Sequence Control

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Alternating Sequence Control for Carboxylic Acid and Hydroxy Pendant Groups by Controlled Radical Cyclopolymerization of a Divinyl Monomer Carrying a Cleavable Spacer

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Abstract: *By utilizing features of the hemiacetal ester (HAE) bond: easy formation from vinyl ether and carboxylic acid and easy cleavage into different functional groups (-COOH and -OH), we achieved control of the alternating sequence of two functional pendant groups of a vinyl copolymer. Methacrylate- and acrylate-based vinyl groups were connected through HAE bonds to prepare a cleavable divinyl monomer, which was cyclo-polymerized under optimized conditions in a ruthenium-catalyzed living radical polymerization. Subsequent cleavage of the HAE bonds in the resultant cyclo-pendant led to a copolymer consisting of alternating methacrylic acid and 2-hydroxyethyl acrylate units as analyzed by ^{13}C NMR spectroscopy. The alternating sequence of -COOH and -OH pendants specifically provided a lower critical solution temperature (LCST) in an ether solvent, which was not observed with the random copolymer of same composition ratio.*

In nature, the "sequence" of macromolecules (i.e., DNA and peptides) is elaborately controlled, and functional substituents at well-defined positions cooperatively play an important role on their functions. Sequence control for synthetic polymers has recently attracted attention toward creation of more advanced functions like those of natural polymers,[1–6] but the control is still challenging in polymer science. Among artificial macromolecules, vinyl polymers are very interesting for this subject, because they consist of repeating units derived from co-monomers carrying various functional pendant groups similar to peptides composed of amino acid-based units. Vinyl polymers are generally synthesized through addition polymerization of vinyl monomers and have been used in plastics, fibers, and rubber as well as functional advanced materials. Monomers are easily co-polymerized via the chain-growth mechanism to give statistical "random" copolymers and the properties can be tuned by combination of co-monomers as well as the averaged composition ratio. Now that the molecular weight and terminal groups can be controlled with living polymerization, the subject of sequence control and sequence-driven functions could be the next destination in polymer science. However, rather unfortunately, the chain-growth mechanism is less appropriate for sequence control because the propagation does not occur in a stepwise manner.

Some concepts or methodologies to control the sequence of vinyl polymers have been reported.[7–20] One simple, but never easy approach, is the iterative single-unit addition on the basis of living polymerization.[7,13–16] This method might be less satisfactory in terms of yield/efficiency because purification and/or diluted condition are required owing to the statistical nature inherent in addition polymerization. Another one relies on not addition polymerization but other polymerizations, such as polyaddition,[9] ring-opening metathesis polymerization (ROMP),[20] acyclic diene metathesis (ADMET) polymerization.[19] Monomers having information of sequence or position are connected with each other and subsequent hydrogenation (for the metathesis mechanism) to give polymers of periodic sequence.

On the other hand, cyclopolymerization of cleavable multi-vinyl monomers where the pendant groups are connected to each other via a cleavable spacer could be an approach to control the periodic sequence by cleaving the resultant cyclo-pendant. This methodology could provide sequence control for high molecular weight polymers, though the sequence pattern is limited to being periodic. We have reported two examples of this concept. One is the AB-divinyl monomer consisting of methacrylate and acrylate whose ester is connected via naphthalene scaffold (Scheme 1 A).[11] The cyclopolymerization was controlled by metal-catalyzed living radical polymerization under diluted condition, followed by cleavage of the ester group, to give AB alternating copolymers consisting of methacrylic and acrylic acid units. A drawback of this design is using same cleavage bond (i.e., ester) resulting in an identical pendant group, carboxylic acid. Another type is ABA-trivinyl monomer based on a palladium complex and the double cyclopolymerization led to the copolymer of ABA periodic sequence of amino methyl styrene (A) and 4-vinyl pyridine (B) units (Scheme 1 B).[12] Although different functional groups (i.e., amine and pyridine) are aligned with ABA sequences, simultaneous control of molecular weight was not achieved because an extremely lower temperature is required to maintain the π–π stacked structure during polymerization.

