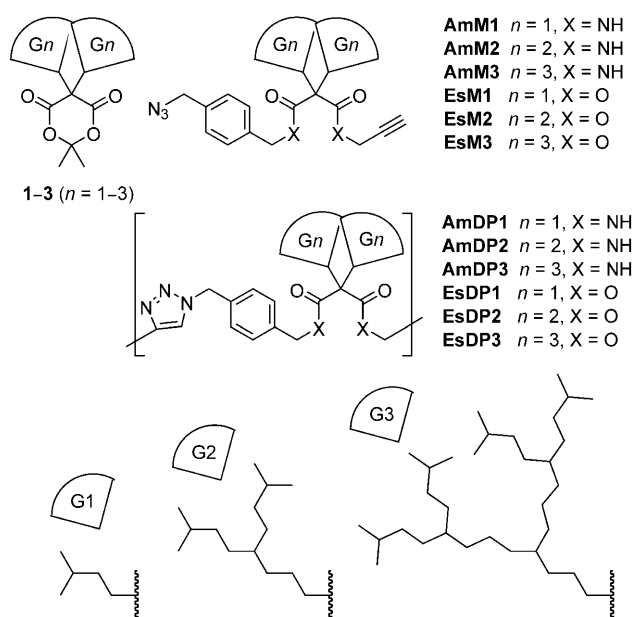


Dendronized Polymer Organogels from Click Chemistry: A Remarkable Gelation Property Owing to Synergistic Functional-Group Binding and Dendritic Size Effects**

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The use of 1,3-dipolar cycloaddition reactions between azides and alkynes (click chemistry) has been extremely successful as a versatile synthetic tool to construct novel polymeric systems.^[1] Whereas the main thrust has been focused on building up highly elaborate polymeric architectures, such as block copolymers, star polymers, dendrimers, and hyper-branched polymers, it is also noted that the physical properties of such poly(triazole)-based materials are little studied.^[1c] Additionally, although there are many examples of the synthesis of dendrimers using click chemistry, only a few concern the preparation of dendronized polymers.^[2] These are polymers incorporating multiple dendron segments stemming from a linear polymer backbone and are commonly prepared by graft-to, graft-from, or macromonomer polymerization approaches.^[3] The major challenges for these approaches are the difficulty in ensuring complete dendron coverage in the graft-to and graft-from strategies, and the sometimes poor polymerization efficiency in the macromonomer strategy. To improve the synthetic efficacy, it is necessary to make use of reactions that offer perfect conversion efficiency (such as click chemistry). Herein we wish to report a) the successful click synthesis of two different series of dendronized polymers (DPs), **AmDP1–AmDP3** and **EsDP1–EsDP3**, from heterobifunctional amide-linked macromonomers (**AmM1–AmM3**) and ester-linked macromonomers (**EsM1–EsM3**), respectively, b) the novel and unique organogelation property of one such poly(triazole)-based dendronized polymer **AmDP2**, c) the remarkable functional-group synergistic effect on polymer interchain H-bonding, owing to the placing of many amide functionalities in close proximity along the polymer chain, and most importantly d) that the macromolecular interactions among the dendronized polymer chains are strongly influenced by the size of

dendritic appendages and the nature of the linker functionality. To our knowledge, synthesis of dendronized polymers by AB-type macromonomer polymerization has not been reported before. Moreover, although physical organogels based on dendrimers^[4] and linear polymers^[5] are known, those based on click poly(triazole) polymers^[6] and dendronized polymers^[7] are extremely rare.



