Switchable Radical Polymerization of *α*-Olefins via Remote Hydrogen Atom or Group Transfer

Silin Song,[a] Shuo Wang,[a] Ziqiang Wang,[a] Hao Sun,*[a] Xianjin Wang,*[a] and Chen Zhu*[a]

Frontiers Science Center for Transformative Molecules, Zhangjiang Institute for Advanced Study, and Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

Abstract: Introducing polar groups into non-polar polyolefins can significantly enhance the important properties of materials. However, producing polyolefin backbones consisting of polar blocks remains elusive, due to the substantial difference of reactivity ratios between polar and non-polar olefin monomers in radical polymerization or the poisoning of transition-metal catalysts by polar groups in coordination polymerization. Herein we present a practical way for the preparation of polyethylene-based polymers with distinct polar groups by radical polymerization of *α*-olefins. A strategy of switchable remote hydrogen atom or group transfer is devised, leading to a diverse range of AAB or ABC sequence-defined carbon-chain polyolefins.
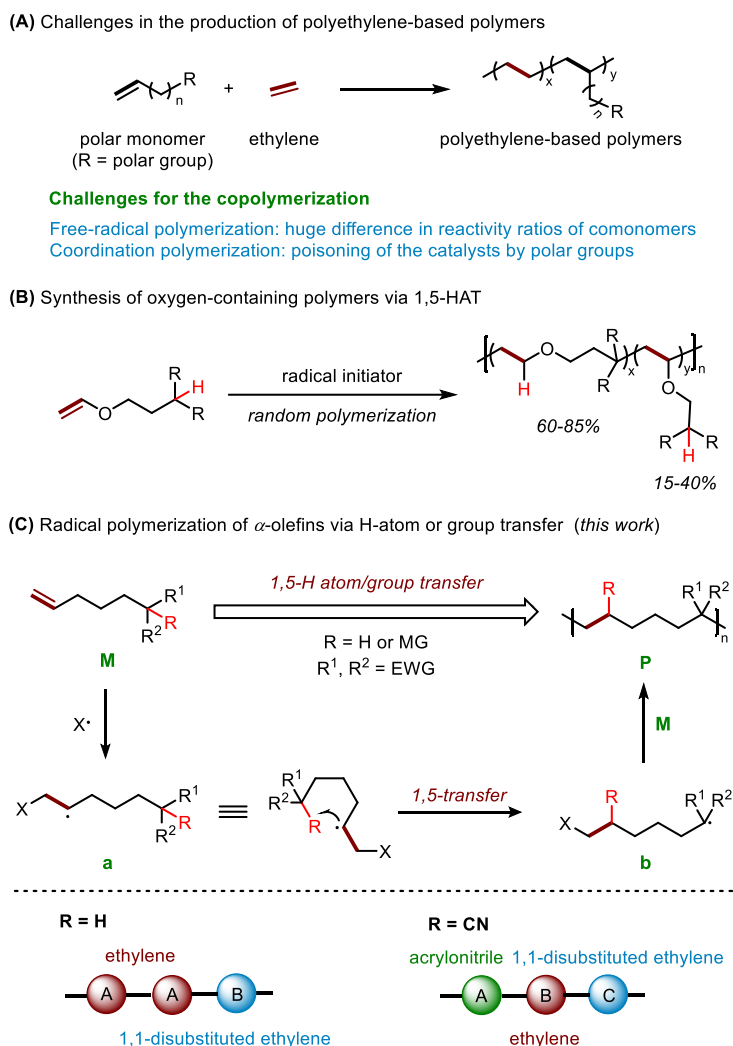
Introduction

Polyethylene-based polymers are the most widely used materials in the world, and their distinctive functions can be gained from the incorporation of various polar groups into the non-polar backbones that modifies the surface properties (e.g., adhesiveness, compatibility, toughness, adhesion, surface properties, etc.) of polyethylene.[1-3] Copolymerization of ethylene with polar vinyl monomers provides a straightforward route to prepare functionalized polyethylene-based polymers. However, the current methods can only produce random copolymers, and is impossible for the synthesis of sequence-defined copolymers (Fig. 1A). For instance, free-radical polymerization can be applied in the production of ethylene/polar monomer (e.g., acrylates, acrylic acid, vinyl acetate) copolymers, this method encounters the substantial difference of reactivity ratios between ethylene and polar vinyl monomers and leads to random polymers with low molecular weights and chains containing a significant amount of branches.[4-6] Moreover, in coordination polymerization the polar groups act detrimentally to the transition-metal catalysts, primarily due to the poisoning of the catalysts.[7-13] In this scenario, the innovation of advanced strategies to produce the polyolefins consisting of polar blocks in accurate sequence control is highly desirable.[14-18]

