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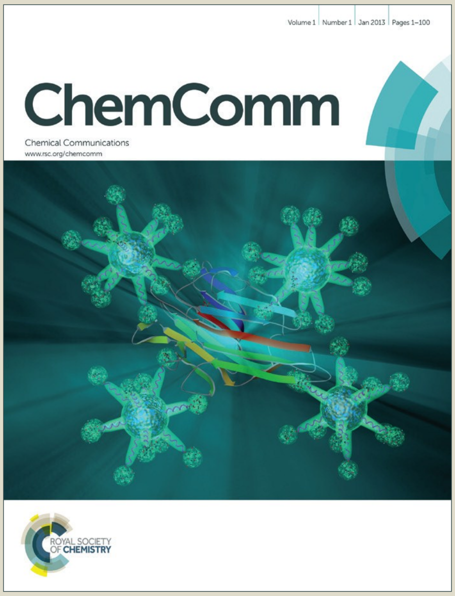

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One-Pot Synthesis of Semicrystalline/Amorphous Multiblock Copolymers via Divinyl-Terminated Telechelic Polyolefins

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A simple, one-pot approach to synthesize random semicrystalline/amorphous multiblock copolymers (12-17 blocks per chain on average) is demonstrated that takes advantage of acyclic diene metathesis (ADMET) polymerization of α,ω-divinyl-terminated telechelic polyolefins. This synthetic approach offers a generic, viable and economical route to polyolefin-based multiblock copolymers and may be extendable to broader families of multiblock materials.

Multiblock copolymers are of interest because of the resulting microphase-separated morphologies and differences in thermal and mechanical properties, relative to homopolymers, homopolymer blends, and simple copolymers such as A-B diblocks.[1] Despite their promise, broad exploration of multiblock copolymers, especially in the important class of polyolefin-based copolymers, has been limited by synthetic accessibility.[2,3] Block copolymer synthesis often requires living or quasi-living polymerization conditions and the sequential addition of distinct monomers.[1b,1c,4] This approach has been used to synthesize multiblock structures with up to 20 blocks, but remains restricted in terms of monomer types and the available methods of polymerization.[5] An alternative synthetic method for multiblock copolymers involves the coupling of individual blocks via telechelic functional groups.[1a, 6] This approach increases the range of segment types, but has been largely restricted to condensation chemistries that are generally not compatible with multiblock synthesis.

Multiblock copolymers that possess soft elastic segments and hard crystalline segments have attracted extensive attention.[1f,7] The amorphous domains provide for elastomeric properties, while the crystalline domains act as physical cross-links that give the material strength.

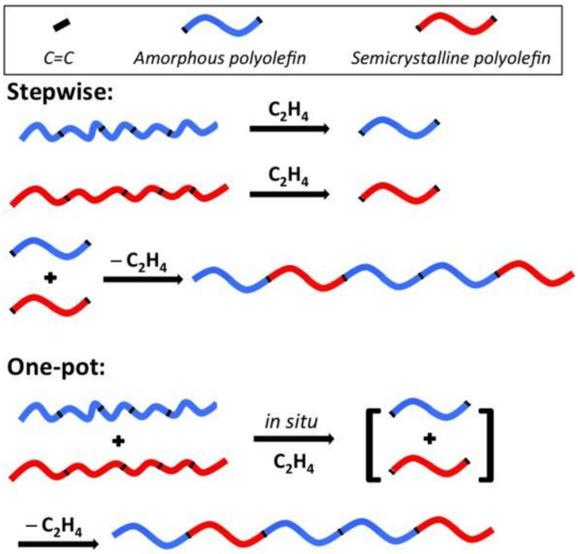

Fig. 1 Schematic illustration of synthetic approaches (stepwise vs. one-pot) to random semicrystalline/amorphous multiblock copolymers via ADMET depolymerization/repolymerization.

