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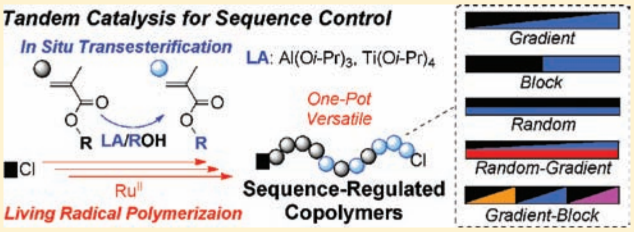
Sequence-Regulated Copolymers via Tandem Catalysis of Living Radical Polymerization and In Situ Transesterification

Kazuhiro Nakatani, Yusuke Ogura, Yuta Koda, Takaya Terashima,* and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Supporting Information



ABSTRACT: Sequence regulation of monomers is undoubtedly a challenging issue as an ultimate goal in polymer science. To efficiently produce sequence-controlled copolymers, we herein developed the versatile tandem catalysis, which concurrently and/or sequentially involved ruthenium-catalyzed living radical polymerization and in situ transesterification of methacrylates (monomers: RMA) with metal alkoxides (catalysts) and alcohols (ROH). Typically, gradient copolymers were directly obtained from the synchronization of the two reactions: the instantaneous monomer composition in feed gradually changed via the transesterification of R_1MA into R_2MA in the presence of R_2OH during living polymerization to give R_1MA/R_2MA gradient copolymers. The gradient sequence of monomers along a chain was catalytically controlled by the reaction conditions such as temperature, concentration and/or species of catalysts, alcohols, and monomers. The sequence regulation of multimonomer units was also successfully achieved in one-pot by monomer-selective transesterification in concurrent tandem catalysis and iterative tandem catalysis, providing random-gradient copolymers and gradient-block counterparts, respectively. In contrast, sequential tandem catalysis via the variable initiation of either polymerization or in situ transesterification led to random or block copolymers. Due to the versatile adaptability of common and commercially available reagents (monomers, alcohols, catalysts), this tandem catalysis is one of the most efficient, convenient, and powerful tools to design tailor-made sequence-regulated copolymers.

■ INTRODUCTION

Natural polymers such as proteins, enzymes, and genes own perfectly controlled primary structures. Therein the sequence regulation of repeat units (monomers) along the main chain, or the spatial placement of functionality, is a key factor to create their exquisite functions like efficient and selective catalysis and transmission of genetic information. In synthetic polymers, recent development of precision polymerization such as living radical polymerization[1−8] has allowed us to control most of their primary structures including molecular weight, molecular weight distribution, terminal structure, and three-dimensional architectures. The sequence regulation along a single polymer chain is, however, still a remaining and challenging issue among the ultimate goals for polymer synthesis.[9] Besides conventional random, alternating, and gradient copolymerizations, some new approaches to sequence regulation are quite recently emerging:[9] (1) the iterative in situ addition of monomers in living polymerization;[3c,10,11] (2) the polymerization of templated multifunctional monomers;[12,13] (3) the selective radical addition of monomers with template initiators carrying recognition units;[14] and (4) the selective single addition of non or less-homopolymerizable monomers and the post-modification of the pendant groups to generate reactive terminals for the next monomer addition.[15,16] Though promising and elegant, these methodologies often involve multistep procedures or elaborate syntheses of substrates and monomers.

The catalysis and synthesis for designed functional materials should be, ideally, efficient, convenient, and versatile with the use of common reagents. In terms of efficiency and convenience, tandem catalysis[17] is among these to realize multiple reactions that proceed sequentially and/or concurrently in one-pot without any isolation of intermediates. Tandem strategies have been actually applied to precision polymerizations in conjunction with hydrogenation,[18] racemization,[19] click reaction,[20] and other polymerization systems.[21−23] Recent examples in this line include metal-catalyzed living radical polymerization, where the high tolerance of selected catalysts toward functional groups leads to a variety of designed functional polymers.[1−4] For example, ruthenium catalysts achieves the synthesis of well-defined functional (co)polymers in alcohol[24] and in aqueous media.[25] In these systems, cocatalysts (additives)[26,27] are often employed as key players to control the catalysis, typically metal alkoxides such as Al(O*i*-Pr)$_3$ and Ti(O*i*-Pr)$_4$.[25a,26] As is well-known in organic chemistry, such metal alkoxides also catalyze the transesterification of carboxylate esters in the presence of alcohols: $RCOOR_1 + R_2OH \rightarrow RCOOR_2 + R_1OH$ (R, R_1, R_2 = alkyl).[28−31]

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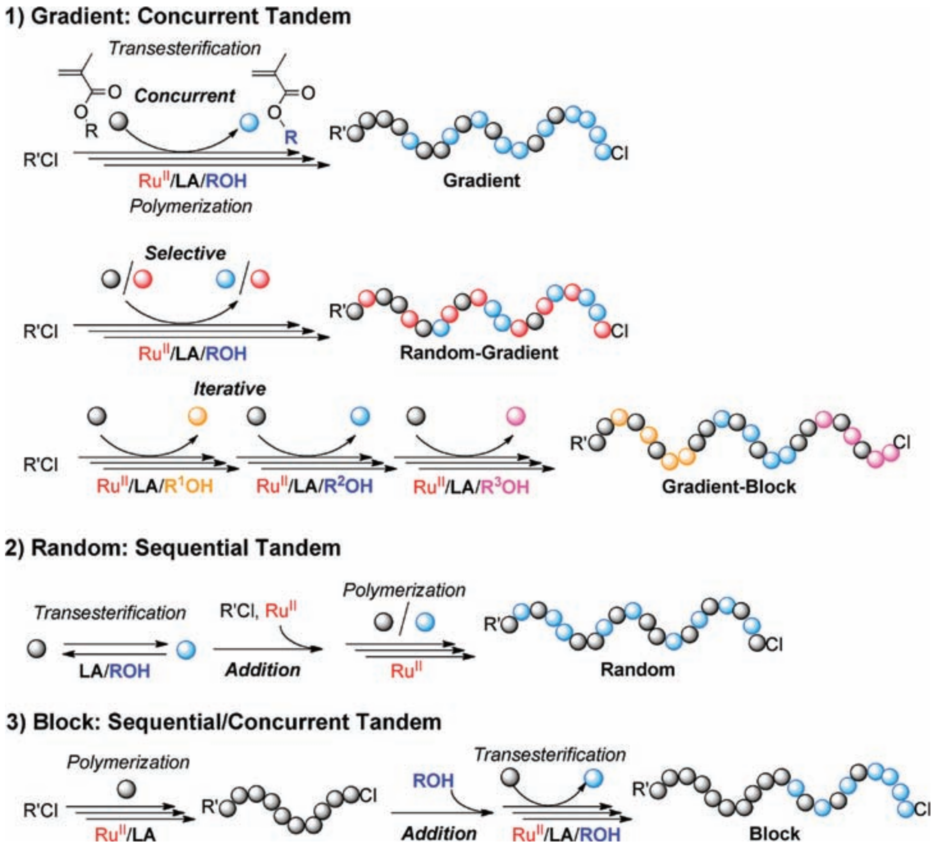
Scheme 1. Sequence-Controlled Copolymers via Tandem Catalysis of Ruthenium-Catalyzed Living Radical Polymerization and In Situ Metal Alkoxide-Catalyzed Transesterification



Transesterification is conventional, however, quite powerful to produce ester-compounds in not only laboratory uses but also industrial fields.

