Direct Synthesis of Polar Functionalized Polyethylene Thermoplastic Elastomer

Shengyu Dai,* Shuaikang Li, Guoyong Xu, and Changle Chen*

Read Online

ACCESS | 📊 Metrics & More | 📖 Article Recommendations | 🆂�🆘 Supporting Information
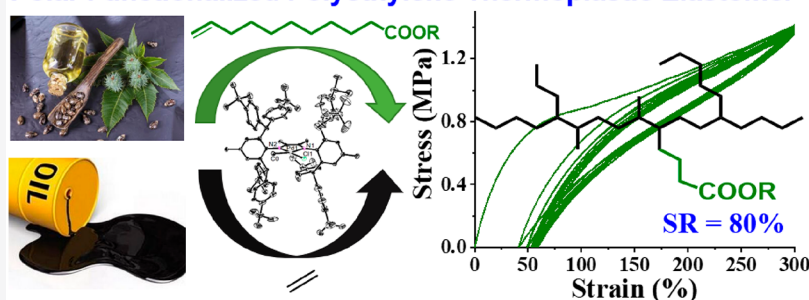
ABSTRACT: Thermoplastic elastomers (TPE) can be easily molded, extruded, and reused like plastics and exhibit typical elastic properties like rubbers. They are widely used in the automotive sector and household appliances sector. The synthesis of thermoplastic polyolefin elastomers using only ethylene as feedstock in a single step is a fascinating concept. The synthesis of polyethylene thermoplastic elastomers through α-diimine nickel catalyzed ethylene polymerization has been successfully achieved in recent years. However, the utilization of α-diimine palladium catalysts for this purpose is much more challenging due to their greater chain-walking tendency versus the nickel counterpart, thereby leading to the formation of highly branched polyolefins with poor mechanical properties. In this contribution, we report the direct synthesis of polyethylene thermoplastic elastomers through α-diimine palladium catalyzed ethylene polymerization. With exquisite catalyst design and polymerization regulation, polyethylene thermoplastic elastomers with great mechanical and elastic properties can be obtained. Most importantly, polar functionalized polyethylene thermoplastic elastomers bearing great elastic properties can be generated through copolymerization of ethylene with biomass-derived comonomers.

■ INTRODUCTION

Thermoplastic elastomer (TPE) is a class of polymeric material that exhibits rubber elasticity at room temperature and can be plasticized at high temperature. Therefore, such polymers have some of the characteristics of both thermoset rubbers and thermoplastics. They are widely used in industry as spanning tires, rubber, clothing, insulators, and many others.[1,2] The distinguishing structural feature of thermoplastic elastomer is that the polymer chains are connected in series or grafted with some chemically different plastic segments (hard segments) and rubber segments (soft segments).[3] The majority of polyolefin-based TPEs are generated by the copolymerization of ethylene with higher α-olefins by using metallocene catalysts.[4−7] Most of these copolymers are composed of crystalline polyethylene or polypropylene as "hard" segments to create physical cross-links needed for elastic recovery and amorphous atactic polypropylene or ethylene−higher α-olefin copolymer as the "soft" segments with low T_g value. Thermoplastic polyolefin elastomers are essentially branched polyethylene. Some late-transition-metal-based catalysts exhibit unique "chain walking" properties, generating branched

polyethylene in ethylene homopolymerization.[8,9] Recently, the Ricci group[10] and Coates group[11] developed a multiple-step strategy for the synthesis of thermoplastic polyolefin elastomers using α-diimine nickel catalysts, in which higher α-olefins (1-decene or 1-dodecene) are required. The synthesis of thermoplastic polyolefin elastomers in one step using only ethylene as the feedstock is a fascinating concept and holds great potentials for practical applications. For example, some asymmetric α-diimine nickel catalysts (Scheme 1, **A** and **B**)[12,13] led to the formation of polyethylene elastomers with great elastic properties (strain-at-break values of 300%−1800% and elastic recovery of 42%−85% after 10 cycles at 300% strain). Some highly sterically hindered acenaphthene-based α-
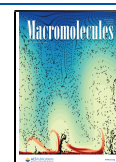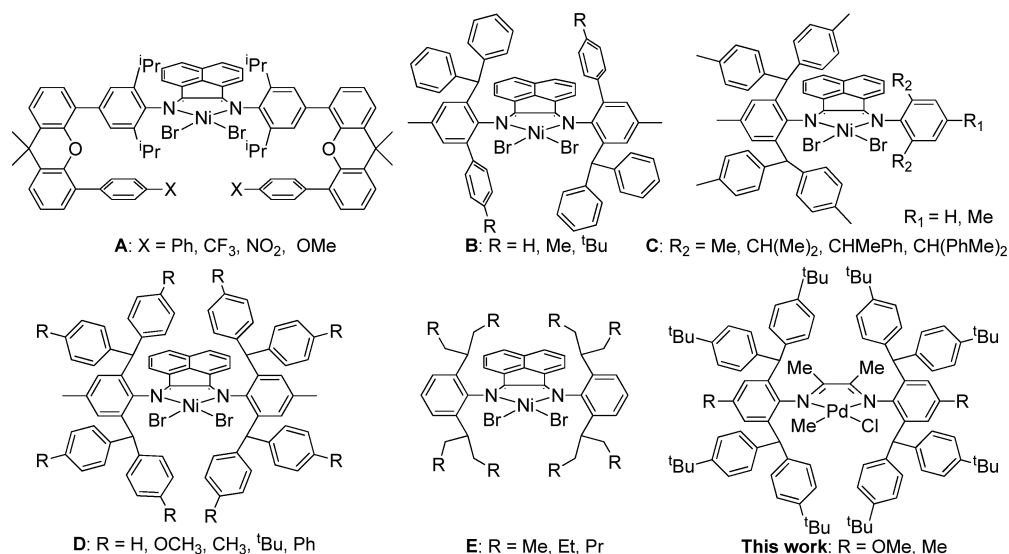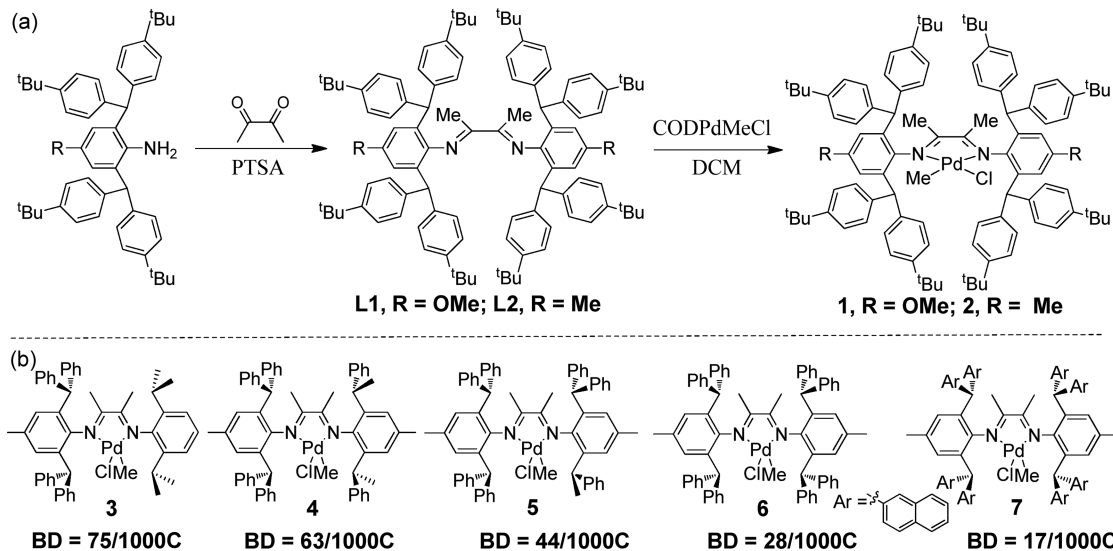
Scheme 1. α-Diimine Nickel Catalysts with Capabilities of Generating Thermoplastic Polyethylene Elastomer from Only Ethylene as Feedstock

