Polymer Vol. 37 No. 23, pp. 5255–5259, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

S0032-3861(96)00399-7

Introduction of silver nano-clusters into poly(vinyl alcohol) core–polystyrene shell type microspheres

Reiko Saito*, Shin-ichi Okamura and Koji Ishizu
Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12 Ookayama, Meguro-ku, Tokyo 152, Japan
(Received 19 September 1995; revised 26 February 1996)

Silver nano-clusters were introduced into the core part of the poly(vinyl alcohol) [PVA] core–polystyrene [PS] shell type microspheres. The introduction of silver nano-clusters was observed by energy dispersive X-ray spectrometry (EDX) and wide angle X-ray scattering (WAXS). The maximum content of the silver (17 wt%) was obtained at 9 mol% of PS shell content. The silver content in the film was governed by the shell thickness (PS content), the crosslinking density of the core, the composition of used solvent and the presence of hydroxide ions in the film. Copyright © 1996 Elsevier Science Ltd.

(Keywords: silver nano-cluster; polystyrene/poly(vinyl alcohol); metal–polymer composite material)

INTRODUCTION

Hybridization of polymer gels and noble metal nano-clusters is very beneficial and interesting in the development of polymer conductors, optical materials and catalyst carriers. In order to control the functionality of these composite materials, the location of the metal nano-clusters in the gels should be controlled. In the most published work[1–3], such a control is not complete. However, the strict control of the localization of the noble metal nano-clusters was successful in some cases.

Cohen *et al.*[4–6] succeeded in introducing several types of metal nano-clusters into the lamella and spherical microdomains in polymer films of functionalized phosphine-containing poly(*racemic* 2-exo-3-endo-bis(diphenylphosphino)bicyclo-[2, 2, 1]-heptene-*b*-methyltetracyclododecene) diblock copolymers. In their work[4–6], the metal nano-clusters only existed in the norbornene microphases. We also succeeded in producing silver nano-clusters in the limited crosslinked poly(2-vinyl pyridine) (P2VP) phases (hydrogel phases) of microphase separated films of poly(styrene-*b*-2-vinyl pyridine) [P(S-*b*-2VP)] block copolymers[7–10]. For both cases, the microphase separated structures of the AB block copolymers were used as templates. These methods are beneficial because the size and shapes of the microphase separation are expected based on the predictions of 'Molau's law'[11].

The particular features of our method are: (a) the P2VP microdomains were chemically crosslinked, thus the P2VP microdomains holding the silver nano-clusters were stable in good solvents for both PS and P2VP; (b) the content of silver nano-clusters could be controlled by varying the introduction conditions such as the crosslink density of P2VP phases, the silver ion concentration and the solvent composition of the soaking solution.

By using the P(S-*b*-2VP) block copolymer with P2VP spheres in PS matrix morphology, the P2VP core–PS shell type polymer microspheres containing the silver nano-clusters into the core part could be synthesized[9,10]. The core–shell type polymer microspheres can be used as composite materials for super lattice formation in solution and in the solid state by blending with other homopolymers and block copolymers[12–15] because of their specific structures[16,17]. Therefore, it is expected to design the high functional materials by combining the super lattice formation technique of the microspheres and introduction of the metal nano-clusters into the microspheres. However, there is one major disadvantage for P(S-*b*-2VP) block copolymers in that the pyridine groups form the complex with silver[18,19]. From this viewpoint, the pyridine core should be avoided.

Poly(vinyl alcohol) (PVA) is the conventional non-ionic hydrophilic polymer as the carrier for the noble metal nano-clusters. If it is possible to use the PVA for the core of the microspheres instead of P2VP, the complex formation between silver and the core sequences can be neglected. Based on this consideration, we have already synthesized the PVA core–PS shell type microspheres with varying PS contents and crosslink densities[20].

In this paper, we aim to introduce the silver nano-clusters into PVA cores in the PVA core–PS shell type microspheres. The progress of introduction of silver nano-clusters was estimated by energy dispersive X-ray (EDX) and wide angle X-ray scattering (WAXS).