Designing new α-olefins by integration of polar moieties into non-polar olefins backbone transforms the original copolymerization of ethylene with polar vinyl

monomers into homopolymerization, and may overcome the sequence control problem in radical polymerization. Nevertheless, the homopolymerization of *α*-olefins is generally impeded by significant chain transfer process, in which the formation of more stable allylic radicals via hydrogen atom transfer (HAT) presents a major barrier to the successful assembly of polymer chains.[19] In 1990s, Sato *et al.* reported the radical polymerization of vinyl ethers via 1,5-HAT, aiming to generate the oxygen-containing polymers (Fig. 1B).[20-22] However, the polymerization proceeded through different pathways, leading to the polymers consisting of two chain structures. Moreover, these seminal studies were not applied to the construction of carbon-chain polyolefins.

We conceive to develop an efficient method for radical polymerization of *α*-olefins and construct sequence-defined polyethylene-based polymers with diverse polar blocks. In the hypothesis (Fig. 1C), strategically designed hexene derivatives substituted with two electron-deficient groups are employed as monomers. Mechanistically, the *in-situ* generated secondary alkyl radical abstracts H-atom from remote site, mainly via 1,5-HAT, to form a new tertiary alkyl radical species (**b**) that engages in the chain propagation. The driving force for the HAT has two folds: the tendency of H-abstraction from electron-deficient carbon by nucleophilic alkyl radical and the formation of a more stable tertiary alkyl radical. As a result, the fast intramolecular HAT suppresses the intermolecular chain transfer and facilitates the desirable polymerization of α-olefins. Alternatively, if the C-H bond is absent, the group transfer takes place instead of HAT to induce the polymerization.

Herein, we provide the proof-of-concept studies. When R is a H-atom, the polymerization proceeds via 1,5-HAT, leading to the AAB sequence-defined polymers, analogous to the ordered copolymers of ethylene and 1,1-disubstituted ethylene. When R is a cyano group, the polymerization proceeds via 1,5-cyano transfer, leading to the ABC sequence-defined polymers, analogous to the terpolymer comprising of ethylene, acrylonitrile, and 1,1-disubstituted ethylene. Of note, all these sequence-defined polyethylene-based polymers are difficult to prepare by current methods.

(A) Challenges in the production of polyethylene-based polymers

polar monomer
(R = polar group)

ethylene

polyethylene-based polymers

Challenges for the copolymerization

Free-radical polymerization: huge difference in reactivity ratios of comonomers
Coordination polymerization: poisoning of the catalysts by polar groups

(B) Synthesis of oxygen-containing polymers via 1,5-HAT

radical initiator
random polymerization

60-85%

15-40%

(C) Radical polymerization of α-olefins via H-atom or group transfer (*this work*)

1,5-H atom/group transfer
R = H or MG
R^1, R^2 = EWG

M

P

X·

1,5-transfer

a

b

R = H

ethylene

1,1-disubstituted ethylene

R = CN

acrylonitrile 1,1-disubstituted ethylene

ethylene

Figure 1. Preparation of polyethylene-based polymers. (A) Challenges in the production of polyethylene-based polymers; (B) Synthesis of oxygen-containing polymers via 1,5-HAT; (C) Radical polymerization of *α*-olefins via H-atom or group transfer. EWG = electron-withdrawing group; MG = migrating group.

Results and Discussion

Our study begun with an examination of the optimal conditions for the homopolymerization of methyl 2-cyanohept-6-enoate **M1**. This substrate can be conveniently synthesized within one step through the reaction of methyl cyanoacetate with 5-bromo-1-pentene. The polymerization employed azobis(isobutyronitrile) (AIBN) as the initiator at 65 °C for 12 h, leading to a white solid polymer with a 55% conversion. Characterization by gel permeation chromatography (GPC) demonstrated the number-average molecular weight (M_n) of 11.2 kg/mol and distribution ($Đ$) of 1.57 (Table 1, entry 1). Additional trials using other azo initiators such as 2,2'-azobisisoheptonitrile (ABVN) and dimethyl 2,2'-azobis(2-methylpropionate) (V601) did not improve conversion (Table 1, entries 2 and 3). We further explored the influence of peroxide-based initiators at 100 °C (Table 1, entries 4-8). Among these, *tert*-butyl peroxy benzoate (TBPB) provided the best results, elevating the conversion to 76% (Table 1,

