Macromolecules

pubs.acs.org/Macromolecules Article

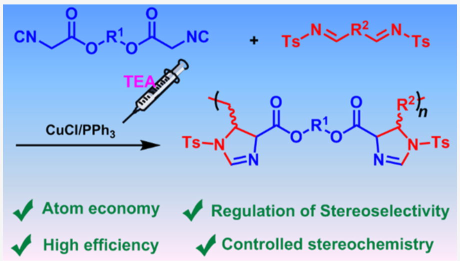
# Stereochemistry-Tunable Isocyanide-Based Polymerization

Tianyu Cheng, Tianwen Bai, Die Huang, Anjun Qin,* Jun Ling,* and Ben Zhong Tang*

Cite This: https://doi.org/10.1021/acs.macromol.1c01721 Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

**ABSTRACT:** Regulation of stereochemistry is one of the most important research focuses in synthetic polymer chemistry; however, this area should be further developed. In this work, a new polymerization of diisocyanoacetates and disulfonimines with tunable stereochemistry was developed. Diisocyanoacetates and disulfonimines could easily undergo polycycloaddition in the presence of CuCl/PPh$_3$, and polyimidazolines with high weight-average molecular weights ($M_w$, up to 43 900) were produced in excellent yields (up to 99%). Moreover, the stereochemistry of the polymerization and the stereoregularity of the resultant polymers can be fine-tuned by triethylamine (TEA). In addition, TEA could also significantly promote the polymerization, from which polymers with much higher molecular weights ($M_w$ up to 155 400) could be obtained in higher yields. This work not only promotes the development of the isocyanide chemistry and enriches the family of polymerizations based on triple-bond building blocks but also provides an opportunity to study the structure−property relationship of the polyimidazolines.



## ■ INTRODUCTION

The significance of stereochemistry in polymer science is well-defined by scientists.[1−4] For example, the stereochemical difference between natural rubber and gutta-percha (the cis- and trans-isomers of polyisoprene, respectively) results in remarkable variation in their mechanical properties, with the former being used as an elastic material while the latter being used as a hard material.[5] Furthermore, the origin of a biosystem, that is, DNA, requires the chirality of the deoxyribose sugar in its backbone to ensure that the double-helical structure can be formed by the hydrogen-bonding interaction between base pairs.[5] The direct influence of the stereochemistry in polymeric materials on their structures and properties makes the stereoselectivity in polymer synthesis extremely meaningful.[6−9] However, control over stereochemistry and its potential to influence properties of the resultant polymers are not fully realized. Therefore, exploring new polymerization reactions with controlled stereochemistry toward new polymers with well-defined stereoregular structures is of vital significance in polymer science.

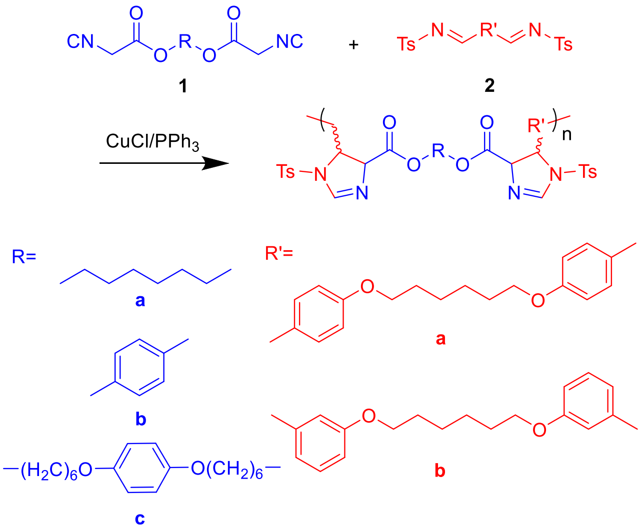
The stereochemistry also plays key roles in the polymerizations based on triple-bond building blocks, on which our groups have been working for years and remarkable progresses have been made.[10−14] One of the feasible strategies to establish new polymerization reactions is getting inspiration from reported highly efficient organic reactions. Among the triple-bond compounds, isocyanides ($-N^{+}\equiv C^{-}$) have long been proved to be irreplaceable building blocks in modern organic chemistry and various highly efficient organic reactions based on them have been reported.[15−19] However, only a handful of isocyanide-based reactions have been developed into polymerizations, such as Passerini reaction,[20] Ugi reaction,[21] and so on.[22] Thus, the polymerizations based on isocyanide monomers still need to be further expanded.

During the process of exploring new polymerization reactions based on isocyanide monomers, we are attracted by the reactions based on isocyanoacetates.[23] In our previous work, we have successfully established efficient polymerizations using isocyanoacetate derivatives as monomers, and functional nitrogen-containing heterocyclic polymers have been prepared.[24,25] Encouraged by these results, we attempted to explore more innovative polymerizations based on isocyanoacetates.

It is reported that methyl isocyanoacetate can readily react with sulfonimine in the presence of Cu(I) species, from which both *cis*- and *trans*-imidazolines could be produced in almost quantitative yields.[26,27] Since this reaction enjoys the advantages of high efficiency and atom economy and could be carried out under mild reaction conditions, it well meets the requirement for developing into a polymerization reaction.[28] Indeed, after systematical optimization of reaction conditions, we succeeded in transferring it into a new and efficient polymerization reaction (Scheme 1). Simply mixing diisocyanoacetates **1** and disulfonimines **2** in the presence of a catalytic system of CuCl/PPh$_3$ at 40 °C readily produced soluble polyimidazolines with high weight-average molecular weights ($M_w$, up to 43 900) in excellent yields (up to 99%) in 8 h.

