

Note

ACYCLIC DIENE METATHESIS POLYMERIZATION OF TAILOR-MADE MONOMERS TOWARDS SEQUENCE-REGULATED VINYL COPOLYMERS*

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Abstract Acyclic diene metathesis polymerization (ADMET) enables convenient transfer of sequential information of the designed monomers to the corresponding sequence-regulated copolymers. In this study, two structurally symmetric monomers, M1 and M2, were synthesized *via* atom transfer radical addition (ATRA) of diethyl *meso*-2,5-dibromohexanedioate with 1,5-hexadiene and 1,7-octadiene, respectively. Thus, sequenced segment of VB-EA-EA-VB (VB and EA represent vinyl bromide and ethyl acrylate, respectively) was incorporated into the ADMET diene monomers. ADMET polymerization of these two monomers with Grubbs first generation catalyst (Grubbs-I) was performed in CH₂Cl₂ at 40°C for 5 days under nitrogen purge. Effects of catalyst amount, monomer concentration and methanol precipitation on the M_p and PDI of polymers were investigated by GPC, and the structures of the formed polymers were characterized by NMR. Our results indicate that using 3.0 mol% of Grubbs-I to monomer can afford polymers with high M_p . Moreover, selective precipitation in methanol enables complete removal of low molecular weight components from the crude products. Meanwhile, M2 exhibits higher ADMET polymerization reactivity than M1 due to its capability of suppressing negative neighboring group effect.

Keywords: ADMET; ATRA; Sequence-regulated copolymers.

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Vinyl polymers are among the most widely used synthetic materials in industry and daily life. Besides the most well-known bulk materials of homopolymers like polyethylene and polypropylene, mixtures of homopolymers have also been commonly used as polymer blend or “polymer alloy”. Depending on the nature of homopolymers, these mixtures may be molecularly compatible or phase-separated at the macromolecular level. More importantly, copolymerization of a set of two or more monomers can provide copolymers with chain heterogeneity, and thus become an important method to modulate the polymer properties and obtain advanced materials. A typical example is SBS thermal plastic elastomer prepared by the sequential anionic polymerization of styrene and 1,3-butadiene. Coexistence of the rigid polystyrene segment (PS) and flexible polybutadiene segment (PB) in a designed SBS sequence endows the materials with crystallinity and viscoelasticity, respectively. However, synthetic polymers still fall very much behind biomacromolecules in respect of hierarchical structures and precise functions^[1, 2]. For instance, the fine chemical structures of proteins are mono-

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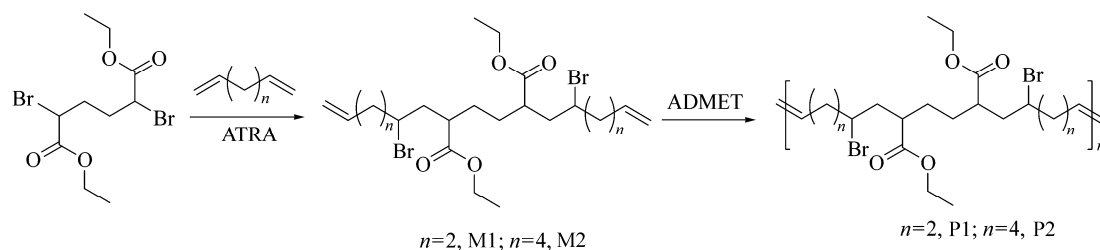
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disperse, stereo-specific, and sequence-defined polypeptides, affording assemblies of high structural complexity and functions with high specificity and efficiency. In this context, the chemical structures of synthetic polymers are far beyond perfectly controlled at an atomic level as compared to biomacromolecules, and thus polymer chemists are still miles away to mimic both the structure and the function of the elegant natural examples.

