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Well-Defined Polyamide Synthesis from Diisocyanates and Diacids Involving Hindered Carbodiimide Intermediates

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ABSTRACT: We have uncovered a novel polycondensation strategy for the synthesis of well-defined polyamides of narrow molecular weight distributions based on modifications of our sequential self-repetitive reaction ("SSRR") previously developed for diisocyanate−dicarboxylic acid polymerization. In our newly discovered SSRR polyamide formation mechanism, a small amount of hindered carbodiimide, *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) or a hindered isocyanate such as 2,6-diisopropylphenyl isocyanate (iPr-NCO), was introduced to the polymerization as an initiator, followed by simultaneous addition of diisocyanates and diacids monomers. By using this new reaction mode, the SSRR mechanism produces polyamide products of narrow molecular weight distributions with their dispersities reduced to 1.2−1.4, which is far lower than a range of >2.5 found in regular SSRR reactions. Significantly different from a conventional step-growth or standard SSRR reaction, the formation of a polymer backbone is preferential when the diacid is added to the requisite iPr-CDI in the first step, followed by a rearrangement to form amide and fragmented components for SSRR. The control of molecular weight is mainly attributed to the acid addition favoring the unhindered poly-CDI intermediates in the middle of the growing chains over the hindered-CDI at the chain terminals. It appears that the formation of a "hindered isocyanate" and the subsequent formation of a "new hindered-CDI" at the terminal end of growing amide-chains in each SSRR cycle force the acid again toward the preferred unhindered CDI sites dictating the observed outcome. This simple polyamide synthesis methodology is unique and unconventional, and it could significantly facilitate the development of tailored-made polyamides from a variety of diisocyanates and diacids.

Introduction

In recent years, synthesis of structurally well-defined polymers has been one of the most active areas of polymer research. Particularly, living free radical polymerizations such as atom-transfer radical polymerization (ATRP),[1,2] nitroxide-mediated free radical polymerization (NMRP),[3,4] and reversible addition−fragmentation chain transfer polymerization (RAFT)[5−7] have been extensively developed to synthesize polymers with narrow molecular weight distributions. All of these synthetic methods are based on vinyl monomer addition to the terminal active sites of the growing backbones. This vinyl monomer addition polymerization differs from the conventional condensation polymerizations which proceed through a step-growth mechanism that allows monomers and the growing oligomers to react randomly with each other simultaneously. This random step-growth mechanism in the condensation polymerization produces polymers with a wide range of molecular weight distributions. However, Yokozawa et al.[8−16] have recently demonstrated the ability to control molecular weights and dispersities of condensation polymers such as polyamides, polyesters, and polyethers by "chain-growth condensation" of para-substituted AB-type aromatic monomers. They manipulated the condensation reaction through introduction of an activated functional group in the polymerization steps; thereby creating a preferred site and thus a sequence for the new monomer addition. This general principle has inspired and ushered in new efforts for finding "controlled" condensation polymerization.[17]

In our previous paper in this series, we described a "sequential self-repetitive reaction (SSRR)" for the synthesis of polyamide through condensation of diisocyanate with diacid in the presence of a carbodiimide (CDI) catalyst.[18,19] The standard "SSRR" reaction involves three basic repetitive yet sequential reactions including: (i) condensation of two isocyanates into a CDI in the presence of a CDI catalyst (DMPO)[20] (ii) addition of acid to the CDI to yield *N*-acylurea and (iii) thermal fragmentation of the *N*-acylurea to form amide and isocyanate fragments both in half of the original molar amount, (Scheme 1). It was observed that step i and step ii were very facile even at a ambient temperature, whereas step iii could only be effective at a temperature of greater than 140 °C.[21−23] However, when this three-step cycle repeats under heated conditions with sufficient acid, all of the isocyanate and CDI are converted into amide as the final product in excellent conversion and selectivity.[18,19] By extending this unique methodology, we have devised a new twist to the SSRR process by addition of small amount of a hindered carbodiimide (CDI) such as *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide, iPr-CDI **1**, or a hindered isocyanate such as 2,6-diisopropylphenyl isocyanate, iPr-NCO **7**. Doing so creates terminally new hindered-CDIs (PiPr-CDI type **10**, Scheme 4) on the growing polymer chains. Introduction of the terminally new hindered-CDIs has been found to form "less-reactive" CDI-sites than those of the unhindered CDI counterparts on the regular polymer chains for the "SSRR" cycles. These sterically new hindered-CDIs were found to control the site and sequence of the acid addition. As the consequence, polyamides **4a**′**−4f**′ of low dispersities were prepared from varieties of diacids **2a−2f** and methylene diphenylene diisocyanate (MDI) **3** as shown in Scheme 2.

Results and Discussion

The new DMPO-catalyzed polycondensations from diisocyanates and dicarboxylic acids are basically the same as those of the regular SSRR,[18,19,24−26] where both intermediates were added

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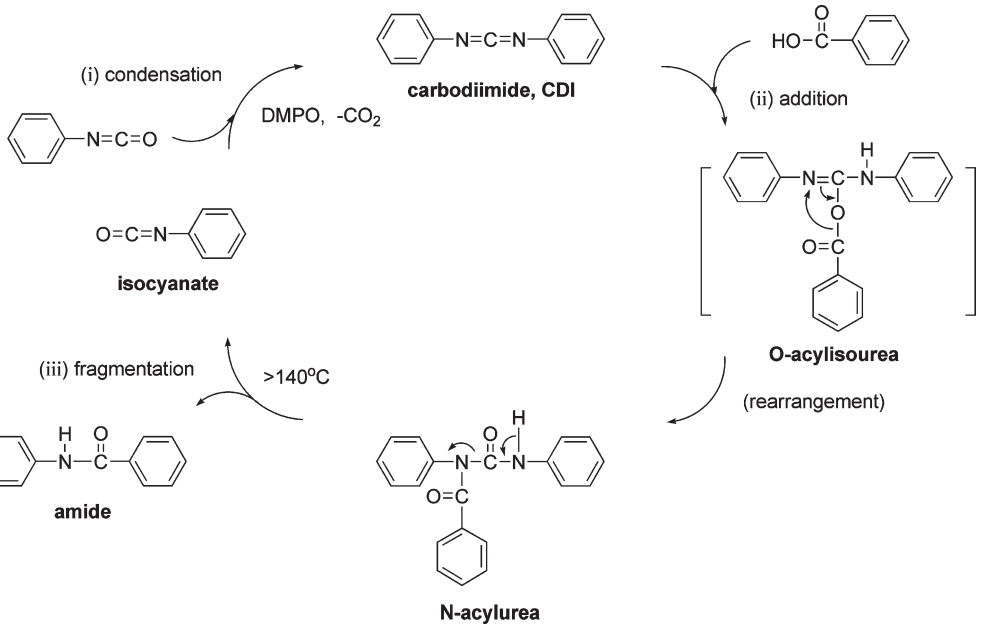
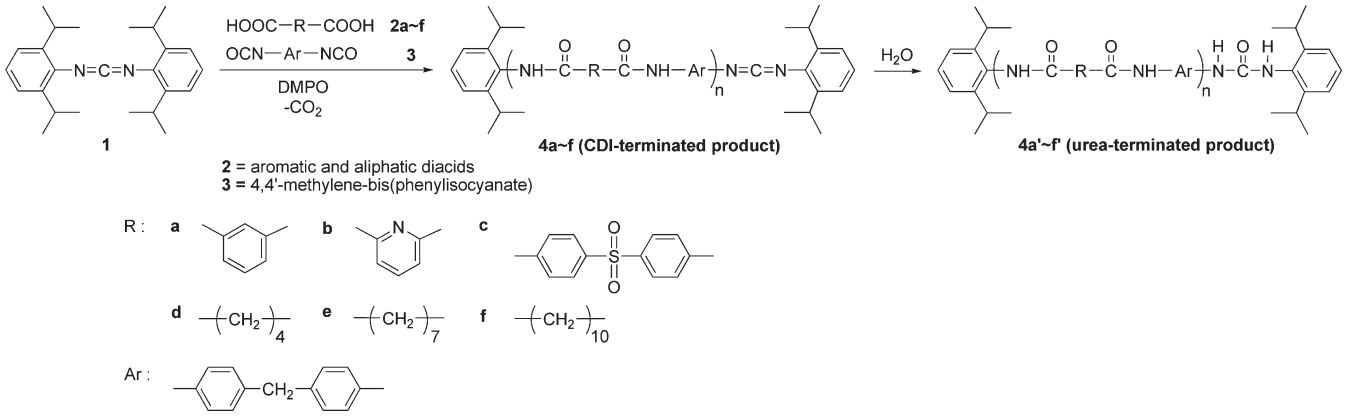
Scheme 1. The Standard "SSRR" Reaction



Scheme 2. New "SSRR" Polyamide Synthesis with a Hindered Carbodiimide Initiated Polymerization of Diisocyanate and Diacid

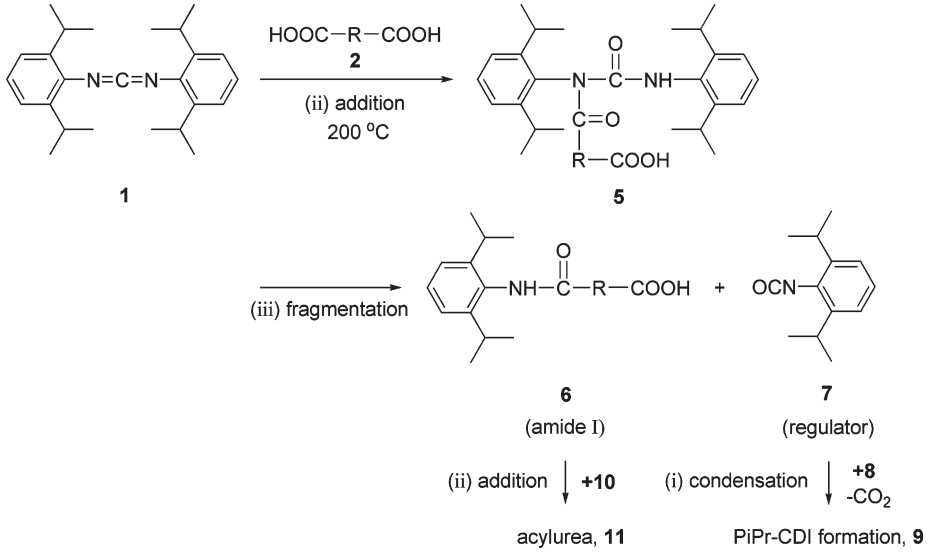


into a solution containing a catalyst at about 180−200 °C. However, due to the new addition of iPr-CDI **1** in the beginning of the new reaction, iPr-CDI **1** reacted with diacid **2** forming an amide terminated monoacid **6** as one of the initiation steps of the polymerization (Scheme 3). In the meantime, 2,6-diisopropylphenyl isocyanate (iPr-NCO, **7**) generated was found to slowly create new hindered-CDI at the terminal end of the growing polymer chains as shown in Scheme 4, Scheme 5 and Scheme 6. Therefore, two types of CDIs, the diisopropyl-phenyl containing new hindered-CDI type at the terminal ends of the polymer chains and the unhindered CDIs type, such as **10**, **13** or **16** at the midportions of their growing chains were both created in the new SSRR polymerization process mainly through cross-condensation involving iPr-NCO **7**.