EXPERIMENTAL

Materials

PVA core–PS shell type microsphere: the microspheres used in this paper were synthesized and characterized

---

* To whom correspondence should be addressed

Table 1 Characteristics of PVA core–PS shell type microspheres

Sample name	PS content (mol%)	[TPA]/[-OH] (mol%)[a]	Diameter of PVA core (nm)[b]	Q_W of PVA core (wt/wt)[c]	Q_w of film (wt/wt)[c]
G1-1	9.0	1.0	120	3.51	2.93
G1-5	9.0	5.0	106	1.50	1.25
G2-1	16.7	1.0	110	2.20	1.57
G2-5	16.7	5.0	96	1.78	1.27
G3-1	23.0	1.0	110	2.25	1.41

[a] Telephthal aldehyde concentration to alcohol group in PVA
[b] Estimated by TEM
[c] Swelling degree of the film in water for 2 days at 35°C

elsewhere[20]. Composition of the microsphere, diameter of core, shell thickness and degree of swelling of the microspheres are shown in *Table 1*. All microspheres were spherical and their diameter distributions (D_w/D_n) were less than 1.2.

Introduction of the silver nano-cluster in the film

For beneficial treatment, the microsphere film was prepared by casting the microsphere/benzene solution (polymer concentration 10 wt%). The films were about 120 μm thick. In order to introduce the hydroxide ion in the film, the film was soaked in the 3 wt% caesium hydroxide/THF–water solution for 2 h at room temperature in the dark. Films were washed with water and dried completely at room temperature in the dark. For introducing the silver ions into the film, the films were soaked in the silver nitrate/THF–water solution for 4 days in the dark. The concentration of silver nitrate was 1.0×10^{-1} mol l^{-1}. After being soaked in the silver ion solution, the films were washed with water, dried, and soaked into the 2.5 hydroquinone/THF–water solutions for 2 h at 35°C for the reduction.

The silver nano-cluster contents and the morphologies of the films were decided as similar to the previous methods[7].

Wide angle X-ray scattering measurement

Wide angle X-ray scattering (WAXS) intensity distribution was measured with a rotating-anode X-ray generator (Rigaku Denki, Rotaflex RT. 300 RC) operated at 40 kV and 100 mA. The X-ray source was monochromatized to CuKα ($\lambda = 1.54$ Å) radiation. The WAXS patterns were taken with a fine-focused X-ray source using a flat plate camera (Rigaku Denki, RU-100).

Morphological observation

The solution of sample (polymer concentration 1 wt%) was dropped on the copper microgrid coated with carbon, and dried gradually. In order to investigate the morphology on the cross-section of the sample, an ultra-thin film specimen was prepared by cutting the film with a microtome (Reichert-Nissei Co., Ultracut N). The morphological results were obtained with a Hitachi H-500 TEM at 75 kV.

The cross-section of the film, obtained by breaking the film in liquid nitrogen, was observed by scanning electron microscopy (SEM) (JEOL JSM-T220). Ag and Cs atoms on the cross-section of the film were analysed by energy dispersive X-ray (EDX) (Philips EDAXPV9900IL).

RESULTS AND DISCUSSION

Introduction of silver nano-clusters into the microsphere films

Figure 1 shows the schematic process of the introduction of the silver nano-clusters in the PVA core parts of the PVA core–PS shell type microspheres. As described in the Introduction, the most important feature of this study is to introduce the silver ions into only PVA core parts. Previously, the silver ions were trapped in the certain domains with halogen ions for the P(S-*b*-2VP) films[7-9]. However, no ions existed in the PVA core. Thus, first, we loaded hydroxide ions as the trap for the silver ion into the PVA core. Pre-treatment of the film with hydroxide aqueous solution is the most popular method for trapping the silver ions in PVA gels. Taking into account the solubility in the THF–water mixture and the convenience for EDX observation, we chose caesium hydroxide for this purpose instead of potassium hydroxide or sodium hydroxide.

