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Letter

Proton Transfer Anionic Polymerization of Methyl Methacrylate with Ligands for Dual Control of Molecular Weight and Tacticity

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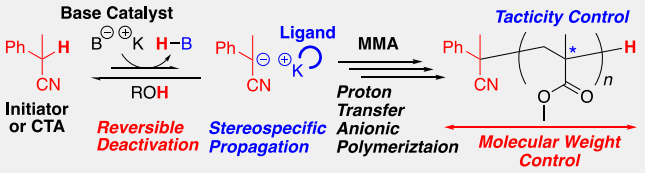
ABSTRACT: Dual control of the molecular weight and tacticity in proton transfer anionic polymerization (PTAP) of methyl methacrylate (MMA) was investigated by using various ligands in the presence of a bulky potassium base catalyst and an organic compound with a weakly acidic C−H bond as dormant species in toluene at 0 °C. The tacticity of the resulting poly(MMA) (PMMA) produced without ligands was nearly atactic (*rr*/*mr*/*mm* = 22/54/24). However, the use of 18-crown-6 as a ligand afforded predominantly syndiotactic PMMA (*rr* ≈ 58%), whereas the use of chiral bis(oxazoline) ligands gave slightly isotactic-rich PMMA (*mm* ≈ 32%). Molecular weight control of PMMA was achieved (*Đ* = 1.1−1.2) by adding 1,1-diphenylethanol as a reversible terminator while maintaining control of the tacticity with the above ligands. Stereoblock PMMA consisting of atactic and syndiotactic segments was successfully synthesized via sequential PTAP using macroinitiator/macro-CTA methods.



KEYWORDS: *living polymerization, anionic polymerization, stereospecific polymerization, methacrylate, stereoblock polymer*

Novel methods for precision polymerization that allow control of the molecular weight, stereochemistry, monomer sequence, and chain-end structure of the resulting polymers are still needed for more precise and facile synthesis of functional polymer materials with controlled structures.[1−11] In particular, control of multiple structural parameters specific to macromolecules is demanded to further develop polymer materials analogous to natural macromolecules with superior functions derived from their highly controlled structures.

The roots of precision polymerization can be traced back to the living anionic polymerization of styrene with sodium and naphthalene as initiators in sealed glassware under harsh conditions without moisture and air, which was reported by Szwarc in 1956.[12−14] Since then, living anionic polymerizations have been developed for various vinyl monomers, including not only hydrocarbon monomers, such as styrene and isoprene, but also polar monomers, such as methacrylate and acrylate using appropriate initiators.[15−17] Furthermore, dual control of the molecular weight and stereochemical tacticity has been achieved in anionic polymerization of (meth)acrylic monomers by using metal-based initiators in the presence of selected additives and in specific solvents.[18] For example, isospecific living anionic polymerization of methyl methacrylate (MMA) is achievable by using *t*BuMgBr in toluene[19,20] or lithium enolates in the presence of lithium trimethylsilanolate in toluene.[21,22] Additionally, syndiospecific living anionic polymerization of MMA can be achieved via the use of metal-based initiating systems such as diphenylhexyl lithium (DPHLi) in THF,[23] *t*BuLi/R_3Al in toluene,[24,25] and organolanthanide complexes in toluene.[26] In these stereospecific living anionic polymerizations, the propagating anionic or enolate species accompanied by metals and additives should be in charge of both living and stereospecific chain growth. The metal compound must thus be present in at least an equal amount to the polymer chain. In addition, metal-based initiating species are often difficult to synthesize and/or handle. A novel strategy to address these issues is thus desired.

