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Synthesis and Thermoreversible Gelation Properties of Main-Chain Poly(pyridine-2,6-dicarboxamide-triazole)s

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Abstract: A series of main-chain poly(amide-triazole)s were prepared by copper(I)-catalyzed alkyne–azide AABB-type copolymerizatons between five structurally similar diacetylenes **1**–**5** with the same diazide **6**. The acetylene units in monomers **1**–**5** possessed different degrees of conformational flexibility due to the different number of intramolecular hydrogen bonds built inside the monomer architecture. Our study showed that the conformational freedom of the monomer had a profound effect on the polymerization efficiency and the thermoreversible gelation properties of the resulting copolymers. Among all five diacetylene monomers, only the one, that is, **1**-$Py(NH)_2$ which possesses the pyridine-2,6-dicarboxamide unit with two built-in intramolecular H bonds could produce the corresponding poly(amide-triazole) Poly-$(PyNH)_2$ with a significantly higher degree of polymerization (DP) than other monomers with a lesser number of intramolecular H bonds. In addition, it was found that only this polymer exhibited excellent thermoreversible gelation ability in aromatic solvents. A self-assembling model of the organogelating polymer Poly-$(PyNH)_2$ was proposed based on FTIR spectroscopy, XRD, and SEM analyses, in which H bonding, π–π aromatic stacking, hydrophobic interactions, and the structural rigidity of the polymer backbone were identified as the main driving forces for the polymer self-assembly process.

Keywords: catalysis · click chemistry · copper · polymers · supramolecular chemistry

Introduction

The introduction of the 'click chemistry' concept by Sharpless in 2001[1] has led to discovery of new chemical reactions that allow the coupling of basic chemistry building blocks in an extremely effective manner.[2] One of the most popular methods is the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) between azides and alkynes, which results in the formation of 1,4-disubstituted 1,2,3-triazoles[3] in high yields and with excellent regioselectivity. This method has been employed extensively in polymer synthesis.[4] At the same time, the properties of the product triazole unit have also begun to attract a lot of research attention. Various examples have shown that oligo- and polytriazole compounds exhibited interesting conformational and supramolecular properties.[5] For example, oligotriazoles could act as hosts for anions[6] and were capable of forming head-to-tail dimeric structures,[7] whereas polytriazoles were able to act as hydro-[8] and organogelators.[9] Due to its bioisosterecity with the amide functionality,[10] the triazole moiety can be used to replace some of the amide units in a polyamide chain and produce a new class of hybrid molecule poly(amide-triazole), with new functional and supramolecular properties. Earlier we reported the synthesis of several dendronized poly(amide-triazole)s and exemplified the effect of the dendron side chain, the H bonding amide unit, and the relative orientation of triazole motifs on the self-assembling and thermoreversible gelation properties,[11] which demonstrates that the interplay between the amide and triazole functionalities was a key factor for such poly(amide-triazole)s to display rich chemistry. However, the preparation of triazole-rich polymers is not without challenge. One key issue was the formation of cyclic oligomeric byproducts from structurally flexible monomers.[12] This led to poor polymerization efficiencies and most often polymers with low DP values were formed.[13] Herein we wish to report the synthesis of a new class of poly(pyridine-2,6-dicarboxamide-triazole) **1**-$Py(NH)_2$ with intramolecularly H-bonded, structurally rigid pyridine-2,6-dicarboxamide units along the polymer main chain. It was shown that this structurally rigid motif, in comparison to other structurally more flexible dicarboxamide

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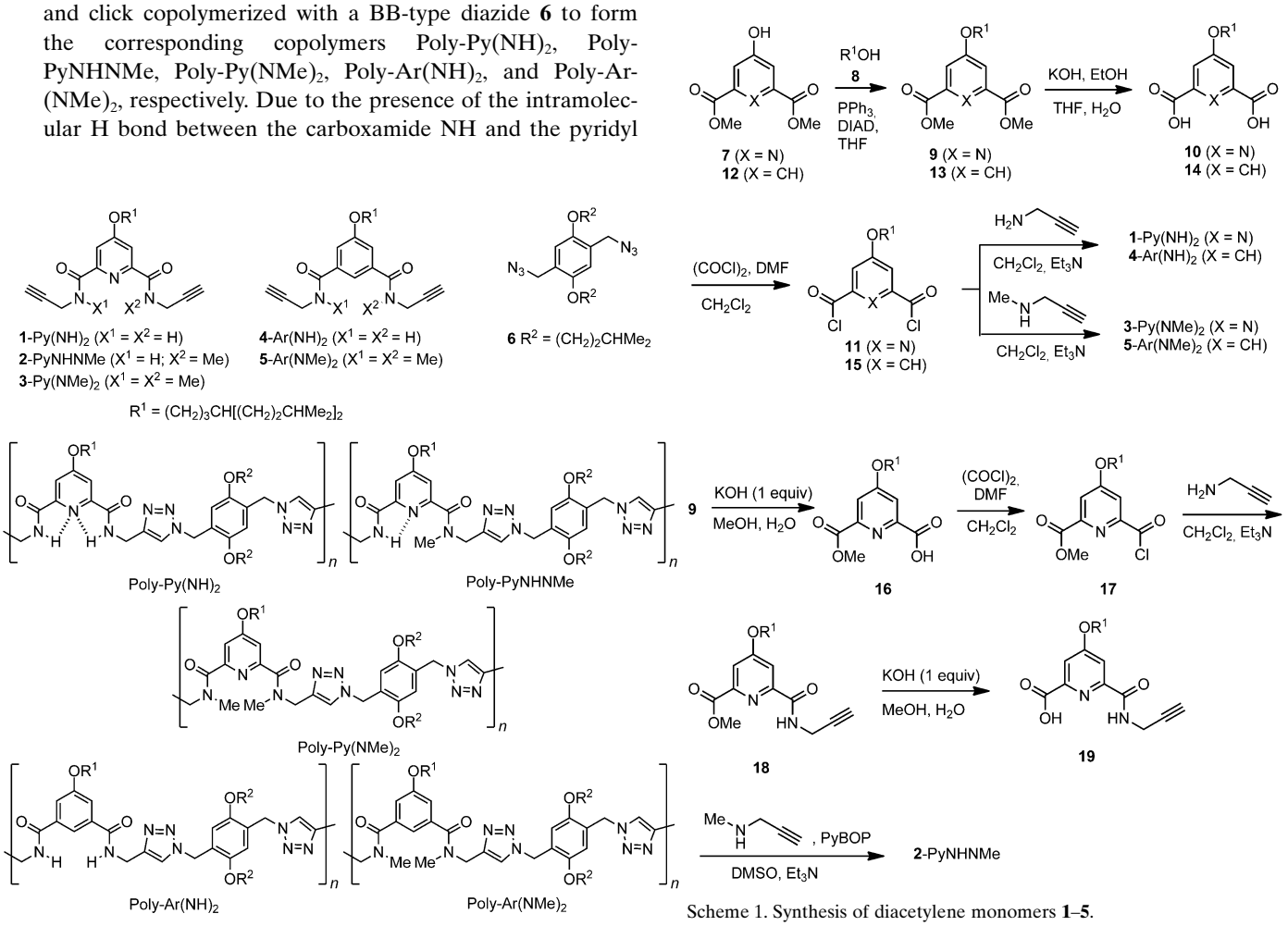
motifs (i.e. **2**–**5**), produced the corresponding polymer Poly-Py(NH)$_2$ with a significantly higher DP value. Furthermore, it was also found that only this polymer Poly-Py(NH)$_2$ could form strong thermoreversible polymer gels[14] with aromatic solvents. The other structurally closely related polymer, Poly-Ar(NH)$_2$, despite containing the same number of carboxamide and triazole units along the main chain but devoid of two intramolecular H bonds, in sharp contrast, was nongelating. It was proposed that the two intramolecular H-bonds in the pyridine-2,6-dicarboxamide moieties were responsible for holding the polymer chain in an extended conformation to facilitate its self-assembling into a three-dimensional network gel structure. This work further highlights new and additional factors in the self-assembly of multifunctional polymers, and should offer insights to the design and preparation of new polymer-based physical gelating materials.