We have quite recently combined these two features of our metal-assisted polymerization (alcohols as solvent and the dual roles of metal alkoxides) to develop a novel concurrent tandem catalysis for gradient copolymerization, in which a metal alkoxide not only works as a cocatalyst for promoting propagation but also concurrently catalyzes in situ monomer transformation that in turn provides a second monomer for the copolymerization (Scheme 1).[31] Typical systems involve a metal alkoxide and an alcohol solvent (ROH) in ruthenium-catalyzed living radical polymerization of methyl methacrylate (MMA). Under selected conditions, the dual catalysis by the alkoxide renders the propagation and the monomer transformation "synchronized", thereby the instantaneous comonomer composition in feed changes gradually while living copolymerization proceeds, to give gradient copolymers. Importantly, the selective transesterification of the pendent esters of monomers in the presence of the polymers is mandatory for the successful gradient copolymerization. This tandem catalysis is categorized as the new method to catalytically induce gradient copolymerization in one pot, clearly apart from the following conventional two methods:[32−36] (1) spontaneous gradient copolymerization via the different reactivity of comonomers (i.e., copolymerization of methacrylates and acrylates);[33] (2) gradient copolymerization via the continuous feeding of a second monomer to change the comonomer composition in the solution.[34] Due to the gradual change of comonomer composition along a chain, gradient copolymers turn to be attractive materials with unique properties in solution[31,35] and solid state,[31,36] different from random and block counterparts. The conventional methods may be, however, applicable to a limited range of comonomers of different reactivity (not frequent in radical polymerization) and may require cumbersome procedures such as continuous feed of comonomers.

Herein, we report the synthesis of sequence-regulated copolymers via tandem catalysis that consists of metal alkoxides-mediated transesterification of methacrylates with alcohols and ruthenium-catalyzed living radical polymerization of their comonomers (Scheme 1). Discussion was first directed to the catalytic control of the monomer sequence in gradient copolymers via reaction temperature and species and/or concentration of metal alkoxides (cocatalyst), monomers, and alcohols. Thanks to the high versatility and controllability, the tandem catalysis further applied to the one-pot synthesis of multisequence-regulated copolymers such as random-gradient copolymers and gradient-block counterparts, that were difficult to be prepared before now without any preparation and isolation of comonomers and/or prepolymers. Random and block copolymers were also facilely obtained from the control of the initiation timing of tandem catalysis.

■ RESULTS AND DISCUSSION

Transesterification for Tandem Catalysis. We have recently found that gradient copolymers are obtained from concurrent tandem catalysis consisting of living radical polymerization and in situ monomer transesterification.[31] In principle, the efficient preparation involves the following factors:

(i) Transesterification is selectively active for monomers and inert for the polymers, or much more active for monomers than the polymers, independent of polymerization stage (monomer concentration) (ii) Transesterification and the cocatalyst never deactivate or retard living radical copolymerization. (iii) The transesterification of a precursor monomer into a second monomer is kinetically synchronized with the copolymerization of the two monomers. Thus, we first examined the factor (i) and (ii) on the transesterification of methyl methacrylate (MMA) and poly(MMA)s with metal catalysts and ethanol (EtOH).

Aluminum and titanium isopropoxides, Al(O*i*-Pr)$_3$ and Ti(O*i*-Pr)$_4$, originally work as cocatalysts for ruthenium-catalyzed living radical polymerization.[1,26] Focused on the adaptability with regard to factor (ii), Al(O*i*-Pr)$_3$ and Ti(O*i*-Pr)$_4$ were employed as catalysts for the transesterification of MMA in EtOH/toluene (1/1, v/v) at 80 °C (Figure 1A). The concentration of MMA ([MMA]$_0$) was set as 20 or 2000 mM, and that of the catalysts ([Al(O*i*-Pr)$_3$ or Ti(O*i*-Pr)$_4$]$_0$) was as 20 mM. Both catalysts efficiently transformed MMA into ethyl methacrylate (EMA), independent of MMA concentration (20 or 2000 mM). This result suggests that the in situ transesterification of MMA should efficiently proceed even in the latter stage of concurrent tandem catalysis. Ti(O*i*-Pr)$_4$ was much more active than Al(O*i*-Pr)$_3$ (faster reaction, higher yield).

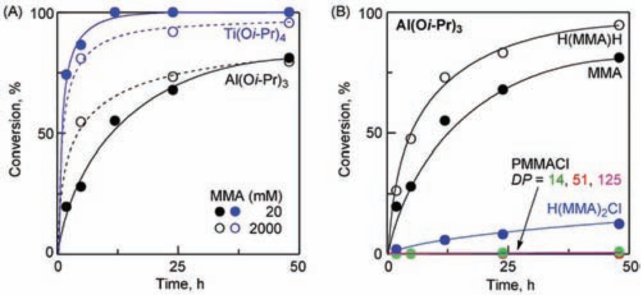


Figure 1. (A) Transesterification of MMA catalyzed by Al(O*i*-Pr)$_3$ (black) or Ti(O*i*-Pr)$_4$ (blue) with EtOH: [MMA]/[Al(O*i*-Pr)$_3$ or Ti(O*i*-Pr)$_4$]$_0$ = 20 (filled circles) or 2000 (open circles)/20 mM in toluene/EtOH (1/1, v/v) at 80 °C. (B) Al(O*i*-Pr)$_3$-catalyzed transesterification of methyl isobutyrate [H(MMA)H], H(MMA)$_2$Cl, PMMACls (DP = 14, 51, 125) with EtOH: [H(MMA)H or H(MMA)$_2$Cl or PMMACl]$_0$/[Al(O*i*-Pr)$_3$]$_0$ = 20/20 mM in toluene/EtOH (1/1, v/v) at 80 °C.

Factor (i) was further evaluated by Al(O*i*-Pr)$_3$/EtOH-mediated transesterification of a MMA dimer chloride [H(MMA)$_2$Cl] and chlorine-capped MMA homopolymers (PMMACls) with different degree of polymerization (*DP*) (*DP* = [MMA units]/[PMMACl] = 14, 51, 125) (Figure 1B). The concentration of PMMACl chains and H(MMA)$_2$Cl was kept constant ([PMMACl or H(MMA)$_2$Cl]$_0$ = 20 mM), which faithfully correspond to the concentration of gradient copolymers formed in tandem catalysis. Tacticity on polymers often affects reactivity on the post modification of the side chains.[37] Thus, the PMMACls were synthesized by the same Ru(Ind)Cl(PPh$_3$)$_2$-catalyzed living radical polymerization [without Al(O*i*-Pr)$_3$ and EtOH] as that employed for tandem catalysis, giving the tacticity (*mm*/*mr*/*rr* ~ 4/37/59) presumably identical to that of gradient copolymers.

All of the PMMACls (*DP* > 14) were indeed inert and the MMA dimer was also almost inactive, while methyl isobutyrate [H(MMA)H, a saturated ester of one MMA unit] and MMA were smoothly transformed into ethyl isobutyrate [H(EMA)H] and EMA, respectively. Ti(O*i*-Pr)$_4$ also never induced the transesterification of PMMACl (*DP* = 125) with EtOH. Methyl ester groups on PMMACls are sterically hindered by methacrylate backbones and neighboring side chains, which would prevent catalysts accessing the esters. The inert reactivity of PMMACls, obtained with living radical polymerization, is a crucial factor to produce gradient copolymers via the objective concurrent tandem catalysis with in situ transesterification.

