

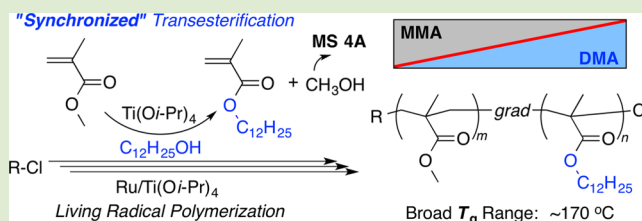
Synchronized Tandem Catalysis of Living Radical Polymerization and Transesterification: Methacrylate Gradient Copolymers with Extremely Broad Glass Transition Temperature

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S Supporting Information

ABSTRACT: Gradient copolymers with differential sequences linearly changing from methyl methacrylate (MMA) to dodecyl methacrylate (DMA) were efficiently synthesized by a concurrent tandem catalysis in the ruthenium-catalyzed living radical (co)polymerization coupled with the in situ transesterification of MMA with 1-dodecanol assisted by titanium isopropoxide [Ti(Oi-Pr)₄]. The key is to perfectly synchronize the two reactions throughout the tandem catalysis by using molecular sieves (MSs), which facilitates the MMA transesterification into DMA by removing the resulting methanol. The MMA/DMA gradient copolymers had an extremely broad glass transition temperature range (i.e., hardly detectable by differential scanning calorimetry (DSC)), in sharp contrast to the random and the block counterparts of similar compositions.



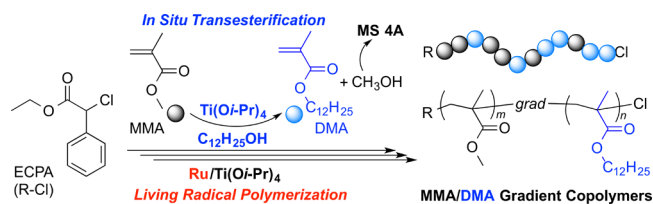
Gradient copolymers are a class of sequence-regulated copolymers where the differential comonomer composition along the backbone gradually and continuously changes from one terminal to the other.^{1–16} Owing to this particular sequence distribution, gradient copolymers often exhibit intriguing physical properties in the solid state and/or in solution and thus differ from the corresponding random and block copolymers.^{1,2,6–15} Typically, A–B gradient copolymers often exhibit broad glass transition temperature (T_g) for monomer pairs whose homopolymers have very different T_g .^{2,10–12} The breadth of the T_g range is dependent on not only comonomer combination but also their sequence distribution and the degree of polymerization (DP). Such polymeric materials with broad T_g range would be quite effective for vibration or acoustic damping.^{17,18}

In general, gradient copolymers have been obtained in living polymerization by the following two methods: the “spontaneous” gradient formation from two monomers with different reactivity^{4,7,8} and the “forced” gradient formation via a continuous feed of a second monomer into a living polymerization system of another (first) monomer.^{3,5,6,9–14} In radical polymerization, in particular, the two methodologies are often combined^{19–26} by taking advantage of facile cross-propagation, but this approach involves drawbacks such as limited monomer combinations and cumbersome procedures, sometimes spoiling the versatility of radical polymerization where a wide variety of monomers are applicable.

As a new, efficient, and versatile strategy for gradient copolymers, we have recently developed the concurrent tandem catalysis that combines the ruthenium-catalyzed living radical polymerization with the in situ transformation of an initially fed methacrylate (R_1MA) into another (R_2MA) via transesterification with an alcohol (R_2OH) and a metal alkoxide [Al(Oi-

Pr)₃, Ti(Oi-Pr)₄, etc.] (Scheme 1).^{15,16} In this system, these metal alkoxides, originally employed as polymerization

Scheme 1. MMA/DMA Gradient Copolymers via Synchronized Tandem Catalysis of Living Radical Polymerization and Transesterification



cocatalysts (additives),^{27,28} concurrently catalyze the transesterification²⁹ from R_1MA into R_2MA . The instantaneous comonomer composition thereby continuously changes from R_1MA alone to an R_2MA -rich mixture. The seamless change of the monomer composition is directly reflected in the instantaneous monomer-unit composition (gradient sequence distribution) because methacrylates usually have similar reactivity independent of the pendent ester alkyl group and because the transesterification takes place specifically for monomers.^{15,16}

