A Convergence of Photo-Bergman Cyclization and Intramolecular Chain Collapse Towards Polymeric Nanoparticles

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ABSTRACT: Employing enediynes as crosslinking precursors, a novel yet efficient strategy, namely photo-triggered Bergman cyclization, was integrated with intramolecular chain collapse to yield polymeric nanoparticles with the size regime below 20 nm. Enediyne motif was designed delicately to possess a high photo-reactivity, with the double bond locked in a methyl benzoate ring while triple bonds substituted with phenyls. Single electron transfer-living radical polymerization was conducted to provide linear acrylate copolymers with controlled molecular weights and narrow polydispersities. Poly(butylarylate-*co*-**5**) went through UV-irradiation with a concurrent Bergman cyclization, resulting in well-defined ultrafine polymeric nanoparticles. Results from NMR, Raman scattering, photolumines-

INTRODUCTION Avid interest has been devoted to the exploitation of advanced organic chemistry in polymer science and materials recently.^{1,2} The main driving force is that the synthetic organic chemistry has the capability to exquisitely control the composition of small molecules, thus fabricate well-defined materials. One of the classic examples is the formation of ultra-fine polymeric nanoparticles through intramolecular cross-linking or single chain collapse. This is not surprising since the intramolecular chain collapse technique provides a facile strategy for preparing polymeric nanoparticles within the critical size regime of 1-20 nm, which showed multiple applications ranging from catalysts and drug delivering systems,³⁻⁸ light- and energy-harvesting,⁹ and nanoporous low dielectric constant materials for micro electric applications.¹⁰ A key requirement for an effective intramolecular chain collapse involves an easy and controllable incorporation of appropriate cross-linking precursors into an individual polymer chain. So far, several typical precursors and synthetic tools have been designed and applied to induce such a coil-to-globule transition, resulting in the so called unimolecular nanoparticles.¹⁰⁻²⁷ Vinyl functionalizations, such as acrylate,¹⁰ as well as benzocyclobutane (BCB)¹² were successfully investigated to form such kinds of nanoparticles through free-radical cross-linking. In the BCB

cence and UV-vis spectra corroborated the presence of conjugative structures in the polymeric nanoparticles, indicating the occurrence of photo-induced Bergman cyclization. A series of other acrylate-based nanoparticles were investigated to confirm the applicability of such a unique strategy in thermal sensitive but UV-stable polymeric structures, making photo-Bergman cyclization a promising tool towards polymeric nanoparticles. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 5330–5338, 2011

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system, no initiator or catalyst was required except for the high heating temperature (250 °C) to trigger the crosslinking without side product formation. Meanwhile, benzosulfones were utilized as precursors to form the same stable benzocyclooctadiene cross-linked entities as obtained from BCB, resulting in polyelectrolyte nanoparticles¹⁶ or 3D architectures.¹⁹ It should be noted that ultra-dilute reaction conditions or a continuous addition technique must be requested to favor intramolecular coupling against intermolecular cross-linking. To avoid the harsh conditions, isocyanates were then selected as cross-linkers to go through a much more moderate, room temperature condition.²⁰ In addition to the covalent bonding, multiple hydrogen bonding was also employed to produce metastable supramolecular polymeric nanoparicles.²² This technique was later expanded with the combination of the living radical polymerization and "click" chemistry to produce supramolecular polymeric nanoparticles under UV irradiation.²³ As functionalized polymeric nanoparticles have been regarded as versatile building blocks for scores of nanotechnological structures, much more diversified precursors and milder reaction conditions are still in urgent need.

Intrigued by the multiple applications of polymeric nanoparticles, we successfully expanded thermal Bergman cyclization

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into the "tool box" of preparing single chain polymeric nanoparticles in our previous work.²¹ Bergman cyclization is the intramolecular cyclization of enediyne derivatives to generate a highly reactive aromatic 1,4-diradical intermediate.²⁸ Significant amount of aromatic oligomers or polymers will be obtained even with large excess of radical terminators, such as 1,4-cyclohexadiene. Bergman cyclization is reckoned to be an attractive and promising synthetic tool for material sci $ence^{29-31}$ as the polymerization of aromatic 1,4-diradical can give polyphenylenes and polynaphthalenes without the need of exogenous catalyst or reagent. The structural variability of enediyne monomers also allows introduction of multi functionalities through substitution, leading to soluble and processable aromatic polymers. Hitherto, Bergman cyclization has been reported to fabricate aromatic polymers and carbonaceous materials, such as poly-p-phenylenes, polynaphthalenes, conjugated brush polymers, carbon nanotubes and glassy carbons.32-41

However, the harsh reaction condition (>200 °C) previously encountered may suppress the universality of Bergman cyclization in the field of polymers and materials, since the high temperature required will go against most of the thermal sensitive polymers, such as poly(*t*-butyl acrylate). To solve this problem, herein we attempt to investigate the capability of an alternative synthetic method, namely photo-induced Bergman cyclization,²⁸ to form unimolecular nanoparticles.