**Received:** August 15, 2021
**Revised:** November 28, 2021

**Scheme 1. Cu(I)-Catalyzed Polymerization of Diisocyanoacetates and Disulfimides**



Through structural characterization, we found that both *cis*- and *trans*-imidazoline units in the polymer chains existed. Excitingly, *cis*-imidazolines can be partially transformed to *trans*-isomers in the presence of triethylamine (TEA) with a ratio of *cis*- and *trans*-isomers ($R_{cis/trans}$) from 70:30 to 14:86.[29] Notably, the polymerization could also be dramatically promoted by TEA, and polymers with higher $M_w$ (up to 155 400) could be obtained in higher yields. Thus, in this work, we successfully built up a new stereochemistry-controlled isocyanoacetate−sulfonimine polymerization reaction.

## RESULTS AND DISCUSSION

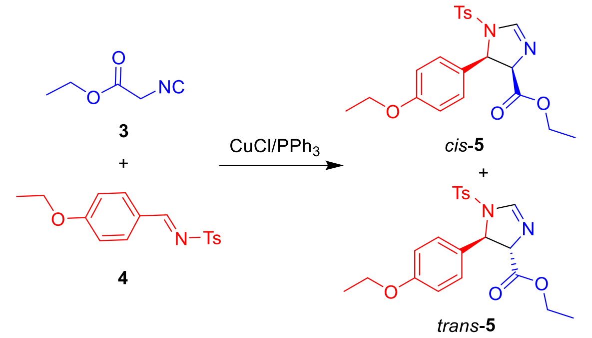
**Polymerization of Diisocyanoacetates and Disulfimides.** To develop the polymerization of isocyanoacetates and sulfonimines, we first synthesized monomers of diisocyanoacetates **1a**−**1c** according to our reported methods.[24] Meanwhile, the co-monomers of disulfonimines **2a**−**2b** were prepared following the routes shown in Scheme S1. According to our experience in the development of new polymerizations, the conditions of organic reactions are not fully suitable for the polymerization. Thus, to generate soluble polyimidazolines with high $M_w$, we systematically investigated the polymerization conditions using diisocyanoacetate **1a** and disulfonimine **2a** as model monomers (Scheme 1). The catalyst system, solvent, temperature, reaction time, and monomer concentration on the polymerization results were fully studied (Tables S1−S5), from which the optimal conditions were obtained, that is, [**1a**] = [**2a**] = 0.1 M, [CuCl] = 0.01 M, [$PPh_3$] = 2[CuCl], the solvent is dichloromethane (DCM), and the reaction time and temperature are 8 h and 40 °C, respectively. Using the optimized reaction conditions, we polymerized diisocyanoacetates **1** and disulfonimines **2** to confirm their universality and generality. As shown in Table 1, all the polymerizations propagated smoothly and polymers with high $M_w$ values (Figure S1) were produced in high yields.

**Table 1. Polymerizations of Diisocyanoacetates 1a−1c and Disulfonimines 2a−2b**[a]

| entry | monomer | Polymer | yield (%) | $M_w$[b] | $Đ$[b] | $R_{cis/trans}$[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** + **2a** | P**1a2a** | 98 | 38 300 | 1.51 | 70:30 |
| 2 | **1a** + **2b** | P**1a2b** | 87 | 15 700 | 1.54 | 75:25 |
| 3 | **1b** + **2a** | P**1b2a** | 99 | 43 900 | 1.96 | 60:40 |
| 4 | **1b** + **2b** | P**1b2b** | 79 | 22 000 | 1.62 | 65:35 |
| 5 | **1c** + **2a** | P**1c2a** | 93 | 16 100 | 1.53 | 72:28 |
| 6 | **1c** + **2b** | P**1c2b** | 90 | 13 700 | 1.48 | 79:21 |

[a]Carried out in DCM under nitrogen at 40 °C for 8 h. [M] = 0.1 M. Catalyst: [CuCl] = 1/2[$PPh_3$] = 0.01 M. [b]Estimated by gel-permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a PMMA calibration; $M_w$ = weight-average molecular weight; $M_n$ = number-average molecular weight; and $M_w/M_n$ = polydispersity index ($Đ$). [c]$R_{cis/trans}$ represents the ratio of cis- and trans-isomers in the polymers and is deduced from $^1H$ NMR spectra.

**Scheme 2. Model Reaction of Ethyl Isocyanoacetate 3 and Sulfonimine 4**



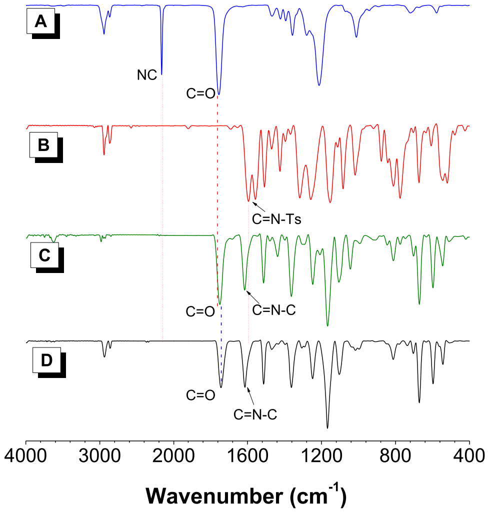


**Figure 1.** FT-IR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **5**, and (D) polymer P**1a2a**.

The resultant polymers are soluble in commonly used organic solvents, such as chloroform, DCM, DMF, and DMSO. They are also thermally stable. As evaluated by thermogravimetric analysis (TGA) (Figure S2), the temperatures for 5% weight loss of P**1a2a**−P**1c2b** are between 245 and 270 °C under nitrogen, which will facilitate their general applications.

