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ORIGINAL CONTRIBUTION

Micelle formation induced by photo-Claisen rearrangement of poly(4-allyloxystyrene)-*block*-polystyrene

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Abstract A novel micelle formation induced by the photo-Claisen rearrangement was attained using a poly(4-allyloxystyrene)-*block*-polystyrene (PASt-*b*-PSt) diblock copolymer. The photoreaction was performed in cyclohexane at room temperature without a catalyst. The conversion of the 4-allyloxystyrene units reached 90% by irradiation for 24 h. The photo-Claisen rearrangement of PASt-*b*-PSt into poly(3-allyl-4-hydroxystyrene)-*block*-PSt quantitatively proceeded up to a 20% conversion; however, the elimination of the allyl groups competitively occurred over the 20% conversion. The degrees of the photorearrangement and elimination showed good agreement in their material balance throughout the course of the reaction. Both of the photorearrangement and elimination finally reached ca. 50% degrees over 60% conversion. The light-scattering studies demonstrated that the PASt-*b*-PSt copolymer with a 36-nm hydrodynamic diameter as unimers formed micelles with a 98-nm diameter by irradiation.

Keywords Photo-Claisen rearrangement · Self-assembly · Micelle formation · Poly(4-allyloxystyrene)-*block*-polystyrene · Elimination · Light scattering

Introduction

The photochemical reaction is a green-sustainable and energy-saving process for manufactures involving chemical reactions accompanied by mass transfer. The reactions have been widely used in many fields such as photoimaging [1, 2] and the curing of coatings [2], inks [2, 3], and adhesives [4]. Among a variety of the photochemical reactions, photorearrangements are excellent for occurring without catalysts. A number of publications have reported the photo-Fries rearrangement [5–8] and photo-Claisen rearrangement [8–10]. In particular, the photo-Fries rearrangement is important for investigating the causes of the coloring of aromatic polyesters in sunlight or during exposure to ultra-violet light [11]. The photorearrangements have also been observed for *N*-aryl lactams [12, 13], the carboxylic acid derivatives of *N*-aryl amides [14, 15], enol esters [16, 17], enol lactones [18, 19], enamides [20, 21], and the sulfonic acid derivative of *N*-aryl amides [22].

Molecular self-assembly is also an environmentally clean system for forming high-dimensional structures of molecules through non-covalent bonding such as the van der Waals interaction, electrostatic attraction, and hydrogen bonding. The self-assembly of molecules produced a great variety of supramolecules: micelles [23–28], molecular necklaces [29], molecular shuttles [30], supramolecular cylinders [31], cyanuric acid–melamine lattices [32, 33], and both double [34] and triple helices [35]. Recently, the self-assembly induced by chemical reactions has attracted considerable attention as new triggers that lead to molecular associations. Examples include the micellization induced by the oxidation [36], reduction [37], and disproportionation of radicals [38]. The self-assembly induced by the photoreactions has also been discovered using photoisomerization [39–41], photoscission [42–44], and photolysis [45, 46]. The self-assembly combined with these photoreactions has the potential to create new photo-based materials for use in optical data storage [47], sensors [48–50], and electronic devices with molecular switching [51, 52].

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This paper describes a novel micelle formation induced by the photo-Claisen rearrangement as a new trigger for the poly(4-allyloxystyrene)-*block*-polystyrene (PASt-*b*-PSt) diblock copolymer through the photochemical reaction.

Experimental

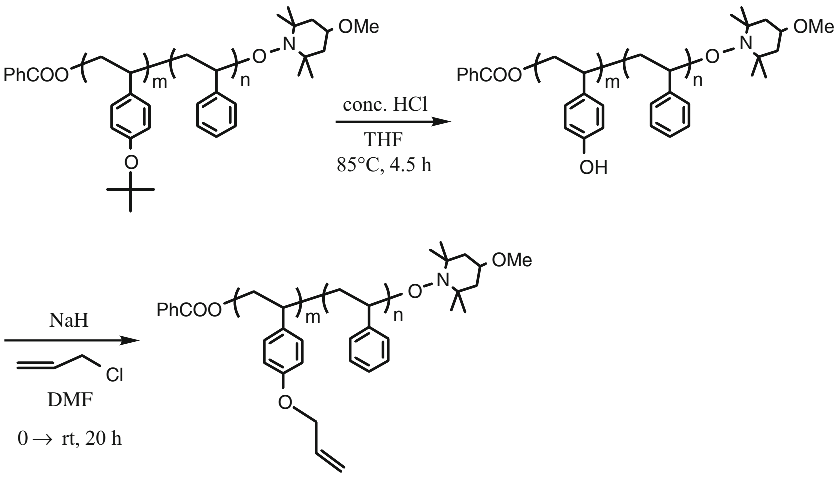
Instrumentation The ^{1}H NMR measurements were conducted using a Varian 300 FT NMR spectrometer. Light-scattering measurements were performed with a Photal Otsuka Electronics ELS-8000 electrophoretic light-scattering spectrophotometer equipped with a system controller, an ELS controller, and a He–Ne laser operating at λ=632.8 nm. The irradiation reaction was carried out using a Wacom HX-500 illuminator with a 500-W high-pressure mercury lamp at 7.0 A. The wavelength range of the lamp was 200–450 nm.