Sequence-controlled polymerization arouses the research enthusiasm of polymer chemists in recent years^[1, 2]. Among them, vinyl copolymers with sequenced microstructures are the most challengeable since direct copolymerization of even two monomers will certainly result in copolymers with chain heterogeneity due to the difference of reactivity ratios^[3–8]. Synthetic wisdom has been reflected in some elegant examples to manipulate chain propagation processes by controlling the selectivity of carbon-carbon bond formation^[9–14]. Nevertheless, rather limited monomers could be selected for sequence control *via* chain-growth mechanism.

Acyclic diene metathesis polymerization (ADMET), an efficient and convenient method to obtain polyolefin *via* step-growth mechanism, has been systematically investigated over the past two decades^[15]. Many kinds of functionalized polyethylene, polyolefin with complex topology, and advanced polymeric materials have been reported^[16]. Taking advantage of high tolerance to polar groups of ruthenium-based catalysts and wide accessibility of organic reactions to obtain diene monomers, ADMET has been utilized to afford vinyl copolymers with pendant groups separated by methylene spacer of defined length, the structures of which are unattainable through chain-growth copolymerization methodology^[17–22]. Therefore, ADMET has proved to be a simple method towards perfectly controlling the polymer chain microstructures at an atomic level with wide options by rational design. However, in most cases, the previously reported diene monomers bear only a single functional entity by tedious synthetic procedures, while polyolefins with more complicated microstructures are scarcely seen in literature. Thus, we hypothesized that the built-in sequence of diene monomers *via* simple organic synthesis will certainly satisfy the urgent demand of sequence-regulated vinyl copolymers with microstructures consisting of several common vinyl monomers. As a first effort, we describe herein the synthesis of two diene monomers with the built-in sequenced segment of VB-EA-EA-VB (VB and EA represent vinyl bromide and ethyl acrylate, respectively) and their ADMET to produce a new type of sequence-regulated vinyl copolymers.

The two diene monomers, M1 and M2, were synthesized by the copper-catalyzed atom transfer radical addition (ATRA) reactions of *meso*-2,5-dibromohexanedioate with 1,5-hexadiene or 1,7-octadiene, respectively^[23]. Each monomer contains a sequenced segment of VB-EA-EA-VB, and after ADMET polymerization, this sequence information will transfer into the polymer to yield the sequence-regulated copolymers. Polymer P1 can be considered as a periodic copolymer of VB, EA and 1,3-butadiene; and in polymer P2, an additional ethylene unit is incorporated (Scheme 1). For a successful ATRA reaction, multiple additions of olefins and reactivation of the newly formed carbon halide should be suppressed to ensure that the most abundant product is the desired monoadduct. In this work, chemically dormant α,ω -diene was selected for ATRA reaction to completely prohibit multiple additions and reactivation of the formed bromides. Excesses of α,ω -dienes were used, and the reactions proceeded smoothly in THF at 40°C as catalyzed by copper powder, CuBr₂ and PMDETA. After standard chromatography separation of the yellowish crude products, pure products were obtained as viscous colorless oil in 70% yields (see supplementary material for details).



Scheme 1 Monomer synthesis and ADMET

Figure 1 shows the ^1H - and ^{13}C -NMR spectra of the two monomers, characteristic peaks of the terminal olefins are clearly identified at $\delta = 5.0$ – 5.1 and $\delta = 5.7$ – 5.8 , respectively. Peaks of the ester ethyl groups appear at $\delta = 4.1$ – 4.2 for the methylene protons and $\delta = 1.2$ – 1.3 for the methyl group protons. Importantly, peaks at $\delta = 3.9$ – 4.0 and $\delta = 2.6$ – 2.8 assigning to the methine groups of C–Br and α position of the ester group provide direct evidences for the expected structures. All the afore-mentioned groups can be identified by the corresponding peaks in ^{13}C -NMR spectra. Their ESI-MS spectra shown in Fig. 2 are also consistent with the expected structures of M1 and M2. It should be noted that in the NMR spectra, the methylene protons in the main chain are splitted into a complicated fashion due to ambiguous stereochemistry of neighboring groups, and it is thus difficult to distinguish them in the NMR spectra. Nevertheless, in this work, control of stereo-selectivity of the ATRA reactions is not our concern.

