Preparation and morphologies of 4- and 12-armed styrene–isoprene star-shaped block copolymers

Y. Matsushita*, T. Takasu†, K. Yagi‡, K. Tomioka§ and I. Noda
Department of Applied Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
(Received 5 July 1993; revised 8 November 1993)

Styrene(S)–isoprene(I) star-shaped block copolymers of the $(SI)_4$ and $(SI)_{12}$ types were prepared by an anionic polymerization technique. Linear SI arm molecules were prepared with sec-butyllithium as an initiator in benzene, followed by a coupling reaction with the 4-functional linking agent 1,2-bis(methyldichlorosilyl)ethane and the 12-functional 1,1,2,2-tetrakis(2-(trichlorosilyl)ethyl)silane, respectively, under vacuum. The star-shaped block copolymers were isolated by precipitational fractionation from as-polymerized crude products using benzene–methanol mixtures. They were confirmed to have the designed molecular structures by careful characterization. Using a transmission electron microscope it was observed that the microphase-separated structures of solvent-cast films of the samples are polystyrene (PS) cylinders in a polyisoprene (PI) matrix, alternating lamellar structures and PI cylinders in a PS matrix for 4-armed star-shaped block copolymers when the values of the volume fraction of PS, ϕ_s, are 0.23, 0.47 and 0.78, respectively, and lamellar structures for the 12-armed star-shaped block copolymers when the ϕ_s values are ~0.5. Small-angle X-ray scattering studies revealed that lamellar domain spacings of the star-shaped block copolymers are essentially the same as those of the arm molecules, that is, linear diblock copolymers, irrespective of the number of arms.

(Keywords: preparation; morphology; star-shaped block copolymers)

INTRODUCTION

Studies on microphase-separated structures of block copolymers have mainly focused on linear diblock copolymers. The variation of morphology with composition has been extensively studied. Hasegawa *et al.*[1] examined the compositional dependence of the microphase-separated structures precisely for styrene(S)–isoprene(I) diblock copolymers and found four different structures, i.e. spherical, cylindrical, bicontinuous and lamellar.

The molecular weight dependence of lamellar domain spacing has also been well investigated both theoretically and experimentally. Although several theoretical equations were derived by using different theoretical approaches[2–5], all the equations have similar domain spacing (D)–molecular weight (M) relationships, given by a power law as:

$$D \propto M^{\nu} \qquad (1)$$

In this equation, the exponent ν is 2/3 or close to 2/3 in the strong segregation limit where the thickness of the interface between different microdomains is reasonably thin compared with the domain spacing. Experimental results on SI diblock copolymers[6] and on styrene–2-vinylpyridine diblock copolymers[7] agree well with the theoretical predictions.

The significant feature of $(AB)_n$ star-shaped block copolymers in microphase-separated structures in contrast to those of linear diblock copolymers is that a B block polymer has no free end: one end is anchored on the A–B domain boundary and the other end is connected in the B domain. However, the A block polymer has a free end. A block and B block polymers are not equivalent even in lamellar microdomains, therefore, it is interesting and worthwhile to clarify the effect of this restriction by comparing the morphological features of star-shaped block copolymers with those of linear ones.

Recently, Herman *et al.*[8] studied microphase-separated structures of star-shaped block copolymers of the $(AB)_n$ type and reported that the morphologies of 18-armed star-shaped molecules change with composition in almost the same way as those of the corresponding linear diblock copolymers, though the ordered-bicontinuous double-diamond (OBDD) structures tend to be found easily by increasing the number of arms[9,10]. They also studied the effect of arm number and arm molecular weight on domain spacings for cylindrical and OBDD structures but not for lamellar structure[11].

In this work, therefore, we studied the lamellar domain spacings of star molecules with 4 and 12 arms in comparison with those of linear molecules. For this purpose, we examined the composition range which gave lamellar structures for 4-armed star-shaped block copolymers first. The polymer samples were prepared by

---

* To whom correspondence should be addressed

† Present address: Sanyo Chemical Industries Ltd, 11-1 Ikkyo Nomoto-cho, Higashiyama-ku, Kyoto 605, Japan

‡ Present address: Rinnai Co. Ltd, 2-26 Fukuzumi-cho, Nakagawa-ku, Nagoya 454, Japan

§ Present address: Kao Corporation, Wakayama Research Laboratories, 1334 Minato, Wakayama 640, Japan

