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NOTES

Synthesis of Model A_5B_1 Heteroarm Star Copolymers Using Living Radical Polymerization Mediated by 2,2,6,6-Tetramethylpiperidine-1-oxyl

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Considerable attention has been paid to heteroarm star copolymers, since they are expected to promote different microphase segregation from linear block copolymers. There are many publications on heteroarm star copolymers. Rempp *et al.* found star copolymers of the A_2B_2 type where A was polystyrene and B poly(*n*-butyl methacrylate) using divinyl benzene,[1] while Quirk and his co-workers prepared the A_2B_2 comprising polystyrene and 1,4-polybutadiene using 1,3-bis(1-phenylethenyl)benzene as the core.[2] Hadjichristidis *et al.* succeeded in preparing the A_8B_8-type of star copolymer using a multi-functional chlorosilane compound.[3] They have also prepared copolymers of the ABC[4] and ABCD types[5] where A is polystyrene, B polyisoprene, C polybutadiene, and D poly(4-methylstyrene). Isono *et al.* prepared the ABC type of copolymer consisting of polystyrene, poly(dimethylsiloxane), and poly(*t*-butyl methacrylate).[6] Dumas *et al.* have recently released a publication on the synthesis of a triarm star copolymer comprising polystyrene, poly(ethylene oxide), and poly(ε-caprolactone).[7] These copolymers were all prepared through living anionic polymerization. The synthesis of the A_8B_8 heteroarm star copolymers through living cationic polymerization has been reported. The copolymer, prepared by Sawamoto *et al.* comprised two types of poly(vinyl ether).[8] We found the synthesis of model A_5B_1 copolymers by the radical polymerization using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) attached to cyclotriphosphazene. Cyclotriphosphazene is a monomer for an inorganic–organic composite polymer with main chains consisting of P=N.[9] This compound is convenient for preparing heteroarm star copolymers, because it is easy to control the number of heteroarms in the star copolymer by choosing the number of TEMPO molecules introduced into cyclotriphosphazene. This paper describes the synthesis of model star copolymers of the A_5B_1 type where A is poly(ethylene oxide) and B polystyrene, through the radical polymerization using TEMPO-supported cyclotriphosphazene as the core.

EXPERIMENTAL

Measurements

Gel permeation chromatography (GPC) was performed with Tosoh HLC-802A equipped with an RI detector and with a Tosoh CP-8000 chromato processor. Two polystyrene gel columns of Tosoh TSK gel $G4000H_8$ and $G2000H_8$ were used with tetrahydrofuran (THF) as the eluent at 42°C. ESR spectra were recorded on a Jeol JES-TE 300 ESR spectrometer based on M_n^{2+}, and ^1H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer. Gas chromatography (GC) was performed with a Shimadzu GC-6A.

Materials

4-Hydroxy-TEMPO was prepared by the method reported previously.[10] The oil used for storing the sodium hydride was removed by washing with hexane. Sodium hydride (*ca.* 60 wt% in oil) was suspended in hexane and stirred with a magnetic stirrer at room temperature for 5 min. The hexane was removed by decantation. The bare sodium hydride was dried *in vacuo* immediately before use. THF was purified by refluxing on sodium for several hours and distilled over sodium. Commercial grade styrene was washed with aqueous alkaline solution and water, and distilled over calcium hydride. Benzoyl peroxide (BPO) was precipitated from chloroform into methanol and recrystallized at 0°C. Extrapure grade hexachlorocyclotriphosphazene, sodium methoxide, triethylene glycol monomethyl ether, and phenylhydrazine for ^1H NMR studies were used without further purification.

Synthesis of 4-Pentachlorocyclotriphosphazoxyl-TEMPO

4-Hydroxy-TEMPO (914 mg, 5.31 mmol) dissolved in 10 mL of THF was added to sodium hydride (220 mg, 9.17 mmol) suspended in THF (4 mL), and the mixture was stirred at room temperature for 1 h under nitrogen. To a red suspension of 4-sodium oxy-TEMPO was added a solution of hexachlorocyclotriphosphazene (2.22 g, 6.39 mmol) in THF (10 mL) at 0°C. The mixture was stirred at 0°C for 5 min, kept at room temperature for 23 h, and heated at 50°C for the next 115 h. After confirming no spot of 4-hydroxy-TEMPO by TLC, the white precipitate in the mixture was filtered off with suction. The filtrate was concentrated by evaporation, and dried *in vacuo* for several hours. A crude product (2.96 g) was obtained. 4-Pentachlorocyclotriphosphazoyl-TEMPO (CPT) was separated by a silica gel column with hexane and then with mixed solvent (benzene : ethyl

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acetate = 50 : 1, v/v) as the eluent. CPT of 1.44 g (yield 56%) was obtained as red crystals. m/z = 483, 328 ($-C_9H_{17}NO$), 312 (–O). mp = 75°C.