In sharp contrast to PMMACls, a poly(methyl acrylate) (*DP* = 100) was transesterified by metal alkoxides [Al(O*i*-Pr)$_3$ or Ti(O*i*-Pr)$_4$] in the presence of EtOH (Figure S1). This is probably because polyacrylates have no α-methyl groups on the backbones to be more flexible and less hindered than polymethacrylates. Additionally, other Lewis acids including tin(IV), zinc chlorides ($SnCl_4$, $ZnCl_2$), boron trifluoride diethyl etherate (BF_3OEt), and aluminum, antimony(III), iron(III) oxides (Al_2O_3, Sb_2O_3, and Fe_2O_3), except for titanium(IV) chlorides ($TiCl_4$), were not effective as cocatalysts for the transesterification of MMA with EtOH (Figure S2). From these results, it was found that the aluminum and titanium alkoxides are the most suitable catalysts for in situ transesterification of MMA.

Concurrent Tandem Catalysis for Gradient Copolymers. Metal alkoxide-catalyzed transesterification of methacrylates (R_1MA) with alcohols (R_2OH) undergoes an equilibrium process, in which R_1MA is efficiently transformed into R_2MA and R_1OH in the presence of excess amounts of alcohols (R_2OH).[28] Thus, we systematically investigated reaction conditions in terms of temperature, concentration and/or species of catalysts, alcohols, and monomers, to catalytically control the monomer sequences in gradient copolymers via concurrent tandem catalysis with in situ monomer transesterification.

Effects of Temperature. We first examined effects of reaction temperature on the monomer sequences of MMA/EMA gradient copolymers (Figure 2, Table 1 entries 1−4). MMA was polymerized with a ruthenium catalyst [Ru(Ind)Cl(PPh$_3$)$_2$, Ind = η^5-C_9H_7][26b] and a chloride initiator (ECPA: ethyl 2-chloro-2-phenylacetate) in the presence of Al(O*i*-Pr)$_3$[26] as a catalyst for the transesterification of MMA and a cocatalyst for the polymerization in EtOH/toluene mixture (1/1, v/v) at various temperatures (40, 50, 60, and 80 °C). The degree of polymerization (*DP* = [MMA]$_0$/[ECPA]$_0$) was set as 100.

As shown in Figure 2, panels A and C, polymerization smoothly proceeded up to over 90% conversion at all the temperatures to give well-controlled polymers ($M_n \approx 10000$) with narrow molecular weight distribution (MWD, M_w/M_n = 1.2−1.4). The controllability was independent of the temperature, though the polymerization rate decreased with decreasing temperature. The polymerization solutions were analyzed by proton nuclear magnetic resonance (^{1}H NMR) to directly determine both EMA contents in monomers and those in products.[31] Figure 2B shows EMA contents in monomers (100[EMA]$_t$/[MMA]$_t$ + [EMA]$_t$) as a function of total monomer conversion. EMA was gradually generated in solutions by the in situ transesterification of MMA at over 50 °C as polymerization proceeded. The EMA contents increased in whole processes with increasing reaction temperature. This tendency is fully consistent with the separate transesterification of MMA with Al(O*i*-Pr)$_3$ and EtOH (Figure S3).

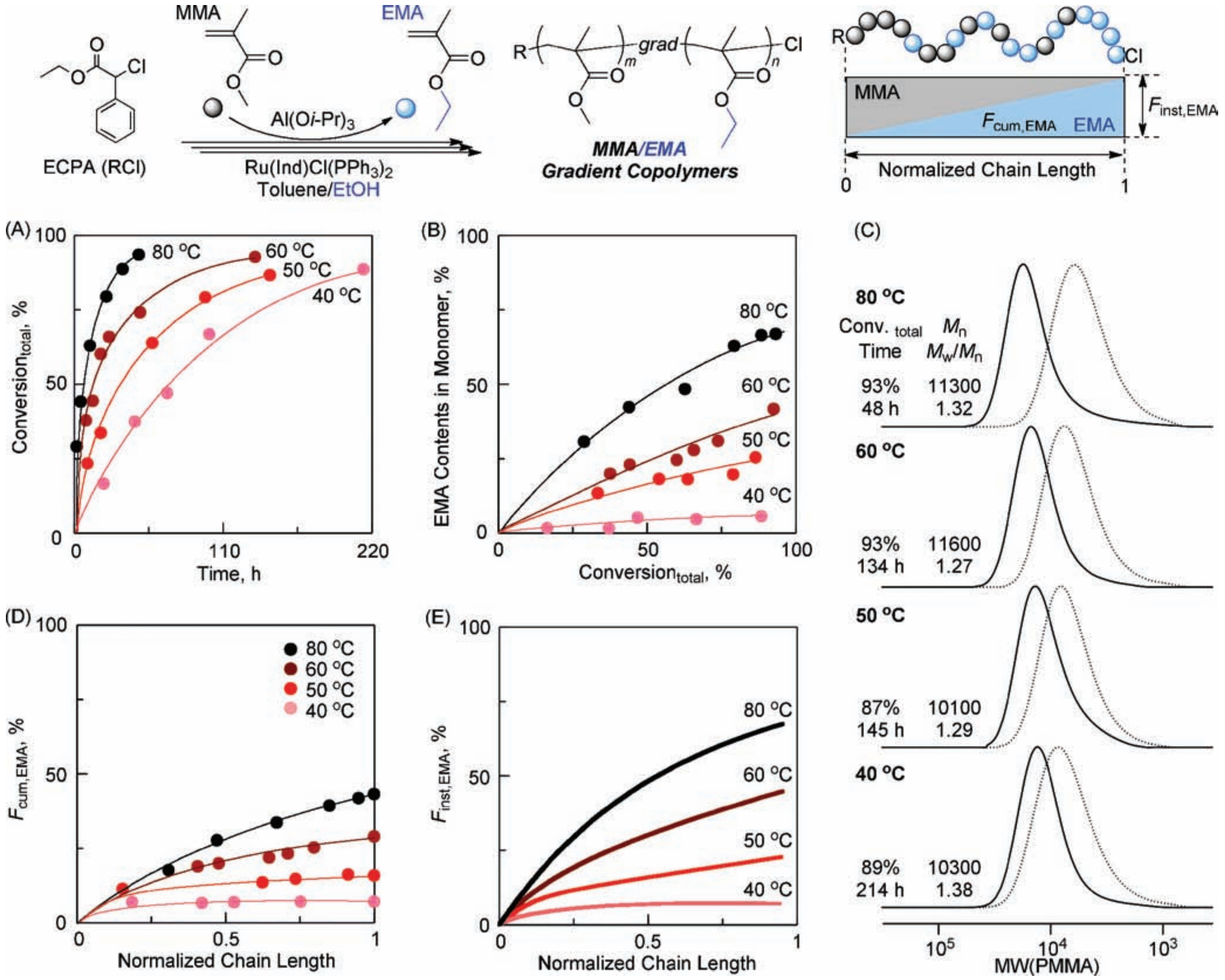


Figure 2. Effects of reaction temperature on MMA/EMA gradient copolymers obtained from tandem catalysis of ruthenium-catalyzed living radical polymerization and in situ transesterification of MMA with Al(O*i*-Pr)$_3$ and EtOH: (A) total monomer conversion as a function of reaction time; (B) EMA contents in monomer as a function of total monomer conversion; (C) SEC curves of products (dash lines: products at 30−50% conversion); (D) cumulative EMA contents ($F_{cum,EMA}$); and (E) instantaneous EMA contents ($F_{inst,EMA}$) in products as a function of normalized chain length; [MMA]$_0$/[ECPA]$_0$/[Ru(Ind)Cl(PPh$_3$)$_2$]$_0$/[Al(O*i*-Pr)$_3$]$_0$ = 2000/20/2.0/20 mM in toluene/EtOH (1/1, v/v) at 40, 50, 60, and 80 °C.