Results and Discussion

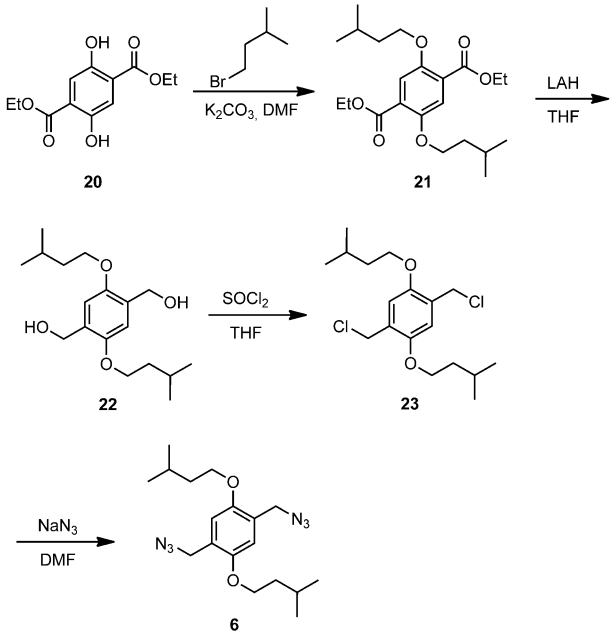
To investigate whether the conformational flexibility of the monomers could exert any effects on CuAAC polymerization efficiency, AA-type diacetylene monomers **1**–**5** with different extents of intramolecular H bonding were prepared and click copolymerized with a BB-type diazide **6** to form the corresponding copolymers Poly-Py(NH)$_2$, Poly-PyNHNMe, Poly-Py(NMe)$_2$, Poly-Ar(NH)$_2$, and Poly-Ar-(NMe)$_2$, respectively. Due to the presence of the intramolecular H bond between the carboxamide NH and the pyridyl nitrogen atom,[15] amongst the monomers **1**–**3**, the conformational flexibility of the two acetylene functionalities should follow the order: **1**-Py(NH)$_2$ < **2**-PyNHNMe < **3**-Py(NMe)$_2$. To further demonstrate the importance of the pyridyl nitrogen atom on the self-assembling properties, the corresponding benzene-1,3-dicarboxamide analogues of **1** and **3** (i.e. **4**-Ar(NH)$_2$ and **5**-Ar(NMe)$_2$, respectively) were also prepared and subjected to the same click copolymerization reaction. Due to the inherent poor solubility of poly(triazole)s, a hydrophobic aliphatic side chain[16] (R^1) was anchored to the monomers to improve the solubility of the resulting polymers.

Preparation of monomers: The various diacetylene **1**–**5** and diazide **6** monomers were readily prepared from commercially available starting materials by simple functional-group transformations (Scheme 1). Hence, the pyridine-2,6-dicarboxamide monomers **1** and **3** could be obtained from dimethyl chelidamate **7** in 65 and 63% yields, respectively, whereas the benzene-1,3-dicarboxamide monomers **4** and **5** were synthesized in 75 and 72% yields, respectively, from dimethyl isophthalate **12**. For the unsymmetrical monomer **2**-PyNHNMe, a reaction sequence involving the sequential introduction of the propargyl amine and *N*-methylpropargyl



Scheme 1. Synthesis of diacetylene monomers **1**–**5**.

amine was carried out, and the overall yield was 66% from compound **9**. On the other hand, the diazide monomer **6** could be prepared from diethyl 2,5-dihydroxyterephthalate **20** in 75% yield in four steps (Scheme 2). Details of the synthetic preparations and characterization data of monomers **1**–**6** can be found in the Supporting Information.



Scheme 2. Synthesis of diazide monomer **6**.

Copolymerizations and polymer characterizations: The click 1:1 copolymerizations between **1**–**5** and **6** were carried out under optimized conditions (~100 mM, $CuSO_4$, sodium ascorbate, DMF/H_2O 9:1, 25°C). The copolymerizations were repeated two-to-six times and the results were reproducible as confirmed by size-exclusion chromatographic analysis (SEC). After polymerization, the product was isolated by dissolving the mixture in a small amount of DMF followed by precipitation with water. Their structures were characterized by ^{1}H NMR spectroscopy and SEC. In all the ^{1}H NMR spectra, the original acetylenic proton signal ($\delta = 2.2$–2.6 ppm) due to the diacetylene monomers disappeared, which confirmed that the copolymerization proceeded to a high degree (>98%) of conversion. Incidentally, the appearance of the triazolyl proton signal at around $\delta = 7.2$–8.0 ppm was noted. Moreover, a significant downfield shift of the N*H* resonance signal was observed for the polymeric compounds when compared to that of the corresponding diacetylene monomer at the same NH concentration. For example, the intramolecular H-bonded N*H* signal of **1**-Py(NH)$_2$, initially located at $\delta = 9.1$ ppm, was further downfield shifted to $\delta = 9.2$–10.9 ppm in Poly-Py(NH)$_2$ (Figure 1). The non-H bonded N*H* signal of 4-Ar(NH)$_2$, which was initially at $\delta =$ 8.1 ppm, was similarly shifted to $\delta = 8.3$–8.5 ppm. Such a downfield shift of the N*H* resonance signals upon polymerization could be attributed to a strengthening of inter- or intramolecular H bonding due to the presence of multiple NH and triazole units in close proximity, a synergistic zip-templating effect that has been reported by Hunter[17] and us[11] before.

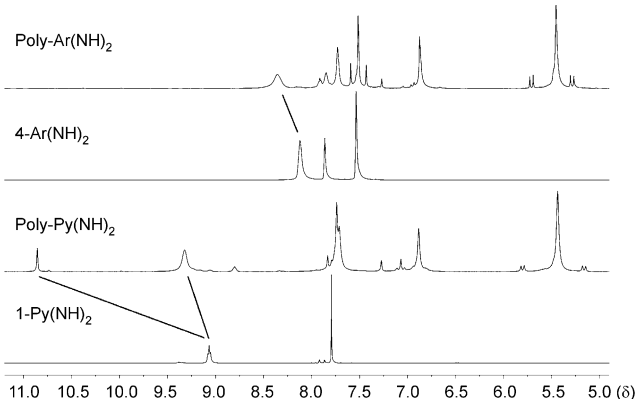


Figure 1. Partial stacked ^{1}H NMR spectra (400 MHz, [D_8]THF, 25°C) of (from top to bottom) Poly-Ar(NH)$_2$, 4-Ar(NH)$_2$, Poly-Py(NH)$_2$, and 1-Py(NH)$_2$. All spectra were recorded at the same total NH concentration (60 mM).