Herein, we present a simple but effective design to control the periodic sequence for different functional side chains as well as the molecular weight and the sequence-driven

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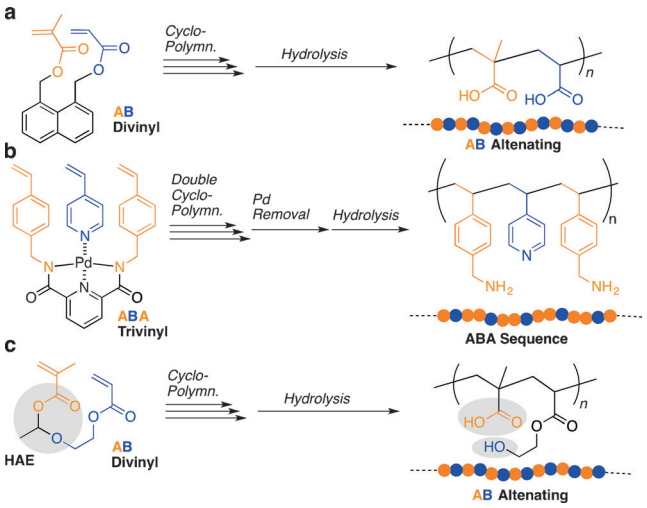

Scheme 1. Cyclopolymerizations to control the alternating sequence. a) Cyclopolymerization of AB-type divinyl monomer with naphthalene spacer, b) double-cyclopolymerization of ABA-type trivinyl monomer based on a palladium complex, c) cyclopolymerization of AB-type divinyl monomer with HAE spacer (this work).

properties. Crucial is the introduction of a cleavable spacer between two vinyl groups in the divinyl monomer and control of the cyclopolymerization. Herein, the hemiacetal ester (HAE) bond is the key as the cleavable bond, since the bond is cleaved into carboxylic acid and hydroxy groups under acidic conditions and is easily formed from vinyl ether and carboxylic acid. Given by the previous design with the combination of methacrylate and acrylate for AB alternating sequences, the two vinyl monomer components are connected via an HAE bond to prepare the AB divinyl monomer **1** (Scheme 1 C). The cyclopolymerization of **1** followed by cleavage of the HAE bond is expected to give an alternating sequence of methacrylic acid (MAA) and 2-hydroxyethyl acrylate (HEA).

We thus studied the conditions to realize the cyclopolymerization of **1**, such as selection of initiator/cocatalyst and concentrations of components, in a ruthenium-catalyzed living radical polymerization (see Supporting Information, Table S1). First, a bromine-based initiator [H-$(MMA)_2$-Br] was used in conjunction with $[RuCp^*(Cl)(PPh_3)_2]$ ($Cp^* = C_5Me_5$) and $Al(O\textit{i}\text{-}Pr)_3$ (cocatalyst), and the polymerization of **1** was performed in toluene at 60 °C with the following concentrations: $[\mathbf{1}]_0/[\text{H-}(MMA)_2\text{-Br}]_0/[RuCp^*(Cl)(PPh_3)_2]_0/[Al(O\textit{i}\text{-}Pr)_3]_0 = 100/2.0/1.0/10$ mM. Consumptions of the both vinyl groups (i.e., methacrylate (M) and acrylate (A)) were individually determined with ^{1}H NMR spectroscopy, and the two vinyl groups were consumed at almost same rate, indicating control of cyclopolymerization. However, $Al(O\textit{i}\text{-}Pr)_3$ caused ester-exchange with **1** during polymerization to give a non-cyclo unit carrying an isopropyl pendant, which was detected in the conversion analysis by ^{1}H NMR spectroscopy. Thus, $Al(O\textit{t}\text{-}Bu)_3$ was tried as the cocatalyst, because it works in MMA polymerization without an ester exchange reaction.[21] In this polymerization, damage to **1** as a result of ester exchange reaction was not observed, however the molecular weight distribution (MWD) of polymer obtained was broad ($M_w/M_n = 2.93$). Chlorine-based H-$(MMA)_2$-Cl or iodine-based (H-EMA-I) initiator was also tested instead of H-$(MMA)_2$-Br. The H-$(MMA)_2$-Cl gave slower polymerization and broad MWD of obtained polymer ($M_w/M_n = 2.65$), and in contrast, the H-EMA-I gave faster polymerization and narrower MWD ($M_w/M_n = 1.59$). In spite of such acceleration, the two vinyl groups were consumed in parallel and an insoluble gel was not formed during polymerization. As the concentration of **1** or initiator was higher, the MWDs were broader probably due to cross-linking reactions but moderately diluted conditions allowed narrower MWDs of polymers to be obtained.

