



## **One-Pot Radical Polymerization of One Inimer to Form One-Dimensional Polymeric Nanomaterials**

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Inspired by their unique properties and widespread applications ranging from biological sciences to materials engineering, onedimensional (1D) organic nanomaterials kept attracting much interest of researchers in developing novel synthetic strategies which would have far-reaching impact in broad fields.<sup>[1]</sup> 1D polymer nanoparticles were usually obtained via either tedious organic chemistry approaches to obtain covalently linked moieties, such as dendronized polymers and fullerenebased one-dimensional nanopolymers;<sup>[2,3]</sup> or supramolecular/ self-assembly approaches,<sup>[4]</sup> or physical confinement,<sup>[5]</sup> etc. Molecular congregating under the influence of multifarious intermolecular forces, for example, self-assembly of di/multiblock copolymers or polymer brushes, formed colloidal 1D nanoparticles.<sup>[4]</sup> Physical confinement, for example, electrospinning or crystallization inside cylindrical nanopores, could likewise form nanofibers.<sup>[5]</sup> Though polymers played important roles, as architectural units or templates, etc, in all the abovementioned strategies, few approaches were reported to form covalent 1D nanomaterials in a one-pot way directly from monomers as polymerization chemistry usually does.

Free radical polymerization is perhaps the most common and facile reaction for making a wide variety of different polymers directly from monomers. Extension of the power of polymer chemistry has long been the target of research efforts, and research in the field is ever increasing with new types of materials and methodologies being continually discovered.<sup>[6,7]</sup> It is well established that self-condensing polymerization of an inimer yielded hyperbranched polymers.<sup>[6]</sup> Living radical polymerizations, including atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition fragmentation transfer polymerization (RAFT), and their concurrent/successive combinations have become powerful tools for the design of macromolecular architectures, especially topological structures.<sup>[7]</sup> However, generally only crosslinked structures or hyperbranched polymers could be obtained in pursuing three-dimensional macromolecular structures via one-pot polymerization chemistry.<sup>[8]</sup>

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In this work, we intend to synthesize 1D nanomaterials via one-pot concurrent living/controlled polymerizations of inimers. It is proposed that the 1D nanomaterials could be formed by the linkage of hyperbranched polymeric intermediates via trapping active end groups in the one-pot free radical polymerization (Scheme 1). This approach could form 1D pearl-necklace polymers directly whose molecular configuration could be more stable than polymer brushes, especially in solutions. Moreover, the 1D nano-structures could be constituted with not only "homogeneous" building blocks but also "copolymeric" units.

We consider the concurrent living free radical polymerizations of an inimer bearing an ATRP/NMP initiating site in the presence of a RAFT chain transfer agent (CTA). Both ATRP and NMP can directly generate free radicals for propagation if capping groups are activated; whereas RAFT seems to regulate the propagating way of radicals through balanced reactions with existing radicals. Because of the balance as illustrated in Scheme 1c, the contents of free radicals for either RAFT or ATRP/NMP are the same. Both the kinetic length of chains stemming from either RAFT or ATRP/NMP and the probability of branching are nearly the same. Thus most probably, no heterogeneous propagation directions can be distinguished in the formation of hyperbranched polymers. Though the intermolecular linkage of hyperbranched polymers through the combination of active ATRP/NMP sites is suppressed to the lowest possibility, however, RAFT CTA sites are apt to trap radicals generated from active ATRP/NMP sites by nature. Especially the so-called cross-termination can form stable bonds between CTA and radicals.<sup>[9]</sup> Thus one hyperbranched polymer can joint other hyperbranched polymers one by one to form a pearl-necklace structure constituted of repeating hyperbranched polymer "pearls" (Scheme 1d). The diameter of the 1D nanostructure is determined by the size of the hyperbranched polymeric intermediates. The ideal case is that only one RAFT CTA site in a hyperbranched polymer can bind any one active ATRP/NMP site in another hyperbranched polymer to form a linkage. This is possible in a general RAFT system with a molar ratio of monomer to CTA, for example, 100 or higher. An NMP inimer is used in this work instead of ATRP inimers because of two considerations, i.e. the ease in the view of the stoichiometry and avoidance of metal ions' interferences with RAFT CTA.

To verify the feasibility, we synthesized an inimer bearing an NMP initiating site, 2,2,6,6-tetramethyl-1-(4-vinyl-benzyloxy)piperidine(PSt), via spin-trapping of the radicals generated in a redox reaction between the chloride group of 4-vinylbenzyl chloride and a transition metal catalyst. PSt was obtained as colorless liquid. The yield of pure PSt was 64.2%. The structure of PSt was verified by 2D <sup>1</sup>H-<sup>13</sup>C correlation NMR, and MS (Figure S1-S3 in the Supporting information).