The PS shell chains in the microspheres were attached to PVA core with ester bonds. These ester bonds would be hydrolysed during the caesium hydroxide treatment. Thus, the possibility of the hydrolysis of the microsphere film with caesium hydroxide was investigated. The microsphere film of G1 of 120 μm thickness, which was colourless and transparent, was soaked in the caesium hydroxide/THF–water mixture for a week.

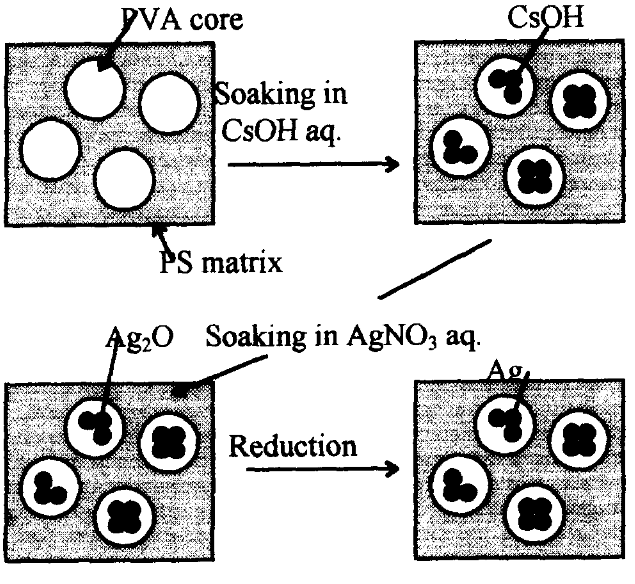

Figure 1 Scheme for introduction of silver nano-clusters in this paper

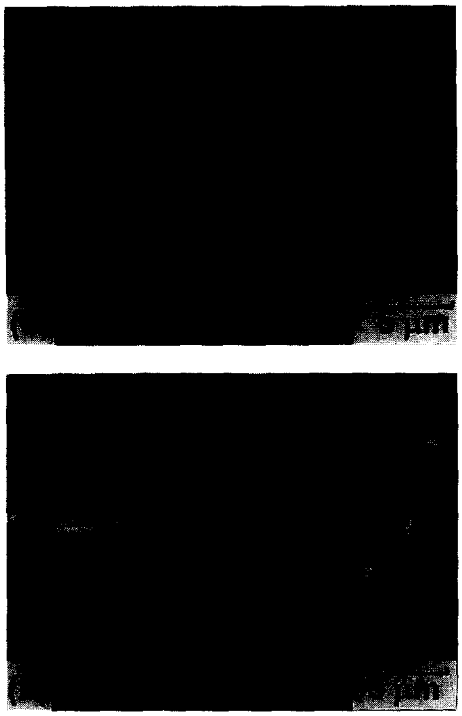

Figure 2 SEM micrographs of G3-5 after soaking in the caesium hydroxide solution: (a) near the surface of the film; (b) in the centre of the film