Consequently, controlled cyclopolymerization of **1** was realized under optimized condition: $[\mathbf{1}]_0/[\text{H-EMA-I}]_0/[RuCp^*(Cl)(PPh_3)_2]_0/[Al(O\textit{t}\text{-}Bu)_3]_0 = 100/2.0/1.0/10$ mM in toluene at 60 °C (Figure 1). The vinyl groups from the methacrylate and acrylate units were consumed at almost the same rate (Figure 1 a) despite their inherently different reactivity, which is due to intramolecular propagation on the spacer connection.[22] The polymerization proceeded without giving any insoluble polymers and the propagation seemed to be controlled: the number-averaged molecular weight (M_n) was increased as the conversion increased Figure 1 b and SEC curves of obtained polymers shifted to higher molecular

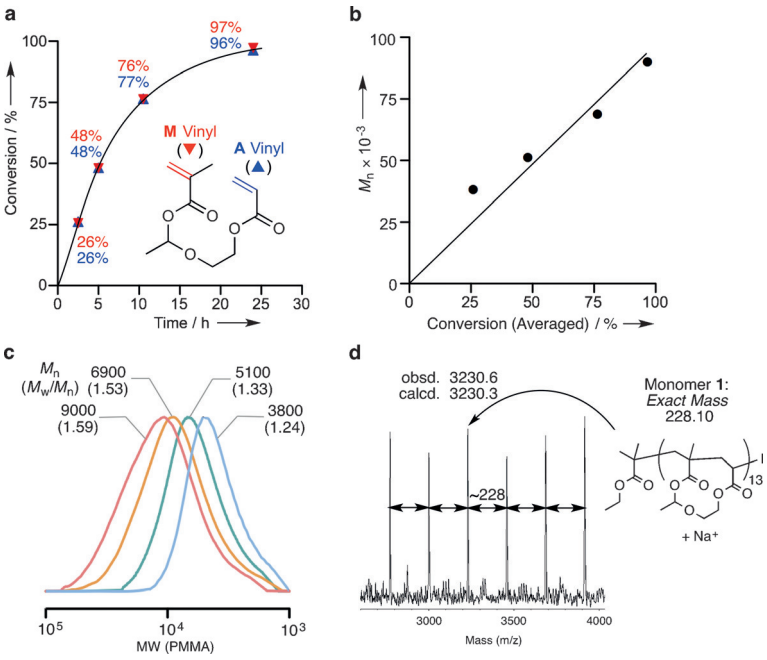

Figure 1. Ruthenium-catalyzed cyclopolymerization of **1**: $[\mathbf{1}]_0/[\text{H-EMA-I}]_0/[RuCp^*(Cl)(PPh_3)_2]_0/[Al(O\textit{t}\text{-}Bu)_3]_0 = 100/2.0/1.0/10$ mM in toluene at 60 °C. a) time-conversion plot, b) conversion versus M_n plot, c) SEC curves of polymers obtained, d) MALDI-TOF-MS spectrum of the polymer obtained. The sample of MALDI-TOF-MS [Conv. (M) = 27 %, Conv. (A) = 26 %; $M_n = 3700$; $M_w/M_n = 1.20$] was prepared with iodine-based ruthenium complex instead of $[RuCp^*(Cl)(PPh_3)_2]$ to avoid a halogen exchange reaction: $[\mathbf{1}]_0/[\text{H-EMA-I}]_0/[[Cp^*Ru(\mu_3\text{-I})]_4]_0/[PPh_3]_0 = 100/2.0/1.0/8.0$ mM.