entry 7). Increase of TBPB concentration from 2% to 4% significantly increased the conversion of **M1** to 91% (Table 1, entry 9). Extending the polymerization duration to 18 and 24 h yielded conversions of 79% and 90%, respectively (Table 1, entries 10 and 11). Elevated polymerization temperatures at 110 °C and 120 °C facilitated conversions reaching 90% and 96%, with increases in molecular weight to 18.1 kg/mol and 18.6 kg/mol (Table 1, entries 12 and 13). Additionally, this radical polymerization process proved effective in various solvents, including *N*, *N*-dimethylformamide (DMF), 2-butanone (MEK), chlorobenzene (PhCl), and toluene (Table 1, entries 14-17).

Table 1. Optimization of radical homopolymerization of methyl 2-cyanohept-6-enoate. [a]

Entry	Initiator	Solvent	Conv. (%) [b]	M_n (kg/mol) [c]	Đ [c]
1	AIBN	-	55	11.2	1.57
2	ABVN	-	47	10.2	1.52
3	V601	-	46	11.8	1.53
4	BPO	-	74	12.7	1.78
5	DPO	-	45	11.2	1.58
6	TBPA	-	74	14.1	1.75
7	TBPB	-	76	14.9	1.76
8	DTBP	-	26	14.1	1.53
9[d]	TBPB	-	91	15.8	1.87
10[e]	TBPB	-	79	15.0	1.77
11[f]	TBPB	-	90	16.1	1.85
12[g]	TBPB	-	90	18.1	2.03
13[h]	TBPB	-	96	18.6	1.96
14[h]	TBPB	DMF	84	8.0	1.33
15[h]	TBPB	MEK	81	8.4	1.57
16[h]	TBPB	PhCl	72	13.4	1.59
17[h]	TBPB	Toluene	74	13.2	1.56

[a] Reaction conditions: monomer concentration [M] = 2 M (if applicable), initiator (2 mol %), under N_2 for 12 h at 65 or 100 ºC. [b] The monomer conversion was determined by ^{1}H NMR spectroscopy using 1, 3, 5-trimethoxybenzene as internal standard. [c] M_n and Đ were determined by GPC in THF with polystyrene as an internal standard at 40 ºC. [d] TBPB (4 mol %). [e] 18 h. [f] 24 h. [g] 110 ºC. [h] 120 ºC.

The structural characterization of the polymer chain was elucidated through ^{1}H nuclear magnetic resonance (NMR) spectroscopy. In the spectrum, the aliphatic resonance observed between 3.49-3.52 ppm was attributed to the hydrogen atoms (denoted as H_f) adjacent to the cyano and ester groups. Notably, this signal was absent in the ^{1}H NMR spectrum of the polymerized sample (Fig. 2A), indicating alterations in the chemical environment of these hydrogen atoms consequent to the polymerization process. A peak spacing (m/z = 167) that corresponds to the designated repeating unit was identified in the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis (Fig. S1). As shown in Fig. 2B, polymers with M_n of 10 kg/mol were reached even at low conversion, which indicated a typical radical polymerization process.
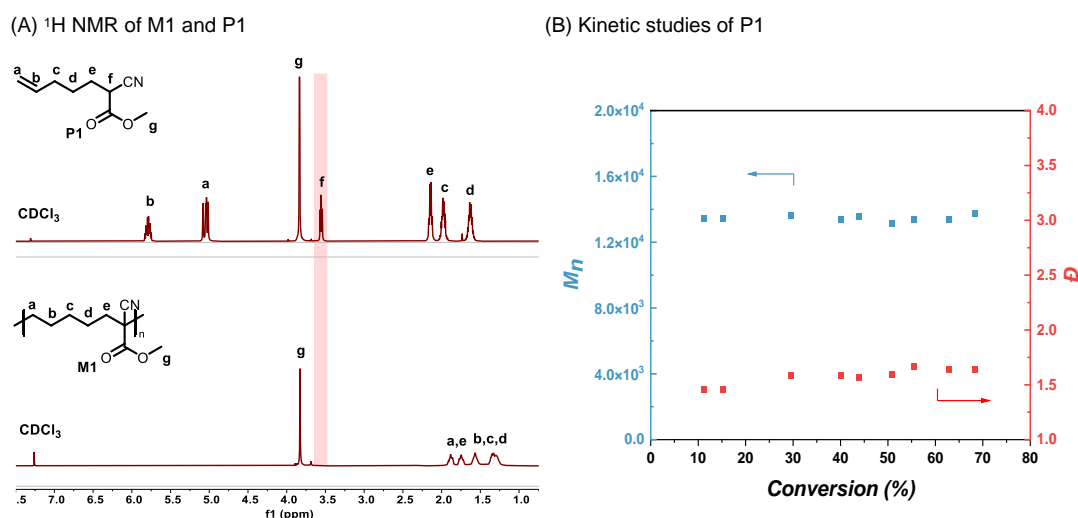
Figure 2. Polymer chain structure and type determination. (A) ^{1}H NMR of **M1** and **P1**; (B) Kinetic studies of **P1**.