A: X = Ph, CF₃, NO₂, OMe

B: R = H, Me, ᵗBu

C: R₂ = Me, CH(Me)₂, CHMePh, CH(PhMe)₂　　R₁ = H, Me

D: R = H, OCH₃, CH₃, ᵗBu, Ph

E: R = Me, Et, Pr

This work: R = OMe, Me

Scheme 2. Ethylene Copolymerization with 10-Undecenoic Acid and Its Derivatives Derived from Castor Oil

Extract

pyrolysis

R = H, OMe

Cat. Pd

Biomass Functionalized Elastomer
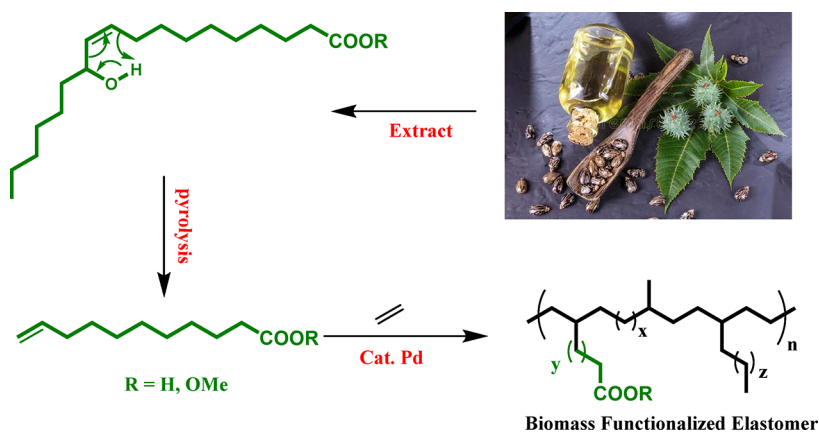
Scheme 3. (a) Synthesis of the ᵗBu-Substituted α-Diimine Ligands (L1 and L2) and the Corresponding Palladium Complexes (1 and 2); (b) Selected α-Diimine Palladium Catalysts That Can Generate Polyethylenes with Different Branching Densities

(a)

PTSA

CODPdMeCl
DCM

L1, R = OMe; L2, R = Me

1, R = OMe; 2, R = Me

(b)

3
BD = 75/1000C

4
BD = 63/1000C

5
BD = 44/1000C

6
BD = 28/1000C

Ar =

7
BD = 17/1000C

diimine nickel complexes catalyzed ethylene polymerization to generate thermoplastic polyethylene elastomers (Scheme 1, **C**, **D**, and **E**).[14−17] The thermoplastic polyethylene elastomer produced by these catalysts have high molecular weight (M_w up to 450.5×10^4 g mol^{-1}) and great elastic properties. Sun and co-workers also reported some α-diimine nickel catalysts with similar properties.[18]

Currently, most polymeric materials are derived from nonrenewable fossil resources. With the shortage of fossil resources and the deterioration of the environment, the use of biorenewable compounds for polymer synthesis is receiving increasing attention.[19−21] Among various renewable resources, plant oils and their derivatives have become more and more popular in the field of polymer synthesis.[22−25] 10-Undecenoic acid (UA) can be obtained by the pyrolysis of ricinoleic acid derived from castor oil (Scheme 2).[26,27] It has been used in the manufacture of many pharmaceuticals, personal hygiene products, cosmetics, perfumes, and polymers such as nylon-11.[26,28] The "soft" long alkyl structure of UA might result in low glass transition temperature (T_g) of the polymers derived from it. A series of 10-undecenoic acid derivatives can be obtained by chemical transformations such as esterification and amidation, which serve as important starting materials in the preparation of biodegradable elastomers, hydrogels, adhesives, emulsifiers, and photosensitive materials.[29,30]

Compared with α-diimine nickel catalysts, α-diimine palladium counterparts possess a much higher tendency to chain walk, thereby leading to the formation of highly branched polyethylenes with poor mechanical/elastic properties.[31,32] One superior feature of α-diimine palladium catalysts over the nickel counterparts is their good copolymerization capability with polar comonomers. Although some α-diimine nickel catalysts have been shown to be able to copolymerize ethylene with polar comonomers, a large amount of aluminum cocatalyst is required. Moreover, the presence of polar comonomers will greatly reduce polymer molecular weights for the case of nickel catalysis,[15,33,34] which is detrimental to mechanical and elastic properties. In this work, we reported the synthesis of thermoplastic polyethylene elastomers using some specially designed α-diimine palladium catalysts (Scheme 3). Furthermore, the synthesis of polar functionalized thermoplastic polyethylene elastomers was demonstrated through ethylene copolymerization with 10-undecenoic acid and its derivatives.

■ RESULTS AND DISCUSSION

Catalysts Synthesis. 2,6-Bis(di-p-tert-butylphenyl)-4-methylaniline and 2,6-bis(di-p-tert-butylphenyl)-4-methoxylaniline were prepared according to the literature procedures.[35] Ligands **L1** and **L2** were prepared from the reactions of anilines with 0.5 equiv of 2,3-butanedione at 78% and 65% yields by using the method developed by our group (Scheme 3).[36,37] The palladium complexes **1** and **2** were obtained at 61% and 55% yields from reactions of the corresponding ligands with 1 equiv of (COD)PdMeCl (COD = 1,5-cyclooctadiene). These palladium complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and mass spectrometry. For comparison, the previously reported palladium complexes **3−7**[37,38] were prepared to screen the optimum catalysts for the synthesis of polyethylene thermoplastic elastomers. The molecular structure of complex **2** is shown in Figure 1. The Pd center adopts a slightly distorted

square-planar geometry, and the effective blockage of the axial positions of the Pd center can be observed from the structure.
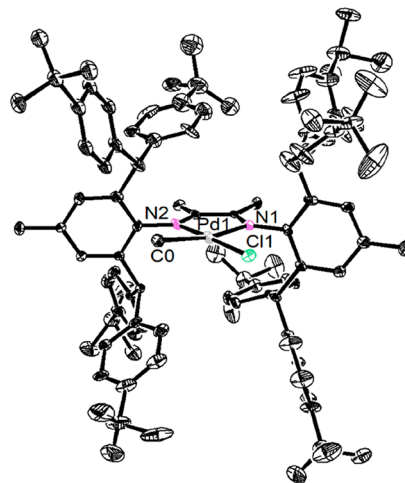

Figure 1. Molecular structure of complex **2** in the solid state. Hydrogen atoms have been omitted for clarity. Atoms are drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Pd1−N1 2.057(2), Pd1−C0 2.088(19), Pd1−N2 2.045(3), Pd1−Cl1 2.253(3), C0−Pd1−N2 92.4(5), N2−Pd1−N1 79.10(10), N1−Pd1−Cl1 97.61(10), and C0−Pd1−Cl1 91.4(5).