weight keeping the unimodal shapes (Figure 1c). In addition, an iodine-based catalyst[23] was used instead of [RuCp*(Cl)-$(PPh_3)_2$] to aid analysis of the structure of the polymer by mass spectrometry: there was one series of peaks whose interval is the molecular weight of **1** and the mass of each peak agreed with the molecular weight of ideal polymer (the Na^+ adduct) of **1** carrying the initiator moieties at the terminals (Figure 1d). From these analyses, it was concluded that the cyclopolymerization of **1** was fairly controlled. Another type of divinyl monomer **2**, in which an HAE bond was introduced at a different position from **1**, was also tested for cyclopolymerization under the same conditions, and similar results, that is, parallel consumption and molecular weight control, were observed (Table S1 and Figure S4).

Figure 2a shows ^{1}H NMR spectrum of the cyclopolymer (40% conversion of the two vinyl groups, $M_n = 6400$; $M_w/M_n = 1.30$). Some signals assigned to the repeating-unit protons were observed, but the shapes were much broader than common vinyl (co)polymers as a result of the cyclostructure. Importantly, methine (*c*) and methyl (*d*) (see Figure 2a) in repeating HAE bond were clearly identified, indicating the HAE bond was maintained during the radical polymerization process. Minor signals around 6.4 ppm were attributed to unreacted acrylate (*h′*, *g′*) branch on the copolymer. This implies the cyclopropagation was not perfect, however, the "apparent" error ratio was estimated at less than 5%, and so the degree of cyclopropagation was relatively high.

Then, the HAE bond in the repeating unit is cleaved with trifluoroacetic acid (TFA) and the structure of the resultant copolymer was characterized with ^{1}H NMR spectroscopy (in CD_3OD, Figure 2b). The signals from HAE bond disappear, and instead a peak (*i*) from the proton of the resultant hydroxy group appeared. An integration ratio of the characteristic signals (*b′* and *e′*, *f′*, Figure 2b) certainly supported the formation of the copolymer of MAA and HEA with 1:1 composition ratio.

To verify the sequence of MAA and HEA units, the structure was analyzed with ^{13}C NMR spectroscopy (Figure 2c). The signals from the carbonyl group (C=O) were compared with those for the random copolymer of MAA and HEA with 1:1 composition ratio as well as for the respective homopolymers of MAA and HEA. The random copolymer was prepared via ruthenium-catalyzed living radical polymerization of *tert*-butyl methacrylate (TBMA) and HEA, and subsequent deprotection of TBMA unit in the resultant random copolymer: $M_n = 4600$, $M_w/M_n = 1.29$, $DP_{n,TBMA}:DP_{n,HEA} = 51:49$ (before deprotection, see Supporting Information). Importantly, the copolymer from **1** provided no NMR signals for the MAA sequential homo unit at around 182 ppm, in sharp contrast to the random copolymer. As for the signal arising from the HEA sequential unit at around 178 ppm, the analysis was hampered by the lower signal-to-noise ratio but almost no signals were observed around this region. In addition, signals at 179–181 ppm were quite different from those of the random copolymer. Considering the polymerization behaviors together, such as parallel consumption of the two vinyl groups and no formation of insoluble product, these structural analyses with ^{13}C NMR spectroscopy support an alternating sequence of MAA and HEA.

