

# Photo Nitroxide-Mediated Living Radical Polymerization of Hindered Amine-Supported Methacrylate

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**Abstract:** With the aim of obtaining giant polymer vesicles supporting a hindered amine that is converted into a redox catalyst on the vesicle shells, the living nature of the photo nitroxide-mediated living radical polymerization (photo NMP) of a monomer containing a hindered amine and the formation of the vesicles consisting of an amphiphilic diblock copolymer by the polymerization-induced self-assembly were investigated. The photo NMP of 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TPMA) was performed in methanol using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator, 2,2'-azobis[2-(2-imidazolin-2-yl)propane] (V-61) as the initiator, and (4-*tert*-butylphenyl)diphenylsulfonium triflate as the accelerator by UV irradiation at room temperature. The first-order time-conversion plots had an induction period in which the MTEMPO molecules were captured by the initiator radicals and the monomer radicals generated by the initiation. It was confirmed that the polymerization proceeded by a living mechanism based on linear correlations of the molecular weight of the poly(TPMA) (PTPMA) versus the monomer conversion and the reciprocal of the initial concentration of V-61. Based on the livingness of the polymerization, the photo NMP-induced self-assembly for the block copolymerization of methyl methacrylate (MMA) using the PTPMA end-capped with MTEMPO was carried out in methanol to produce microsized giant spherical vesicles consisting of the amphiphilic PTPMA-*block*-poly(MMA) diblock copolymer. A differential scanning calorimetry study demonstrated that the vesicles had a single bilayer structure.

**Keywords:** 2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TPMA), Hindered amine, Photo nitroxide-mediated living radical polymerization (photo NMP), Photo NMP-induced self-assembly, Giant vesicles, Single bilayer structure.

## INTRODUCTION

2,2,6,6-Tetramethyl-4-piperidyl methacrylate (TPMA) is an important monomer that provides polymers supporting the hindered amine with functions of a light stabilizer and an antioxidant in plastics manufacturing [1, 2]. Some polymers of TPMA were prepared by radical (co)polymerization using commercial monomers of methyl methacrylate (MMA), vinyl acetate, styrene, acrylamide, 4-vinyl pyridine, and acrylonitrile for the purpose of improving the photoprotecting efficiency and the compatibility with the plastics [3, 4]. The hindered amine is oxidized with hydrogen peroxide into 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [5] that acts as a redox catalyst for oxidation of the alcohol by Cu(II) and Fe(III) [6, 7].

Microsized giant vesicles are possible artificial models of biomembranes for cells and organelles based on the similarities in their size and structure [8]. In particular, the giant vesicles consisting of an amphiphilic poly(methacrylic acid)-*block*-poly(methyl methacrylate-*random*-methacrylic acid) diblock copolymer have advantages over the vesicles of small molecular amphiphiles regarding their structural

stability and great variety of molecular designs of the block copolymer [9, 10]. The polymer vesicles have the similarities to the biomembrane not only regarding their structural features, but also about their stimuli-responsive behavior [11, 12] and the formation by budding separation [13]. Based on these similarities and advantages, many morphologies were produced by self-assembly induced by the photo nitroxide-mediated living radical polymerization (photo NMP). Examples include the spherical vesicles [8], the elliptical [14], worm-like [15-17], cup-like [17], and key-shaped [15], coupled with the villus-like structure [18] and anastomosed tubular networks continuing with a fenestrated sheet [12]. The studies of the polymer giant vesicles also created an artificial sterol model employing the segmented random copolymer [19] and a model of a membrane protein for endocytosis [20]. The giant vesicles supporting the hindered amine as a precursor of the redox catalyst on their shells foster the establishment of the artificial biomembrane model using the polymer vesicles because *in vivo* the redox reactions involved in respiration and photosynthesis are caused by oxidoreductase embedded in the biomembranes of the mitochondria and thylakoid [21-23]. With the aim of obtaining the giant vesicles having the hindered amine on their shells by the photo NMP-induced self-assembly of an amphiphilic block copolymer, the living nature for the photo NMP of TPMA was investigated. This paper describes the

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photo-NMP of TPMA using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator and the formation of the giant vesicles through the polymerization-induced self-assembly of the amphiphilic diblock copolymer containing poly(methyl methacrylate) (PMMA).

## EXPERIMENTAL

### Instrumentation

The photo NMP was performed using a BA-H502 Ushio optical module, an OPM2-502H illuminator with a UI-OP2SL high-illumination lens, and a 500W super high-pressure UV lamp (USH-500SC2, Ushio Co., Ltd.).  $^1\text{H}$  NMR measurements were conducted using Jeol ECS400 and ECS500 FT NMR spectrometers. Gel permeation chromatography (GPC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and an RI-8020 refractometer. Two polystyrene gel columns, Tosoh TSK gel  $\alpha$ -M, were used at 40°C with an eluent of *N,N*-dimethylformamide (DMF) containing lithium bromide (50 mM) and triethylamine (10 mM). The molecular weight and its distribution were estimated on the basis of PMMA standards. Field emission scanning electron microscopy (FE-SEM) measurements were performed using a Hitachi SU8000 scanning electron microscope. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60 instrument equipped with a TA-60WS system controller and an FC-60 nitrogen flow controller.