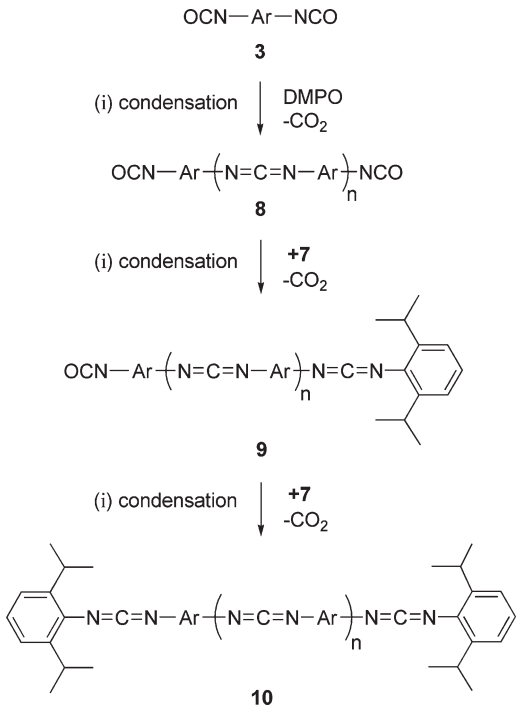
First, condensation of MDI **3** monomer under the catalyst of DMPO was converted into poly-CDI products **8** at a rapid rate. iPr-NCO **7** being the "less-reactive" isocyanate serves as a regulator in the polymerization by facilitating the capping of poly-CDI **8** and residual isocyanates **9** slowly under the catalytic action of DMPO (Scheme 4). Both condensation reactions create unsymmetrically new hindered-CDI groups at the terminal end of poly-CDI-chains **10**. PiPr-CDI terminated poly-CDI **10** was found to go forward with the chain-growth reaction with the monoacid 6 in formation of acylureas **11** thereby starting the SSRR sequence as shown in Scheme 5. By this mechanism, the propagation of the growing polyamide chains takes place preferentially at the unhindered CDI-sites (such as **13**) through SSRR. Overall as shown in Schemes 5 and 6, the mode of polymerization constitutes controlled insertions of diacid **2** onto unhindered polyamide-CDIs sites at the midportions of the polymer chains followed by fragmentation of the resulting acylureas to form polyamide **16** and new isocyanates **12** for further repetitive reactions leading to **4** as the final product.

The proof of the proposed mechanism operative in this new SSRR is shown in the isolated polyamides which all possess diisopropyl-phenyl groups at their terminal ends as evidenced by the NMR spectroscopy of polymer products featured either in part a or part b of Figure 1 as a urea-terminated PA due to water treatment. This result confirms that iPr-CDI **1** indeed was involved in the major polymerization process. The FT-IR monitoring of the reaction mixture provided additional evidence of the proposed reaction mechanism. Our FT-IR spectral analysis based on authentic and synthesized model compounds, Figure 2 revealed that the initial CDI absorption at 2169 cm^{-1} of iPr-CDI **1** disappeared rapidly upon addition of diacid **2**, indicating that iPr-CDI **1** was consumed readily. Coinciding with the disappearance of the iPr-CDI **1** absorption is the emergence of a new isocyanate absorption of iPr-NCO **7** at 2290 cm^{-1} confirming the initiation reaction of iPr-CDI **1** (Figure 2a). Meanwhile, at the

Scheme 3. Initiation Mechanism of New SSRR through iPr-CDI 1 and Diacid 2



Scheme 4. Propagation Mechanism of PiPr-CDI Terminated 10 Formation through Capping of 8 and 9 by iPr-NCO 7

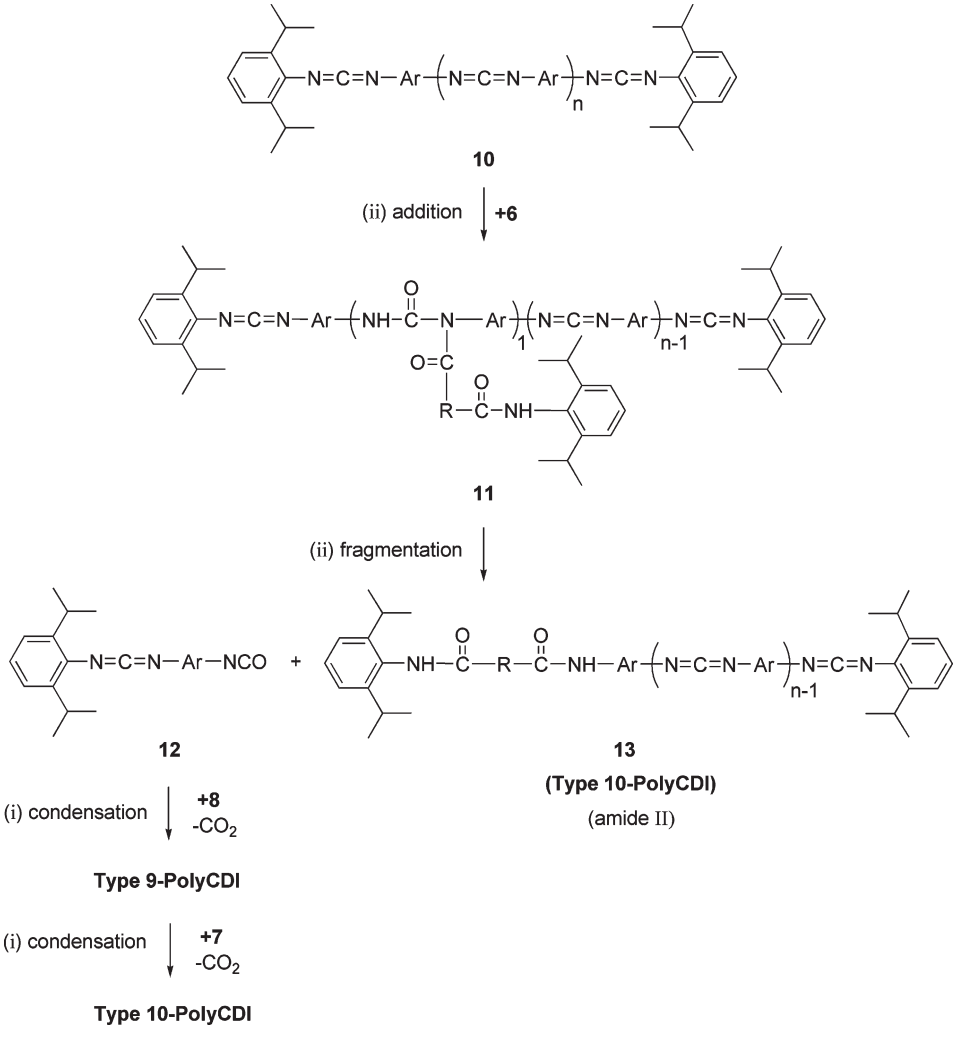


early stage of adding MDI **3**/diacid **2** monomers to the reaction mixture, the isocyanate IR absorption at 2260 cm^{-1} corresponding to MDI **3** though visible, was converted into poly-CDI products **8** at a rapid rate, evidenced by the appearance of strong IR doublet absorptions at 2136 and 2112 cm^{-1} (Figure 2a). This observation is indicative of a rapid conversion of MDI **3** into unhindered poly-CDI oligomers **8**. Upon further propagation between MDI **3** and diacids **2** at 190 °C, the hindered isocyanate absorption of iPr-NCO **7** at 2290 cm^{-1} became gradually diminished as shown in Figure 2d. Toward the end of the reaction, twin CDI peaks at 2136 and 2112 cm^{-1} which both correspond to the poly-CDI **8** absorptions originating from MDI **3** merged gradually into one new peak at 2152 cm^{-1}. This absorption was attributed to polymers such as **10**, **13**, **16** or **4** with unsymmetrically new hindered-CDI type at the terminal of the polymer chains. This IR spectral assignment is consistent with that of the model unsymmetrical *N*′-phenyl-*N*-(2,6-diisopropylphenyl) CDI, (PiPr-CDI) **20** as shown in Figure 3b, and this model unsymmetrical *N*′-phenyl-*N*-(2,6-diisopropylphenyl) CDI (PiPr-CDI) **20**, and this model unsymmetrical *N*′-phenyl-*N*-(2,6-diisopropylphenyl) CDI, (PiPr-CDI) **20**, was synthesized and isolated in 58% according to the reactions shown in Scheme 7.[27] The new hindered-CDI absorption at 2151 cm^{-1} (Figure 2, parts c−f) persists in the polymeric solution toward the end of polymerization at 200 °C. These observations are consistent with our proposed new SSRR mechanism shown in Schemes 3, 4, 5, and 6 showing the initiation, CDI active-site formations, propagation, and then the termination.

Most unexpectedly, the generated polyamides **4**′ by this new SSRR process were found to have narrow molecular weight (MW) distributions of less than 1.40 in molar ratios of iPr-CDI/MDI/IA of 1/5/5 and 1/10/10 respectively by GPC analysis shown in Figure 4, parts a and b. The molecular weights increased linearly indicating that the controlled mechanism is operative from 3838 molecular weight for 1/5/5 for iPr-CDI/MDI/PA up to 6424 for 1/20/20 (Figure 5, parts a and b). These dispersities of less than 1.40 are substantially different from those without the use of hindered CDI **1** as the initiator such as in part c of Figure 4 showing a dispersity of >2.5. This general synthetic procedure has been successfully extended to synthesize polyamides **4**′ with a variety of diacids **2** including isophthalic acid (IA), 2,6-pyridinedicarboxylic acid (PA) and 4,4′-sulfonyldibenzoic acid (SA), adipic acid (AA), azelaic acid (AZA), and 1,10-decanedicarboxylic acid (DA), all with MDI **3** as the common diisocyanate, and all producing well-defined polyamides **4a**′−**4f**′ with narrow MW distributions of less than 1.4 as shown in Table 1.[28]

Other pieces of data supporting the proposed mechanism were found through our model study shown in Scheme 8a where benzoic acid **22** was added to a mixed solution containing five molar excess of both unhindered diphenyl carbodiimide (diphenyl CDI) **21** and the hindered iPr-CDI **1** in a competitive reaction. Through the amide product analyses in HPLC after the reaction, it was found that the relative addition rates of benzoic acid **22** to these two CDIs was determined to be in a ratio of as large as 4 to 1 at 140 °C in favor of unhindered phenyl CDI **21** in formation of the amides **23**. Furthermore, in a similar model competitive study for Scheme 8b between two addition sites of internal unsymmetrical PiPr-CDI **20**, the preferred addition site to form acylurea is also shown to favor the unhindered side of intermolecular dissymmetrical PiPr-CDI **20** by a ratio of 2.4 to 1.0 in formation

Scheme 5. Propagation Mechanism of iPr-amide Terminated Poly-CDI Formation 13 through Addition of Monoacid 6



of their respective amides.[29] Thus, both these data support our proposed mechanism that the unhindered CDIs are favored kinetically in the addition reaction in Schemes 5 and 6.