To discuss the sequence distribution of monomers in products from the α-end (an initiating fragment, R) to the ω-end (a terminal halogen, Cl) along a chain, we plotted cumulative EMA contents in gradient copolymers ($F_{cum,EMA}$) and instantaneous EMA contents in counterparts ($F_{inst,EMA}$) as a function of normalized chain lengths in Figure 2, panels D and E, respectively.[31−34] $F_{cum,EMA}$ was determined by ^{1}H NMR from the signal intensity ratio of EMA units in products.[31] $F_{inst,EMA}$ was in turn calculated from the following equation: $F_{inst,EMA} = [\mathrm{Conv}_{total,i}F_{cum,EMA,i} - \mathrm{Conv}_{total,i\text{-}1}F_{cum,EMA,i\text{-}1}]/[\mathrm{conv}_{total,i} - \mathrm{conv}_{total,i\text{-}1}]$, where conv$_{total}$ is the total conversion of both monomers (MMA and EMA).[31,32,34b] It should be noted that $F_{inst,EMA}$ curves as a function of normalized chain length (Figure 2E) virtually shows true gradient profiles along a chain in contrast to $F_{cum,EMA}$.

$F_{cum,EMA}$ and $F_{inst,EMA}$ gradually increased with increasing normalized chain length at over 50 °C, meaning that EMA contents in copolymers gradually increased and MMA counterparts in turn decreased from the α-end to the ω-end. As well as EMA contents in monomers, both $F_{cum,EMA}$ and $F_{inst,EMA}$ increased in entire processes with increasing reaction temperature [Table 1, $F_{cum,EMA}$ at ~90% conv$_{total}$ = 6% (40 °C), 16% (50 °C), 29% (60 °C), and 43% (80 °C)]. Gradient copolymers obtained at 80 °C typically had about 70% of $F_{inst,EMA}$ adjacent to the ω-end (Figure 2E). More importantly, the $F_{inst,EMA}$ curves obtained at 40−80 °C were fully consistent with the respective EMA contents in monomers (Figure 2, panels B and E). This result strongly supports that the gradient distribution of EMA in copolymers is just controlled by EMA contents in monomers: i.e. the propagating radicals of polymer chains react with MMA or EMA on the basis of their composition in solutions at the moment due to the identical reactivity of MMA and EMA in radical copolymerization.[31,38] Incorporation of EMA units into all polymer chains was further confirmed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) (Figure S4).

Table 1. RMA/EMA Gradient Copolymers Obtained from Concurrent Tandem Catalysis of Living Radical Polymerization and In Situ Transesterification of RMA with Metal Alkoxides and EtOH[a]

entry	RMA	$M(OR)_n$	$[M(OR)_n]_0$ (mM)	$[EtOH]_0$ (M)	temp. (°C)	time (h)	$Conv_{total}$ (%)[b]	M_n[c]	M_w/M_n[c]	$F_{cum,RMA}/F_{cum,EMA}$ (%/%)[b]
1	MMA	Al(O*i*-Pr)$_3$	20	6.5	40	214	89	10 300	1.38	94/6
2	MMA	Al(O*i*-Pr)$_3$	20	6.5	50	145	87	10 100	1.29	84/16
3	MMA	Al(O*i*-Pr)$_3$	20	6.5	60	134	93	11 600	1.27	71/29
4	MMA	Al(O*i*-Pr)$_3$	20	6.5	80	48	93	11 300	1.32	57/43
5	MMA	Al(O*i*-Pr)$_3$	10	6.5	80	34	91	11 400	1.43	94/6
6	MMA	Al(O*i*-Pr)$_3$	15	6.5	80	43	95	10 200	1.35	81/19
7	MMA	Al(O*i*-Pr)$_3$	40	6.5	80	49	90	11 300	1.43	52/48
8	MMA	Al(O*i*-Pr)$_3$	20	2.0	80	51	93	12 200	1.24	85/15
9	MMA	Al(O*i*-Pr)$_3$	20	4.0	80	48	92	11 700	1.34	65/35
10	MMA	Ti(O*i*-Pr)$_4$	20	6.5	80	48	96	11 100	1.42	25/75
11	DMA	Ti(O*i*-Pr)$_4$	20	6.5	80	24	90	17 800	1.25	50/50
12	*i*-PrMA	Ti(O*i*-Pr)$_4$	20	6.5	80	48	96	11 800	1.47	56/44
13	*t*-BuMA	Ti(O*i*-Pr)$_4$	20	6.5	80	48	89	16 900	2.02	96/4

[a] $[RMA]_0$ = 2.0 M; $[ECPA]_0$ = 20 mM; $[Ru(Ind)Cl(PPh_3)_2]_0$ = 2.0 mM; $[M(OR)_n]_0$ = 10 - 40 mM; $[EtOH]_0$ = 2.0 - 6.5 M in toluene at 40 - 80 °C. RMA: methyl methacrylate (MMA); dodecyl methacrylate (DMA); isopropyl methacrylate (*i*-PrMA); *tert*-butyl methacrylate (*t*-BuMA). [b] Determined by ^{1}H NMR. [c] Determined by SEC in chloroform with PMMA standards.

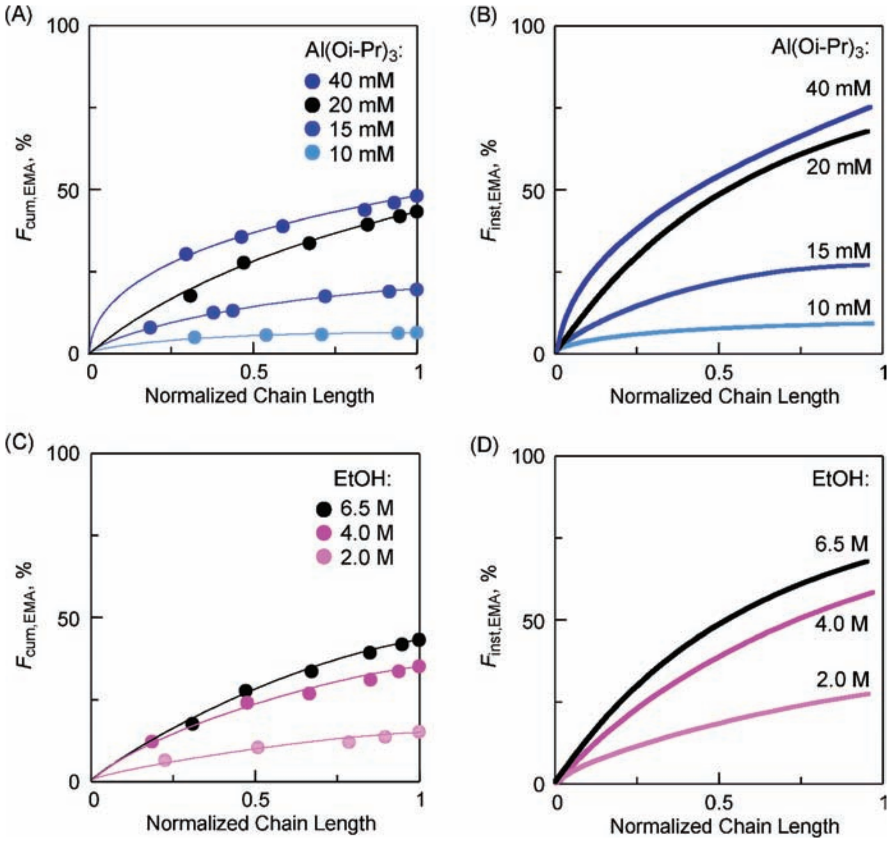


Figure 3. Effects of Al(O*i*-Pr)$_3$ (A and B) or EtOH (C and D) concentration on MMA/EMA gradient copolymers obtained from tandem catalysis of ruthenium-catalyzed living radical polymerization and in situ transesterification of MMA with Al(O*i*-Pr)$_3$ and EtOH. (A and C) cumulative EMA contents ($F_{cum,EMA}$) and (B and D) instantaneous EMA contents ($F_{inst,EMA}$) as a function of normalized chain length. (A and B) $[MMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[Al(Oi\text{-}Pr)_3]_0$ = 2000/20/2.0/10, 15, 20, and 40 mM in toluene/EtOH (1/1, v/v: $[EtOH]_0$ = 6.5 M) at 80 °C. (C, D) $[MMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[Al(Oi\text{-}Pr)_3]_0$ = 2000/20/2.0/20 mM in toluene/EtOH ($[EtOH]_0$ = 2.0, 4.0, and 6.5 M) at 80 °C.