### Materials

TPMA was purchased from Tokyo Chemical Industry and used without further purification. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] (V-61) and (4-*tert*-butylphenyl)diphenylsulfonium triflate ( $^t\text{BuS}$ ) were purchased from Wako Pure Chemical Industries and Sigma-Aldrich, respectively, and used as received. 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) was prepared as previously reported [24]. MMA was washed with a 5% NaOH aqueous solution and water. After drying using anhydrous  $\text{MgSO}_4$ , the MMA was distilled over calcium hydride. The purified MMA was degassed with Ar for 15 min during stirring just before use. Methanol (MeOH) was refluxed over magnesium with a small amount of iodine for several hours, then distilled. (2*RS*,2'*RS*)-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (*r*-AMDV) was obtained by separation from a mixture of the racemic and meso forms of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) [25]. Extra

pure Ar gas with over 99.999 vol% purity was purchased from the Taiyo Nippon Sanso Corporation.

### Photo NMP of TPMA: General Procedure

TPMA (1.000 g, 4.44 mmol), V-61 (11.2 mg, 0.0447 mmol), MTEMPO (9.0 mg, 0.0483 mmol),  $^t\text{BuS}$  (12.0 mg, 0.0256 mmol), and MeOH (1 mL) were placed in a 30-mL test tube joined to a high vacuum valve. The contents were degassed several times using a freeze-pump-thaw cycle, then charged with Ar. The polymerization was carried out at room temperature for 6.5 h by irradiation with a 500W super high-pressure UV lamp at 9.2 amperes by reflective light using a mirror in order to avoid any thermal polymerization caused by direct irradiation [26]. After MeOH (5 mL) was added to the resulting viscous solution, part (ca. 0.2 mL) of the solution was withdrawn to determine the conversion (86%) by  $^1\text{H}$  NMR. The residual solution was poured into petroleum (500 mL) to isolate the polymer. The precipitate was collected and dried in vacuo for several hours to obtain the polymer (0.808 g).

### Photo NMP-Induced Self-Assembly of PTPMA-block-PMMA

TPMA (1.000 g, 4.44 mmol), V-61 (11.2 mg, 0.0447 mmol), MTEMPO (9.0 mg, 0.0483 mmol),  $^t\text{BuS}$  (12.0 mg, 0.0256 mmol), and MeOH (1 mL) were placed in a 30-mL test tube connected to a high vacuum valve. The contents were degassed several times using a freeze-pump-thaw cycle, then charged with Ar. The polymerization was carried out at room temperature for 5.5 h by irradiation at 9.2 amperes. After MeOH (9 mL) was added to the resulting solution, part (ca. 1 mL) of the solution was withdrawn to determine the conversion (78%) by  $^1\text{H}$  NMR and the molecular weight ( $M_n = 36,600$ ,  $M_w/M_n = 2.36$ ) by GPC based on PMMA standards. The solution (4 mL containing 0.391 mmol of the unreacted TPMA) and MMA (1.404 g, 14.0 mmol) were placed in a 30-mL test tube connected to a high vacuum valve under flowing Ar. The contents were degassed several times using a freeze-pump-thaw cycle and finally charged with Ar. The polymerization was carried out for 7 h at room temperature with a 600-rpm stirring speed by UV irradiation at 9.2 amperes. After the polymerization, part (ca. 0.2 mL) of the resulting dispersion solution was withdrawn to determine the monomer conversions by  $^1\text{H}$  NMR. MeOH (20 mL) was added to the dispersion solution to precipitate the aggregates. The aggregates were cleaned with MeOH by a repeated sedimentation-

redispersion process. The aggregates were stored in the presence of a small amount of MeOH.

### Poly(TPMA-random-MMA)

MMA (1.123 g, 11.2 mmol), TPMA (70.4 mg, 0.312 mmol), MTEMPO (3.6 mg, 0.0193 mmol), *r*-AMDV (5.6 mg, 0.0182 mmol), and <sup>t</sup>BuS (4.8 mg, 0.0102 mmol) were placed in a 30-mL test tube connected to a high vacuum valve. The contents were degassed several times using a freeze-pump-thaw cycle, then charged with Ar. The polymerization was carried out at room temperature for 21 h with UV irradiation at 9.3 amperes. After the product was completely dissolved in chloroform (10 mL), part (ca. 1 mL) of the solution was withdrawn to determine the monomer conversions (conversion = 76% for MMA and 78% for TPMA). The solution was poured into hexane (500 mL) to isolate the copolymer. The precipitate was collected and dried in vacuo for several hours to obtain the copolymer (0.876 g).