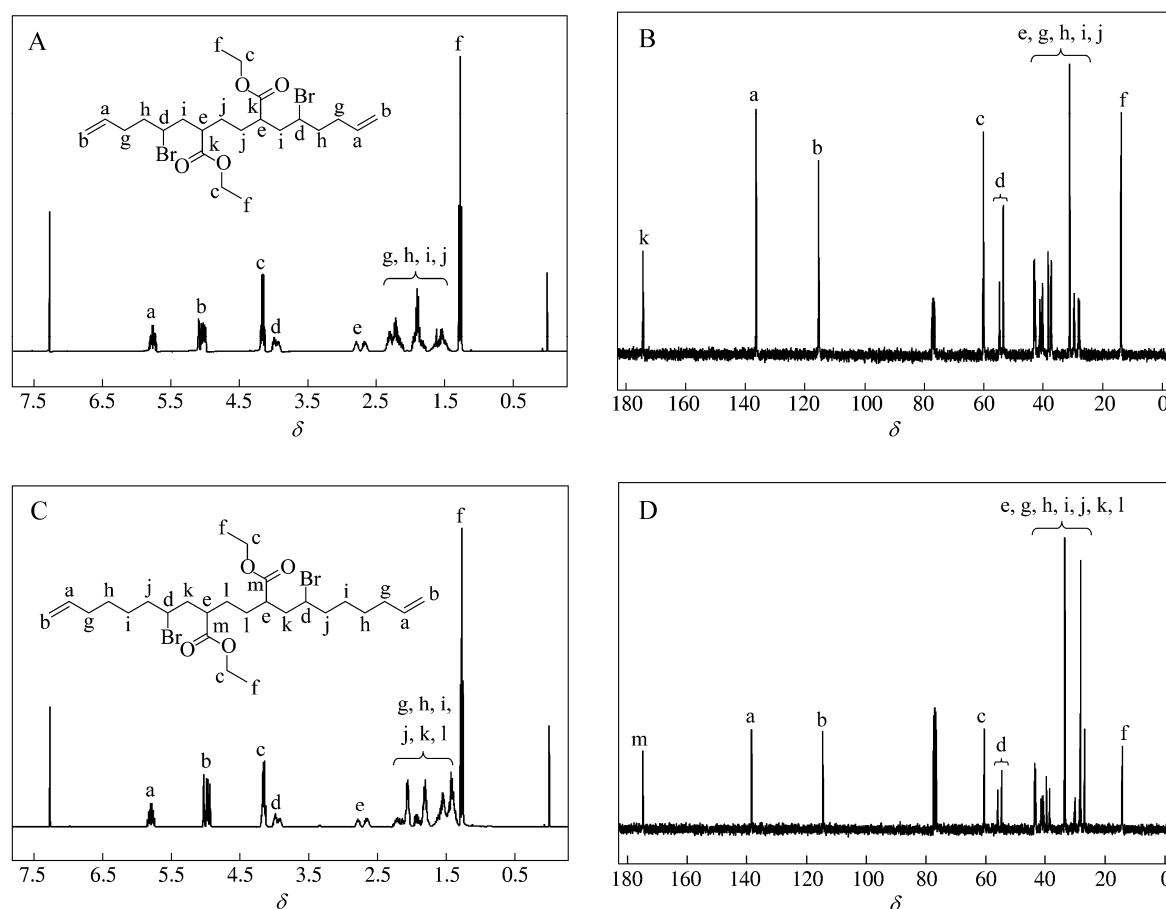


Fig. 1 ^1H - and ^{13}C -NMR spectra of monomers M1 (A and B) and M2 (C and D) (solvent: CDCl_3)