The weight-average molecular weight (M_w), polydispersity index (PDI), and DP values of the click polymers were then determined by SEC analysis (Table 1 and Figure 2). No notable difference in the SEC chromatograms was observed with samples of Poly-Py(NH)$_2$ of 20 times difference in concentration (i.e. 1.0 and 0.05 mg mL^{-1}), which indicated that the samples were free of aggregation under the SEC experimental conditions. Several interesting findings deserved attention. First, low molecular weight (LWM) oligomers (arbitrarily defined as $M_w \leq 4$ kD) were found in various amounts (<0.4–23%), but the relative % was strongly dependent on the structure of the diacetylene monomer. Hence, the structurally more rigid Poly-Py(NH)$_2$ contained <0.4% of such LWM oligomers, whereas the one without intramolecular H-bonds on the polymer backbone (i.e. Poly-Ar(NMe)$_2$) consisted of 23% weight of LWM oligomers. As the molecular masses of the cyclic oligomers are exactly the same as those of the corresponding linear oligomers, we were unable to

Table 1. SEC data of the click polymers.[a]

Polymer	M_w [kD]	PDI	DP	Weight % of LMW fraction[b]	Yield [%]
Poly-Py(NH)$_2$	37	2.2	45	<0.4	84
Poly-PyNHNMe	14	1.3	17	3	85
Poly-Py(NMe)$_2$	13	1.3	15	5	83
Poly-Ar(NH)$_2$	13	1.3	16	7	85
Poly-Ar(NMe)$_2$	8	1.1	10	23	83
Poly([Py(NH)$_2$]$_4$-*ran*-[Py(NMe)$_2$]$_1$)	21	1.6	25	2	84
Poly([Py(NH)$_2$]$_1$-*ran*-[Py(NMe)$_2$]$_1$)	16	1.4	20	3	82

[a] All SEC measurements were performed in THF at 40°C by using polystyrene standards for calibrations. [b] LMW fraction with $M_w \leq 4$ kD.

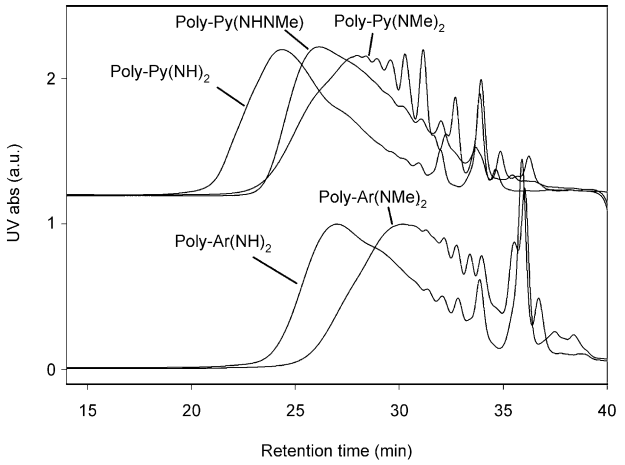
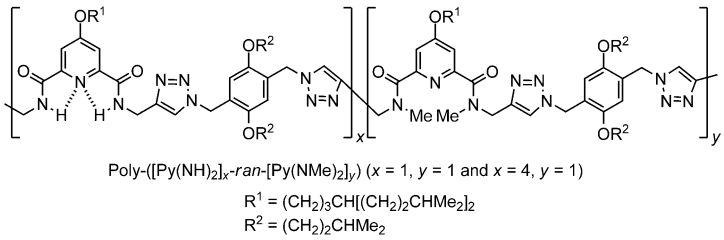


Figure 2. Stacked SEC chromatograms of (top) Poly-Py(NH)$_2$, Poly-PyNHNMe, Poly-Py(NMe)$_2$ and (bottom) Poly-Ar(NH)$_2$, Poly-Ar-(NMe)$_2$. The relative % of LMW oligomers is exaggerated in the plot as the *x*-axis is on a logarithm scale of polymer M_w.

provide conclusive proof that these were cyclic oligomers by MS analysis. However, judging from the complete absence of the acetylenic ^{1}H NMR spectroscopic signals in the NMR spectra and the lack of N_3 absorption from the IR spectra, it was likely that these were cyclic oligomers as those reported earlier by other groups.[12] This finding also highlighted the inherent cyclic oligomerization problem associated with such structurally flexible monomers. In our case, flexible monomers **2**–**5** were simply poor candidates for click linear polymerizations. This could also be reflected in the significant deviation of their corresponding polymer PDI values (1.1–1.3) from the theoretical value (2.0) typical of a step-growth polymerization process. It should be noted that once cyclization occurred, no further addition of monomer was possible. Second, monomers containing more H-bonded NH functionalities produced the corresponding polymer with a higher DP value. Hence, for the pyridine series, the DP value of Poly-Py(NH)$_2$ was higher than that of Poly-PyNHNMe, which in turn was higher than that of Poly-Py-(NMe)$_2$. Similarly, for the benzene series, Poly-Ar(NH)$_2$ had a higher DP value than Poly-Ar(NMe)$_2$. Third, the DP value of the pyridine series was consistently higher than that of the benzene series bearing the same number of NH moieties. Among the five diacetylene monomers, **1**-Py(NH)$_2$ was found to form the corresponding polymer Poly-Py(NH)$_2$ with the highest M_w and DP values. On the other hand, monomer 2-Py(NHNMe), containing only one intramolecular H bond, and 4-Ar(NH)$_2$, containing two NH groups but lacking the pyridyl nitrogen atom required for intramolecular H bonding, polymerized with significantly lower efficiencies. All these results indicated that the polymerization efficiency could be significantly enhanced by imposing conformational rigidity by intramolecular H bonding on the monomer. It should be mentioned here that previous literature examples involving structurally preorganized monomers generally led to the preferential formation of LMW cyclic oligomers,[18] in contrast to the results we encountered here.

To further evaluate the effect of the pyridine-2,6-dicarboxamide H bonding unit on the polymerization, two random copolymers, Poly-([Py(NH)$_2$]$_4$-*ran*-[Py(NMe)$_2$]$_1$) and Poly-([Py(NH)$_2$]$_4$-*ran*-[Py(NMe)$_2$]$_1$), with reduced intramolecular H bonding content, were prepared by mixing 4:1 and 1:1 molar ratios of **1**-Py(NH)$_2$ and **3**-Py(NMe)$_2$, respectively, and copolymerized with 1.0 equivalent of diazide **6**. The structure of the copolymers and the relative amount of NH versus NMe functionality in them, were confirmed by ^{1}H NMR spectroscopy (see the Supporting Information for details). The M_w of these two polymers were found to be in between Poly-Py(NH)$_2$ and Poly-Py(NMe)$_2$, and increased with increasing **1**-Py(NH)$_2$ content, further proving that the rigidity of the pyridine-2,6-dicarboxamide H-bonding unit did improve the DP value.