**Model Reaction.** It is reported that both *cis*- and *trans*-imidazolines were yielded through the reaction of ethyl isocyanoacetate and sulfonimine.[27] To figure out the structures of the polymers and the $R_{cis/trans}$, a model compound **5** was prepared by the reaction of ethyl isocyanoacetate **3** and sulfonimine **4** under the reaction conditions similar with polymerization (Scheme 2). The $^1H$ NMR spectra of the crude

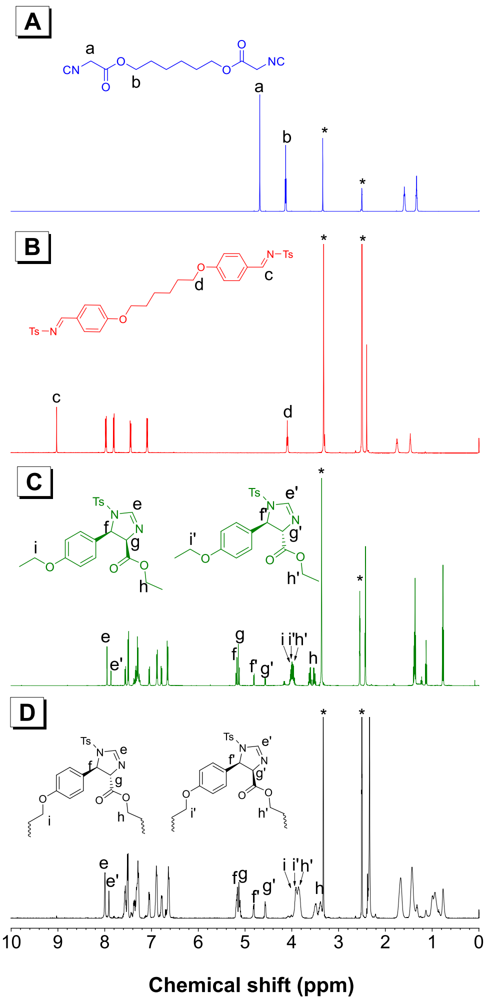


**Figure 2.** $^1$H NMR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **5**, and (D) polymer P**1a2a** in DMSO-$d_6$. The solvent peaks are marked with asterisks.

product (Figure S3) indicated that both *cis*- and *trans*-imidazolines were obtained and the ratio was deduced to be 70:30. Although we have tried very hard, no pure isomer could be obtained due to their very similar polarity.

**Structural Characterization.** The resultant polymers are characterized by Fourier transform infrared (FT-IR) and NMR spectroscopic methods. Since similar results were obtained for all the polymers (Figures S4–S18), the characterization of P**1a2a** is shown here as an example.

The FT-IR spectra of P**1a2a** and its monomers **1a** and **2a** as well as model compound **5** are presented in Figure 1. The absorption bands of **1a** associated with $-N^+{\equiv}C^-$ and C=O stretching vibrations are observed at 2187 and 1755 cm$^{-1}$, respectively. Meanwhile, the −CH=N-Ts stretching vibration peak of **2a** emerges at 1600 cm$^{-1}$. However, in the spectra of P**1a2a** and **5**, $-N^+{\equiv}C^-$ and −CH=N-Ts stretching vibration peaks become very weak. Meanwhile, a new peak belonging to the −CH=N−C stretching vibration of imidazoline appears at 1620 cm$^{-1}$. Furthermore, since the C=O group is conjugated with the newly formed imidazoline ring, its stretching vibration peak in **1a** shifted from 1755 to 1740 cm$^{-1}$ in P**1a2a**. These results indicate that most of the $-N^+{\equiv}C^-$ and −C=N-Ts groups in **1a** and **2a** have been transformed into the imidazoline rings in P**1a2a** by polymerization.