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**Scheme 1.** Self-condensing polymerization of an inimer in the presence of RAFT CTA.

The free radical polymerization of PSt was carried out at 130 °C with addition of RAFT CTA ([PSt] = 0.244 M, molar [PSt]/[CTA] = 110) to form concurrent RAFT and NMP dual controlled polymerization systems. The [PSt]/[CTA] feed ratio was chosen based on optimized results in the literature. TEMPO-based NMP systems demanded high polymerization temperature (125-145 °C) for the dissociation of the C-O bond in the NMP initiating site. Two other kinds of polymerization were carried out as well as control tests: TEMPO-mediated selfcondensing vinyl polymerization of PSt at 130 °C to form hyperbranched polymers, and RAFT polymerization of PSt at 50 °C with addition of azobisisobutyronitrile (AIBN) as the initiator to form linear polymers. N-methyl-2-pyrrolidone was used as the reaction media. When N-methyl-2-pyrrolidone was used as the reaction media, the polymer yields in the concurrent NMP and RAFT reached nearly 100% in 36 hours without gelling.

Gel permeation chromatography (GPC) was used to monitor the weight average molecular weight  $(M_w)$  and its distribution

 $(M_w/M_n)$  during self-condensing NMP and concurrent NMP/ RAFT of *PSt* (Figure 1). GPC data manifested that the concurrent NMP/RAFT of *PSt* showed typical kinetic characteristics of step condensation polymerization, differing from the kinetic characteristics of the formation of hyperbranched polymers in the self-condensing NMP. At the early stage of the concurrent NMP and RAFT, the polymers showed narrow molecular weight distribution ( $M_w/M_n \sim 1.1$ ) which indicated a tightly controlled manner in the dual controlled polymerization systems. The widening of molecular weight distribution in longer polymerization time was not because of out-of-control on the free radical polymerization. Concerning that the low  $M_w$  peak always appeared in the wide molecular weight distribution, our assumption that the polymers were formed by step-combination of hyperbranched pearls was reasonable.

Because of rigidity in structures, mainly signals arising from TEMPO end groups and phenyl groups were observed in either solid or solution <sup>13</sup>C NMR of these polymers (Figure S4).

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**Figure 1.** Molecular weight and structural analysis via FTIR. (A) and (B) were the GPC chromatograms of polymers obtained inconcurrent NMP/RAFT system and self-condensing NMP, respectively. Polymerization time in A (hours): a: 6; b: 12; c: 19.5; d: 30; e: 31; f: 34; and in B: g: 6; h: 12; i: 24; j: 32; k: 40. C and D was calibrated from A and B, respectively. (E) FTIR absorbance of the polymers obtained in the concurrent NMP/RAFT systems in polymerization time of 6 (a), 10 (b), 15 (c), 20 (d), and 25 hours (e), and (F) The ratios of the absorbance at 1134 cm<sup>-1</sup> to that at 1512 cm<sup>-1</sup> versus polymerization time.

In contrast, FTIR was an efficient tool to monitor the structural changes during the concurrent living polymerizations of inimers. We studied the FTIR spectra of these polymers, TEMPO and the monomer. A peak at 1134 cm<sup>-1</sup> arose from the skeletal vibration in TEMPO. Another peak at 1512 cm<sup>-1</sup> was due to a vibration mode of aromatic rings (Figure 1E). The two peaks were sharp and strong, and were not affected by overlap with other peaks; thus the absorbance ratios of them (Abs<sub>1134</sub>/ Abs<sub>1512</sub>) could be used to characterize the structural changes during polymerization. The Abs<sub>1134</sub>/Abs<sub>1512</sub> for the monomer *PSt* was about 2.1, whereas was greater than 2.8 for a linear polymer obtained by RAFT polymerization at relative low temperature. Along with elongated polymerization time in the concurrent living polymerizations, the absorbance ratios in these polymers were observed to decrease, and to reach a constant value of ~0.5. This indicated that the contents of aromatic structures increased with polymerization time, or vice versa, the contents of TEMPO groups decreased. The trends elucidated in the curve of  $Abs_{1134}/Abs_{1512}$  versus time were in accord with the analysis of the fractions of terminal groups in SCVP.<sup>[10]</sup> The FTIR results revealed a highly branched nature of the polymers obtained in the concurrent dual controlled polymerization. Fast developed molecular weight but constant  $Abs_{1134}/Abs_{1512}$  value at the later stage of the polymerization supported the mechanism of combination of hyperbranched intermediates.