Materials A poly(4-*tert*-butoxystyrene)-*block*-polystyrene diblock copolymer was prepared as reported previously [45]. The molecular weight of the copolymer was Mn (PBSt-*b*-PSt)=15,400-*b*-96,600 by ^{1}H NMR, while the molecular weight and its distribution were Mn=58,000, and Mw/Mn=1.36 by gel permeation chromatography based on polystyrene standards [45]. The degrees of polymerization for the PBSt and PSt blocks were 87.3 and 927.9, respectively. Tetrahydrofuran (THF) and cyclohexane were distilled over sodium. *N*,*N*-Dimethylformamide (DMF) was distilled over calcium hydride under reduced pressure. Allyl chloride was also distilled over calcium hydride.

Synthesis of a poly(vinylphenol)-block-polystyrene diblock copolymer (PVPh-b-PSt) PVPh-PSt was prepared as reported previously [53]. The PBSt-*b*-PSt (2.00 g) was dissolved in THF (70 mL). Concentrated hydrochloric acid (7 mL) was added to the copolymer solution. The mixture was heated at 85°C for 4.5 h. The resulting solution was concentrated to ca. 30 mL by an evaporator and was poured into water (1 L) to precipitate a polymer. The precipitates were collected by filtration, and then freeze-dried with 1,4-dioxane. PVPh-*b*-PSt (1.593 g) was obtained. The molecular weight of the PVPh-*b*-PSt was determined to be Mn (PVPh-*b*-PSt)=10,500-*b*-96,600 by ^{1}H NMR.

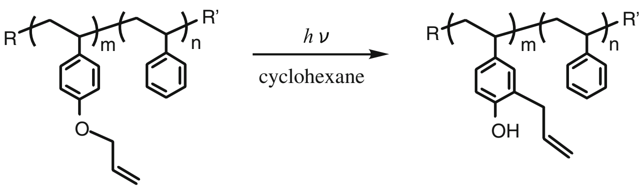
Synthesis of PASt-b-PSt The PVPh-*b*-PSt (0.70 g) was dissolved in DMF (15 mL). Sodium hydride (0.414 g, 17.3 mmol) was added to the copolymer solution at 0°C under nitrogen atmosphere. The suspension was stirred at 0°C for 5 min and was further stirred at room temperature for 1 h. Allyl chloride (1.41 g, 18.4 mmol) in DMF (5 mL) was added to the suspension at 0°C. The mixture was stirred at 0°C for 5 min and was further stirred at room temperature for 20 h. The resulting solution was poured into methanol (1 L) to precipitate a polymer. The precipitates were collected by filtration and then dried in vacuo for several hours. PASt-*b*-PSt (0.68 g) was obtained. The molecular weight of the PASt-*b*-PSt was determined to be Mn(PASt-*b*-PSt)=14,000-*b*-96,600 by ^{1}H NMR.

Irradiation reaction of PASt-b-PSt: general procedure Cyclohexane was deoxygenated by bubbling with nitrogen for 15 min. The PASt-*b*-PSt (8.2 mg) was dissolved in the deoxygenated cyclohexane (5 mL). This copolymer solution was stirred at room temperature for 30 min under nitrogen atmosphere to deoxygenate it again. The solution was irradiated with a high-pressure mercury lamp at room temperature for a definite time. The resulting solution was concentrated with an evaporator and was freeze-dried with 1,4-dioxane. The resulting copolymer was subjected to ^{1}H NMR and light-scattering measurements.