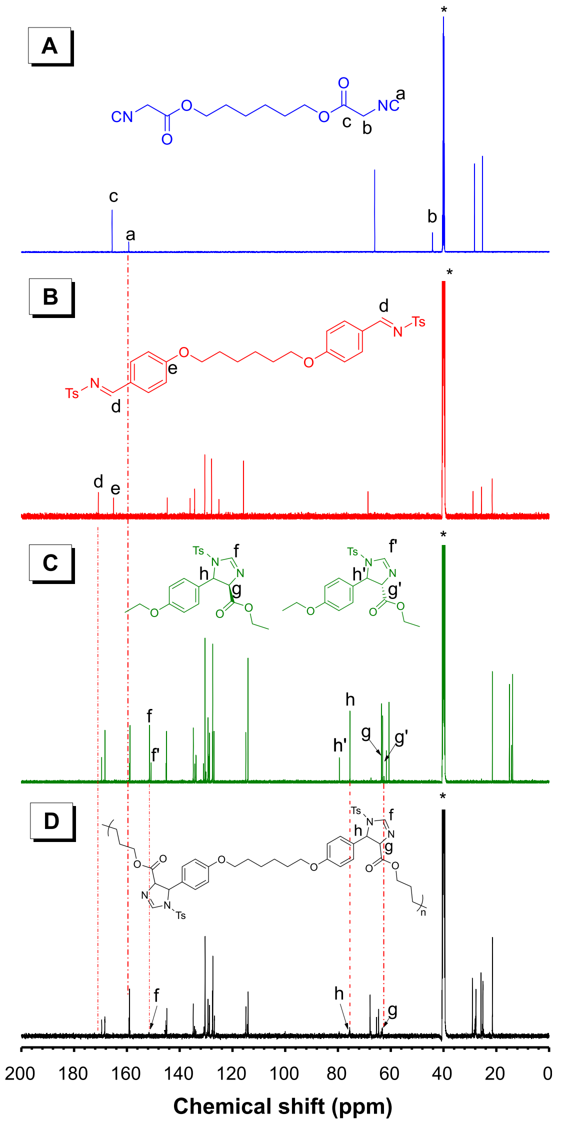


**Figure 3.** $^{13}$C NMR spectra of (A) monomer **1a**, (B) monomer **2a**, (C) model compound **5**, and (D) polymer P**1a2a** in DMSO-$d_6$. The solvent peaks are marked with asterisks.

More detailed information about the polymer structures could be obtained from NMR spectroscopy. Figure 2 shows the $^1$H NMR spectra of P**1a2a**, **1a**, **2a**, and **5**. The −C*H*=N-Ts protons of **2a** resonated at *δ* 9.02 could not be found in the spectra of P**1a2a** and **5**. Instead, new peaks at *δ* 7.99, 5.16, and 5.13 were assigned to the resonances of the newly formed *cis*-imidazoline and emerged peaks at *δ* 7.91, 4.81, and 4.57 represented the resonances of the newly formed *trans*-isomer appeared in the spectra of P**1a2a** and **5**.[29] From the integral, the $R_{cis/trans}$ was calculated to be 70:30 in P**1a2a**, which is similar to that of its model compound **5**. These results suggest that polyimidazolines were successfully obtained through the polymerization of isocyanoacetates and sulfonimines.

The $^{13}$C NMR spectra of **1a**, **2a**, **5**, and P**1a2a** further substantiate the conclusions drawn from the FT-IR and $^1$H NMR spectra. The isocyanine carbon atom of **1a** resonated at *δ* 159.23 and the imine carbon atom of **2a** at *δ* 170.99 are hardly found in the spectra of P**1a2a** and **5** (Figure 3). Meanwhile, new peaks are observed at *δ* 150.8, 75.9, and 63.1, which are assignable to the resonances of the newly formed *cis*-

### Table 2. Treatment of the Polymer P**1a2a** by TEA[a]

| entry | $t$ (h) | $M_w$[b] | Đ[b] | $R_{cis/trans}$[c] |
|---|---|---|---|---|
| 1 | 0 | 43 100 | 1.82 | 70:30 |
| 2 | 0.5 | 53 400 | 1.84 | 52:48 |
| 3 | 1 | 62 800 | 1.83 | 42:58 |
| 4 | 2 | 63 300 | 1.93 | 32:68 |
| 5 | 3 | 63 800 | 2.33 | 30:70 |
| 6 | 4 | 63 900 | 2.34 | 22:78 |
| 7 | 5 | 60 900 | 2.58 | 21:79 |
| 8 | 6 | 59 500 | 2.80 | 19:81 |
| 9 | 8 | 52 800 | 2.16 | 17:83 |
| 10 | 10 | 50 200 | 2.14 | 14:86 |
| 11 | 12 | 46 500 | 2.12 | 14:86 |
| 12 | 24 | 5000 | 2.01 | |

[a]Carried out in DCM under nitrogen in 40 °C. [P**1a2a**] = 0.1 M. [TEA] = 0.01 M. [b]Estimated by gel-permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a PMMA calibration; $M_w$ = weight-average molecular weight; $M_w/M_n$ = polydispersity index (Đ); and $M_n$ = number-average molecular weight. [c]$R_{cis/trans}$ represents the ratio of cis- and trans-isomers in the polymers and is deduced from $^1$H NMR spectra.

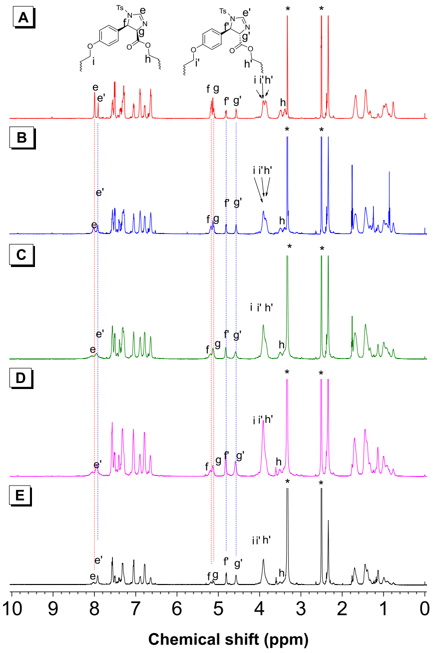


**Figure 4.** $^1$H NMR spectra of P**1a2a** treated with TEA at (A) 0, (B) 0.5, (C) 1, (D) 2, and (E) 3 h in DMSO-$d_6$. The solvent peaks are marked with asterisks.