The click macromonomer polymerization is basically a step-growth polymerization. Therefore, to achieve a higher degree of polymerization (DP), it must be ensured that the AB-hetero-bifunctional monomers **AmM1–AmM3** are of perfect purity and structural homogeneity. For this purpose, we made use of the symmetrical aliphatic hydrocarbon-based Meldrum's acids **1–3**^[8] as our starting materials. Simple functional-group transformations then led to the target amide-linked macromonomers **AmM1–AmM3** in good yields and high purities (see Supporting Information). The macromonomers **AmM1–AmM3** were then polymerized in the presence of sodium ascorbate and CuSO_4 in a 1:1:1 solvent mixture of THF, DMF, and water at 25°C for 4 days. To counteract the poor solubility of the products, DMF was added to maintain a homogenous reaction mixture, at least during the initial stage of the polymerizations. The dendronized polymers **AmDP1** (70% yield) and **AmDP2** (62% yield)

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were isolated by precipitation from the reaction mixture, whereas **AmDP3** (81 % yield) was obtained as a solid by solvent extraction. For comparison studies, the corresponding ester-linked macromonomers **EsM1–EsM3** were also prepared and polymerized to give the corresponding click dendronized polymers **EsDP1–EsDP3** (see Supporting Information). Both the ester-linked **EsM1–EsM3** and, to a lesser extent, the amide-linked **AmM1–AmM3** were shown to undergo thermal self-clicking when stored as neat oils at 25 °C. The presence of the amide and triazole repeating units rendered the dendronized polymers quite polar. For **AmDP1**, solubility was so poor that its characterization could only be conducted in DMF or DMSO solution. However, because of the presence of larger, nonpolar hydrocarbon sectors, better solubilities were observed for **AmDP2** and **AmDP3**.

The structure of the amide-linked dendronized polymers were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and size-exclusion chromatography (SEC). The ^1H NMR spectra revealed the complete disappearance of the acetylenic proton signal at approximately $\delta = 2.2$ ppm and the appearance of the triazole proton signal at approximately $\delta = 7.9$ ppm (in $[\text{D}_6]\text{DMSO}$) or 7.4–7.7 ppm (in $[\text{D}_8]\text{THF}$), indicating that all monomer was consumed during the polymerization (Figure 1). However, there was a notable

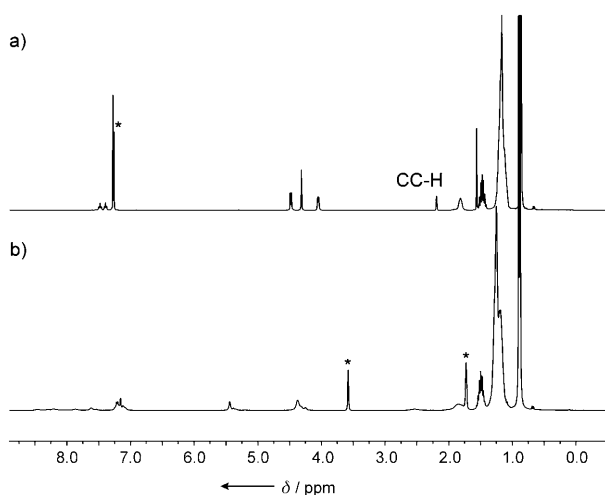


Figure 1. ^1H NMR spectra of a) third generation (G3) macromonomer **AmM3** (in CDCl_3) and b) dendronized polymer **AmDP3** (15% w/v in $[\text{D}_8]\text{THF}$ at 50 °C). Peaks marked with an asterisk are signals due to residual solvent.

difference between the ^1H NMR spectra (at 50 °C) of **AmDP2** and **AmDP3** (see Supporting Information). While all N–H signals from **AmDP3** (15% w/v in $[\text{D}_8]\text{THF}$) resonated between $\delta = 7.7$ and $\delta = 8.5$ ppm, two additional, but unusually downfield N–H signals were found at approximately $\delta = 10.6$ ppm for **AmDP2** when the sample concentration was > 3% w/v in $[\text{D}_8]\text{THF}$. Additionally, **AmDP2** was also found to form a partial gel when the concentration was > 3% in $[\text{D}_8]\text{THF}$. It was interesting to note that such downfield N–H signals were not found for **AmDP2** when the concentration was < 3%, at which concentration the sample was non-

gelating in $[\text{D}_8]\text{THF}$, indicating that the amide hydrogen atoms must be involved in a stronger H-bonding environment in **AmDP2** than those in **AmDP3**. Surprisingly, the SEC chromatographs of **AmDP2** and **AmDP3** showed the presence of 2–4 wt % of oligomeric species (Figure 2). In both