To verify the step-combination mechanism, the hyperbranched "pearls" were isolated and purified, and then were subjected to the polymerization conditions. The well-isolated



polymer b with narrow molecular weight distribution (b in Figure 1) was chosen. After being heated at 130 °C for 30 hours, polymer parts with Mw above 106 were observed via GPC in the solution of polymer b; whereas M<sub>w</sub> of the hyperbranched polymer h obtained in Figure 1 was almost not changed in the same conditions. This experiment verified the recombination mechanism, as illustrated in Scheme 1(d). Obviously, if different hyperbranched polymer "pearls" obtained from different inimers were combined in the polymerization, a pearl-necklace structure constituted of "copolymeric" building blocks could be produced. By using molecular weight control techniques, Janus particles could be possibly obtained as well.

The sulfur contents due to RAFT CTA in the polymers were measured with X-ray photoelectron spectroscopy (XPS), and were found to be  $0.13 \pm 0.1$  atom% in the polymers obtained from dually controlled systems (Figure S7), which were close to the value ( $0.14 \pm 0.1$  atom%) found in the linear polymers obtained via RAFT polymerization. The additional results proved that RAFT CTA was involved in the dually controlled polymerization systems.

The obtained polymers were mixtures of hyperbranched polymers and polymer nanorods, as evidenced by GPC and TEM observation. The polymer nanorods were well soluble in tetrahydrofuran (THF), N-methyl-2-pyrro-

lidone and toluene, but not in dimethylformamide (DMF). Thus the polymer nanorods were obtained by classification of a THF solution of the raw polymers with precipitation of DMF. The nanorods obtained from the sample d in Figure 1 were found to have a length of about 137 nm and a diameter of about 30 nm in average according to statistics on TEM image (Figure 2A). If the concentrations of both [PSt] and [CTA] were doubled, Mw and  $M_w/M_n$  obtained in the polymerization of 30 hours at 130 °C were 16000 and 2.4, respectively, and we obtained nanorods with lengths around 60 nm and diameters of around 15 nm, indicative of regulatory lengths of these rods via the concurrent controlled polymerization methodology (Figure 2C). SCVP of an inimer was usually related to equilibrium between the activation and deactivation processes. High initiator (inimer) concentration favored a shift of the equilibrium toward the active radicals, leading to a higher concentration of radicals,<sup>[11]</sup> a faster polymerization rate but smaller molar mass.

Actually, hyperbranched blocks could randomly attach towards each other to afford three kinds of topological arrangements of hyperbranched blocks, including nanorods, botryoidal shapes and budding grafting shapes. However, the botryoidal shape could lose its identity from hyperbranched polymers. If one branch of the botryoidal shape grew up to form "budding", a budding grafting shape could be obtained, as illustrated in Figure 2D. The budding grafting shapes relied on the development of huge molar mass. Overall, nanorods were the most

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**Figure 2.** (A) TEM of sample d with average length of  $137 \pm 15$  nm and width of  $30 \pm 5$  nm. (B) AFM of sample d. The sample was prepared by spin-coating THF solution of polymer d (0.1 mg/mL) on mica. The particle in a cycle mark has a length of 125 nm and width of 25 nm. (C) TEM of the products from the concurrent controlled polymerization in 30 hours where [*PSt*] and [CTA] were twice as those for sample d. (D) Budding grafting structures found in the concurrent controlled polymerization. (E) Optical microscopy image of self-aggregated aqueous suspension derived from sample d. Magnification 100X.

probably obtained structures after classification. AFM observations were performed on polymer d as well. The sample was prepared by spin-coating THF solution of polymer d (0.1 mg/ mL) on mica, and the corresponding image was shown in Figure 2B. The sample was scanned at different directions for recognizing and avoiding possible AFM artifacts. The image showed nanometer-sized rod-like particles with length of about 130 nm, and width between several to 30 nm. The average sizes were coincided with TEM observation.

