

Multicomponent Cyclopolymerization of Alkynes, Isocyanides and Isocyanates toward Heterocyclic Polymers

Xiaoheng Wang,[†] Baixue Li,[†] Jianwen Peng,[†] Bingnan Wang,[†] Anjun Qin^{†} and Ben Zhong
Tang^{†,‡}*

[†] State Key Laboratory of Luminescent Materials and Devices, Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, SCUT-HKUST Joint Research Institute, AIE Institute, Center for Aggregation-Induced Emission, South China University of Technology (SCUT), Guangzhou 510640, China. E-mail: msqinaj@scut.edu.cn

[‡] Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, Institute for Advanced Study, and Department of Chemical and Biological Engineering, The Hong Kong University of Science & Technology (HKUST), Hong Kong, Kowloon, Hong Kong 999077, China

Abstract:

Multicomponent cyclopolymerization (MCCP) based on isocyanides, among the tremendous synthetic methodologies, is a powerful tool for the preparation of functional heterocyclic polymers like poly(maleimide)s (PMDs), which should be further developed. In this work, an atom-economic and catalyst-free MCCP of activated alkynes, diisocyanides and diisocyanates was fully explored. The PMDs with high weight-average molecular weights (M_w up to 29 000) were facilely produced in satisfactory yields (up to 85%). The resultant polymers showed excellent solubility, high thermal stability, and good film-forming ability, and their thin films possessed high refraction indices (RI) in a range of 1.613 to 1.708 at 632.8 nm. Therefore, this work not only supplements the isocyanide-based multicomponent cyclopolymerizations but also enriches the family of polymerization reactions based on triple-bond building blocks.

Introduction

The exploration of new polymerization reactions for the synthesis of functional polymers with specific structures and excellent properties are fundamental in polymer chemistry materials sciences.¹⁻⁴ Triple-bonded building blocks such as isocyanides, nitriles and alkynes have been admitted to be significant monomers in synthetic polymer chemistry, owing to their excellent reactivity, adaptable reaction types and simple synthesis, *etc.*⁵⁻¹⁰ Over the past years, plentiful of polymerization reactions based on triple-bond building blocks have been developed.¹⁵⁻¹⁸ As an isomer of nitrile, isocyanides have a high reactivity, unusual valence structure and are often used as a structural unit for the synthesis of heteroatom-containing compounds. However, compared with their huge number of organic reactions, the polymerizations based on isocyanides still need to be further expanded.

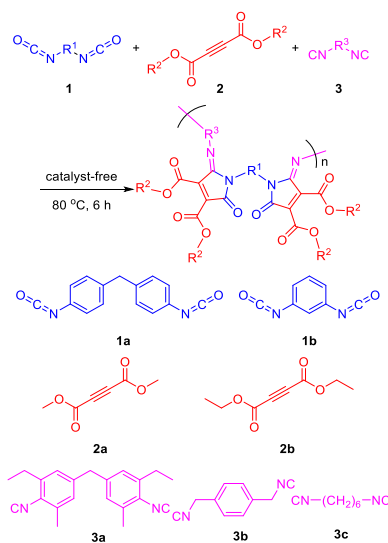
The isocyanide-based multicomponent polymerizations (MCPs),^{19,20} as an emerging topic of synthetic polymer chemistry, have gained wide popularity recently. Besides the merits inherited from multicomponent reactions (MCRs), such as high atom economy, step effectiveness, environmental benefits, simple and inexpensive reactants, operational simplicity and synthetic efficiency, such MCPs compared to other polymerizations is the great structural diversity of the products that could be obtained through various combinations of multiple monomers.^{21,22} Most importantly, instead of only linking functional monomeric units together in a polymer chain, MCPs could build new functional units embedded in the main chains of polymers directly. With these advantages, MCPs could perform as a powerful tool for the development of functional polymer materials with great efficiency and synthetic simplicity.

Although a great deal of research on the isocyanide-based MCR,²³⁻³⁰ which plays a crucial role in organic synthesis, drug discovery and materials science, have been reported,³¹⁻³⁵ there have been few empirical investigations into isocyanide-based multicomponent cyclopolymerization reactions.³⁶⁻⁴⁰ Among the reported isocyanide-based reactions, we were intrigued by a catalyst-free cyclization of isocyanides, isocyanates and alkynes, in which maleimide derivatives can be efficiently produced in high yields.⁴¹ Such reaction holds great potential to be developed into a multicomponent cyclopolymerization (MCCP),⁴² which could furnish functional heterocyclic polymers that are applicable in the genes delivery, controlled drug release, photoelectric materials, coatings and adhesives, etc.⁴³⁻⁴⁸ Moreover, the monomers for the polymerization are easily accessible, and with merely a rational design of diisocyanides.

Encouraged by the efficient organic reactions of isocyanides and diversified polymerization structures using triple-bonded building blocks, we accordingly attempted to develop a one-pot catalyst-free MCCP based on isocyanides, isocyanates, and alkynes. Delightfully, we successfully established such a polymerization after a systematic optimization of the reaction conditions, such as solvent, temperature, reaction time, monomer concentration, atmosphere and monomer. Simply mixing diisocyanates **1**, dialkyl acetylenedicarboxylates **2** and diisocyanides **3** (their synthetic routes are shown in Schemes S1 and S2) at 80 °C readily produced soluble poly(maleimide)s (PMDs) with high weight-average molecular weights (M_w up to 29 000) in satisfactory yields (up to 85%) after 6 h (Scheme 1). Notably, this polymerization is atom economic as no byproduct was generated. The resultant PMDs possess high thermal stability with decomposition

temperatures (T_d , the temperatures for 5% weight loss) as high as 312 °C, excellent film-forming ability, and high refractive indices (RI) with the values ranging from 1.613 to 1.708 at 632.8 nm. Therefore, this work not only developed a new and efficient MCCP but also enriches the family of polymerization reactions based on triple-bond building blocks.