Acyclic diene metathesis (ADMET) polymerization offers a synthetic route for the polymerization of low molecular weight α,ω-terminated diene monomers.[8] However, examples of ADMET polymerization of telechelic macromonomers remain rare.[9] Recently, it was demonstrated that α,ω-divinyl-terminated telechelic polyolefins can be obtained from terpolymers containing ethylene, 1-octene, and butadiene by an olefin metathesis strategy using ethylene, namely ethenolysis.[10]

In this contribution, we report a convenient one-pot protocol to prepare random semicrystalline/amorphous multiblock copolymers containing, on average, more than 10 blocks via sequential ADMET depolymerization/repolymerization process. As shown in Fig. 1, the process can be carried out via isolation of telechelic intermediates, or, more simply, in one pot with the addition/removal of ethylene. The thermal and mechanical properties of the new multiblock copolymers are evaluated. They exhibit similar

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Table 1. Characterization Data of Starting Polymers.

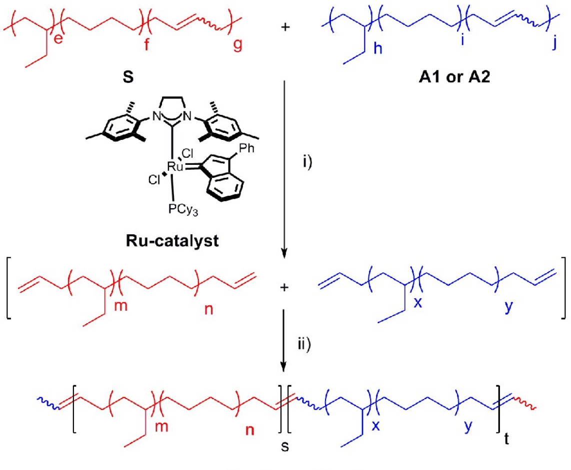
Polymer	1-Butene[a] (mol%)	Tetramethylene[a] (mol%)	1,3-Butadiene[a] (mol%)	M_n (kg mol^{-1})[b]	$Đ$[b]	T_m (°C)[c]	T_g (°C)[c]	ΔH_m (J g^{-1})[c]
S	10	86	4	202	1.8	91	-	64
A1	52	40	8	56	1.8	-	-49	-
A2	57	35	8	197	1.6	-	-61	-

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by GPC analysis at 150 °C in 1,2,4-trichlorobenzene versus polystyrene standards. [c]Determined from the second heating cycle of DSC measurements at a heating/cooling rate of 10 °C min^{-1}.

melting temperatures (T_m) as the starting semicrystalline polymers, and similar glass transition temperatures (T_g) as the starting amorphous polymers. These copolymers offer significantly improved mechanical properties when compared to a physical blend of the two corresponding starting polymers. Moreover, mechanical properties of the resulting copolymers can be tuned by simply varying the input weight ratio of the two starting materials.

Semicrystalline (**S**) and amorphous polymers (**A1**) and (**A2**) were prepared via partial hydrogenation [11] of three commercially available polybutadienes (**PBD**) with different vinyl content, *i.e.* arising from 1,2-inserted butadiene. Partial hydrogenation of PBD was performed using Wilkinson's catalyst ($RhCl(PPh_3)_3$) under a H_2 atmosphere (200 psi) inside a Parr reactor. Monitoring the reactions as a function of reaction time allows one to convert the vinyl groups into ethyl branches, but not to completely reduce the 1,4-inserted butadiene units. Thus, the three resulting polymers, **S**, **A1** and **A2** may be represented as random terpolymers of 1-butene, tetramethylene, and 1,3-butadiene, and the percentages of these three components are listed in Table 1. The molar percentage of 1,3-butadiene remaining after hydrogenation impacts both the segment length and the fraction of divinyl telechelic segments generated after ethenolysis. Note that ethenolysis provides two mono-vinyl polymeric segments per chain, which act as chain terminating segments in the subsequent ADMET reaction.

