Polymer Chemistry

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Cite this: *Polym. Chem.*, 2025, **16**, 3172

Synthesis of high MFI polyolefin elastomers using dibenzosuberyl iminopyridyl Ni(II) catalysts†

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Recently, nickel-based α-diimine catalysts have been widely used in the preparation of polyolefin elastomer materials. However, the polyolefin materials obtained from this system often exhibit high molecular weights, leading to a low melt flow index (MFI) and difficulties in film processing. Herein, we first report the synthesis and characterization of a class of nickel dibenzosuberyl iminopyridyl catalysts, featuring backbones and arylamine substituents with varying electronic effects. These catalysts demonstrate high activity (10^6 g mol^{-1} h^{-1}) in ethylene polymerization and enable the synthesis of polyethylene elastomers with moderate molecular weights (53.8–156.9 kg mol^{-1}) and branching densities (55–87/1000 C). The electronic properties of the catalyst backbone and the arylamine substituents have a general influence on ethylene polymerization and the properties of the resulting products. However, increasing the polymerization temperature significantly reduced the polymerization activity and altered the molecular weight and branching density of the obtained polyethylene elastomers. Mechanical property tests of these polyethylene elastomers reveal excellent elongation at break (1617%–1729%) and moderate tensile strength at break (5.46–10.58 MPa) and elastic recovery ratios (30%–45%). MFI tests, as well as transmittance and volume resistivity measurements, indicate that the obtained polyethylene elastomer materials possess high MFR (16–22 g per 10 min), high transmittance (84–89%), and high volume resistivity (151–321 × 10^{15} Ω m), making them suitable for use as photovoltaic encapsulant films.

Received 24th January 2025,
Accepted 6th June 2025

DOI: 10.1039/d5py00083a

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1. Introduction

Polyolefin elastomers (POEs) are a versatile class of materials that combine the elasticity of rubber with the processability of thermoplastics, offering advantages such as excellent flexibility, durability, and recyclability.[1,2] Their unique combination of properties makes them highly important in various applications, ranging from automotive parts and consumer electronics to packaging and photovoltaic encapsulants, where they enhance product performance, design flexibility, and sustainability. Polyolefin elastomers are typically synthesized *via* advanced polymerization techniques, such as solution polymerization or suspension polymerization, where ethylene or propylene is copolymerized with smaller amounts of alpha-olefins and diene monomers.[1–3] This process carefully controls the molecular structure to achieve a balance of elastomeric properties, including high flexibility, good mechanical strength, and excellent resilience, making them suitable for a wide range of applications.

Recently, late transition metal catalysts with chain-walking capabilities have emerged as promising alternatives for the synthesis of polyolefin elastomers.[4–19] These catalysts eliminate the need for expensive higher-order α-olefins, attracting significant attention from both academia and industry. As a result, various nickel-based catalysts with diverse ligand structures have been developed, leading to substantial progress in polyolefin elastomer synthesis (Chart 1).[7–10,20–22] However, a notable challenge arises with these nickel-based catalysts: they often produce polyethylene elastomers with exceptionally high weight-average molecular weights, frequently exceeding 300 kg mol^{-1}.[7–10] For instance, in the nickel α-diimine system, axial steric hindrance is correlated not only with the molecular weight of the resulting polyethylene but also with its branching density. Consequently, obtaining highly branched polyethylene often comes with the trade-off of a high molecular weight, creating a dilemma.[7] This high molecular weight makes elastomers difficult to process and handle in practical applications. An exceptional case was reported by Fu *et al.*, who developed a class of 1,2-diketopyracene-based α-diimine nickel catalysts capable of simultaneously achieving both a

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† Electronic supplementary information (ESI) available: Full experimental details for the synthetic procedures, materials, analytical methods, NMR and mass spectra (Fig. S1–S34) of the synthetic compounds, and NMR (Fig. S35–S43), DSC (Fig. S44–S52) and GPC (Fig. S53–S66) curves of polyethylene elastomers. See DOI: https://doi.org/10.1039/d5py00083a