0032-3861/94/13/2862–05

anionic block copolymerization followed by a coupling reaction between the chain end of living polymers and linking agents. The samples were carefully purified and characterized in order to be used for morphological observations by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

EXPERIMENTAL

Sample preparation

The purification methods for the S and I monomers and benzene, and the polymerization procedure used to prepare SI linear diblock copolymers are almost the same as those described in a previous paper[12]. The coupling agents 1,2-bis(methyldichlorosilyl)ethane and 1,1,2,2-tetrakis(2-(trichlorosilyl)ethyl)silane (Shinetsu Chemical Co.) were both stored in evacuated ampoules on receipt and used as tetrahydrofuran (THF) solutions without any further purification. Since block copolymerization reactions were carried out in the order of S and I, star molecules were synthesized by coupling reactions between living polyisoprenyl anions and the coupling agents so that the outer block polymer was polystyrene (PS) and the inner block polymer was polyisoprene (PI). These reactions were always designed to satisfy the condition that the number of living ends is $\sim 10\%$ more than that of functional chlorine atoms in the coupling agents to avoid the production of star molecules with less arms. A fraction of homopolymers and SI diblock molecules were isolated as precursors for characterization.

Fractionation and characterization

Precipitational fractionations were carried out to remove the polymer impurities such as linear molecules, which were produced by the procedure described above, from crude polymer mixtures as polymerized. The solvent is a benzene–methanol mixture ($\sim$1:3 v/v). The molecular weight distributions of the polymers at each fractionation stage were checked by g.p.c. (Tosoh HLC-802A with $\mathrm{GMH_{XL}} \times 2$ columns) and those of purified products were also examined by sedimentation patterns (Beckman Spinco Model E ultracentrifuge) in cyclohexane at 35°C. The number-averaged molecular weights of arms and stars were measured by a membrane osmometer (Hewlett-Packard model 502) in toluene at 25°C and the weight-averaged molecular weight of stars with large molecular weight were measured by a light scattering photometer (Fica model 50) in THF at 25°C. PS contents were determined by u.v. absorbance experiments in THF at 25°C with a Shimadzu UV-240. The microstructures of PI blocks were also determined by ^{1}H n.m.r. (Varian Gemini 200).

Morphological observation

Film specimens of the star molecules and their arms for morphological observations were cast from a dilute solution of toluene under air and also under argon atmosphere on a Petri dish for 4 or 5 days and dried under vacuum: the so-called as-cast films. Some of the specimens were further annealed at 120°C for 1 week under vacuum so as to have structures thermodynamically at equilibrium: the so-called annealed films. SAXS measurements were carried out at room temperature with a Kratky U-slit camera (Anton Paar). X-rays were incident parallel to the film surface; this geometry is called edge-view. As-cast and annealed films were stained with osmium tetroxide and cut normal to the film surface into ultrathin sections. Microphase-separated structures of these specimens were observed by TEM with a JEOL 2000FX. Details of SAXS measurements and TEM observations have been described previously[7,13].

RESULTS

Preparation and characterization of samples

Figure 1 shows g.p.c. chromatograms of an as-polymerized polymer and its precursors. *Figure 2* compares the molecular weight distributions before and after fractionation for the same sample as shown in *Figure 1*. From *Figure 2* it is clear that the star molecule was isolated from the crude product by the fractionation procedure, though the yield of the purified fraction was only 1.9 g out of 42 g. The molecular characteristics of the samples thus obtained are listed in *Table 1*. The ratios of the number-averaged molecular weight of the purified star molecules to those of the arms are all close to 4 for five samples of the $(\mathrm{SI})_4$ type and close to 12 for three samples of the $(\mathrm{SI})_{12}$ type. The apparent molecular weight distributions (M_w/M_n) of arm molecules estimated from g.p.c. chromatograms by using a calibration curve of PS are all fairly narrow, and the measured PS contents of stars agree well with the designed values within experimental error. The microstructures of PI blocks were determined to be on the average 60, 28 and 12%

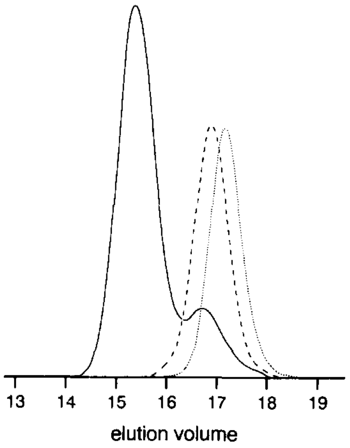


Figure 1 G.p.c. chromatograms of as-prepared crude product for a star-shaped block copolymer, $(\mathrm{SI})_4$-3, and its precursors: (······) PS precursor; (– – –) linear SI precursor; (——) as-prepared crude polymer