ADMET polymerization of dienes is a well-established method to produce polyolefins with internal alkenes in polymer main chain, this internal alkene can be considered as a structural unit formed by the 1,4 addition of 1,3-butadiene (Scheme 1). Here, we select Grubbs-I as the catalyst to suppress olefin isomerization^[24, 25]. The polymerizations were conducted in CH_2Cl_2 under nitrogen purge (a technique applied to remove the generated ethylene) for 5 days to get polymers with high molecular weights. As the polymerization proceeded, CH_2Cl_2 was gradually evaporated and the polymeric products became solidified. These polymer samples can be dissolved in THF, and GPC measurements were used to investigate the effects of catalyst amount, monomer concentration and reprecipitation on the M_p and PDI of the crude polymers.

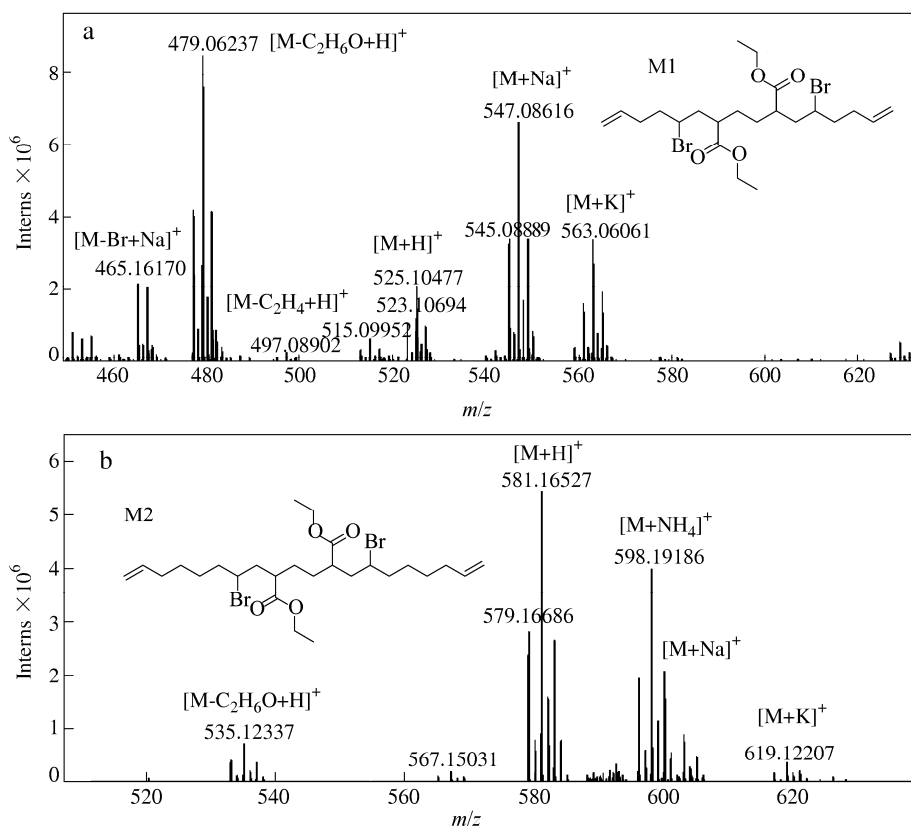


Fig. 2 ESI-MS spectrum of M1 (a) and M2 (b)