With the optimized polymerization conditions in hand, we investigated the broader application of 1,5-HAT-mediated radical polymerization (Fig. 3). The polymerization of monomer **M1** was successfully scaled up to 100 grams, achieving a yield of 93%. Monomers with ethyl, n-octyl, and isopropyl ester exhibited good reactivity, achieving polymer conversions ranging from 82% to 95% (**P2-P4**). Furthermore, substituting with either a phosphonate or an amide group lead to the synthesis of the corresponding polymers, although with moderate conversions of 58% and 43%, respectively. When the substituents are only esters, polymers **P7** and **P8** were synthesized with conversions of 86% and 80%. The thermal characteristics of these polymers were characterized using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The diverse substitutions along the polymer backbones resulte in a broad range of observed glass transition temperatures (T_g), spanning from -34.8 ºC to 73.9 ºC. The experimental data reveal a clear trend: as the alkyl chain length progressively increases from **P1** to **P3**, the T_g notably decreases. This trend indicates a corresponding increase in the overall flexibility of the molecular chains, offering valuable insights into how structural modifications can significantly impact material properties at the molecular level (Fig. S3-S5). Overall, most of the polymers display exceptional thermal stabilities

with decomposition temperatures ($T_{d,5\%}$) exceeding 280 °C. The polymers are soluble in polar aprotic solvents such as *N*, *N*-dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM) and dimethyl sulfoxide (DMSO), while not soluble in relatively polar protic solvents such as water and methanol. We also investigated analogous radical polymerization via 1,4 and 1,6-HAT process, but they did not entirely follow the reaction mode of intramolecular hydrogen atom transfer (Fig. S6-S7).
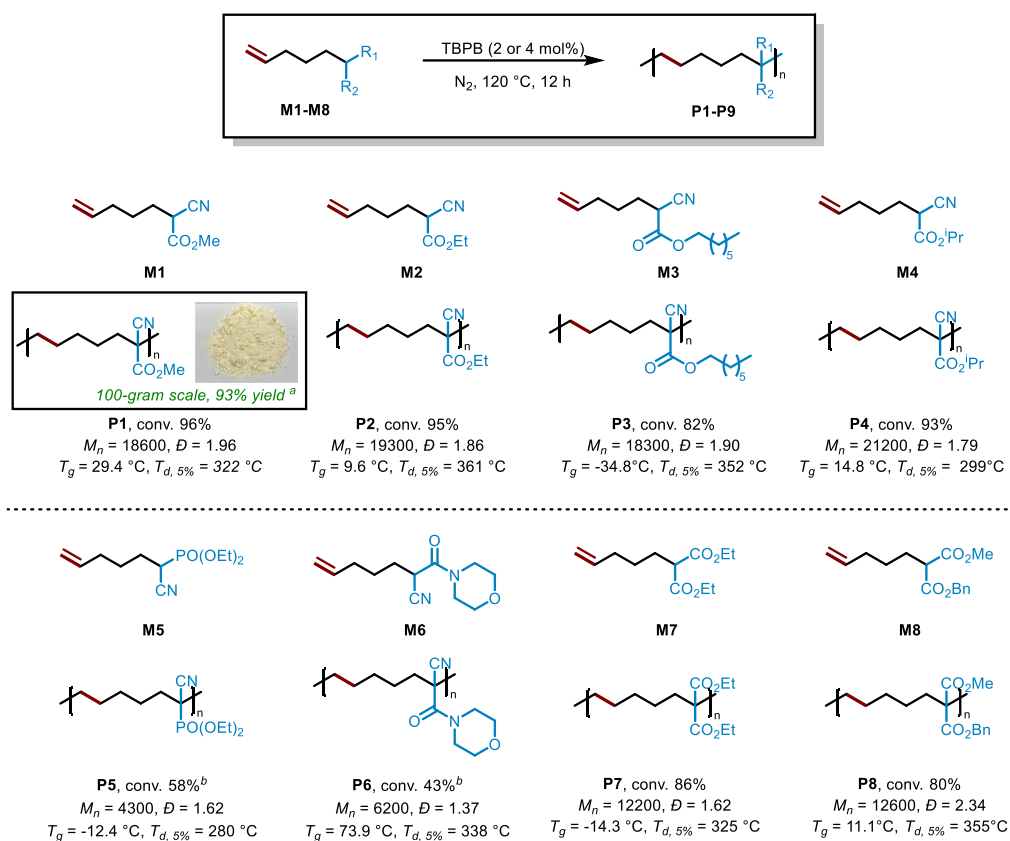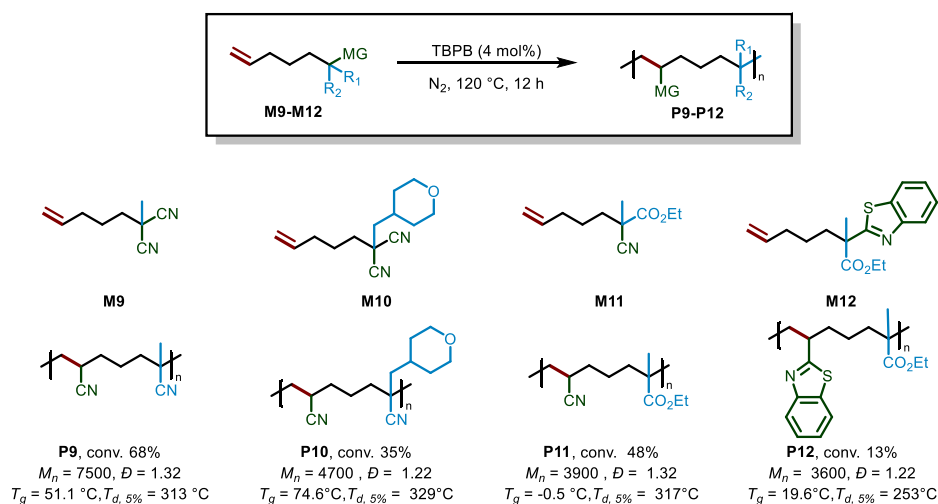

Figure 3. Scope of radical polymerization via 1,5-HAT. Reaction conditions: monomer (4 mmol) and TBPB (2 mol %) in a 4 mL vial under N_2 for 12 h at 120 ºC. [a] 100-gram scale; the yield of isolated product after precipitation with methanol is given. [b] TBPB (4 mol %).

