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Anionic Polymerization of 4-Methacryloyloxy-TEMPO Using an MMA-Capped Initiator

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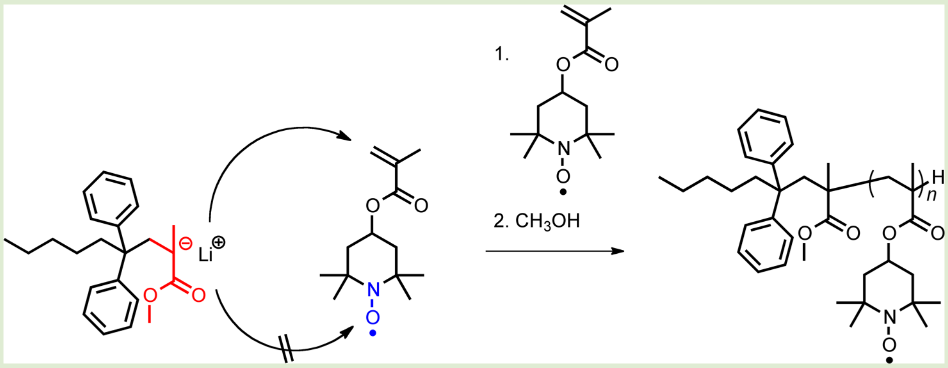
Supporting Information



ABSTRACT: Anionic polymerization of 4-methacryloyloxy-TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) was successfully carried out using methyl methacrylate-capped 1,1-diphenylhexyllithium (DPHLi/MMA), of which nucleophilicity is moderate enough to suppress the side reaction between the nitroxide radical of TEMPO moiety and the carbanion of DPHLi, to yield the radical polymer with well-controlled molecular weight, narrow polydispersity index (PDI < 1.10), high yield (>95%), and almost 1.0 radicals per monomer unit.

Organic radical molecules represented by 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) have recently attracted considerable attention due to their reversible redox reactions.[1,2] This fascinating feature of the radical molecules motivated us to utilize them, particularly in the form of a polymer bearing densely populated pendant radicals as electroactive materials for organic-based secondary batteries, solar cells, and nonvolatile memories.[3] In particular, we proposed poly(4-methacryloyloxy-TEMPO) (PTMA) as a cathode-active material, which has been widely studied owing to the fast charging/discharging, the high output voltage, and the long cycle-life performances essential for secondary batteries.[4] Typically, PTMA was synthesized via free or controlled radical polymerizations of the secondary amine-containing radical precursor, and following oxidation of the resultant polymer.[5,6] Potential reactivity between the nitroxide radical of TEMPO moiety and propagating carbon radicals inhibited radical polymerizations of the 4-methacryloyloxy-TEMPO monomer (TMA). Furthermore, the oxidation process often triggered side reactions such as cross-linking of PTMA. Limited radical concentration originated from the reaction on polymer is an inherent problem.

Anionic polymerization and group transfer polymerization of TMA were reported; the resultant polymers still contained the nitroxide radicals which survived throughout the polymerizations.[7] These results indicate that anionic polymerization has potential of direct polymerization of the radical monomer to prepare well-defined PTMA as high molecular-weight polymer and block copolymer based on the competent living nature. However, butyllithium, a typical initiator for vinyl monomers on anionic polymerization, has the high nucleophilicity enough to attack the polarized carbonyl group of methacrylate moiety and then to terminate the polymerization.[8] Furthermore, a reaction between butyllithium and TEMPO through one-electron transfer from the carbanion of butyllithium to the nitroxide radical of TEMPO moiety was reported.[9] Indeed, in our previous study, PTMA synthesized by anionic polymerization using butyllithium had 0.81 radicals per monomer unit which implied the presence of the undesired side reaction relevant to the nitroxide radical.[10] Hence, a more reasonable system of anionic polymerization for the synthesis of PTMA is required to avoid the side reaction.