The one-pot synthesis of olefin-based semicrystalline/amorphous multiblock copolymers is outlined in Scheme 1. The depolymerization (ethenolysis) reaction was performed in a toluene solution of a semicrystalline polymer **S** and an amorphous polymer **A** ([polymer]$_{S+A}$ = 30 g L^{-1}) at 90 °C under 25 psi ethylene in the presence of a ruthenium catalyst (2.2 mol% relative to 1,3-butadiene unsaturation in the starting polymers). The choice of ruthenium catalyst was based on commercial availability, high thermal stability and functional group tolerance.[10,12] After 2 h, additional catalyst (1.0 mol% relative to 1,3-butadiene unsaturation in the starting polymers) was added. The ethylene atmosphere was switched to argon via sparging through the solution, in order to remove ethylene and drive the reaction equilibrium toward polymerization. The solvent was evaporated over a period of 30 min by carefully adjusting the argon flow rate. The polymer residue was dissolved in a minimum amount of toluene, and precipitated in methanol, filtered, and dried under vacuum overnight. In these studies, **P(S-A1)** was prepared from **S** and **A1** at a 1:1 weight ratio, while **P1(S-A2)** and **P2(S-A2)** were prepared from **S** and **A2** at 1:1 and 3:2 weight ratios, respectively.



Scheme 1. *In situ* Synthesis of Random Semicrystalline/Amorphous Multiblock Copolymers via Ethenolysis and ADMET Polymerization. Reagents and conditions: i) C_2H_4 (25 psi), Ru-catalyst (2.2 mol% relative to 1,3-butadiene unsaturation in S and A), toluene (([polymer]$_{S+A}$ = 30 g L^{-1}), 90 °C, 2h; ii) Ar, Ru-catalyst (1.0 mol% relative to 1,3-butadiene unsaturation in S and A), toluene, 90 °C, 30 min.

To verify the overall sequence of steps proposed in the one-pot synthesis illustrated in Fig. 1, we also examined the stepwise ethenolysis/ADMET polymerization of **P(S-A1)**. We found no significant differences between these two methods (one-pot vs. stepwise) by analysis of ^{1}H NMR spectroscopy and gel-permeation chromatography (GPC). Note that the stepwise ethenolysis procedure required the synthesis of each telechelic polyolefin in a separate pot together with isolation and drying of the resulting telechelic products. Moreover, in the subsequent ADMET polymerization step, the two resulting telechelic polymers must be homogeneously mixed in dry toluene, which requires heating the mixture at 90 °C to enable full dissolution before the ruthenium catalyst is added.

Confirmation of chemical structures was sought by using ^{1}H NMR spectroscopy and GPC. ^{1}H NMR spectra were acquired at 120 °C in tetrachloroethane-*d*2, while high-temperature GPC was performed at 150 °C in 1,2,4-trichlorobenzene versus polystyrene standards. The ^{1}H NMR (Fig. 2) of the aliquot during the preparation of **P(S-A1)** showed the characteristic peaks of terminated vinyl groups (H_2C=CH-, 5.00 and 5.85 ppm), along with the internal unsaturated peaks (-HC=CH-, 5.45 ppm), due to incomplete depolymerization. The molar ratio of the terminal H_2C=CH- vs. the internal -HC=CH- was estimated to be approximately 2:0.7 from ^{1}H NMR integration of the corresponding unsaturated protons. GPC analysis of the same aliquot showed a sharp decrease in molecular weight (M_n = 3305 g mol^{-1}, $Đ$ = 2.2), compared to the starting polymers **S** and **A1** (Fig. S6).

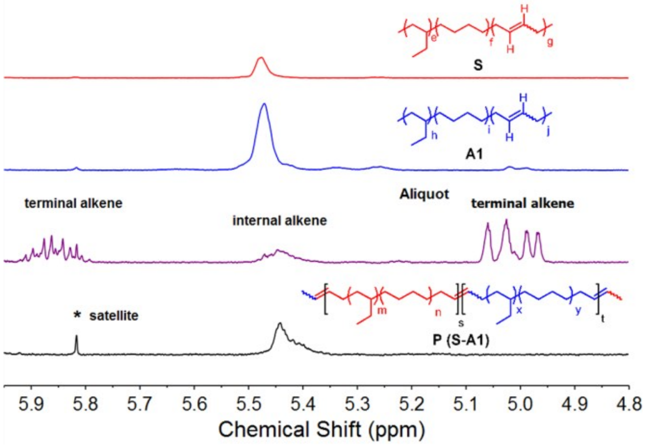


Fig. 2 Representative ^{1}H NMR spectra in the range of 4.80-5.95 ppm in tetrachloroethane-*d*2 at 120 °C.