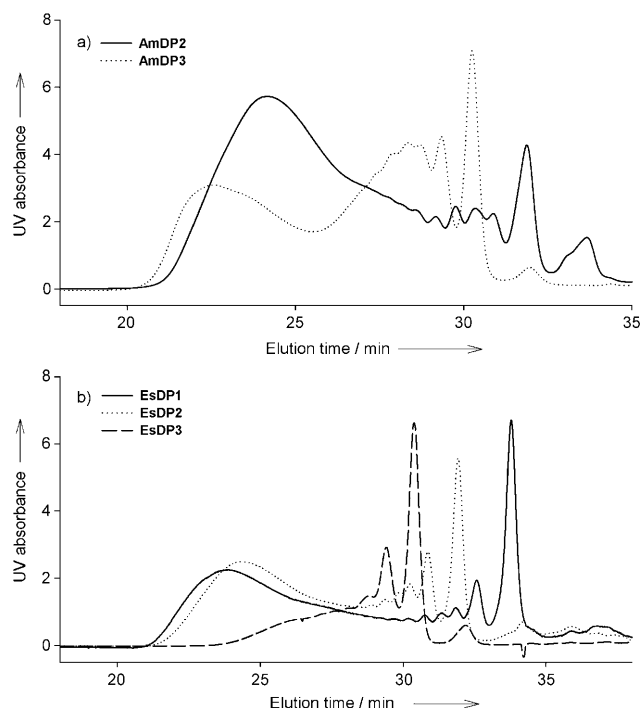


Figure 2. Stacked SEC chromatographs of a) **AmDP2** and **AmDP3** and b) **EsDP1–EsDP3**. The wt % of the oligomers are exaggerated in these plots as the x-axis (elution time) is on a logarithm scale of polymer molecular weight.

cases, there was even a peak with a longer retention time than that of the monomer (see Supporting Information). In addition, subjecting the initial click dendronized polymer **EsDP2** to reaction in the presence of CuSO_4 for an additional 48 h did not change the appearance of the SEC chromatograph, indicating that these oligomeric species were most likely cyclic. The formation of cyclic oligomers using click chemistry has been reported before.^[9] Disregarding the signals of the lower molecular weight oligomers up to the hexamer, the SEC data of the dendronized polymers were tabulated (Table 1). The polydispersity values (PDI) were close to 2, a typical value expected from a step-growth polymerization. The degree of polymerization (DP) for the amide-linked compounds was generally higher than for the ester-linked series of the same generation (G_n), owing mainly to the lower tendency of amide-linked monomers to form cyclic oligomers. As cyclization was an inevitable side reaction, the DP values were generally low (30–60). However, as many previous studies revealed that SEC measurements tend to underestimate the actual M_w values by a factor of 2–8,^[3d] the actual DP values could be between 50 and 500, and therefore click chemistry could still be considered an efficient polymerization process. The DP values dropped with increasing dendrimer generation, suggesting that steric hindrance

Table 1: SEC data of dendronized polymers **AmDP1–AmDP3** and **EsDP1–EsDP3**.^[a]

Polymer	M_w	PDI	DP	Weight % of LMW fraction ^[b]
AmDP1 ^[c]	—	—	—	—
AmDP2	27 300	1.84	40	2
AmDP3	43 700	2.21	37	4
EsDP1	28 000	2.19	66	2
EsDP2	24 300	1.71	36	4
EsDP3	14 000	1.11	12	49

[a] All experiments were conducted in THF using polystyrenes as calibration standards. [b] Low MW fraction up to hexamer. See Supporting Information for details of calculation. [c] Not determined because of poor solubility in THF.

was a dominant retardation factor for the polymerization process. In fact, oligomers (49% by weight) were the major products from the ester-linked G3 monomer **EsM3**.