Owing to the diversity of alcohols and methacrylates along with the catalytic control of monomer sequence, the tandem catalysis can potentially provide tailor-made gradient copolymers with wide comonomer combinations, as well as interesting

Received: September 18, 2013

Accepted: October 16, 2013

Published: October 21, 2013

sequences, from such common reagents as alcohols for polymeric functional materials.

Herein, we report the design of gradient copolymers via a well-synchronized tandem catalysis of living radical polymerization and the $\text{Ti}(\text{O}i\text{-Pr})_4$ -catalyzed in situ transesterification of MMA into dodecyl methacrylate (DMA) with 1-dodecanol and molecular sieves (MSs) (Scheme 1). It should be noted that MSs are newly employed to efficiently assist the transesterification into the latter monomer by removing the resulting methanol by absorption. The synchronized catalysis is of vital importance in achieving a linearly shifting sequence distribution from MMA into DMA along the backbone. Given a large difference in T_g between PMMA and PDMA (+116 and -52 °C, respectively), MMA/DMA gradient copolymers are expected to have a quite broad T_g range.² In fact, it was found that, in sharp contrast to random and block counterparts of the same composition, MMA/DMA gradient copolymers with a linear sequence change have an extremely broad glass transition breadth (ΔT_g), showing virtually no detectable DSC transition signals.

For MMA/DMA gradient copolymers, concurrent tandem polymerization of MMA (2.0 M) was examined with $\text{Ru}(\text{Ind})\text{Cl}(\text{PPh}_3)_2$, $\text{Ti}(\text{O}i\text{-Pr})_4$, and ethyl 2-chloro-2-phenylacetate (ECPA) in toluene/1-dodecanol (1/1 v/v, $[\text{1-dodecanol}]_0 = 1.7$ M) at 80 °C (Figures 1 and 2, Table 1,

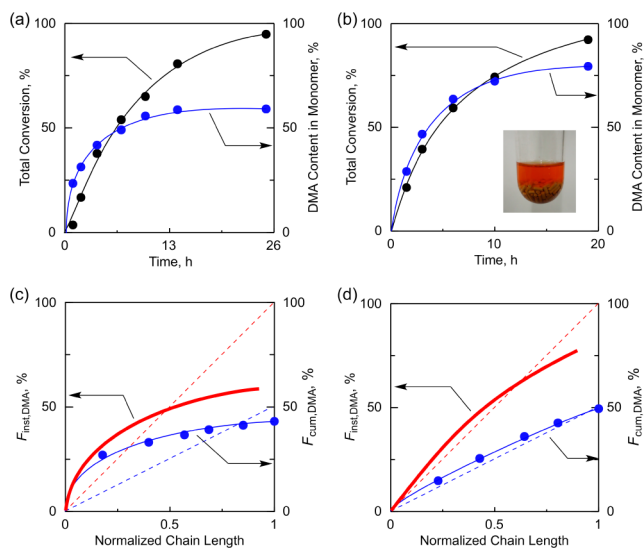


Figure 1. Effects of MS 4A on concurrent tandem living radical polymerization for MMA/DMA gradient copolymers: (a, b) total monomer conversion and DMA content in monomer; (c, d) cumulative ($F_{\text{cum,DMA}}$) and instantaneous ($F_{\text{inst,DMA}}$) DMA content in products; $[\text{MMA}]_0/[\text{ECPA}]_0/[\text{Ru}(\text{Ind})\text{Cl}(\text{PPh}_3)_2]/[\text{Ti}(\text{O}i\text{-Pr})_4]_0 = 2000/20/2.0/(a, c) 20$ or (b, d) 5.0 mM (a, c) without or (b, d) with MS 4A (0.33 g/mL) in toluene/1-dodecanol (1/1 v/v, $[\text{1-dodecanol}]_0 = 1.7$ M) at 80 °C. Inset picture in (b): tandem polymerization with MS 4A.

and Figures S2–S5, Supporting Information). Polymerization efficiently proceeded in high yield to give a well-controlled polymer with narrow molecular weight distribution (a typical result with Ti of 20 mM: total conversion = 95%; 25 h; $M_n = 15\,000$ and $M_w/M_n = 1.25$ by size-exclusion chromatography (SEC) in CHCl_3 ; Table 1, entry 7, Figure 1a,c).