Effects of Catalyst and EtOH Concentration. Next, concurrent tandem catalysis for MMA/EMA gradient copolymers was conducted by varying either Al(O*i*-Pr)$_3$ concentration (10, 15, 20, and 40 mM) or EtOH counterpart (2.0. 4.0, and 6.5 M) at 80 °C (Figure 3, Table 1, Figure S5). The concentrations of MMA (2.0 M), a ruthenium catalyst ($[Ru(Ind)Cl(PPh_3)_2]_0$ = 2.0 mM), and an initiator ($[ECPA]_0$ = 20 mM) were kept constant (identical to those in Figure 2), thus *DP* was also set as 100. All conditions efficiently induced polymerization of monomers in high yield (>90%) and in situ transesterification of MMA into EMA with EtOH (Figure S5A and S5B) to give well-controlled MMA/EMA gradient

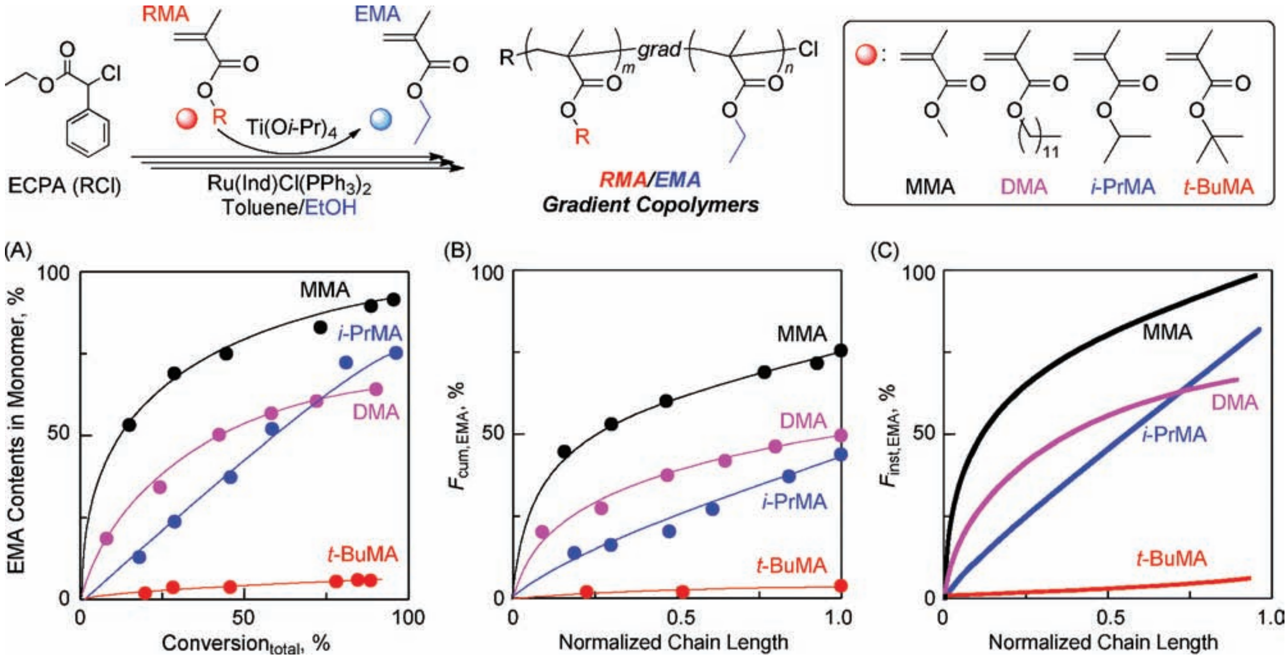


Figure 4. Effects of monomers (RMA: MMA; DMA; *i*-PrMA; *t*-BuMA) on RMA/EMA gradient copolymers obtained from tandem catalysis of ruthenium-catalyzed living radical polymerization and in situ transesterification of RMA with Ti(O*i*-Pr)$_4$ and EtOH: (A) EMA contents in monomer as a function of total monomer conversion; (B) cumulative EMA contents ($F_{\mathrm{cum,EMA}}$); and (C) instant EMA contents ($F_{\mathrm{inst,EMA}}$) in products as a function of normalized chain length; $[\mathrm{RMA}]_0/[\mathrm{ECPA}]_0/[\mathrm{Ru(Ind)Cl(PPh_3)_2}]_0/[\mathrm{Ti(O}i\text{-}\mathrm{Pr})_4]_0$ = 2000/20/2.0/20 mM in toluene/EtOH (1/1, v/v) at 80 °C.

copolymers with narrow MWDs (Figure S5, Table 1, entries 4−9). Both of $F_{\mathrm{cum,EMA}}$ and $F_{\mathrm{inst,EMA}}$ increased along a chain (Figure 3). The gradient distribution of EMA along a chain ($F_{\mathrm{inst,EMA}}$) gradually turned steep as the concentration of Al(O*i*-Pr)$_3$ or EtOH increased.

Effects of Catalysts. Ti(O*i*-Pr)$_4$ was more active as a catalyst for EtOH-mediated transesterification of MMA than Al(O*i*-Pr)$_3$ (Figure 1A). Thus, to increase EMA contents on gradient copolymers, we employed Ti(O*i*-Pr)$_4$ for ruthenium-catalyzed polymerization of MMA in EtOH/toluene (1/1) at 80 °C (Figures 4 and S6, Table 1, entry 10). As predicted, MMA was faster converted into EMA than that treated with Al(O*i*-Pr)$_3$ (Figure 4A, compared with Figure 2B black line). The EMA contents in gradient copolymers rapidly increased around the initial α-end and finally reached up to almost 95% of $F_{\mathrm{inst,EMA}}$ around the ω-end (Figure 4C).

Therefore, the monomer sequence on MMA/EMA gradient copolymers was efficiently, conveniently, and catalytically controlled by the conditions including reaction temperature, concentration of metal alkoxides and EtOH, and catalyst species, which successfully modulated the equilibrium on in situ transesterification of MMA to EMA. It should be noted that this system directly leads to "perfectly seamless" MMA/EMA gradient copolymers in one-pot, in contrast to the continuous feed technique of a second monomer with a syringe pump.[34]

Effects of Monomers. In general, transesterification is strongly affected by the steric hindrance of substrates and the boiling temperature of alcohols released from substrates.[28,39] To survey effects of monomer structures on gradient copolymerization, we employed dodecyl methacrylate (DMA), isopropyl methacrylate (*i*-PrMA), and *tert*-butyl methacrylate (*t*-BuMA) as precursor monomers (RMA), on behalf of MMA, for Ti(O*i*-Pr)$_4$/EtOH-mediated concurrent tandem polymerization (Figures 4 and S6, Table 1, entries 11−13). All of the monomers were efficiently polymerized in high yield (>90%), giving controlled products. However, the efficiency on in situ monomer transesterification was dependent on monomer structures. DMA and *i*-PrMA were slower transformed into EMA than MMA, and *t*-BuMA was hardly done, owing to the high boiling temperature of alcohols released from monomers and/or the steric hindrance of the bulky alkyl pendants (Figure 4A). Both DMA and *i*-PrMA provided their corresponding RMA/EMA gradient copolymers, in which the EMA contents more gently increased along a chain than those with MMA (Figure 4C). It should be noteworthy that the tandem system for gradient copolymers is quite versatile due to high applicability of various alcohols[31] and primary or secondary-alkyl methacrylates. In addition, the selective transesterification of primary or secondary methacrylates, except for tertiary counterparts, is rather intriguing to regulate multimonomer sequences in copolymers as shown later.