### Table 3. Effect of TEA Concentration on the Polymerization of **1a** and **2a**[a]

| entry | [TEA] (M) | yield (%) | $M_w$[b] | Đ[b] | $R_{cis/trans}$[c] |
|---|---|---|---|---|---|
| 1 | 0 | 97 | 36 400 | 1.50 | 70:30 |
| 2 | 0.025 | 99 | 97 400 | 2.05 | 29:71 |
| 3 | 0.05 | 99 | 97 500 | 2.04 | 21:79 |
| 4 | 0.1 | 99 | 98 400 | 2.09 | 20:80 |
| 5 | 0.2 | 99 | 69 200 | 2.43 | 18:82 |

[a]Carried out in DCM under nitrogen in 40 °C for 6 h. [M] = 0.1 M. Catalyst: [CuCl] = 1/2[$PPh_3$] = 0.01 M. [b]Estimated by gel-permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a PMMA calibration; $M_w$ = weight-average molecular weight; $M_w/M_n$ = polydispersity index (Đ); and $M_n$ = number-average molecular weight. [c]$R_{cis/trans}$ represents the ratio of cis- and trans-isomers in the polymers and is deduced from $^1$H NMR spectra shown in Figure S19.

### Table 4. Time Course of Polymerization of **1a** and **2a** in the Presence of TEA[a]

| entry | $t$ (h) | yield (%) | $M_w$[b] | Đ[b] | $R_{cis/trans}$[c] |
|---|---|---|---|---|---|
| 1 | 2 | 99 | 95 300 | 2.08 | 30:70 |
| 2 | 4 | 99 | 96 600 | 2.02 | 24:76 |
| 3 | 6 | 99 | 96 500 | 2.03 | 21:79 |
| 4 | 8 | 99 | 98 000 | 2.02 | 18:82 |
| 5 | 10 | 99 | 98 200 | 1.98 | 16:84 |
| 6 | 12 | 99 | 98 500 | 1.87 | 11:89 |

[a]Carried out in DCM under nitrogen in 40 °C. [M] = 0.1 M. Catalyst: [CuCl] = 1/2[$PPh_3$] = 0.01 M. [b]Estimated by gel-permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a PMMA calibration; $M_w$ = weight-average molecular weight; $M_w/M_n$ = polydispersity index (Đ); and $M_n$ = number-average molecular weight. [c]$R_{cis/trans}$ represents the ratio of cis- and trans-isomers in the polymers and is deduced from $^1$H NMR spectra shown in Figure S19.

### Table 5. Cu(I)-Catalyzed Polymerizations of Diisocyanoacetates **1a**−**1c** and Disulfonimines **2a**−**2b** in the Presence of TEA[a]

| entry | monomers | polymer | yield (%) | $M_w$[b] | Đ[b] | $R_{cis/trans}$[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** + **2a** | P**1a2a**′ | 99 | 92 400 | 1.77 | 11:89 |
| 2 | **1a** + **2b** | P**1a2b**′ | 88 | 44 700 | 3.18 | 14:86 |
| 3 | **1b** + **2a** | P**1b2a**′ | 99 | 155 400 | 2.51 | 12:88 |
| 4 | **1b** + **2b** | P**1b2b**′ | 92 | 100 600 | 2.33 | 15:85 |
| 5 | **1c** + **2a** | P**1c2a**′ | 94 | 36 400 | 1.92 | 10:90 |
| 6 | **1c** + **2b** | P**1c2b**′ | 92 | 33 700 | 2.03 | 14:86 |

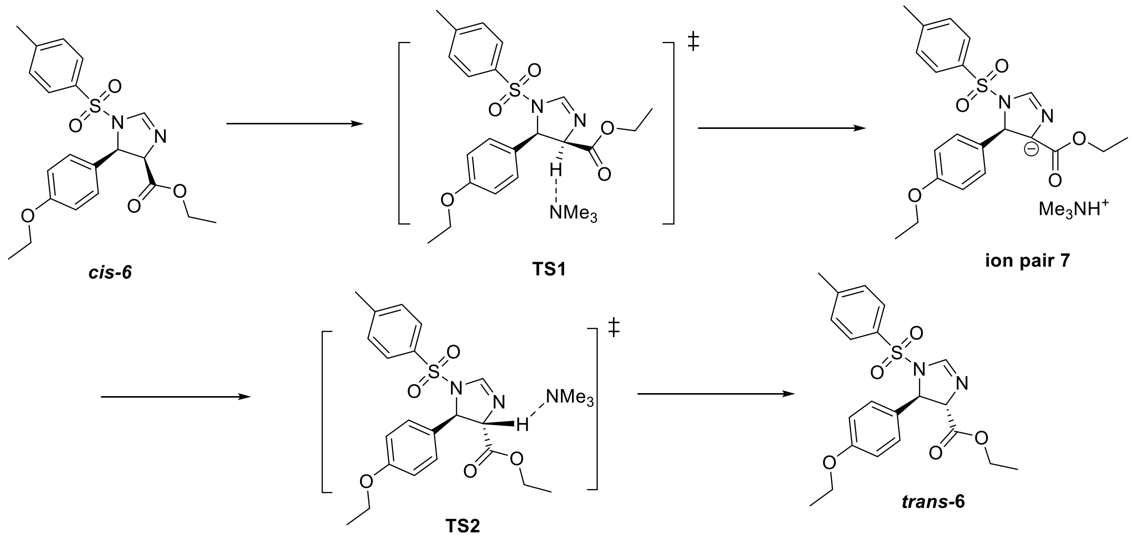
[a]Carried out in DCM under nitrogen at 40 °C for 12 h. [M] = 0.1 M. Catalyst: [CuCl] = 1/2[$PPh_3$] = 0.01 M. [b]Estimated by gel-permeation chromatography (GPC) in DMF containing 0.05 M LiBr on the basis of a PMMA calibration; $M_w$ = weight-average molecular weight; $M_w/M_n$ = polydispersity index (Đ); and $M_n$ = number-average molecular weight. [c]$R_{cis/trans}$ represents the ratio of cis- and trans-isomers in the polymers and is deduced from $^1$H NMR spectra shown in Figures S9−S18.

imidazoline rings. It is worth noting that the peaks for *trans*-isomers are too weak to be assigned. These results again confirm the conversion of the $-N^+{\equiv}C^-$ of **1a** and the $-CH{=}$N-Ts of **2a** into the imidazoline rings in P**1a2a** and the success of polymerization of isocyanoacetates and sulfonimines.