Thermoreversible gelating properties: Other than better polymerization efficiency, it was also found that only Poly-Py(NH)$_2$ was able to form physical gels in aromatic solvents. The polymer sample was extracted with Na_2EDTA (sodium ethylenediaminetetraacetic acid) solution to remove trace amounts of Cu salt that might interfere with the gelation process.[19] The minimum gelation concentration (MGC) was in the range of 0.5–2 % *w*/*v* (Table 2). As the polymer exhibited excellent gelation power only in aromatic solvents, which implied π–π stacking interactions might play a significant role in the gelation process. In contrast, the di-NMe analogues, Poly-Py(NMe)$_2$ and Poly-Ar(NMe)$_2$, simply dissolved in most of the common organic solvents, whereas Poly-Ar(NH)$_2$ showed poor solubilities in most organic solvents. Interestingly, the two random copolymers were also found to be nongelating (up to 50 mg mL^{-1}) even though they contained a certain percentage of pyridine-2,6-dicar-

Table 2. MGC values of Poly-Py(NH)$_2$.[a]

Solvent	MGC[b]	Solvent	MGC
benzene	10 (CG)	ethanol	P
toluene	5 (CG)	acetone	P
o-xylene	10 (CG)	THF	S
m-xylene	10 (CG)	CH_2Cl_2	S
p-xylene	5 (CG)	DMF	S
o-dichlorobenzene	20 (CG)	*n*-hexane	I

[a] CG = transparent gel, P = precipitated upon cooling, S = solubility $\geq$ 50 mg mL^{-1}, I = insoluble. [b] MGC value was expressed in mg mL^{-1}.

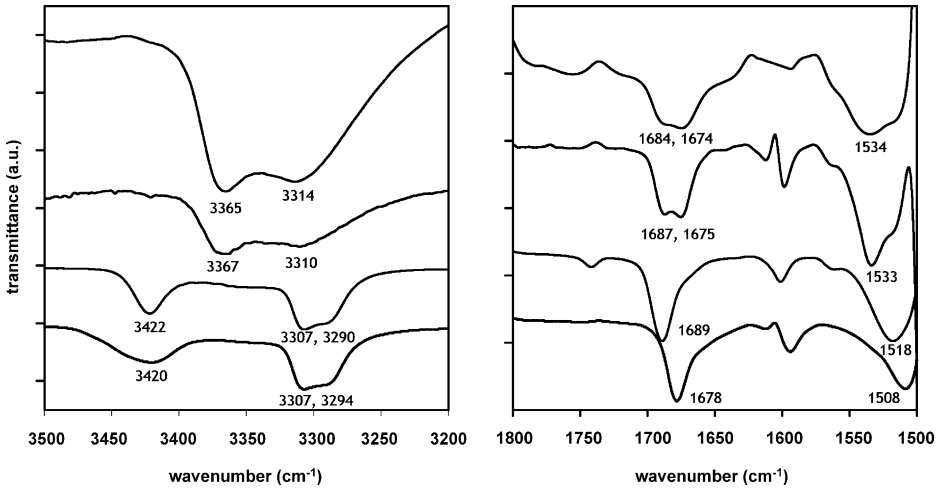


Figure 3. Stacked FTIR spectra of (top to bottom) 10% gel of Poly-Py(NH)$_2$ in toluene; 0.5% toluene solution of Poly-Py(NH)$_2$; 1% toluene solution of 1-Py(NH)$_2$; and 1% toluene solution of 4-Ar(NH)$_2$.

boxamide intramolecular H-bond motif in their backbone structure.

FTIR studies were performed to reveal the extent of H bonding in monomers **1**-Py(NH)$_2$, **4**-Ar(NH)$_2$, and the gelating polymer Poly-Py(NH)$_2$ in various physical states (Figure 3). As expected, in 1% toluene solution, both monomers **1** and **4** did not exhibit any intermolecular H bonding. Hence, the NH (3420, 3290 cm^{-1}) and C=O (1678, 1689 cm^{-1}) stretching frequencies were located at typical non-H-bonded regions. The NH stretching at 3290 cm^{-1} was due to band splitting but not H bonding, and was a typical IR spectral characteristic of symmetrical AA-type diacetylene monomers.[11b,20] It should be noted that although **1**-Py(NH)$_2$ was involved in intramolecular H bonding, the NH stretching frequency was not significantly redshifted because of the nonlinear alignment of the N–H···N H-bonding system. On the other hand, the intramolecular H-bonding nature of **1**-Py(NH)$_2$ could be revealed by examining the NH bending frequency (1518 cm^{-1}), which was blueshifted[21] relative to that of the non-H-bonded **4**-Ar(NH)$_2$ (1508 cm^{-1}). Incidentally, both the NH (from 3420 to 3370/3310 cm^{-1}) and C=O stretching frequencies (from 1689 to 1674 cm^{-1}) experienced redshift, whereas the NH bending exhibited blueshift (from 1518 to 1534 cm^{-1}) in both the solution and gel IR spectra of Poly-Py(NH)$_2$, which indicated that the presence of strong intermolecular H-bonding interactions in the polymer and gel state. It was also noted that part of the C=O stretching remained unchanged ($\approx$1684 cm^{-1}) in Poly-Py(NH)$_2$, which suggested some C=O moieties might not be involved in the intermolecular H bonding in the gel state. In fact, it had been reported that only one of the carbonyl groups was involved in H bonding in the crystal structure of *N*,*N*′-dimethylpyridine-2,6-dicarboxamide.[22]

XRD analyses were carried out to gain further insight on the packing arrangement of Poly-Py(NH)$_2$. For the freeze-dried sample of the 1% gel in toluene, two peaks ($2\theta = 4.00$ and 19.59°) were found, which corresponded to a regular spacing of 22.1 and 4.5 Å, respectively (Figure 4). The *d* spacing of 4.5 Å falls within the range of π–π stacking interaromatic distance,[23] and could be assigned to the distance between the backbones of two neighboring polymer chains. Meanwhile, the *d* spacing of 22.1 Å was roughly two times equal to the span of the hydrophobic side chain. Based on this information, a packing model of Poly-Py(NH)$_2$ was proposed (Figure 5). Because of the presence of the two intramolecular H bonds that hold the polymer chain in extended conformation, the backbone of the polymer will be stiffened to adopt a wormlike structure. The polymer chains are then stacked onto each other with a spacing of approximately 4.5 Å by interchain π–π aromatic stacking and H-bonding interactions

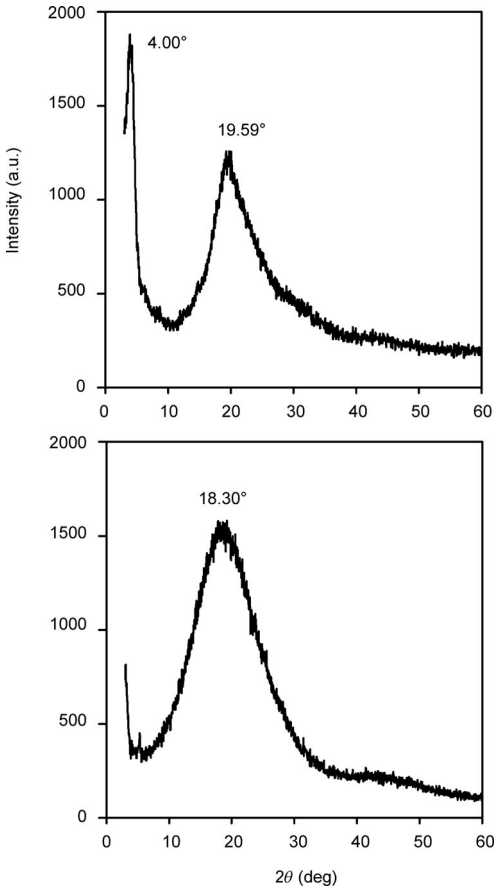


Figure 4. Powder XRD diffractograms of (top) freeze-dried Poly-Py(NH)$_2$ from 1% gel in toluene and (bottom) Poly-Py(NH)$_2$ gel in 1% toluene inside a capillary tube.