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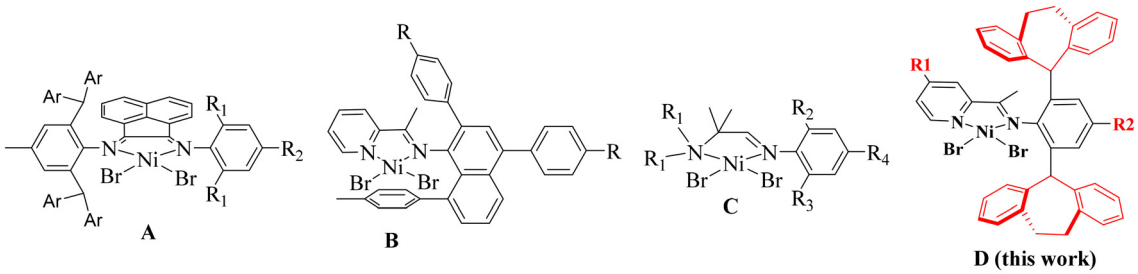


Chart 1 Typical nickel-based catalysts with diverse ligand structures in polyolefin elastomer synthesis (A–D).

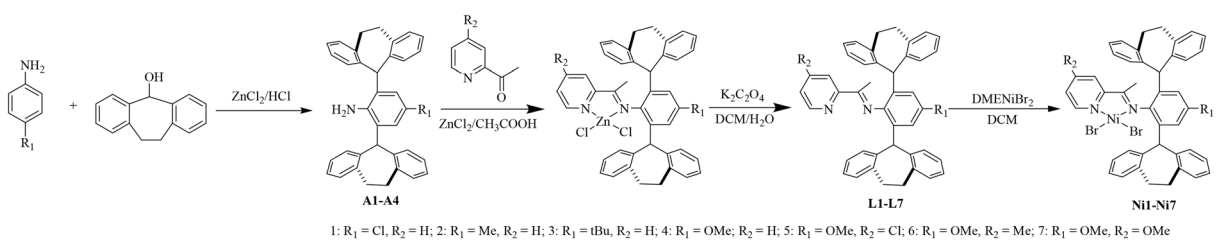
relatively low molecular weight and a high branching density in polyethylene synthesis.[23] Furthermore, α-diimine nickel catalysts are reported to be susceptible to deactivation in the presence of hydrogen, making them unsuitable for regulating molecular weight through hydrogen.[24] This limitation restricts the methods available for adjusting the melt index of the resulting elastomers. High-molecular-weight polyolefin materials are typically challenging to process, with their processability often characterized by the melt flow index (MFI). The MFI is a critical indicator of polyolefin melt flowability, expressed in grams per 10 minutes (g per 10 min). It measures the weight of the melt passing through a standardized orifice under specific temperature and pressure conditions. A high MFI is crucial for efficient and uniform material distribution during molding, extrusion, and other processing operations. Polyolefins with high MFI values are particularly suitable for applications requiring thin-wall parts, such as packaging materials, disposable medical devices, and consumer electronics, as their enhanced processability allows for the production of complex geometries and tight tolerances.

To overcome the issues associated with high molecular weight and high branching in late transition metal catalysts, we have designed a class of nickel iminopyridyl catalysts substituted with dibenzosuberyl groups. These catalysts, despite featuring large steric hindrance, are capable of catalyzing the preparation of relatively low-molecular-weight polyethylene and are prone to undergoing chain walking processes to generate highly branched polyethylene, similar to many reported bulky nickel iminopyridyl catalysts.[25–29] This design enables the production of high-MFI polyethylene elastomers, addressing the processing difficulties associated with high-molecular-weight elastomers and enhancing their applicability in various industrial applications.