Scheme 1. Multicomponent cyclopolymerization of diisocyanates **1**, activated alkynes **2** and diisocyanide **3**.



Results and Discussion

Multicomponent cyclopolymerization. It is well-known that the conditions for a highly efficient organic reaction could not be copied for corresponding polymerization.⁴² We thus systematically investigated the reaction conditions for the catalyst-free one-pot MCCP using 4,4'-diphenylmethane diisocyanate (**1a**), diethyl acetylenedicarboxylate (**2b**) and bis(3-ethyl-4-isocyano-5-methylphenyl)methane (**3a**) as representative monomers. The effect of solvent on the polymerization was firstly investigated, and the data are shown in Table 1. Four different solvents, namely dichloromethane (DCM), toluene, dichloroethane (DCE), and tetrahydrofuran (THF), were selected to transmit the MCCP. The cyclopolymerization did not happen in THF (Table 1, entry 4), probably because the activity of diisocyanide monomers was too low for polymerization in the polar solvent.⁴⁹ Meanwhile, the highest yield (70%)

and the highest M_w (10 200) of the polymer were achieved in DCE (Table 1, entry 3). Although the cyclopolymerization also occurred in low polar solvents, such as toluene and DCM, both the yields and M_w s of the products were significantly decreased (Table 1, entries 1 and 2). Therefore, DCE was used as the proper cyclopolymerization solvent in the subsequent studies.

Table 1. The Effect of Solvent on the Polymerization of 1a, 2b and 3a^a

entry	solvent	yield (%)	M_w^b	\bar{D}^b
1	toluene	61	8400	1.34
2	DCM ^c	70	9000	1.48
3	DCE	70	10 200	1.38
4	THF	-	-	-

^a Carried out at 80 °C for 12 h under nitrogen. $[1a] = [3a] = 0.2$ M, $[1a]/[2b] = 1/2$. ^b Estimated by Advanced Polymer Chromatography (APC) in THF on the basis of a polystyrene (PS) calibration. M_w = weight-average molecular weight; polydispersity index (\bar{D}) = M_w/M_n , M_n = number-average molecular weight. ^c Carried out at 38 °C.

In addition to the solvent, temperature is also an important factor in producing a polymer with a high molecular weight in a high yield. Thus, the polymerization temperature was studied from room temperature to 80 °C, and the consequences are given in Table 2. When the polymerization was carried out at 25 °C, the yield and M_w of the obtained the polymer were considerably low (Table 2, entry 1), which raised in stepwise with increasing temperatures from 25 to 80 °C (Table 2, entries 1–4). Apparently, higher temperatures permitted the cyclopolymerization to quickly overcome the energy gap and contributed to higher reaction efficiency. When the reaction temperature was set as 80 °C, soluble polymer was obtained in the highest yield. The M_w values and yields of the products might improve if further increasing the reaction temperature, but considering the energy saving and product possibility, we did not further elevate the temperature. Therefore, 80 °C was singled out as

the cyclopolymerization temperature for the following explorations.

Table 2. The Effect of Reaction Temperature on the Polymerization of 1a, 2b and 3a^a

entry	<i>T</i> (°C)	yield (%)	<i>M_w</i> ^b	<i>Đ</i> ^b
1	25	52	7200	1.27
2	40	65	11 500	1.54
3	60	75	15 500	1.66
4	80	81	29 900	2.21

^a Carried out in DCE for 12 h under nitrogen. [1a] = [3a] = 0.2 M, [1a]/[2b] = 1/2. ^b Estimated by Advanced Polymer Chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene (PS) calibration. *M_w* = weight-average molecular weight; polydispersity index (*Đ*) = *M_w*/*M_n*, *M_n* = number-average molecular weight.

The reaction time is another important parameter in the polymerization. So, the time course of the polymerization was also examined, and the results are presented in Table 3. With the polymerization time increasing steadily from 1 h to 12 h, both the yields and *M_w* of the polymers were remarkably improved (Table 3, entries 1–5). Nevertheless, the polymers using 3c as one of the monomers had poor solubility when the reaction time was 8 h. Furthermore, because of the high efficiency of the MCCP, the resultant polymers reached relatively high *M_w* and yields at 6 h. Considering the solubility of the generated polymers, 6 h was ultimately adopted as the preferred polymerization time.

Table 3. Time Course of the Polymerization of 1a, 2b and 3a^a

entry	<i>t</i> (h)	yield (%)	<i>M_w</i> ^b	<i>Đ</i> ^b
1	4	75	15 300	1.63
2	6	77	16 700	1.71
3	8	78	20 900	1.78
4	10	80	26 700	1.93
5	12	83	28 200	2.11

^a Carried out in DCE at 80 °C under nitrogen. [1a] = [3a] = 0.2 M, [1a]/[2b] = 1/2. ^b Estimated by Advanced Polymer Chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene (PS) calibration. *M_w* = weight-average molecular weight; polydispersity index (*Đ*) = *M_w*/*M_n*, *M_n* = number-average molecular weight.