Scheme 1 Synthesis of the PASt-*b*-PSt diblock copolymer

Light-scattering measurements The light-scattering measurements were performed at 40°C at the angle θ=90°. The hydrodynamic diameter of the copolymer was estimated by the cumulant analysis, while the scattering intensity distribution of hydrodynamic diameter was obtained by the Marquadt analysis [54].



Scheme 2 The photo-Claisen rearrangement of PASt-*b*-PSt

Results and discussion

The PASt-*b*-PSt was prepared by the reaction of PVPh-*b*-PSt and allyl chloride (Scheme 1). The ^{1}H NMR spectra of PASt-*b*-PSt and PVPh-*b*-PSt are shown in Fig. 1. The spectra were obtained using 1,4-dioxane-d_8 as the solvent in order to prevent the PVPh-*b*-PSt from aggregating. The signal at 7.2–7.5 ppm originating from the hydroxyl group of PVPh-*b*-PSt completely disappeared by the reaction with allyl chloride, suggesting the quantitative conversion of the vinylphenol units into the allyloxystyrene. Signals of the tetramethyl protons of the 4-methoxy-TEMPO attached to the chain end of the copolymer were discerned at 0.8–1.0 ppm. The signals based on the allyloxy group were also observed at 4.3–4.7, 5.1–5.5, and 5.9–6.2 ppm. Those were attributed to the allyl protons, the α-proton of the vinyl, and its β-protons. The conversion of the vinylphenol units into the allyloxystyrene was estimated to be 99.5% based on the degrees of polymerization for the PBSt and PSt blocks and on the signal intensity at 4.3–6.2 ppm for the allyl protons and at 6.3–7.9 ppm for the aromatic protons.

It was found that the allyloxystyrene units underwent the photo-Claisen rearrangement by irradiation of a cyclohexane solution containing the PASt-*b*-PSt copolymer (Scheme 2). Figure 2 shows the ^{1}H NMR spectrum of the resulting copolymer by the irradiation of PASt-*b*-PSt. The irradiation was performed at room temperature for 18 h. In addition to the signals of the allyloxy groups, the signals originating from the allylbenzyl groups were observed at 3.1–3.8 ppm. The allylbenzyl groups were attributed to the 3-allyl-4-hydroxystyrene units generated by the photo-rearrangement of the allyloxystyrene units. A signal for the hydroxyl groups of the 3-allyl-4-hydroxystyrene units was not observed due to the too low intensity and the fact that it overlapped with the signals of the aromatic protons. Accordingly, the conversion of the allyloxystyrene units was estimated on the basis of the proportion of the decrease in the signal intensity of the allyl protons at 4.3–4.7 ppm to that of the aromatic protons at 6.3–7.9 ppm. The conversion was 66% at the 18-h irradiation time. The time–conversion plots of the allyloxystyrene units for the photoreaction are shown in Fig. 3. The conversion linearly increased over time. However, the proportion of the increase in the signal intensity of the allylbenzyl protons to the decrease in that of the allyl protons was only 45% at the 18-h irradiation time. This unquantitative proportion of the increase in the signal intensity suggests that part of the allyl groups was eliminated during the reaction. The elimination is considered to produce the vinylphenol units when it is taken into account that the photo-Claisen rearrangement of allyl phenyl ether partly caused the formation of phenol by the allyl group elimination [55].

The degrees of the rearrangement and elimination of the allyl groups were determined by ^{1}H NMR. Figure 4 shows the plots of degrees of the rearrangement and

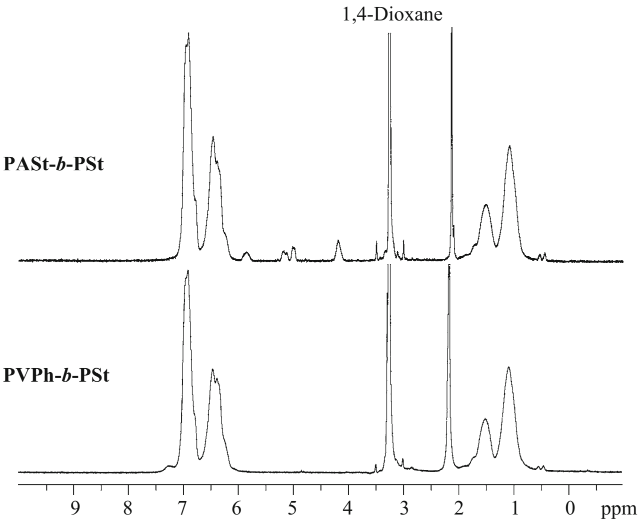


Fig. 1 ^{1}H NMR spectra of the PASt-*b*-PSt and PVPh-*b*-PSt diblock copolymers. Solvent: 1,4-dioxane-d_8