Recently, we developed a novel method to control the molecular weight during anionic polymerization of methacrylates by using organic compounds with weakly acidic C−H bonds as initiators and/or chain-transfer agents (CTAs) in the presence of a catalytic amount of simple bulky bases such as potassium hexamethyldisilazide (KHMDS, $K^+(Me_3Si)_2N^-$) and potassium *tert*-butoxide (KO*t*Bu).[27] This polymerization was coined proton transfer anionic polymerization (PTAP), which is analogous to proton transfer anionic addition in organic synthesis.[28] The molecular weight is controlled via proton transfer between the propagating anionic species and the dormant species with C−H bonds. Accordingly, one polymer chain forms from one molecule of the organic compounds, while the metal compounds catalytically work for the polymer chain. The amount of metal compounds per chain is thus significantly decreased. Unlike conventional living anionic polymerization, water does not have to be completely

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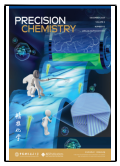

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Scheme 1. Proton Transfer Anionic Polymerization of Methyl Methacrylate with Ligands for Dual Control of Molecular Weight and Tacticity

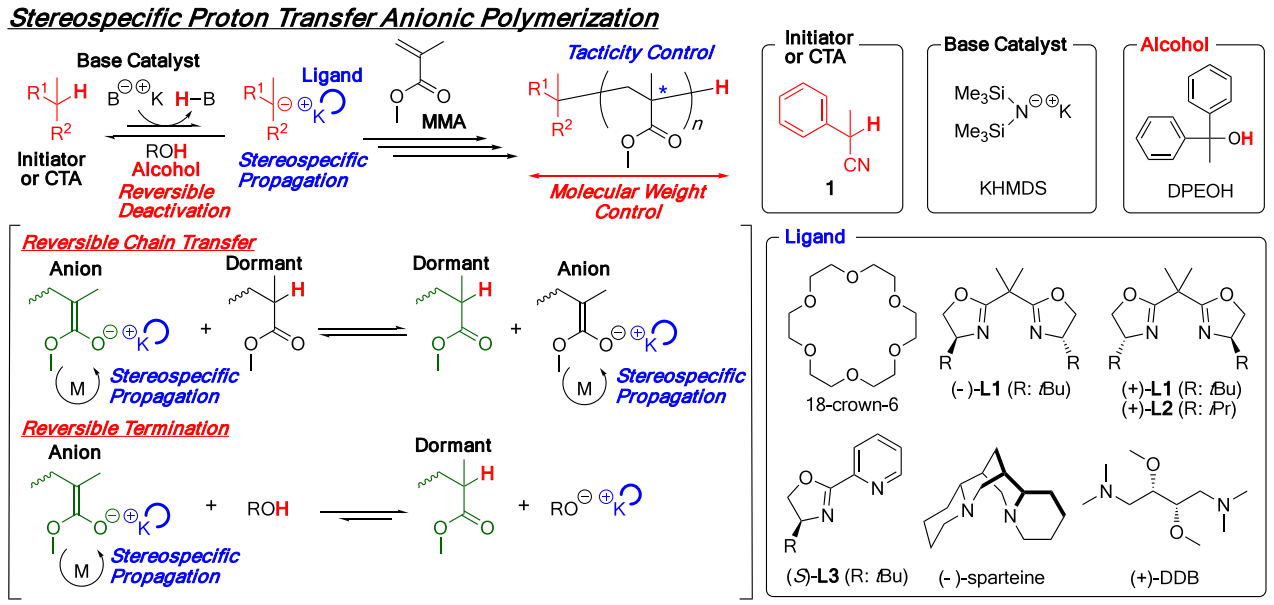

Table 1. PTAP of MMA Using KHMDS with Various Ligands and Alcohols[a]

entry	solvent	ligand	alcohol	time	conv. (%)[b]	M_n(calcd)[c]	M_n[d]	$Đ$[d]	*rr*/*mr*/*mm*[e]
1	toluene	none	none	77 h	88	2300	3600	2.54	22/54/24
2	toluene	18-crown-6	none	10 min	>99	2600	3800	4.08	58/35/7
3	toluene	(−)-**L1**	none	21 h	93	2500	2600	8.57	19/49/32
4	toluene	(+)-**L2**	none	67.5 h	68	1800	1800	3.21	20/53/27
5	toluene	(*S*)-**L3**	none	46 h	73	2000	2300	6.57	19/51/30
6	toluene	(+)-**L1**	none	22 h	96	2500	4100	6.96	20/48/32
7[f]	toluene	**L1**	none	22 h	93	2500	4400	8.06	20/49/31
8	toluene	(−)-sparteine	none	76 h	96	2500	2300	5.51	21/53/26
9	toluene	(+)-DDB	none	76 h	96	2500	4800	8.88	22/50/28
10	THF	none	none	7 h	>99	2600	2500	4.44	31/57/12
11	THF	18-crown-6	none	10 min	>99	2600	3000	4.52	55/40/5
12	THF	(−)-**L1**	none	2 h	>99	2600	2800	4.91	30/57/13
13[g]	toluene	none	DPEOH	282 h	95	2500	1800	1.17	21/55/24
14[g]	toluene	18-crown-6	DPEOH	6 h	>99	2600	2100	1.13	55/39/6
15[g]	toluene	(−)-**L1**	DPEOH	358 h	95	2500	2100	1.75	21/53/26