2. Results and discussion

2.1. Synthesis and characterization of Ni(II) complexes

The dibenzosuberyl arylamines **A1–A4** were synthesized through the dialkylation of 4-R-aniline with dibenzocycloheptanol, catalyzed by Lucas' reagent (a mixture of zinc chloride and hydrochloric acid) (Scheme 1). These dibenzosuberyl arylamines were obtained in high yields (87–90%), eliminating the necessity for column chromatography separation during the synthetic procedure. Characterization and determination of these compounds were achieved using high-resolution mass spectrometry (HRMS), and hydrogen and carbon nuclear magnetic resonance (NMR) spectroscopy. Subsequently, the iminopyridine ligands **L1–L7** were synthesized *via* a template-type method, which involved the formation of zinc template complexes followed by demetallation reactions (Scheme 1), as reported in references.[30,31] However, the yields for ligands **L5–L7** were less satisfactory, ranging from 15% to 20%. Attempts to improve the yields using an acid-catalyzed condensation approach directly yielded similar results (15–32%). This is likely attributable to the insufficient imine formation and decreased ligand stability caused by substituents with varying electronic effects on the pyridine backbone. All the new ligands were characterized and identified using HRMS, hydrogen NMR spectroscopy, and carbon NMR spectroscopy. Under a nitrogen atmosphere at room temperature, ligands reacted with $(DME)NiBr_2$ in anhydrous dichloromethane, then the



Scheme 1 Synthesis of dibenzosuberyl iminopyridyl Ni(II) complexes.

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solvent was removed, and the residue was treated to yield iminopyridyl Ni(II) complexes **Ni1–Ni7** as yellow powders upon filtration (Scheme 1). The isolated Ni(II) complexes were obtained in good yields, ranging from 84% to 92%. Their purity and structural integrity were confirmed through elemental analysis and high-resolution MALDI-TOF mass spectrometry.

2.2. Polyethylene elastomer synthesis

A series of dibenzosuberyl iminopyridyl Ni(II) complexes were activated with 500 equivalents of methylaluminoxane (MAO), paving the way for ethylene polymerization. Under controlled conditions of 6 atm ethylene pressure and temperatures ranging from 30 to 50 °C, these catalysts exhibited high activity (10^6 g mol^{-1} h^{-1}) in the polymerization process, yielding polyethylene materials characterized by their high branching (55–87/1000 C) and moderate melting points (30–77 °C) (Table 1). As the reaction temperature rose from 30 to 50 °C, a sharp decline in the catalytic activity for ethylene polymerization was observed across various catalysts, indicating a significant loss of catalytic potency at this higher temperature (Fig. 1a and 2a). This observation underscores the weak thermal stability of these iminopyridyl nickel catalysts within

Table 1 Polyethylene elastomer synthesis[a]

Entry	Complex	T/°C	Yield/g	Activity[b]	M_n[c]	M_w/M_n[c]	B[d]	T_m[e]/(°C)
1	**Ni1**	30	2.11	2.11	115	1.60	74	51
2	**Ni1**	50	1.06	1.06	65.8	1.56	83	38
3	**Ni2**	30	1.41	1.41	99.6	1.43	76	52
4	**Ni2**	50	0.52	0.52	63.4	1.50	87	33
5	**Ni3**	30	1.78	1.78	70.9	1.64	64	51
6	**Ni3**	50	0.87	0.87	59.4	1.44	78	30
7	**Ni4**	30	1.72	1.72	108.2	1.65	55	77
8	**Ni4**	50	0.84	0.84	81.2	1.65	77	44
9	**Ni5**	30	1.64	1.64	126.2	1.73	74	54
10	**Ni5**	50	0.69	0.69	53.8	1.55	78	37
11	**Ni6**	30	1.42	1.42	156.9	1.74	73	55
12	**Ni6**	50	0.72	0.72	103.6	1.60	84	53
13	**Ni7**	30	0.73	0.73	136.7	1.60	64	72
14	**Ni7**	50	0.48	0.48	88.8	1.57	80	50

[a] Conditions: Ni(II) catalyst (2 μmol), 500 eq. MAO, 1 mL CH_2Cl_2, 20 mL toluene, 6 atm, and polymerization time (30 min). [b] Activity (Act.) = 10^6 g per (mol Ni h). [c] M_n is in units of kg mol^{-1}, determined by GPC in trichlorobenzene at 150 °C. [d] B = branches per 1000 carbons, determined by ^{1}H NMR spectroscopy, $B = 1000 \times 2(I_{CH_3})/3(I_{CH_2+CH} + I_{CH_3})$. [e] Determined by differential scanning calorimetry (DSC), broad peak.