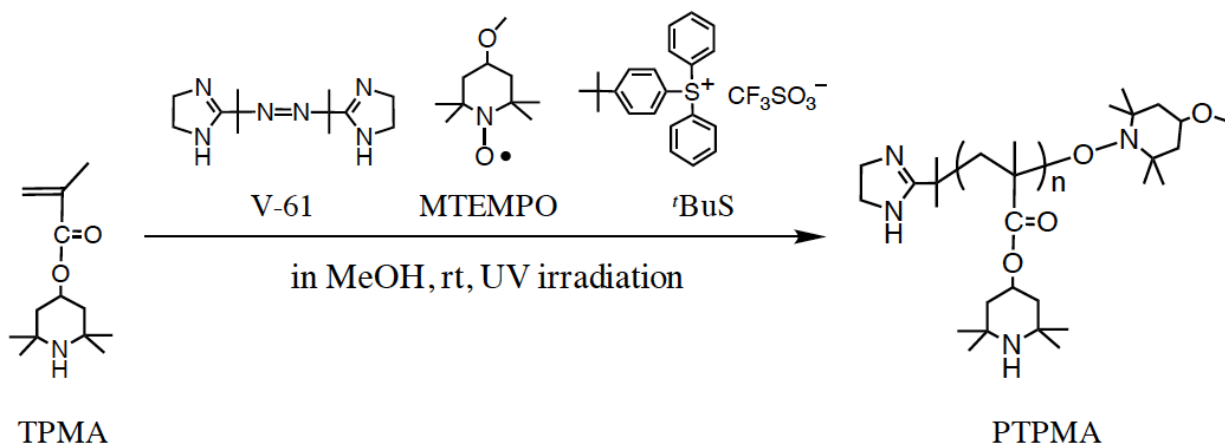
### SEM Observations

The aggregates obtained as the precipitates were dried in air and subjected to the FE-SEM measurements. The morphologies and particle size were determined by FE-SEM observation at 1.0 kV without any coating. The size distribution was calculated as previously reported [27].

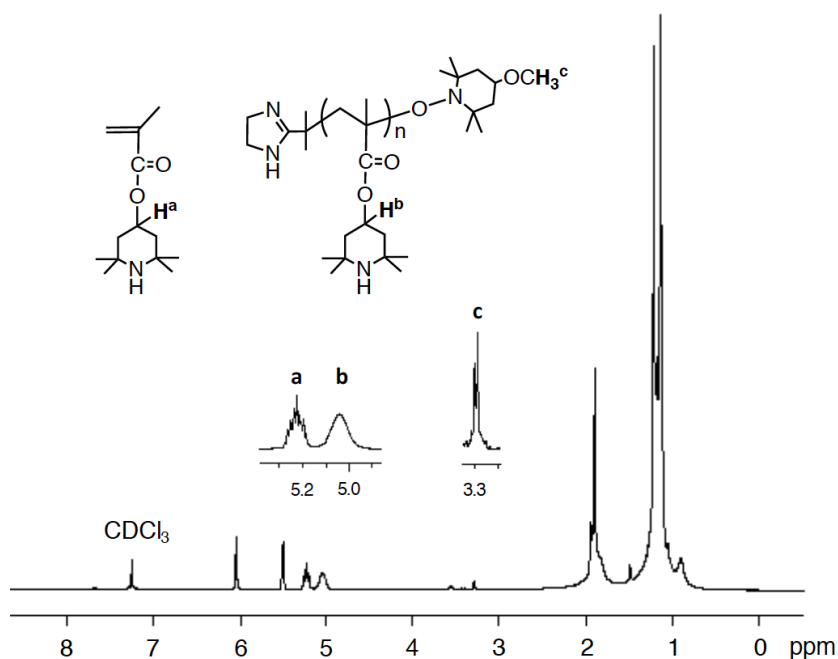
## RESULTS AND DISCUSSION

In order to investigate the living nature of the photo NMP for TPMA, the photo radical polymerization of TPMA was performed in MeOH using V-61 as the initiator, MTEMPO as the mediator, and <sup>t</sup>BuS as the accelerator by UV irradiation at room temperature