Synthesis of 4-Pentamethoxycyclotriphosphazoyl-TEMPO

Sodium methoxide (859 mg, 15.9 mmol) was added at 0°C to CPT (1.08 g, 2.23 mmol) dissolved in 20 mL of THF, and the mixture was stirred at 0°C for 5 min, and kept at room temperature for 12 h under nitrogen. The white precipitate was filtered off, and the filtrate was concentrated by evaporation. The residue was purified by a silica gel column with a mixed solvent (benzene : ethyl acetate = 50 : 1, v/v) to give 4-pentamethoxycyclotriphosphazoyl-TEMPO (MPT) of 0.934 g (yield 91%) as red crystals. ^{1}H NMR ($CDCl_3$) δ 4.55 (1H, m, TEMPO C*H*), 3.68 (15H, s, OCH_3), 2.09 (2H, d, J = 12.6 Hz, CH_2^{eq}), 1.78 (2H, t, J = 11.5 Hz, CH_2^{ax}), 1.30 (6H, s, CH_3^{eq}), 1.24 (6H, s, CH_3^{ax}). m/z = 462 (M + 1), 461, 290 ($-C_9H_{17}NO_2$). mp = 58°C.

Synthesis of 4-Penta[oligo(oxyethylene)]cyclotriphosphazoxyl-TEMPO

Triethylene glycol monomethyl ether (4.52 g, 27.5 mmol) dissolved in 60 mL THF was added to sodium hydride (1.27 g, 52.9 mmol) suspended in THF (6 mL), and the mixture was stirred at 0°C for 45 min under nitrogen. To a white suspension of sodium oxytriethylene glycol monomethyl ether was added a solution of CPT (2.21 g, 4.57 mmol) in THF (30 mL) at 0°C. The mixture was stirred at 0°C for 5 min, and kept at room temperature for 20 h. The white precipitate in the mixture was filtered off with suction. The filtrate was concentrated by evaporation, and dried *in vacuo* for several hours. 4-Penta[oligo(oxyethylene)]cyclotriphosphazoxyl-TEMPO (OPT) was separated by a silica gel column with ethyl acetate, and then with acetone. OPT of 4.37 g (yield 85%) was obtained as a viscous red liquid. ^{1}H NMR ($CDCl_3$) δ 4.50 (1H, m, TEMPO C*H*), 4.30 (10H, s, $POCH_2CH_2$–), 3.5—3.9 (50H, OCH_2), 3.37 (15H, s, OCH_3), 2.06 (2H, d, J = 8.4 Hz, CH_2^{eq}), 1.72 (2H, t, J = 12.6 Hz, CH_2^{ax}), 1.25 (6H, s, CH_3^{eq}), 1.20 (6H, s, CH_3^{ax}). m/z = 1123 (M + 1), 1107 (–O), 967 ($-C_9H_{18}N$).

Radical Polymerization of Styrene by BPO and TEMPO-Supported Phosphazene: General Procedure

Styrene (0.5 mL, 4.36 mmol), BPO (10 mg, 0.0413 mmol), and MPT (22 mg, 0.0477 mmol) were placed in an ampule. After degassing, the ampule was sealed *in vacuo*. Polymerization was carried out at first for 3.5 h at 95°C, then for 50 h at 125°C, and terminated by cooling with liquid nitrogen. The product was dissolved in 5 mL dichloromethane, purified by repeated precipitation from dichloromethane into hexane, and dried *in vacuo* for several hours. A polymer (0.318 g, yield 70%) was obtained. After the addition of toluene as the internal standard, the dichloromethane solution was subjected to GC to estimate the conversion of styrene.