We first performed ADMET polymerization of M1 in 0.2 mL of CH_2Cl_2 with different amounts of Grubbs-I catalyst (feed ratio of catalyst to monomer: 0.5%, 1.0%, 3.0%, and 5.0%) and the GPC traces of the crude polymers are shown in Fig. 3(a). In all the cases, polymers were obtained, but with a portion of oligomers. Low molecular weight components account for larger proportions in the cases of Grubbs-I feed ratio set at 0.5% and 1.0%, at a ratio of 3.0% or above, P1 with M_p up to 6300 can be obtained. We also changed the monomer concentration by using different amounts of CH_2Cl_2 (0.1, 0.2, 0.5, and 1.0 mL), roughly corresponding to $[\text{M1}]_0 = 5.0, 2.5, 1.0, \text{ and } 0.5 \text{ mol/L}$. Figure 3(b) shows the GPC traces of the crude polymer samples. Theoretically, step-growth polymerization should be performed at high concentrations to afford high molecular weight products; however, in this study, small amount of CH_2Cl_2 promotes polymerization. Previously, we performed ADMET polymerization of M1 in bulk, but dimer and trimer are the most abundant products. Since mixture of monomer and catalyst themselves is heterogeneous, solvent enables polymerization system with homogeneity. This family of GPC traces clearly shows that 2.5 mol/L monomer concentration benefits the ADMET polymerization mostly. Selective reprecipitation is a common method to remove low molecular weight components from crude products, thus narrowing the PDIs. We selected methanol as precipitant to purify the crude polymer samples. Components with molecular weight lower than 1000 are totally removed after three times of reprecipitation, and the PDI decreases to 1.41 without altering M_p (Fig. 3c). To compare the ADMET polymerization of M1 and M2, we polymerized equal molar amount (0.5 mmol/L) of the two monomers with 15 $\mu\text{mol/L}$ Grubbs-I both in 0.2 mL of CH_2Cl_2 at 40°C for 24 h. The GPC traces of both crude polymer samples shown in Fig. 3(d) clearly indicate that M2 exhibits higher polymerization reactivity. Since long alkyl chain is able to minimize negative neighboring group effect, this result is in accordance with the literature results^[26]. All these results are summarized in Table 1.