Photo-induced Bergman cyclization was uncovered in the 1990s by Sugiura,⁴² Nicolaou,⁴³ and Wender.⁴⁴ Later, Turro and Nicolaou revealed that simple artificial enediynes could also undergo cycloaromatization upon photo-irradiation.45 Subsequently, plenty of arene-fused or nonbenzenoid, locked or acyclic enediynes were explored and investigated under photoirradiation.46-56 Photo-Bergman cyclization was deemed to be similar in mechanism to that of the thermal induced. However, most of the work aimed at cycloaromatization products and treated polymers formed during the procedures as by-products without further investigation. As we have been acknowledged, only one report was issued employing photo Bergman cyclization to yield a sparingly soluble polymeric materials by Zaleski et al.⁵⁷ They excited metalloenediynes in solid state with a 785 nm diode laser where both the metal ions and the laser acted as stimuli. While here, employing enediynes as cross-linkers, we report for the first time the utilization of a pure photo-triggered Bergman cyclization route in ultra-dilute solution to fabricate single chain polymeric nanoparticles with interior conjugated oligomers. A couple of vinyl monomers are used to further verify its applicability, including methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), and tert-butylacrylate (*t*BA).

RESULTS AND DISCUSSION

The design of an appropriate parent compound turns out to be very essential in virtue of the fact that upon photo-irradiation, enediynes would likely go through a Bergman-type rearrangement to yield benzene derivatives as expected from the thermal Bergman cyclization, or a triple bond photo-



SCHEME 1 Synthesis of enediyne-containing G-1 (5) and G-2 (11) dendrimers.

reduction, resulting in uncyclized substances,⁵⁸ whereas others may even suffer from a cis, trans-isomerization of the double bond.⁵⁹ It's already been well-documented that both the types of photolytic products and the yield of the Bergman-type product were dependent on the substituents on the triple bonds. Specifically, the photoreduction products were eliminated when the double bond was confined in a benzene ring along with the triple bonds were substituted with phenyl groups. Herein, 1,2-bis(2-phenylethynyl)benzene⁶⁰ and its derivatives were taken for our ideal models. However, the yield of the cyclized product under photo-irradiation in our experiment was as low as been reported elsewhere.⁶¹ Considering that an extended conjugative effect and wider range of UV absorption might somewhat enhance the photo-reactivity of the enediynes (Supporting Information Fig. S1), we incorporated the double bond into a ring of methyl benzoate instead of benzene. Accordingly, enediyne 3 was synthesized immediately employing Pd-mediated Sonogashira coupling reaction (Scheme 1). Both 3 and 1,2-bis(2phenyl ethynyl)benzene were UV-triggered in THF for 6 h with the same amount. The reaction mixtures were concentrated under vacuum to yield the products, which were later characterized with ¹H NMR without further purification. There's no significant change for 1,2-bis(2-phenylethynyl)benzene before and after UV irradiation in the corresponding ¹H NMR spectrum. Whereas for 3, apparent new peaks around 8.1 and 8.9 ppm were presented after UV-irradiation, indicating the formation of naphthyl (Supporting Information Fig. S2). Hereby a novel yet efficient cross-linker, which not only possessed high reactivity but also required only two high-yield steps from a commercially available starting material, was exploited.