RESULTS AND DISCUSSION

We prepared three TEMPO-supported cyclotriphosphazenes: 4-Pentachlorocyclotriphosphazoyl-TEMPO (CPT), 4-pentamethoxycyclotriphosphazoyl-TEMPO (MPT), and 4-penta[oligo(oxyethylene)]cyclotriphosphazoxyl-TEMPO (OPT). CPT and MPT were obtained as solid crystals, and OPT as a viscous liquid. The compounds were red in color, and showed typical three sharp signals in ESR spectra (Figure 1). Hyperfine coupling constants (A_N) and g are listed in Table I. The values were close to those of 4-methoxy-TEMPO (A_N = 16.0 G, g = 2.007). This indicates that these phosphazene compounds have the potential to serve as counter radicals for polymerization of styrene, giving polymers with narrow polydispersities, in the same manner as 4-methoxy-TEMPO. Polymerization of styrene was performed in the presence of CPT, MPT, or OPT by BPO as an initiator (Scheme 1). Time-conversion plots are shown in Figure 2. The polymerization by CPT proceeded rapidly in comparison with those by MPT and OPT. This implies that scission occurs more easily when the linkage is between CPT and the growing radical than when it is with MPT and OPT. This may be accounted for by the fact that triphosphazene pentachloride of CPT acts as a Lewis acid for the growing chain end to advance polymerization, when it is taken into consideration that an acid[11] and organic acid salt[12] forwards TEMPO-mediated polymerization. Polymer-

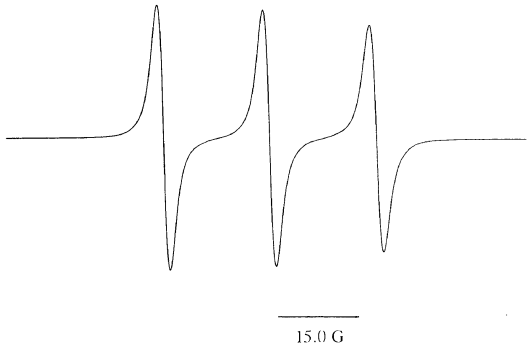
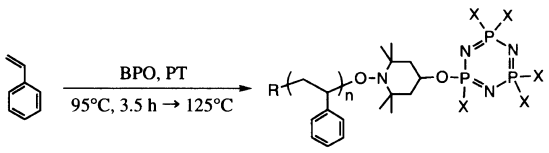


Figure 1. ESR spectrum of OPT (solvent: benzene, at room temperature).

Table I. Characterization of TEMPO-supported cyclotriphosphazenes by ESR

PT	A_N / G	g
CPT	15.7	2.007
MPT	15.7	2.007
OPT	15.9	2.007



CPT: X = Cl
MPT: X = OMe
OPT: X = $O(CH_2CH_2O)_3CH_3$

R = Benzoyl group or thermal initiator.

Scheme 1.

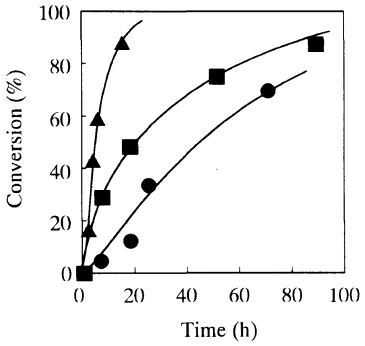


Figure 2. Time-conversion plots for the polymerization of styrene by BPO using CPT (▲), MPT (●), and OPT (■).

Table II. Conversion, molecular weights, and polydispersity of polystyrenes obtained from CPT, MPT, and OPT[a]

PT	Conversion[b] / %	M_n[c]	M_w/M_n[c]
CPT	17	3600	1.25
	43	4900	1.23
	58	7500	1.37
	88	9600	1.52
MPT	6	600	1.01
	14	2100	1.26
	35	5800	1.33
	71	11000	1.22
OPT	31	4000	1.11
	50	6900	1.23
	77	9900	1.19
	89	11000	1.21

[a] $[PT]_0/[BPO]_0 = 1.1$ in all cases. [b] Estimated by GC. [c] Estimated by GPC based on polystyrene standards.