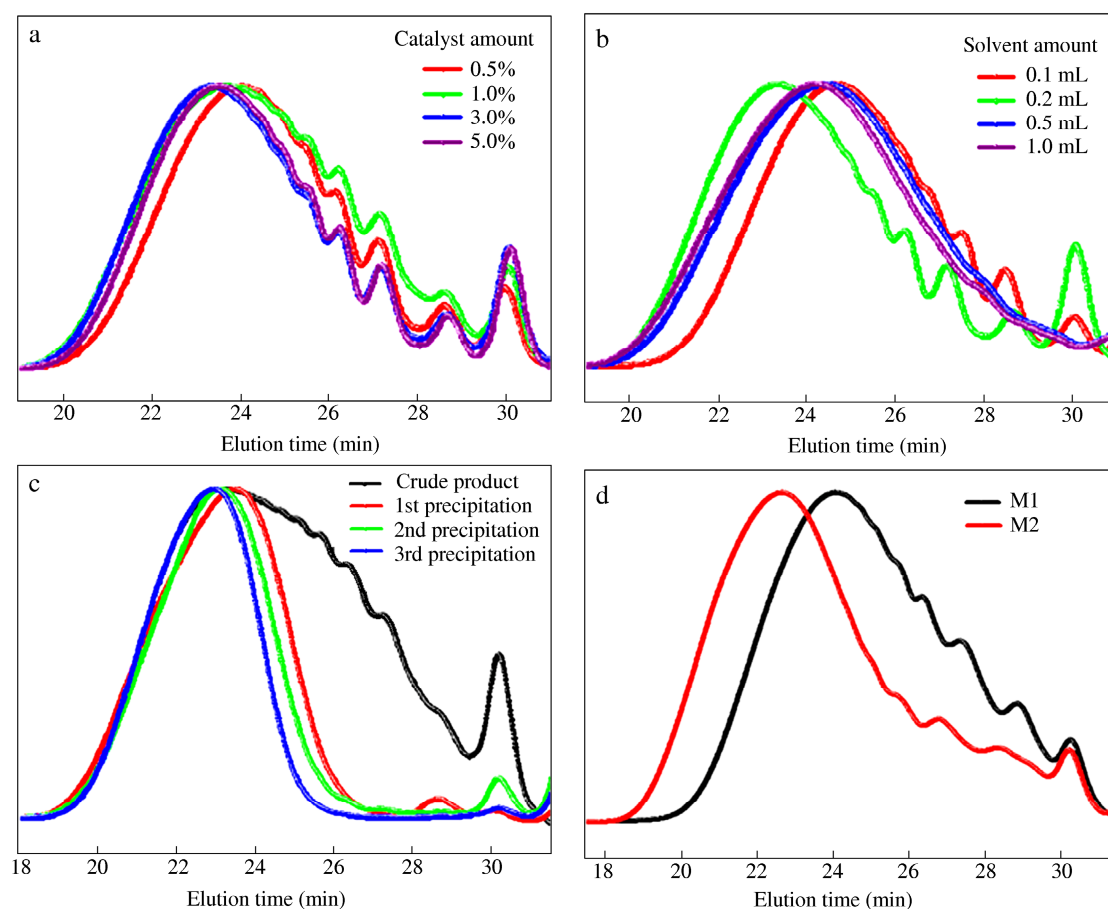


Fig. 3 GPC traces of crude polymer samples from the ADMET polymerizations of M1 at 40°C for 5 days: (a) $[\text{cat.}]/[\text{M1}] = 0.5\%$, 1.0% , 3.0% , and 5.0% ; (b) $[\text{M1}]_0 = 5.0$, 2.5 , 1.0 , and 0.5 mol/L; (c) effects of precipitation in methanol; (d) GPC traces of two crude polymer samples: M1 or M2 (0.5 mmol/L), Grubbs-I (15 $\mu\text{mol/L}$) in 0.2 mL of CH_2Cl_2 at 40°C for 24 h, respectively

Table 1. Molecular weights of polymers obtained by ADMET*

Entry	Monomer	Grubbs-I (mg)	CH_2Cl_2 (mL)	M_p^a	PDI ^a
1	M1	2.1	0.2	4700	2.16
2	M1	4.1	0.2	5400	2.52
3	M1	12.3	0.2	6300	2.58
4	M1	20.5	0.2	5900	2.46
5	M1	12.3	0.1	3700	2.45
6	M1	12.3	0.5	4000	2.26
7	M1	12.3	1.0	4400	2.38
8 ^b	M1	—	—	6500	3.10
9 ^c	M1	—	—	5800	1.58
10 ^d	M1	—	—	6800	1.47
11 ^e	M1	—	—	6600	1.41
12 ^f	M1	12.3	0.2	4600	2.40
13 ^f	M2	12.3	0.2	8400	3.26

* ADMET polymerization time is set at 5 days unless otherwise noted;

^a Determined *via* GPC; ^b Crude polymer sample; ^c Polymer sample after precipitation in methanol for one time;

^d Polymer sample after twice precipitation in methanol; ^e Polymer sample after three times precipitation in methanol; ^f Crude polymer samples after 24 h polymerization

Figure 4 shows the ^1H - and ^{13}C -NMR spectra of polymers derived from M1 and M2, respectively. Signals of internal alkenes are clearly identified at chemical shifts ranging from $\delta = 5.2$ to 5.4 with most of them adopting *trans* conformation. However, calculation of the *E/Z* ratio was not successful due to severe signal overlap. Meanwhile, terminal olefins exhibit comparable signal strength to the internal ones, indicating a limited degree of polymerization as discussed above. Besides the peaks of the double bonds, all the other characteristic peaks appear at the same chemical shifts as those in the NMR spectra of the corresponding monomers, but with obvious signal broadening. Moreover, the similarity of ^{13}C -NMR spectra of polymer and monomers demonstrates that ADMET polymerization did not alter the chemical structures of the built-in sequenced information in the monomers.