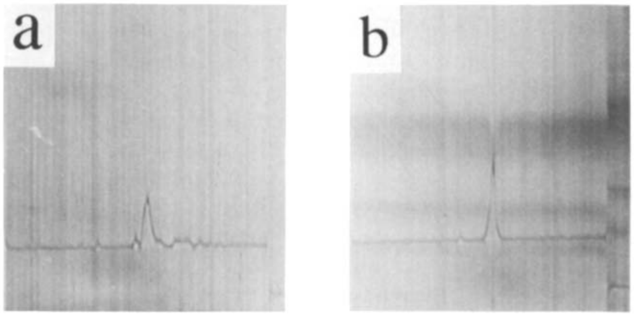


Figure 2 Comparison of sedimentation patterns of a 4-armed star-shaped block copolymer before and after fractionation. (a) As-prepared crude product for $(\mathrm{SI})_4$-3; (b) fractionated $(\mathrm{SI})_4$-3. Solvent, cyclohexane; temperature, 35°C; speed of rotation, 59 780 rev min^{-1}; angle, 80°; time, 94 min; concentration, (a) 0.4 g dl^{-1}, (b) 0.3 g dl^{-1}

Table 1 Molecular characteristics of the samples

Sample code	$M_n (\times 10^{-3})$ Arm	Star	$M_{n,s}/M_{n,a}$	M_w/M_n	ϕ_s[b]
$(SI)_4$-2	102	410	4.0	1.02	0.23 (0.25)
$(SI)_4$-6	58	227	3.9	1.09	0.51 (0.51)
$(SI)_4$-1	114	438	3.9	1.10	0.47 (0.46)
$(SI)_4$-4	209	830[a]	4.0	1.04	0.56 (0.51)
$(SI)_4$-3	94	351	3.7	1.02	0.78 (0.75)
$(SI)_{12}$-3	27	316	11.7	1.03	0.46 (0.48)
$(SI)_{12}$-1	73	810[a]	11.1	1.03	0.50 (0.52)
$(SI)_{12}$-2	127	1450[a]	11.4	1.04	0.45 (0.48)

[a] The numbers are weight-averaged molecular weight values measured by light scattering

[b] Volume fraction of PS blocks; the numbers in parentheses are the volume fraction of monomers added

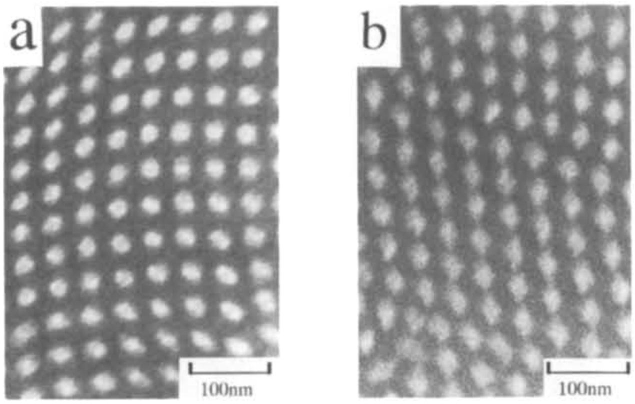
for *cis*-1,4, *trans*-1,4 and 1,2 or 3,4 configurations, respectively.