Monomer concentration is also critical to the outcome of the polymerization reaction. The

monomer concentration was then investigated, and the results are summed up in Table 4. When reducing the monomer concentration, both the yield and the M_w of the product decreased considerably (Table 4, entries 1–2). Notably, the polymerization was gelled when the **1a** concentration was enhanced to 0.4 M (Table 1, entry 5). Thus, 0.3 M was profitable to cyclopolymerization, and the monomer concentration was applied in the following research.

Table 4. The Effect of Monomer Concentration on the Polymerization of 1a, 2b and 3a^a

entry	[1a]/(M)	yield (%)	M_w^b	\bar{D}^b
1	0.05	54	4700	1.37
2	0.10	65	7400	1.45
3	0.20	75	17 900	1.84
4	0.30	84	29 000	2.44
5	0.40	gel	-	-

^a Carried out in DCE at 80 °C under nitrogen for 6 h. [**1a**] = [**3a**], [**1a**]/[**2b**] = 1/2. ^b Estimated by Advanced Polymer Chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene (PS) calibration. M_w = weight-average molecular weight; polydispersity index (\bar{D}) = M_w/M_n , M_n = number-average molecular weight.

Above experiments were carried out under nitrogen, we were curious whether this polymerization could be performed in air. Then, we investigated the effect of the atmosphere of the polymerization reaction. As shown in Table 5, polymers with high M_w could be obtained in high yields in air or under nitrogen conditions, indicating that the polymerization reaction is robust and could efficiently proceed even in air conditions (Table 5, entries 1–2).

Table 5. The Effect of Atmosphere on the Polymerization of 1a, 2b and 3a^a

entry	atmosphere	yield (%)	M_w^b	\bar{D}^b
1	nitrogen	85	28 000	2.34
2	air	84	26 900	2.48

^a Carried out in DCE at 80 °C for 6 h. [**1a**] = [**3a**] = 0.3 M, [**1a**]/[**2b**] = 1/2. ^b Estimated by Advanced Polymer Chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene (PS) calibration. M_w = weight-average molecular weight; polydispersity index (\bar{D}) = M_w/M_n , M_n = number-average molecular weight.

Eventually, the monomer scope of this MCCP was further extended to test its general

applicability. Two diisocyanates of **1a** and **1b**, two alkynes of **2a** and **2b**, and aromatic and aliphatic diisocyanides **3a**, **3b** and **3c** were applied for the MCCP under the optimized conditions. The data for the resultant polymers are listed in Table 6. In general, all the MCCP proceeded smoothly with varied combinations of monomers, affording excellent soluble products with high M_w (up to 29 000 g/mol) in high yields (up to 85%). Based on these results, we could conclude that this MCCP enjoyed a great atom economy and broad universality.

Table 6. The Polymerizations of the Monomers 1, 2 and 3^a

entry	monomer	polymer	yield (%)	M_w^b	\bar{D}^b
1	1a + 2a + 3a	P1a2a3a	85	18 300	2.14
2	1a + 2a + 3b	P1a2a3b	77	15 400	1.93
3	1a + 2a + 3c	P1a2a3c	73	15 000	1.66
4	1a + 2b + 3a	P1a2b3a	85	29 000	2.44
5	1a + 2b + 3b	P1a2b3b	77	19 100	2.16
6	1a + 2b + 3c	P1a2b3c	71	15 100	1.57
7	1b + 2a + 3a	P1b2a3a	85	21 500	2.15
8	1b + 2a + 3b	P1b2a3b	68	14 100	1.97
9	1b + 2b + 3a	P1b2b3a	85	22 400	2.20
10	1b + 2b + 3b	P1b2b3b	84	20 000	2.05

^a Carried out in DCE at 80 °C under nitrogen for 6 h. $[1] = [3] = 0.3$ M, $[1]/[2] = 1/2$. ^b Estimated by Advanced Polymer Chromatography (APC) in tetrahydrofuran (THF) on the basis of a polystyrene (PS) calibration. M_w = weight-average molecular weight; polydispersity index (\bar{D}) = M_w/M_n , M_n = number-average molecular weight.

Established on the mechanism of the reported organic reaction,⁴¹ we also came up with a one-pot MCCP process of diisocyanates, dialkyl acetylenedicarboxylates and diisocyanides (Scheme S3). Mechanistically, diisocyanides initially attack the triple-bond of dialkyl acetylenedicarboxylates to give a zwitterionic intermediate **I**.⁵⁰ Then, both the positively and negatively charged carbons of the intermediate **I** attack with the nitrogen and the carbon atom of diisocyanates, respectively. Afterward, cyclization of the latter leads to a structural unit of

the polymer in the intermediate **III**. Repeating these transforms finally forms the polymers.

