymers quoted from *Ref.* [10]. In order to lock the ordered lattice of PI stars into a solid matrix, it seems advantageous to employ vinyl monomers that not only have higher k_p values but also a closer compatibility

Table 4 Polymerization conditions for locking an ordered lattice of PI stars

Expt.	PI star		Monomer	Initiator (wt.% of monomer)	CBr_4 or EGDM (wt.% of monomer)
	Code	Polym. conc. (wt.%)			
LS-11	$(\mathrm{SI08})_{237}$	15	BA	V-70; 3	CBr_4; 3
LS-12	$(\mathrm{SI67})_{116}$	5	MMA	V-70; 3	CBr_4; 3
LS-21	$(\mathrm{SI27})_{91}$	12	MMA	BPO; 3	EGDM; 6
LS-22	$(\mathrm{SI08})_{237}$	15	MMA	BPO; 3	EGDM; 6
LS-31	$(\mathrm{SI27})_{91}$	12	Styrene	BPO; 3	DVB; 3
LS-32	$(\mathrm{SI42})_{111}$	7	Styrene	BPO; 3	DVB; 3
LS-41[a]	$(\mathrm{SI67})_{116}$	5	MMA	BPO; 3	EGDM; 6

[a] Poly(I–b–MMA): IM1 diblock copolymer (1 wt.% of monomer) was added to the polymerization system

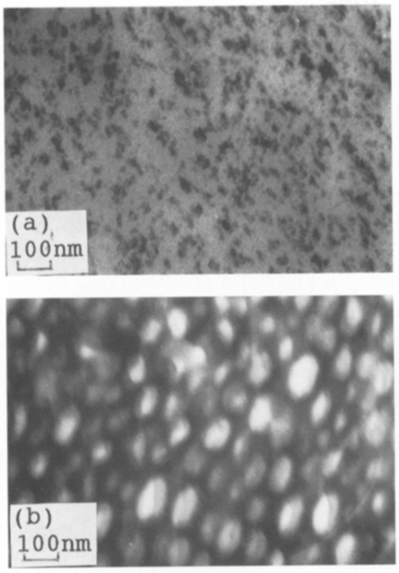

Figure 1 TEM micrographs of (a) LS-11 and (b) LS-12

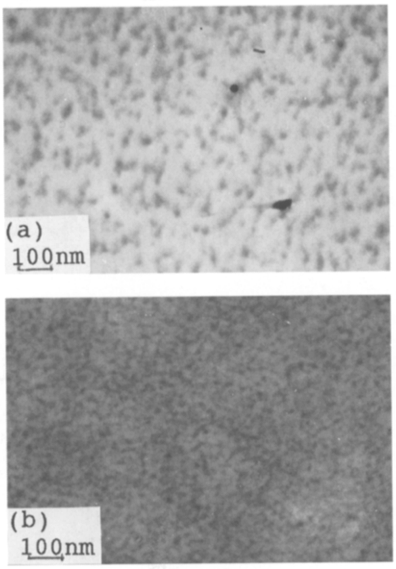

Figure 2 TEM micrographs of (a) LS-21 and (b) LS-22

with the PI stars. In general, the smaller the difference in the cohesive energy densities between PI and each matrix polymer becomes, the more the compatibility increases. In previous work[8], it was concluded from SAXS measurements that PI stars (*n* above about 90) formed a superlattice of BCC structure near *C** in solution. Moreover, it was found that the addition of a chain transfer agent had the effect of preventing polymerization-induced phase separation during the locking of the core-shell microspheres due to a shortening in the propagating chain length of the vinyl monomers[3].

We examined first the preliminary experiments, carried out using V-70 as initiator (method 1), on the polymerization-induced phase separation. The polymerization conditions for the LS-11 and LS-12 specimens are listed in *Table 4*. *Figure 1a* and *1b* show TEM micrographs of LS-11 and LS-12, respectively. The dark portions correspond to PI phases selectively stained with OsO_4. It is found from *Figure 1a* that the PI star particles are dispersed in a poly(*t*-butyl acrylate) (PBA) matrix but are connected to several

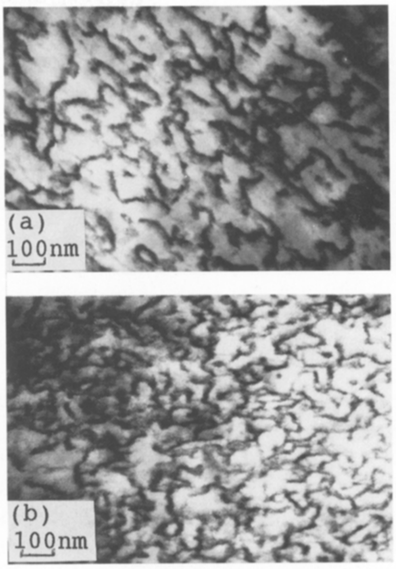

Figure 3 TEM micrographs of (a) LS-31 and (b) LS-32

particle units. This hybrid film possessed poor mechanical strength due to a low T_g of the PBA. The LS-12 specimen, inversely, shows a morphology of large poly(methyl methacrylate) (PMMA) particles dispersed in a continuous PI matrix (see *Figure 1b*). The arm number of the PI stars for the LS-11 system is higher than that for the LS-12 system. These phenomena can be explained as follows. In the LS-12 system, the driving force of phase separation between the PI and PMMA domains overcomes the entropy of rearrangement of the PI stars. As a result, such a specimen shows a thermal equilibrium morphology due to polymerization-induced phase separation. On the other hand, the k_p of BA is high in the extreme compared to that of the MMA monomer. In the LS-11 system, the ordered lattice of PI stars may be locked by the PBA matrix in a non-thermal-equilibrium state. It seems from both polymerization systems that the locking of the PI stars depended on not only on the k_p of the vinyl monomers but also on the arm numbers. However, void formation was observed in both films due to the decomposition of the azo initiators. The following experiments were then performed by method (2), *i.e.* the photopolymerization of MMA or styrene with irradiation by a u.v. beam using BPO as initiator.