In this paper, we report living anionic polymerizations of TMA where the side reaction involving the nitroxide radical of TEMPO moiety was significantly suppressed. First, anionic polymerization of TMA was initiated by a common initiator for living anionic polymerization of methyl methacrylate (MMA), 1,1-diphenylhexyllithium (DPHLi),[11] which was regarded as an appropriate initiator to suppress the side reaction involving the nitroxide radical of TEMPO moiety owing to the bulky

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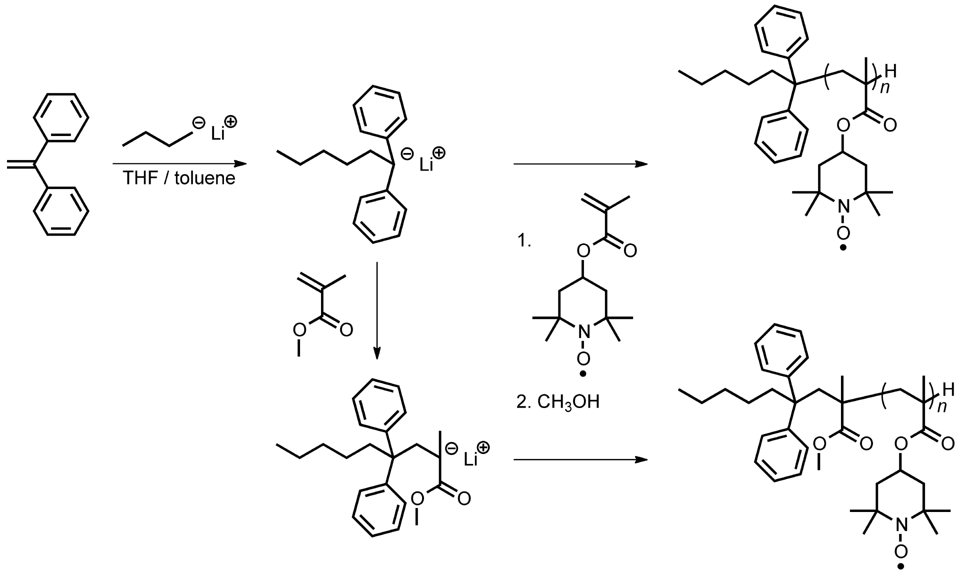
Scheme 1. Anionic Polymerization of 4-Methacryloyloxy-TEMPO Using DPHLi or DPHLi/MMA



structure and the reduced basicity according to a previous report (Scheme 1).[12]

Table 1. Anionic Polymerization of TMA[a]

entry	initiator	$[M]_0/[I]_0$	yield (%)	$M_n \times 10^3$ calcd	$M_n \times 10^3$ obsd[b]	PDI[b]	radical concn[c] (%)
1	DPHLi	13	100	3.4	4.5	1.24	93
2	DPHLi	20	100	5.0	6.0	1.18	92
3	DPHLi	42	100	10.3	23.5	1.11	93
4	DPHLi	52	100	12.7	26.2	1.16	89
5	DPHLi	78	100	19.0	30.4	1.16	94
6	DPHLi/MMA	13	100	3.5	3.0	1.06	99
7	DPHLi/MMA	20	100	5.1	3.6	1.08	98
8	DPHLi/MMA	42	100	10.4	9.5	1.07	98
9	DPHLi/MMA	52	95	12.8	10.6	1.10	100
10	DPHLi/MMA	78	100	19.1	16.5	1.04	99

[a] $[LiCl]/[I] = 1$, in THF/toluene = 10/1(v/v), monomer concentration = 0.17 M, −61 °C. [b] Determined by GPC in THF elusion. [c] Estimated by ESR.

The results of the polymerization are summarized in entries 1−5 of Table 1. PTMA has the relatively lower solubility in the polymerization solvent than those of common polymers such as polystyrene and poly(methyl methacrylate) especially at low temperature required for anionic polymerization. Hence, the slightly higher temperature of −61 °C than −78 °C (the latter is the typical temperature for anionic polymerization of methacrylate derivatives) was selected as an appropriate temperature for the polymerization of TMA to improve the solubility and to control the polymerization. PTMA was quantitatively obtained regardless of the initial molar ratio between TMA and DPHLi ($[M]_0/[I]_0$, entries 1−5 in Table 1).