[a]Polymerization condition: $[M]_0/[\mathbf{1}]_0/[KHMDS]_0/[ligand]_0$ = 750/30/5.0/5.5 mM at 0 °C. [b]Determined by ^{1}H NMR. [c]M_n(calcd) = MW(MMA) × ($[M]_0/[\mathbf{1}]_0$) × conv. + MW(**1**). [d]Determined by SEC. [e]Triad tacticities (*rr*/*mr*/*mm*) were determined by ^{13}C NMR. [f]$[ligand]_0$ = $[(-)\text{-}\mathbf{L1}]_0$ + $[(+)\text{-}\mathbf{L1}]_0$ = 2.75 + 2.75 mM. [g]$[DPEOH]_0$ = 10 mM.

removed from the polymerization mixture because the C−H terminals generated via termination with water can also serve as dormant species. Moreover, an added alcohol works as a reversible terminator, which tames the fast polymerization of reactive monomers such as MMA, resulting in a dormant C−H terminal and a conjugate base as a catalyst. However, stereochemical control in PTAP has not been studied. In particular, the tacticity may be tuned by additives, whereas the molecular weight can be controlled by the proton transfer process. This approach will lead to dual control of the tacticity and molecular weight in PTAP, similar to how stereospecific living radical polymerization has been achieved via the use of additives in ATRP and RAFT polymerization.[3,29,30]

In this study, we examined the effects of additives, such as crown ether and chiral oxazoline derivatives, as ligands for countercations on PTAP of MMA for simultaneous control of the molecular weight and tacticity of poly(MMA) (PMMA) (Scheme 1). The key to success is to search for ligands that can alter the tacticity of the resulting PMMA and find conditions under which the control of the molecular weight in PTAP is maintained. Hopefully, the stereochemistry is tuned by the interaction between the growing anionic species and the countercation associated with ligands, whereas the molecular weight is controlled by the reversible deactivation of the anionic species, which can be enhanced by further addition of alcohol. Furthermore, the synthesis of stereoblock PMMA by sequential PTAP using PMMA obtained under different conditions as a macroinitiator or a macro-CTA with a different tacticity was investigated.

To determine the effects of ligands, a series of anionic polymerizations of MMA using various ligands, such as 18-crown-6 and chiral bisoxazoline (Box) derivatives (**L1**−**L3**), analogous to those used in catalytic asymmetric Mannich reactions, was examined.[31] The polymerizations were carried

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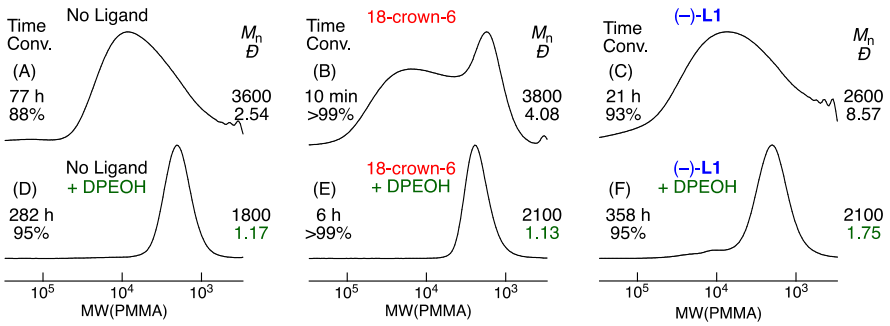

Figure 1. SEC curves of PMMA obtained by PTAP of MMA using KHMDS with various ligands in the absence (A–C) or presence (D–F) of DPEOH: $[MMA]_0/[\mathbf{1}]_0/[KHMDS]_0/[ligand]_0/[DPEOH]_0$ = 750/30/5.0/0 or 5.5/0 or 10 mM in toluene at 0 °C.