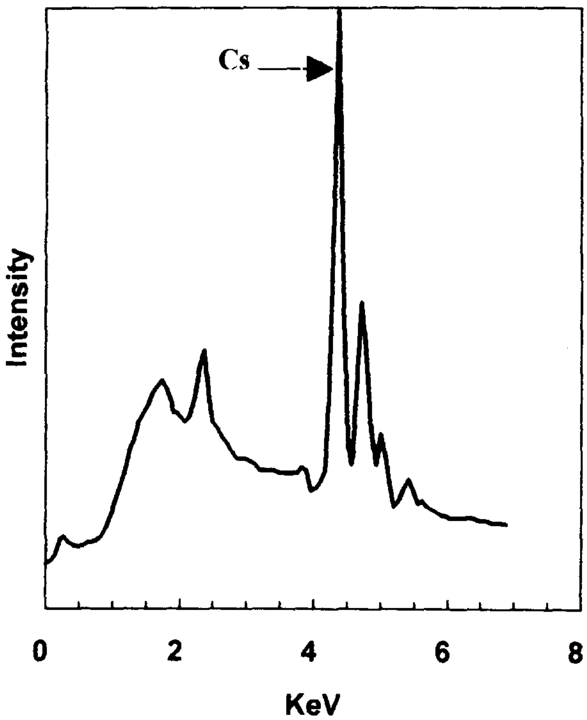

Figure 3 EDX profile of the G3-5 after soaking in the caesium hydroxide solution

The compositions of this mixture were 3 wt% of caesium hydroxide and 50 vol% of THF. After soaking, the film was dissolved into the THF/DMSO mixture and detached PS chains were extracted with THF. The g.p.c. measurement was carried out for detection of the detached PS chains in THF. As no PS chain was detected in the THF solution by g.p.c. with RI and u.v. detectors, it was concluded that the microsphere films were stable in the caesium hydroxide solution under these conditions. From these results, the 3 wt% caesium hydroxide solution was used for soaking in this work.

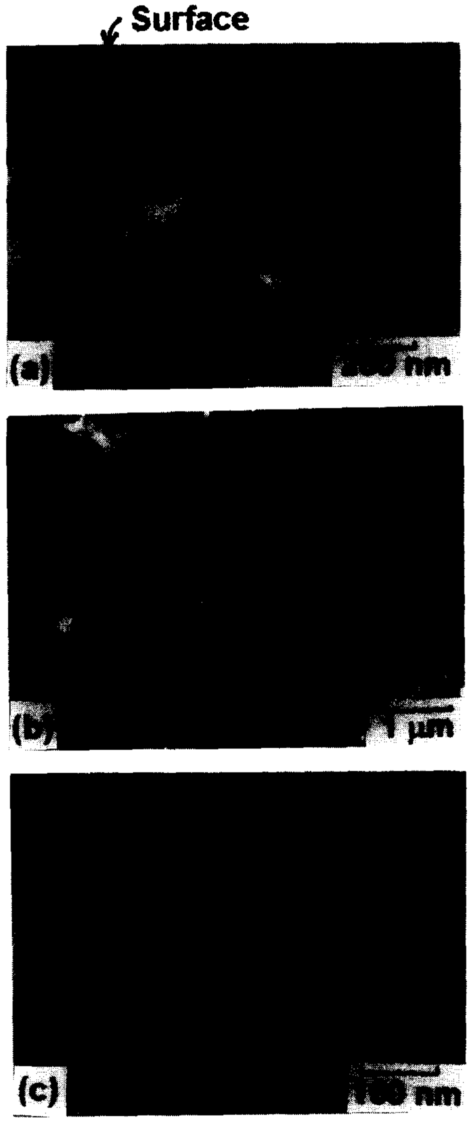

Figure 4 The micrograph of the cross-section of the film G3-5. (a) TEM micrograph after soaking in the silver nitrate solutions. (b) SEM micrograph after the reduction. (c) TEM micrograph after the reduction

Next, the introduction of the caesium hydroxide into the films was confirmed by SEM. *Figure 2* shows the SEM micrographs of the vertical cross-section of G3-5 films after the caesium hydroxide treatment (THF 30 vol%). The bright spots are observed not only near the surface (*Figure 2a*) but also in the centre of the film (*Figure 2b*). The elements of the bright spots were determined by the EDX method (*Figure 3*). The clear peak due to the Cs–Kα appeared at 4.2 keV. The bright spots were caesium hydroxide. Consequently, the caesium hydroxide was introduced through the film.