Ethylene Polymerization. Palladium complexes **1−7** are highly active in ethylene polymerization when activated by the addition of 2.0 equiv of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAF) (Table 1). For complexes **1** and **2**, polymerization parameters are not very sensitive toward ethylene pressure (Table 1, entries 1−6). Complex **2** exhibited decreasing polymerization activities over 3 h, while the polyethylene molecular weights increased from 14.29×10^4 to 45.43×10^4 Da (Table 1, entries 7−9 and 5). The most notable feature of these two catalysts is the production of moderately branched and high-molecular-weight polyethylenes (B = ca. 60/1000C, M_n > 300 kDa) with low T_g values (−64 to −43 °C). The low melting enthalpies (24−45 J/g) of these polyethylenes are attributed to the branched polymer microstructures. The ethylene pressure and ligand electronic effect can slightly affect polymer branching density, with the higher pressure and electron-donating substituent favoring the formation of lower branching polymer products. Complexes **3−7** were strategically selected for comparison because they afford polyethylenes with similar molecular weights as **1/2** but with varied branching densities (Table 1, entries 10−14).

Ethylene/Polar Monomer Copolymerization. The α-diimine palladium catalysts have been widely used in copolymerization of ethylene with polar comonomers due to their great polar group tolerance.[36−40] The incorporation of polar comonomers can modify many important properties of nonpolar polyethylenes such as surface properties, adhesion, and compatibility with other materials.[41−49] In this system, **1** and **2** can mediate efficient copolymerizations of ethylene with 10-undecenoic acid (UA) and its derivative 10-methyl undecanoate (MU) at 6 atm and 30 °C. These catalysts showed moderate activities (ca. 10^4 g/(mol Pd·h)), producing high-molecular-weight copolymers (M_n up to 341 kDa) with moderate comonomer incorporations (ca. 1%) (Table 2, entries 1−4). Catalyst **2** produced copolymers with slightly higher molecular weights and slightly higher comonomer

## Table 1. Ethylene Homopolymerization Using Palladium Complexes 1−7[a]

entry	cat.	time (h)	P (atm)	yield (g)	activity[b]	M_n^c (×10⁻⁴)	PDI	B^d	T_m^e (°C)	enthalpy[e] (J/g)	T_g^e (°C)
1	**1**	3	2	3.10	1.03	33.58	1.97	63	33	24	−63
2	**1**	3	4	4.30	1.43	45.58	1.95	62	38	32	−64
3	**1**	3	6	4.12	1.37	31.74	2.00	59	42	41	−45
4	**2**	3	2	3.15	1.05	42.29	1.82	67	28	34	−52
5	**2**	3	4	3.96	1.32	45.43	1.94	65	35	45	−50
6	**2**	3	6	4.37	1.46	44.48	2.44	64	38	40	−43
7	**2**	0.5	4	2.08	4.16	14.29	1.91				
8	**2**	1	4	2.70	2.70	28.92	1.81				
9	**2**	2	4	3.53	1.77	31.34	1.84				
10	**3**	3	6	4.37	1.46	23.96	1.97	75	−13	14	−65
11	**4**	3	6	5.67	1.89	27.67	2.28	63	28, 63	39	−63
12	**5**	3	6	6.24	2.08	48.56	1.99	44	61	44	
13	**6**	3	6	7.28	2.43	47.09	1.86	28	85	44	
14	7	3	6	8.97	2.99	53.78	1.77	17	107	68	

[a]Conditions: 10 μmol of precatalyst, 2.0 equiv of NaBAF, 2 mL of CH_2Cl_2, 40 mL of toluene, 30 °C. [b]Activity = 10^5 g/(mol Pd·h). [c]Molecular weight was determined by GPC in trichlorobenzene at 150 °C by using polystyrene standards. [d]B = branches per 1000 carbons, determined by ^{1}H NMR spectroscopy. [e]Determined by differential scanning calorimetry, second heating.

Table 2. Ethylene/Polar Comonomer Copolymerization[a]

entry	cat.	time (h)	P (atm)	comon	[M] (mol/L)	yield (g)	activity[b]	X_M^c (%)	M_n^d (×10⁻⁴)	PDI	B^e	T_m^f (°C)	enthalpy[f] (J/g)	T_g^f (°C)
1	**1**	12	6	UA	0.5	1.58	1.32	1.2	6.65	2.25	53	33	37	−64
2	**1**	12	6	MU	0.5	1.77	1.48	1.3	25.40	1.52	61	20	43	−50
3	**2**	12	6	UA	0.5	2.68	2.23	1.3	16.25	2.15	61	24	10	−65
4	**2**	12	6	MU	0.5	1.17	0.98	1.4	34.09	1.38	64	14	41	−48
5	**2**	12	6	UA	1.0	1.02	0.85	3.2	3.71	2.30	70	g	g	g
6	**2**	12	4	UA	0.5	1.43	1.19	2.8	4.12	2.15	72	g	g	g
7	**2**	12	2	UA	0.5	0.47	0.39	3.8	1.17	1.98	76	g	g	g
8	**2**	2	6	UA	0.5	0.72	3.60		3.30	2.47				
9	**2**	4	6	UA	0.5	1.12	2.80		5.11	1.83				
10	**2**	6	6	UA	0.5	1.66	2.77		6.08	2.25				
11	**2**	8	6	UA	0.5	1.92	2.40		12.31	1.90				
12	**2**	10	6	UA	0.5	2.36	2.36		14.04	2.27				
13	**2**	2	6	MU	0.5	0.18	0.90		5.11	1.67				
14	**2**	4	6	MU	0.5	0.46	1.15		8.75	1.28				
15	**2**	6	6	MU	0.5	0.68	1.13		14.48	1.44				
16	**2**	8	6	MU	0.5	0.92	1.15		18.21	1.51				
17	**2**	10	6	MU	0.5	1.08	1.08		23.74	1.48				