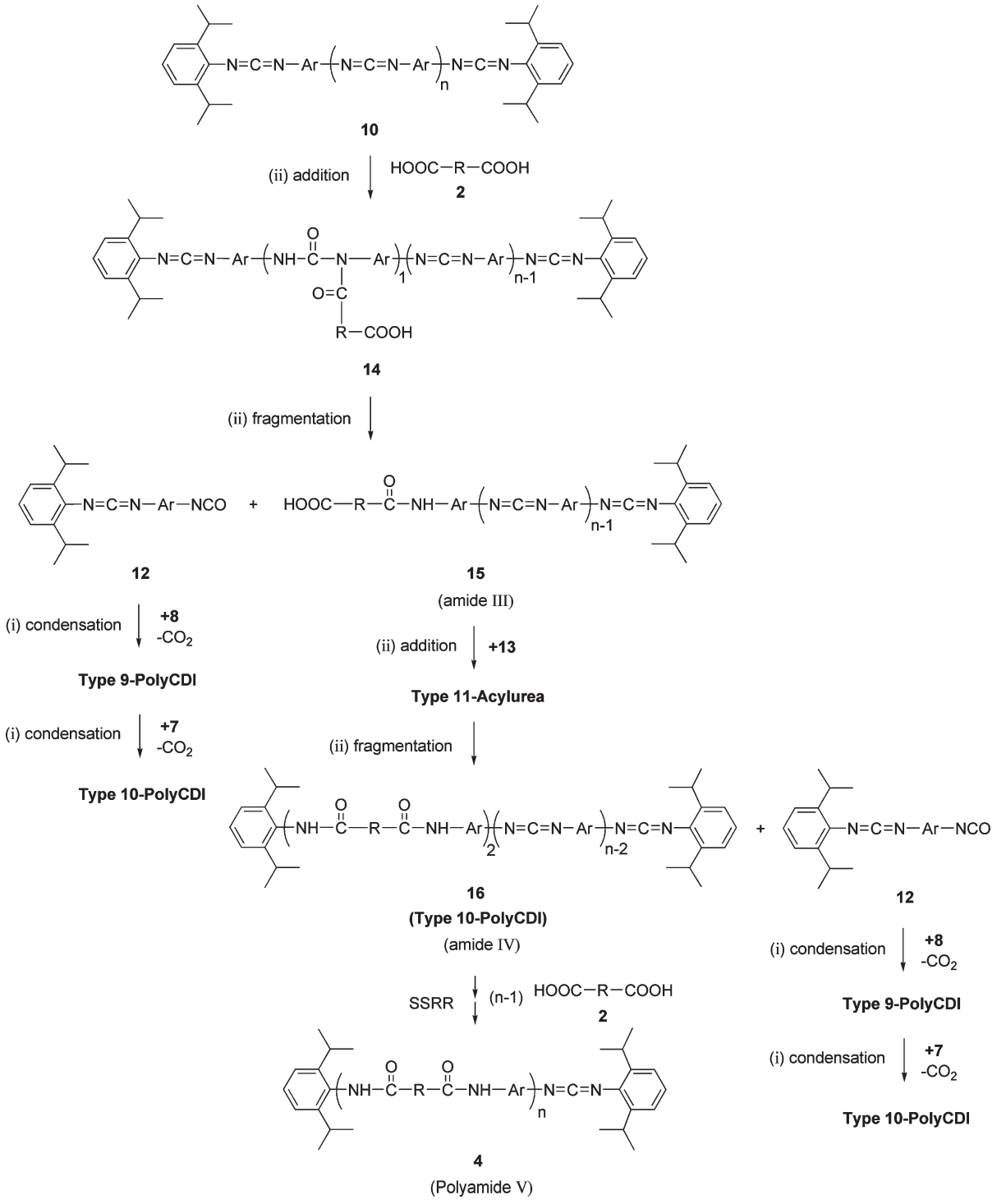
Moreover, DMPO catalyzed trans-CDI disproportion reaction shown in Scheme 9a should also be taken into account in overall mechanism because this disproportion reaction will also lead to the formation of new hindered-CDI **20**.[30] This model study shown in Scheme 9a was carried out by addition of DMPO catalyst into the 1:1 molar mixture of mixed iPr-CDI **1** and diphenyl CDI **21** solution at 140 °C. It was found that 32% of PiPr-CDI **20**, the trans-CDI disproportion product, was found in the reaction solution after 4 h of equilibration. Furthermore, mixing of iPr-NCO **7** and diphenyl CDI **21** in mole ratio of 2 to 1 at 140 °C for an hour has also resulted in an isocyanate-CDI exchange reaction in formation of unsymmetrical CDI **20** as the major product (83%) in the mixture shown in Scheme 9b.[31] Therefore, this trans-CDI disproportion reaction along with the isocyanate-CDI exchange reaction are capable of shifting the long poly-CDI chains **8** toward terminally hindered-CDI compounds such as **10**. In another words, these reactions are alternative paths of forming intermediates of new hindered-CDI type **10** with two discernible CDI-reaction sites.

Finally, proof of our proposed mechanism was further reinforced by a controlled polymerization experiment, where high molecular weight unhindered poly-CDI containing polyamides **26** was prepared first by mixing excess MDI **3** and diacids **2c** in the molar ratio of 10 to 8 at 180 °C in solution with DMPO. As indicated by GPC in Figure 6a, several high molecular unhindered poly-CDI containing polyamide components **26** were observed, but the major fraction is the one having a molecular weight of 52 373 and a dispersity of 2.15. After the reaction was stabilized, a small amount of iPr-CDI initiator **1** together with the rest of requisite diacid **2c** were added to the reaction mixture as the second step. We observed the reshuffling of the product distribution in the ensuing reactions at 180 °C, and after 3 h of stirring, a new polyamide **4c′-2** with M_n = 18,538 with dispersity of 1.22 (shown in Figure 6b) was isolated. On the basis of the results revealed in GPC analysis in Figure 6, we could postulate reaction sequences of the change in Scheme 10 and this result reinforces the fact that iPr-CDI **1** is essential and critical in our controlled polyamide formation. However, it is important to point out that the addition of iPr-CDI **1** works in those cases, only when polyamides still possess CDI or isocyanate groups in its main chains. This is due to the need for the regulator to operate through trans-CDI disproportion reaction and isocyanate-CDI exchange reaction. We also found that this controlled polymerization could be also accomplished by replacing iPr-CDI **1** by iPr-NCO **7** as the initiator which achieves the same result (see example polyamide **4c′-3**) because interconversion of iPr-NCO **7** and PiPr-CDI **20** is rapid as shown in Scheme 9b.

Conclusions

A unique and simple methodology has been found for synthesizing well-defined polyamides from diisocyanates such as MDI

Scheme 6. Polyamide 4 Formation through Selective Addition of Diacid 2 to iPr-amide Terminated Poly-CDI 13 in The New SSRR Cycles



and diacids to form polyamides of narrow molecular weight distributions (dispersity < 1.4). The new SSRR mechanism involves creation of two types of CDIs of different reactivity toward carboxylic acid, i.e. the new hindered-CDI and unhindered CDIs, through the introduction of iPr-CDI, followed by sterically controlled addition of carboxylic acid to the preferred unhindered CDI initially. In this new process, the new hindered-CDI sites play a regulating role until unhindered CDIs are consumed preferentially. This preferred reaction at center each time will generate intermediates and products of type **10** and type **13** of approximately the same lengths, and thus it results in the formation of controlled polyamides with low dispersities. The chemistry behind the new mechanism seems complex; however, the process itself is straightforward, with high-yield and versatility for making final well-defined polyamides. More results of this developed polymerization strategies in other polymer applications will be reported shortly.

Experimental Section

Materials. *N*,*N*′-Bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** was supplied under the trade name of Stabaxol 1 by Rhein Chemie Rheinau GmbH and used without further purification. Isophthalic acid (IA) **2a** was purchased from Lancaster,

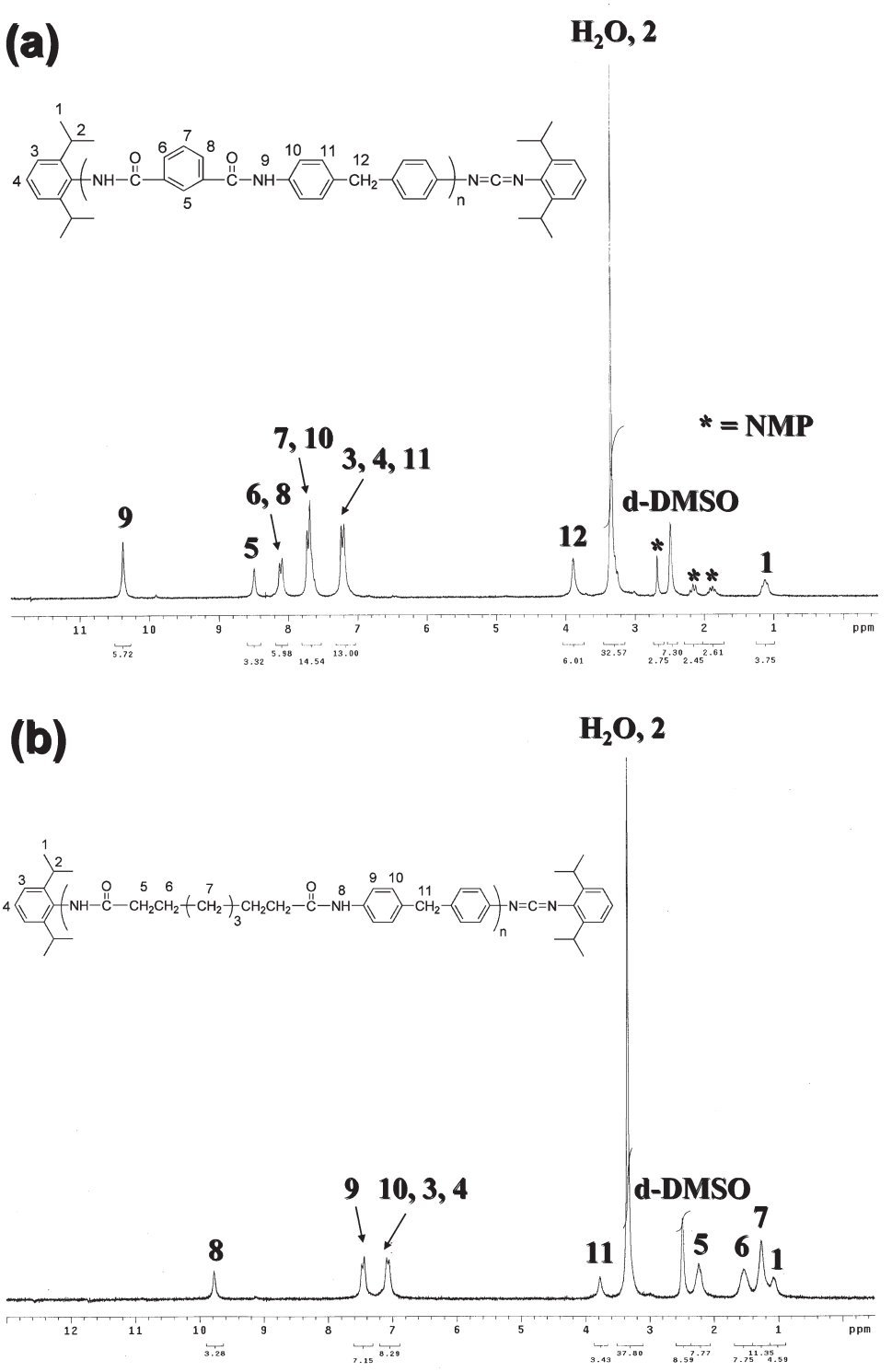


Figure 1. ^{1}H NMR spectra for (a) aromatic polyamide **4a′-2** (iPr-CDI/MDI/IA = 1/10/10) and (b) aryl-aliphatic polyamide **4e′** (iPr-CDI/MDI/AZA = 1/10/10).