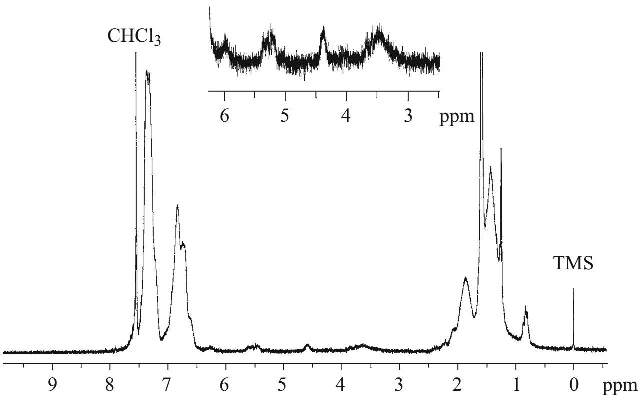


Fig. 2 ^{1}H NMR spectrum of the copolymer obtained by the irradiation of PASt-*b*-PSt. Solvent: $CDCl_3$

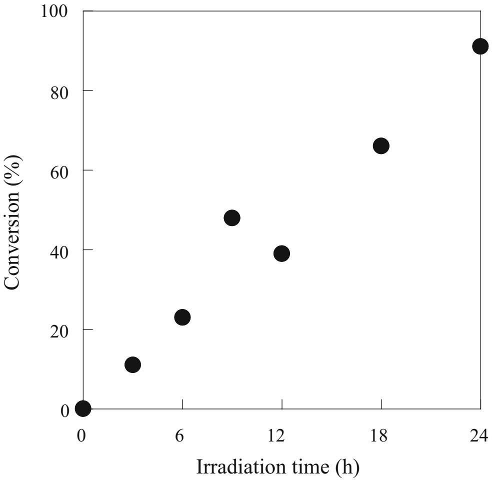


Fig. 3 The time–conversion plots of the allyloxystyrene units for the photorearrangement. $[\text{copolymer}]_0 = 1.64$ g/L

elimination vs. the conversion of the allyloxystyrene units. No elimination occurred up to ca. 20% conversion and the quantitative rearrangement proceeded. However, over the 20% conversion, the degree of rearrangement decreased with the increase in the conversion. On the contrary, the degree of elimination increased with the increasing conversion. The degrees of the rearrangement and elimination were in good agreement regarding their material balance throughout the course of the reaction. Both of the rearrangement and elimination finally reached ca. 50% degrees when the conversion was over 60%. The result of the rearrangement and elimination degrees to 50% implies that the elimination occurs during the process of the allyl rearrangement, rather than after the rearrangement was completed.

The light-scattering studies demonstrated that the PASt-*b*-PSt copolymer formed micelles during the photoreaction.

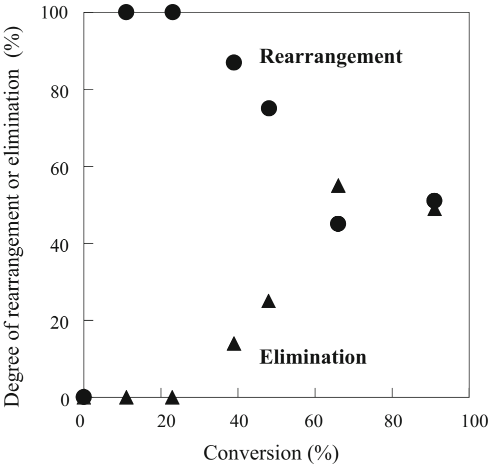


Fig. 4 The plots of degrees of the rearrangement and elimination vs. the conversion of the allyloxystyrene units. $[\text{copolymer}]_0 = 1.64$ g/L