Among the three amide-linked dendronized polymers, only **AmDP2** was found to form strong organogels in organic solvents, with minimum gelation concentration (MGC) down to 5 mg mL⁻¹ (Table 2), whereas **AmDP1** and **AmDP3** did

Table 2: Minimum gel concentration (MGC) values [mg mL⁻¹] of dendronized polymer **AmDP2** in organic solvents.^[a]

Solvent	MGC	Solvent	MGC
<i>n</i> -hexane	I	toluene	5 (CG)
CHCl ₃	S ^[b]	<i>o</i> -xylene	5 (CG)
EtOAc	10 (OG)	<i>m</i> -xylene	5 (CG)
acetone	10 (OG)	<i>p</i> -xylene	5 (CG)
EtOH	20 (OG)	<i>o</i> -DiClbenzene	5 (CG)
THF	50 (OG)	anisole	10 (CG)
benzene	10 (CG)	nitrobenzene	10 (TG)

[a] CG = transparent gel; TG = translucent gel; OG = opaque gel; S = soluble; I = insoluble. [b] Solubility ≥ 50 mg mL⁻¹.

not exhibit any gelation in any of the solvents tested. Interestingly, stirring a sample of **AmDP2** in a CHCl₃/aqueous ethylenediaminetetraacetic acid (EDTA) biphasic solution for 24 h at 25 °C did not reduce its gelation power, indicating that gelation was not due to cross-linking of the dendronized polymer chains through Cu complexation to the triazole moieties.^[6] Moreover, the three ester-linked dendronized polymers **EsDP1–EsDP3** were also devoid of gelation properties. Therefore the key structural element that was responsible for gelation must be the amide-linker functionality. It was also noted that weak, opaque gels were formed with non-aromatic solvents, such as CHCl₃ or EtOH, while strong transparent gels were formed with aromatic solvents, suggesting that the π – π stacking effect between the benzene/triazole units and aromatic solvents may also contribute to the gelation mechanism.^[10]

FT-IR studies were carried out on the monomers and the amide-linked polymers (Figure 3 and Table 3). 5–20% solutions of the monomers in toluene showed four characteristic IR absorptions at approximately 3430, 3310, 2100, and 1680 cm⁻¹, which could be attributed to N–H, \equiv C–H, N₃, and C=O stretching vibrations, respectively. In particular, the

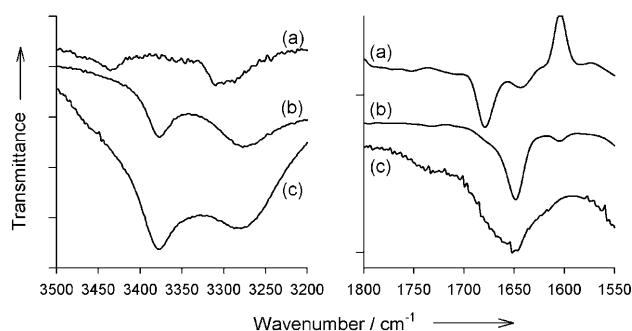


Figure 3. Two regions of the FT-IR spectra of a) **AmM2** (5% solution in toluene); b) **AmDP2** (1% gel in toluene) and c) **AmDP2** (solid in KBr disc).

Table 3: FT-IR data [cm⁻¹] of macromonomers and dendronized polymers in different physical states.