Structure Characterization. All polymers were determined by standard spectroscopic techniques, consisting of FT-IR, ^1H and ^{13}C NMR spectroscopies. To assist the structural characterization of the generated polymers, a model compound **4** was produced under comparable polymerization conditions (Scheme S4 and Figure S1). Since the spectral profiles of the polymers are similar, herein, **P1a2b3a** is taken as an example. Figure 1 illustrates the FT-IR spectra of **P1a2b3a** (E) and its monomers (A–C), as well as that of model compound **4** (D). The stretching vibrations of $-\text{N}=\text{C}=\text{O}$ group in **1a**, the $\text{C}\equiv\text{C}$ in **2b** and the $-\text{N}^+\equiv\text{C}^-$ in **3a** were observed at 2270, 2190 and 2235 cm^{-1} , respectively. All these characteristic peaks became much weaker or disappeared in the spectra of **4** and **P1a2b3a**. The peak at 1723 cm^{-1} in the spectrum of **2b** assignable to the stretching vibration of $\text{C}=\text{O}$ was split into doublet peaks at 1727 and 1744 cm^{-1} in the spectra of **4** and **P1a2b3a**. That is mainly because there are two types of carbonyl groups in **4** and **P1a2b3a**.⁵¹ Meanwhile, the $\text{C}=\text{N}$ stretching vibration was detected at 1665 cm^{-1} in the spectrum of **4** and **P1a2b3a**, which proved their correct structures. Similar results were observed in the FT-IR spectra of **P1a2a3a**–**P1a2b3c** (Figures S2–S10).

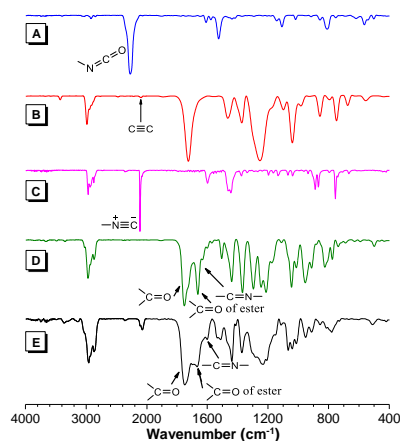


Figure 1. FT-IR spectra of **1a** (A), **2b** (B), **3a** (C), model compound **4** (D) and **P1a2b3a** (E).

The polymer **P1a2b3a** was further characterized by NMR spectroscopy. Figure 2 demonstrates the ^1H NMR spectra of monomers of **1a**, **2b**, and **3a** and their polymer. The peaks at δ 3.93, 1.20 and 4.17, which were referred to the resonances of H_a , H_d and H_e in **1a** and **2b**, shifted to δ 3.78 and 3.93, δ 1.08 and 1.10, δ 4.30 and 4.44 in **P1a2b3a**, respectively mainly owing to their particular chemical environments in the cyclic structural units. Likewise, the resonance of H_f , H_g , H_h and H_i in **3a** at δ 1.24, 2.38, 2.74 and 3.86 were split into two peaks with location at δ 1.26 and 1.39, δ 2.00 and 2.07, δ 2.35 and 2.45, δ 3.72 and 3.85 in **P1a2b3a**, respectively. Compared with that of **1a** and **3a**, the other resonances belong to the remaining protons of the aromatic rings appeared in the downfield region of **P1a2b3a**.

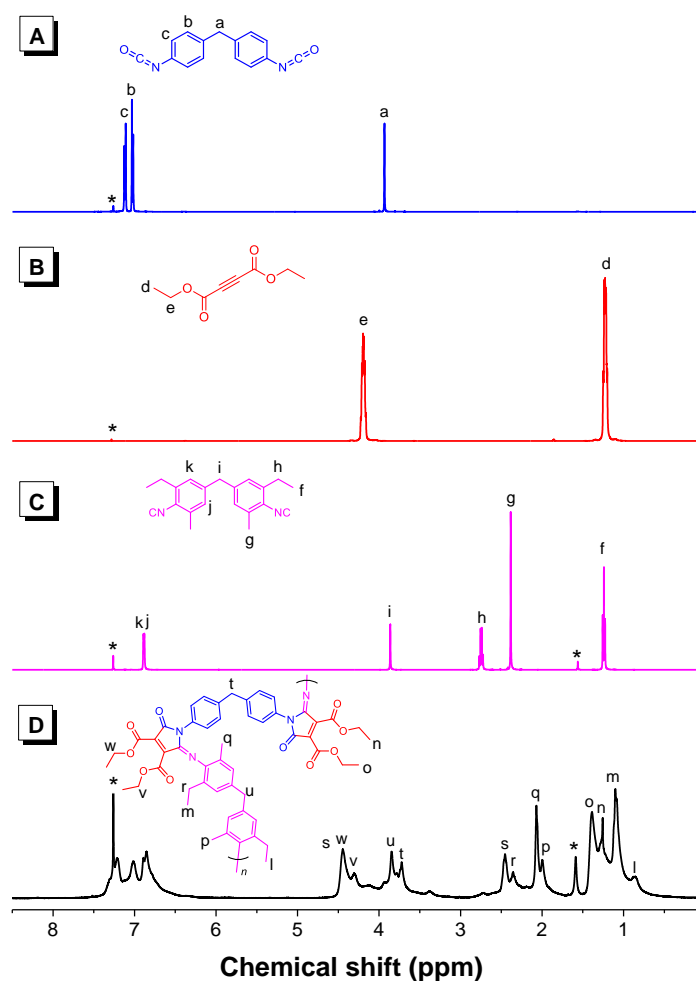


Figure 2. ^1H NMR spectra of **1a** (A), **2a** (B), **3a** (C) and **P1a2b3a** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

The virtue of the ^{13}C NMR spectra confirmed the formation of the cyclic structural units (Figure 3). All peaks at δ 138.43, 74.30 and 167.78 assigned to the resonance of C_b , C_f , C_l in **1a**, **2b** and **3a** disappeared in **P1a2b3a**. The peak at δ 151.49 attributed to the resonances of C_g in **2a** was split into two peaks at δ 159.82 and 160.29 in **P1a2b3a**. New peaks at δ 149.00, and 146.82 were assigned to the resonances of C_s and C_r in **P1a2b3a**, respectively. Other NMR spectra of the resultant polymers showed similar results, as presented in Figures S11–S28 in the supporting information. These results gave full evidence that cyclopolymerization was performed successfully, from which target polymers were actually produced.