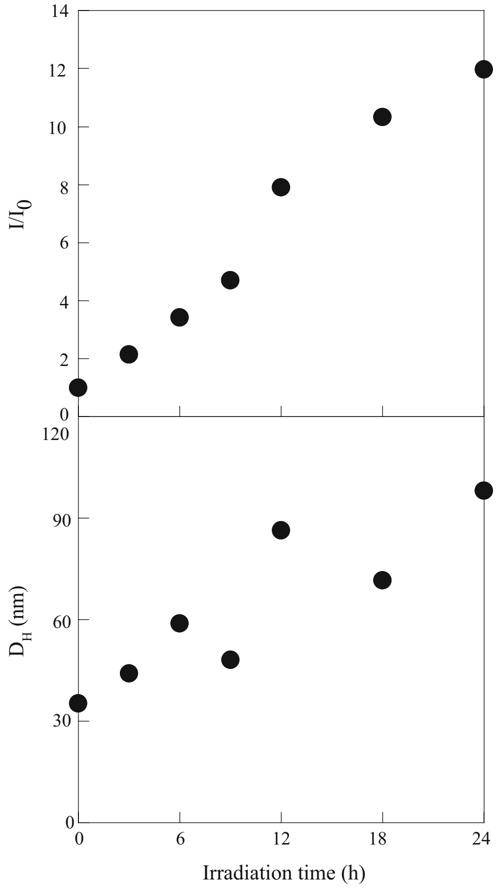


Fig. 5 The variation in the relative scattering intensity and hydrodynamic diameter of the copolymer. $[\text{copolymer}]_0 = 1.64$ g/L

The variation in the relative scattering intensity (I/I_0) and hydrodynamic diameter (D_H) of the copolymer is shown in Fig. 5. The light-scattering measurements were performed at 40°C. The copolymer showed no self-assembly in cyclohexane at 40°C and existed as unimer with a 35.3-nm diameter. The presence of the copolymer as unimer was also confirmed by the ^{1}H NMR analysis based on the fact that the signal intensity ratios of the protons composing the copolymer were in good agreement with the structure. The scattering intensity increased with time, indicating aggre-

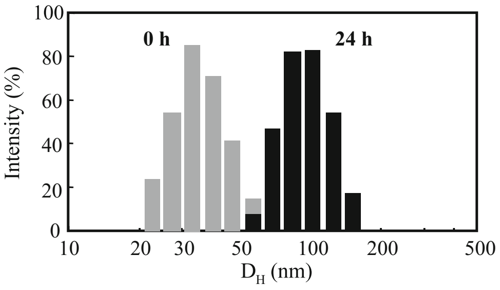


Fig. 6 The scattering intensity distribution for the hydrodynamic diameter of the copolymer before and after the irradiation. The irradiation time 24 h. $[\text{copolymer}]_0 = 1.64$ g/L

gation of the copolymer. The hydrodynamic diameter of the copolymer also increased with time, although there was some scatter in the plots. The Marquadt analysis also proved the formation of the micelles. Figure 6 shows the scattering intensity distribution for the hydrodynamic diameter of the copolymer before and after the irradiation. Before the irradiation, the distribution of the hydrodynamic diameter was observed around 35 nm based on the unimers. After irradiation for 24 h, the hydrodynamic diameter distribution was shifted to around 100 nm, attributed to the micelles. The exact hydrodynamic diameter of the micelles was estimated to be 98.1 nm.

Conclusion

A novel micellization induced by the photo-Claisen rearrangement was attained for the PASt-*b*-PSt diblock copolymer. The photoreaction proceeded without catalysts. The photorearrangement of the allyloxystyrene units quantitatively proceeded up to a 20% conversion to produce the 3-allyl-4-hydroxystyrene units, while the elimination of the allyl groups competitively occurred over the 20% conversion. The photorearrangement and elimination degrees showed good agreement in their material balance throughout the course of the reaction. The light-scattering studies demonstrated that the block copolymer formed micelles due to the photoreaction, since the scattering intensity of the copolymer increased with the irradiation time. The isolated copolymer with a 35-nm hydrodynamic diameter aggregated into micelles with a 98-nm diameter. This is the first study employing the photo-Claisen rearrangement for micelle formation.