As most of the precedents involving photo-Bergman cyclization were carried out mainly to obtain benzene or





FIGURE 1 ¹H (left) and ¹³C (right) NMR spectrum of compound 3 (a) and its polymeric products (b) after UV irradiation.

naphthalene rather than their oligomers or polymers, they were conducted particularly with hydrogen donors such as 1,4-cyclohexadiene in a solvent or with a solvent bearing good H-donatability, with THF and iso-propanol (i-PrOH) being the routines. However, such kinds of H-donors and solvents will quench the biradical formed during the Bergman cyclization immediately, making polymerization almost impossible. Therefore, to perform an effective chain collapse within a single chain, the solvent circumstance must be chosen prudently. Toluene was regarded as a good candidate for a couple of reasons. First of all, according to its UV absorption spectrum, toluene is able to filter out most of the short wavelengths below 280 nm that might cause polymer degradation. Second, toluene is a good solvent for most of the hydrophobic polymers. The most important thing is that protons bearing on toluene are less reactive than those of THF or i-PrOH, thus making them harder to trap the biradical immediately. Enediyne 3 was UV-triggered in toluene to con-

firm our hypothesis. Polymeric products were obtained via a flash chromatography (silica gel, hexane: ethyl acetate 5/1) and characterized with NMR, ESI-MS, GPC, UV-vis, and Raman. The photolytic product showed broad rather than distinct peaks from 6.5 to 8.5 ppm assigned to the protons on arene, so did the methyl ester part locating around 3.9 ppm (Fig. 1). That might be ascribed to longer relaxation time of the conjugated structure upon biradical coupling. As can be seen in the ¹³C NMR spectra, peaks at 96.6, 94.4, 87.9, and 87.5 ppm corresponding to the triple bond totally disappeared after the reaction. Further characterization with Raman scattering presented an extensive intensity reduction for the triple bond (2,200 cm^{-1}) after photo-Bergman cyclization (Fig. 2). The existence of the peak around 2,200 cm^{-1} suggested an incomplete photo-Bergman cyclization, however, it did little harm on the intramolecular chain collapse (vide infra). A main peak around 1500 Da along with two small peaks at 809, 439 Da showed up in GPC trace (vs. PS



FIGURE 2 Raman scattering of compound 3 before (left) and after (right) UV irradiation.



FIGURE 3 Photoluminescence emission spectra of compound 3 (solid line) and its polymeric products (dashed line) after UV irradiation.

in THF), which was later reckoned as tetramers, trimers and dimmers, respectively. It should be noted that, as the oligomers have more compact structures and thus smaller hydrodynamic values when compared to PS, the actual molecular weights of the oligomers ought to be higher than the values obtained from GPC. The cyclized conjugative structure was also evidenced by a red shift from 456 to 516 nm in Photoluminescence spectra (Fig. 3) after the irradiation. The formation of these oligomers (Scheme 2) dropped a hint that it's enough for us to investigate the intramolecular chain collapse with this photo-initiated Bergman cyclization.

The synthesis of enediyne containing acrylate 5 and its copolymers with BA was depicted in Scheme 1. Acrylate monomer species were selected because of the multiple mature synthetic strategies, such as SET-LRP, to precisely control over the molecular weight and the polydispersity (PDI).⁶² The copolymerization of **5** with BA was conducted in a binary solvent of acetone and water (9/1, vol).⁶³ Small amount of hydrazine hydrate was added as a reducing agent to reduce the Cu (II) generated during the polymerization, affording highly controllable molecular weight as well as narrow PDI.⁶⁴ The incorporation of the enediyne moieties was evidenced by the appearance of aromatic protons between 6.8 and 8.5 ppm in the ¹H NMR analysis (Supporting Information Fig. S3). The incorporation ratios of the enediyne monomers calculated from ¹H NMR analysis were found to be the same as that of the feeding amount, representing a comparative reactivity of the monomers during a SET-LRP technique. Molecular weights, PDIs and the amount of enediynes in each copolymer chain were detailed in Table 1.

Linear precursor PBA-**5** was then subjected to UV-irradiation in toluene (0.06 mg/mL). To check the efficiency of the photo-reaction, Bergman cyclization was carried out for 3 h and 6 h, respectively. After the UV exposure, the copolymers were assumed to be compact globules with conjugated cross-linkers, resulting in an apparent decrease in the hydrodynamic volumes, which was able to be distinguished by GPC analysis. As shown in Figure 4, the retention time of the polymeric nanoparticles was much longer than that of the linear copolymers. The products obtained after 6 hours' irradiation, as expected, were even longer in retention time than that from the 3 h. Statistically, the apparent molecular weight decreased about 19% after 3 h UV irradiation (entry 1) while 26% after 6 h (entry 2). Whereas another longer irradiation time (>6 h) caused no further apparent molecular weight change in our experimental systems, thus subsequent photo-Bergman cyclizations were all performed for 6 h. Variant fractions of enediyne moieties were incorporated into the linear copolymers to tailor the nanoparticles. However, no clear relationship between the ratio of the cross-linker and the decrease fraction in the apparent molecular weight of polymeric nanoparticles was disclosed here.