Thermal Analysis. Differential scanning calorimetry (DSC) was conducted for MMA/RMA gradient copolymers obtained with various alcohols [ROH: EtOH, benzyl alcohol (BzOH), 1-dodecanol ($C_{12}H_{25}OH$), poly(ethylene glycol) methyl ether (PEG−OH: M_n = 550)][31] (Table 2, Figure S7). All samples showed one broad glass transition temperature (T_g) between T_g for MMA homopolymers (PMMAs, ∼105 °C)[40] and that for RMA counterparts (PRMAs). Such broad T_gs are the typical evidence of gradient copolymers, different from random or block counterparts.[31,36a,b] T_gs for MMA/EMA gradient copolymers decreased with increasing EMA contents (entry 1−4). T_gs for gradient copolymers containing almost identical MMA contents (∼55%) were dependent on RMA species (entries 3, 5, and 6), i.e. decreased with decreasing T_gs for PRMAs[40] [T_g = 65 °C (PEMA),[41] 54 °C (PBzMA),[42]

Table 2. DSC Analyses of MMA/RMA Gradient Copolymers[a]

entry	ROH	M_n[b]	M_w/M_n[b]	$F_{cum,MMA}/F_{cum,RMA}$ (%)[c]	T_g [T_m] (°C)[d]
1	EtOH	10 300	1.28	94/6	105
2	EtOH	11 200	1.27	71/29	91
3	EtOH	11 300	1.32	57/43	88
4	EtOH	11 100	1.42	25/75	64
5	BzOH	12 900	1.45	55/45	59
6	1-dodecanol	20 700	1.21	56/44	18
7	PEG−OH	28 000	1.17	69/31	−59[11]

[a] Polymerization: $[\mathrm{MMA}]_0/[\mathrm{ECPA}]_0/[\mathrm{Ru(Ind)Cl(PPh_3)_2}]_0/[\mathrm{Al}(\mathrm{O}i\text{-}\mathrm{Pr})_3$ (entries 1−3) or $\mathrm{Ti}(\mathrm{O}i\text{-}\mathrm{Pr})_4$ (entries 4−8)$]_0$ = 2000/20/2.0/20 mM in toluene/alcohol (ROH) (1/1, v/v) (entries 1−7) or in alcohol (entry 8) at 40 (entry 1), 60 (entry 2), and 80 (entries 3−8) °C. RMA: Monomers generating from in situ transesterification of MMA with ROH. [b] Determined by SEC in chloroform with PMMA standards. [c] Determined by ^{1}H NMR. [d] Glass transition temperature (T_g) and melting temperature (T_m).

and −59 °C ($PC_{12}H_{25}MA$)[43]. PEG-bearing gradient copolymers further showed a melting temperature (T_m) derived from PEG chains (entry 7). Thus, solid properties of copolymers were successfully modulated by the sequence regulation of monomers and the monomer species.

Multisequence-Controlled Copolymers. *Random-Gradient Copolymers: Selective Transesterification.* The selective transesterification of monomers (Figure 4) encouraged us to directly conduct random-gradient copolymerization via concurrent tandem catalysis (Figure 5). For this, MMA and *t*-BuMA ($[\mathrm{MMA}]_0/[t\text{-BuMA}]_0$ = 1M/1M) were copolymerized with a ruthenium catalyst in the presence of Al(O*i*-Pr)$_3$ and EtOH at 80 °C (Figure 5, panels A and C). Importantly, the transesterification of monomers into EMA was selectively active for MMA even in the presence of *t*-BuMA (*t*-BuMA contents in monomer, ∼50%). As a result, this system provided random-gradient copolymers [(PMMA-*grad*-PEMA)-*ran*-P*t*-BuMA: M_n = 15200; M_w/M_n = 1.8; $F_{cum,MMA}/F_{cum,EMA}/F_{cum,t\text{-}BuMA}$ = 18/30/52] consisting of both the gradient sequence from MMA to EMA and the uniform counterpart of *t*-BuMA along a chain. This tandem catalysis afforded such a complex multisequence regulation without any external supply of comonomers.

Gradient-Block Copolymers: Iterative Tandem Catalysis. Thanks to the high catalyst stability and the controllability (end-functionality), ruthenium-catalyzed living radical polymerization realizes one-pot block copolymerization via in situ addition of a second monomer into a prepolymer solution.[1,24b] Thus, we further extended our tandem catalysis to the synthesis of gradient triblock copolymers containing three different gradient segments via the iterative addition of MMA and different alcohols (ROH) (Figure 6). In the presence of Ti(O*i*-Pr)$_4$, MMA/*i*-PrMA gradient copolymers (first block: M_n = 8700, M_w/M_n = 1.30) were first prepared by ruthenium-catalyzed polymerization of MMA with a chloride initiator (ECPA) in isopropanol (*i*-PrOH) and toluene (1/1, v/v) at 80 °C. After the remaining MMA and solvents were removed by evaporation, a fresh MMA, and EtOH and toluene (1/1, v/v) were subsequently added into the reaction vessel. Tandem catalysis was then conducted again at 80 °C to prepare a second MMA/EMA gradient segment (MMA/*i*-PrMA-MMA/EMA gradient diblock copolymers: M_n = 16 100, M_w/M_n = 1.32), further followed by the identical treatment with MMA and BzOH for a third block. The SEC curves of the products exhibited unimodal distributions and gradually shifted to higher molecular weight as the iterative tandem catalysis