**Stereoregulation of Polyimidazolines.** Based on the abovementioned structural characterization, we could conclude that the resultant polymers contain both *cis*- and *trans*-isomers and the former is dominated. Fine-tuning the stereoregularity of the polymers will be attractive because their properties might be different. Interestingly, it is reported that the *cis*-imidazolines could be isomerized into *trans*-ones upon treatment with TEA.[29] We thus attempted to adjust the stereoregularity of the polymers by the addition of TEA using P**1a2a** as a model. As shown in Table 2, after adding TEA into the DCM solution of P**1a2a**, the $M_w$ of the polymer increases slightly in the first 3 h. This phenomenon could be explained as that the presence of TEA together with the residual catalysts might promote the reaction of the polymer with the terminated unreacted groups. Afterward, the polymer remained stable in next 3 h but degraded slightly in 6 h probably due to the basic

https://doi.org/10.1021/acs.macromol.1c01721
*Macromolecules* XXXX, XXX, XXX−XXX

**Scheme 3. Theoretical Mechanism of Configuration Transformation of Imidazoline in the Presence of Trimethylamine**



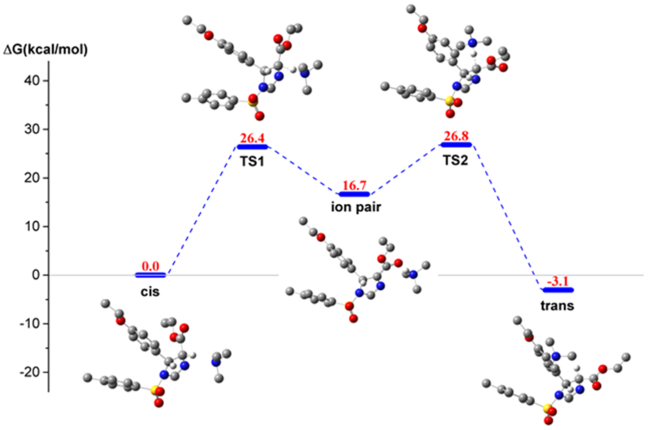


**Figure 5.** DFT-calculated Gibbs free-energy profiles of configuration transformation under B3LYP/6-311++G(2df,pd)//B3LYP/6-31+G-(d,p) in THF. All mentioned intermediates and **TS**s are illustrated using 3D models where some hydrogen atoms are omitted for clarity.

condition. After treatment for 24 h, the polymer degraded completely.

The change in the cis- and trans-isomer ratio of the polymer could be clearly observed in the $^1$H NMR spectra (Figure 4). We can intuitively see that with the extension of the treatment time, the characteristic peak of cis-isomers gradually decreased; meanwhile, the resonant peak of trans-isomers increased and the latter become dominated after 3 h. These results fully demonstrate that the regulation of the polymer structure could be realized by changing the treatment time of polymers with TEA.

**Control over Stereochemistry during Polymerization.** Inspired by the fact that upon the addition of TEA, not only the stereoregularity of P**1a2a** changed but also its molecular weight enhanced in 3 h, we anticipated that TEA could also promote the polymerization of isocyanoacetates and sulfonimines besides fine-tuning the stereoregularity of the products. To confirm this hypothesis, we systematically investigated the effect of TEA on polymerization.

First, we studied the effect of TEA concentration on polymerization and the results are summarized in Table 3. By adding a catalytic amount of TEA into the polymerization system, the $R_{\text{cis/trans}}$ of the polymer changed as expected from 70:30 to 18:82. At the same time, TEA also promoted the polymerization reaction significantly. Both the yield and $M_w$ of the product increase. It is worth noting that the $M_w$ could be enhanced to 98 400, which is almost three times higher than the value without TEA.

Second, we followed the time course of the polymerization with the treatment of TEA. As shown in Table 4, when the reaction time extended from 2 to 12 h, the $M_w$ changed slightly, but the $R_{\text{cis/trans}}$ varied dramatically from 30:70 to 11:89. Hence, the stereochemistry of the polymerization could be controlled by adjusting the amount and treatment time of TEA. The results also confirm our anticipation.

Similar results were obtained in the polymerizations of diisocyanoacetates **1a**−**1c** and disulfonimines **2a** and **2b** in the presence of TEA (Table 5 and Figure S20), and polymers of P**1a2a′**−P**1c2b′** with much higher $M_w$ values than those without TEA were produced in excellent yields (Figures S9−S18).

**Mechanism Study.** The polymerization mechanism of isocyanoacetate and sulfonimine monomers could be understood on the basis of the proposed organic reaction (Scheme S2).[26,27] The copper complex first coordinates with isocyanide to form an intermediate **I** which makes the proton of the methylene group adjacent to the isocyanide group easily leave to form a negatively charged intermediate **II** under the basic condition. When the system has no TEA, the weak alkalinity of the sulfonimide monomer itself takes away such protons. As the reaction proceeds, the consumption of sulfonimide monomers gradually weakens the alkalinity of the system which hinders the formation of intermediates **II**, leading the polymerization to terminate early. At the same time, the reaction of sulfonimide monomer with **II** readily results in the intermediate **III**, from which the product is generated after intramolecular cyclization of **IV** and elimination of catalytic species. However, in the presence of TEA, it could serve as a base to attract the proton from **I**, and sulfonimide monomers are no longer required to provide an alkaline environment. Thus, the consumption of sulfonimide monomers does not affect the formation of intermediate **II**, which makes the reaction more fast and complete. As a result, polymers with higher molecular weights are obtained in higher yields.