[a]Conditions: 0.010 mmol of precatalyst, 2.0 equiv of NaBAF, 2 mL of CH_2Cl_2, total volume of toluene and polar monomer: 20 mL, 30 °C. [b]Activity = 10^4 g/(mol Pd·h). [c]X_M = comonomer incorporation (mol %). [d]Molecular weight was determined by GPC in trichlorobenzene at 150 °C by using polystyrene standards. [e]B = branches per 1000 carbons; branching numbers were determined by using ^{1}H NMR spectroscopy; the branches ending with functional groups are added to the total branches. [f]Determined by differential scanning calorimetry (DSC). [g]Not observed at the temperature range of −50 to 120 °C.
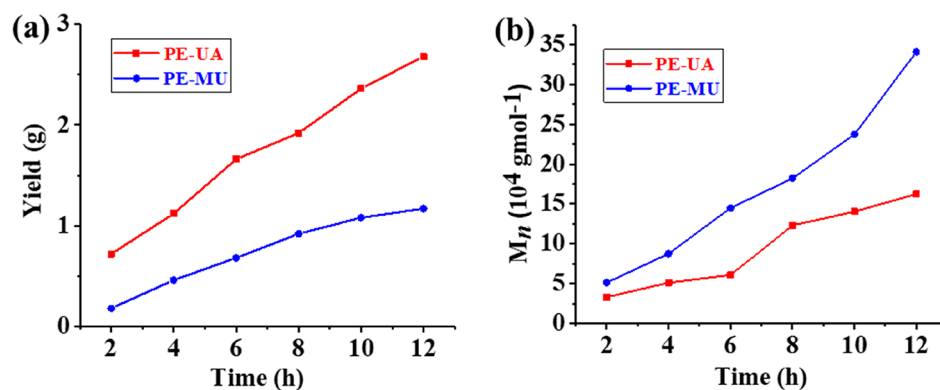
Figure 2. Plots of (a) yield vs time and (b) M_n vs time for **2**-catalyzed ethylene copolymerization with UA (red) and MU (blue).
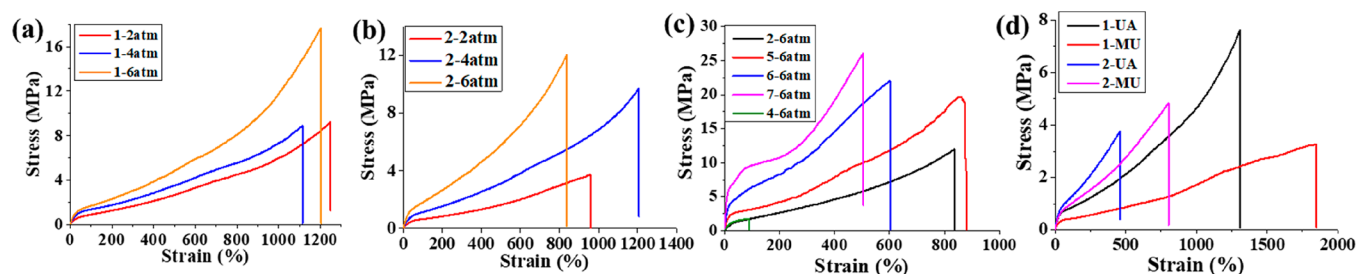
Figure 3. Stress−strain curves for polymers generated by (a) **1** at 2, 4, and 6 atm; (b) **2** at 2, 4, and 6 atm; (c) **2**, **4**, **5**, **6**, and **7** at 6 atm. (d) Stress−strain curves for the polar functionalized copolymers.
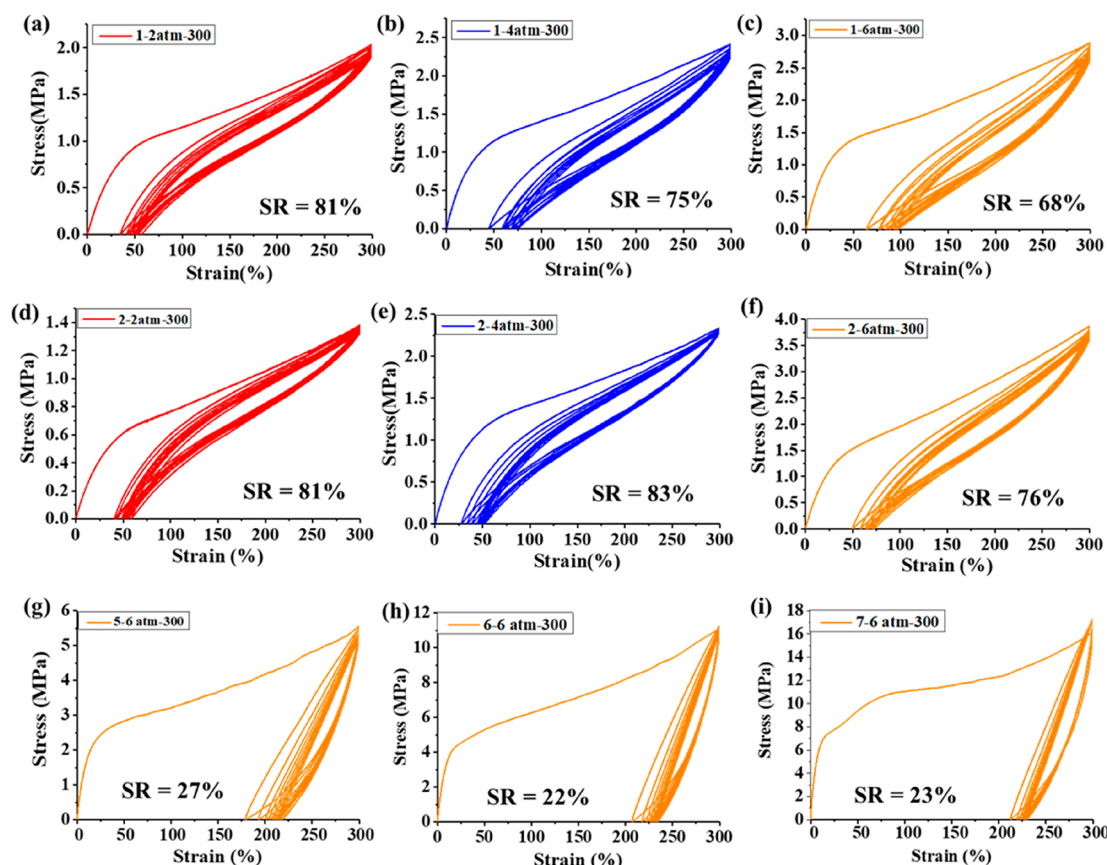

Figure 4. Plots of hysteresis experiments of ten cycles at a strain of 300% for samples generated by **1** at 2 atm (a), **1** at 4 atm (b), **1** at 6 atm (c), **2** at 2 atm (d), **2** at 4 atm (e), **2** at 6 atm (f), **5** at 6 atm (g), **6** at 6 atm (h), and **7** at 6 atm (i).

incorporations, along with slightly higher branching densities and lower melting points comparing with those produced by catalyst **1** under the same conditions (Table 2, entry 3 vs 1 and entry 4 vs 2). As expected, increasing comonomer concentration from 0.5 to 1.0 M led to higher incorporation (3.2 mol %) along with decreased catalytic activity and molecular weight (Table 2, entry 5). When the ethylene pressure was decreased from 6 atm through 4 atm to 2 atm, the comonomer incorporation (up to 3.8 mol %) increased gradually while the catalytic activity and molecular weight decreased dramatically (Table 2, entries 3, 6, and 7). Importantly, the incorporation of UA or MU unit can efficiently improve the surface properties of the thermoplastic elastomer even at low comonomer incorporation. As can be seen from Figure S1 (see the Supporting Information), the water contact angle (WCA) was 105° for homopolyethylene (Table 1, entry 6). In contrast, the incorporation of 1.3% UA comonomer (Table 2, entry 3) can

induce a ca. 20° WCA reduction, and the incorporation of 1.4% MU comonomer (Table 2, entry 4) can induce a ca. 14° WCA reduction.