2,6-pyridinedicarboxylic acid (PA) **2b** from Aldrich, 4,4′-sulfonyldibenzoic acid (SA) **2c** from Acros, adipic acid (AA) **2d** from Showa, azelaic acid (AZA) **2e** from Aldrich, and 1,10-decanedicarboxylic acid (DA) **2f** from Alfa. All of the above chemicals were used without further purification. 4,4′-Methylenebis(phenyl isocyanate) (4,4′-MDI) **3** was received from BASF, and freshly distilled under reduced pressure before use. 1,3-Dimethyl-3-phospholene oxide (DMPO) was received from GRECO of Taichung, Taiwan. 2,6-Diisopropylphenyl isocyanate **7**, phenyl isothiocyanate **17**, and 2,6-diisopropylaniline **18** were purchased from Acros and used without further purification. Sodium hydroxide was purchased from Fisher Chemical and tetra-*n*-butylammonium bromide was received from Alfa. Benzoic acid **22** and sodium hypochlorite solution (12%) were purchased from Showa and used as received. Phenyl isocyanate **25** was purchased from Fluka and used without further purification. Acetonitrile (AN) and dichloromethane (DCM) were purchased from Tedia. Tetrahydrofuran (THF) and chloroform were purchased from Tedia, distilled over calcium hydride and stored on molecular sieves. *N*-Methyl-2-pyrrolidone (NMP) was received from Tedia, distilled

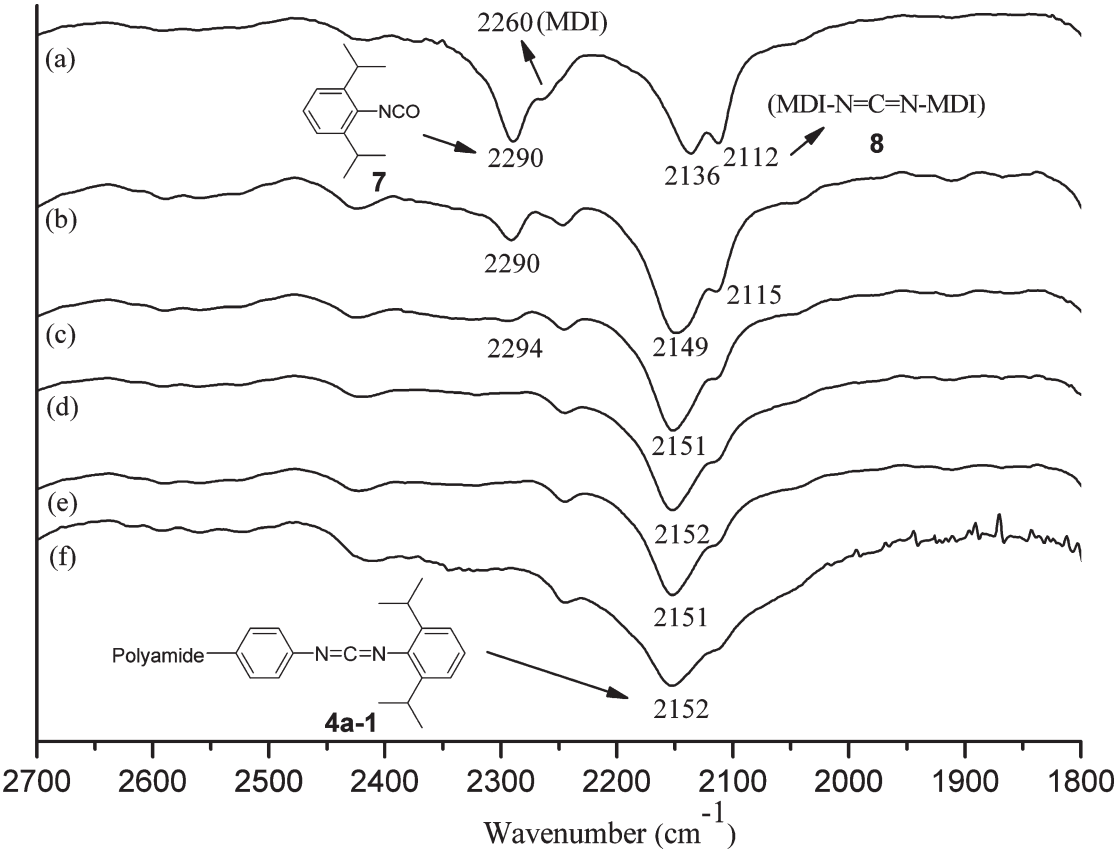


Figure 2. FT-IR monitoring of spectra of polyamides **4a-1** (iPr-CDI/MDI/IA = 1/5/5) after completing addition of monomers at 200 °C: (a) 0 min; (b) 7 min; (c) 15 min; (d) 30 min; (e) 1 h (f) 3 h.

over calcium hydride and stored on molecular sieves before use. *N,N*-Dimethylformamide (DMF) was received from Mallinckrodt Chemicals, distilled over calcium hydride, and stored on molecular sieves before use.

Measurements. ^{1}H NMR spectra was recorded on Varian Inova 200 MHz. Chemical shifts were given in δ, and the coupling constants J were given in Hz. The spectra were recorded in solvents such as $CDCl_3$ or DMSO-d_6 at room temperature, and chemical shifts were given relative to the solvent signals. FT-IR was carried out using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental CHN analysis was performed on a Heraeus CHN-OS rapid analyzer. Electron ionization mass (EIMS) analysis was performed on a ThermoQuest MAT 95XL apparatus. The molecular weights (M_n) were determined by gel permeation chromatography (Shodex GPC with a Shodex RI detector) and calibrated by polystyrene standards. In the GPC analysis, both degassed *N,N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) were used as the eluent and performed at a flow rate of 1.0 mL min^{-1}. NMP was used partly in the cases where less soluble polyamide and analyzed. HPLC was performed using a 5 m spherical particle/100 Å pore size column (Hypersil-100 C18, Thermo Electron Corporation) using a UV detector with its UV band set at 254 nm with 50% or 100% of AN/water as an eluent at a flow rate of 0.5 mL/min. The resulting polyamide products were quenched by pouring into water followed by filtration. Polyamide products were purified by low-polar solvent (chloroform or THF) and were vacuum-dried into polyamide powder before testing.

Synthesis of Polyamides 4a′−4f′ (Scheme 2). *Synthesis of Aromatic Polyamides* ***4a′−4c′***. Reaction of *N,N′*-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and isophthalic acid (IA) **2a** in the molar ratio of iPr-CDI/MDI/IA = 1/10/10 is given here as a typical example. Into a 100 mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer, was placed 10 mL of dry NMP and was heated to 180 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and iPr-CDI **1** (0.363 g, 1 mmol) were added into the hot NMP solution and stirred for 30 s. Freshly distilled MDI **3** (2.500 g, 10 mmol) and IA **2a** (1.660 g, 10 mmol) were dissolved in 20 mL of dry NMP and were then added dropwise into the NMP solution in 6 min at 180 °C. The reaction was further heated to 202 °C for 3 h. The reaction was monitored by FT-IR. The peak absorption at 2112, 2136, 2260, and 2290 cm^{-1} disappeared and was replaced by new hindered-CDI absorption at 2151 cm^{-1} in approximate 30 min. The new peak absorption at 2151 cm^{-1} was persisted to the rest of 2.5 h. The resulting product **4a-2** solution was quenched by 500 mL of water, filtered and dried, to yield 3.582 g (99%) of crude polyamide **4a′-2** (light yellow solid). FT-IR analysis of the crude product showed the CDI peak absorption at 2151 cm^{-1} disappeared and was replaced by urea/amide complex absorption at 1668 cm^{-1}. A small portion of product (0.5 g) was further purified by dissolving in about 5 mL of NMP solvent, following by precipitating from 50 mL of chloroform (70% yields). The detail results of FT-IR, ^{1}H NMR, and GPC for aromatic polyamides were described below.

Synthesis of Aromatic Polyamide ***4a′-1***. Reaction of *N,N′*-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and isophthalic acid (IA) **2a** in the molar ratio of iPr-CDI/MDI/IA = 1/5/5. Yield = 98% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C=O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.05−1.18 (t, 24H, iPr−CH_3), 3.25−3.43 (t, 4H, iPr−CH), 3.90 (s, 2*n*H, Ph−CH_2), 7.20−7.24 (d, (4*n* + 6)H, Ar−H), 7.66−7.73 (t, 5*n*H, Ar−H), 8.10−8.13 (d, 2*n*H, Ar−H), 8.50 (s, 1*n*H, Ar−H), 10.37 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.27, M_w = 18923, M_n = 14900.

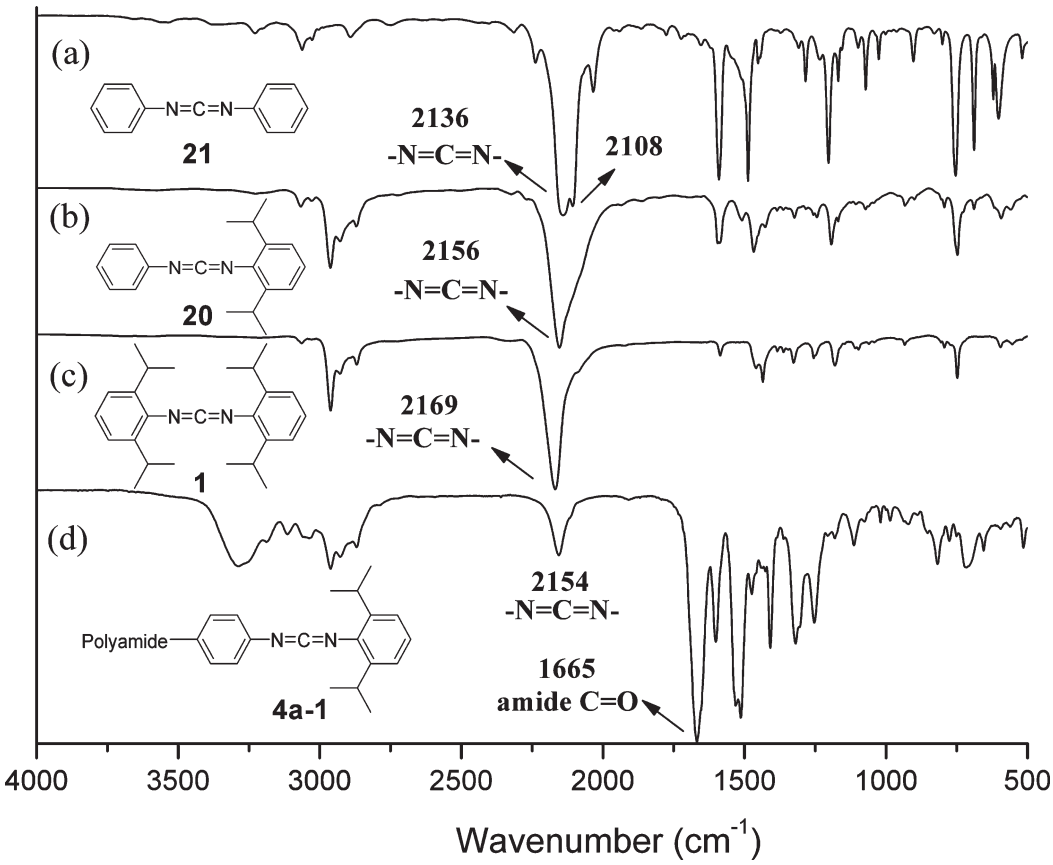
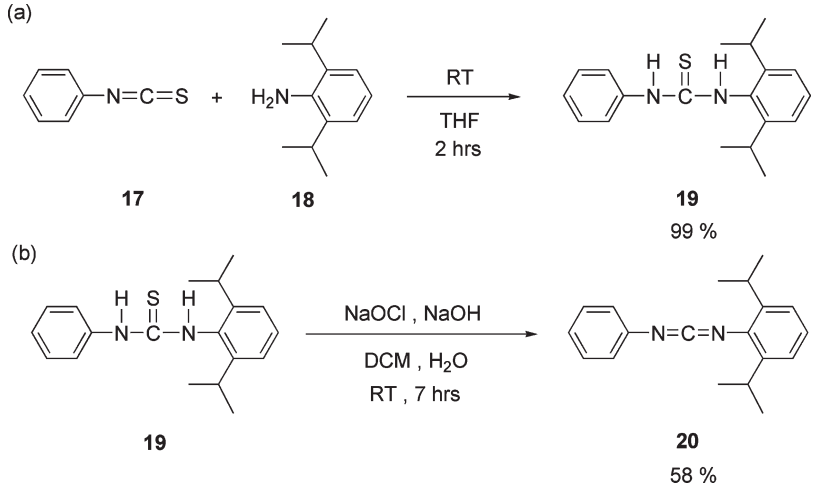


Figure 3. Model FT-IR spectrum of (a) diphenyl carbodiimide **21**; (b) *N*′-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide **20**; (c) *N*,*N*′-bis(2,6-diisopropylphenyl) carbodiimide **1**; and (d) hindered CDI-capped polyamide **4a-1** (iPr-CDI/MDI/IA = 1/5/5).