After ADMET polymerization, the ^{1}H NMR spectra showed no signals attributable to vinyl olefins (Fig. 2), indicative of nearly quantitative consumption of telechelic chains. GPC analysis indicated an increase in molecular weight relative to the aliquot mixture (Fig. S6). The molecular weight of the multiblock polymer **P(S-A1)** was determined to be M_n = 55 kg mol^{-1} ($Đ$ = 2.7), which was estimated to be approximately 17 blocks per chain on average, based on the M_n of the aliquot mixture.

Thermal properties of the polymers were analyzed using differential scanning calorimetry (DSC) (Table 1 and 2 and Fig. S9). All multiblock copolymers displayed a melting peak (T_m) similar to that of the starting semicrystalline polymer **S** at 91 °C. Moreover, the multiblock copolymers showed similar T_g values compared to those of the starting amorphous ones. The crystallinity of the starting semicrystalline polymer **S** was 23%, which was calculated from the heat of fusion ratio $\Delta H_m / \Delta H_m^0$, where ΔH_m^0 is the melting enthalpy of completely crystalline linear polyethylene of (277 J g^{-1}).[13] Both **P(S-A1)** and **P1(S-A2)** synthesized from a 1:1 weight ratio of semicrystalline polymer to amorphous polymer showed a crystallinity of 11% and 10%, respectively. The crystallinities of **P(S-A1)** and **P1(S-A2)** were approximately half that of the starting semicrystalline polymer **S** (23%), which suggests that both semicrystalline and amorphous polymeric segments were incorporated in nearly equivalent quantities. The crystallinity (14%) of the ADMET polymer **P2(S-A2)** prepared from a 3:2 weight ratio of semicrystalline polymer **S** to amorphous polymer **A2** was higher than that of **P1(S-A2)**, as expected.

To evaluate mechanical properties of the multiblock copolymers, tensile testing experiments of a physical blend of **S** and **A1** (**BL(S-A1)**) and its corresponding multiblock copolymer product **P(S-A1)** were performed. It is worth noting that **BL(S-A1)** was prepared by fully dissolving **S** and **A1** (1:1 weight ratio) in toluene at 90 °C, followed by solvent removal. Representative nominal stress versus nominal strain curves of **BL(S-A1)** and **P(S-A1)** were chosen from at least five data sets per sample and are shown in Fig. 3a**. P(S-A1)** exhibited dramatically improved mechanical behavior compared to **BL(S-A1).** Specifically, **P(S-A1)** displayed an ultimate elongation at break (ε) of 430%, while that of **BL(S-A1)** was determined to be 70%. Furthermore, **P(S-A1)** revealed higher ultimate tensile stress (σ = 7 MPa) than that of the **BL(S-A1)** (σ = 1.5 MPa).

Table 2. Characteristic Data for Illustrative ADMET Polymers

Polymer	M_n (kg mol^{-1})^a	$Đ^a$	T_m (°C)^b	T_g (°C)^b	ΔH_m (J g^{-1})^b
P(S-A1)	55	2.7	89	-52	31
P1(S-A2)	45	3.8	93	-52	29
P2(S-A2)	44	3.6	89	-50	39

[a] Determined by GPC analysis at 150 °C in 1,2,4-trichlorobenzene versus polystyrene standards. [b] Determined by DSC (second heating cycle) at 10 °C min^{-1}.

The morphologies of the tensile specimens, **BL(S-A1)** and **P(S-A1)**, were imaged by scanning electron microscopy (SEM). The tensile specimens were fractured in liquid nitrogen, and the resulting cross-sections were similar as indicated in SEM images (Fig. S10). After immersing these fractured samples in toluene at room temperature for 20 min, **BL(S-A1)** and **P(S-A1)** exhibited significantly different morphology changes as shown by SEM (Fig. 3c and 3d). The blend **BL(S-A1)** showed extensive pitting and roughness on the fractured surface after toluene etching (Fig. 3c). This suggests macrophase separation of the amorphous component domains from the crystalline component-rich ones in **BL(S-A1)**, as amorphous component rich domains were expected to be more soluble in toluene than the crystalline counterparts at room temperature. In contrast, the morphology of **P(S-A1)** was maintained after exposure to toluene at room temperature for 20 min (Fig. 3d). Such macrophase separation in **BL(S-A1)** is likely to be responsible for its poorer mechanical properties, when compared to **P(S-A1)**.