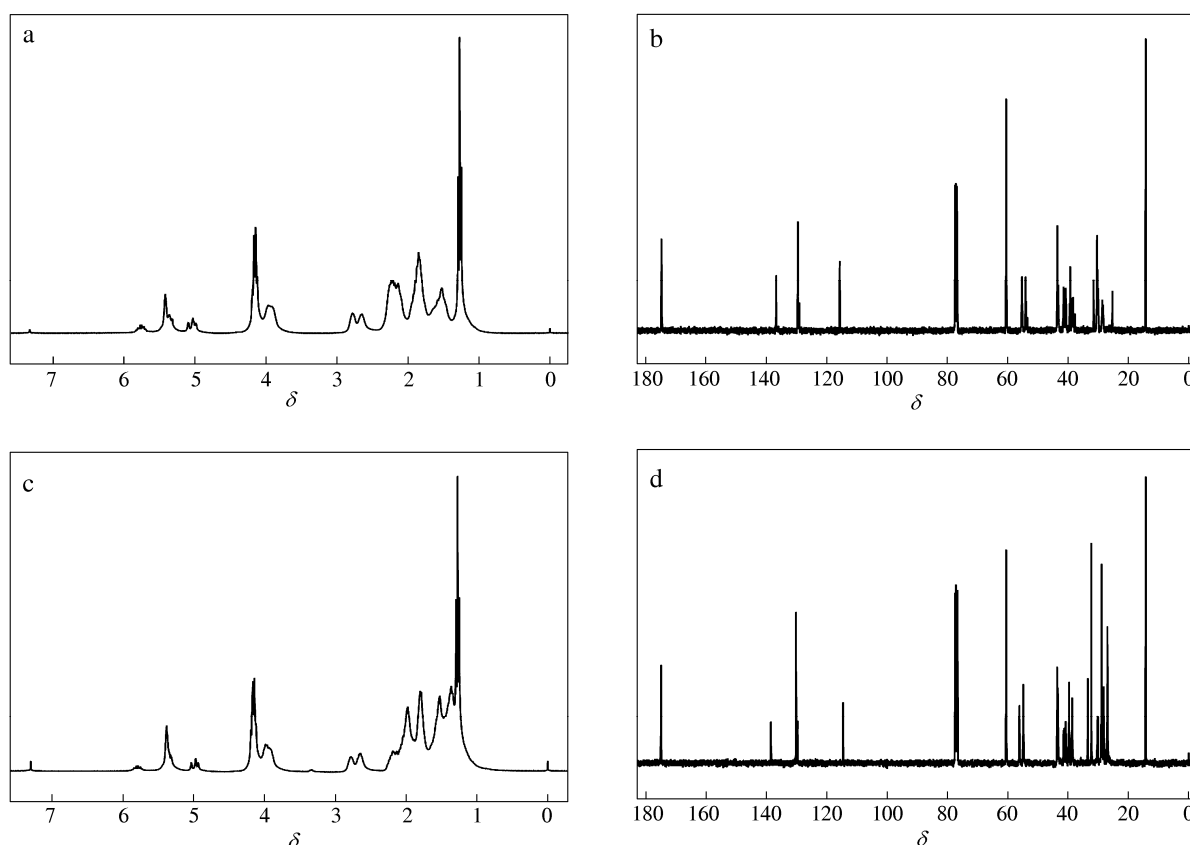


Fig. 4 ^1H - and ^{13}C -NMR spectra of polymers of M1 (a and b) and M2 (c and d), respectively (solvent: CDCl_3)

The fine structures of the polymers were characterized by MALDI-TOF-MS as shown in Fig. 5. A family of peaks with a regular interval of 496 and 552 (theoretical repeating unit mass for M1 and M2, respectively) indicates the integrity of the polymer structures. However, the spectra also exhibit minor series with peak mass shifted from the corresponding major series by a mass of $14 \times n$, implying that different methylene units exist between sequenced segments. This phenomenon also evidences the olefin isomerization during ADMET polymerization even if Grubbs-I was used as the catalyst^[27, 28].