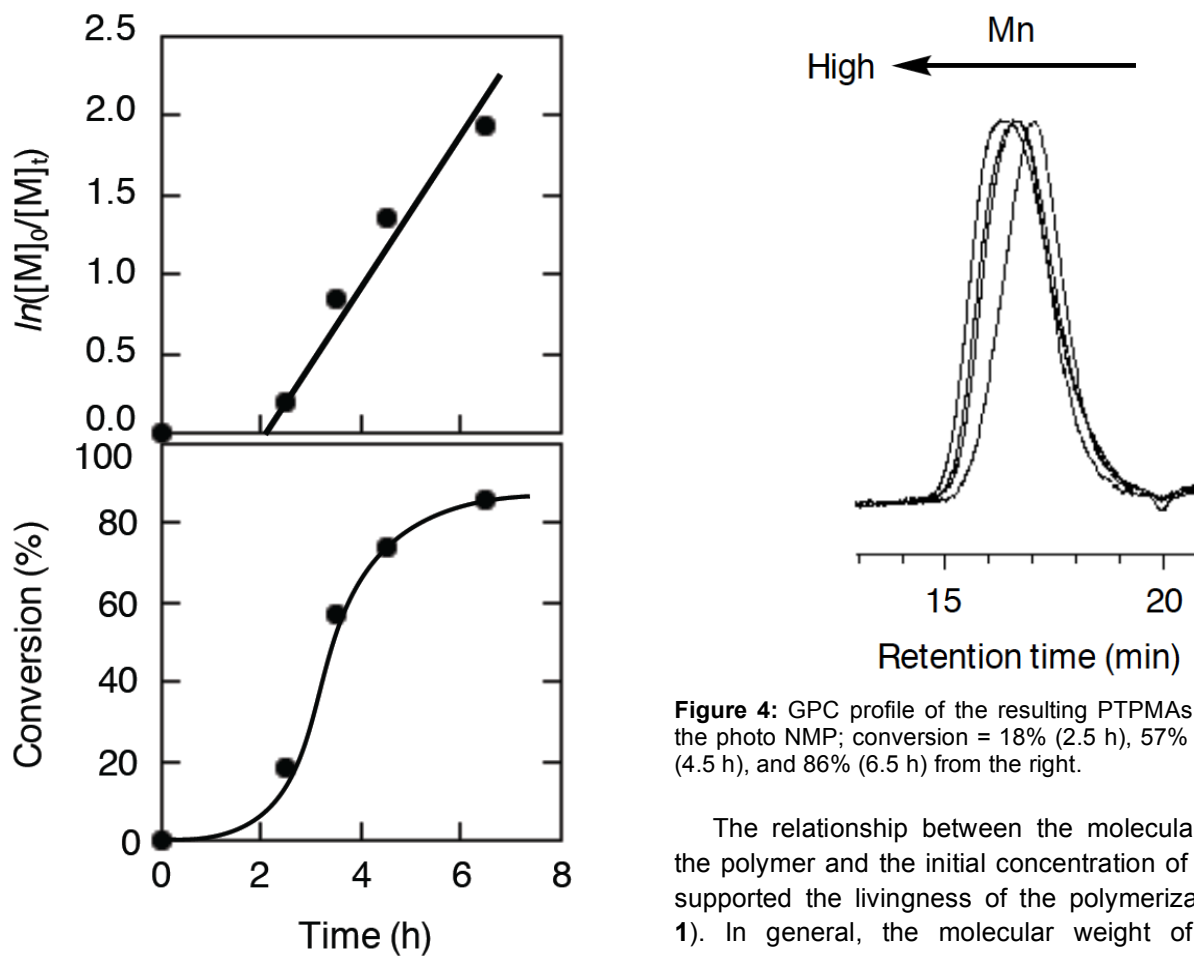
(Figure 1). The orange-colored solution based on MTEMPO turned colorless in 2 h. The solution gradually became viscous during the late stage of the polymerization. A <sup>1</sup>H NMR spectrum of the PTPMA obtained with a 51% conversion for the 4.5-h polymerization is shown in Figure 2. The conversion was estimated using the signals based on the methine proton of the piperidine at 5.22 ppm for the monomer and at 4.90 - 5.15 ppm for the polymer. The molecular weight of this PTPMA was determined to be 9,085 using this methine proton of the polymer and the methyl protons at 3.29 ppm attributed to MTEMPO attached to the polymer chain end. The molecular weight estimated by GPC based on PMMA standards was 26,500. The molecular weight by GPC was about 2.9 times greater than the real molecular weight due to the bulky piperidine rings. Figure 3 shows the time-conversion and its first-order time-conversion plots for the polymerization. The first-order plots had an induction period of ca. 2 h. This period of time was equal to the period until the orange color of the solution faded out. During the induction period, the MTEMPO molecules were captured by the initiator radicals and the monomer radicals produced by the initiation. However, the first order plots showed a linear increase with time, suggesting that the number of polymer chains was constant throughout the course of the polymerization. The GPC profile demonstrated that the curves of the resulting polymers with each conversion were shifted to the higher molecular weight side with the conversion (Figure 4). As shown in Figure 5, the molecular weight of the resulting polymer showed a linear increase with the conversion, indicating that the polymerization proceeded by a living mechanism. The molecular weight distribution also increased with the conversion and was somewhat broad due to the slow initiation.



**Figure 1:** The photo NMP of TPMA.



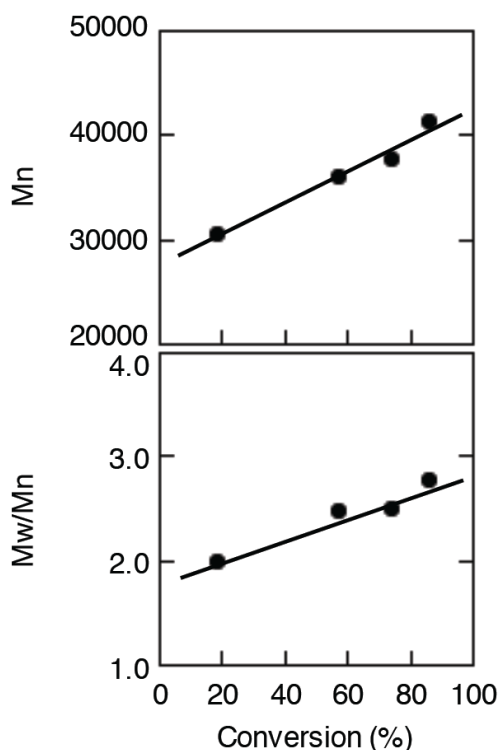
**Figure 2:** A  $^1\text{H}$  NMR spectrum of the PTPMA (conversion = 51%) obtained by the photo NMP (4.5 h,  $[\text{V-61}]_0 = 89.5$  mM,  $[\text{MTEMPO}]_0 = 96.6$  mM, and  $[\text{tBuS}]_0 = 51.2$  mM), followed by freeze-drying with benzene. Solvent:  $\text{CDCl}_3$ .