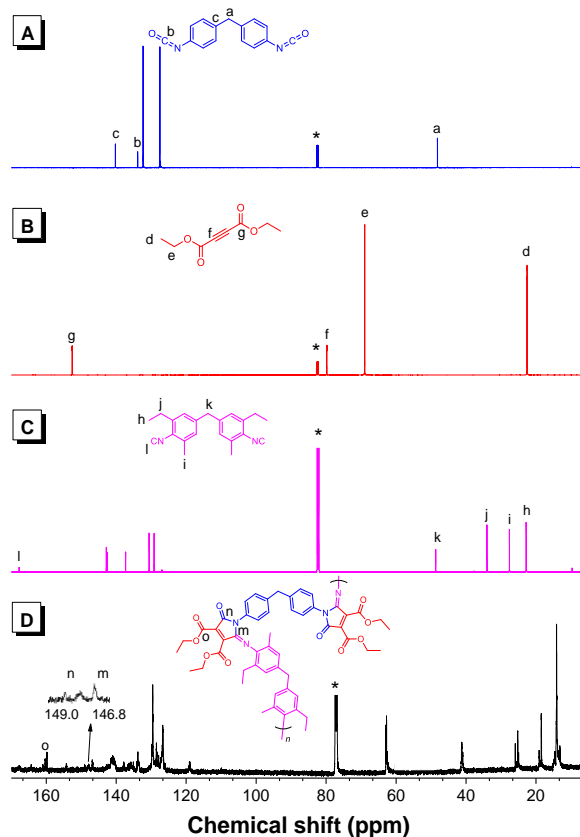


Figure 3. ^{13}C NMR spectra of **1a** (A), **2a** (B), **3a** (C) and **P1a2b3a** (D) in CDCl_3 . The solvent peaks are marked with asterisks.

Kinetic Study. To explore the kinetic process of this cyclopolymerization, *in situ* IR spectrometry was applied to monitor the formation of PMDs. It is clean that two peaks emerged at 1744 and 1665 cm^{-1} in the IR spectra of the polymerization system of **1a**, **2b** and

3a and these two peaks could be promptly attributed to the stretching vibrations of the C=O and C=N bonds of the pentacyclic unit in the polymer, respectively (Figure 4A). The C=O stretching vibration of **2b** at 1723 cm⁻¹ rapidly declined and was shifted to 1727 cm⁻¹ in the spectra of **P1a2b3a**. The kinetic change of the 3D *in situ* IR profiles and the time dependent peak intensity at 1665, 1723, 1727 and 1744 cm⁻¹ were recorded to follow the course of the reaction process at 80 °C. The effects revealed that the strength of the four peaks transformed rapidly and approximately reached to saturation in 6 h, which is reproducible with the one obtained from the condition optimization, suggestive of the fast reaction rate and high efficiency of this MCCP (Figures 4B–D).

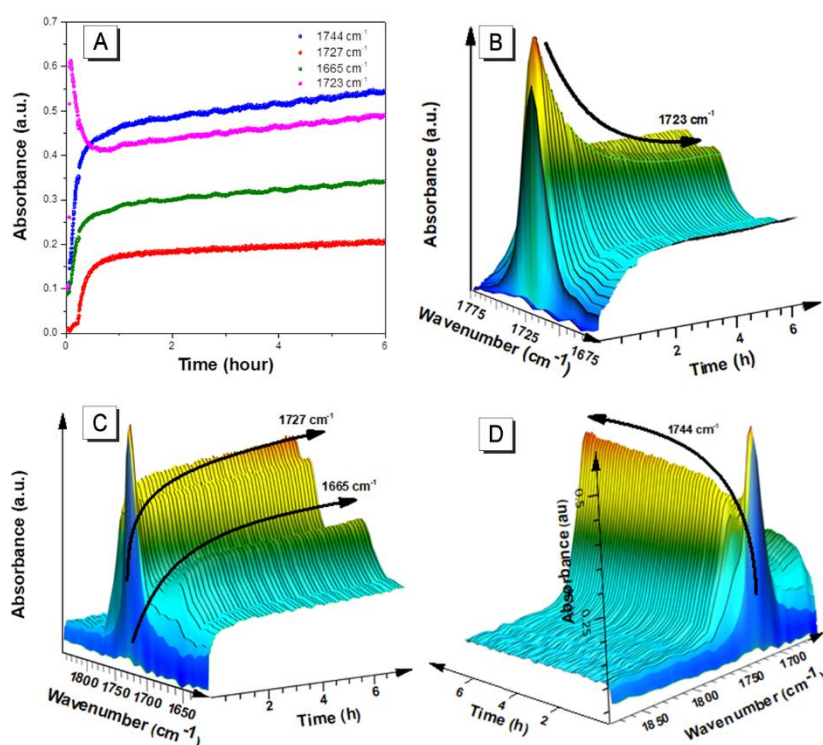


Figure 4. (A) The time-dependent peak intensity changes at 1744, 1727, 1723 and 1665 cm⁻¹. (B) Three-dimensional FT-IR profile of the peaks at 1723 cm⁻¹. (C) Three-dimensional FT-IR profile of the peaks at 1727 and 1665 cm⁻¹. (D) Three-dimensional FT-IR profile of the peaks at 1744 cm⁻¹.