To monitor the progress of polymerization, a small portion of a polymerization solution was separated hourly from 5 to 60 min after the initiation of the polymerization and then supplied for GPC analysis (Figure S1). The peak for polymer shifted toward higher molecular weight and the intensity of the peak for monomer concurrently became smaller as the polymerization progressed and finally disappeared after 60 min. Furthermore, as evidenced by the fact that almost 90% of the initial amount of monomer was consumed in 10 min after the initiation, the time dependency of the polymerization indicates the fast reaction rate of the anionic polymerization.

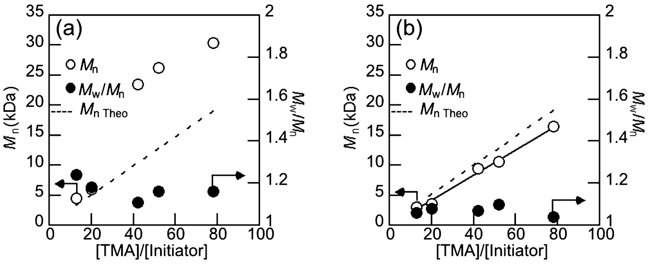
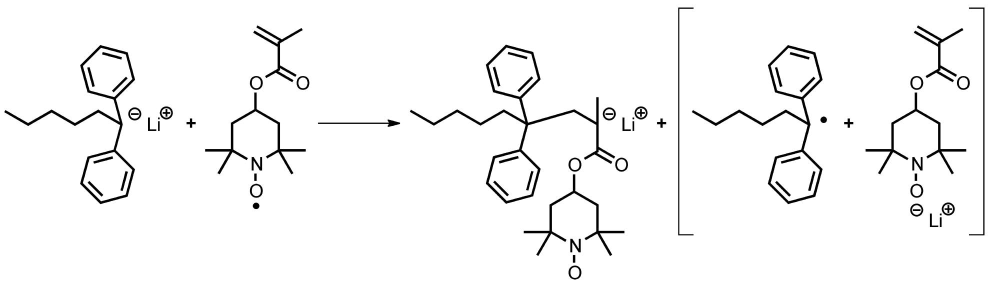


Figure 1. Molecular weight and PDI dependence on the initial molar ratio of [TMA]/[initiator]: (a) using DPHLi and (b) DPHLi/MMA.

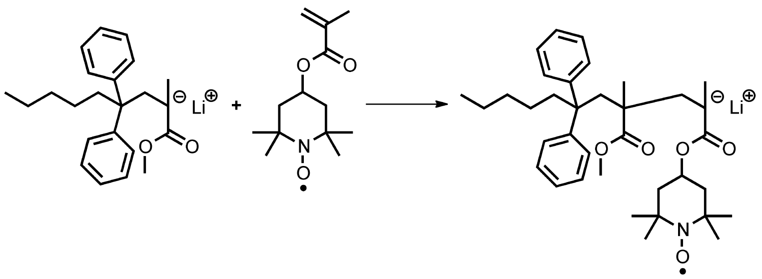
In spite of these features of anionic polymerization, the experimental molecular weights were much higher than the theoretical values estimated by the initial molar ratio of $[M]_0/[I]_0$ (Figure 1a), and the polydispersity indices (PDIs) of PTMA extended to 1.24 were slightly higher than those of general polymers prepared by living anionic polymerization (<1.10). Radical concentration of PTMA was estimated by the intensities of electron spin resonance (ESR) spectra for unpaired electrons of the nitroxide radicals. The broad ESR signal for PTMA emerged at $g = 2.0065$ due to the spin exchange interaction between the unpaired electrons of the neighboring nitroxide groups even in dilute solutions (Figure S3), in contrast to the spectrum obtained for a solution of the monomer with the distinct hyperfine structure. According to the comparison between the value of integrated ESR signal intensity for PTMA and the calibration curve of the value for the standard sample TEMPO, a radical concentration of 0.89 radicals per monomer unit (i.e., 2.23×10^{21} unpaired electrons/g) was obtained for PTMA (entry 4 in Table 1). The radical

Scheme 2. Reactions of 4-Methacryloyloxy-TEMPO with (a) DPHLi and (b) DPHLi/MMA

(a) Using DPHLi initiator



(b) Using DPHLi/MMA initiator



concentration suggests the occurrence of a side reaction related to the nitroxide radical moiety. Considering the relatively high molecular weights, the broad PDIs, and the quantitative yields, it seemed that the side reaction arose in the initiation process; DPHLi competitively reacted with both the nitroxide radical and the methacrylate moieties, while the methacrylate carbanion of the propagating end avoided the side reaction to the nitroxide radical of TEMPO moiety. Therefore, it was likely that the initiator efficiency was reduced by the side reaction of DPHLi with the nitroxide radical moiety in the initiation process.