After the caesium hydroxide treatment, the silver ions were introduced into the films by soaking the film in the silver nitrate solutions. After soaking in the silver nitrate solutions, all films became black and translucent. *Figure 4a* shows the TEM micrograph of the cross-section of the G3-5 after the silver nitrate treatment. The dark small particles dispersing in the film could be observed without

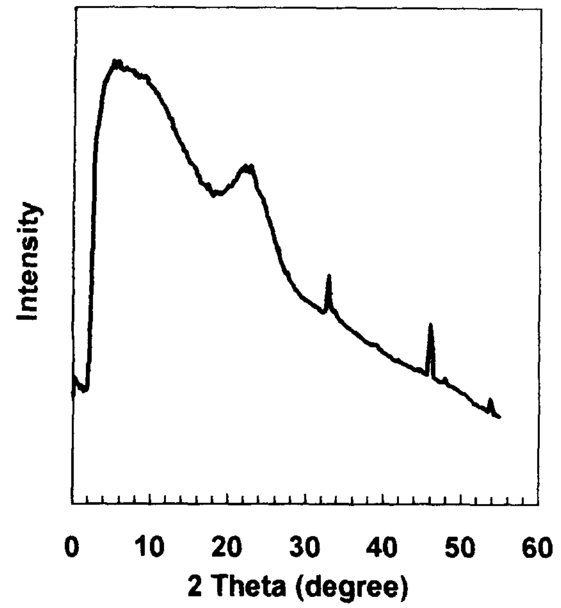

Figure 5 WAXS profile of the G3-5 film after soaking in the silver nitrate solution

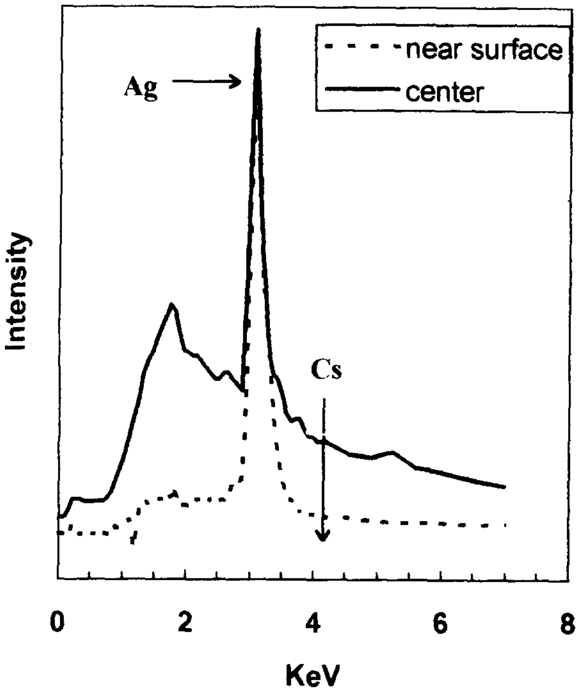

Figure 6 EDX profiles of the G3-5 after the reduction: (a) near the surface of the film; (b) in the centre of the film

Table 2 Conditions and results for silver nano-cluster introduction

Sample number	THF content in $AgNO_3$ (vol%)[b]	Ag/film (wt%)[c]	[Ag]/[VA] (mol%)[d]
G1-1-10	10	2.9	1.5
G1-1-30	30	17.0	8.8
G1-1-50	50	7.1	3.6
G1-1-30B[a]	30	5.4	2.7
G1-5-10	10	1.4	0.7
G1-5-30	30	1.5	0.8
G2-1-0	0	2.2	1.3
G2-1-10	10	2.3	0.8
G3-1-0	0	1.3	0.9
G3-1-10	10	1.5	1.1

[a] Without caesium hydroxide treatment
[b] THF content in the aqueous silver nitrate used for soaking the film
[c] Introduced silver into the film estimated from Volhard's titration
[d] The molar ratio of introduced silver to the vinyl alcohol unit

staining. The average diameter of these particles was 10 nm. As all atoms except silver are transparent on the TEM micrograph under these conditions, the black particles were concluded to be the silver compound. In order to specify these particles, WAXS measurements were carried out. *Figure 5* shows the WAXS chart of the film of G3-5 after soaking in the silver nitrate. The peak observed at 32.9° is due to the silver oxide. No peak based upon the silver nitrate appeared at 29.7°. Consequently, the black particles were not silver nitrate but silver oxide.