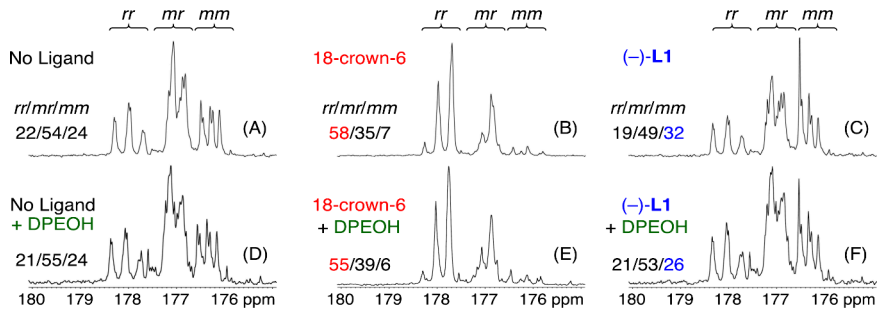

Figure 2. ^{13}C NMR spectra ($CDCl_3$, 55 °C) of PMMA obtained by PTAP of MMA using KHMDS with various ligands in the absence (A–C) or presence (D–F) of DPEOH.

out with a catalytic amount of KHMDS as a base catalyst and 2-phenyl propionitrile (**1**) as an initiator or a CTA with an acidic C–H proton in toluene at 0 °C (Table 1). Without any ligands, the polymerization was very slow, in which the consumption of MMA reached 88% after 77 h, resulting in polymers with broad dispersity ($Đ$ = 2.54) and a number-average molecular weight (M_n = 3600) that was slightly higher than the calculated value for PTAP (entry 1 in Table 1; Figure 1A). The ^{13}C NMR spectrum revealed that a nearly atactic polymer was obtained (*rr*/*mr*/*mm* = 22/54/24) (Figures 2A, S1A, and S2A). Thus, without any ligands, control of the molecular weight and tacticity was difficult under these conditions.

Then, 18-crown-6 was added as a ligand for this polymerization to dramatically increase the polymerization rate (>99% monomer conversion in 10 min), and polymers with a bimodal size-exclusion chromatography (SEC) curve and a similar M_n value were obtained (M_n = 3800, $Đ$ = 4.08) (entry 2; Figure 1B). The high molecular weight part of the bimodal distribution could be due to the polymers produced by fast initiation and propagation with almost no reversible chain transfer, while the low molecular weight part could be attributed to the polymers that underwent sufficient reversible chain transfer. The tacticity of the product changed to a relatively high syndiotactic enchainment (*rr*/*mr*/*mm* = 58/35/7) (Figures 2B, S1B, and S2B). The coordination of 18-crown-6 to the potassium counterion enhanced the formation of free enolate species, thereby promoting syndiospecific propagation through steric repulsion of the side chains.[32]

In contrast, when a chiral Box ligand such as (*S*,*S*)-(−)-2,2-bis(4-*tert*-butyl-2-oxazolin-2-yl)propane ((−)-**L1**) was used as an additive, the isotactic enchainment slightly increased (*rr*/*mr*/*mm* = 19/49/32) (entry 3; Figures 2C, S1C, and S2C). A similar increase in the isotactic content was also observed when using another chiral Box ligand with an isopropyl substituent ((*R*,*R*)-(+)-2,2-bis(4-isopropyl-2-oxazolin-2-yl)propane: (+)-**L2**, *rr*/*mr*/*mm* = 20/53/27) and a chiral pyridyl monooxazoline (Pymox) ligand ((*S*)-4-*tert*-butyl-2-(2-pyridyl)-oxazoline: (*S*)-**L3**, *rr*/*mr*/*mm* = 19/51/30) (entries 4 and 5; Figures S3 and S4). The enantiomer of (−)-**L1**, i.e., (+)-**L1**, resulted in almost the same tacticity (*rr*/*mr*/*mm* = 20/48/32) (entry 6; Figures S5 and S6) as that obtained with (−)-**L1**. In contrast, other chiral amines, such as (−)-sparteine and (*S*,*S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB),[33] afforded nearly atactic polymers (entries 8 and 9; Figures S7 and S8), similar to those obtained without ligands. These results suggest that oxazoline-based ligands enhance the isospecific propagation in toluene.