To investigate the influence of polymerization time, ethylene copolymerizations with UA and MU catalyzed by **2** were conducted in 2, 4, 6, 8, 10, and 12 h at 6 atm and 30 °C. The copolymer yields increased nearly linearly as a function of time over 12 h (Table 2, entries 3−4 and 8−17, Figure 2a). Moreover, the copolymer molecular weights also increased nearly linearly with polymerization time and reached over 16.25×10^4 g mol^{-1} for UA and 34.09×10^4 g mol^{-1} for MU (Table 2, entries 3−4 and 8−17, Figure 2b). This feature is characteristic of living polymerization, yet the PDI values (1.83−2.47 for UA and 1.28−1.67 for MU) are considerably greater than those expected for a living polymerization. This behavior is likely due to rapid precipitation of the high-molecular-weight polymers resulting in inhomogeneous
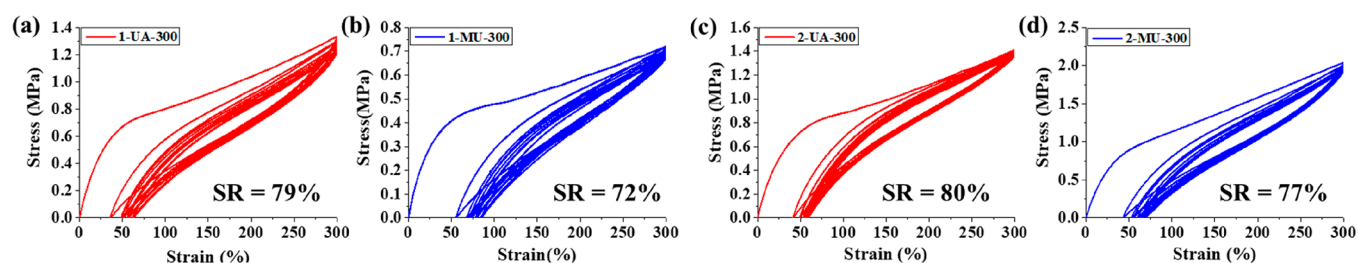
Figure 5. Plots of hysteresis experiments of ten cycles at a strain of 300% for copolymer samples from Table 2, entry 1 (a), Table 2, entry 2 (b), Table 2, entry 3 (c), and Table 2, entry 4 (d).

reaction conditions with a distribution of sites possessing varying activities. The PDI values of ethylene−UA copolymers are larger than those of ethylene−MU copolymers, which may be due to the fact that ethylene−UA copolymers are more likely to precipitate out of toluene. This phenomenon has been previously encountered by Bazan and Brookhart, who have termed this behavior as "quasi-living" polymerization.[50,51]

Properties of the Polymer and Copolymer Products. The polyethylenes and polar functionalized polyethylenes obtained by catalysts **1** and **2** are high-molecular-weight polymers with moderate branching densities and low melting points. Tensile strength analysis was performed for selected polymer samples. The polymer films were melt-pressed at 150 °C under a pressure of 2.5 MPa for 10 min and cooled at a rate of ∼6 °C/min to 25 °C. These films were subsequently cut into dog-bone-shaped tensile bars with 12 mm gauge length, 2 mm width, and thickness of 0.5 mm. Clearly, the mechanical properties of the resulting polyethylene and polar function-alized polyethylene samples produced by catalysts **1** and **2** can be modulated over a very wide range (Figure 3). These samples exhibited low to medium stress-at-break values ranging from 3.3 to 17.6 MPa and high strain-at-break values ranging from 450% to 1850%. Generally, stress-at-break values and Young's modulus increased with increasing ethylene pressure (Figure 3a,b and Table S1). The polyethylenes obtained by **1** have stronger ultimate tensile strength and tensile toughness than those obtained by **2** under otherwise identical conditions. This may originate from the fact that the electron-rich catalyst **1** produces polyethylene with lower branching density and higher melting point than **2**, which is consistent with the above-mentioned ethylene pressure effect. The results reveal that the mechanical properties of the obtained polyethylenes can be modulated by varying polymerization conditions or ligand electronic effect. For comparison, the polyethylene samples generated from **5**−**7** showed stress-at-break values ranging from 19.6 to 26.0 MPa and strain-at-break values ranging from 500% to 860%. The samples from **5**−**7** showed higher stress than those generated from **2** at the same strain (Figure 3c), which is likely due to their lower degree of branching and higher melting points. This is supported by the fact that stress-at-break values and Young's modulus increased with increasing ligand steric bulkiness for **5**−**7** (Figure 3c). The polyethylene product from **3** with high branching density is a sticky solid, which cannot be melt-processed into a test specimen. The sample from **4** is composed of hard and soft components and can be easily broken during the tensile experiment (Figure 3c). Complex **4** is a mixture of isomers, which leads to a mixture of polyethylene chains with different branching density, resulting in poor mechanical properties. This is supported by the presence of two melting points for the polymer product (Table 1, entry 11). The polar functionalized

copolymers generated by **1** and **2** showed lower stress-at-break values than the homopolymer counterparts, probably due to their lower molecular weights and melting points. The copolymers generated by **1** displayed much higher strain at break values and relatively lower Young's modulus than those from **2** (Figure 3d).

To investigate the elastic recovery properties, that is, the capability of returning to the initial state once the force is removed, the polymer and copolymer samples were subjected to hysteresis testing where each sample was extended to 300% strain over 10 cycles (Figures 4 and 5, Table S1). The strain recovery values (SR) can be calculated by SR = $100(\varepsilon_a - \varepsilon_r)/\varepsilon_a$, where ε_a is the applied strain and ε_r is the strain in the cycle at zero load after the 10th cycle. These polymer and copolymer samples obtained by **1** and **2** exhibit a certain amount of unrecovered strain after the first cycle, followed by minimal deformation on each subsequent cycle. A permanent structural change happens during the first cycle, after which better elastomeric properties are created. Overall, the samples obtained by **1** and **2** exhibit SR values ranging from 68% to 83%, which are comparable with previously reported elastic polyethylene materials obtained by the α-diimine nickel catalysts.[12−18] ^{13}C NMR analysis showed that the polyethylene prepared by **2** at 4 atm (Figure 4e) composed of various alkyl branches from C1 to C≥4, even *sec*-butyl (branch on branch structure). Interestingly, high percentages of long chain branches were observed for this case (Table S2). The presence of various alkyl branches and their random distribution in these samples probably contribute to their unique properties (Figure S2). In direct contrast, the samples from **5**−**7** showed very poor elastomeric properties (with SR values ranging from 22% to 27%), despite their great tensile performance. These results suggest that the appropriately branched polymer micro-structures (ca. 60/1000C, proper crystallinity) and high molecular weight ($M_n > 300$ kDa, high entropy elasticity) are critical to achieve good elastic properties of the obtained polyethylene products.