In situ transesterification and the gradient sequence in polymer were analyzed by proton nuclear magnetic resonance

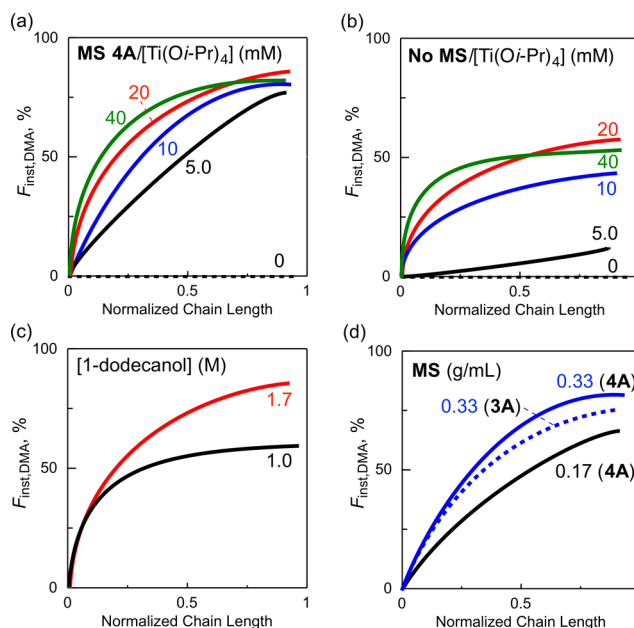


Figure 2. Effects of reaction conditions on $F_{\text{inst,DMA}}$ of MMA/DMA gradient copolymers ($DP = 100$). (a) $\text{Ti}(\text{O}i\text{-Pr})_4$ (0, 5, 10, 20, 40 mM), 1-dodecanol (1.7 M) with MS 4A (0.33 g/mL). (b) $\text{Ti}(\text{O}i\text{-Pr})_4$ (0, 5, 10, 20, 40 mM), 1-dodecanol (1.7 M) without MS 4A. (c) $\text{Ti}(\text{O}i\text{-Pr})_4$ (20 mM), 1-dodecanol (1.7, 1.0 M) with MS 4A (0.33 g/mL). (d) $\text{Ti}(\text{O}i\text{-Pr})_4$ (10 mM), 1-dodecanol (1.7 M) with MS 4A (0.33, 0.17 g/mL) or MS 3A (0.33 g/mL).

(^1H NMR) spectroscopy. The DMA content in the polymerization solution gradually increased (Figure 1a: blue symbols). The cumulative and the instantaneous DMA content in polymer ($F_{\text{cum,DMA}}$ and $F_{\text{inst,DMA}}$, respectively) increased with the normalized chain length, while virtually identical to total conversion (Figure 1c), where the normalized chain length is defined as DP_t/DP_{final} for living copolymers; $DP_t = [\text{MMA}]_0 \times (\text{total conversion}/100)/[\text{ECPA}]_0$; $DP_{\text{final}} = [\text{MMA}]_0 \times (\text{total final conversion}/100)/[\text{ECPA}]_0$. Separate model reactions further support that Ti-mediated transesterification with 1-dodecanol was perfectly selective for MMA in the presence of MMA oligo(poly)mers (DP : 6, 100), while ECPA was also transformed into dodecyl 2-chloro-2-phenylacetate (Figure S1, Supporting Information). Thus, a gradient copolymer from MMA to DMA was actually obtained.