More detailed information about the polymeric nanoparticles was given afterwards by analyzing PBA-5 (entry 2). The results from GPC, ¹H NMR, Raman, and UV-vis were integrated to present some useful structural information. Similar to what has been observed for compound 3, the resonance of aromatic protons in linear copolymers ranging from 6.5 to 8.5 ppm became board after irradiation in ¹H NMR (Supporting Information Fig. S3). The vagueness caused here could also be ascribed to the hindrance arose from the rest part of the polymer structures besides the longer relaxation time of the conjugated structure formed during photo-Bergman cyclization. Significantly, no substantial change of integration value of the four methylene protons on enediyne moieties (around 4.4 ppm) compared to backbone methane protons provided strong evidence that the enediyne moieties didn't break off during the photo-irradiation. Other characterizations, including Raman scattering, UV-vis spectroscopy, and PL emission spectroscopy (Supporting Information Figs. S4-S6), also displayed an analogous change to that of compound 3. Control experiments (entry 7) were done to dig a further insight into the intramolecular chain collapse. BA and tBA were copolymerized respectively with 2-(acryloyloxy)ethyl benzoate and then irradiated under the same reaction conditions. There was no detectable change in the apparent molecular weight of these cases, thus demonstrating that photo-degradation of the polymer backbone didn't occur in our systems and the intramolecular chain collapse was caused by photo-Bergman cyclization of the enediynes.



SCHEME 2 Formation of oligomeric products upon irradiation of enediyne **3** in toluene.

Entry	Copolymer	EDY% ^b	Linear Polymer		Nanoparticle		
			$M_{\rm w}{}^{\rm d}$	PDI ^d	$M_{\rm w}{}^{\rm d}$	PDI ^d	$\Delta M_{\rm w}\%^{\rm c}$
1 ^e	PBA- 5	15	27,200	1.27	21,900	1.23	19.49
2	PBA- 5	15	27,200	1.27	20,100	1.12	26.10
3	PBA- 5	10	21,400	1.22	16,800	1.15	21.50
4	PBA- 5	10	11,900	1.24	8,200	1.29	31.09
5	PBA- 5	20	21,700	1.23	17,100	1.13	21.20
6	PBA- 5	20	38,800	1.37	27,500	1.29	29.12
7	PBA-benzoate	0	22,000	1.32	-	-	NA
8	PMA-5	15	26,800	1.27	20,100	1.11	25.00
9	PEA-5	20	19,800	1.26	13,000	1.19	34.34
10	PtBA-5	17	27,900	1.20	18,000	1.14	35.48
11	PtBA-benzoate	0	22,300	1.34	-	-	NA

TABLE 1 Comparison of Apparent Molecular Weight and PDI of Starting Linear Polymers and Corresponding Nanoparticles^a

^a All reactions were run in toluene under ultra-dilute condition at room temperature for 6 h unless specified.

^b Molar fraction of enediyne (EDY) 5 moiety in copolymer calculated through NMR analysis.

^c Change of apparent molecular weight.

^d Weight average molecular weight and polydispersity index (PDI) measured by GPC using poly(styrene)

as calibration standard.

 $^{\rm e}$ Irradiation for 3 h.

Based on the above results, it can be addressed that phototriggered Bergman cyclization is a feasible and mild pathway for intramolecular chain collapse. To inspect its generality, other acrylate monomers, MA, EA, and *t*BA (entries 8–10) were copolymerized with 15% mol feed ratio of enediyne **5**. However, the fraction of enediyne moieties in each linear copolymer, as shown in Table 1, was slightly higher than 15%, which, in another word, suggested monomers MA, EA, and *t*BA were slightly less reactive than enediyne **5**. Further photo-irradiation of the linear copolymers fabricated more compact nanoparticles with narrow PDIs (Table 1, entries 8–10).