Then, the silver oxide in the films was reduced to the silver nano-clusters with hydroquinone. *Figure 4b* shows the SEM micrograph of the cross-section of the G3-5 near the surface after the reduction. The bright spots still presented homogeneously through the film. *Figure 6* shows the EDX spectra of these bright spots in the film. The peak of caesium atom at 4.2 keV vanished completely and a new peak appeared at 3.0 keV. This new peak is due to the silver atom. Thus, it was found that the caesium atom was removed and only silver compounds remained in the film. *Figure 4c* shows the TEM micrograph of the microsphere of G3-5 reduced and stained with OsO_4. White, grey and black regions are PS phases, PVA phases and the silver nano-clusters, respectively. This micrograph shows that the silver nano-clusters selectively existed in the PVA core. Therefore, the silver nano-clusters were introduced only into the PVA core parts of the film.

Additionally, it should be noticed that the final films were dark red translucent. The u.v. absorption behaviour of these films is discussed below.

Silver contents in the films

Table 2 shows the silver contents in the films. Except for the G1-1 series, the silver was not introduced in the film. According to Kurokawa *et al.*[3], the size and contents of the silver nano-clusters are governed by the crosslinking densities of the gel matrices. In a previous work[9], we reported that high swelling of the film was required for introducing the silver nano-clusters in the film. In this work, the matrices of the films were polystyrene. It was suggested that the PS shells of the microspheres, except G1-1, were too thick to introduce the silver nano-clusters. Among these films, the silver nano-clusters were introduced in only the G1-1 series. The content of silver nano-clusters increased with the THF content. Here, the degree of swelling of the film (Q_W) corresponds to the THF content. For the G1-1 series, the maximum silver nano-cluster content was 17 wt%, when the THF content in the solvent was 30 vol%. Similar to previous work[9], the film partially dissolved in the silver when the THF content in the solution was above 60 vol%.

In this study, the caesium hydroxide was used as the trap of silver ions. In order to make clear the effect of caesium hydroxide, the silver contents of the films of G1-1-30 and G1-1-30B, which were treated with and without caesium hydroxide, respectively, were prepared. As the silver nano-cluster content of the G1-1-30 (17 wt%) with

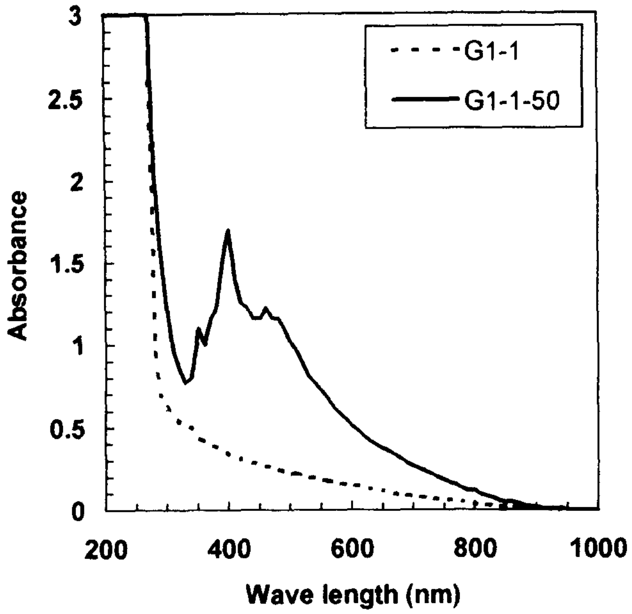

Figure 7 The u.v. absorption of the G1-1-50

the caesium hydroxide treatment was about three times larger than G1-1-30B (5.4 wt%) without caesium hydroxide treatment, the treatment with caesium hydroxide resulted in the increasing of the silver content. Thus, it was found that the hydroxide ion was important for stacking the silver ion in the film and accelerated the silver content.