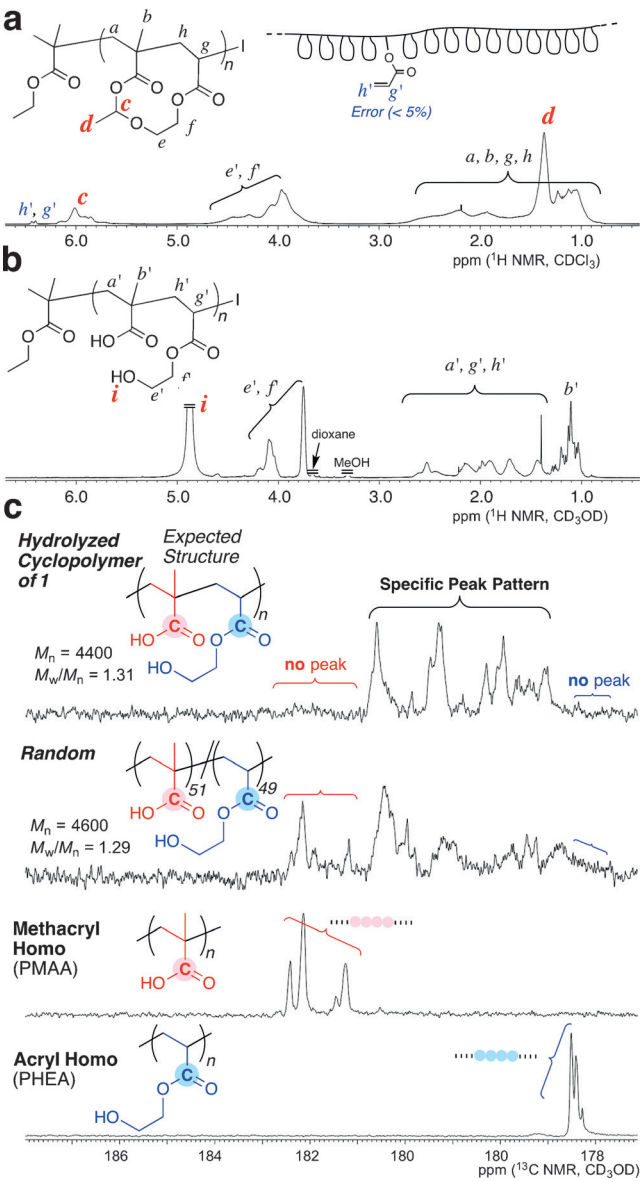

Figure 2. ^{1}H NMR spectrum of a) cyclopolymer of **1** and b) the hydrolyzed copolymer. c) ^{13}C NMR spectra (178–187 ppm) of the hydrolyzed copolymer **1**, random copolymer, homopolymer of MAA, and homopolymer of HEA.

Crucial to obtaining an alternating sequence with this approach is the combination of different vinyl groups, that is, methacrylate and acrylate. Based on by reactivity ratios for combinations of methacrylate and acrylate (e.g., $r_1 = 2.15$, $r_2 = 0.40$ for methyl methacrylate (MMA: M_1) and methyl acrylate (MA: M_2)),[24] both the radical species from methacrylate and acrylate prefer to react with the methacrylate-based vinyl group. Herein, the propagation order of the two vinyl groups on cyclopolymerization of **1** was studied with a model reaction under similar conditions to the polymerization. An acrylate-based iodine initiator (H-EA-I) was used for the reaction with an equimolar amount of **1** under ruthenium catalysis in [D_8]toluene at 60°C and the conver-