In summary, we demonstrated that ADMET polymerizations of monomers with built-in sequence of vinyl monomer units can form periodic polymers with accurate sequence. Two monomers, M1 and M2 with sequenced segment of VB-EA-EA-VB were synthesized by ATRA reaction of structurally symmetric ATRP initiator *meso*-2,5-dibromohexanedioate and 1,5-hexadiene or 1,7-octadiene to incorporate. ADMET polymerizations of the monomers were successfully performed with Grubbs-I as the catalyst at 40°C in CH_2Cl_2 , M2 exhibits higher polymerization reactivity than M1 due to its long alkyl chains that suppress the negative neighboring group

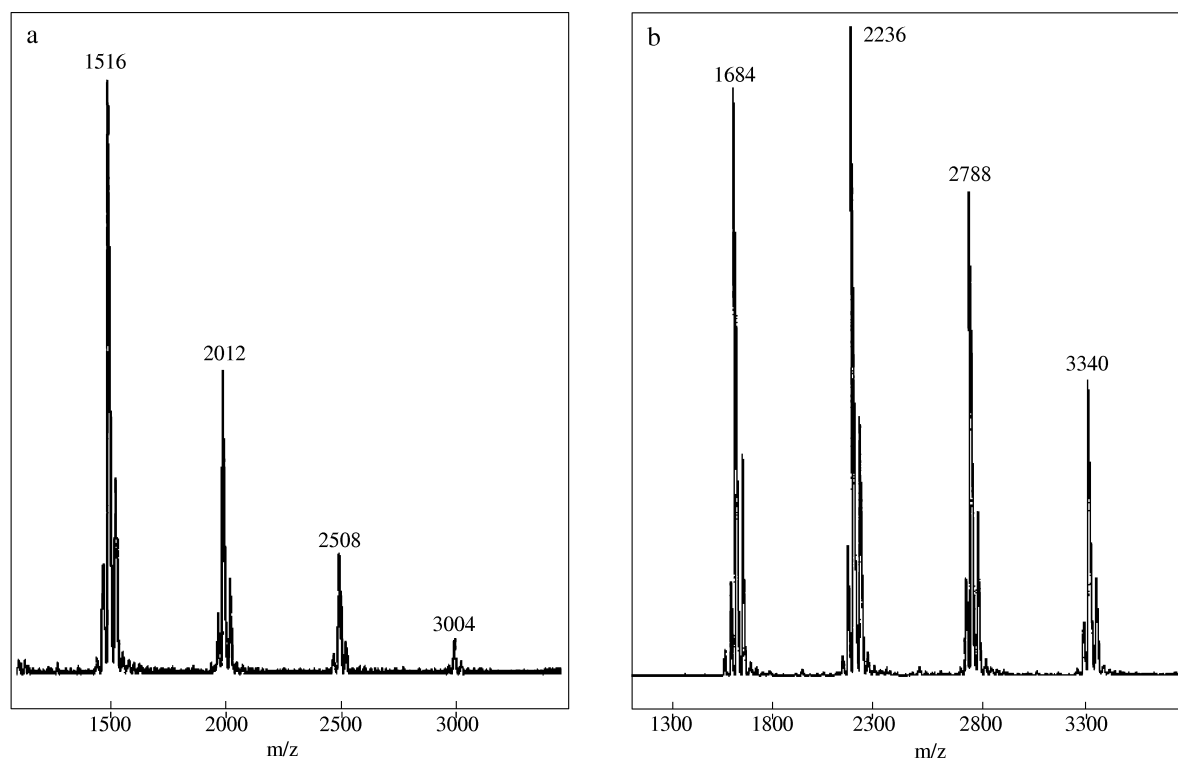


Fig. 5 MALDI-TOF-MS spectra of M1 (a) and M2 (b), respectively

effect. After optimizing the polymerization conditions, moderate to high molecular weight polymers were obtained, and these polymers have well-defined sequence microstructures evolved from the tailor-made monomers. This approach is an efficient method to prepare carbon chain copolymers with specific monomer sequence, and can thus provide unprecedented polymer samples to elucidate the exact structure-property relationship of copolymers at an atomic level.

SUPPORTING INFORMATION General experimental procedures including materials, measurements, synthesis of monomers, and ADMET polymerization

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