It turned out, however, that the instantaneous composition ($F_{\text{inst,DMA}}$) does not change linearly along the polymer backbone; i.e., $F_{\text{inst,DMA}}$ increases sharply at the beginning of the reaction [or at the vicinity of the initiating terminal (α -end)] but more moderately as the reaction is retarded at about 60% conversion. This sequence–distribution shift along the backbone directly reflects time-dependent changes in the instantaneous comonomer composition in the reaction mixture. Namely, the in situ transesterification of MMA into DMA was faster than the copolymerization of the monomers during the early phases (total conversion below 40%) but sharply slowed down and almost stopped beyond conversion over 50% (Figure 1a: black versus blue plots).

Though the final $F_{\text{cum,DMA}}$ and the initial $F_{\text{inst,DMA}}$ indeed increased with increasing concentration of $\text{Ti}(\text{O}i\text{-Pr})_4$ (from 5.0 to 40 mM; Table 1, entries 5–8; Figure S2, Supporting Information), the retardation of $F_{\text{inst,DMA}}$ beyond the middle reaction stage was inevitable (Figure 2b), indicating that the

Table 1. MMA/DMA Gradient Copolymers Obtained from Concurrent Tandem Living Radical Polymerization^a

entry	DP	[Ti(Oi-Pr) ₄] ₀ (mM)	[1-dodecanol] ₀ (M)	MS	MS (g/mL)	time (h)	conv. ^b (%)	M _n ^c	M _w /M _n ^c	F _{cum,DMA} ^d	F _{inst,DMA} ^d
1	100	5.0	1.7	4A	0.33	19	92	19000	1.36	50	77
2	100	10	1.7	4A	0.33	25	95	17700	1.45	61	80
3	100	20	1.7	4A	0.33	14	95	17900	1.42	68	85
4	100	40	1.7	4A	0.33	22	98	23100	1.37	72	82
5	100	5.0	1.7	–	–	22	90	14500	1.27	7	13
6	100	10	1.7	–	–	25	95	14300	1.26	35	44
7	100	20	1.7	–	–	25	95	15000	1.25	45	59
8	100	40	1.7	–	–	34	94	18700	1.22	48	53
9	100	20	1.0	4A	0.33	33	89	18200	1.28	51	59
10	100	10	1.7	4A	0.17	24	93	16900	1.30	45	66
11	100	10	1.7	3A	0.33	22	90	18500	1.38	56	77
12	400	5.0	1.7	4A	0.33	19	91	68500	1.38	54	80
13	400	20	1.7	–	0.33	24	93	84800	1.38	41	52

^a[MMA]₀/[ECPA]₀/[Ru(Ind)Cl(PPh₃)₂]₀/[Ti(Oi-Pr)₄]₀ = 2000/20/2.0 (entries 1–11) or 0.5 (entries 12, 13)/5.0–20 mM with or without MS 4A (or 3A) in toluene/1-dodecanol at 80 °C. ^bTotal monomer conversion: determined by ¹H NMR with an internal standard. ^cDetermined by SEC in CHCl₃ with a PMMA standard calibration. ^dCumulative DMA content (F_{cum,DMA}) and instantaneous DMA content (F_{inst,DMA}) in final products.