U.v.-vis. absorption of the microsphere film containing the silver nano-clusters

It is well known that the polymer films containing well dispersed metallic nano-clusters showed optical nonlinearity with third order optical susceptibility[21,22]. As described above, the original film without any modification was clear and colourless, and the final films containing the silver nano-clusters were dark red. From this colour change, the specific optimal properties, for example optical non-linearity, were expected.

Thus, the u.v.-vis. absorption spectrum was measured for the film G1-1-50 (*Figure 7*). After the introduction of silver nano-clusters, three new peaks appeared at 350 nm, 405 nm and 460 nm. According to the literature[23,24], the peak at 405 nm is due to the surface plasmon resonance of silver nano-clusters. Therefore, the optical nanolinearity of the film is expected. However, the peak at 405 nm was wide and overlapped with the other two peaks. Moreover, the film was too dark to be analysed because the content of the silver nano-clusters in the film was too large. For more detailed investigations, the film with less silver nano-clusters dispersed homogeneously is required.

CONCLUSIONS

The silver nano-clusters were introduced into the poly(vinyl alcohol) core parts of the poly(vinyl alcohol) core–polystyrene shell type polymer microspheres. The introductions of the caesium hydroxide and silver ions into the PVA core–PS shell type microsphere film were confirmed by the SEM micrographs with EDX and the WAXS measurements. The presence of silver nanoclusters in the core parts of the microspheres was estimated with the WAXS measurements and TEM observations. The silver nano-cluster contents increased with increasing the degree of swelling of the film. For the film of G1-1, the optimum THF composition was 30 vol%. The maximum value of the silver nano-cluster content in the film was 17 wt%.

REFERENCES

1 Mueller K. F. *Science* 1984, **225**, 1021
2 Holba, V. *Colloid. Polym. Sci.* 1989, **267**, 456
3 Kurokawa, Y. and Ueno, K. *J. Appl. Polym. Sci.* 1982, **27**, 621
4 Cheang Chan, Ng, Y., Schrock, R. R. and Cohen, R. E. *Chem. Mater.* 1992, **4**, 24
5 Cheang Chan, Ng, Y., Schrock, R. R. and Cohen, R. E. *J. Am. Chem. Soc.* 1992, **114**, 7295
6 Cummins, C. C., Ng, Y., Schrock, R. R. and Cohen, R. E., *Chem. Mater.* 1992, **4**, 27
7 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1992, **33**, 1099
8 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1992, **34**, 1183
9 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1992, **34**, 1189
10 Saito, R. and Ishizu, K., *Polymer*, 1995, **36**, 4119.
11 Molau, G. E. 'Blockpolymers' (Ed. S. E. Aggarwa), Plenum Press, New York, 1970
12 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 1581
13 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 2296
14 Saito, R., Kotsubo, H. and Ishizu, K. *Polymer* 1994, **35**, 1747
15 Ishizu, K., Sugita, M., Kotsubo, H. and Saito, R. *J. Colloid and Interface Sci.* 1995, **169**, 456
16 De la Cruz, M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
17 Witten, T. A., Pincus, P. A., Cates, M. E. *Europhys. Lett.* 1986, **2**, 137
18 Bjerrum, J. *Chem. Rev.* 1950, **46**, 381
19 Hong, P. P., Boerio, F. J., Tirrell, M., Dhoot, S. and Guenous, P. *Macromolecules* 1993, **26**, 3953
20 Saito, R., Okamura, S. and Ishizu, K. *Polymer* 1995, **36**, 4515.
21 Yamazaki, S. and Kurokawa, Y. *Polym. Commun.* 1991, **32**, 524
22 Ogawa, S., Hayashi, Y., Kobayashi, N., Tokizaki, T. and Nakamura, A. *Jpn. J. Appl. Phys.* 1994, **33**, L331
23 Richard, D., Roussignol, P. and Flytzanis, C. *Opt. Lett.* 1985, **10**, 511
24 Bloemer, N. J., Haus, J. W. and Ashley, P. R. *J. Opt. Soc. Am.* 1990, **B7**, 790