Solubility and Thermal Stability. Thanks to the ester side chains, most of the resultant polymers possess excellent solubility in commonly used organic solvents, such as DCM, THF,

N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The polymers also have excellent film-forming ability and high quality of the films could be obtained by the simple spin-coating technique. Furthermore, they are thermally stable. As shown in Figure 5, the thermogravimetric analysis (TGA) suggested that these PMDs display good thermo-stability with the temperatures of 5% weight loss (T_d) in the range of 257 and 312 °C under N_2 atmosphere.^{52,53} Notably, the phenyl ring-containing polymers had higher carbon residual ratio even at 800 °C, which might be useful for the construction of carbon-based nanomaterials. In addition, the differential scanning calorimetry (DSC) results showing in Figure S29 indicated that the glass transition temperatures (T_g) of the polymers range between 112.4 to 130.8 °C, mainly due to the relatively rigid cyclic structures in the polymer main-chains.

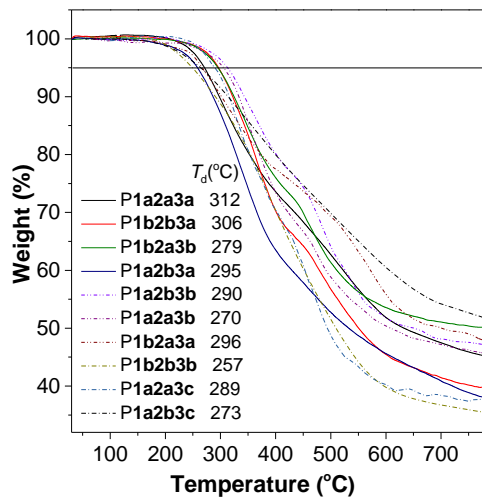


Figure 5. Thermogravimetric analysis (TGA) of P1a2a3a–P1a2b3c. T_d represents the temperatures of 5% weight loss of the polymers.

Light Refractivity. In the design of photonic materials such as lenses, prisms, and waveguides, the refractive index is one of the key factors to be considered. A high RI generally shows up when the polymeric materials containing polar heteroatoms and aromatic rings.⁵⁴ Considering the high nitrogen and oxygen content of the obtained PMDs, the light

refraction properties of these PMDs were studied. The results showed that thin films of all polymers possessed large RI values (n) between 1.613 and 1.708 at 632.8 nm, which are much higher than those of commercially important optical plastics like polycarbonate ($n = 1.581$ at 632.8 nm). Therefore, the PMDs generated by our established MCCP could be potentially applicable in advanced photonic areas.

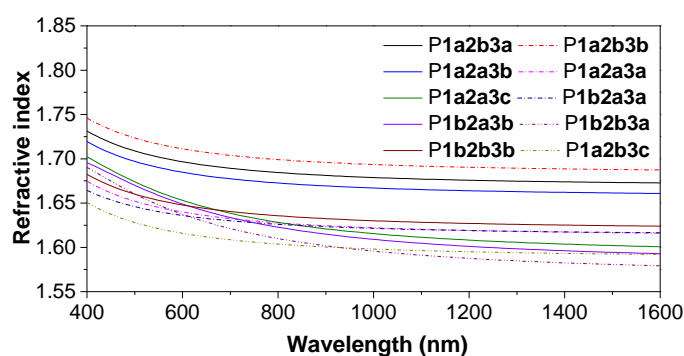


Figure 6. Refractive indexes of P1a2a3a–P1a2b3c.

Conclusions

We successfully developed an efficient catalyst-free one-pot MCCP of easily available diisocyanates, activated alkynes and diisocyanides. This MCCP can be applied to versatile aliphatic isocyanides, and aromatic isocyanides, producing a series of PMDs with excellent M_w (up to 29 000) in satisfactory yields (up to 85%) at 80 °C after 6 h. More importantly, the *in situ* FI-IR measurement suggested that the PMDs can also be finished rapidly in air in 6 h, indicative of its fast polymerization rate and high efficiency. The resultant PMDs are soluble in commonly used organic solvents and possess good thermal stability with T_d up to 312 °C. What's more, these polymers show excellent film-forming ability and their thin films with high quality show high refractive indices with values ranged between 1.613 and 1.708 at 632.8 nm. Thus, this work not only enriches the family of polymerization reactions based on

triple-bond building blocks, but also performs as an important components of heterocyclic polymers that are potentially applicable in diverse areas.

Experimental Section

Materials. Benzyltriethylammonium chloride (TEBAC) was purchased from J&K Scientific Ltd; 4,4'-methylenebis(2-ethyl-6-methylaniline) and 1,4-benzenedimethanamine were purchased from TCI; 1,6-diisocyanohexane (**3c**) was purchased from Sigma-Aldrich; 4,4'-diphenylmethane diisocyanate (**1a**), 1,3-phenylene diisocyanate (**1b**), dimethyl acetylenedicarboxylate (**2a**) and diethyl acetylenedicarboxylate (**2b**) were purchased from Energy Chemical; dichloromethane, toluene, dichloroethane, tetrahydrofuran, chloroform, NaOH and HCl (36-38 wt %) were purchased from Guangzhou Chemical Reagent Factory.