The structural order of the polymers produced in the concurrent NMP/RAFT system at different time was investigated with X-ray powder diffraction (XRD). Wide-angle XRD patterns of these polymers showed only a broad peak at around 20° corresponding to non-crystalline of the polymer molecular chains without short range order. However, after being simply orientated by rotary evaporation from THF solutions which was conducive to orientation of nanorods, the polymers showed diffraction peaks in small angles XRD (SA-XRD) at 2Q around 1.3° correspondent to periodic spacing of about 6.6 nm (Figure 3A), indicative of typical features of structures with long-range orders. There was no long-range order presented in either the hyperbranched polymer or the linear polymer of PSt. SA-XRD in combination with wide-angle XRD results indicated that the long-range order possibly stemmed from the nanorod-close-packing conformation. The structures seemed more regular than expected. The polymer formed from a normal system in 30 hours showed the



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**Figure 3.** Structural order in the polymer nanorods. (A) Small-angle X-ray powder diffraction patterns of polymer powders obtained in the concurrent NMP/RAFT system in different polymerization time: (m) 24, (d) 30, (e) 31, (f) 34 hours. Curve n arose from the polymer obtained by recombination polymerization of a hyperbranched polymer in 30 hours. (B) Wider XRD spectrum of curve d. (C) D-spacing correspondent to the maximum in (A). (F) Orthogonal polarizing microscopy image of polymer d, and (E) its nature view; (D) Optical density varies cyclically as the specimen is rotated against the polarizers.

best regularity, evidenced by the appearance of multilevel diffraction peaks (d in Figure 3). However, we must point out that if these nanorod samples were stored as dry powder, the periodic spacing could continue to increase possibly because of combination among close-packed nanorods. The periodic spacing of sample m increased from 6.4 nm to about 10.6 nm after about 4 months. These samples were stable if stored in solutions.

The SA-XRD of the sample obtained by recombination of the isolated hyperbranched polymer b in Figure 1A in 30 hours yielded a 2Q peak at about 1.6° correspondent to periodic spacing of about 5.0 nm (n in Figure 3A), significantly smaller than other rod-like samples obtained with continuous addition reaction of monomers.

One intriguing characteristic of the polymers m, d, e, f, and e (correspondent to the samples in Figure 1A and Figure 3A) obtained in the concurrent NMP/RAFT system were that they showed liquid crystalline orientation in a polarizing microscope (Figure 3F). When sample d was observed with 360-degree

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rotation through crossed polarizers, the orientated sample changed from bright to extinction cyclically. We measured the optical density change of a certain place at each 5° rotation of sample stage (Figure 3D). The variation of optical density was cyclical and symmetrical, indicative of high orientation order.

The end TEMPO groups could initiate further polymerization. We attached poly(Nisopropylacrylamide), PNIPAM, to these nanorods via NMP of N-isopropylacrylamide. The obtained PNIPAM-modified nanorods could be easily emulsified in water. However, the aqueous suspension of PNIPAM-modified nanorods could also easily aggregate to form macroscopic 1D structures following the direction of the external magnetic field (Figure 2E). The 1D aggregated structure could be ascribed to these polymer nanorods. However, the easy aggregation process was likely related to the magnetic properties of these nanorods. Because of the attachment of TEMPO groups at the chain ends, those nanorods showed super-paramagnetic properties, whereas TEMPO itself is a paramagnetic material (Figure S8).

In conclusion, polymer nanorods were formed by facile concurrent NMP/RAFT polymerization of a styrene-based inimer. Comprehensive analysis in combination with TEM observation suggested that 1D nanostructures were preferentially formed from those systems with high monomer concentrations and suitable proportion of [*PSt*]/[CTA]. The lengths of nanorods were regulatory via adjustment of feed ratios or polymerization time. The approach proposed in this work was conducive to making novel nanomaterials. These rigid polymeric nanorods could also reinforce composites. We tested reinforcement of epoxy resins by addition of pol-

ymer d of only 0.1 wt%, and found that the storage modulus in a wide range from room temperature to 150 °C were increased by 2-1.5 fold (Figure S9).

Furthermore, many different nitroxides other than TEMPO have been designed for the initiators of NMP or NMP based inimers, and have flourished NMP systems for the synthesis of block copolymers and macromolecular architectures.<sup>[12]</sup> Basically the inimers based on these newly emerging nitroxides are applicable for the approach of this work. Overall, the approach and nanorods obtained in this approach are worthy of further study, and will find widespread applicability.

#### **Experimental Section**

Synthesis of 2,2,6,6-tetramethyl-1-(4-vinyl-benzyloxy)-piperidine (PSt): A flask was charged with 2,2,6,6-tetramethyl-1-piperidine-N-oxyl (TEMPO) (5 g, 0.032 mol), 4-vinylbenzyl chloride (5 g, 0.033 mol), [2,2']bipyridinyl