THF was also used in place of toluene for several polymerizations. The polymerization without ligands resulted in PMMA with a slightly increased *rr* content (*rr*/*mr*/*mm* = 31/57/12) (entry 10; Figures S9A and S10A) compared with that obtained in toluene, most likely due to the coordination of THF to potassium cations. The addition of 18-crown-6 gave PMMA with almost the same tacticity (*rr*/*mr*/*mm* = 55/40/5) (entry 11; Figures S9B and S10B) as that obtained in toluene with 18-crown-6. However, there was almost no effect of (−)-**L1** on the tacticity (*rr*/*mr*/*mm* = 30/57/13) (entry 12; Figures S9C and S10C) of the PMMA obtained in THF. These results indicate that 18-crown-6 has a greater coordination ability than THF, whereas the coordination ability of (−)-**L1** is lower than that of THF. Further investigation is required to elucidate the mechanism for the stereospecific propagation.

The tacticity of PMMA was thus changed from atactic to syndiotactic and then to slightly *m*-rich enchainment by the addition of ligands. However, in all cases, the molecular weight distribution was broad, although the M_n value was close to the

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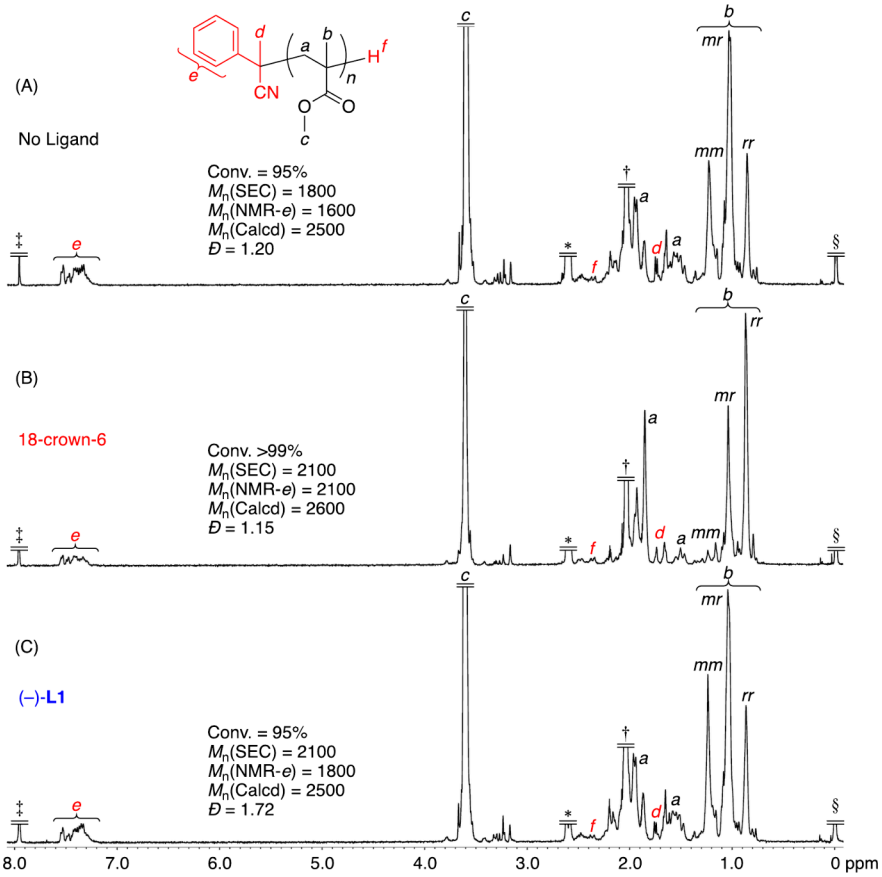