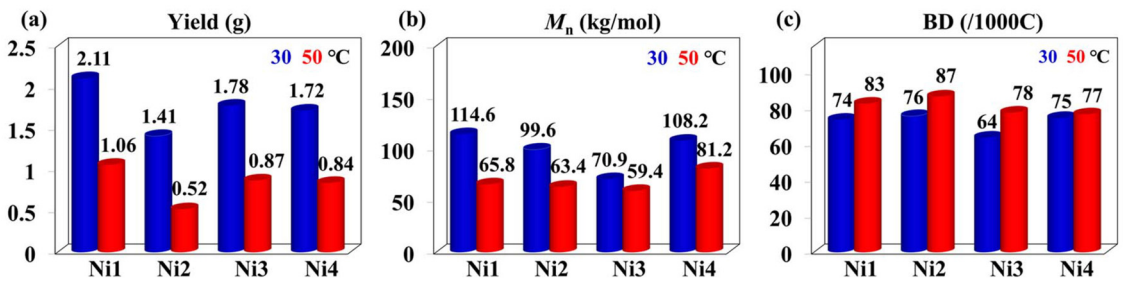

Fig. 1 Comparison of the yield (a), molecular weight (b), and branching density (c) of polyethylene generated using **Ni1–Ni4** at 30 and 50 °C.

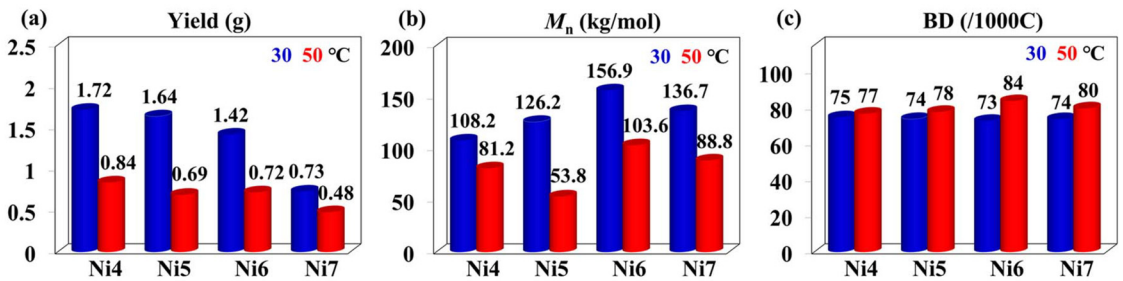

Fig. 2 Comparison of the yield (a), molecular weight (b), and branching density (c) of polyethylene generated using **Ni4–Ni7** at 30 and 50 °C.

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the 30–50 °C range, leading to pronounced catalyst deactivation. Furthermore, the reduced solubility of ethylene at elevated temperatures contributed, in part, to this observed phenomenon. The polymerization kinetics of the **Ni1** catalyst were investigated at 50 °C over time intervals of 10, 20, 30, and 60 minutes (ESI, Fig. SA†). The results demonstrated a progressive increase in polymer yield, albeit with a gradually diminishing rate. Notably, only marginal yield enhancement was observed beyond 30 minutes, indicating near-complete deactivation of the majority of active catalytic species within this period. Under these precisely controlled conditions, the nickel catalysts facilitated the production of a diverse array of high molecular weight polyethylenes (53.8–156.9 kg mol^{-1}), exhibiting varying degrees of branching.