Sample	State	N–H	\equiv CH	N ₃	C=O
AmM1	5% solution in PhMe	3430	3307	2098	1676
AmM2	5% solution in PhMe	3436	3310	2099	1679
AmM3	20% solution in PhMe	3431	3314	2098	1679
AmDP1	solid	3338	—	—	1668
AmDP2	1% gel in PhMe	3378, 3285	—	—	1649
	1% freeze dried gel in PhMe	3378, 3287	—	—	1653
	solid in KBr disc	3377, 3279	—	—	1652
AmDP3	solid	3350	—	—	1653
	40% solution in PhMe	3418, 3328	—	—	1676

N–H and C=O absorption peaks match very well to those of non-hydrogen-bonded secondary amides,^[11] indicating that the monomers did not form H-bond aggregates in toluene. After click polymerization, the peaks corresponding to the \equiv C–H and N₃ absorptions disappeared, and the N–H and C=O absorptions were significantly red-shifted (50–150 cm⁻¹ for N–H, 10–30 cm⁻¹ for C=O) in the solid samples of **AmDP1–AmDP3**, indicating the presence of interchain H-bonds in the solid state. For the organogel and xerogel samples obtained from 1% **AmDP2** in toluene, the N–H absorption was split into two peaks. Both peaks were red-shifted (60 and 140 cm⁻¹) relative to the monomer, as was the C=O absorption (30 cm⁻¹). In contrast, the corresponding red-shift values of a 40% solution sample of **AmDP3** in toluene were much smaller (ca. 10 and 100 cm⁻¹ for N–H, and 3 cm⁻¹ for C=O), suggesting that the extent of interchain H-bonding was significantly weaker than that for **AmDP2**. This finding was consistent with those obtained from the ¹H NMR spectroscopic data. Unfortunately, we were unable to record the FT-IR spectrum of **AmDP1** in solution in toluene, as the compound is insoluble in nonpolar solvents.

The morphology of the supramolecular dendronized polymer gel **AmDP2** was visualized by scanning electron microscopy (SEM) (Figure 4). The xerogels obtained from freeze drying of a 1% sample in *p*-xylene showed the presence of three dimensional networks formed by the entanglement of fibers with length of tens of micrometers and diameter ranging from 50–70 nm. The diameter of such nanofibers was much larger than expected for a single dendronized polymer chain, and suggested that the xerogels

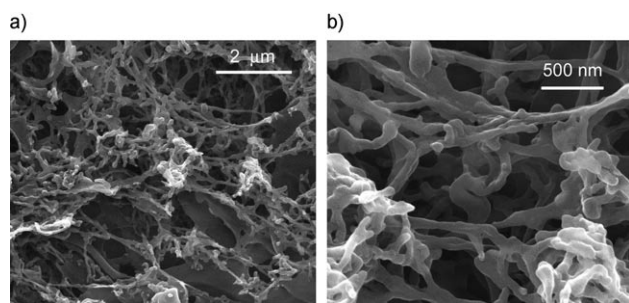


Figure 4. SEM Images of a) freeze-dried 1% **AmDP2** gel in *p*-xylene at $\times 35\,000$ magnification and b) the same sample at $\times 121\,000$ magnification.

were super-bundles formed from the intertwining of many polymer chains. However, it is not certain whether these were present in the native gel or formed during the sample drying stage.

Based on the facts that only **AmDP2** formed strong organogels and that the monomers were all non-aggregating in the solution state, a gelation model was postulated (Figure 5). Since the monomers contain only two H-bonding amide units that are not pre-organized by a rigid spacer, there is little cooperative binding effect. Hence **AmM1–AmM3** showed little self-association in the solution state, as confirmed by FT-IR study. After click polymerization, the dendronized polymers contain a large number of H-bonding amide units packed at regular intervals along the polymer chain, producing a zip templating effect, as initial interchain H-bonding between a few amide units would facilitate bindings of those located further down the polymer chain, provided that the steric size of the dendrons did not interfere with the binding process. In addition, aliphatic hydrocarbon dendrons also provided a highly nonpolar hydrophobic