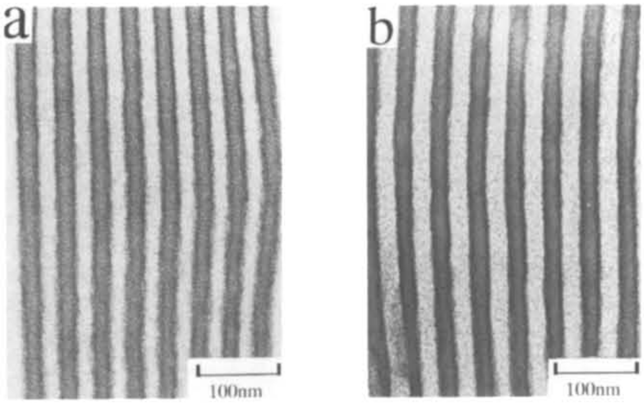
Morphological observation

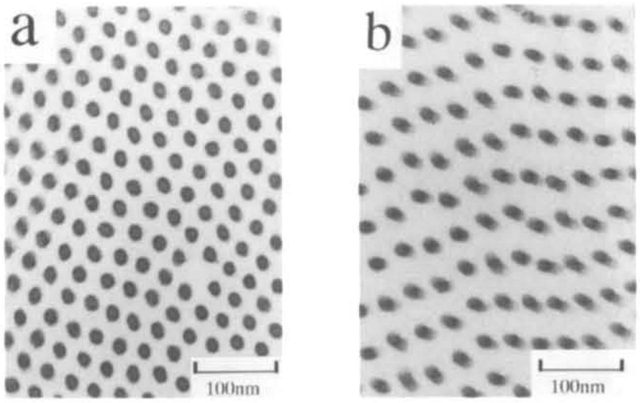
Figures 3–5 show the transmission electron micrographs from as-cast films of 4-armed star molecules and their arms. From these figures it is clear that the star molecules have qualitatively the same microphase-separated structures as those of linear diblock copolymers; their structures are PS cylinders in a PI matrix for $(SI)_4$-2, an alternating lamellar structure for $(SI)_4$-1 and PI cylinders in a PS matrix for $(SI)_4$-3, of which the volume fractions of S are 0.23, 0.47 and 0.78, respectively. This composition dependence is in accordance with the results of Herman *et al.* for SI star-shaped block copolymers with 18 arms[8]. *Figure 6* compares the microphase-separated structures from as-cast films of a 12-armed star molecule and its arm. Apparently, both are alternating lamellar structures and they seem to be equivalent to each other. Thus it can be concluded that the microphase-separated structures of 12-armed star-shaped block copolymers as well as 4-armed molecules are at least qualitatively the same as those of linear diblock copolymers.

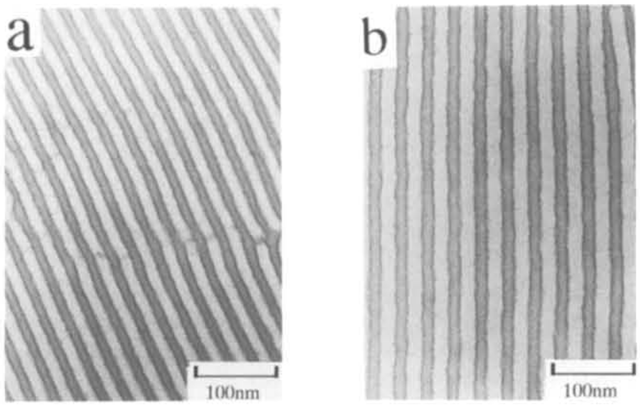
Figure 7 compares the SAXS diffraction patterns from as-cast films of a 12-armed block copolymer and its arm molecule. This figure reveals that the Bragg peak positions of the star molecule appear at higher q values than those of the linear molecule, where $q\ [=(4\pi/\lambda)\sin(\theta/2)]$ is the magnitude of the scattering vector. This means that the domain spacing (D) of the star molecule is smaller than that of the arm molecule for as-cast films. On the other hand, *Figure 8* compares the diffraction patterns of star and arm molecules for annealed films prepared under argon atmosphere. The peak positions of both molecules are almost the same in this case, implying that the D values of the star and its arm are equal to each other. The D values evaluated from SAXS experiments are plotted double-logarithmically against the number-averaged molecular weight of arm molecules ($M_{n,a}$) in *Figure 9*. From this figure it was found that the D values of the annealed films are larger than those of the as-cast films not only for star molecules but also for arm molecules. However, the D values of the annealed films for stars are almost the same as those of the corresponding arms for all 4- and 12-armed stars.