The polar functionalized polyethylene products obtained by catalysts **1** and **2** exhibit SR values ranging from 72% to 80%, which are comparable to those of polyethylene samples obtained by using the same catalysts. These copolymers also have appropriately branched microstructure (ca. 60/1000C) and high molecular weight ($M_n > 66$ kDa). The microstructure analysis of these copolymers based on ^{13}C NMR showed the existence of methyl, long chain (>C₄) branches, and function-alized long chain branches. The polar functionalized group was located at the chain-end position of the copolymers obtained by these α-diimine palladium catalysts (Figure S3).

CONCLUSIONS

In summary, we reported the synthesis and characterization of polyethylene thermoplastic elastomers and polar functionalized polyethylene thermoplastic elastomers using some specially designed α-diimine palladium catalysts with *tert*-butyl substituents. In ethylene polymerization, the α-diimine palladium complexes **1** and **2** showed moderate activities (ca. 10^5 g/(mol Pd·h)), generating polyethylene with high molecular weight (M_n up to 45.58×10^4) and moderately branched microstructures (ca. 60/1000C). These branched polyethylenes displayed characteristics of thermoplastic elastomers with great elastic recovery properties (SR = 68%−83%). The ethylene pressure and ligand electronic effect can efficiently tune the mechanical properties. In ethylene−biomass comonomer copolymerization, complexes **1** and **2** produced high molecular weight (M_n up to 34.09×10^4) copolymers with moderately branched microstructures (ca. 60/1000C) and moderate comonomers incorporation (ca. 1%). The polar functionalized polyethylenes also displayed characteristics of thermoplastic elastomers with great elastic recovery properties (SR = 72%−80%). The key factors contributing to the success of this palladium system are the fine control of the polymer branching structures and the capability of achieving high polymer molecular weights. This work demonstrates the great potentials of generating polar functionalized polyethylene thermoplastic elastomers in a single step by using only ethylene and biomass-derived comonomers as the feedstock.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00083.

Full experimental details for the synthesis of palladium complexes and polymers (PDF)
checkCIF/PLATON report (PDF)
Crystallograhic data for complex **2** (CIF)

AUTHOR INFORMATION

Corresponding Authors

Shengyu Dai − *Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui 230601, China;* orcid.org/0000-0003-4110-7691; Email: daiyu@ustc.edu.cn

Changle Chen − *Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China;* orcid.org/0000-0002-4497-4398; Email: changle@ustc.edu.cn

Authors

Shuaikang Li − *Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui 230601, China*

Guoyong Xu − *Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, Anhui University, Hefei, Anhui 230601, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.macromol.0c00083

Notes

The authors declare no competing financial interest.
The CCDC number of **2** is 1950703. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

REFERENCES

(1) Geoffrey, H. *Applied Plastics Engineering Handbook*; William Andrew: 2011.

(2) Craver, C.; Carraher, C. *Applied Polymer Science: 21st Century*; Elsevier Science: Oxford, 2000.

(3) Brobny, J. G. *Handbook of Thermoplastic Elastomers*; William Andrew: New York, 2007.

(4) Harney, M. B.; Zhang, Y.; Sita, L. R. Discrete, multiblock isotactic−atactic stereoblock polypropene microstructures of differing block architectures through programmable stereomodulated living Ziegler−Natta polymerization. *Angew. Chem., Int. Ed.* **2006**, *45*, 2400−2404.

(5) Rose, J. M.; Deplace, F.; Lynd, N. A.; Wang, Z.; Hotta, A.; Lobkovsky, E. B.; Kramer, E. J.; Coates, G. W. C2-Symmetric Ni(II) α-Diimines featuring cumyl-derived ligands: synthesis of improved elastomeric regioblock polypropylene. *Macromolecules* **2008**, *41*, 9548−9555.

(6) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. Catalytic production of olefin block copolymers via chain shuttling polymerization. *Science* **2006**, *312*, 714−719.

(7) Ohtaki, H.; Deplace, F.; Vo, G. D.; LaPointe, A. M.; Shimizu, F.; Sugano, T.; Kramer, E. J.; Fredrickson, G. H.; Coates, G. W. Allyl-terminated polypropylene macromonomers: a route to polyolefin elastomers with excellent elastic behavior. *Macromolecules* **2015**, *48*, 7489−7494.

(8) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. Chain walking: a new strategy to control polymer topology. *Science* **1999**, *283*, 2059−2062.

(9) Xu, Y.; Xiang, P.; Ye, Z.; Wang, W. J. Hyperbranched-linear polyethylene block polymers constructed with chain blocks of hybrid chain topologies via one-pot stagewise chain walking ethylene "living" polymerization. *Macromolecules* **2010**, *43*, 8026−8038.

(10) Leone, G.; Mauri, M.; Bertini, F.; Canetti, M.; Piovani, D.; Ricci, G. Ni(II) α-diimine-catalyzed α-olefins polymerization: thermoplastic elastomers of block copolymers. *Macromolecules* **2015**, *48*, 1304−1312.

(11) O'Connor, K. S.; Watts, A.; Vaidya, T.; LaPointe, A. M.; Hillmyer, M. A.; Coates, G. W. Controlled chain walking for the synthesis of thermoplastic polyolefin elastomers: synthesis, structure, and properties. *Macromolecules* **2016**, *49*, 6743−6751.

(12) Lian, K. B.; Zhu, Y.; Li, W. M.; Dai, S. Y.; Chen, C. L. Direct synthesis of thermoplastic polyolefin elastomers from nickel-catalyzed ethylene polymerization. *Macromolecules* **2017**, *50*, 6074−6080.

(13) Fang, J.; Sui, X. L.; Li, Y. G.; Chen, C. L. Synthesis of polyolefin elastomers from unsymmetrical α-diimine nickel catalyzed olefin polymerization. *Polym. Chem.* **2018**, *9*, 4143−4149.

(14) Guo, L. H.; Lian, K.; Kong, W.; Xu, S.; Jiang, G.; Dai, S. Y. Synthesis of Various Branched Ultra-High-Molecular-Weight Polyethylenes Using Sterically Hindered Acenaphthene-Based α-Diimine Ni (II) Catalysts. *Organometallics* **2018**, *37*, 2442−2449.

(15) Gong, Y.; Li, S.; Gong, Q.; Zhang, S.; Liu, B.; Dai, S. Systematic Investigations of Ligand Steric Effects on α-Diimine Nickel Catalyzed Olefin Polymerization and Copolymerization. *Organometallics* **2019**, *38*, 2919−2926.