When using **M9** as the monomer, where the tertiary C-H bond is absent, polymer **P9** was obtained under the above polymerization conditions. We confirmed that 1,5-cyano migration occurred in the polymerization by [1]H & [13]C nuclear magnetic resonance (NMR) spectroscopy, [1]H-^{1}H correlation spectroscopy (COSY), [1]H-^{13}C heteronuclear single quantum coherence (HSQC), and [1]H-^{13}C heteronuclear multiple bond correlation (HMBC) (Fig. 4). The aliphatic peak of 2.77 ppm was assigned to H_b next to the cyano group. The HSQC spectra showed that the carbon coupled to hydrogen next to the cyano group. The HMBC spectra showed that the carbon of the cyano group coupled to H_a, H_b and H_c. By analyzing the results of the NMR, we confirmed that the occurrence of 1,5-cyano migration process, and the construction of ABC (acrylonitrile-ethylene-methacrylonitrile) sequence was established.
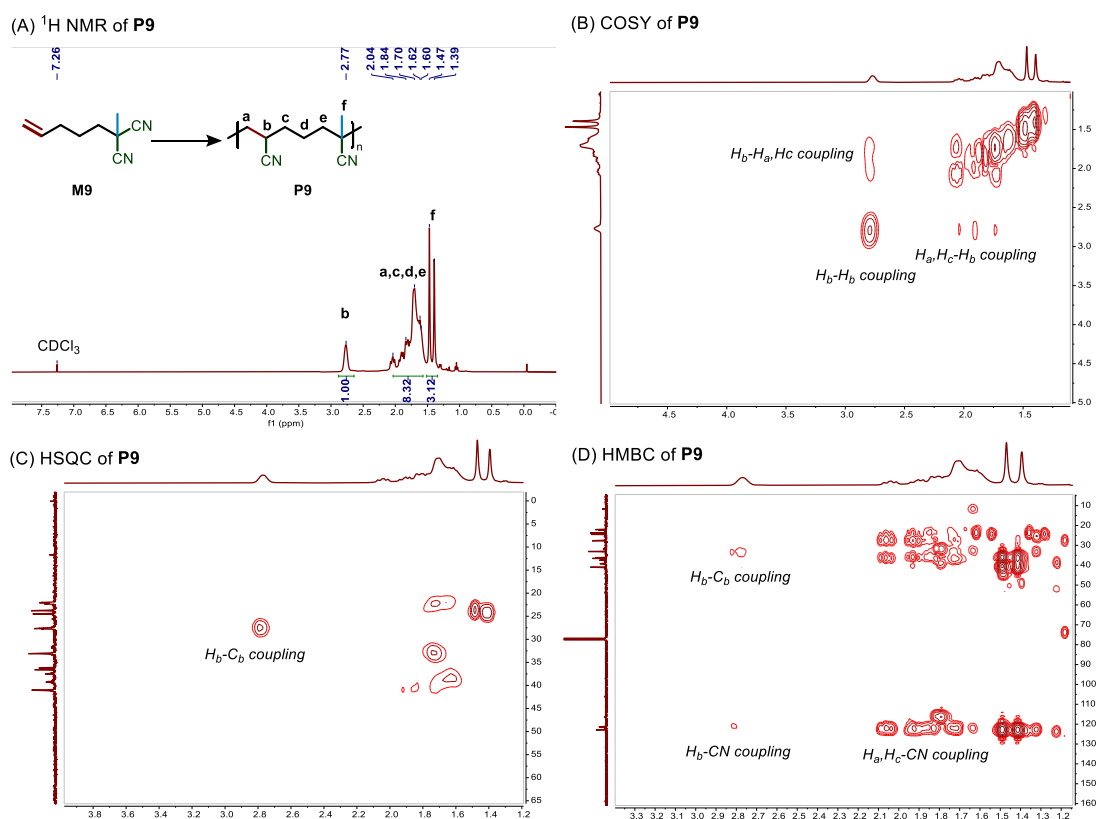
Figure 4. Polymer chain structure and type determination (A-D) ^{1}H NMR, COSY, HSQC and HMBC spectra of **P9** verifying the polymer chain sequences.

Subsequently, the suitability of various monomers for radical polymerization via 1,5-group transfer was evaluated (Fig. 5). Polymerization was achieved with a bulky tetrahydropyran substituent (**P10**), highlighting the robustness of this method. Furthermore, the sequential polymer composed of acrylonitrile, ethylene, and ethyl methacrylate units (**P11**) was synthesized with a conversion of 48%. Interestingly, the presence of benzothiazole group was also suitable for 1,5-migration process, leading to the corresponding polymer **P12**, albeit with a low conversion. To characterize the thermal properties of the resultant polymers, which were ABC sequence-defined, TGA and DSC were also applied. The analyses reveal that all polymers exhibited remarkable thermal stability, with a $T_{d, 5\%}$ exceeding 250 °C.

Figure 5. Scope of radical polymerization via 1,5-group transfer. Reaction conditions: monomer (4 mmol) and TBPB (4 mol %) in a 4 mL vial under N_2 for 12 h at 120 °C.

Conclusion

We have devised a strategy of switchable remote hydrogen atom or group transfer, which is applicable for the production of polyethylene-based polymers consisting of various polar blocks. A variety of new α-olefin monomers are designed for the radical polymerization. This innovative technique facilitates the construction of a diverse array of AAB or ABC sequence-defined carbon-chain polyolefins. All these sequence-defined polyethylene-based polymers are difficult to prepare by current methods. These research endeavors pave a new avenue for the precise synthesis functionalized polyolefins, potentially opening the prospects of the fabrication of high-performance materials.