References

1. Delzenne GA (1979) Adv Photochem 11:1
2. Pappas SP (ed) (1978) UV curing: science and technology. Technology Marketing, Norwalk, CT
3. Wentink SG, Koch SD (eds) (1981) UV curing in screen printing for printed circuits and the graphic arts. Technology Marketing, Norwalk, CT
4. Garrison LR (1980) Radiat Curing 7:26
5. Anderson JC, Reese CB (1960) Proc Chem Soc 217.
6. Arai T, Tobita S, Shizuka H (1994) Chem Phys Lett 223:521
7. Magdy M, Malik A, Mayo P (1983) Can J Chem 62:1275
8. Pitchumani K, Warri M, Ramamurthy V (1996) J Am Chem Soc 118:9428
9. Pincock AL, Pincock JA, Stefanova R (2002) J Am Chem Soc 124:9768
10. Sanchez AM, Veglia AV, Rossi RH (1997) Can J Chem 75:1151
11. Miranda MA (1995) In: Horspool WM, Song PS (eds) CRC handbook of organic photochemistry and photobiology. CRC, Boca Raton, p 570
12. Fischer M (1968) Tetrahedron Lett 4295.
13. Fischer M, Mattheus A (1969) Chem Ber 102:342
14. Bellus D, Schaffner K (1968) Helv Chim Acta 51:221
15. Kan RO, Furey RL (1966) Tetrahedron Lett 2573.
16. Finnegan RA, Hagen AW (1963) Tetrahedron Lett 365.
17. Gorodetsky M, Mazur Y (1964) J Am Chem Soc 86:5213
18. Rigaudy J, Derible P (1965) Bull Chem Soc France 3047.
19. Yogev A, Mazur Y (1965) J Am Chem Soc 87:3520
20. Eschenmoser A (1963) Pure Appl Chem 7:297
21. Bertele E, Boos H, Dunitz JD, Elsinger F, Eschenmoser A, Felner I, Gribi HP, Gschwend H, Meyer EF, Pesaro M, Scheffold R (1964) Angew Chem 76:393
22. Nozaki H, Okada T, Noyori R, Kawanishi M (1966) Tetrahedron 22:2177
23. Zhang L, Eisenberg A (1995) Science 268:1728
24. Jenekhe SA, Chen XL (1998) Science 279:1903
25. Yoshida E, Kunugi S (2002) Macromolecules 35:6665
26. Yoshida E, Ohta M, Terada Y (2005) Polym Adv Technol 16:183
27. Yoshida E, Tanaka M, Takata T (2005) Colloid Polym Sci 284:51
28. Yoshida E, Naito T (2008) Colloid Polym Sci 286:1203
29. Harada A, Li J, Kamachi M (1992) Nature 356:325
30. Philp D, Stoddart JF (1991) Synlett 445.
31. Percec V, Ahnm CH, Unger G, Yeardley DJP, Moller M, Sheiko SS (1998) Nature 391:161
32. Seto CT, Whiteside GM (1990) J Am Chem Soc 112:6409
33. Seto CT, Whiteside GM (1991) J Am Chem Soc 113:712
34. Koert U, Harding MM, Lehn JM (1990) Nature 346:339
35. Prakash G, Kool ET (1991) J Chem Soc Chem Commun 1161.
36. Yoshida E, Tanaka T (2006) Colloid Polym Sci 285:135
37. Yoshida E, Tanaka T (2008) Colloid Polym Sci 286:827
38. Yoshida E, Ogawa H (2007) J Oleo Sci 56:297
39. Leclair S, Mathew L, Giguere M, Motallebi S, Zhao Y (2003) Macromolecules 36:9024
40. Eastoe J, Dominguez MS, Wyatt P, Beeby A, Heenan R (2002) Langmuir 18:7837
41. Szczubialka K, Nowakoaska M (2003) Polymer 44:5269
42. Dunkin IR, Gittinger A, Sherrington DC, Wittaker P (1994) J Chem Soc Chem Commun 19:2245
43. Veronese A, Berclaz N, Luisi PL (1998) J Phys Chem B 102:7078
44. Haubs M, Ringsdorf H (1987) New J Chem 11:151
45. Yoshida E, Kuwayama S (2007) Colloid Polym Sci 285:1287
46. Yoshida E, Kuwayama S (2008) Colloid Polym Sci 286:1621
47. Matsuyama T, Kawata Y (2006) Appl Phys Lett 88:123113
48. Ahlheim M, Hellensleben ML (1992) Makromol Chem 193:779
49. Isahara M, Nakanishi K, Ono K, Sato M, Kikuchi M, Sito Y, Yura H, Matsui T, Hattori H, Uenoyama M, Kurita A (2002) Biomaterials 23:833
50. Yuan K, Hu Z, Li Y (1999) Appl Phys Lett 74:2233
51. Feringa BL, Jager WF, De Lange B (1993) Tetrahedron 49:8267
52. Liang L, Feng XD, Liu J, Rieke PC, Fryxell GE (1998) Macromolecules 31:7845
53. Yoshida E, Kunugi S (2002) J Polym Sci Part A Polym Chem Ed 40:3063
54. Marquardt DW (1963) J Soc Ind Appl Math 11:431
55. Pitchumani K, Warrier M, Ramamurthy V (1999) Res Chem Intermed 25:623