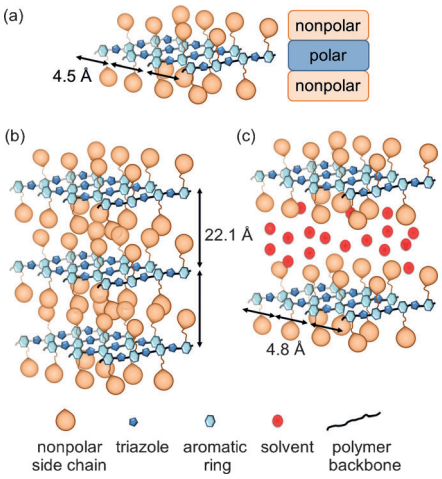


Figure 5. Proposed stacking structure of Poly-Py(NH)$_2$: a) Formation of the sandwich structure by H-bonding and π–π stacking interactions; b) package arrangement of the sandwich structures in the freeze-dried gel state; c) package arrangement of the sandwich structures in 1% toluene gel.

(Figure 5a). Due to the highly hydrophobic nature of the side chains, they would segregate from the polar poly(amide-triazole) backbone and form sandwichlike structures. These sandwichlike layers then stacked onto each other with a spacing of 22.1 Å separated by a thickness of two nonpolar layers (Figure 5b). On the other hand, only one diffraction pattern at $2\theta = 18.30°$ could be observed when a 1% gel sample of Poly-Py(NH)$_2$ was analyzed inside a capillary tube. This translated to a *d* spacing of 4.8 Å that could similarly be attributed to the interchain π–π aromatic stacking distance. This suggested that in the gel state, the polymer chains could still pack in a side by side manner with a slightly lengthened interchain distance of 4.8 Å, whereas the weaker van der Waals interaction between the nonpolar layers was disrupted in the presence of nonpolar aromatic solvents (Figure 5c).[24] Incidentally, SEM images of the freeze-dried gel showed the presence of fiberlike structures with a diameter of 5–10 nm (see the Supporting Information for details). The results further confirmed that these fibers were formed by the regular stacking of the polymer chains by a combination of H bonding, π–π aromatic stacking, and hydrophobic interactions. Based on all these studies, it was proposed that intramolecular H bonding in Poly-Py(NH)$_2$ induced a preorganization of the polymer backbone, and allowed it to pack in an orderly manner to facilitate their further self-assembly. On the other hand, no discernible XRD peaks could be identified in all the other non-gelating polymers.

Conclusion

In summary, we reported here the synthesis and novel organogelating properties of a new class of poly(pyridine-2,6-dicarboxamide-triazole) compounds, Poly-Py(NH)$_2$. The structural rigidity of the intramolecularly H-bonded motif along the polymer backbone could promote the polymerization efficiency by suppressing LMW oligomers formation, and facilitate the packing of the rigidified polymer chain into a three dimensional gel network. More interestingly, the mere presence of secondary amide and triazole functionalities in a polymer does not guarantee it to become gelating, as judging from the nongelating examples of Poly-PyNHNMe and Poly-Ar(NH)$_2$. In addition to the side-chain steric effect[11a] and polymer backbone symmetry effect[11b] reported earlier by us, here in this present work it was found out that the backbone rigidity could also play an important factor in controlling their thermoreversible gelating and self-assembling properties. These new findings should help us in further understanding and unveiling the fundamental factors of polymer self-assembling behavior.

Experimental Section

All reactions were carried out under N_2 at 25 °C unless otherwise stated. The progress of the reactions was monitored by TLC analysis performed on Merck pre-coated silica gel 60F_{254} plates, and compounds were visualized by using a spray of 5% (*w*/*v*) dodecamolybdophosphoric acid in ethanol followed by subsequent heating. Flash column chromatography was carried out on columns of Merck Kwiselgel 60 (230–400 mesh). All reagents were purchased from commercial suppliers and used without further purification unless otherwise stated. THF was freshly distilled prior to use from sodium/benzophenone ketyl under N_2. Dichloromethane was freshly distilled from CaH_2 under N_2.

Compound 1-Py(NH)$_2$: Oxalyl chloride (1.50 mL, 17.29 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a stirred solution of the diacid **10** (2.19 g, 5.77 mmol) in CH_2Cl_2 (20 mL) at 0 °C followed by the addition of one drop of DMF. The reaction mixture was stirred for 4 h from 0 to 25 °C, and then concentrated under reduced pressure to give the diacyl chloride **11** as a yellow solid. Compound **11** was then used directly by mixing with triethylamine (10 mL) at 0 °C. After the mixture had been stirred for 10 min, a solution of propargylamine (1.00 mL, 15.61 mmol) in CH_2Cl_2 (5 mL) was added dropwise at 0 °C. The reaction mixture was allowed to stir for 10 h at 25 °C, and was then quenched with aqueous HCl (30 mL, 1.2 M). The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic extracts were washed with saturated NaCl solution, dried (Na_2SO_4), filtered, and evaporated under reduced pressure to give a brown oil. The oil was purified by flash column chromatography (hexane/EtOAc 3:1 gradient to 1:1) to generate **1**-Py(NH)$_2$ (2.14 g, 4.72 mmol, 82% in two steps) as a pale-yellow oil. R_f: 0.50 (hexane/EtOAc 2:1); ^{1}H NMR: $\delta = 0.87$ (12H, d, $J = 6.8$ Hz; CH_3), 1.08–1.18 (4H, m; CH_2), 1.18–1.31 (5H, m; CH_2, CH_2CHCH_2), 1.31–1.42 (2H, m; CH_2), 1.41–1.53 (2H, m; $CHMe_2$), 1.72–1.82 (2H, m; OCH_2CH_2), 2.25 (2H, br s; C≡CH), 4.08 (2H, t, $J = 6.4$ Hz; OCH_2), 4.29 (4H, dd, $J = 5.6$, 2.4 Hz, $NHCH_2C{\equiv}CH$), 7.84 (2H, m; ArH), 8.05–8.15 ppm (2H, br s; NH); ^{13}C NMR: $\delta = 22.6$, 25.8, 28.2, 29.0, 29.4, 30.9, 35.6, 37.4, 69.4, 71.1, 79.3, 111.4, 150.3, 164.0, 167.8 ppm; ESI: *m*/*z* (%): 476 $[M+Na]^+$ (100); HRMS (ESI): *m*/*z*: calcd for $C_{27}H_{39}N_3O_3+Na^+$: 476.2884; found: 476.2891.