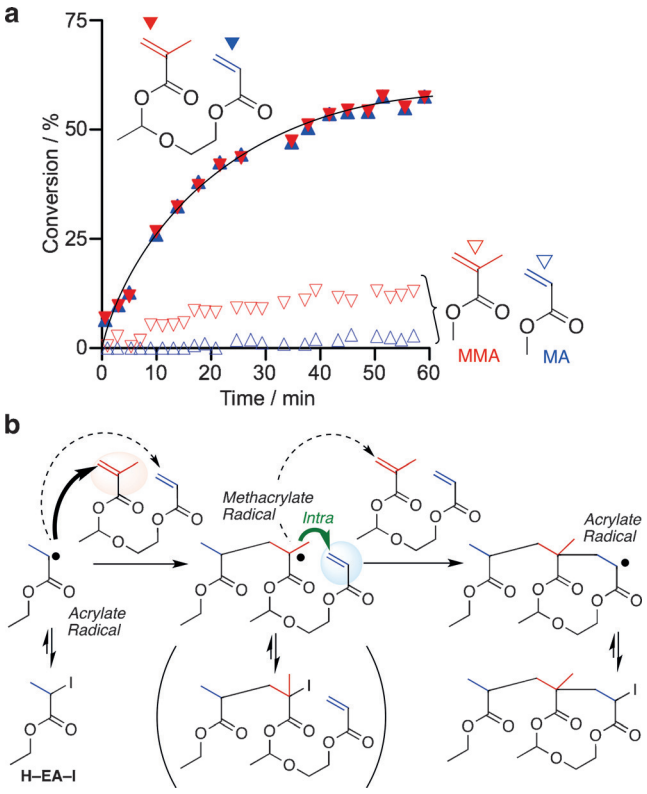

Figure 3. Ruthenium-catalyzed radical addition reaction of **1** with EA-I as a model reaction: $[\mathbf{1}]_0/[\text{EA-I}]_0/[\text{RuCp*(Cl)}(\text{PPh}_3)_2]_0/[\text{Al}(O\textit{t}\text{-Bu})_3]_0 = 10/10/1.0/10$ mM in [D$_8$]toluene at 60 °C. Control experiment: MMA and MA were used instead of **1**; $[\text{MMA}]_0/[\text{MA}]_0/[\text{EA-I}]_0/[\text{RuCp*(Cl)}(\text{PPh}_3)_2]_0/[\text{Al}(O\textit{t}\text{-Bu})_3]_0 = 10/10/\ 10/1.0/10$ mM in [D$_8$]toluene at 60 °C. a) Time conversion plots, b) proposed propagation mechanism with **1**.

sions of two vinyl groups (methacrylate and acrylate) were directly monitored: $[\text{H-EA-I}]_0/[\mathbf{1}]_0 = 10/10$ mM. As shown in the time-conversion plots (Figure 3a), both of the vinyl groups were smoothly consumed and the rate was almost same for each (parallel consumption), just as in the polymerization. A similar model reaction was also performed with an equimolar mixture of MMA and MA instead of **1**: $[\text{H-EA-I}]_0/[\text{MMA}]_0/[\text{MA}]_0 = 10/10/10$ mM. In sharp contrast to the reaction with **1**, only MMA was consumed, whereas MA was not, and the consumption rate of MMA was much slower than **1**. From these model reactions, the following mechanism was proposed (Figure 3b): the acrylate-based radical species from EA-I preferably reacts with the methacrylate vinyl group rather than the acrylate, a situation which is supported by the model reaction with MMA and MA. Considering that the consumption for both of the vinyl groups in **1** is the same, the resultant methacrylate radical species could react intramolecularly with the acrylate vinyl group, independent of the inherent preference to methacrylate, owing to the neighboring effect and/or enthalpy gain via the cyclization. Most probably, the intramolecular propagation on **1** smoothly proceeded without going through methacrylate-based dormant species that are formed via halogen capping to methacrylate-based radical species in the presence of Ru^{III}. The resultant acrylate radical or the dormant species could repeat the cyclopropagation in the order from methacrylate to acrylate, eventually to give the alternating sequence.[25]

Finally, the solubility of the resultant alternating copolymer of MAA and HEA ($M_n = 4400$, $M_w/M_n = 1.31$ before HAE cleavage) was examined in comparison with the random copolymer, which was used for the sequence analysis by ^{13}C NMR spectroscopy.

The alternating copolymer exhibited good solubility in alcohols, such as methanol and isopropanol, as did the random copolymer. However, the alternating copolymer showed different solubility from the random copolymer in the ether solvents tetrahydrofuran (THF), 1,4-dioxane, and dimethyl ether (DME), as well as in acetone: the alternating copolymer was more soluble for the ether solvents but less soluble in acetone. The alternating copolymer was more soluble than the random copolymer in acidic water (pH 3; Figure 4a). Most interestingly, the solution of the alternating copolymer in DME was turbid at room temperature, but it became transparent when it was put in ice bath (Figure 4b). The thermosensitive solubility in DME was then evaluated with temperature-dependent UV/Vis measurements, in which the transmittance of the solution was monitored at $\lambda = 670$ nm upon heating ($[\text{polymer}] = 8\ \text{mg mL}^{-1}$, heating speed $= 1\ ^\circ\text{C min}^{-1}$). Consequently, the solution phase-separated in DME upon heating, though the response was not quick. In contrast, the DME solution of the random copolymer was completely turbid regardless of temperature.