Instruments. The FT-IR spectra were collected on a Bruker Vector 22 spectrometer (KBr disks). The ^1H and ^{13}C NMR spectra were measured on a Bruker ADVANCE2B spectrometer in CDCl_3 using tetramethylsilane (TMS, $\delta = 0$) as internal reference. The weight- and number-average molecular weights (M_w and M_n) and polydispersity index (D , M_w/M_n) of the polymers were estimated by a Waters advanced polymer chromatography system equipped with photo-diode array detector, using monodisperse polystyrene as calibration and THF as the eluent at a flow rate of 0.5 mL/min. Thermo-gravimetric analysis measurements were carried out on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 20 $^\circ\text{C}/\text{min}$. Differential scanning calorimetry analysis was performed on a DSCAQ20 apparatus at a heating rate of 10 $^\circ\text{C}/\text{min}$ under dry nitrogen. Refractive index values were determined on a J.A. Woollam V-VASE variable angle ellipsometry measurement system. The polymer films were prepared by spin-coating on crystalline silicon wafer using 1,2-dichloroethane as

solvent. The Cauchy dispersion law was applied to analyze the polymer layers from the visible to the IR spectroscopic region.

Polymerization. Unless otherwise stated, all the polymerizations of diisocyanates **1**, activated alkynes **2** and diisocyanides **3** were conducted under nitrogen using standard Schlenk techniques. Typical experimental procedures for the cyclopolymerization of **1a**, **2b** and **3a** are given below as an example. Into a 30 mL schlenk tube equipped with a magnetic stir bar, 4,4'-diphenylmethane diisocyanate (25.0 mg, 1 mmol), bis(3-ethyl-4-isocyano-5-methylphenyl)methane (30.2 mg, 1 mmol), DCE (3.3 mL) and diethyl acetylenedicarboxylate (34.0 mg, 2 mmol) were added successively. The reaction mixture was heated at 80 °C for 6 h under N₂, and then cooled to room temperature. Then the mixture was poured into 100 mL of methanol under vigorous stirring. The precipitate was filtered, washed with methanol, and dried to a stable weight under vacuum to afford the target polymers.

Characterization Data of P1a2a3a. A dark yellow powder was obtained in 85% yield. M_w : 18 300; \bar{D} : 2.14. FT-IR (KBr disk), ν (cm⁻¹): 2930, 1744, 1727, 1723, 1230, 1018. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.21, 7.01, 6.85, 3.98, 3.85, 3.73, 2.45, 2.35, 2.06, 1.99, 1.09. ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 160.81, 160.32, 156.81, 154.19, 151.25, 148.89, 147.84, 147.22, 146.64, 145.06, 140.93, 138.83, 137.95, 134.78, 133.73, 132.34, 129.59, 128.52, 127.85, 126.70, 119.05, 53.58, 41.14, 25.20, 24.92, 18.45, 14.24, 13.23.

Characterization Data of P1a2a3b. A dark yellow powder was obtained in 77% yield. M_w : 15 400; \bar{D} : 1.93. FT-IR (KBr disk), ν (cm⁻¹): 2989, 1748, 1729, 1724, 1241, 1022. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.19, 7.16, 7.13, 7.09, 6.94, 6.92, 4.67, 4.44, 3.85, 3.84,

3.82, 3.76, 3.70, 3.50, 1.53. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 161.06, 160.22, 149.69, 148.84, 141.66, 140.27, 135.90, 135.34, 133.66, 129.54, 128.13, 127.34, 126.21, 125.10, 57.65, 53.56, 52.67, 41.07, 33.83, 25.54.

Characterization Data of P1a2a3c. A dark yellow powder was obtained in 73% yield. M_w : 15 000; D : 1.66. FT-IR (KBr disk), ν (cm^{-1}): 2998, 1742, 1726, 1719, 1212, 1030. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.31, 7.26, 7.16, 7.09, 4.40, 4.36, 4.30, 4.23, 4.11, 3.90, 3.72, 3.57, 3.46, 3.32, 1.33, 1.25. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.35, 159.83, 154.25, 152.77, 149.58, 148.67, 147.68, 144.15, 142.07, 139.92, 138.89, 137.80, 136.35, 134.53, 133.66, 129.56, 129.39, 127.18, 125.77, 123.92, 122.75, 119.02, 62.66, 62.59, 52.32, 50.92, 50.04, 40.95, 30.28, 28.19, 27.37, 25.71, 14.12, 14.07.

Characterization Data of P1a2b3a. A dark yellow powder was obtained in 85% yield. M_w : 29 000; D : 2.44. FT-IR (KBr disk), ν (cm^{-1}): 2933, 1747, 1723, 1721, 1223, 1010. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.26, 7.21, 7.02, 6.89, 6.85, 4.44, 4.30, 3.85, 3.78, 3.72, 2.45, 2.35, 2.07, 2.00, 1.39, 1.26, 1.10, 1.08. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.29, 160.04, 159.82, 159.17, 154.34, 149.00, 147.78, 146.82, 141.01, 139.09, 137.82, 137.08, 135.79, 134.49, 133.80, 132.26, 129.80, 129.56, 128.49, 127.89, 126.68, 122.17, 118.98, 62.91, 62.73, 41.21, 40.94, 25.93, 25.24, 24.99, 19.12, 18.51, 14.67, 14.49, 14.14, 13.17.