**Figure 3:** The time-conversion and its first order time-conversion plots for the photo NMP of TPMA ( $[\text{V-61}]_0 = 44.7$  mM,  $[\text{MTEMPO}]_0 = 48.3$  mM, and  $[\text{tBuS}]_0 = 25.6$  mM)

**Figure 4:** GPC profile of the resulting PTPMAs obtained by the photo NMP; conversion = 18% (2.5 h), 57% (3.5 h), 74% (4.5 h), and 86% (6.5 h) from the right.

The relationship between the molecular weight of the polymer and the initial concentration of the initiator supported the livingness of the polymerization (Table 1). In general, the molecular weight of the living polymers is determined by the following equation using the concentration of the consumed monomer and the initial concentration of the initiator.



**Figure 5:** Plots of the molecular weight and molecular weight distribution versus the conversion for the photo NMP of TPMA.

**Table 1: Photo NMP of TPMA**

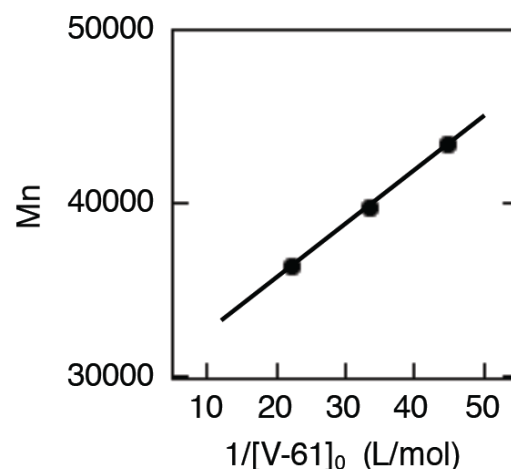
[V-61] <sub>0</sub> (mmol/L)	1/[V-61] <sub>0</sub> (L/mol)	Conversion (%)	Mn <sup>a</sup>	Mw/Mn <sup>a</sup>
22.4	44.7	93	43,400	3.57
30.0	33.4	90	39,700	3.45
44.7	22.4	80	36,300	3.21

[TPMA]<sub>0</sub> = 4.44 mol/L, MTEMPO/V-61 = 1.08, <sup>t</sup>BuS/MTEMPO = 0.53.  
<sup>a</sup>Estimated by GPC based on PMMA standards.

$$MW(\text{polymer}) = ([\text{Monomer}]/[\text{Initiator}]_0) \times MW(\text{monomer}) \quad (1)$$

The molecular weight showed a linear correlation with the reciprocal of [V-61]<sub>0</sub> (Figure 6), verifying the living nature of the polymerization.

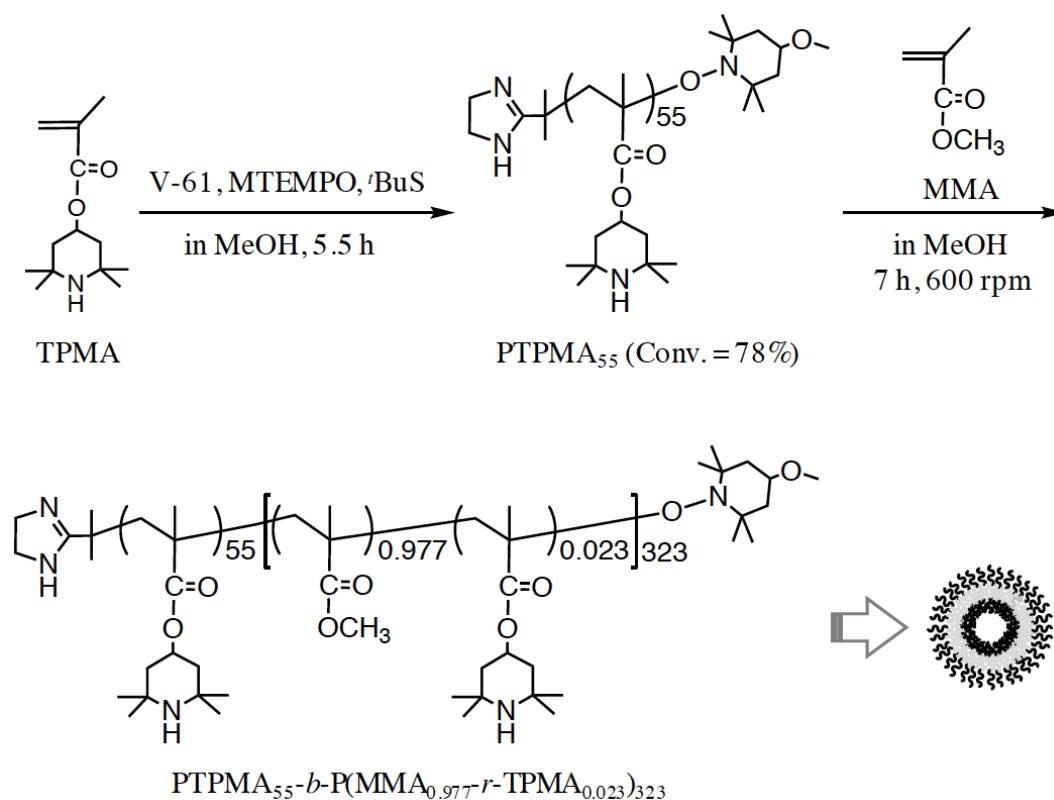
Based on the livingness of the polymerization, the photo NMP-induced self-assembly was performed using the PTPMA as the prepolymer (Figure 7). The sequential block copolymerization with MMA was carried out in methanol at room temperature for 7 h at a 600-rpm stirring speed using the PTPMA prepolymer obtained with a 78% conversion. The molecular weight and its distribution were Mn = 36,600 and Mw/Mn = 2.36 by GPC. The real molecular weight was calculated to be 12,620 based on the difference in the molecular