FIGURE 4 GPC traces of linear P(BA-r-5) (solid line) and corresponding nanoparticles for 3 hr irradiation (dashed line, entry 1) and 6 hr irradiation (dotted line, entry 2)

Glass transition temperatures (T_g) were also measured by differential scanning calorimetry (DSC) to indicate the morphology change from coil to globular. Diverse linear acrylate backbones exhibited different T_{g} s (-15.82 °C for PBA-5, 13.28 °C for PEA-5, 37.04 °C for PMA-5, 60.38 °C for PtBA-5). Meanwhile, large exothermic peaks were observed above 300 °C for all the linear copolymers, relating to the corresponding thermal Bergman cyclization. While for PtBA-5, an additional endothermic peak showed up at 238 °C, as a result of the thermal degradation of the *t*BA moieties. All the polymeric nanoparticles exhibited neither measurable glass transition temperatures nor characteristic exothermal peak of Bergman cyclization in DSC curves (Supporting Information Fig. S7). The disappearance of the $T_{\rm g}$ must be ascribed to the decreased segmental chain mobility for the highly cross-linked nanoparticles. While the vanishing of characteristic exothermal peaks of Bergman cyclization indicated the complete consumption of the enediyne moieties. In all these DSC curves, unexpected exothermal peaks around 215 °C appeared for polymeric nanoparticles. At current stage, we can only speculate that other reactions (e.g., formation of five-membered rings⁶⁵) besides Bergman cyclization may have taken place since the mechanism of photo-Bergman cyclization remains poorly understood.

AFM is a powerful method to characterize the assembly of polymer chains.^{66–69} After the photo-crosslinking, the as-prepared nanoparticles were dissolved in THF and spin-coated onto a hexamethyldisilazane modified silica wafer at the speed of 2,000 rpm for 30 s. Figure 5 displayed tens of welldefined spherical-like polymeric nanoparticles. Taking the shape of the particles as half an ellipsoid, nanoparticles in



FIGURE 5 AFM phase image (left) and 3D height image (right) of nanoparticles (entry 6) on silicon wafer.

Figure 5 would possess a calculated diameter of ~ 10 nm following the Meijer's method,²² which was slightly larger, yet in the same order of magnitude, than that deduced from GPC. The deviation in diameters might be caused by the large extent of rigid structures in the nanoparticles that made them irregular balls rather than half ellipsoids.

EXPERIMENTAL

Materials

All of the reactions and manipulations were carried out with Schlenk techniques under Nitrogen unless otherwise mentioned. Tetrahydrofuran (THF) and toluene were distilled over Na under nitrogen before use. *N*,*N*-dimethylforamide (DMF) and triethylamine (Et₃N) were distilled over Calcium hydride under nitrogen before use. MA, EA, BA, and *t*BA were washed with a 5% aqueous NaOH solution to remove the inhibitor and distilled under vacuum before use. Tris[2-(dimethylamino)ethyl]amine (Me₆-TREN) was synthesized according to literature procedures.⁷⁰ All other reagents were commercially available and used as received.

Characterization

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) measurements were performed on a Bruker AVANCE 400 FT-NMR spectrometer with CDCl₃ as solvent. Gel permeation chromatography (GPC) was conducted at 40 °C in THF on a WATERS 1515 system equipped with a series of PS gel columns. The molecular weights of both the polymers and polymeric nanoparticles were calculated in relative to linear polystyrene (PS) standards. Differential scanning calorimetry (DSC) studies were carried out on a Mettler-Toledo thermal analysis workstation equipped with a model 822e DSC module. Glass transition temperatures were measured under a constant nitrogen flow with a heating rate of 10 °C/min. Mass spectra were obtained from a Micromass LCTTM mass spectrometer employing ESI method. UV analyses were performed using a UNICO UV-21-2 PCS spectrometer in THF at room temperature. AFM images of nanoparticles were acquired on a Multimode Nanoscope V scanning probe microscopy system using the tapping mode. Fluorescence spectra were recorded on a Varian Cary eclipse fluorescence spectrophotometer.

Synthesis of Methyl 3,4-dibromobenzoate (2)

Compound **2** was synthesized according to a literature procedure.⁷¹ The crude product was recrystallized from ethyl acetate-hexane to give pure white crystals.

¹H NMR (CDCl₃, δ ppm): 8.27 (d, ⁴*J* = 1.9 Hz, Ph-*H*, 1H,), 7.81 (dd, ³*J* = 8.3 Hz, ⁴*J* = 1.9 Hz, Ph-*H*, 1H), 7.70 (d, ³*J* = 8.3 Hz, Ph-*H*, 1H), 3.9 (s, OCH₃, 3H).