Comparison of **P1(S-A2)** and **P2(S-A2)** shows that the mechanical properties of the multiblock copolymers can be tuned by varying the weight ratios of the starting semicrystalline polymer **S** and the amorphous polymer **A2**. Monotonic and step-cycle tensile mechanical tests were carried out with at least 5 dog-bone specimens. Representative curves of monotonic mechanical tests are shown in Fig. 3a, while the elastic recovery[14] calculated from step-cycle tensile testing (Fig. S11 and S12) is given in Fig. 3b. **P1(S-A2)** and **P2(S-A2)** were able to stretch to 520% and 580%, respectively. The tensile stress at break (σ) and Young's modulus (E) of **P2(S-A2)** were both higher than those of **P1(S-A2)** (Fig. 3a). Of particular interest is that the elastic recovery of **P1(S-A2)** was calculated to be 80% at a strain of 200% with an initial Young's modulus of 11.6 ± 0.1 MPa (Fig. 3b). Similarly, the elastic recovery of **P2(S-A2)** was over 80% at a strain of 150%, with an initial Young's modulus of 18.7 ± 0.1 MPa. **P1(S-A2)** and **P2(S-A2)** are therefore highly elastic materials, yet the higher semicrystalline block content in **P2(S-A2)** increases σ and E, while reducing elastic recovery.

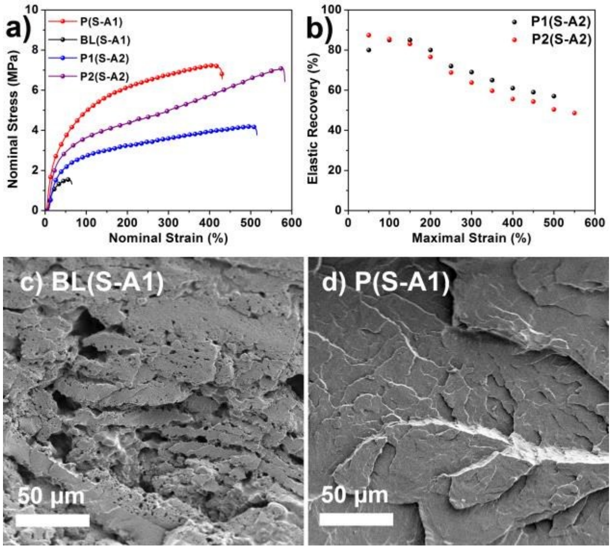


Fig. 3 a) Representative tensile stress-versus-strain curves for P(S-A1), BL(S-A1), P1(S-A2) and P2(S-A2). b) Elastic recovery of P1(S-A2) and P2(S-A2) as a function of maximum tensile strain. c) and d) SEM images of the cross-section of tensile specimens for BL(S-A1) and P(S-A1) after etching in toluene for 20 min at room temperature.

In summary, we have developed a convenient one-pot protocol to prepare random semicrystalline/amorphous multiblock copolymers from telechelic macromonomers. The overall process is a depolymerization/repolymerization/scrambling of polymer segments bound by internal olefins in the starting polymers. The results show that repolymerization of olefin-based α,ω-divinyl telechelics to produce the multiblock copolymers with more than ten blocks can be realized via ADMET polymerization. All the produced polymers showed melting temperatures close to the parent semicrystalline polymer (91 °C) and similar T_g values (≤ -50 °C) to the starting amorphous polymers. The multiblock copolymers offer significantly improved mechanical properties relative to the corresponding physical blend, consistent with the more intimate relationship between semicrystalline and amorphous segments as a result of covalent constraints. By varying the weight ratio of the starting polymers, the tensile properties of the generated copolymers can be tuned. Ultimate elongation at break up to 580%, and 80% elastic recovery at 200% stain with Young's modulus higher than 10 MPa were obtained. This synthetic strategy provides a generic and viable route to multiblock copolymers and expands the synthetic tool kit in this area.

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TOC graphic:

A one-pot synthesis of random semicrystalline/ amorphous multiblock copolymers is demonstrated via acyclic diene metathesis (ADMET) polymerization of α,ω-divinyl-terminated telechelic polyolefins.