**Figure 6:** Plots of the molecular weight versus the reciprocal of [V-61]<sub>0</sub>.

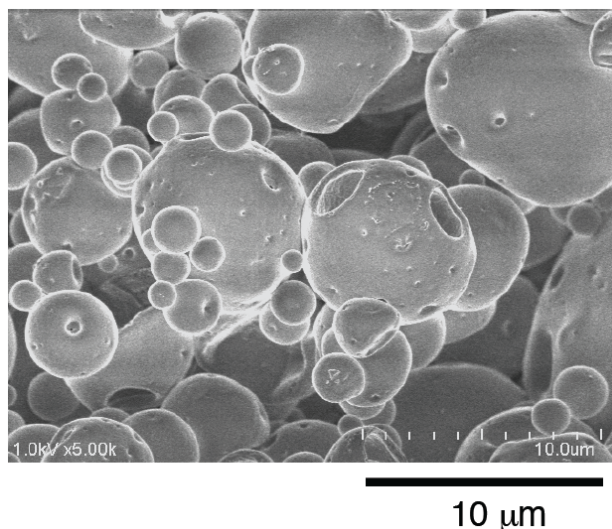
weight estimated by GPC. The degree of polymerization (DP) was determined to be 55 using this real molecular weight. The colorless solution containing MMA and the PTPMA became cloudy within 1 h, then a suspension formed. The monomer conversions were 57% for MMA and 47% for TPMA based on the <sup>1</sup>H NMR spectrum using the ester methyl protons for MMA and the piperidine methine proton for TPMA. The structure of the block copolymer was determined to be PTPMA<sub>55</sub>-*b*-P(MMA<sub>0.977</sub>-*r*-TPMA<sub>0.023</sub>)<sub>323</sub> using these conversions. The PMMA block contained a slight amount of the TPMA units because the unreacted TPMA monomers were also polymerized along with MMA during the block copolymerization. The molecular weight and its distribution of the block copolymer were Mn = 38,500 and Mw/Mn = 1.83 by GPC, respectively. The aggregates formed in the resulting dispersion were purified by a repeated sedimentation-redispersion process using MeOH.

The FE-SEM observation demonstrated that the photo NMP-induced self-assembly of the diblock copolymer produced microsized giant spherical vesicles. An FE-SEM image of the vesicles is shown in Figure 8. The diameter of the vesicles was D<sub>n</sub> = 3.07 μm and the size distribution was D<sub>w</sub>/D<sub>n</sub> = 2.13. The vesicles had various large and small holes in their surfaces. Some holes passing through the surface indicated that they were bilayer vesicles. The thickness of the bilayer was estimated to be 411 nm based on the walls of the holes passing through the surfaces. The reason for the formation of the vesicles, rather than micelles is due to the presence of the TPMA units in the hydrophobic block. The hydrophilic TPMA units increased the hydrophilicity of the hydrophobic block, causing a change in the critical packing shape [28]

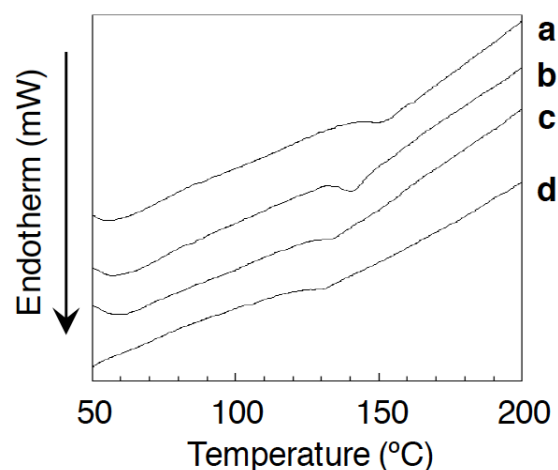


**Figure 7:** The photo NMP-induced self-assembly of PTPMA-*b*-PMMA.

from a cone to a truncated cone to provide vesicles. The result that the hydrophilic units in the hydrophobic block promoted the formation of vesicles agreed with the previous result for the vesicles consisting of amphiphilic poly(methacrylic acid)-*block*-poly(methyl methacrylate)-*random*-methacrylic acid [8, 9]. The somewhat broad size distribution of the vesicles should be due to the broad distribution of the hydrophilic PTPMA block.



**Figure 8:** An FE-SEM image of the vesicles composed of PTPMA<sub>55</sub>-*b*-P(MMA<sub>0.977</sub>-*r*-TPMA<sub>0.023</sub>)<sub>323</sub>.