Scheme 7. Synthesis of Model Unsymmetrical *N*′-Phenyl-*N*-(2,6-diisopropylphenyl) Carbodiimide (PiPr-CDI) 20: (a) Synthesis of *N*′-Phenyl-*N*-(2,6-diisopropylphenyl) Thiourea 19; (b) Synthesis of Model *N*′-Phenyl-*N*-(2,6-diisopropylphenyl) Carbodiimide (PiPr-CDI) 20



*Synthesis of Aromatic Polyamide **4a′-2***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and isophthalic acid (IA) **2a** in the molar ratio of iPr-CDI/MDI/IA = 1/10/10. Yield = 99% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C=O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.05−1.18 (t, 24H, iPr−CH_3), 3.26−3.32 (t, 4H, iPr−CH), 3.90 (s, 2*n*H, Ph−CH_2), 7.19−7.24 (d, (4*n* + 6)H, Ar−H), 7.66−7.72 (d, 5*n*H, Ar−H), 8.10−8.14 (d, 2*n*H, Ar−H), 8.50 (s, 1*n*H, Ar−H), 10.37 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.30, M_w = 22880, M_n = 17600.

*Synthesis of Aromatic Polyamide **4a′-3***. Reaction of 4,4′-methylenebis(phenylisocyanate) (MDI) **3** with isophthalic acid (IA) **2a** in the molar ratio of iPr-CDI/MDI/IA = 0/1/1. The detail procedure for preparing polyamide **4a′-3** was described below. Yield = 98% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C=O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 3.90 (s, 2*n*H, Ph−CH_2), 7.20−7.24 (d, (4*n* + 6)H, Ar−H), 7.62−7.73 (m, 5*n*H, Ar−H), 8.10−8.13 (d, 2*n*H, Ar−H), 8.50 (s, 1*n*H, Ar−H), 10.37 (s, 2*n*H, N−H). GPC (DMF): dispersity = 6.06, M_w = 122419, M_n = 20201.

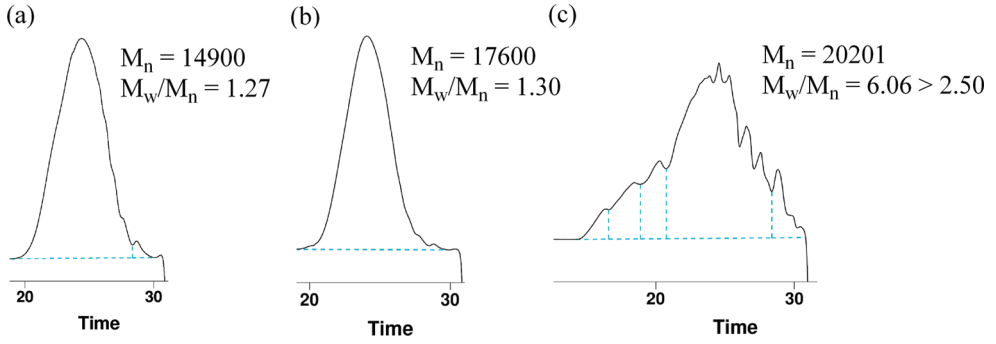


Figure 4. GPC profiles (DMF) of polyamides **4a′-1**−**4a′-3** prepared by new SSRR: (a) polyamide **4a′-1** of iPr-CDI/MDI/IA = 1/5/5; (b) polyamide **4a′-2** of iPr-CDI/MDI/IA = 1/10/10; (c) polyamide **4a′-3** of iPr-CDI/MDI/IA = 0/1/1 (no iPr-CDI **1** as initiator).

*Synthesis of Aromatic Polyamide **4b′-1***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/5/5. Yield = 91%of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.13−1.15 (s, 24H, iPr−CH_3), 3.23−3.42 (t, 4H, iPr−CH), 3.95 (s, 2*n*H, Ph−CH_2), 7.27−7.30 (d, (4*n* + 6)H, Ar−H), 7.79−7.83 (d, 4*n*H, Ar−H), 8.28−8.34 (t, 3nH, Ar−H), 10.97 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.29, M_w = 4951, M_n = 3838.

*Synthesis of Aromatic Polyamide **4b′-2***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/7.5/7.5. Yield = 93% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.12−1.15 (d, 24H, iPr−CH_3), 3.23−3.42 (t, 4H, iPr−CH), 3.95 (s, 2*n*H, Ph−CH_2), 7.27−7.30 (d, (4*n* + 6)H, Ar−H), 7.79−7.83 (d, 4*n*H, Ar−H), 8.29−8.34 (t, 3nH, Ar−H), 10.97 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.29, M_w = 5270, M_n = 4085.

*Synthesis of Aromatic Polyamide **4b′-3***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/10/10. Yield = 96% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 11.11−1.14 (d, 24H, iPr−CH_3), 3.30−3.38 (t, 4H, iPr−CH), 3.93 (s, 2*n*H, Ph−CH_2), 7.25−7.28 (d, (4*n* + 6)H, Ar−H), 7.78−7.82 (d, 4*n*H, Ar−H), 8.28−8.32 (d, 3nH, Ar−H), 10.96 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.30, M_w = 6042, M_n = 4648.

*Synthesis of Aromatic Polyamide **4b′-4***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/12.5/12.5. Yield = 95% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.13 (s, 24H, iPr−CH_3), 3.26−3.40 (t, 4H, iPr−CH), 3.94 (s, 2*n*H, Ph−CH_2), 7.26−7.29 (d, (4*n* + 6)H, Ar−H), 7.78−7.82 (d, 4*n*H, Ar−H), 8.33 (s, 3nH, Ar−H), 10.96 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.35, M_w = 6817, M_n = 5049.

*Synthesis of Aromatic Polyamide **4b′-5***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/15/15. Yield = 94% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.13 (s, 24H, iPr−CH_3), 3.36 (s, 4H, iPr−CH), 3.94 (s, 2*n*H, Ph−CH_2), 7.29 (s, (4*n* + 6)H, Ar−H), 7.78−7.82 (d, 4*n*H, Ar−H), 8.33 (s, 3nH, Ar−H), 10.96 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.38, M_w = 7176, M_n = 5200.

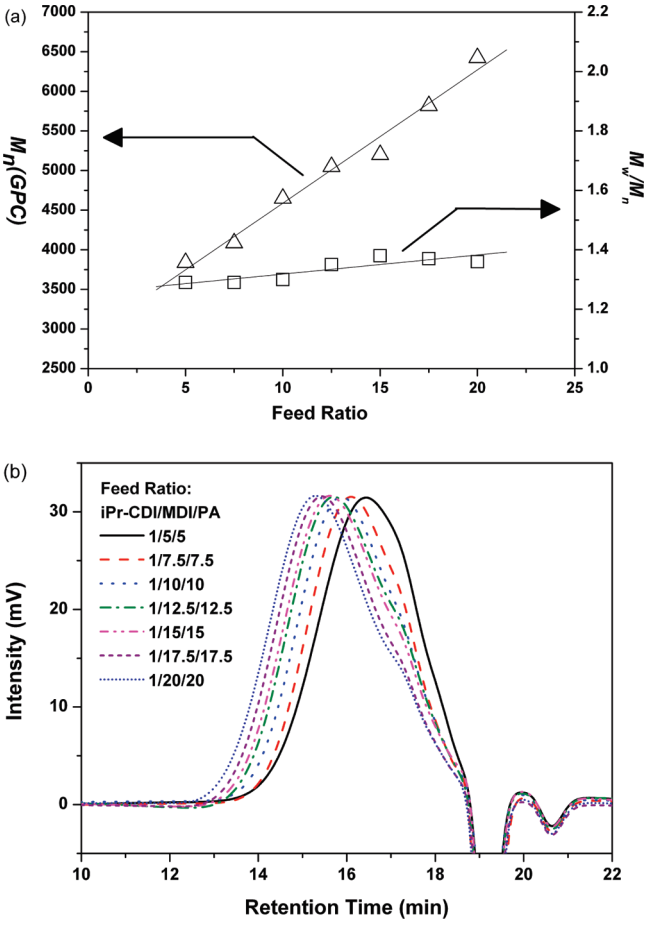


Figure 5. GPC results (NMP) of polyamides **4b′-1**∼**b′-7**: (a) M_n and M_w/M_n values as a function of the feed ratio of MDI/PA to iPr-CDI; (b) GPC profiles obtained as a function of the feed ratio of iPr-CDI/MDI/PA.

*Synthesis of Aromatic Polyamide **4b′-6***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/17.5/17.5. Yield = 93% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.08−1.13 (d, 24H, iPr−CH_3), 3.35−3.38 (d, 4H, iPr−CH), 3.93 (s, 2*n*H, Ph−CH_2), 7.25−7.28 (d, (4*n* + 6)H, Ar−H), 7.78−7.81 (d, 4*n*H, Ar−H), 8.28−8.32 (d, 3nH, Ar−H), 10.95 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.37, M_w = 7971, M_n = 5818.

Table 1. Molecular Weights and Polydispersities of Polyamides 4a′−4j′[a]

entry	composition	molar ratio	feed [min]	M_w	M_n	dispersity [M_w/M_n]
4d′	iPr-CDI/MDI/AA[b]	1/10/10	7	17 650	14 355	1.23
4e′	iPr-CDI/MDI/AZA[b]	1/10/10	7	13 621	12 197	1.11
4f′	iPr-CDI/MDI/DA[b]	1/10/10	7	11 264	10 444	1.08
4a′-2	iPr-CDI/MDI/IA[b]	1/10/10	7	22 800	17 600	1.30
4c′-1	iPr-CDI/MDI/SA[b]	1/10/10	7	22 821	18 860	1.21
4b′-1	iPr-CDI/MDI/PA[c]	1/5/5	7	4951	3838	1.29
4b′-3	iPr-CDI/MDI/PA[c]	1/10/10	7	6042	4648	1.30
4b′-5	iPr-CDI/MDI/PA[c]	1/15/15	7	7176	5200	1.38
4b′-7	iPr-CDI/MDI/PA[c]	1/20/20	7	8737	6424	1.36

[a] Aliphatic diacids **2d**−**2f**: AA = adipic acid **2d**, AZA = azelaic acid **2e**, DA = 1,10-decanedicarboxylic acid **2f**. Aromatic diacids **2a**−**2c**: IA = isophthalic acid **2a**, SA = 4,4′-sulfonyldibenzoic acid **2c**, PA = 2,6-pyridinedicarboxylic acid **2b**. [b] Measured by GPC of *N*-dimethylformamide (DMF) was used as the eluent. [c] Measured by GPC of *N*-methyl-2-pyrrolidone (NMP) was used as the eluent for less soluble polyamide.