Although the polymerization mechanism is clear, there is still another question, that is, why TEA could fine-tune the stereoregularity of the polymers? To have an insight into the underneath mechanism, we applied a DFT calculation. To simplify the calculation, trimethylamine instead of TEA was used. As shown in Scheme 3, the acidic proton of the imidazoline ring of *cis*-**6** could be captured by the trimethylamine via a transition state **TS1** to form an ion pair intermediate **7**. The ester group in **7** could freely rotate and there are two positions to recombine the protons. The DFT calculation results show that the difference of the Gibbs energy barrier between *cis*-intermediate **TS1** to **7** and trans-intermediate **TS2** to **7** is only 0.4 kcal/mol (Figure 5), suggesting that **TS1** and **TS2** are randomly formed. However, from **TS2** to *trans*-**6**, the energy released is 29.9 kcal/mol, which is higher than the energy barrier of 26.4 kcal/mol between **TS1** and *cis*-**6**. These results indicate that the thermodynamic stability of *trans*-**6** is higher than that of *cis*-**6**. Thus, it is more likely to form *trans*-**6** with better thermodynamic stability.

## CONCLUSIONS

We successfully developed an efficient Cu(I)-catalyzed polymerization of isocyanoacetates and sulfonimines. The polymerization could be performed under mild reaction conditions and readily furnish soluble and thermally stable polyimidazolines of P**1a2a**−P**1c2b** with high $M_w$ values in high yields at 40 °C in 8 h. Moreover, the stereoregularity of the polymers and stereochemistry of the polymerization could be fine-tuned by TEA. Moreover, the polymerization could be dramatically promoted by TEA and polymers P**1a2a′**−P**1c2b′** with higher molecular weights than P**1a2a**−P**1c2b** could be produced. Notably, the fine-tuning of the stereoregularity of the polymers could be well-explained by employing DFT calculation. This new polymerization of isocyanoacetates and sulfonimines with controlled stereochemistry furnishes us a new method to prepare functional polymeric materials with different stereoregular structures and offers us a new platform to study the structure−property relationship of polymers, which is our next goal.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c01721.

> Materials, instrumentation, experimental procedures, characterization data, and calculation details; polymerization condition optimization on a catalyst system, solvent, temperature, reaction time, and monomer concentration; GPC traces, FT-IR, $^1$H, and $^{13}$C NMR spectra of monomers and polymers; TGA thermograms of polymers; and optimized geometries (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

**Anjun Qin** − *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, AIE Institute, Center for Aggregation Induced Emission, South China University of Technology, Guangzhou 510640, China;* orcid.org/0000-0001-7158-1808; Email: msqinaj@scut.edu.cn

**Jun Ling** − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China;* orcid.org/0000-0002-0365-1381; Email: lingjun@zju.edu.cn

**Ben Zhong Tang** − *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, AIE Institute, Center for Aggregation Induced Emission, South China University of Technology, Guangzhou 510640, China; Shenzhen Institute of Aggregate Science and Technology, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, Shenzhen City, Guangdong 518172, China;* Email: tangbenz@cuhk.edu.cn

### Authors

**Tianyu Cheng** − *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, AIE Institute, Center for Aggregation Induced Emission, South China University of Technology, Guangzhou 510640, China*

**Tianwen Bai** − *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China*

**Die Huang** − *State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, AIE Institute, Center for Aggregation Induced Emission, South China University of Technology, Guangzhou 510640, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.1c01721

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (21788102 and 21525417), the Natural Science Foundation of Guangdong Province (2019B030301003 and 2016A030312002), and the Innovation and Technology Commission of Hong Kong (ITCC-NERC14S01).

## REFERENCES

(1) Jenkins, A. D. Stereochemical Definitions and Notations Relating to Polymers. *Pure Appl. Chem.* **1981**, *53*, 733−752.

(2) Wulff, G. N. Main-Chain Chirality and Optical Activity in Polymers Consisting of C-C Chains. *Angew. Chem., Int. Ed.* **1989**, *28*, 21−37.

(3) Coates, G. W.; Waymouth, R. M. Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene. *Science* **1995**, *267*, 217−219.

(4) Cornelissen, J. J. L. M.; Donners, J. J. J. M.; de Gelder, R.; Graswinckel, W. S.; Metselaar, G. A.; Rowan, A. E.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. β-Helical Polymers from Isocyanopeptides. *Science* **2001**, *293*, 676−680.

(5) Worch, J. C.; Prydderch, H.; Jimaja, S.; Bexis, P.; Becker, M. L.; Dove, A. P. Stereochemical Enhancement of Polymer Properties. *Nat. Rev. Chem.* **2019**, *3*, 514−535.

(6) Stubbs, C. J.; Worch, J. C.; Prydderch, H.; Becker, M. L.; Dove, A. P. Unsaturated Poly(ester-urethanes) with Stereochemically Dependent Thermomechanical Properties. *Macromolecules* **2020**, *53*, 174−181.