Figure 3. ^{1}H NMR spectra ($(CD_3)_2CO$, 50 °C) of PMMA obtained by PTAP of MMA without ligand (A) and with 18-crown-6 (B) and **L1** (C) in the presence of DPEOH: $[MMA]_0/[\mathbf{1}]_0/[KHMDS]_0/[ligand]_0/[DPEOH]_0$ = 750/30/5.0/5.5/10 mM in toluene at 0 °C: (§) tetramethylsilane, (†) acetone, (*) H_2O, (‡) $CHCl_3$.

calculated value. This could be due to slow interconversion between the growing species and dormant C−H terminals. To further control the molecular weight by enhancing the reversible deactivation process relative to propagation,[27] 2 equiv of 1,1-diphenylethanol (DPEOH) to KHMDS was added to the polymerizations under the conditions without ligands and with 18-crown-6 or (−)-**L1**. DPEOH was selected because it is a bulky alcohol and is unlikely to undergo undesirable transesterification in the side chains and initiation from the alkoxide. While the addition of DPEOH significantly retarded the polymerization, all of the resulting polymers exhibited unimodal SEC curves (Figures 1D−1F). The added DPEOH works as a reversible terminator, which not only reacts with the propagating anionic species to suppresses the fast polymerization but also reversibly forms the dormant C−H terminal to thereby control the molecular weight.[27] Although the dispersity was slightly large (Đ = 1.75) for the polymer obtained with (−)-**L1** owing to the slight lead in the SEC curve, those of the polymers obtained without ligands and with 18-crown-6 were small (Đ = 1.17 and 1.13, respectively).

The shapes of the ^{13}C NMR spectrum of the carbonyl carbons remained almost unchanged upon the addition of DPEOH in all cases (Figures 2D−F and S11 vs Figure 2A−C), indicating that addition of the alcohol allowed molecular weight control without significantly affecting the tacticity, which was mainly governed by the added ligands. The synthesis of high molecular weight polymer was investigated by increasing the feed ratio of MMA and **1** to 200 in the presence of 18-crown-6 and DPEOH at −20 °C (Figure S12). The resulting polymer also had a narrow dispersity (Đ = 1.25) and an M_n(SEC) of 19 000, close to the calculated value (M_n(calcd)) of 20 200. The ^{13}C NMR spectrum showed a higher syndiotacticity (*rr*/*mr*/*mm* = 63/33/4) (Figures S13 and S14) due to the lower polymerization temperature.

The terminal structures of the obtained polymers were analyzed by ^{1}H NMR. All spectra showed small peaks (*e* and *f*) assignable to the unit originating from **1** at the *α*- and *ω*-chain ends of the polymer chain in addition to large peaks (*a*, *b*, and *c*) of the PMMA main chains (Figure 3). The M_n values calculated from the ratio of the integral of the terminal phenyl proton peak (*e*) to that of the main-chain methyl ester proton peak (*c*) were in good agreement with those obtained by SEC, indicating the quantitative incorporation of **1** as an initiator and/or a CTA at the *α*-chain end. In addition, the MALDI-TOF-MS spectra of the polymers obtained with 18-crown-6 in the presence of DPEOH revealed that the main peaks were separated by the molar mass of MMA and agreed well with the theoretical values for the *α*- and *ω*-chain ends derived from **1** (Figure S15). These results indicate that anionic polymerization was initiated from **1**. Thus, dual control of the molecular weight and tacticity of PMMA was achieved with PTAP using **1** and KHMDS in the presence of appropriate ligands and alcohols.