Characterization Data of P1a2b3b. A dark yellow powder was obtained in 77% yield. M_w : 19 100; D : 2.16. FT-IR (KBr disk), ν (cm^{-1}): 2944, 1740, 1677, 1589, 1222, 1018. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.30, 7.26, 7.20, 7.17, 7.11, 7.10, 4.77, 4.41, 4.37, 4.00, 3.93, 3.72, 1.68, 1.36, 1.34, 1.26. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.23, 159.97,

159.74, 155.54, 154.26, 151.23, 150.40, 149.73, 147.42, 143.77, 141.93, 141.40, 140.00, 139.61, 139.13, 137.73, 137.44, 136.79, 136.32, 135.54, 134.78, 132.07, 129.61, 129.45, 128.91, 127.98, 126.53, 125.68, 125.58, 123.29, 119.06, 62.75, 62.65, 58.87, 53.19, 52.65, 52.37, 49.10, 41.32, 41.00, 40.02, 14.13, 14.10.

Characterization Data of P1a2b3c. A dark yellow powder was obtained in 71% yield. M_w : 15 100; \bar{D} : 1.57. FT-IR (KBr disk), ν (cm^{-1}): 2926, 1730, 1657, 1584, 1217, 1023. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.21, 7.01, 6.85, 3.98, 3.85, 3.73, 2.45, 2.35, 2.06, 1.99, 1.09. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.99, 160.14, 153.81, 151.60, 148.62, 142.40, 142.06, 136.59, 129.56, 127.26, 126.13, 125.71, 123.41, 119.25, 119.04, 68.31, 62.76, 55.97, 52.37, 47.83, 40.96, 36.89, 29.44, 25.74, 14.14.

Characterization Data of P1b2a3a. A dark yellow powder was obtained in 85% yield. M_w : 21 500; \bar{D} : 2.15. FT-IR (KBr disk), ν (cm^{-1}): 2925, 1731, 1657, 1554, 1243, 1048. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.27, 7.26, 6.85, 4.00, 3.86, 3.72, 2.44, 2.35, 2.05, 1.69, 1.09, 0.96. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.41, 160.19, 154.94, 153.85, 152.82, 147.67, 145.77, 143.97, 143.11, 140.72, 139.36, 138.02, 135.01, 133.80, 131.40, 129.29, 128.45, 127.58, 127.23, 126.64, 126.22, 58.32, 53.62, 52.42, 41.06, 25.92, 25.16, 18.99, 18.43, 15.13, 14.79, 14.18, 13.23.

Characterization Data of P1b2a3b. A dark yellow powder was obtained in 68% yield. M_w : 14 100; \bar{D} : 1.97. FT-IR (KBr disk), ν (cm^{-1}): 2978, 1752, 1662, 1554, 1220, 1021. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.29, 7.26, 7.05, 7.00, 4.79, 4.75, 3.91, 3.71, 1.73. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.57, 160.24, 160.06, 154.04, 153.67, 150.21, 149.26,

147.93, 147.58, 144.58, 143.92, 138.94, 133.33, 129.45, 128.18, 126.31, 122.86, 121.13, 120.03, 119.29, 117.25, 116.48, 114.87, 53.52, 52.43.

Characterization Data of P1b2b3a. A dark yellow powder was obtained in 85% yield. M_w : 22 400; \bar{D} : 2.20. FT-IR (KBr disk), ν (cm^{-1}): 2945, 1743, 1658, 1621, 1234, 1014. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 6.87, 6.74, 4.35, 4.21, 4.03, 3.71, 3.70, 3.64, 3.63, 2.34, 2.23, 1.96, 1.94, 1.29, 1.18, 0.99. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 159.69, 159.18, 153.88, 151.37, 147.86, 146.59, 144.15, 143.61, 140.71, 138.44, 137.96, 137.44, 135.96, 135.39, 133.87, 132.74, 129.40, 128.47, 127.84, 127.26, 126.64, 62.96, 62.81, 62.53, 52.42, 41.06, 38.52, 25.73, 25.20, 18.47, 15.25, 14.67, 14.15, 13.15.

Characterization Data of P1b2b3b. A dark yellow powder was obtained in 84% yield. M_w : 20 000; \bar{D} : 2.05. FT-IR (KBr disk), ν (cm^{-1}): 2924, 1747, 1675, 1576, 1223, 1030. ^1H NMR (500 MHz, CDCl_3), δ (TMS, ppm): 7.29, 7.00, 6.99, 4.80, 4.76, 4.38, 4.17, 3.71, 1.35, 1.21. ^{13}C NMR (125 MHz, CDCl_3), δ (ppm): 160.07, 159.68, 159.33, 154.00, 153.69, 150.30, 149.46, 148.15, 146.23, 144.65, 143.23, 138.76, 137.68, 137.39, 135.73, 135.66, 132.76, 129.39, 128.05, 123.33, 119.97, 118.25, 117.08, 115.87, 114.78, 62.78, 53.17, 52.43, 14.12, 14.09.

ASSOCIATED CONTENT

Supporting Information. Detailed synthetic routes to monomers **3a** and **3b**, model compound. FT-IR, ^1H NMR and ^{13}C NMR spectra of **3a**, **3b**, model compound **4** and **P1a2a3a-P1a2b3c**. HRMS spectrum of model compound **4**, polymerization mechanism, DSC curves, RI values. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: msqinaj@scut.edu.cn (A.J.Q.)

Notes

The authors declare no competing financial interest.

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