microenvironment that further enhanced the strength of H-bonding.^[12] In practice, the G3 dendrons were too bulky, and prevented sufficiently close contacts among the polymer chains to form a stable H-bond network structure in the solution state, as confirmed by the smaller red shift values of N–H and C=O stretchings in the FT-IR spectrum of **AmDP3** in toluene solution. With regard to the gelation-specificity of the **AmDP2** dendronized polymer, the G2 branching hydrocarbon residue seemingly possessed the optimized size to allow close contacts of the dendronized polymer chains, and hence the formation of a stronger H-bond-mediated network structure in the solution state, as confirmed by FT-IR study of **AmDP2** in toluene solution. At the same time, the internal voids created within the network were of the appropriate size to accommodate solvent molecules and therefore physical gels were formed. For **AmDP1**, with the smallest hydrocarbon side chains that did not hinder chain associations, interchain H-bonding was very strong and hence network packing was much denser. Hence **AmDP1** is a highly insoluble compound and the internal voids within it are too small to accommodate any solvent molecules. In addition, the role of solubility should also play a role in controlling gelation. The different hydrophobic side chains could modulate the solubility of the resulting dendronized polymers. Hence, **AmDP1** does not have enough hydrophobic functionality to dissolve and therefore is a solid, whereas **AmDP3** has too much hydrophobicity, interacts too effectively with the solvent, and simply dissolves.

In summary, we have reported herein the first efficient synthesis of G1–G3 dendronized polymers starting from AB-type heterobifunctional macromonomers using click polymerization. A significant functional-group synergistic effect was noted on the interchain hydrogen-bonding capability of the many amide functionalities in the resulting dendronized polymers. Despite their structural similarities, the strength of the hydrogen-bond networks, and hence the physical properties of the three dendronized polymers, were different and were controlled by the size of the dendritic appendage. It is of interest to note that our findings are reminiscent to those made for the hydrogelating properties of poly(*N*-alkyl)acrylamides, wherein their gelating properties are dependent on the amide N–H hydrogen bonding and the nature of the alkyl side chains.^[13] Notably, the G2 dendronized polymer **AmDP2** was found to have very strong organogelating properties, with MGC values down to 5 mg mL^{-1} . We believe the new findings can provide valuable insights into the self-assembly of dendronized polymers, and offer new understandings of the intricate mechanism of polymer–polymer hydrogen-bonding interactions.

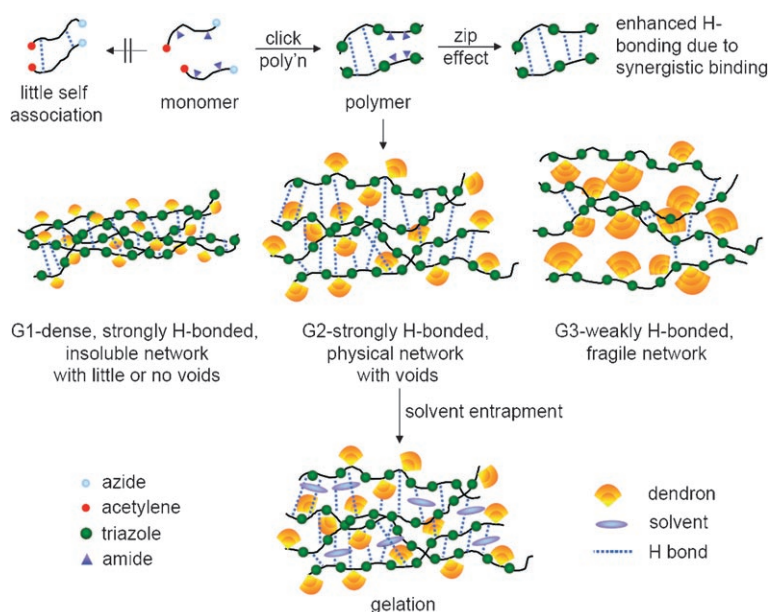


Figure 5. Proposed gelation model of **AmDP2**. For clarity, some dendrons are omitted in some of the structures.

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