The detailed mechanism of the lower critical solution temperature (LCST) behavior of the alternating sequence is currently unclear, but most probably it is related to a balance of the following two hydrogen bonding interactions:1) intra-

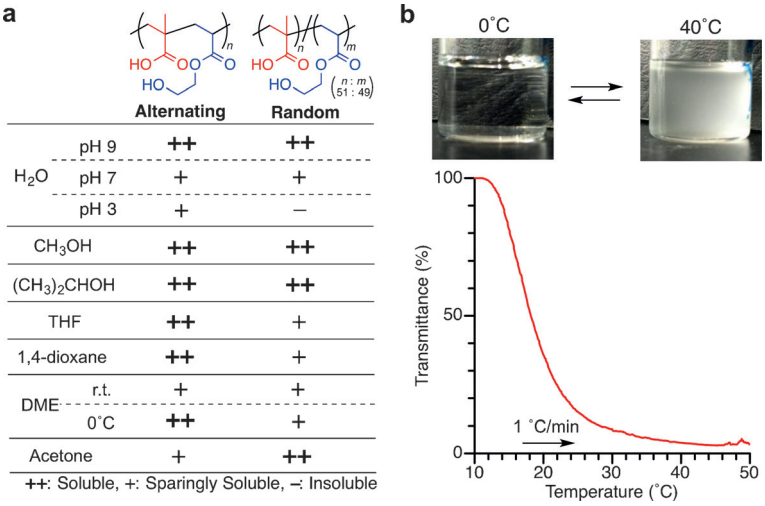

Figure 4. a) The solubility of the alternating and random copolymer of MAA and HEA, b) transmittance measurement of DME solution of the alternating copolymer (8 mg mL^{-1}) as a function of temperature. Heating process at 1 °C min^{-1} from 10 °C to 50 °C. Inset: photographs of DME solutions of the alternating copolymer at different temperatures.

chain interaction between neighboring pendants, that is, -COOH and -OH and 2) inter-chain interaction between -COOH pendants (so-called "carboxylic dimer") that would cause precipitation or phase separation. The neighboring hydroxy group could affect the inter-chain interaction between -COOH pendants through its hydrogen bonding with the acid and/or its solvation, and the interaction preference might be changed depending on temperature of the DME solution leading to LCST behavior. In general, LCST behavior of polymers in organic solvents is not common, and a specific combination of polymer structure and solvent are required, such as poly(vinyl ether) having ionic liquid pendant in chloroform,[26] PEG pendant polymethacrylate in hydrofluorocarbon,[27] and polyether in ionic liquid.[28] It should be noted that the LCST behavior was observed by using very simple structures composed of MAA and HEA units in the ether solvent and was specific to the "alternating" sequence.

In conclusion, the simple connection of methacrylate and acrylate via and HAE bond in the side chain could lead to an alternating sequence of -COOH and -OH pendant groups through the cyclopolymerization and the cleavage of the HAE bond in the repeating cyclo-units. The alternating sequence of the two functional groups provided a unique solubility behavior, which was different from the random sequence of same composition ratio. This approach would open the door to the development of sequence control for vinyl copolymers and the creation of sequence-oriented functions or properties.

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[22] When a 1:1 copolymerization of methyl methacrylate (MMA) and methyl acrylate (MA) was performed under the same conditions, such a parallel consumption was not observed (MMA was polymerized faster than MA) and the copolymerization was much slower (Figure S3). The smooth and parallel consumption of the two vinyl groups of **1** is likely due to the intramolecular propagation effect, as discussed with model reaction.

[23] The iodine-based ruthenium catalyst was used only for MALDI-TOF-MS analysis to suppress the halogen exchange reaction which makes the analysis complicated. See Table S1 Entry 7. For usual cyclopolymerizations, [RuCp*(Cl)(PPh_3)$_2$] was used because it is commercially available.
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