Compound 2-PyNHNMe: Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP; 180 mg, 0.37 mmol) was added to a stirred solution of **19** (103 mg, 0.25 mmol) and *N*-methylpropargylamine (0.10 mL, 1.18 mmol) in DMSO (5 mL). Triethylamine (0.1 mL) was then added to the solution mixture. After 10 h, EtOAc (15 mL) and H_2O (15 mL) were added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with EtOAc (2×15 mL). The combined organic extracts were washed with saturated NaCl, dried (Na_2SO_4), and concentrated under reduced pressure to afford the target

compound **2**-PyNHNHMe (106 mg, 0.23 mmol, 94%) as a pale-yellow oil. R_f=0.42 (hexane/EtOAc 2:1); **2**-PyNHNHMe exists as a mixture of rotational isomers which causes complications of the signal splitting in the ^{1}H and ^{13}C NMR spectra; ^{1}H NMR: δ=0.87 (12H, d, J=6.8 Hz; CH_3), 1.09–1.19 (4H, m; CH_2), 1.19–1.33 (5H, m; CH_2, CH_2CHCH_2), 1.33–1.42 (2H, m; CH_2), 1.42–1.53 (2H, m; $CHMe_2$), 1.73–1.83 (2H, m; OCH_2CH_2), 2.23–2.53 (total 2H, m; C≡CH), 3.12, 3.22 (total 3H, s; NCH_3). 4.09 (2H, t, J=6.4 Hz; OCH_2), 4.15–4.45 (4H, m; $CH_2C{\equiv}C$), 7.23–7.42 (total 1H, m; ArH), 7.74–7.78 (total 1H, m; ArH), 8.04, 8.49 ppm (total 1H, t, J=5 Hz; NH); ^{13}C NMR: δ=22.8, 26.0, 28.4, 29.1, 29.3, 29.6, 31.1, 34.0, 35.9, 36.2, 36.8, 37.5, 41.7, 69.4, 71.7, 71.8, 72.6, 73.1, 78.1, 79.3, 79.5, 79.9, 109.5, 110.2, 112.8, 113.7, 149.7, 150.2, 153.0, 153.9, 163.4, 167.2, 167.5, 167.7, 167.8 ppm; MS (ESI): m/z (%): 468 $[M+H]^+$ (100); HRMS (ESI): m/z: calcd for $C_{28}H_{41}N_3O_3+H^+$: 468.3221; found: 468.3231.

Compound 3-Py(NMe)$_2$: Compound **11** was prepared from the diacid **10** (641 mg, 1.69 mmol) by using the same procedure as above. Triethylamine (2 mL) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of **11** in CH_2Cl_2 (5 mL) at 0°C. After 15 min, a solution of *N*-methylpropargylamine (0.40 mL, 4.74 mmol) in CH_2Cl_2 (3 mL) was added dropwise at 0°C. The reaction mixture was stirred for 10 h at 25°C and quenched with aqueous HCl (10 mL, 1.2 M). The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic extracts were washed with saturated NaCl solution, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give a brown liquid. The brown liquid was then purified by flash column chromatography (hexane/EtOAc 3:1 gradient to 1:1) to produce **3**-Py(NMe)$_2$ (654 mg, 1.36 mmol, 80% in two steps) as a pale-brown liquid. R_f=0.35 (hexane/EtOAc 2:1). Compound **3**-Py(NMe)$_2$ exists as a mixture of three rotational isomers which causes the complication of unequal sized splitting in the ^{1}H and ^{13}C NMR spectra; ^{1}H NMR: δ=0.87 (12H, d, J=6.8 Hz; CH_3), 1.07–1.18 (4H, m; CH_2), 1.18–1.32 (5H, m; CH_2, CH_2CHCH_2), 1.32–1.42 (2H, m; CH_2), 1.42–1.53 (2H, m; $CHMe_2$), 1.72–1.82 (2H, m; OCH_2CH_2), 2.23–2.36 (total 2H, m; C≡CH), 3.12, 3.15, 3.17 (total 6H, s; NMe), 4.05 (2H, t, J=6.4 Hz), 4.28–4.40 (total 4H, m; $CH_2C{\equiv}C$), 7.27–7.30 ppm (total 2H, m; ArH); ^{13}C NMR: δ=22.6, 25.9, 28.3, 29.5, 31.0, 33.4, 35.7, 36.1, 36.2, 36.79, 36.84, 37.3, 40.7, 69.1, 72.28, 72.33, 72.86, 72.89, 78.09, 78.11, 78.26, 111.1, 111.5, 111.6, 153.6, 153.9, 154.0, 166.7, 166.8, 166.9, 167.52, 167.57, 167.63, 167.7 ppm; MS (ESI): m/z (%): 482 $[M+H]^+$ (100); HRMS (ESI): m/z: calcd for $C_{29}H_{43}N_3O_3+H^+$: 482.3377; found: 482.3374.

Compound 4-Ar(NH)$_2$: Oxalyl chloride (0.11 mL, 1.29 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of diacid **14** (222 mg, 0.59 mmol) in CH_2Cl_2 (5 mL) at 0°C followed by the addition of one drop of DMF. The reaction mixture was allowed to stir for 4 h at 0–25°C and concentrated under reduced pressure to give compound **15** as a deep-orange solid which was then used directly without purification. Triethylamine (1 mL) in CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of **15** in CH_2Cl_2 (5 mL) at 0°C. After 10 min, a solution of propargylamine (0.10 mL, 1.56 mmol) in CH_2Cl_2 (5 mL) was added dropwise at 0°C. The reaction mixture was allowed to stir for 10 h at 25°C and then quenched by the addition of aqueous HCl (10 mL, 1.2 M). The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2× 10 mL). The combined organic extracts were washed with saturated NaCl solution, dried (Na_2SO_4), filtered, and evaporated under reduced pressure to give a deep-brown liquid. The liquid was purified by flash column chromatography (hexane/EtOAc 3:1 gradient to 1:1) to generate **4**-Ar(NH)$_2$ (239 mg, 0.53 mmol, 90% in two steps) as a white solid. M.p. 67–69°C; R_f=0.62 (hexane/EtOAc 2:1); ^{1}H NMR: δ=0.87 (12H, d, J=6.4 Hz; CH_3), 1.09–1.19 (4H, m; CH_2), 1.19–1.34 (5H, m; CH_2, CH_2CHCH_2), 1.34–1.42 (2H, m; CH_2), 1.42–1.54 (2H, m; $CHMe_2$), 1.71–1.81 (2H, m; OCH_2CH_2), 2.29 (2H, t, J=2.4 Hz; C≡CH), 4.00 (2H, t, J=6.4 Hz; OCH_2), 4.24 (4H, dd, J=2.4, 4.8 Hz; $CH_2C{\equiv}C$), 6.50–6.62 (2H, brs; NH), 7.46 (2H, brs; ArH), 7.73 ppm (1H, brs; ArH); ^{13}C NMR: 22.7, 26.3, 28.4, 29.8, 29.9, 31.0, 35.8, 37.6, 69.0, 71.9, 79.4, 116.9, 117.3, 135.2, 159.5, 166.8 ppm; MS (ESI): m/z (%): 453 $[M+H]^+$ (100); HRMS (ESI): m/z: calcd for $C_{28}H_{40}N_2O_3+H^+$: 453.3112; found: 453.3111; elemental analysis calcd (%) for $C_{28}H_{40}N_2O_3$: C 74.30, H 8.91, N 6.19; found: C 73.99, H 9.14, N 6.13.