(16) Dai, S.; Li, S.; Xu, G.; Wu, C.; Liao, Y.; Guo, L. Flexible Cycloalkyl Substituents in Insertion Polymerization with α-Diimine Nickel and Palladium Species. *Polym. Chem.* **2020**, *11*, 1393−1400.

(17) Guo, L.; Sun, W.; Li, S.; Xu, G.; Dai, S. Bulky yet flexible substituents in insertion polymerization with α-diimine nickel and palladium systems. *Polym. Chem.* **2019**, *10*, 4866−4871.

(18) Wang, X. X.; Fan, L. L.; Ma, Y. P.; Guo, C. Y.; Solan, G. A.; Sun, Y.; Sun, W. H. Elastomeric polyethylenes accessible via ethylene homo-polymerization using an unsymmetrical α-diimino-nickel catalyst. *Polym. Chem.* **2017**, *8*, 2785−2795.

(19) Miller, S. A. Sustainable Polymers: Replacing Polymers Derived from Fossil Fuels. *Polym. Chem.* **2014**, *5*, 3117−3118.

(20) Gandini, A.; Lacerda, T. M. From Monomers to Polymers from Renewable Resources: Recent Advances. *Prog. Polym. Sci.* **2015**, *48*, 1−39.

(21) Wool, R.; Sun, X. S. *Bio-based Polymers and Composites*; Academic Press: Boston, 2011.

(22) Miller, S. A. Sustainable Polymers: Opportunities for the Next Decade. *ACS Macro Lett.* **2013**, *2*, 550−554.

(23) Yu, L.; Dean, K.; Li, L. Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* **2006**, *31*, 576−602.

(24) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schafer, H. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3854−3871.

(25) Stempfle, F.; Ortmann, P.; Mecking, S. Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. *Chem. Rev.* **2016**, *116*, 4597−4641.

(26) Anneken, D. J.; Both, S.; Christoph, R.; Fieg, G.; Steinberner, U.; Westfechtel, A. *Fatty Acids in Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2006.

(27) Chauvel, A.; Lefebvre, G. *Petrochemical Processes: Technical and Economic Characteristics*; Gulf Publishing Company: Paris, 1989.

(28) Kohlpaintner, C.; Schulte, M.; Falbe, J.; Lappe, P.; Weber, J. *Aldehydes, Aliphatic in Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2008.

(29) Liu, Y.; Mecking, S. A Synthetic Polyester from Plant Oil Feedstock by Functionalizing Polymerization. *Angew. Chem., Int. Ed.* **2019**, *58*, 3346−350.

(30) Quinzler, D.; Mecking, S. Renewable resource-based poly (dodecyloate) by carbonylation polymerization. *Chem. Commun.* **2009**, *36*, 5400−5402.

(31) Tan, C.; Chen, C. L. Emerging Palladium and Nickel Catalysts for Copolymerization of Olefins with Polar Monomers. *Angew. Chem., Int. Ed.* **2019**, *58*, 7192−7200.

(32) Wang, F. Z.; Chen, C. L. A continuing legend: the Brookhart-type α-diimine nickel and palladium catalysts. *Polym. Chem.* **2019**, *10*, 2354−2369.

(33) Long, B. K.; Eagan, J. M.; Mulzer, M.; Coates, G. W. Semi-Crystalline Polar Polyethylene: Ester-Functionalized Linear Poly-olefins Enabled by a Functional-Group-Tolerant, Cationic Nickel Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55*, 7106−7110.

(34) Zhong, L.; Li, G.; Liang, G.; Gao, H.; Wu, Q. Enhancing thermal stability and living fashion in α-diimine-nickel-catalyzed (co)polymerization of ethylene and polar monomer by increasing the steric bulk of ligand backbone. *Macromolecules* **2017**, *50*, 2675−2682.

(35) Guo, L. H.; Kong, W. Y.; Xu, Y. J.; Yang, Y. L.; Ma, R.; Cong, L.; Dai, S. Y.; Liu, Z. Large-scale synthesis of novel sterically hindered acenaphthene-based α-diimine ligands and their application in coordination chemistry. *J. Organomet. Chem.* **2018**, *859*, 58−67.

(36) Dai, S. Y.; Sui, X. L.; Chen, C. L. Highly robust palladium(II) α-diimine catalysts for slow-chain-walking polymerization of ethylene and copolymerization with methyl acrylate. *Angew. Chem., Int. Ed.* **2015**, *54*, 9948−9953.

(37) Dai, S. Y.; Zhou, S. X.; Zhang, W.; Chen, C. L. Systematic investigations of ligand steric effects on α-diimine palladium catalyzed olefin polymerization and copolymerization. *Macromolecules* **2016**, *49*, 8855−8862.

(38) Dai, S.; Chen, C. Direct Synthesis of Functionalized High-Molecular-Weight Polyethylene by Copolymerization of Ethylene with Polar Monomers. *Angew. Chem., Int. Ed.* **2016**, *55*, 13281−13285.

(39) Muhammad, Q.; Tan, C.; Chen, C. L. Concerted steric and electronic effects on α-diimine nickel- and palladium-catalyzed ethylene polymerization and copolymerization. *Sci. Bull.* **2020**, *65*, 300−307.

(40) Hyatt, M. G.; Guironnet, D. Silane as chain transfer agent for the polymerization of ethylene catalyzed by a palladium(II) diimine catalyst. *ACS Catal.* **2017**, *7*, 5717−5720.

(41) Keyes, A.; Basbug, A. H. E.; Ordonez, E.; Ha, U.; Beezer, D. B.; Dau, H.; Liu, Y. S.; Tsogtgerel, E.; Jones, G. R.; Harth, E. Olefins and vinyl polar monomers: bridging the gap for next generation materials. *Angew. Chem., Int. Ed.* **2019**, *58*, 12370−12391.

(42) Liu, B.; Qiao, K. N.; Fang, J.; Wang, T. T.; Wang, Z. C.; Liu, D. T.; Xie, Z. G.; Maron, L.; Cui, D. M. Mechanism and Effect of Polar Styrenes on Scandium-Catalyzed Copolymerization with Ethylene. *Angew. Chem., Int. Ed.* **2018**, *57*, 14896−14901.

(43) Rünzi, T.; Mecking, S. Saturated Polar-Substituted Poly-ethylene Elastomers from Insertion Polymerization. *Adv. Funct. Mater.* **2014**, *24*, 387−395.

(44) Wang, X.; Nozaki, K. Selective Chain-End Functionalization of Polar Polyethylenes: Orthogonal Reactivity of Carbene and Polar Vinyl Monomers in Their Copolymerization with Ethylene. *J. Am. Chem. Soc.* **2018**, *140*, 15635−15640.

(45) Chen, M.; Chen, C. L. Direct and Tandem Routes for the Copolymerization of Ethylene with Polar Functionalized Internal Olefins. *Angew. Chem., Int. Ed.* **2020**, *59*, 1206−1210.