ization by OPT is faster than that by MPT. The mobility of the counter radical influenced the rate of polymerization: Bulkiness of the groups on which TEMPO was supported diminished the mobility of TEMPO, causing rate of polymerization to increase. In fact, rate enhancement was observed in styrene polymerization using TEMPO attached to polymers at the chain end.[13-16] The rate enhancement by OPT probably resulted from restraint on the mobility of TEMPO by supporting it on the phosphazene ring with bulky tetraethylene oxide chains. The relationships between conversion, molecular weight, and polydispersity are shown in Table II. Polydispersities of the polystyrenes obtained from the polymerizations by MPT and OPT were near to or less than 1.3 in the entire region of conversion, while the polymerization by CPT gave rise to the polymers with broad polydispersity. In particular, polydispersity was much broader at the late stage of the polymerization. The molecular weight linearly increased with conversion, suggesting that the polymerization proceeds in accordance with a living mechanism. Relationship between molecular weight and initial concentration of the counter radicals ($[PT]_0$) was also studied. This investigation is based on our previous results that molecular weight is in proportion to the reciprocal of the initial concentration of TEMPO if the polymerization proceeds in a living manner. The relations are shown in Table III. Conversions were high enough to

Table III. Relationship between molecular weight and $[PT]_0$

PT	$[PT]_0$ / $\times 10^2$ mol L^{-1}	Time / h	Conversion[a] / %	M_n[b] / $\times 10^{-4}$	M_w/M_n[b]
CPT	3.21	21	82	3.2	1.58
	4.63	25	100	2.3	1.64
	9.60	48	93	1.6	1.54
	19.2	70	100	1.1	1.43
MPT	1.95	47	89	2.2	1.32
	2.38	50	76	1.9	1.25
	4.77	70	71	1.1	1.22
	9.54	141	93	0.92	1.27
OPT	3.21	39	88	3.8	1.24
	4.63	65	84	2.4	1.22
	9.60	50	77	0.99	1.19
	18.9	86	88	0.76	1.24

[a] Estimated by GC. [b] Estimated by GPC based on polystyrene standards.

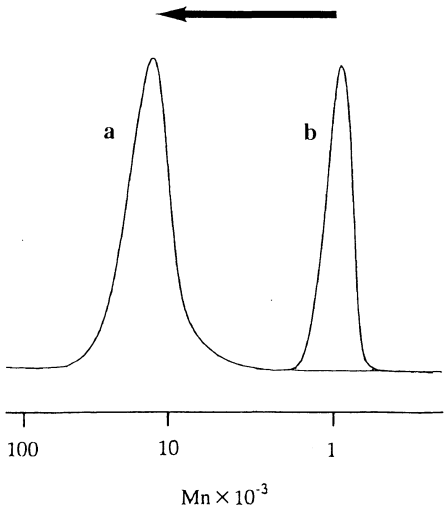


Figure 3. GPC profiles of polymers obtained (a) and OPT (b).

compare molecular weights. Molecular weights were in inverse proportion to $[PT]_0$. All the polymerizations thus undoubtedly proceed in accordance with a living mechanism. The entirety of the TEMPO-supported triphosphazenes was engaged in the polymerizations, because GPC of the resulting polymers showed no peak in the field of the phosphazene compounds. Figure 3 shows GPC of OPT and the resulting polymer before isolated. Observation of unimodal GPC originating from the polymer was made only on the higher molecular weight side. ^1H NMR analysis clarified that the polymers have the TEMPO-supported triphosphazenes and benzoyl group. The spectrum of the polymer obtained from OPT is shown in Figure 4. Signals at 7.5 and 7.9 ppm are due to benzoyl group, assigned to aromatic protons at *meta* and *ortho* positions, respectively. The signals at 0.2, 0.4, 0.9, and 1.1 ppm are attributed to tetramethyl protons of TEMPO. Observation of signals based on tetraethylene oxide was also made at 3.3—4.1 ppm. The sharp signal at 3.35 ppm was assigned to terminal methoxy group, and the signals at 3.55 and 3.68 ppm to the methylenes. The signal at 4.00 ppm is attributed to another oxymethylene attached to the phosphazene ring. The protons of the polystyrene terminal methine bonded to TEMPO moiety