One of the characteristic features of PTAP is that the resulting polymers can be isolated and used as macroinitiators or macro-CTAs because the chain ends consist of stable and similarly acidic C−H bonds.[27] Finally, the synthesis of stereoblock PMMA by sequential polymerization was inves-

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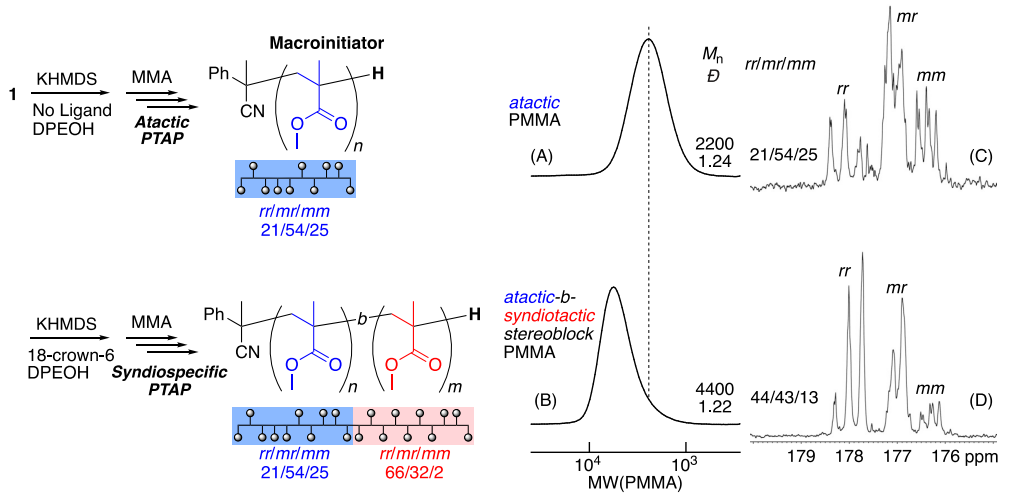

Figure 4. SEC curves (A and B) and ^{13}C NMR spectra ($CDCl_3$, 55 °C) (C and D) of atactic PMMA (A and C) and atactic-*b*-syndiotactic stereoblock PMMA (B and D): $[MMA]_0/[\mathbf{1}]_0/[KHMDS]_0/[DPEOH]_0$ = 750/30/5.0/10 mM in toluene at 0 °C. $[MMA]_0/[macroinitiator]_0/[KHMDS]_0/[18\text{-crown-6}]_0/[DPEOH]_0$ = 750/30/5.0/5.5/10 mM in toluene at 0 °C.

tigated under different conditions. As the first step, PTAP of MMA was carried out using **1** and KHMDS without ligands in conjunction with DPEOH in toluene at 0 °C, resulting in atactic PMMA with a controlled molecular weight (M_n = 2200, $Đ$ = 1.24, *rr*/*mr*/*mm* = 21/54/25) (Figures 4A, 4C, S16A, and S17A). The obtained atactic PMMA, which was purified via preparative high-performance liquid chromatography in size-exclusion mode, was subsequently used as a macroinitiator for syndiospecific PTAP of MMA using KHMDS with 18-crown-6. The second polymerization also smoothly proceeded such that the SEC curve shifted to the high-molecular-weight region while maintaining a narrow dispersity (M_n = 4400, $Đ$ = 1.22) (Figure 4B). This result indicates the success of the chain extension reaction of C−H bonds at the PMMA chain ends. After chain extension, the total *rr* content increased (*rr*/*mr*/*mm* = 44/43/13) (Figures 4D, S16B, and S17B). The tacticity of the second PMMA segment formed with 18-crown-6 was then calculated using the tacticity and the number-average degree of polymerization for each segment (n = 21, m = 22) (Figure S16). The triad value of the second segment was syndiotactic rich (*rr*/*mr*/*mm* = 66/32/2), which was close to that obtained under the same conditions as above. These results indicate the formation of atactic-*b*-syndiotactic stereoblock PMMA via sequential PTAP under different conditions using macroinitiators or macro-CTAs with different tacticities.

In conclusion, the tacticity of PMMA was tuned by adding ligands in PTAP of MMA using an acidic C−H compound as an initiator or a CTA and KHMDS as a base catalyst. Dual control of the tacticity and molecular weight in PTAP was thus achieved via the use of appropriate ligands and alcohols as reversible deactivators. Furthermore, synthesis of stereoblock PMMA was also achieved via sequential PTAP.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/prechem.4c00066.

Materials, experimental procedures, SEC curves, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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