(7) Teator, A. J.; Varner, T. P.; Jacky, P. E.; Sheyko, K. A.; Leibfarth, F. A. Polar Thermoplastics with Tunable Physical Properties Enabled by the Stereoselective Copolymerization of Vinyl Ethers. *ACS Macro Lett.* **2019**, *8*, 1559−1563.

(8) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. Chiral Architectures from Macromolecular Building Blocks. *Chem. Rev.* **2001**, *101*, 4039−4070.

(9) Lv, J.-a.; Liu, Y.; Wei, J.; Chen, E.; Qin, L.; Yu, Y. Photocontrol of Fluid Slugs in Liquid Crystal Polymer Microactuators. *Nature* **2016**, *537*, 179−184.

(10) Liu, J.; Lam, J. W. Y.; Tang, B. Z. Acetylenic Polymers: Syntheses, Structures, and Functions. *Chem. Rev.* **2009**, *109*, 5799−5867.

(11) Qin, A.; Lam, J. W. Y.; Tang, B. Z. Click Polymerization. *Chem. Soc. Rev.* **2010**, *39*, 2522−2544.

(12) Qin, A.; Tang, B. Z. Special Topic on Research Frontier in Polymer Science in China. *Sci. China Chem.* **2016**, *59*, 1529−1530.

(13) Liu, Y.; Qin, A.; Tang, B. Z. Polymerizations Based on Triple-Bond Building Blocks. *Prog. Polym. Sci.* **2018**, *78*, 92−138.

(14) Song, B.; Qin, A.-J.; Tang, B. Z. Green Monomer of $CO_2$ and Alkyne-Based Four-Component Tandem Polymerization toward Regio- and Stereoregular Poly(aminoacrylate)s. *Chin. J. Polym. Sci.* **2021**, *39*, 51−59.

(15) Lygin, A. V.; de Meijere, A. Isocyanides in the Synthesis of Nitrogen Heterocycles. *Angew. Chem., Int. Ed.* **2010**, *49*, 9094−9124.

(16) Boyarskiy, V. P.; Bokach, N. A.; Luzyanin, K. V.; Kukushkin, V. Y. Metal-Mediated and Metal-Catalyzed Reactions of Isocyanides. *Chem. Rev.* **2015**, *115*, 2698−2779.

(17) Gu, Z.; Ji, S. Recent Advances in Cobalt Catalyzed Isocyanide Coupling Reactions. *Acta Chim. Sin.* **2018**, *76*, 347−356.

(18) Wang, Y.; Liu, Y. Metal-Free C2-H Aminocarbonylation of Pyridines for the Synthesis of Picolinamides. *Acta Chim. Sin.* **2019**, *77*, 418−421.

(19) Zhang, J.; Wang, Y.-Y.; Sun, H.; Li, S.-Y.; Xiang, S.-H.; Tan, B. Enantioselective Three-Component Ugi Reaction Catalyzed by Chiral Phosphoric Acid. *Sci. China Chem.* **2020**, *63*, 47−54.

(20) Kreye, O.; Tóth, T.; Meier, M. A. R. Introducing Multicomponent Reactions to Polymer Science: Passerini Reactions of Renewable Monomers. *J. Am. Chem. Soc.* **2011**, *133*, 1790−1792.

(21) Sehlinger, A.; Dannecker, P.-K.; Kreye, O.; Meier, M. A. R. Diversely Substituted Polyamides: Macromolecular Design Using the Ugi Four-Component Reaction. *Macromolecules* **2014**, *47*, 2774−2783.

(22) Cai, Z.; Ren, Y.; Li, X.; Shi, J.; Tong, B.; Dong, Y. Functional Isocyanide-Based Polymers. *Acc. Chem. Res.* **2020**, *53*, 2879−2891.

(23) Gulevich, A. V.; Zhdanko, A. G.; Orru, R. V. A.; Nenajdenko, V. G. Isocyanoacetate Derivatives: Synthesis, Reactivity, and Application. *Chem. Rev.* **2010**, *110*, 5235−5331.

(24) Cheng, T.; Chen, Y.; Qin, A.; Tang, B. Z. Single Component Polymerization of Diisocyanoacetates toward Polyimidazoles. *Macromolecules* **2018**, *51*, 5638−5645.

(25) Cheng, T.; Chen, Y.; Ding, J.; Qin, A.; Tang, B. Z. Isocyanoacetate-Aldehyde Polymerization: A Facile Tool toward Functional Oxazoline-Containing Polymers. *Macromol. Rapid Commun.* **2020**, *41*, 2000179.

(26) Ito, Y.; Matsuura, T.; Saegusa, T. $ZnCl_2$ and CuCl Promoted Aldol Reactions of Isocyanoacetate with $\alpha,\beta$-Unsaturated Carbonyl Compounds. *Tetrahedron Lett.* **1985**, *26*, 5781−5784.

(27) Benito-Garagorri, D.; Bocokić, V.; Kirchner, K. Copper(I)-Catalyzed Diastereoselective Formation of Oxazolines and *N*-sulfonyl-2-imidazolines. *Tetrahedron Lett.* **2006**, *47*, 8641−8644.

(28) Qin, A.; Liu, Y.; Tang, B. Z. Regioselective Metal-Free Click Polymerization of Azide and Alkyne. *Macromol. Chem. Phys.* **2015**, *216*, 818−828.

(29) Hayashi, T.; Kishi, E.; Soloshonok, V. A.; Uozumi, Y. Erythro-Selective Aldol-Type Reaction of *N*-Sulfonylaldimines with Methyl Isocyanoacetate Catalyzed by Gold(I). *Tetrahedron Lett.* **1996**, *37*, 4969−4972.