**Figure 9:** DSC spectra of PTPMA<sub>54</sub> (a,  $M_n = 36,300$ ,  $M_w/M_n = 3.12$ ), the giant vesicles of PTPMA<sub>55</sub>-*b*-P(MMA<sub>0.977</sub>-*r*-TPMA<sub>0.023</sub>)<sub>323</sub> (b, the first scanning and c, the second scanning), and P(MMA<sub>0.972</sub>-*r*-TPMA<sub>0.028</sub>)<sub>454</sub> (d,  $M_n = 29,800$ ,  $M_w/M_n = 1.82$ ).

The DSC analysis revealed that the vesicles had a single bilayer structure. Figure 9 shows the DSC spectra of the vesicles, a PTPMA<sub>54</sub> homopolymer ( $T_g = 136.5^\circ\text{C}$ ), and P(MMA<sub>0.972</sub>-*r*-TPMA<sub>0.028</sub>)<sub>454</sub> random copolymer ( $T_g = 122.1^\circ\text{C}$ ). The vesicles only showed a glass transition temperature ( $T_g$ ) attributed to the PTPMA block at  $133.4^\circ\text{C}$  throughout the first scanning.

No observation was made for the  $T_g$  originating from the random copolymer block of P(MMA<sub>0.977</sub>-*r*-TPMA<sub>0.023</sub>)<sub>323</sub>. The  $T_g$  of the random copolymer block was 125.8°C instead of the  $T_g$  of the PTPMA block by the second scanning. The random copolymer blocks forming the vesicle cores were covered with the PTPMA blocks so that the  $T_g$  of the random copolymer block was observed after the PTPMA blocks had mobility. No observation of the  $T_g$  originating from the PTPMA block was made during the third scanning and later, thus supporting the formation of single layer vesicles.

## CONCLUSION

The photo NMP of the methacrylate ester supporting the hindered amine light stabilizer was found to proceed by a living mechanism based on the fact that the molecular weight showed linear correlations versus the monomer conversion and the reciprocal of the initial concentration of the initiator. The molecular weight distribution was somewhat broad due to the slow initiation during the MTEMPO molecules were captured by the initiator radicals and monomer radicals. The photo NMP-induced self-assembly for the block copolymerization of MMA using the PTPMA prepolymer produced microsized giant spherical vesicles. The vesicles consisted of the hydrophilic PTPMA block and hydrophobic PMMA containing a slight amount of the TPMA unit. It was found that the vesicles had a single bilayer structure based on SEM observations of the holes passing through the surface and on the DSC analysis. It is expected that the vesicles supporting the hindered amine on their shells not only produce a new artificial model of the oxidoreductase-supporting biomembrane, but also develop a new carrier having the function of electron transfer in drug and gene delivery systems.

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## CONFLICT OF INTEREST

The author has no conflict of interest in this study.

## REFERENCES

- [1] Minagawa M. New developments in polymer stabilization. *Polym Degrad Stab* 1989; 25: 121-41. [https://doi.org/10.1016/S0141-3910\(89\)81004-3](https://doi.org/10.1016/S0141-3910(89)81004-3)
- [2] Padron AJC. Performance and mechanisms of hindered amine light stabilizers in polymer photostabilization. *J Macromol Sci Rev Macromol Chem* 1990; C30: 107-54. <https://doi.org/10.1080/07366579008050906>
- [3] Lee CS, Lau WWY, Lee SY, Goh SH. Polymerization behavior of 2,2,6,6-tetramethylpiperidiny methacrylate: A monomer carrying a hindered amine group. *J Polym Sci, Part A, Polym Chem* 1992; 30: 983-8. <https://doi.org/10.1002/pola.1992.080300604>
- [4] Jiangqing P, Cheng W, Song Y, Hu X. Preparation and characterization of new copolymers containing hindered amine. *Polym Degrad Stab* 1993; 39: 85-91. [https://doi.org/10.1016/0141-3910\(93\)90128-6](https://doi.org/10.1016/0141-3910(93)90128-6)
- [5] Kurosaki T, Lee KW, Okawara M. Polymers having stable radicals. I. Synthesis of nitroxyl polymers from 4-methacryloyl derivatives of 2,2,6,6-tetramethylpiperidine. *J Polym Sci, Polym Chem Ed* 1972; 10: 3295-310. <https://doi.org/10.1002/pol.1972.170101116>
- [6] Yoshida E, Takata T, Endo T. Efficient and selective oxidation of a polymeric terminal diol with Cu(II) mediated by nitroxyl radical. *J Polym Sci, Part A Polym Chem Ed* 1992; 30: 1193-7. <https://doi.org/10.1002/pola.1992.080300627>
- [7] Yoshida E, Takata T, Endo T. Oxidation of polymeric terminal diols with iron(III) or copper(II) salts mediated by the nitroxyl radical. *Macromolecules* 1992; 25: 7282-5. <https://doi.org/10.1021/ma00052a032>
- [8] Yoshida E. Giant vesicles prepared by nitroxide-mediated photo-controlled/living radical polymerization-induced self-assembly. *Colloid Polym Sci* 2013; 291: 2733-9. <https://doi.org/10.1007/s00396-013-3056-0>
- [9] Yoshida E. Morphology control of giant vesicles by manipulating hydrophobic-hydrophilic balance of amphiphilic random block copolymers through polymerization-induced self-assembly. *Colloid Polym Sci* 2014; 292: 763-9. <https://doi.org/10.1007/s00396-013-3154-z>
- [10] Yoshida E. Preparation of giant vesicles containing quaternary ammonium salt of 2-(dimethylamino)ethyl methacrylate through photo nitroxide-mediated controlled/living radical polymerization-induced self-assembly. *J. Polym Res* 2018; 25: 109 (1-12). <https://doi.org/10.1007/s10965-018-1509-3>
- [11] Yoshida E. PH response behavior of giant vesicles comprised of amphiphilic poly(methacrylic acid)-*block*-poly(methyl methacrylate-*random*-methacrylic acid). *Colloid Polym Sci* 2015; 293: 649-53. <https://doi.org/10.1007/s00396-014-3482-7>
- [12] Yoshida E. Fabrication of anastomosed tubular networks developed out of fenestrated sheets through thermo responsiveness of polymer giant vesicles. *ChemXpress* 2017; 10(1): 118 (1-11). <http://www.tsijournals.com/articles/fabrication-of-anastomosed-tubular-networks-developed-out-of-fenestrated-sheets-through-thermo-responsiveness-of-polymer.pdf>
- [13] Yoshida E. Fission of giant vesicles accompanied by hydrophobic chain growth through polymerization-induced self-assembly. *Colloid Polym Sci* 2014; 292: 1463-8. <https://doi.org/10.1007/s00396-014-3216-x>
- [14] Yoshida E. Morphology transformation of micrometer-sized giant vesicles based on physical conditions for photopolymerization-induced self-assembly. *Supramol Chem* 2015; 27: 274-80. <https://doi.org/10.1080/10610278.2014.959014>
- [15] Yoshida E. Morphology control of giant vesicles by composition of mixed amphiphilic random block copolymers of poly(methacrylic acid)-*block*-poly(methyl methacrylate-*random*-methacrylic acid). *Colloid Polym Sci* 2015; 293: 249-56. <https://doi.org/10.1007/s00396-014-3403-9>
- [16] Yoshida E. Giant vesicles comprised of mixed amphiphilic poly(methacrylic acid)-*block*-poly(methyl methacrylate-*random*-methacrylic acid) diblock copolymers. *Colloid Polym Sci* 2016; 293: 3641-8. <https://doi.org/10.1007/s00396-015-3763-9>