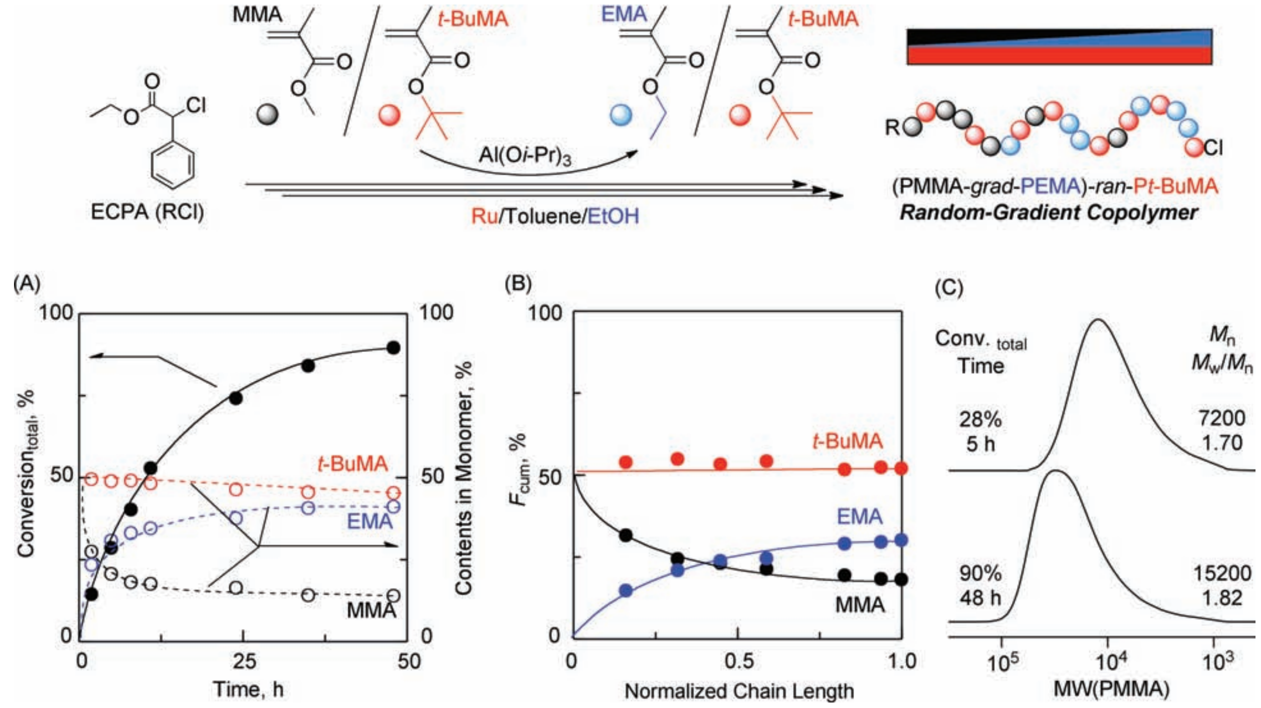


Figure 5. Random-gradient copolymers synthesized by tandem catalysis of ruthenium-catalyzed living radical copolymerization and selective transesterification of MMA with EtOH in the presence of *t*-BuMA: (A) total conversion and monomer contents as a function of reaction time; (B) cumulative monomer contents in products (F_{cum}) as a function of normalized chain length; (C) SEC curves of products; $[\mathrm{MMA}]_0/[t\text{-BuMA}]_0/[\mathrm{ECPA}]_0/[\mathrm{Ru(Ind)Cl(PPh_3)_2}]_0/[\mathrm{Al}(\mathrm{O}i\text{-}\mathrm{Pr})_3]_0$ = 1000/1000/20/2.0/20 mM in toluene/EtOH (1/1, v/v) at 80 °C.

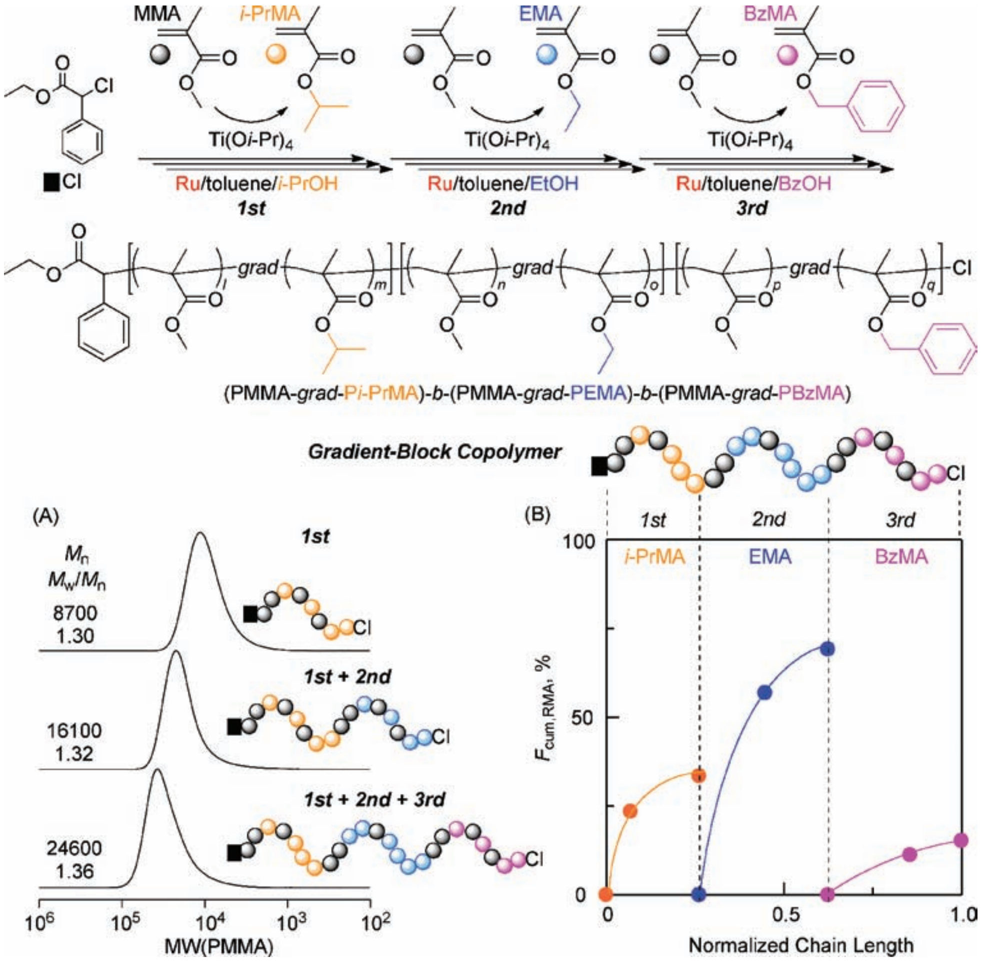


Figure 6. Gradient-triblock copolymers (l/m = 27/14, n/o = 18/39, p/q = 50/9) synthesized by iterative tandem catalysis of ruthenium-catalyzed living radical polymerization and in situ transesterification of MMA with Ti(Oi-Pr)$_4$ and alcohols (ROH: i-PrOH, EtOH, BzOH): (A) SEC curves of products; (B) cumulative RMA contents in products ($F_{\mathrm{cum,RMA}}$) as a function of normalized chain length; [MMA]$_0$/[ECPA or macroinitiators]$_0$/[Ru(Ind)Cl(PPh$_3$)$_2$]$_0$/[Ti(Oi-Pr)$_4$]$_0$ = 2000/20/2.0/20 mM in toluene/alcohols (1/1, v/v) at 80 °C.

proceeded (Figure 6A). Confirmed by ^{1}H NMR, the cumulative contents of monomers (RMA) ($F_{\mathrm{cum,RMA}}$) gradually increased from the starting points in the respective block segments (Figure 6B). As a result, the iterative process efficiently provided unique gradient triblock copolymers [M_n = 24 600, M_w/M_n = 1.36, $(F_{\mathrm{cum,MMA}}/F_{\mathrm{cum,iPrMA}})_{\mathrm{first}}/(F_{\mathrm{cum,MMA}}/F_{\mathrm{cum,EMA}})_{\mathrm{second}}/(F_{\mathrm{cum,MMA}}/F_{\mathrm{cum,BzMA}})_{\mathrm{third}}$ = $(66/34)_{\mathrm{first}}/(31/69)_{\mathrm{second}}/(85/15)_{\mathrm{third}}$]. It must be further emphasized that in situ metal alkoxide-catalyzed transesterification never interferes in controllability and end-functionality on ruthenium-catalyzed living radical polymerization.

Random or Block Copolymers: Sequential Tandem Catalysis. Gradient copolymers are efficiently prepared by the concurrent tandem catalysis that synchronize living radical polymerization and in situ transesterification of monomers from the initial stage. On the contrary, the sequential tandem catalysis to variably start either polymerization or in situ transesterification leads to random copolymers or block counterparts, respectively (Figure 7). Namely, the former is obtained from the sequential polymerization after pretransesterification of monomers, and the latter is from the in situ transesterification of monomers after the middle stage of polymerization.