We studied mainly the effect of the arm number of the PI stars on the polymerization-induced phase separation. The polymerization conditions for LS-21 and LS-22 are also listed in *Table 4*. In these systems, the arm length of the PI stars for LS-22 ($\bar{M}_n = 8 \times 10^3$) is shorter than that for LS-21 ($\bar{M}_n = 2.7 \times 10^4$). In both systems, the MMA monomers as a dispersion medium were cross-linked with EGDM as a cross-linking agent. *Figure 2a* and *2b* show TEM micrographs of the LS-21 and LS-22 specimens, respectively. It is found from both textures that the $(SI08)_{237}$ stars are dispersed homogeneously with the shape of unimolecules in the PMMA networks (*Figure 2b*). That is to say, the result for LS-22 is better than that for LS-21, although the $(SI08)_{237}$ star has a higher arm number and a shorter chain length than $(SI27)_{91}$. However, the BCC structure of the PI stars is somewhat disturbed after the locking treatment. The PI stars behaved as hard spheres in solution on increasing the arm numbers[8]. Moreover, the star polymers are expected

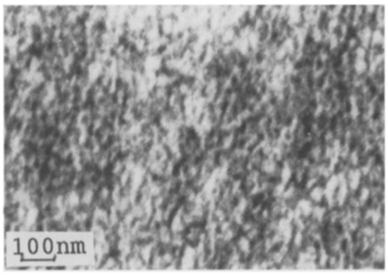

Figure 4 TEM micrographs of LS-41

theoretically to form a crystalline array, when they not only have many arms but also long arm lengths[5]. It is concluded from the above results that the effect of the arm number on the locking of the PI stars is stronger than that of the chain length. The network formation is advantageous to the locking of the PI stars in comparison with the addition effect of the chain transfer agent (see LS-21 and LS-12).

Subsequently, we studied the locking of the PI stars by the photocopolymerization of styrene with DVB. The polymerization conditions for LS-31 and LS-32 are also listed in *Table 4*. *Figure 3a* and 3*b* show TEM micrographs of the LS-31 and LS-32 specimens, respectively. Both specimens show thermal equilibrium morphologies such as PI layer-like structures regardless of arm number. The k_p value of styrene is small compared to those of the MMA and BA monomers. Moreover, polystyrene (PS) has a poor compatibility to PI (see *Table 3*). It then seems difficult to lock the ordered lattice of PI stars in PS networks by radical polymerization.

Lastly, we studied the addition effect of poly(I–b–MMA): IM1 diblock copolymer as a compatibilizer on the polymerization-induced phase separation. The polymerization conditions for LS-41 are also listed in *Table 4*. *Figure 4* shows TEM micrograph of the LS-41 specimen. It is found from the texture that the PI star particles (arm number $n = 116$) are dispersed homogeneously in the PMMA networks. Poly(I–b–MMA) diblock copolymers may be located at the interface boundary between the PI and the PMMA domains. In a comparison of LS-41 (PI star: $n = 237$) and LS-22 (PI star: $n = 116$), the PI star having the higher arm number is superior in locking its ordered lattice even with no addition of compatibilizer.

In this work, we could not lock an ordered lattice of PI stars with the arrangement of a BCC structure in a polymer matrix. However, PI stars could be locked microscopically with the shape of unimolecular micelles in a polymer matrix under some polymerization conditions. From the results obtained in this work, it is expected that one of the best methods for the locking of a lattice is one in which the star polymers themselves play the role of the cross-linker. We are preparing functional PI stars having a vinylbenzyl group at each arm end. The results of such investigations will be reported in the near future.

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REFERENCES

1. Ishizu, K., Sugita, M., Kotsubo, H. and Saito, R., *J. Colloid Interface Sci.*, 1995, **169**, 456.
2. Ishizu, K., *Macromol. Rep.*, 1995, **A32**, 759.
3. Ishizu, K., Ikemoto, T. and Ichimura, A., *Polymer*, 1998, in press.
4. Daoud, M. and Cotton, J. P., *J. Phys. (Les Ulis)*, 1982, **43**, 531.
5. Witten, T. A., Pincus, P. A. and Cates, M., *Europhys. Lett.*, 1986, **2**, 137.
6. Willner, L., Jucknischeke, O., Richter, D., Farago, B., Fetters, L. J. and Huang, J. S., *Europhys. Lett.*, 1992, **19**, 297.
7. Willner, L., Jucknischeke, O., Richter, D., Roovers, J., Zhou, L. -L., Toporowski, P. M., Fetters, L. J., Huang, J. S., Lin, M. Y. and Hadjichristidis, N., *Macromolecules*, 1994, **27**, 3821.
8. Ishizu, K., Ono, T. and Uchida, S., *J. Colloid Interface Sci.*, 1997, **192**, 189.
9. Grubisic, Z., Rempp, P. and Benoit, H., *J. Polym. Sci., Part B*, 1967, **5**, 753.
10. Brandrup, J. and Immergut, E. H. (ed.), in *Polymer Handbook*, 2nd edn., Wiley, New York, 1975.