*Synthesis of Aromatic Polyamide **4b′-7***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 2,6-pyridinedicarboxylic acid (PA) **2b** in the molar ratio of iPr-CDI/MDI/PA = 1/20/20. Yield = 96% of a light red brown solid. FT-IR (KBr cm^{-1}): 1677 (amide, C═O), 3297 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.12−1.14 (d, 24H, iPr−CH$_3$), 3.25−3.43 (m, 4H, iPr−CH), 3.93 (s, 2*n*H, Ph−CH$_2$), 7.25−7.28 (d, (4*n* + 6)H, Ar−H), 7.78−7.81 (d, 4*n*H, Ar−H), 8.27−8.32 (d, 3nH, Ar−H), 10.95 (s, 2*n*H, N−H). GPC (NMP): dispersity = 1.36, M_w = 8737, M_n = 6424.

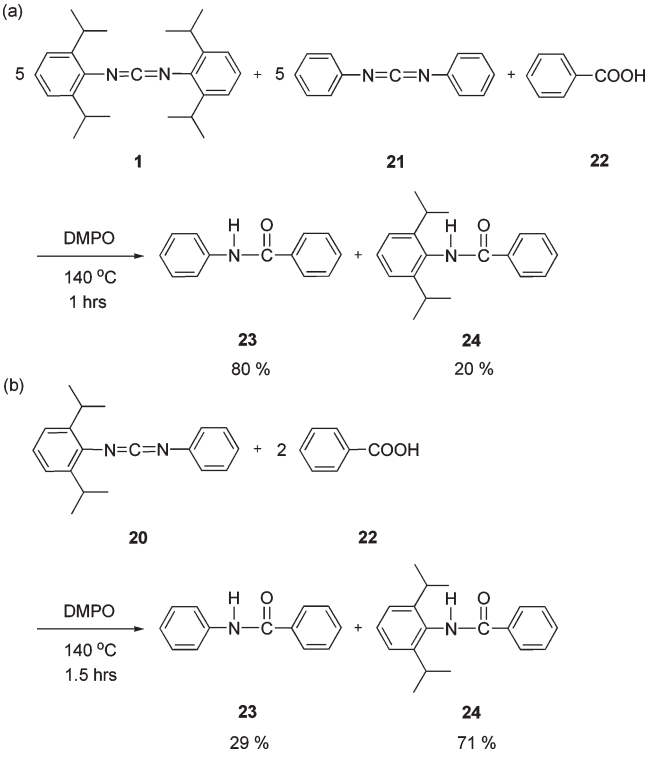
*Synthesis of Aromatic Polyamide **4c′-1***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 4,4′-sulfonyldibenzoic acid (SA) **2c** in the molar ratio of iPr-CDI/MDI/SA = 1/10/10. Yield = 95% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C═O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.06−1.14 (t, 24H, iPr−CH$_3$), 3.28−3.40 (m, 4H, iPr−CH), 3.87 (s, 2*n*H, Ph−CH$_2$), 7.16−7.20 (d, (4*n* + 6)H, Ar−H), 7.62−7.66 (d, 4*n*H, Ar−H), 8.07−8.17 (t, 9nH, Ar−H), 10.40 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.21, M_w = 22821, M_n = 18860.

*Synthesis of Aromatic Polyamide **4c′-2***. Reaction of *N*,*N*′-bis(2,6-diisopropylphgenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 4,4′-sulfonyldibenzoic acid (SA) **2c** in the overall molar ratio of iPr-CDI/MDI/SA = 1/10/10. The detail procedure for preparing polyamide **4c′-2** was described below. Yield = 92% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C═O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.05−1.13 (t, 24H, iPr−CH$_3$), 3.31−3.35 (d, 4H, iPr−CH), 3.87 (s, 2*n*H, Ph−CH$_2$), 7.17−7.21 (d, (4*n* + 6)H, Ar−H), 7.62−7.66 (d, 4*n*H, Ar−H), 8.09−8.17 (t, 8nH, Ar−H), 10.40 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.22, M_w = 22617, M_n = 18538.

*Synthesis of Aromatic Polyamide **4c′-3***. Reaction of 2,6-diisopropylphenyl isocyanate **7** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 4,4′-sulfonyldibenzoic acid (SA) **2c** in the molar ratio of iPr-NCO/MDI/SA = 2/10/10. The detail procedure for preparing polyamide **4c′-3** was described below. Yield = 95% of a light yellow solid. FT-IR (KBr cm^{-1}): 1668 (amide, C═O), 3288 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.06−1.14 (t, 24H, iPr−CH$_3$), 3.44 (s, 4H, iPr−CH), 3.88 (s, 2*n*H, Ph−CH$_2$), 7.17−7.21 (d, (4*n* + 6)H, Ar−H), 7.63−7.66 (d, 4*n*H, Ar−H), 8.12 (s, 8nH, Ar−H), 10.42 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.27, M_w = 22275, M_n = 17466.

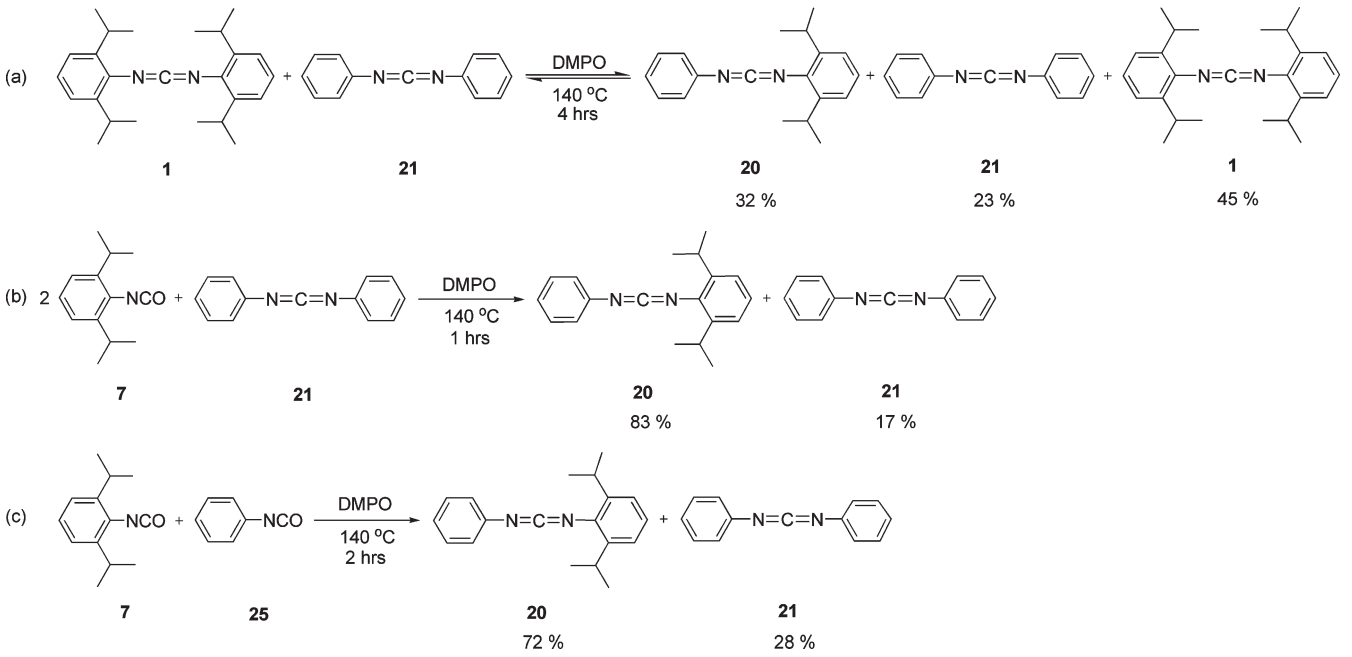
*Synthesis of Aliphatic Polyamides **4d′−4f′***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and azelaic acid (AZA) **2e** in the molar ratio of iPr-CDI/MDI/AZA = 1/10/10 is given here as a typical example. Into a 100 mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer, was placed 10 mL of dry NMP and was heated to 180 °C.

Scheme 8. Model Competitive Studies: (a) Reaction of iPr-CDI 1 and Diphenyl CDI 21 with Benzoic Acid 22; (b) Reaction of PiPr-CDI 20 with Benzoic Acid 22



1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and iPr-CDI **1** (0.363 g, 1 mmol) were added into the hot NMP solution and stirred for 30 s. Freshly distilled MDI **3** (2.500 g, 10 mmol) and AZA **2e** (1.880 g, 10 mmol) were dissolved in 20 mL of dry NMP and were then added dropwise into the NMP solution in 6 min at 180 °C. The reaction was further heated to 202 °C for 3 h. The reaction was monitored by FT-IR. The peak absorption at 2112, 2136, 2260, and 2290 cm^{-1} disappeared and was replaced by new hindered-CDI absorption at 2151 cm^{-1} in approximate 30 min. The new peak absorption at 2151 cm^{-1} was persisted to the rest of 2.5 h. The resulting product **4e** solution was quenched by 500 mL of water, filtered, and dried, to yield 3.752 g (98%) of crude polyamide **4e′** (white solid). FT-IR analysis of the crude product showed the CDI peak absorption at 2151 cm^{-1} disappeared and was replaced by urea/amide complex absorption at 1660 cm^{-1}. A small portion of product (0.5 g) was further purified by dissolving in about 5 mL of NMP solvent, following by precipitating from 50 mL of chloroform (80% yields). The detailed results of FT-IR, ^{1}H NMR, and GPC studies for aliphatic polyamides were described below.

Scheme 9. Trans-CDI Disproportion and Isocyanate-CDI Exchange Reactions: (a) Reaction of iPr-CDI 1 with Diphenyl CDI 21; (b) Reaction of iPr-NCO 7 with Diphenyl CDI 21; (c) Reaction of iPr-NCO 7 with Phenyl Isocyanate 25



Synthesis of Aliphatic Polyamide ***4d′***. Reaction of *N*,*N*′-bis-(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and adipic acid (AA) **2d** in the molar ratio of iPr-CDI/MDI/AA = 1/10/10. Yield = 91% of a white solid. FT-IR (KBr cm^{-1}): 1658 (amide, C═O), 3301 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.05−1.08 (d, 24H, iPr−CH_3), 1.58 (s, 4*n*H, −CH_2−), 2.27 (s, 4*n*H, −CH_2−), 3.34 (s, 4H, iPr−CH), 3.78 (s, 2*n*H, Ph−CH_2), 7.05−7.09 (d, 4*n*H, Ar−H), 7.44−7.48 (d, 4*n*H, Ar−H), 9.78 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.23, M_w = 17650, M_n = 14355.

Synthesis of Aliphatic Polyamide ***4e′***. Reaction of *N*,*N*′-bis-(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and azelaic acid (AZA) **2e** in the molar ratio of iPr-CDI/MDI/AZA = 1/10/10. Yield = 98% of a white solid. FT-IR (KBr cm^{-1}): 1660 (amide, C═O), 3301 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.07 (s, 24H, iPr−CH_3), 1.27 (s, 6nH, −CH_2−), 1.55 (s, 4*n*H, −CH_2−), 2.25 (s, 4*n*H, −CH_2−), 3.34 (s, 4H, iPr−CH), 3.78 (s, 2*n*H, Ph−CH_2), 7.06−7.10 (d, 4*n*H, Ar−H), 7.45−7.49 (d, 4*n*H, Ar−H), 9.76 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.11, M_n = 12197, M_w = 13621.

Synthesis of aliphatic polyamide ***4f′***. Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 1,10-decanedicarboxylic acid (DA) **2f** in the molar ratio of iPr-CDI/MDI/DA = 1/10/10. Yield = 92% of a white solid. FT-IR (KBr cm^{-1}): 1660 (amide, C═O), 3301 (amide, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.10 (s, 24H, iPr−CH_3), 1.24 (s, 12*n*H, −CH_2−), 1.54 (s, 4*n*H, −CH_2−), 2.24 (s, 4*n*H, −CH_2−), 3.20−3.42 (t, 4H, iPr−CH), 3.78 (s, 2*n*H, Ph−CH_2), 7.05−7.09 (d, 4*n*H, Ar−H), 7.44−7.48 (d, 4*n*H, Ar−H), 9.75 (s, 2*n*H, N−H). GPC (DMF): dispersity = 1.08, M_w = 11264, M_n = 10444.