Supporting Information

Experimental procedures, compound characterized data, copies   of spectra including NMR, TG, and DSC were included.

Acknowledgements

Keywords: radical polymerization, hydrogen atom transfer, group transfer, α-olefins, sequence-defined polymers.

References

[1]   A. Schöbel, M. Winkenstette, T. M. J. Anselment, B. Rieger, in: Matyjaszewski K. Möller M. Polymer Science: A Comprehensive Reference, *Elsevier*, **2012**, 779-823.

[2]   R. S. Birajdar, S. H. Chikkali, *Eur. Polym.* **2021**, *143*, 110183.

[3]   G. Ji, Z. Chen, X.-Y. Wang, X.-S. Ning, C.-J. Xu, X.-M. Zhang, W.-J. Tao, J.-F. Li, Y. Gao, Q. Shen, X.-L. Sun, H.-Y. Wang, J.-B. Zhao, B. Zhang, Y.-L. Guo, Y. Zhao, J. Sun, Y. Luo, Y. Tang.

Nat. Commun. **2021**, *12*, 6283.

[4]　S. L. Aggarwal, O. J. Sweeting, *Chem. Rev.* **1957**, *57*, 665-742.

[5]　M. Ghiass, R. A. Hutchinson, *Polym. React. Eng.* **2003**, *11*, 989-1015.

[6]　A. Zarrouki, E. Espinosa, C. Boisson, V. Monteil, *Macromolecules* **2017**, *50*, 3516-3523.

[7]　N. M. G. Franssen, J. N. H. Reek, B. de Bruin, *Chem. Soc. Rev.* **2013**, *42*, 5809-5832.

[8]　J.-I. Imuta, N. Kashiwa, Y. Toda, *J. Am. Chem. Soc.* **2002**, *124*, 1176-1177.

[9]　B. Liu, K. Qiao, J. Fang,T. Wang, Z. Wang, D. Liu, Z. Xie, L. Maron, D. Cui, *Angew. Chem. Int. Ed.* **2018**, *57*, 14896-14901.

[10] J. Demarteau, P. B. V. Scholten, A. Kermagoret, J. De Winter, M. A. R. Meier, V. Monteil, C. Detrembleur, *Macromolecules* **2019**, *52*, 9053-9063.

[11] J. Chen, Y. Gao, T. J. Marks, *Angew. Chem. Int. Ed.* **2020**, *59*, 14726-14735.

[12] X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z, Wang, Z. Xie, Y. Tang, *Angew. Chem. Int. Ed.* **2009**, *48*, 8099-8102.

[13] H. Terao, S. Ishii, M. Mitani, H. Tanaka, T. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 17636-17637.

[14] J. A. Gladysz, Z. T. Ball, G. Bertrand, S. A. Blum, V. M. Dong, R. Dorta, F. E. Hahn, M. G. Humphrey, W. D. Jones, J. Klosin, I. Manners, T. J. Marks. J. M. Mayer, B. Rieger, J. C. Ritter, A. P. Sattelberger, J. M. Schomaker, V. W.-W. Yam, *Organometallics* **2012**, *31*, 1-18.

[15] J.-F. Lutz, M. Ouchi, D. R. Liu, M. Sawamoto, *Science* **2013**, *341*, 1238149.

[16] K. Nishimori, M. Ouchi, *Chem. Commun.* **2020**, *56*, 3473-3483.

[17] M. Ouchi, *Polym. J.* **2021**, *53*, 239-248.

[18] M. Kamigaito, *Polym. J.* **2022**, *54*, 1391-1405.

[19] A. Tardy, J. Nicolas, D. Gigmes, C. Lefay, Y. Guillaneuf, *Chem. Rev.* **2017**, *117*, 1319-1406.

[20] T. Sato, H. Takahashi, H. Tanaka, T. Ota, *J. Polym. Sci. Polym. Chem. ED.* **1988**, *26*, 2839-2847.

[21] T. Sato, D. Ito, M. Kuki, H. Tanaka, T. Ota, *Macromolecules* **1991**, *24*, 2963-1967.

[22] T. Sato, Y. Nakagawa, T. Kawachi, M. Seno, *Eur. Polym. J.* **1996**, *32*, 827-835.