To investigate the side reaction between the carbanions and TEMPO, we examined reactions of both DPHLi and MMA-capped DPHLi (DPHLi/MMA) with TEMPO by adding TEMPO to slightly excess molar equivalents of DPHLi and DPHLi/MMA in THF at −78 °C, respectively (Figure S4). DPHLi/MMA was intended as an approximated methacrylate carbanion moiety in the propagation process of the anionic polymerization of TMA. The red color of each DPHLi and TEMPO solutions disappeared immediately after the addition of the TEMPO solution to the DPHLi solution, while the mixture of DPHLi/MMA and TEMPO colored red. The red color of the mixture of DPHLi/MMA and TEMPO was derived from TEMPO considering the colorless solution of DPHLi/MMA. The difference between these two experiments confirms that the carbanion of DPHLi reacted with TEMPO despite the steric hindrance of the bulky structure of DPHLi, while TEMPO was stable against the carbanion of the methacrylate moiety. The radical concentration of the mixture of DPHLi and TEMPO and that of DPHLi/MMA and TEMPO, estimated by ESR immediately after quenched by methanol, were 0.70 radicals per molecular unit (i.e., 2.70×10^{21} unpaired electrons/g) and 0.98 radicals per molecular unit (i.e., 3.78×10^{21} unpaired electrons/g), respectively. The radical concentrations agreed with the changes in color and concluded that the radicals were degraded in the DPHLi initiator solution.

Based on this result, DPHLi/MMA was adopted as an initiator for anionic polymerization of TMA. 1.1−1.2 mol equiv of MMA were added to a DPHLi solution and then red color derived from DPHLi instantly faded. The disappearance of red color ensured that DPHLi was perfectly capped by MMA. Subsequently, we added a TMA solution to the DPHLi/MMA initiator solution and then obtained PTMA. This initiation system demonstrated the well-controlled polymerization with quantitative yield. The experimental molecular weights were very close to the theoretical values and proportional to $[M]_0/[I]_0$ with the low PDIs (<1.10), which are unique to living anionic polymerization (entries 6−10 in Table 1 and Figure 1b). Molecular weight of PTMA estimated by MALDI-TOF MS analysis indicates that the DPHLi/MMA initiator segment contained one or two MMA monomers for each polymer chain (Figure S5). The NMR spectrum of the PTMA (entry 6 in Table 1) supported both the controlled molecular weight ($M_n = 3.7 \times 10^3$) and the MMA-capping reaction of DPHLi (Figure S6b). The high radical concentration of 0.98 radicals per monomer unit (i.e., 2.46×10^{21} unpaired electrons/g) obtained for PTMA was estimated using a both superconducting quantum interference device (SQUID) magnetometer and the ESR signal intensity (entry 8 in Table 1 and Figure S7). These results reveal that the nucleophilicity of the methacrylate carbanion is strong enough for polymerization of TMA and also moderate enough to suppress the side reaction with the nitroxide radical moiety in significantly contrast to the DPHLi which reacts with the nitroxide radical moiety through one-electron transfer (Scheme 2). The dimerization of the diphenylhexyl radicals generated from the electron transfer was supported by FAB-MS spectrometry, and the TEMPO anion is expected to be stable under the aprotic condition of the anionic polymerization. Other following side reactions affecting the resultant radical concentration are to be studied in our continuous research.

In summary, the anionic polymerization of TMA was improved by using the DPHLi/MMA initiator, to prepare well-defined PTMA radical polymers characterized by controlled molecular weight, quantitative yield, narrow PDI, and high radical concentration. The DPHLi/MMA initiator system has the appropriate nucleophilicity to react with just methacrylate moiety, and therefore, the resultant polymers have controlled molecular weight. A high molecular weight PTMA demonstrated the high charging/discharging performance and the long cycle life (Figure S8). This living polymerization could also enable formation of a block copolymer and a brush polymer of the radical moieties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, additional figures, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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