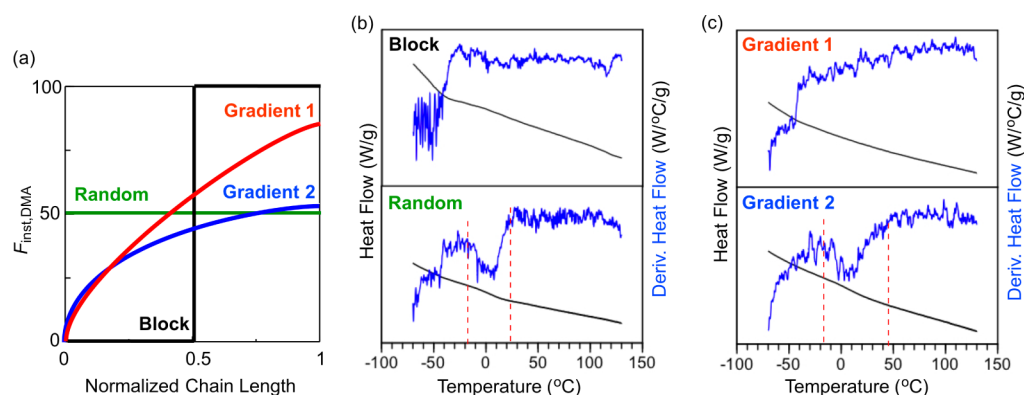


Figure 3. (a) Sequence distribution of MMA/DMA copolymers employed for DSC measurements (DP = 400, Block, Random, **Gradient 1**: entry 12, **Gradient 2**: entry 13). DSC heating curves (black line) and the first derivatives of DSC heating curves (blue line) with temperature for (b) **Block** and **Random** and (c) **Gradient 1** and **Gradient 2**.

increased Ti(Oi-Pr)₄ concentration could accelerate the transesterification just in the early phases of polymerization alone. This is because, under these conditions, the transesterification is reversible and soon reaches equilibrium well before the MMA–DMA copolymerization has been completed.

To enhance DMA formation, or to shift the MMA–DMA transformation equilibrium far to the latter monomer, we employed molecular sieves (MS 4A or 3A) that would remove the resulting methanol by absorption during the transesterification.^{30,31} In fact, separate experiments showed that MS 4A efficiently accelerated the transesterification of MMA into DMA (Figure S1, Supporting Information). Thus, for example, the concurrent tandem polymerization starting from MMA with Ru(Ind)Cl(PPh₃)₂, Ti(Oi-Pr)₄, and 1-dodecanol was examined in the presence of MS 4A (nominal concentration 0.33 g/mL) (see the inset picture in Figure 1b); note that herein the alkoxide concentration was kept rather low (5 mM) relative to the standard conditions (20 mM; see above).

The use of MS 4A at a low Ti(Oi-Pr)₄ concentration almost perfectly synchronized polymerization and transesterification throughout the tandem catalysis (Figure 1b), to produce a well-controlled gradient copolymer with sequence distribution linearly changing from MMA to DMA (Figure 1d and Table 1, entry 1; total conversion = 92%; 19 h; M_n = 19 000; M_w/M_n = 1.36; F_{cum,DMA} = 50; F_{inst,DMA} = 77%). Without the methanol

absorbent, in contrast, in situ transesterification hardly proceeded with such a low Ti(Oi-Pr)₄ concentration (Figure 2b, Table 1, entry 5). Another finding with the use of molecular sieves was that gradient copolymers rich in DMA content from the initiating terminal (F_{cum,DMA} = ~70%; F_{inst,DMA} = ~85%) can be obtained by increasing Ti(Oi-Pr)₄ concentration from 10 to 40 mM, where 82% of 1-dodecanol was incorporated into DMA (Figure 2a; Table 1, entries 2–4). In this tandem catalysis, the tuning of Ti(Oi-Pr)₄ concentration and the use of MS are almost independent of polymerization rate and controllability to conveniently afford the control of gradient sequence on demand.

The gradient sequence can also be controlled by the amount of MS 4A or 3A. For example, decreasing MS 4A from 0.33 to 0.17 g/mL reduced F_{inst,DMA} (Figure 2d, Table 1, entries 10 and 11; Figure S5, Supporting Information). These results demonstrate that molecular sieves efficiently and selectively entrap methanol in the presence of various chemical reagents in our tandem catalysis.

The gradient monomer sequence could also be controlled by decreasing the amount of 1-dodecanol from 1.72 to 1 M (Figure 2c; Table 1, entry 9; with MS 4A). In this case, the in situ transesterification into DMA hardly proceeded beyond the middle stages of the tandem catalysis; thus F_{inst,DMA} remained unchanged with normalized chain length above 0.5 (Figure S4, Supporting Information), where 1-dodecanol was converted

into DMA almost completely (~91%). The product was therefore a virtual block copolymer consisting of a gradient-sequence segment from the α -end to the middle point and a random-sequence segment from the middle to the ω -end (Figure 2c).