Compound 5-Ar(NMe)$_2$: The diacyl chloride **15** was prepared from diacid **14** (201 mg, 0.53 mmol) by using the same procedure as described previously. Triethylamine (1 mL) in CH_2Cl_2 (1 mL) was added dropwise to a stirred solution of **15** in CH_2Cl_2 (5 mL) at 0°C. After 15 min, a solution of *N*-methylpropargylamine (0.10 mL, 1.18 mmol) in CH_2Cl_2 (3 mL) was added dropwise at 0°C. The reaction mixture was stirred for 10 h at 25°C and quenched by the addition of aqueous HCl (10 mL, 1.2 M). The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2×10 mL). The combined organic extracts were washed with saturated NaCl solution, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give a brown liquid which was then purified by flash column chromatography (hexane/EtOAc 3:1 gradient to 1:1) to produce **5**-Ar(NMe)$_2$ (223 mg, 0.46 mmol, 87% in two steps) as a pale-yellow liquid. R_f=0.48 (hexane/EtOAc 2:1); **5**-Ar(NMe)$_2$ exists as a mixture of three rotational isomers which causes the complication of the unequal sized splitting in the ^{1}H and ^{13}C NMR spectra; ^{1}H NMR: δ=0.87 (12H, d, J=6.4 Hz; CCH_3), 1.09–1.19 (4H, m; CH_2), 1.19–1.33 (5H, m; CH_2, CH_2CHCH_2), 1.33–1.42 (2H, m; CH_2), 1.42–1.53 (2H, m; $CHMe_2$), 1.70–1.80 (2H, m; OCH_2CH_2), 2.20–2.40 (total, 2H, m; C≡CH), 3.00–3.20 (total, 6H, m; NCH_3), 3.97 (2H, t, J=6.4 Hz; OCH_2), 3.95–4.40 (total 4H, m; $CH_2C{\equiv}C$), 7.00–7.15 ppm (total 3H, m; ArH); ^{13}C NMR: δ= 22.6, 26.6, 28.4, 30.1, 31.3, 31.5, 33.9, 34.4, 35.1, 35.3, 36.1, 37.8, 39.3, 69.2, 72.8, 73.4, 73.6, 78.4, 115.0, 117.5, 137.4, 159.5, 170.1 ppm; MS (ESI): m/z (%): 481 $[M+H]^+$ (100); HRMS (ESI): m/z: calcd for $C_{30}H_{44}N_2O_3+H^+$: 481.3425; found: 481.3414.

Compound 6: A solution of compound **22** (2.04 g, 6.57 mmol) in THF (10 mL) was added dropwise to a solution of $SOCl_2$ (5 mL) in THF (10 mL) at 0°C. The reaction mixture was stirred for 2 h and then poured into iced water (20 mL). The mixture was extracted with diethyl ether (3×20 mL) and the combined organic extracts were washed with saturated Na_2CO_3 and saturated NaCl, dried ($MgSO_4$), and concentrated under reduced pressure to give the dichloride **23** (2.19 g, 6.31 mmol, 96%) as a pale-yellow solid. R_f=0.95 (hexane/EtOAc 2:1); compound **23** was found to be unstable in the presence of silica gel and was, therefore, used directly without further purification. A mixture of sodium azide (1.40 g, 21.5 mmol) and **23** (2.19 g, 6.31 mmol) in DMF (15 mL) was stirred for 48 h. Water (20 mL) was added to quench the reaction and the mixture was extracted with diethyl ether (3×20 mL). The combined organic extracts were washed with saturated NaCl, dried ($MgSO_4$), and then concentrated under reduced pressure to give a yellow solid. The solid was then purified by flash column chromatography (hexane/CH_2Cl_2 6:1 gradient to 4:1) to afford the desired diazide monomer **6** (2.08 g, 5.74 mmol, 91%) as a pale-yellow solid. M.p. 47–48°C; R_f=0.40 (hexane/CH_2Cl_2 4:1); ^{1}H NMR: 0.97 (12H, d, J=6.4 Hz; CH_3), 1.69 (4H, q, J=6.4 Hz; CH_2CH_2CH), 1.77–1.92 (2H, m; $CHMe_2$), 3.99 (4H, t, J=6.8 Hz; OCH_2), 4.36 (4H, s; $ArCH_2N_3$), 6.83 ppm (2H, s; ArH); ^{13}C NMR: δ=22.7, 25.2, 38.2, 50.1, 67.3, 113.5, 124.8, 150.8 ppm; MS (ESI): m/z (%): 383 $[M+Na]^+$ (50); HRMS (ESI): m/z: calcd for $C_{18}H_{28}N_6O_2+K^+$: 399.1905; found: 399.1905.

Compound Poly-Py(NH)$_2$: Aqueous $CuSO_4$ (0.50 mL, 0.056 M) was added to a stirred solution of **1**-Py(NH)$_2$ (194 mg, 0.43 mmol), **6** (154 mg, 0.43 mmol), and sodium ascorbate (10 mg, 0.05 mmol) in DMF (4.5 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture to form a clear solution and the solution was poured into water (30 mL). The solid was then filtered and dried under reduced pressure to give Poly-Py(NH)$_2$ (292 mg, 84%) as a pale-yellow powder. ^{1}H NMR ([d_8]THF): δ=0.70–1.02 (24H, m; CCH_3), 1.14–1.94 (21H, m), 3.70–4.04 (4H, m; OCH_2), 4.07–4.25 (2H, m; OCH_2), 4.37–4.80 (4H, m; NCH_2Triaz), 5.30–5.65 (4H, m; $ArCH_2$Triaz), 6.74–7.02 (2H, m; ArH), 7.02–7.14, 7.25–7.33, 7.78–7.90 (total 2H, m; TriazH), 7.60–7.80 (2H, m; ArH), 8.77–8.90, 9.10–9.60, 10.85–10.95 ppm (total 2H, m; NH).

Compound Poly-Py(NMe)$_2$: Aqueous $CuSO_4$ (0.10 mL, 0.070 M) was added to a stirred solution of **3**-Py(NMe)$_2$ (51 mg, 0.11 mmol), **6** (37 mg, 0.11 mmol), and sodium ascorbate (5 mg, 0.03 mmol) in DMF (0.9 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture to give a clear solution, and then the solution mixture was poured into water (10 mL). The solid was then filtered

and dried under reduced pressure to give Poly-Py(NMe)$_2$ (75 mg, 83%) as a pale-yellow glassy solid. ^{1}H NMR ([d$_8$]THF): δ = 0.80–1.00 (24H, m; CCH_3), 1.14–1.90 (21H, m), 2.60–3.10 (6H, m; NCH_3), 3.74–4.02 (4H, m; OCH_2), 4.02–4.22 (2H, m; OCH_2), 4.31–4.76 (4H, m; NCH_2Triaz), 5.25–5.75 (4H, m; $ArCH_2$Triaz), 6.66–6.99 (2H, m; ArH), 7.00–7.44 (2H, m; TriazH), 7.60–7.90 ppm (2H, m; ArH).