Synthesis of Model Unsymmetrical *N*′-Phenyl-*N*-(2,6-diisopropylphenyl) Carbodiimide (PiPr-CDI) (Scheme 7). *Synthesis of N*′*-Phenyl-N-(2,6-diisopropylphenyl) Thiourea* ***19*** *(Scheme 7a).* Into a 250 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet, an ice bath, and a magnetic stirrer were placed phenyl isothiocyanate **17** (8.03 g, 58 mmol) and 10 mL of dry THF. After the mixture was cooled to 0−4 °C, 2,6-diisopropylaniline **18** (10.19 g, 52 mmol) dissolved in 10 mL of dry THF was added dropwise to the stirred solution. After the addition, the reaction was continued at room temperature for 2 h. The resulting solution was then poured into 100 mL of petroleum ether. The precipitated product was filtered and dried at room temperature under vacuum. The yield of *N*′-phenyl-*N*-(2,6-diisopropylphenyl) thiourea **19** was 99% (16.36 g). Mp = 173−174 °C. FT-IR (KBr cm^{-1}): 1330 (thiourea, C═S), 3340 (thiourea, N−H). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.12−1.23 (m, 12H, iPr−CH_3), 3.06−3.13 (t, 2H, iPr−CH), 7.17−7.35 (m, 6H, Ar−H), 7.59−7.62 (d, 2H, Ar−H), 8.41,9.00 (s, 2H, N−H), 9.60,9.84 (s, 2H, N−H). Anal. Calcd for $C_{19}H_{24}N_2S$: C, 73.03; H, 7.74; N, 8.97; S, 10.26. Found: C, 73.07; H, 7.73; N, 8.92; S, 10.25. Mass spectrum (*m*/*e*): 312 (M^+, 100% relative abundance).

Synthesis of N′*-Phenyl-N-(2,6-diisopropylphenyl) Carbodiimide (PiPr-CDI)* ***20*** *(Scheme 7(b)).* Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, and a magnetic stirrer were added *N*′-phenyl-*N*-(2,6-diisopropylphenyl) thiourea **19** (9.36 g, 30 mmol) and 50 mL of DCM. After the mixture was cooled to 0−4 °C in an ice bath, sodium hydroxide (2.40 g, 60 mmol) and tetra-*n*-butylammonium bromide (0.10 g, 3 mmol) dissolved in 50 mL of H_2O were added dropwise to the stirred solution. To this solution was then added 12% of sodium hypochlorite solution (55.83 g, 90 mmol), and the combined solution was maintained at room temperature with stirring for 7 h until the color of the solution changing from deep orange to light yellow. The reaction mixture was extracted three times with dichloromethane (DCM). The organic layer was dried with $MgSO_4$. The crude product was purified by rapidly passing through a short chromatograph column packed with silica gel with DCM as the eluent. After evaporation of DCM, *N*′-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide (PiPr-CDI) **20** (4.84 g; 58%) was isolated as a colorless viscose liquid. FT-IR (KBr cm^{-1}): 2156, (carbodiimide, −NCN−). ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.17−1.20 (d, 12H, iPr−CH_3), 3.23−3.39 (m, 2H, iPr−CH), 7.16 (s, 6H, Ar−H), 7.31−7.38 (t, 2H, Ar−H). Mass spectrum (*m*/*e*): 278 (M^+, 100% relative abundance).

Experiments on Model Competitive Study (Scheme 8). *Diphenyl Carbodiimide (Phenyl-CDI)* ***21*** *and N,N*′*-Bis(2,6-diisopropylphenyl)-Carbodiimide (iPr-CDI)* ***1*** *Reacted with Benzoic Acid* ***22*** *(Scheme 8a).* Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, an oil

bath, and a magnetic stirrer was placed 4 mL of dry NMP, and the flask was heated to 140 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and benzoic acid **22** (0.12 g, 1.0 mmol) were added into the solution and stirred for 5 min. *N*,*N*′-Bis(2,6-diisopropylphenyl)carbodiimide **1** (1.81 g, 5.0 mmol) and diphenyl carbodiimide **21** (0.97 g, 5.0 mmol) dissolved in 6 mL of dry NMP and were then added into the reaction mixture at 140 °C. The reaction was monitored by FT-IR. The peak of CDI absorption at 2102, 2137, and 2166 cm^{-1} did not diminish in 60 min. The resulting mixture was quenched by concentrated H_2SO_4 (1 mL) and H_2O (4 mL) and poured into 200 mL of water, filtered, and dried, to yield 2.75 g of crude amide product. FT-IR analysis of the crude product showed the CDI peak absorptions at 2102, 2137, and 2166 cm^{-1} have been converted into urea absorption at 1641 cm^{-1}. HPLC analysis of the crude reaction products showed the yields ratios of 80:20 for phenyl benzamide **23** and *N*-(2,6-diisopropylphenyl) benzamide **24** respectively.

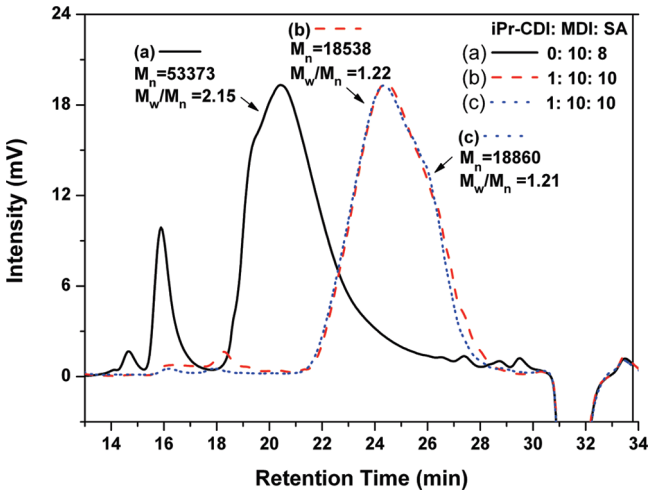
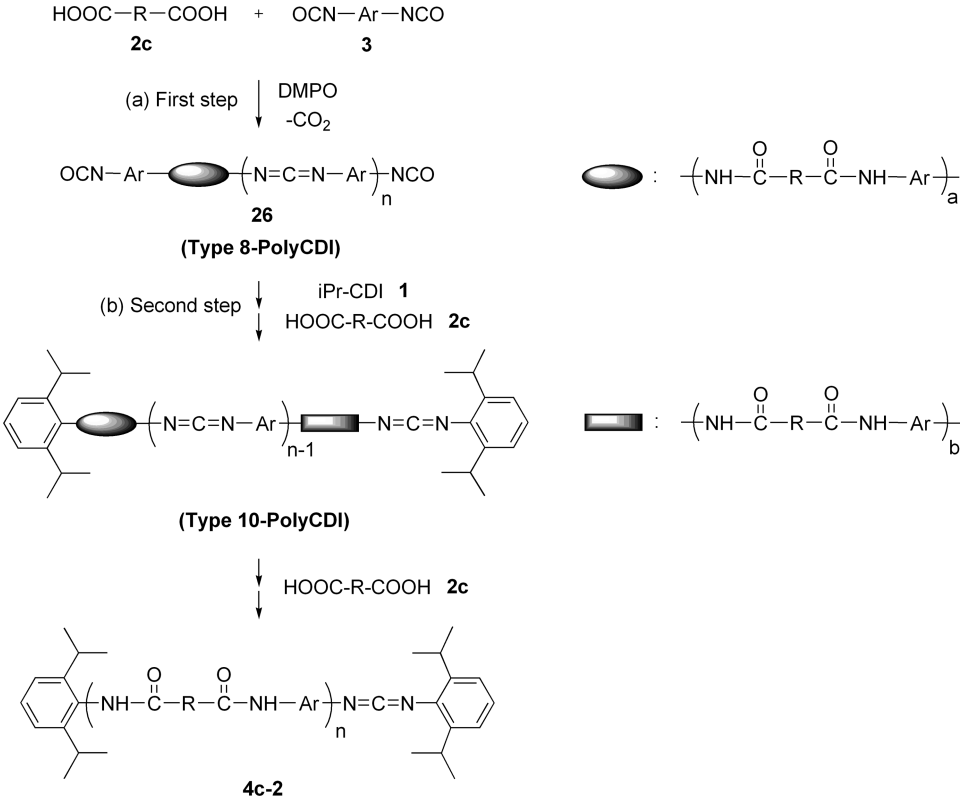


Figure 6. GPC spectra (DMF) of polyamide **4c′-2** (iPr-CDI/MDI/SA = 1/10/10) prepared by a two step method: (a) the first step: synthesis of polyamides **26** with unhindered poly-CDI containing (iPr-CDI/MDI/SA = 0/10/8); (b) second step: addition of iPr-CDI initiator **1** and SA diacids **2c** to control the molecular weight (iPr-CDI/MDI/SA = 1/10/10). (c) One step method by new SSRR for polyamide **4c′-1** (iPr-CDI/MDI/SA = 1/10/10).

*N′-Phenyl-N-(2,6-diisopropylphenyl) Carbodiimide (PiPr-CDI) **20** Reacted with Benzoic Acid **22** (Scheme 8(b))*. Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, an oil bath, and a magnetic stirrer was placed 3 mL of dry NMP, and the flask was heated to 140 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and *N′*-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide (PiPr-CDI) **20** (1.01 g, 3.63 mmol) were added into the solution and stirred for 5 min. Benzoic acid **22** (3.63 g, 7.26 mmol) dissolved in 2 mL of dry NMP and was then added into the reaction mixture at 140 °C. The reaction was monitored by FT-IR. The peak of PiPr-CDI absorption at 2156 cm^{-1} and isocyanate absorption at 2260 and 2290 cm^{-1} disappeared to finish reaction in 90 min. The resulting mixture was quenched by the addition of concentrated H_2SO_4 (0.5 mL) and H_2O (2 mL) and poured into 200 mL of water, filtered, and dried, to yield 5.56 g of crude amide product. FT-IR analysis of the crude product showed amide absorption at 1653 cm^{-1}. HPLC analysis of the crude reaction products showed yield ratios of 29:71 for phenyl benzamide **23** and *N*-(2,6-diisopropylphenyl) benzamide **24**, respectively.

Experiments on Trans-CDI Disproportion and Isocyanate-CDI Exchange Reactions (Scheme 9). *Reaction of N,N′-Bis-(2,6-diisopropylphenyl)Carbodiimide (iPr-CDI) **1** with Diphenyl Carbodiimide (diphenyl CDI) **21** (Scheme 9a)*. Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, an oil bath, and a magnetic stirrer was placed 8 mL of dry NMP, and the flask was heated

Scheme 10. Mechanism of the Two Step Method: (a) First Step, Synthesis of Polyamides 26 Containing Unhindered Poly-CDI; (b) Second Step, Addition of iPr-CDI Initiator 1 and Residual Diacids 2c To Control The Molecular Weight and Finish the Reaction



to 140 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and diphenyl carbodiimide **21** (2.02 g, 10.4 mmol) were added into the solution and stirred for 5 min. *N*,*N*′-Bis(2,6-diisopropylphenyl)carbodiimide **1** (3.77 g, 10.4 mmol) dissolved in 12 mL of dry NMP and was then added into the reaction mixture at 140 °C. The reaction was monitored by FT-IR. The peak absorption at 2107, 2137, and 2166 cm^{-1} were converted into new CDI absorption at 2156 cm^{-1} in 240 min. The resulting mixture was quenched by concentrated H_2SO_4 (1 mL) and H_2O (4 mL) and poured into 200 mL of water, filtered and dried, to yield 4.89 g of crude urea product. FT-IR analysis of the crude product showed the new CDI peak absorption at 2156 cm^{-1} have been converted into urea absorption at 1643 cm^{-1}. The urea product ratios of 32:23:45 for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) urea, diphenyl urea, and *N*,*N*′-bis-(2,6-diisopropylphenyl) urea respectively were measured by HPLC analysis. This ratio of 32:23:45 was assumed to be the ratio of the corresponding CDIs for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide (PiPr-CDI) **20**, diphenyl carbodiimide **21** and *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide **1** respectively before their hydrolysis.