To investigate effects of gradient sequence distribution on copolymers' thermal properties, MMA/DMA gradient copolymers were analyzed by DSC, in comparison to the random and the block counterparts (Figure 3). For this, we prepared two samples of MMA/DMA copolymers with total DP of 400: One sample had a sequence distribution linearly changing from MMA to DMA over the backbone from the α -end to the ω -end, obtained from the well-synchronized catalysis with MS 4A as discussed above (**Gradient 1**: $M_n = 68\,500$; $M_w/M_n = 1.38$; $F_{\text{cum,DMA}} = 54\%$; $F_{\text{inst,DMA}} = 80\%$; Table 1, entry 12). The second sample had a retarded DMA distribution obtained without MS 4A, where the DMA content in the segment closer to the ω -end is smaller than in the first sample and slightly richer near the α -end (**Gradient 2**: $M_n = 84\,800$; $M_w/M_n = 1.38$; $F_{\text{cum,DMA}} = 41\%$; $F_{\text{inst,DMA}} = 52\%$; Table 1, entry 13).

As seen in the heat flow charts (heating rate $10\text{ }^\circ\text{C}/\text{min}$, Figure 3c, black lines), **Gradient 1** did not show a clear T_g , whereas **Gradient 2** seemed to have a broad T_g range. In contrast, the corresponding random copolymer (**Random**: $M_n = 56\,800$; $M_w/M_n = 1.19$; $F_{\text{cum,DMA}} = 51\%$) had one T_g at $6\text{ }^\circ\text{C}$, and the block counterpart (**Block**: $M_n = 64\,400$; $M_w/M_n = 1.36$; $F_{\text{cum,DMA}} = 50\%$) showed two T_g 's at $-52\text{ }^\circ\text{C}$ for DMA and $116\text{ }^\circ\text{C}$ for MMA (Figure 3b), both identical to those for their homopolymers.

The difference in thermal properties was more visible in the first derivatives of heating curves (the blue lines in Figures 3b and 3c). **Gradient 2** clearly showed a signal originating from glass transition, and the width ($\Delta T_g = \sim 65\text{ }^\circ\text{C}$) was larger than that for **Random** ($\Delta T_g = \sim 40\text{ }^\circ\text{C}$). **Gradient 1** in turn hardly showed glass transition. However, the T_g range for **Gradient 1** apparently spread over 170° , due to the difference in T_g between MMA ($116\text{ }^\circ\text{C}$) and DMA ($-52\text{ }^\circ\text{C}$) homopolymers. Therefore, "synchronized" gradient MMA/DMA copolymerization afforded unique polymeric materials with an extremely broad T_g range resulting from a sequence distribution almost linearly changing along the backbone from α - to ω -ends.

In conclusion, we have successfully achieved sequence control of MMA/DMA gradient copolymers via concurrent tandem catalysis of the ruthenium-catalyzed living radical polymerization and the in situ transesterification of MMA with $\text{Ti}(\text{O}i\text{-Pr})_4$ and 1-dodecanol. Importantly, the combination of molecular sieves and a small amount of $\text{Ti}(\text{O}i\text{-Pr})_4$ induced well-synchronized catalysis, to give MMA/DMA gradient copolymers with the sequence distribution linearly changing from MMA to DMA along the backbone. These gradient copolymers turned out to have an extremely large breadth of T_g and thus would be potentially attractive as vibration or acoustic damping materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, time–conversion curves, monomer composition analysis in polymers, and SEC data for the present study are given. 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.

■ ACKNOWLEDGMENTS

This research was supported by the Ministry of Education, Science, Sports and Culture through a Grant-in-Aid for Scientific Research (A: 24245026) and Young Scientist (B) (No.24750104) and by Mizuho Foundation for the Promotion of Sciences, for which T.T. is grateful. We also thank Prof. Rintaro Inoue and Prof. Daichi Ida (Department of Polymer Chemistry, Kyoto University) for helpful discussion about DSC measurements.

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