As expected, the molecular weight of the resulting polyethylene significantly decreased with increasing temperature, which was attributed to the acceleration of chain transfer relative to chain growth as the temperature rose (Fig. 1b and 2b). The degree of branching in the resulting polyethylenes was profoundly influenced by the catalysts' chain walking and chain growth capabilities. Notably, as the polymerization temperature increased, the degree of branching in the polyethylene increased (Fig. 1c and 2c). This observation suggests a direct correlation between the relative rates of chain walking and chain growth with increasing temperature. Consequently, the melting points of these polymers decreased correspondingly with increasing branching (Table 1). It is noteworthy that the **Ni1** catalyst with a chloro substituent at the 4-position of the arylamine exhibits the highest polymerization activity among these catalysts under identical conditions (Fig. 1a and 2a), and the **Ni6** catalyst with a methyl substituent at the 4-position of the pyridine backbone can achieve the preparation of polyethylene with the highest molecular weight under the same conditions (Fig. 1b and 2b). This may be attributed to the synergistic effect of different electronic substituents on the backbone and arylamine; in general, electron-withdrawing substituents on the aryl group can enhance the electrophilicity of the nickel catalytic center, thereby reducing the energy barrier for ethylene insertion and consequently increasing the activity of ethylene polymerization. In contrast, electron-donating groups on the pyridine backbone help to elevate the electron density at the nickel catalytic center, suppressing β-H elimination during polymerization. This effectively inhibits chain transfer during the polymerization process, leading to an increase in the molecular weight of the resulting polyethylene.[4]

2.3. Mechanical and processing properties of polyethylene elastomers

As presented in Table 1, the synthesized polyethylene materials uniformly exhibit moderately high branching densities along with medium-to-low melting points, suggesting their promising potential for utilization as elastomer materials. To gain deeper insights into the mechanical attributes of these materials, we subjected the polyethylene samples derived from **Ni1–4** to mechanical testing. The results of these tests, as illustrated in Table 2 and Fig. 3, reveal that the polyethylenes synthesized using **Ni1–4** demonstrate stress at break values ranging from 5.46 to 10.58 MPa, accompanied by exceptionally high strain at break values spanning from 1617% to 1729%. These findings indicate that the obtained polyethylene materials possess outstanding tensile properties and moderate material strength. Furthermore, the stress–strain curves of the samples exhibited no yielding and displayed characteristics typical of elastomers (Fig. 3). Additional hysteresis tensile tests

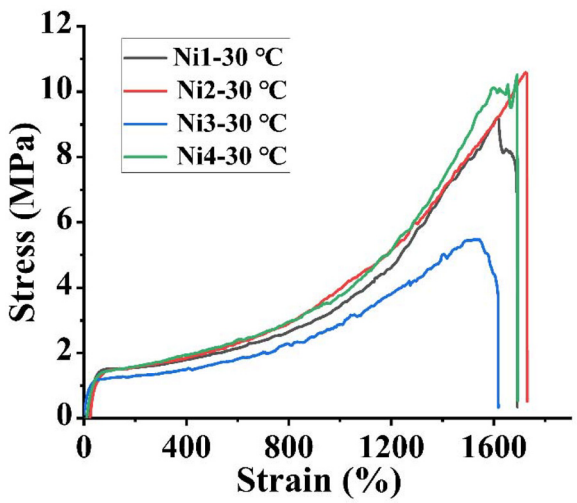

Fig. 3 Stress–strain curves of polyethylenes generated using **Ni1–Ni4** at 30 °C.

Table 2 Mechanical and processing properties of polyethylene elastomers[a]

Ent.	Precatalyst	Strain[b] (%)	Stress[b] (MPa)	SR[c] (%)	MFI[d]	Transmittance[e]	ρ_V[f]
1	**Ni1**	1664	9.13	35	16	84	151
2	**Ni2**	1729	10.58	37	18	87	182
3	**Ni3**	1617	5.46	45	22	89	321
4	**Ni4**	1691	10.51	30	17	86	213

[a] Conditions: performed at 5 mm min^{-1} by means of a universal test machine (UTM2502) at room temperature (25 °C). [b] Strain and stress at break values. [c] The strain recovery (SR) values can be calculated using 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. [d] MFI of polyethylene samples is in units of g per 10 min, determined using a melt index tester: temperature, 190 °C; weight pressure, 2.16 kg. [e] Light transmittance in the 380–760 nm bands. [f] Volume resistivity is in units of 10^{15} Ω cm.