Microdomain spacings of the annealed films are always larger than those of the as-cast films for both star and arm molecules, but the difference in D for the former is









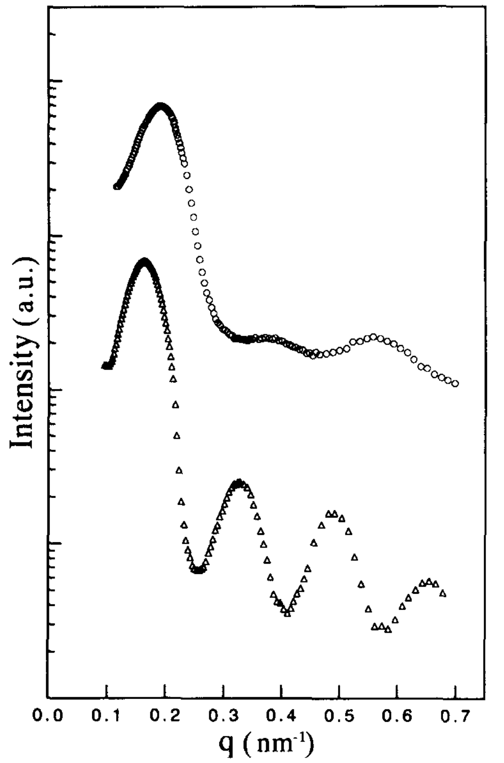


Figure 7 SAXS intensity profiles of a 12-armed star-shaped block copolymer and its arm for as-cast films: (○) $(SI)_{12}$-1; (△) arm molecule

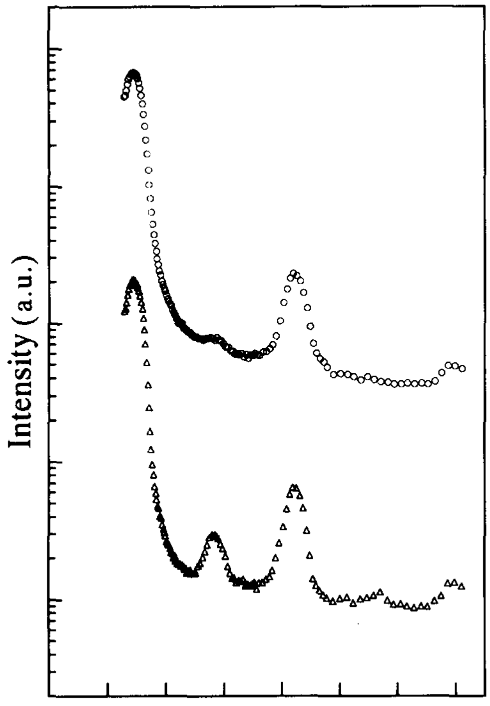


Figure 8 SAXS intensity profiles of a 12-armed star-shaped block copolymer and its arm for annealed films: (○) $(SI)_{12}$-1; (△) arm molecule

larger than in the latter. This phenomenon was also observed for SI multiblock copolymers of the $(SI)_n$ type[14], and this effect may be ascribed to non-equilibrium factors introduced during the solvent-casting procedure adopted in this study and they can be considered to be removed by the annealing treatment. By careful analysis of g.p.c. chromatograms of the film samples, however, we found that chain scission occurs during this process remarkably for the films cast under air, and, in particular, the star molecules cast under air were greatly decomposed. The fraction of decomposed polymer increases with increasing molecular weight of arms and/or increasing number of arms and was found to be between 20% and 50%. However, the fraction of decomposed polymer of films cast under argon atmosphere was found to be between 5% and 10%, so that we can assume that degradation does not affect the result below.

The solid line in *Figure 9* denotes the empirical relationship between D and M including the data for 4-armed stars, 12-armed stars and their arms, determined by using the least-squares method given by:

$$D = 0.0207M^{0.68}\,(\mathrm{nm}) \qquad (2)$$

DISCUSSION

The decomposition of polymers by annealing treatment can be conceived to have two origins. One may be ascribed to the chain scission due to the allyl radical on the 1,4-PI sequence. The radical reaction could occur easily as the hydrogen abstraction reaction by oxygen which was possibly introduced into films during casting under air. The other may be the breakage of junction points owing to concentration of mechanical stress during the formation of microdomains. This reason was considered and speculated because a number of arm molecules were observed in the g.p.c. chromatograms of the annealed star molecules.