Synthesis of Methyl 3,4-bis(2-phenylethynyl)benzoate (3)

Compound **2** (0.75 g, 2.5 mmol), $PdCl_2(PPh_3)_2$ (0.183 g, 0.25 mmol), CuI (0.143 g, 0.75 mmol), and KI (1.245 g, 7.5 mmol) were mixed with a mixture solvent Et_3N/DMF (1/5, 10 mL) in a 50 mL schlenk flask under nitrogen. Subsequent freeze-pump-thaw techniques were conducted for three times, and then phenylacetylene (1.02 g, 10 mmol) was added under nitrogen. The solution was later subjected to an 80 °C oil bath overnight. After dilution with ethyl acetate, the organic layer was washed with 1 N HCl, brine and dried over MgSO₄. The crude product was purified through silica gel column chromatography (ethyl acetate/petroleum ether = 1:20, $R_f = 0.6$) to give the pure product as a brown-red powder (0.61 g, 73%).

¹H NMR (CDCl₃, δ ppm): 8.24 (s, Ph—*H*, 1H), 7.97 (d, ³*J* = 8.0 Hz, Ph—*H*, 1H), 7.59 (m, Ph—*H*, 5H), 7.37 (m, Ph—*H*, 6H), 3.95 (s, OC*H*₃, 3H). ¹³C NMR (CDCl₃, δ ppm): 166.0, 132.9, 131.8, 131.8, 131.8, 130.1, 129.5, 129.0, 128.7, 128.5, 128.5, 126.1, 123.0, 122.8, 96.6, 94.4, 87.9, 87.5, 52.4. MS: *m/z* calcd. for C₂₄H₁₆O₂(M+H)⁺: 337.1; found: 337.1.

Synthesis of 3,4-Bis(2-phenylethynyl)benzoic acid (4)

To a stirring solution of **3** (1.38 g, 4.1 mmol) in CH₂Cl₂/ CH₃OH (150 mL, v/v ~9:1) was added a methanolic solution of NaOH (1.31 g, 32.8 mmol). After 15 min, the solution became cloudy and the sodium salt of the carboxylic acid started to precipitate. The solvents were removed under vacuum after stirring overnight. The reaction mixture was dissolved in water and acidified to pH = 2-3 with dilute HCl, whereupon the crude product was extracted with ethyl acetate and dried over anhydrous MgSO₄. Further concentration over a rotary evaporator under a high vacuum afforded acid **4** as a pale yellow solid (1.24 g, 93%).



¹H NMR (CDCl₃, δ ppm): 8.31 (d, ⁴*J* = 1.6, Ph—*H*, 1H), 8.03 (dd, ³*J* = 8.2 Hz, ⁴*J* = 1.7 Hz, Ph—*H*, 1H), 7.66 (d, ³*J* = 8.1 Hz, Ph—*H*, 1H), 7.59 (m, Ph—*H*, 4H), 7.37 (m, Ph—*H*, 6H).

Synthesis of 2-(Acryloyloxy)ethyl 3,4-bis (2-phenylethynyl)benzoate (5)

To a solution of **4** (0.99 g, 3.08 mmol) in DMF was added 1ethyl-3-[3-dimethylaminopropyl] carbodiimide (0.71 g, 3.70 mmol), *N*,*N*-dimethylaminopyridine (0.08 g, 0.62 mmol) and 2-hydroxyethyl acrylate (1.29 mL, 12.32 mmol) under nitrogen. The mixture was stirred at room temperature overnight. The resulting solution was then washed with brine and extracted with ethyl acetate. The organic layer was dried over anhydrous MgSO₄ and concentrated under vacuum. Subsequent flash chromatographic purification over silica (1:5 ethyl acetate-petroleum ether, $R_{\rm f} = 0.6$) yielded a yellowish product (0.91 g, 70%).