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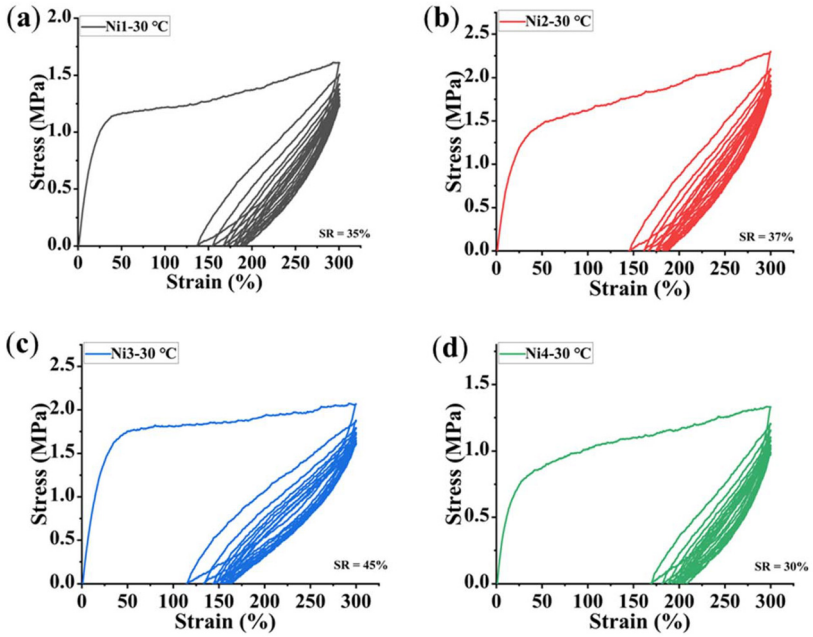

Fig. 4 Plots of hysteresis experiments of ten cycles at 300% strain for polyethylenes generated using **Ni1–Ni4** at 30 °C (a–d).

conducted on these materials revealed a moderate elastic recovery ratio, ranging from 30% to 45% (Fig. 4). The elastic recovery ratio of the obtained polyethylene is lower than that of many reported α-diimine nickel systems, likely due to its relatively low molecular weight.[5–11] We also constructed a correlation plot between the branching density and the elastic recovery ratio, but no direct relationship was observed between these two parameters (ESI, Fig. SB†). The elastic recovery ratio appears to be influenced by additional factors such as molecular weight and crystallinity. Furthermore, the commercially available POE (Dow 8669) exhibits an elastic recovery ratio of around 50%, slightly superior to the polyethylene elastomers obtained in our system.

Notably, all these polyethylene products also exhibited exceptional processing properties. The MFI test results, obtained at a temperature of 190 °C and a weight pressure of 2.16 kg, demonstrated high MFI values ranging from 16 to 22 g per 10 min. This is attributable to their appropriate polymer molecular weight and branching density. Furthermore, the films prepared from these polyethylene materials exhibit high transmittance (84–89%) across the spectral range of 380–760 nm and high volume resistivity (151–321 × 10^{15} Ω m). Collectively, these indicators confirm the suitability of these materials for application in photovoltaic encapsulant film materials.

3. Conclusions

In summary, we have successfully synthesized a series of Ni(II) dibenzosuberyl iminopyridyl catalysts, featuring backbones and arylamine substituents with varying electronic effects and utilized them for the synthesis of polyethylene elastomer materials. These nickel catalysts demonstrate high polymerization activity (10^6 g mol^{-1} h^{-1}) in ethylene polymerization, yielding polyethylenes with moderate molecular weights (53.8–156.9 kg mol^{-1}) and branching densities (55–87/1000 C). The electronic properties of the catalyst backbone and the arylamine substituents exert a moderate influence on the polymerization activity and the properties of the resultant polyethylenes, whereas temperature plays a significant role. Mechanical testing of the obtained polyethylene materials revealed their exceptional strain at break (1617%–1729%), coupled with moderate polymer stress (5.46–10.58 MPa) and elastic recovery (30%–45%). Additionally, the results of MFI tests (16–22 g per 10 min), as well as transmittance (84–89%) and volume resistivity (151–321 × 10^{15} Ω m) measurements, suggest the potential of these materials for application in photovoltaic encapsulant films. This work represents the first instance of employing Ni(II) iminopyridyl catalysts for the production of polyolefin elastomers suitable for high-MFI photovoltaic encapsulant film materials.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no competing financial interests.

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Acknowledgements

This work was supported by the Natural Science Foundation of Anhui Province (2408085MB042).

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