For random copolymerization, Ti(Oi-Pr)$_4$-catalyzed transesterification of MMA with EtOH was first carried out at 80 °C for 8 h to give the mixture of MMA and EMA (EMA: almost saturated at ~50%; Figure 7A). Into the solution, a chloride initiator and a ruthenium catalyst were directly added to start copolymerization of the two monomers. The EMA contents in monomer were almost constant during copolymerization. Thus, the resulting products also had the constant EMA contents ($F_{\mathrm{cum,EMA}}$ = $F_{\mathrm{inst,EMA}}$ = ~50%) along a chain (Figure 7, panels D and E) to be MMA/EMA random copolymers ($M_w/M_n \approx 1.2$) (Figure 7C).

Block copolymers were, in turn, typically synthesized by the direct addition of EtOH into ruthenium-catalyzed polymerization of MMA in the presence of Ti(Oi-Pr)$_4$ at the middle stage (MMA conversion: ~50%). After the addition of EtOH, MMA was rapidly transformed into EMA due to the large excess ratio of the EtOH ([EtOH]$_{\mathrm{add}}$ = 6.5 M) to the remaining MMA ([MMA] = ~1 M). Thus, the EMA contents in resulting copolymers ($F_{\mathrm{inst,EMA}}$) steeply increased from the middle point of the chain to finally reach over 95% around the ω-terminal. Thus, sequential tandem catalysis is regarded as new, facile, and versatile methodologies for both random copolymers and block counterparts, because the monomer units can be facilely designed by the selection of alcohols.

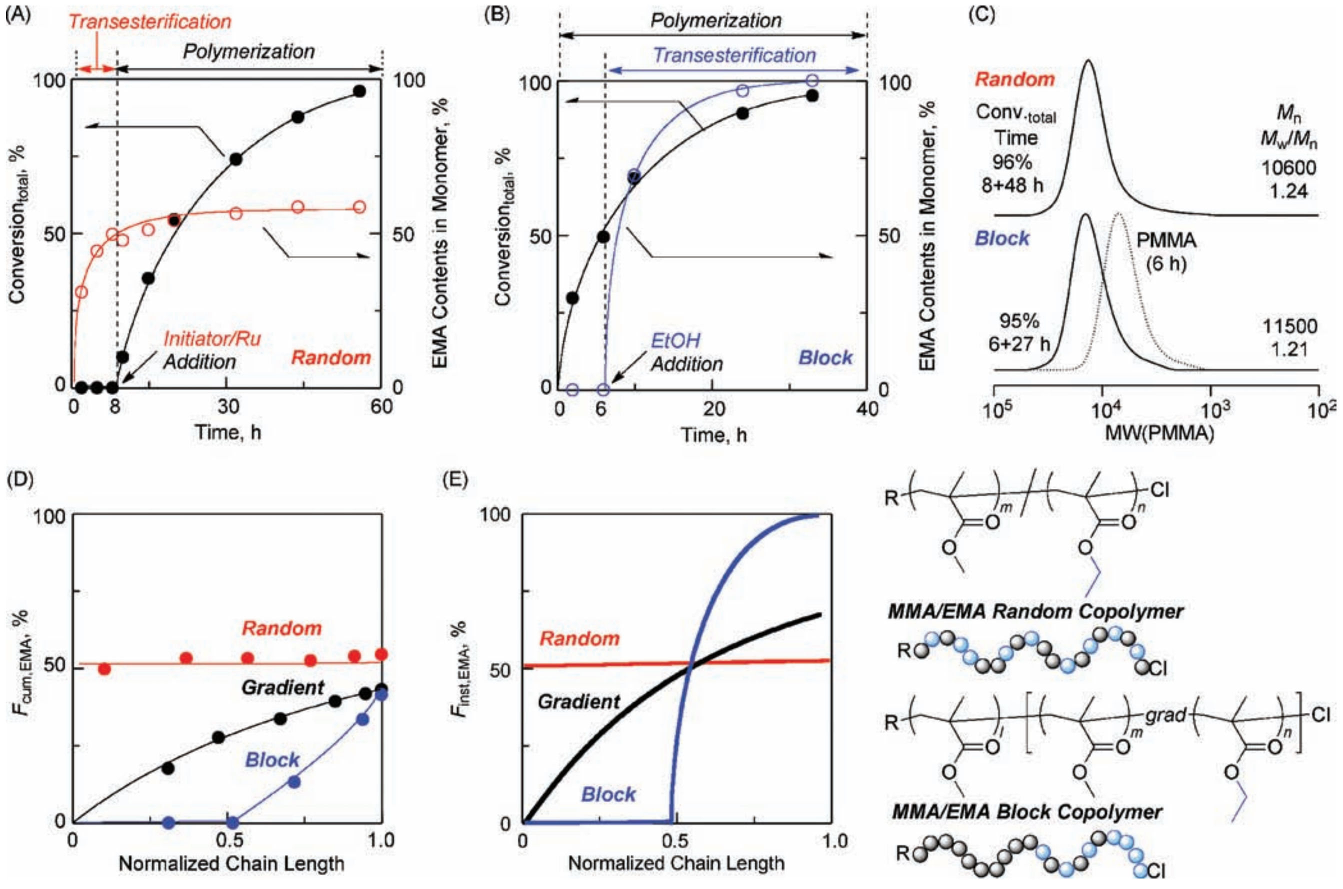


Figure 7. MMA/EMA random or block copolymers prepared by sequential tandem catalysis: (A), (B) total conversion and EMA monomer contents as a function of reaction time; (C) SEC curves of products; (D) cumulative EMA contents ($F_{cum,EMA}$) and (E) instantaneous EMA contents ($F_{inst,EMA}$) in products as a function of normalized chain length. Random: $[MMA]_0/[Ti(O\textit{i}\text{-}Pr)_4]_0/[EtOH]_0/[ECPA]_{add}/[Ru(Ind)Cl(PPh_3)_2]_{add}$ = 2000/20/2000/20/2.0 mM in toluene at 80 °C. Block: $[MMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)_2]_0/[Ti(O\textit{i}\text{-}Pr)_4]_0/[EtOH]_{add}$ = 2000/20/2.0/20/6.5 M in toluene at 80 °C. A gradient copolymer in (D) and (E): corresponding to the sample (entry 4) obtained with Al(O*i*-Pr)$_3$ in Table 1.

■ CONCLUSIONS

We have successfully synthesized various sequence-controlled copolymers in one-pot via tandem catalysis of ruthenium-catalyzed living radical polymerization and metal alkoxide/alcohol-mediated transesterification of methacrylates (Scheme 1). The concurrent, synchronized catalysis efficiently gave "seamless" gradient copolymers, where the monomer sequence was catalytically controlled on demand by the following factors: reaction temperature; species and/or concentration of metal alkoxide catalysts, alcohols, and precursor monomers. The tandem catalysis successfully afforded the direct regulation of multimonomer sequence that was difficult and/or impossible via one-pot process. Typically, random-gradient copolymers were obtained with the highly selective transesterification of primary methacrylates in the presence of tertiary counterparts, and gradient-block copolymers were in turn synthesized via iterative tandem catalysis due to the high controllability of ruthenium-catalyzed living radical polymerization. The tandem catalysis coupled with polymerization and transesterification can be further extended to random or block copolymerization, which are achieved by sequentially and variably starting either polymerization or transesterification, respectively. Therefore, the tandem catalysis, derived from the simple marriage of polymerization and transesterification, is one of the most versatile, efficient direct transformations of common and/or commercially available reagents (monomers, alcohols, catalysts, and an initiator) into sequence-regulated copolymers. Sequence-regulated copolymers with unique properties would open the new vistas in material science.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Transesterification and polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

terashima@living.polym.kyoto-u.ac.jp; sawamoto@star.polym.kyoto-u.ac.jp

Notes

The authors declare no competing financial interest.

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