- [17] Yoshida E. Worm-like vesicle formation by photo-controlled/living radical polymerization-induced self-assembly of amphiphilic poly(methacrylic acid)-*block*-poly(methyl methacrylate-*random*-methacrylic acid). *Colloid Polym Sci* 2016; 294: 1857-63. <https://doi.org/10.1007/s00396-016-3935-2>
- [18] Yoshida E. Fabrication of microvillus-like structure by photopolymerization-induced self-assembly of an amphiphilic random block copolymer. *Colloid Polym Sci* 2015; 293: 1841-5. <https://doi.org/10.1007/s00396-015-3600-1>
- [19] Yoshida E. Morphological changes in polymer giant vesicles by intercalation of a segment copolymer as a sterol model in plasma membrane. *Colloid Polym Sci* 2015; 293: 1835-40. <https://doi.org/10.1007/s00396-015-3577-9>
- [20] Yoshida E. Morphology transformation of giant vesicles by a polyelectrolyte for an artificial model of a membrane protein for endocytosis. *Colloid Surf Sci* 2018; 3: 6-11. <https://doi.org/10.11648/j.css.20180301.12>
- [21] Venditti P, Stefano LD, Meo SD. Mitochondrial metabolism of reactive oxygen species. *Mitochondrion* 2013; 13: 71-82. <https://doi.org/10.1016/j.mito.2013.01.008>
- [22] Bleier L, Dröse S. Superoxide generation by complex III: From mechanistic rationales to functional consequences. *Biochim Biophys Acta* 2013; 1827: 1320-31. <https://doi.org/10.1016/j.bbabi.2012.12.002>
- [23] Rochaix J. Reprint of: Regulation of photosynthetic electron transport. *Biochim Biophys Acta* 2011; 1807: 878-86. <https://doi.org/10.1016/j.bbabi.2011.05.009>
- [24] Miyazawa T, Endo T, Shiihashi S, Ogawara M. Selective oxidation of alcohols by oxoammonium salts (R<sub>2</sub>N:O<sup>+</sup> X<sup>-</sup>). *J Org Chem* 1985; 50: 1332-4. <https://doi.org/10.1021/jo00208a047>
- [25] Kita Y, Gotanda K, Murata K *et al.* Practical radical additions under mild conditions using 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile) [V-70] as an initiator. *Org Process Res Dev* 1998; 2: 250-4. <https://doi.org/10.1021/op970059z>
- [26] Yoshida E. Effects of illuminance and heat rays on photo-controlled/living radical polymerization mediated by 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl. *ISRN Polym Sci* 2012; 102186: 1-6. <https://doi.org/10.5402/2012/102186>
- [27] Kobayashi S, Uyama H, Yamamoto I, Matsumoto Y. Error! Hyperlink reference not valid. *Polym J* 1990; 22: 759-61. <https://doi.org/10.1295/polymj.22.759>
- [28] Israelachvili, JN. *Intermolecular and Surface Forces*. 3rd ed, Waltham: Academic Press 2011.

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