Measured domain spacings of star and arm molecules were compared with the theories for linear diblock copolymers in *Figure 9*. In this figure the dotted line denotes the values calculated by the Helfand–Wasserman theory[3] and the chain line represents the theory of Semenov[4]. Both are obtained by using a value of 0.14 for the Flory–Huggins interaction parameter χ between PS and PI[15] and also using 0.66 nm for the reduced statistical segment length of SI block copolymers, i.e. $b_{SI} = (b_S b_I)^{1/2}$, where b_S (= 0.68 nm) and b_I (= 0.64 nm) are segment lengths of PS[16] and PI[17], respectively. Comparing

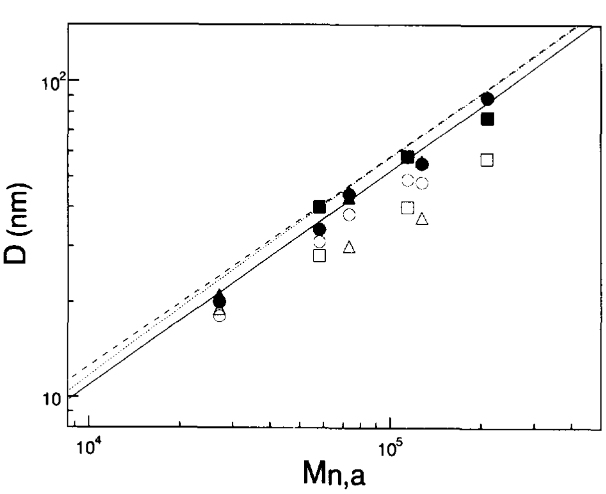


Figure 9 Double-logarithmic plots of domain spacing (D) *versus* number-average molecular weight of arms ($M_{n,a}$). Circles are for arm molecules, squares are for 4-armed star-shaped block copolymers and triangles are for 12-armed molecules. Open symbols are for as-cast films and filled symbols are for annealed films. The solid line denotes equation (2), the dotted line represents the Helfand–Wasserman theory and the chain line represents the theory of Semenov

the experimental data with the theories, we found that the data for star molecules as well as linear molecules agree well with both theories for linear molecules within the molecular weight range adopted in this study. This means that the conformational entropy loss for inner block polymer owing to the presence of the star centres may not be so large as to affect the domain structure even when the arm number is 12. Then we can speculate that the chain dimension of PI block of one arm of a star molecule along the direction perpendicular to the microdomain interface is essentially the same as that of one PI block of a linear diblock copolymer.

ACKNOWLEDGEMENTS

We thank Mr T. Watanabe in the glass-blowing shop in the School of Engineering at Nagoya University for his assistance in making the polymerization system and also Mr H. Choshi for his help in preparing the polymer samples. Y.M. thanks the Ministry of Education, Science and Culture for support through a Grant in Aid for Scientific Research (Grant 63750852), and he also thanks The Ishida Foundation for their support through a Grant in Aid for Encouraging Research.

REFERENCES

1 Hasegawa, H., Tanaka, H., Yamasaki, K. and Hashimoto, T. *Macromolecules* 1987, **20**, 1651

2 Meier, D. J. 'Block and Graft Copolymers' (Eds J. J. Burke and V. Weiss), Syracuse University Press, Syracuse, 1973

3 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879

4 Semenov, A. V. *Sov. Phys.-JETP* 1985, **61**(4), 733

5 Ohta, T. and Kawasaki, K. *Macromolecules* 1986, **19**, 2621

6 Hashimoto, T., Shibayama, M. and Kawai, H. *Macromolecules* 1980, **13**, 1237

7 Matsushita, Y., Mori, K., Saguchi, R., Nakao, Y., Noda, I. and Nagasawa, M. *Macromolecules* 1990, **23**, 4313

8 Herman, D. S., Kinning, D. J., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1987, **20**, 2940

9 Thomas, E. L., Alward, D. B., Kinning, D. J., Martin, D. C., Handlin Jr, D. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 2197

10 Alward, D. B., Kinning, D. J., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 215

11 Kinning, D. J., Alward, D. B., Thomas, E. L., Fetters, L. J. and Handlin Jr, D. L. *Macromolecules* 1988, **19**, 1288

12 Matsushita, Y., Choshi, H., Fujimoto, T. and Nagasawa, M. *Macromolecules* 1980, **13**, 1053

13 Mogi, Y., Kotsuji, H., Kaneko, Y., Matsushita, Y. and Noda, I. *Macromolecules* 1992, **25**, 5408

14 Matsushita, Y., Mogi, Y., Mukai, H., Watanabe, J. and Noda, I. *Polymer* 1994, **35**, 246

15 Helfand, E. *Macromolecules* 1975, **8**, 552

16 Ballard, D. G. H., Wignall, G. D. and Schelten, J. *Eur. Polym. J.* 1973, **9**, 965

17 Prud'homme, J., Roovers, J. E. L. and Bywater, S. *Eur. Polym. J.* 1972, **8**, 901