(46) Takano, S.; Takeuchi, D.; Osakada, K.; Akamatsu, N.; Shishido, A. Dipalladium catalyst for olefin polymerization: Introduction of acrylate units into the main chain of branched polyethylene. *Angew. Chem., Int. Ed.* **2014**, *53*, 9246−9250.

(47) Cui, L.; Chen, M.; Chen, C. L.; Liu, D. T.; Jian, Z. B. Systematic Studies on (Co)Polymerization of Polar Styrene Monomers with Palladium Catalysts. *Macromolecules* **2019**, *52*, 7197−7206.

(48) Zhang, G.; Nam, C.; Petersson, L.; Jämbeck, J.; Hillborg, H.; Chung, T. M. Increasing Polypropylene High Temperature Stability by Blending Polypropylene-Bonded Hindered Phenol Antioxidant. *Macromolecules* **2018**, *51*, 1927−1936.

(49) Zou, C.; Chen, C. L. Polar-Functionalized, Crosslinkable, Self-Healing and Photoresponsive Polyolefins. *Angew. Chem., Int. Ed.* **2020**, *59*, 395−402.

(50) Diamanti, S. J.; Ghosh, P.; Shimizu, F.; Bazan, G. C. Ethylene homopolymerization and copolymerization with functionalized 5-norbornen-2-yl monomers by a novel nickel catalyst system. *Macromolecules* **2003**, *36*, 9731−9735.

(51) Chen, Z.; Mesgar, M.; White, P. S.; Daugulis, O.; Brookhart, M. Synthesis of Branched Ultrahigh-Molecular-Weight Polyethylene Using Highly Active Neutral, Single-Component Ni (II) Catalysts. *ACS Catal.* **2015**, *5*, 631−636.

سنتز مستقیم ترموپلاستیک الاستومر پلی‌اتیلن عامل‌دار شده‌ی قطبی

چکیده:

ترموپلاستیک‌الاستومرها (TPE)[1] را می‌توان به راحتی قالب‌گیری، اکسترود و مانند پلاستیک‌ها مورد استفاده‌ی مجدد قرار داد. همچنین، TPEها می‌توانند خواص الاستیکی مشابه لاستیک‌ها را نشان دهند. آن‌ها به‌طور گسترده‌ای در کاربردهایی مانند خودرو و لوازم خانگی استفاده می‌شوند. سنتز ترموپلاستیک‌الاستومرهای پلی‌اولفینی تنها با استفاده از اتیلن به‌عنوان ماده اولیه و در یک مرحله، مفهومی جذاب است. در سال‌های اخیر، سنتز ترموپلاستیک الاستومرهای پلی‌اتیلن از طریق پلیمریزاسیون اتیلن با استفاده از کاتالیزور آلفا-دی‌ایمین نیکل[2] با موفقیت به دست آمده است. با این‌حال، استفاده از کاتالیزورهای آلفا-دی‌ایمین‌پالادیوم[3] برای این منظور، به دلیل تمایل زیاد آن‌ها به واکینگ زنجیره‌ای[4] (تمایل به قدم زنی زنجیرها) در مقایسه با نوع نیکلی آن، بسیار چالش برانگیزتر است که متعاقبا منجر به تشکیل پلی‌اولفین‌های شاخه‌دار با خواص مکانیکی ضعیف می‌شود. در این مقاله، سنتز مستقیم ترموپلاستیک‌الاستومرهای پلی‌اتیلن از طریق پلیمریزاسیون اتیلن با استفاده از کاتالیزور آلفا-دی‌ایمین‌پالادیوم گزارش شد. با طراحی دقیق کاتالیزور و تنظیم کردن پلیمریزاسیون، ترموپلاستیک‌الاستومرهای پلی‌اتیلن با خواص مکانیکی و الاستیکی عالی را می‌توان به دست آورد. مهمتر از همه، ترموپلاستیک‌الاستومرهای پلی‌اتیلن عامل‌دار شده‌ی قطبی که دارای خواص الاستیک عالی هستند، می‌توانند از طریق کوپلیمریزاسیون اتیلن با کومونومرهای مشتق شده از زیست‌توده[5] تولید شوند.

نتیجه‌گیری

به‌طور خلاصه، سنتز و خصوصیات ترموپلاستیک‌الاستومرهای پلی‌اتیلن و ترموپلاستیک‌الاستومرهای پلی‌اتیلن عامل‌دار شده‌ی قطبی را با استفاده از انواع خاصی از کاتالیزورهای آلفا-دی‌ایمین‌پالادیوم طراحی شده با جایگزین‌های ترت-بوتیل[6]، گزارش گردید. در پلیمریزاسیون اتیلن، کمپلکس‌های آلفا-دی‌ایمین‌پالادیوم 1و 2 فعالیت‌های متوسط (حدود 10^5 g/(mol Pd. h)) را نشان دادند. همچنین آن‌ها منجر به تولید پلی‌اتیلن با وزن

---

[1] Thermoplastic elastomers (TPE)
[2] α-diimine nickel
[3] α-diimine palladium
[4] Chain-walking tendency
[5] Biomass
[6] Tert-butyl

مولکولی بالا (M_n تا $45/58\times10^4$) و میکروساختار شاخه‌دار متوسطی ($60/1000C$) شدند. این پلی‌اتیلن‌های شاخه‌دار، ویژگی‌های ترموپلاستیک‌الاستومرهایی با خواص بازیابی الاستیک بسیار خوبی ($SR^7 = \%68-\%83$) را نشان دادند. فشار اتیلن و اثر الکترونیکی لیگاند می‌تواند به‌طور موثری خواص مکانیکی را تنظیم کند. در کوپلیمریزاسیون کومونومر اتیلن-زیست توده، کمپلکس‌های 1 و 2 کوپلیمرهایی با وزن مولکولی بالا (M_n تا $34/09\times10^4$) و با میکروساختارهای شاخه‌دارمتوسط ($60/1000$ C) را تولید نمودند به گونه‌ای که کومونومرها در حد متوسط (حدود $\%1$) افزوده شدند. پلی‌اتیلن‌های عامل‌دار شده‌ی قطبی ویژگی‌های ترموپلاستیک-الاستومرهایی با خواص بازیابی الاستیک بسیار خوبی ($SR= \%72-\%80$) را نشان دادند. عوامل کلیدی موثر در موفقیت سیستم‌های پالادیوم، کنترل دقیق ساختارهای شاخه‌دار پلیمری و قابلیت دستیابی به جرم‌های مولکولی پلیمری بالا می‌باشد. این مطالعه پتانسیل بسیار خوبی برای تولید ترموپلاستیک‌الاستومرهای پلی‌اتیلن عامل‌دار شده‌ی قطبی را در یک مرحله و تنها با استفاده از کومونومرهای اتیلن و مشتق شده از زیست توده به عنوان ماده اولیه، نشان می‌دهد.

Shengyu Dai, Shuaikang Li, Guoyong Xu, and Changle Chen, "Direct Synthesis of Polar Functionalized Polyethylene Thermoplastic Elastomer", Macromolecules 2020, 53, 2539−2546

---

[7] The strain recovery values