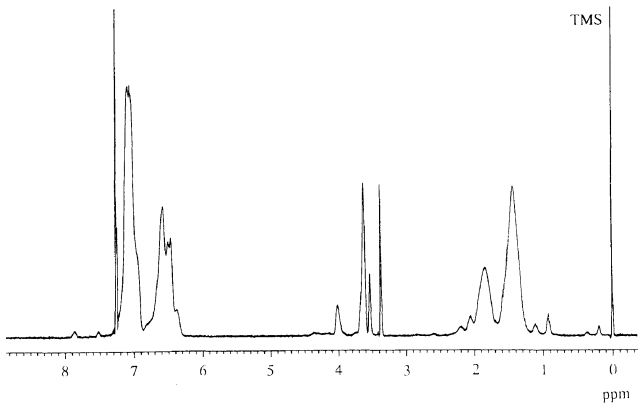


Figure 4. ^{1}H NMR spectrum of the polymer (conversion = 50%, M_n = 6900, and M_w/M_n = 1.23) obtained from OPT. Polymerization was carried out at 125°C for 18 h, after being held at 95°C for 3.5 h (solvent: $CDCl_3$).

and of the methylene attached to benzoyl group are observed at 3.8—4.4 ppm as broad signals. Polystyrene should have a cyclotriphosphazene moiety at the chain end, and the model compounds of a A_5B_1 star copolymer comprising poly(ethylene oxide) and polystyrene were obtained.

CONCLUSIONS

The synthesis of model A_5B_1 heteroarm star copolymers comprising poly(ethylene oxide) and polystyrene was conducted by the radical polymerization using TEMPO-supported cyclotriphosphazene. The polymerization rapidly occurred by the presence of CPT, although the polymers obtained had broad polydispersity. MPT and OPT gave polymers with narrow polydispersity (<1.3). The polymerization proceeded in accordance with a living mechanism, because the molecular weight was in proportion to conversion and reciprocal of the initial concentration of the counter radicals. The polymers were obtained in quantitative efficiency based on GPC. ^{1}H NMR analysis demonstrated that the polymers had the cyclotriphophazene moieties at a chain end, and that model A_5B_1 star copolymers were obtained.

REFERENCES

1. C. Tsitsilianis, P. Chaumont, and P. Rempp, *Makromol. Chem.*, **191**, 2319 (1990).
2. R. P. Quirk, T. Yoo, and B. Lee, *J.M.S.-Pure Appl. Chem.*, **A31**, 911 (1994).
3. A. Avgeropoulos, Y. Poulos, N. Hadjichristidis, and J. Roovers, *Macromolecules*, **29**, 6076 (1996).
4. H. Iatrou and N. Hadjichristidis, *Macromolecules*, **25**, 4649 (1992).
5. H. Iatrou and N. Hadjichristidis, *Macromolecules*, **26**, 2479 (1993).
6. T. Fujimoto, H. Zhang, T. Kazama, Y. Isono, H. Hasegawa, and T. Hashimoto, *Polymer*, **33**, 2208 (1992).
7. O. Lambert, P. Dumas, G. Hurtrez, and G. Riess, *Macromol. Rapid Commun.*, **18**, 343 (1997).
8. S. Kanaoka, T. Omura, M. Sawamoto, and T. Higashimura, *Macromolecules*, **25**, 6407 (1992).
9. H. R. Allcock, J. A. Dodge, I. Manners, and G. H. Riding, *J. Am. Chem. Soc., a*, **113**, 9596 (1991).
10. T. Kurosaki, K. W. Lee, and M. Okawara, *J. Polym. Sci., Polym. Chem.*, **10**, 3295 (1972).
11. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, and M. Saban, *Macromolecules*, **27**, 7228 (1994).
12. P. G. Odell, R. P. N. Veregin, L. M. Michalak, D. Brousmiche, and M. K. Georges, *Macromolecules*, **28**, 8453 (1995).
13. E. Yoshida and A. Sugita, *Macromolecules*, **29**, 6422 (1996).
14. E. Yoshida and M. Nakamura, *Polym. J.*, **30**, 915 (1998).
15. E. Yoshida and Y. Osagawa, *Macromolecules*, **31**, 1446 (1998).
16. E. Yoshida and A. Sugita, *J. Polym. Sci., Polym. Chem. Ed.*, **36**, 2059 (1998).