¹H NMR (CDCl₃, δ ppm): 8.23 (d, Ph—*H*, 1H), 7.96 (dd, ³*J* = 8.2 Hz, Ph—*H*, 1H), 7.60 (m, Ph—*H*, 5H), 7.37 (m, Ph—*H*, 6H), 6.45 (m, ²*J* = 17.3 Hz, -CH=CH–*H*, 1H), 6.17 (m, ²*J* = 17.3 Hz, -CH=CH–*H*, 1H), 6.17 (m, ²*J* = 17.3 Hz, -CH=CH₂, 1H), 5.87 (m, ²*J* = 16.7 Hz, -CH=CH–*H*, 1H), 4.59 (m, Ph–CO₂–CH₂–, 2H), 4.53 (m, -CH₂CH₂–, 2H). ¹³C NMR (CDCl₃, δ ppm): 164.8, 164.1, 131.9, 130.8, 130.7, 130.4, 129.2, 128.0, 128.0, 127.8, 127.7, 127.4, 127.4, 126.9, 125.1, 121.9, 121.7, 95.7, 93.4, 86.8, 86.4, 62.0, 61.1. MS: *m*/*z* calcd. for C₂₈H₂₀O₄(M+H)⁺: 421.1; found: 421.1.

Synthesis of 2-(Acryloyloxy)ethyl benzoate

This compound was synthesized in a manner analogous to that of **5**. The pure product was obtained as a colorless oil.

¹H NMR (CDCl₃, δ ppm): 8.04 (d, ³*J* = 7.2 Hz, Ph—*H*, 2H), 7.56 (t, ³*J* = 7.4 Hz, Ph—*H*, 1H), 7.44(t, ³*J* = 7.82 Hz, Ph—*H*, 2H), 6.43 (m, ²*J* = 17.3 Hz, -CH=CH-H, 1H), 6.14 (m, ²*J* = 17.3 Hz, $-CH=CH_2$, 1H), 5.85 (dd, -CH=CH-H, 1H), 4.55 (m, ³*J* = 9.3 Hz, Ph $-CO_2-CH_2-$, 2H), 4.50 (m, ³*J* = 9.2 Hz, $-CH_2CH_2-$, 2H).

Synthesis of 1,2-Bis(2-phenylethynyl)benzene

This compound was synthesized according to literature procedure.⁶⁰ The pure product was obtained by silica gel chromatography (petroleum ether, $R_{\rm f}=0.8$) as a colorless crystal.

¹H NMR (CDCl₃, δ ppm): 7.46 (m, Ph—*H*, 6H), 7.28 (m, Ph—*H*, 8H).

Representative Procedure for SET-LRP of Poly(acrylate-r-5) (6)

Copolymerizations between enediyne containing monomer **5** and different acrylates were similar. Taken poly(butylacrylate-r-**5**) as an example, a Schlenk flask was successively charged with BA (0.47 ml, 3.27 mmol), **5** (0.24 g, 0.58 mmol), freshly cleaned Cu(0) wires, Me₆-TREN (7 mg, 0.03 mmol), acetone (3 mL) and water (0.1 mL). After three cycles of freeze-pump-thaw, methyl 2-bromoproionate initiator (4 μ L, 0.03 mmol) was added via a degassed syringe. Then the polymerization was carried out at 25 °C for 4–5 h. Several drops of hydrazine hydrate were added during the polymerization. The copolymer was obtained after precipitation in methanol or methanol/water = 1:1 (vol).

General Procedure for Formation of Nanoparticles via UV Triggered Intramolecular Chain Collapse

A solution of polymer **6** (30 mg) in toluene (450 mL) was added to a quartz UV cuvette and sparged with nitrogen. The UV irradiation was conducted in a photo reactor box (Beijing Trusttech, China) using a medium-pressure Hg lamp. The reaction was stirred for 6 h under nitrogen atmosphere.

CONCLUSIONS

We have introduced a novel method to fabricate single chain polymeric nanoparticles based on photo induced Bergman cyclization. Enediyne functionalities were easily incorporated into polymer chains by controllable single electron transfer living radical copolymerization with different kinds of acrylate monomers. Both model small molecular biradical coupling and intramolecular photo-crosslinking in polymer chains were confirmed by various analysis methods. Raman scattering and ¹³C NMR revealed the disappearance of C≡C triple bond after certain UV irradiation, which is one of the most important features of occurring Bergman cyclization, accompanied with sharp decrease of apparent molecular weight recorded by GPC. Through AFM characterization, individual nanoparticles were presented clearly and distinguishable in well defined manner. Furthermore, we expanded this method to thermal sensitive poly(t-butylacrylate) nanoparticles which could not be accomplished by thermal Bergman cyclization. The potential applications of these aromatic functionalized polymer nanoparticles are under exploration in our lab.

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