(8 g, 0.051 mol), Cu(1)Cl (4.5 g, 0.046 mol) and THF (50 mL). The reaction was continued for 72 h at 50 °C under pure N<sub>2</sub>. After solid sediments were removed by filtration, the solution was passed through a column of neutral alumina to remove the copper salts. Pure *PSt* was obtained as colorless liquid by passing through a silica gel column chromatography with petroleum ether as eluent (5.6 g). Yield: 64.2%. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 17.0 (CH<sub>2</sub>), 20.3 (CH<sub>3</sub>), 33.2 (CH<sub>3</sub>), 40.0 (CH<sub>2</sub>), 59.0 (C(CH<sub>3</sub>)<sub>2</sub>), 77.5 (CH<sub>2</sub>-O), 112.5 (CH<sub>2</sub> =). HRMS (EI) m/z (%): 117.0893 (70) [C<sub>9</sub>H<sub>9</sub><sup>+</sup>], 156.1376 (100) [C<sub>9</sub>H<sub>18</sub>NO<sup>+</sup>], [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>27</sub>NO, 273.2093; found, 273.2092.

Concurrent RAFT and NMP dual polymerization at 130 °C to afford nanorod-like polymers: In a typical experiment, a Schlenk flask was flamedried under vacuum and charged with monomer PSt (0.1 g, 0.366 mmol) and RAFT CTA, 2-benzyl-sulfanylthiocarbonylsulfanyl-2-methyl-propionic acid, (0.92 mg,  $3.2 \times 10^{-6}$  mol) dissolved in N-methyl-2-pyrrolidone (1.5 mL). The reaction mixture was degassed by three freeze-pump-thaw cycles. The reaction was carried out at 130 °C. The raw polymers are obtained by precipitation with methanol.

The polymer nanorods were well soluble in THF, N-methyl-2pyrrolidone and toluene, but not in DMF. Thus the polymer nanorods were obtained by precipitation from a THF solution of the raw polymer with DMF, and then isolated by centrifuging at 10000 g.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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- a) J. B. Gilroy, T. Gädt, G. R. Whittell, L. Chabanne, J. M. Mitchels, R. M. Richardson, M. A. Winnik, I. Manners, *Nat. Chem.* **2010**, *2*, 566; b) T. Liu, C. Burgerb, B. Chu, *Prog. Polym. Sci.* **2003**, *28*, 5; c) R. Shen, X. Shen, Z. Zhang, Y. Li, S. Liu, H. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 8627.
- [2] a) W. Stocker, B. Karakaya, B. L. Schürmann, J. P. Rabe,
   A. D. Schlüter, J. Am. Chem. Soc. 1998, 120, 7691; b) H. Frey, Angew.
   Chem. Int. Ed. 1998, 37, 2193.
- [3] a) J. Geng, I. A. Solov'yov, D. G. Reid, P. Skelton, A. E. H. Wheatley, A. V. Solov'yov, B. F. G. Johnson, *Phys. Rew. B* 2010, *81*, 214114;
  b) R. Charvet, S. Acharya, J. P. Hill, M. Akada, M. Liao, S. Seki, Y. Honsho, A. Saeki, K. Ariga, *J. Am. Chem. Soc.* 2009, *131*, 18030.
- [4] a) E. R. Zubarev, M. U. Pralle, L. Li, S. I. Stupp, *Science* 1999, 283, 523; b) J. T. Chen, E. L. Thomas, C. K. Ober, G.-P. Mao, *Science* 1996, 273, 343.
- [5] a) C. Huang, S. Chen, D. H. Reneker, C. Lai, H. Hou, *Adv. Mater.* 2006, *18*, 668; b) S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai, S. Kitagawa, *Nat. Mater.* 2009, *8*, 831.
- [6] J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. R. Leduc, R. B. Grubbs, *Science* **1995**, *269*, 1080.
- [7] a) K. Matyjaszewski, N. V. Tsarevsky, *Nat. Chem.* 2009, 1, 276;
   b) K. Nakatani, T. Terashima, M. Sawamoto, *J. Am. Chem. Soc.* 2009, 131, 13600.
- [8] G. V. Korolev, M. M. Mogilevich, in *Three-Dimensional Free-Radical Polymerization*, Springer, Berlin, Heidelberg 2009.
- [9] F. M. Calitz, J. B. McLeary, J. M. McKenzie, M. P. Tonge, B. Klumperman, R. D. Sanderson, *Macromolecules* 2003, 36, 9687.
- [10] D. Yan, A. H. E. Müller, K. Matyjaszewski, Macromolecules 1997, 30, 7024.
- [11] H. Mori, A. Walther, X. André, M. G. Lanzendörfer, A. H. E. Müller, Macromolecules 2004, 37, 2054.
- [12] a) C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* 2001, 101, 3661; b) J. Nicolas, B. Charleux, O. Guerret, *Angew. Chem. Int. Ed.* 2004, 116, 6312.