Compound Poly-Ar(NH)$_2$: Aqueous $CuSO_4$ (0.50 mL, 0.056 M) was added to a stirred solution of 4-Ar(NH)$_2$ (179 mg, 0.40 mmol), **6** (143 mg, 0.40 mmol), and sodium ascorbate (10 mg, 0.05 mmol) in DMF (4.5 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture until a clear solution was obtained, and then the solution mixture was poured into water (30 mL). The solid was then filtered and dried under reduced pressure to give Poly-Py(NH)$_2$ (274 mg, 85%) as a pale-yellow powder. ^{1}H NMR: ([d$_8$]THF): 0.75–1.10 (24H, m; CCH_3), 1.14–1.90 (21H, m), 3.87–4.10 (6H, m; OCH_2), 4.37–4.70 (4H, m; NCH_2Triaz), 5.25–5.75 (4H, m; $ArCH_2$Triaz), 6.77–6.97 (2H, m; ArH), 7.45–7.56 (2H, m; ArH), 7.67–7.78 (1H, m; ArH), 7.78–7.94 (2H, m; TriazH), 8.20–8.55 ppm (2H, m; NH).

Compound Poly-Ar(NMe)$_2$: Aqueous $CuSO_4$ (0.10 mL, 0.070 M) was added to a stirred solution of **5**-Ar(NMe)$_2$ (48 mg, 0.10 mmol), **6** (36 mg, 0.10 mmol), and sodium ascorbate (5 mg, 0.03 mmol) in DMF (0.9 mL). After 24 h, DMF was added to the mixture until a clear solution was obtained, and the solution mixture was poured into water (10 mL). The solid was then filtered and dried under reduced pressure to give Poly-Ar(NMe)$_2$ (71 mg, 84%) as a pale-yellow glassy solid. ^{1}H NMR ([d$_8$]THF): δ = 0.80–1.02 (24H, m; CCH_3), 1.12–1.95 (21H, m), 2.55–3.10 (6H, m; NCH_3), 3.75–4.12 (6H, m; OCH_2), 4.16–4.71 (4H, m; NCH_2Triaz), 5.25–5.75 (4H, m; $ArCH_2$Triaz), 6.77–6.92 (2H, m; ArH), 6.92–7.00 (1H, m; ArH), 7.00–7.52 (2H, m; TriazH), 7.52–8.20 ppm (2H, m; ArH).

Compound Poly-PyNHNMe: Aqueous $CuSO_4$ (0.15 mL, 0.070 M) was added to a stirred solution of **2**-PyNHNMe (76 mg, 0.16 mmol), **6** (58 mg, 0.16 mmol), and sodium ascorbate (5 mg, 0.03 mmol) in DMF (1.4 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture until a clear solution was formed, and then the solution mixture was poured into water (10 mL). The solid was then filtered and dried under reduced pressure to give Poly-PyNHNMe (114 mg, 85%) as a pale-yellow powder. ^{1}H NMR ([d$_8$]THF): δ = 0.70–1.00 (24H, m; CCH_3), 1.14–1.94 (21H, m), 2.81–3.10 (3H, m; NCH_3), 3.80–4.04 (4H, m; OCH_2), 4.04–4.24 (2H, m; OCH_2), 4.46–4.88 (4H, m; NCH_2Triaz), 5.32–5.70 (4H, m; $ArCH_2$Triaz), 6.70–6.94 (2H, m; ArH), 7.14–7.24, 7.36–7.46 (total 2H, m; TriazH), 7.60–7.90 (2H, m; ArH), 8.65–8.75, 9.48–9.62 ppm (total 1H, m; NH).

Compound Poly([Py(NH)$_2$]$_1$-*ran*-[Py(NMe)$_2$]$_1$): Aqueous $CuSO_4$ (0.10 mL, 0.070 M) was added to a stirred solution of **1**-Py(NH)$_2$ (38.5 mg, 0.085 mmol), **3**-Py(NMe)$_2$ (41.0 mg, 0.085 mmol), **6** (61.1 mg, 0.17 mmol), and sodium ascorbate (5 mg, 0.03 mmol) in DMF (0.9 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture until a clear solution was formed, and then the solution mixture was poured into water (10 mL). The solid was then filtered and dried under reduced pressure to give Poly([Py(NH)$_2$]$_1$-*ran*-[Py(NMe)$_2$]$_1$) (115 mg, 82%) as a pale-yellow powder. ^{1}H NMR ([d$_8$]THF): δ = 0.72–1.10 (48H, m; CCH_3), 1.14–1.90 (42H, m), 2.70–3.15 (6H, m; NCH_3), 3.75–4.03 (8H, m; OCH_2), 4.03–4.24 (4H, m; OCH_2), 4.36–4.90 (8H, m; NCH_2Triaz), 5.35–5.70 (8H, m; $ArCH_2$Triaz), 6.38–7.00 (4H, m; ArH), 7.00–7.42 (4H, m; TriazH), 7.90–7.93 (4H, m; ArH), 8.77–8.84, 9.14–9.54, 9.97–10.01 ppm (total 2H, m; NH).

Compound Poly([Py(NH)$_2$]$_4$-*ran*-[Py(NMe)$_2$]$_1$): Aqueous $CuSO_4$ (0.20 mL, 0.070 M) was added to a stirred solution of **1**-Py(NH)$_2$ (100.2 mg, 0.221 mmol), **3**-Py(NMe)$_2$ (26.6 mg, 0.055 mmol), **6** (99.6 mg, 0.276 mmol), and sodium ascorbate (10 mg, 0.05 mmol) in DMF (1.8 mL). The CuAAC polymerization was allowed to proceed for 24 h. DMF was added to the solution mixture until a clear solution was formed, and then the solution mixture was poured into water (20 mL). The solid was then filtered and dried under reduced pressure to give Poly([Py(NH)$_2$]$_4$-*ran*-[Py(NMe)$_2$]$_1$) (190 mg, 84%) as a pale-yellow powder. ^{1}H NMR ([d$_8$]THF): δ = 0.72–1.10 (120H, m; CCH_3), 1.14–1.90 (105H, m), 2.70–3.10 (6H, m; NCH_3), 3.75–4.04 (20H, m; OCH_2), 4.04–4.25 (10H, m; OCH_2), 4.36–4.80 (20H, m; NCH_2Triaz), 5.25–5.70 (20H, m; $ArCH_2$Triaz), 6.72–7.00 (10H, m; ArH), 7.00–7.33 (10H, m; TriazH), 7.57–7.93 (10H, m; ArH), 8.77–8.84, 9.14–9.54, 9.97–10.01 ppm (total 8H, m; NH).

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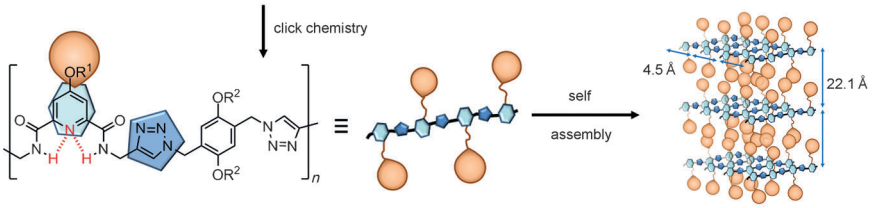

Supramolecular chemistry: The presence of an intramolecular hydrogen-bonding pyridine-2,6-dicarboxamide unit inside a diacetylene monomer promoted its AABB click copolymerization efficiency with a diazide by reducing the amount of low molecular weight oligomers; this structural motif also conferred excellent thermoreversible gelating properties to the resulting poly(amide-triazole) compound (see scheme).