Reaction of 2,6-Diisopropylphenyl Isocyanate (*iPr-NCO*) *7 with Diphenyl Carbodiimide* (*diphenyl CDI*) ***21*** (*Scheme 9b*). Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, and a magnetic stirrer was placed 6 mL of dry NMP and was heated to 140 °C. 1, 3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and diphenyl carbodiimide **21** (0.51 g, 2.64 mmol) were added into the solution and stirred for 5 min. 2,6-Diisopropylphenyl isocyanate **7** (1.07 g, 5.28 mmol) was dissolved in 7 mL of dry NMP and was then added into the reaction mixture at 140 °C. The reaction was monitored by FT-IR. The peak absorption at 2290 cm^{-1} rapidly diminished and disappeared, while a new CDI IR absorption at 2156 cm^{-1} became the major absorption in 60 min. The resulting mixture was quenched by the addition of concentrated H_2SO_4 (0.5 mL) and H_2O (2 mL) to convert all CDIs in the solution into urea derivitives. The resulting solution was poured into 200 mL of water, filtered and dried, to yield 1.22 g of crude urea product. FT-IR analysis of the crude product showed the new CDI peak absorption at 2156 cm^{-1} have been converted into urea absorption at 1643 cm^{-1}. The composition of this urea product mixture was analyzed through HPLC where the relative ratio of ureas were determined to be 83:17 for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) urea and diphenyl urea. This ratio of 83:17 was assumed to be the ratio of the corresponding CDIs for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide (PiPr-CDI) **20** and diphenyl carbodiimide **21** respectively before their hydrolysis.

Reaction of 2,6-Diisopropylphenyl Isocyanate (*iPr-NCO*) *7 with Phenyl Isocyanate* (*Phenyl NCO*) ***25*** (*Scheme 9c*). Into a 100 mL three-necked round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, and a magnetic stirrer was placed 5 mL of dry NMP, and heated to 140 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.05 g) and phenyl isocyanate **25** (0.29 g, 2.43 mmol) were added into the solution and stirred for 5 min. 2,6-Diisopropylphenyl isocyanate **7** (0.50 g, 2.43 mmol) dissolved in 5 mL of dry NMP was then added into the reaction mixture at 140 °C. The reaction was monitored by FT-IR. The peak absorption at 2260 and 2290 cm^{-1} disappeared and was replaced by new CDI absorption at 2156 cm^{-1} in 120 min. The resulting mixture was quenched by concentrated H_2SO_4 (0.5 mL) and H_2O (2 mL) and poured into 200 mL of water, filtered, and dried, to yield 0.51 g of crude urea product. FT-IR analysis of the crude product showed the new CDI peak absorption at 2156 cm^{-1} has been converted into urea absorption at 1643 cm^{-1}. The composition of this urea product mixture was analyzed through HPLC where the relative ratio of urea was determined to be 72:28 for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) urea and diphenyl urea, respectively. This ratio of 72:28 was assumed to be the ratio of the corresponding CDIs for *N*′-phenyl-*N*-(2,6-diisopropylphenyl) carbodiimide (PiPr-CDI) **20** and diphenyl carbodiimide **21** respectively before their hydrolysis.

Synthesis of Polyamide 4a-3 with No iPr-CDI Initiator in Regular SSRR (Figure 4c). *Synthesis of Aromatic Polyamide* ***4a′-3*** *with No iPr-CDI Initiator* ***1*** (*Figure 4c*). Reaction of 4,4′-methylenebis(phenylisocyanate) (MDI) **3** with isophthalic acid (IA) **2a** in the molar ratio of iPr-CDI/MDI/IA = 0/1/1 is given here as a typical example. Into a 100 mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer was placed 10 mL of dry NMP, and the flask was heated to 180 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) was added into the hot NMP solution and stirred for 30 s. Freshly distilled MDI **3** (2.500 g, 10 mmol) and IA **2a** (1.660 g, 10 mmol) were dissolved in 20 mL of dry NMP and were then added dropwise into the NMP solution in 6 min at 180 °C. The reaction was further heated to 202 °C for 3 h. The reaction was monitored by FT-IR. The peak absorption at 2112 and 2136 cm^{-1} disappeared in 10 min. No CDI peak absorption was generated and persisted to the rest of 170 min. The resulting product **4a-3** solution was poured into 500 mL of water, filtered and dried, to yield 3.214 g (98%) of crude polyamide **4a′-3** (light yellow solid). FT-IR analysis of the crude product showed amide absorption at 1668 cm^{-1} and no CDI peak absorption at 2112 and 2136 cm^{-1}. A small portion of product (0.5 g) was further purified by dissolving in about 5 mL of NMP solvent, following by precipitating from 50 mL of chloroform (78% yields). The detail results of FT-IR, ^1H NMR, and GPC for aromatic polyamides **4a′-3** were described above.

Demonstration of the Importance of iPr-CDI to Control The Molecular Weight in New SSRR (Scheme 10). *First Step: Synthesis of Polyamides* ***26*** *with Unhindered Poly-CDI Containing* (*Scheme 10a*). Reaction of 4,4′-methylenebis(phenylisocyanate) (MDI) **3** with 4,4′-sulfonyldibenzoic acid (SA) **2c** in the molar ratio of iPr-CDI/MDI/SA = 0/10/8 is given here. Into a 100 mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer, was placed 6 mL of dry NMP, and the flask was heated to 180 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) was added into the hot NMP solution and stirred for 30 s. Freshly distilled MDI **3** (2.500 g, 10 mmol) and SA **2c** (2.450 g, 8 mmol) were dissolved in 15 mL of dry NMP and were then added dropwise into the NMP solution in 10 s at 180 °C. The reaction was further heated to 202 °C for 2 min. The resulting product solution became viscous and sticky in the process. The resulting product solution was monitored by FT-IR. The peak absorption was converted into poly-CDI absorption at 2112 and 2136 cm^{-1} in 2 min. Taking small resulting product solution (about ~2 mL) was quenched by 50 mL of water, filtered and dried, to yield 0.008 g of high molecular weight polyamide **26** product with unhindered poly-CDI containing (yellow and viscous solid). GPC (DMF): dispersity = 2.15, M_w = 114752, M_n = 52373.

Second Step: Synthesis of Aromatic Polyamide ***4c-2*** *with Adding iPr-CDI Initiator* ***1*** *and SA Diacids* ***2c*** *To Control The Molecular Weight and Finish The Reaction* (*Scheme 10b*). Reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide (iPr-CDI) **1** and 4,4′-sulfonyldibenzoic acid (SA) **2c** with the first step of the resulting product in the overall molar ratio of iPr-CDI/MDI/SA = 1/10/10 is given here. The first step of the resulting product solution was carried onto the second step. Initiator iPr-CDI **1** (0.363 g, 1 mmol) and residual SA **2c** (0.612 g, 2 mmol) were dissolved in 9 mL of dry NMP and were then added dropwise into the NMP solution in 6 min at 202 °C. The reaction was further heated to 202 °C for 3 h. The viscous resulting product solution clarified immediately in the process. The reaction was monitored by FT-IR. The peak absorption at 2112, 2136, and 2290 cm^{-1} disappeared and was replaced by the new hindered-CDI of absorption at 2151 cm^{-1} in 30 min. The new peak absorption at 2151 cm^{-1} was persisted to the rest of 2.5 h.

The resulting product **4c-2** solution was quenched by 500 mL of water, filtered and dried, to yield 4.60 g (92%) of crude polyamide **4c′-2** (light yellow solid). FT-IR analysis of the crude product showed the CDI peak absorption at 2151 cm^{-1} disappeared and was replaced by urea/amide complex absorption at 1668 cm^{-1}. A small portion of product (0.5 g) was further purified by dissolving in about 5 mL of NMP solvent, following by precipitating from 50 mL of THF (80% yields). The detail results of FT-IR, ^{1}H NMR, and GPC for aromatic polyamides **4c′-2** were described above.

Demonstration of iPr-NCO as the Initiator To Control The Molecular Weight in New SSRR (Example Polyamide 4c-3). *Synthesis Aromatic Polyamide 4c′-3 with iPr-NCO 7 as the Initiator*. Reaction of 2,6-diisopropylphenyl isocyanate (iPr-NCO) **7** with 4,4′-methylenebis(phenylisocyanate) (MDI) **3** and 4,4′-sulfonyldibenzoic acid (SA) **2c** in the molar ratio of iPr-NCO/MDI/SA = 2/10/10 is given here. Into a 100 mL, three-necked, round-bottomed flask equipped with a thermometer, a nitrogen gas inlet tube, a reflux condenser, an oil bath, and a magnetic stirrer, was placed 10 mL of dry NMP and was heated to 180 °C. 1,3-Dimethyl-3-phospholene oxide (DMPO, 0.050 g) and iPr-NCO **7** (0.203 g, 2 mmol) were added into the hot NMP solution and stirred for 30 s. Freshly distilled MDI **3** (2.500 g, 10 mmol) and SA **2c** (3.063 g, 10 mmol) were dissolved in 20 mL of dry NMP and were then added dropwise into the NMP solution in 6 min at 180 °C The reaction was further heated to 202 °C for 3 h. The reaction was monitored by FT-IR. The peak absorption at 2112, 2136, 2260, and 2290 cm^{-1} disappeared and was replaced by new hindered-CDI of absorption at 2151 cm^{-1} in 30 min. The new peak absorption at 2151 cm^{-1} was persisted to the rest of 2.5 h. The resulting product **4c-3** solution was quenched by 500 mL of water, filtered, and dried, to yield 4.72 g (95%) of crude polyamide **4c′-3** (light yellow solid). FT-IR analysis of the crude product showed the CDI peak absorption at 2151 cm^{-1} disappeared and was replaced by urea/amide complex absorption at 1668 cm^{-1}. A small portion of product (0.5 g) was further purified by dissolving in about 5 mL of NMP solvent, following by precipitating from 50 mL of THF (78% yields). The detail results of FT-IR, ^{1}H NMR, and GPC for aromatic polyamides **4c′-3** were described above.

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Supporting Information Available: Figures showing NMR spectra for polyamides and model compounds and HPLC spectra for model reactions (including model competitive study, trans-CDI disproportion and isocyanate-CDI exchange reactions). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Note: ^{1}H NMR characterization of model unsymmetrical *N*′-phenyl-*N*-(2,6-diisopropylphenyl) CDI (PiPr-CDI) **20** for Scheme 7 were shown in the Supporting Information, Figure S18 and S19.
(28) Note: ^{1}H NMR characterization for polyamides **4a′**−**4f′** were shown in the Supporting Information, Figures S2−S17.
(29) Note: HPLC analysis of model competitive studies for Scheme 8 were shown in the Supporting Information, Figures S20 and S21.
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(31) Note: HPLC analysis of trans-CDI disproportion and isocyanate-CDI exchange reactions for Scheme 9 were shown in the Supporting Information, Figures S22−S24.