Polymer Chemistry

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Indium-catalyzed Polycyclotrimerization of Diynes: A Facile Route to Prepare 1,3,5-Regioregular Hyperbranced Polyarylenes

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The first example of InCl₃-catalyzed polycyclotrimerization of diynes to generate regioregular hyperbranched polymers was developed. The InCl₃/2-iodophenol-catalyzed polycyclotrimerization of aromatic/aliphatic diynes in chlorobenzene readily furnished soluble 1,3,5-trisubstituted benzene-cored hyperbranched polyarylenes with high weight-averaged molecular weights (up to 37200) in high yields (up to 87.8%). Thanks to its low cost and moisture-tolerance, this catalytic system is anticipated to be widely applied in preparation of regioregular functional hyperbranched polymers with unique properties.

Hyperbranched polymers (HBPs) are a new kind of macromolecules showing architectural beauty and versatile functionality as dendrimers.[1] The unique size-, shape-, and surface-specific properties of HBPs make them applicable in diverse areas including chemical sensing, micellar mimetic, gene delivery, supramolecular assembly, and molecular antenna systems etc, and thus have drawn much attention in recent years.[2] Generally, the HBPs could be prepared by the self-condensation polymerizations of AB$_n$-type monomers (n ≥ 2) via one-pot, single-step process.[3] This strategy is, however, limited by the difficulty of monomer preparation and its self-oligomerization during storage.[4] To overcome these obstacles, the alternative, such as polymerization of A₂ and B$_n$ (n ≥ 2) co-monomers was developed. This method, however, suffers from the strict requirement of stoichiometric balance of the comonomers.[5]

To surmount those drawbacks, a new strategy of polycyclotrimerization (PCT) of A$_n$ (n ≥ 2)-type diynes to produce HBPs was emerged.[6] Many transition metal systems such as palladium, ruthenium, cobalt, nickel, and rhodium have been employed to catalyse the PCTs.[7] However, they are either expensive or must be used under harsh reaction conditions. Moreover, a mixture of 1,3,5- and 1,2,4-trisubstituted benzene isomers in the resulting HBPs are normally yielded.[8]

During the course of development of new polymerization reactions based on triple-bond building blocks, our group has succeeded in preparation of a variety of functional HBPs through PCT of diynes in the presence of transition-metal-catalysts.[9] We have found that PCT of activated diyne of bis(aroylacetylene)s in the presence of ogano instead of metallic catalyst could produce regioregular 1,3,5-trisubstituted hyperbranched poly(aroylarylene)s.[10] The synthesis of these monomers, however, requires many reaction steps and harsh reaction conditions, which has greatly limited its applications. Therefore, cheaper catalytic systems that could facilely catalyse the PCT of traditional diynes regioselectively are in great demand.

In general, most of the polymerizations, if not all, are developed from organic reactions of small molecules. However, great efforts should be taken to develop an organic reaction into a successful polymerization technique because several important issues have to be addressed seriously, for example, the efficiency of catalyst system, the scope and availability of monomer, the tolerance of functional group, the optimization of the polymerization conditions, the control of molecular weights, and regio- and stereo-structures as well as the solubility and processability of the resultant polymers. Thus, an ideal organic reaction for this specific purpose must be highly efficient. The recently reported excellent Indium chloride (InCl₃)/2-iodophenol-catalyzed cyclotrimerization of alkyne,[11] which readily produced solely regioregular 1,3,5-trisubstituted benzene derivatives in high yields,[12] well meets such requirement and is promising to be developed into a new PCT. Specifically, the alkynes used in this reaction were traditional aromatic or aliphatic alkynes. Moreover, InCl₃ is commercially available and much cheaper than many other transition metal complexes. It is worth noting that although InCl₃ has been used for the preparation of linear polymers from alkynes,[13] as far as we know, there is no report on employing it for the synthesis of HBPs via PCT of diynes.

Attracted by the features of this catalytic system and the efficient and regioselective InCl₃/2-iodophenol catalyzed cycloaddition of alkynes, in this work, we tried to develop it into a facile PCT for the

preparation regioregular hyperbranched polyarylenes. To get familiar with this reaction, we first repeated the organic reaction using phenylacetylene as reactant (Scheme S1, Electronic Supplementary Information, ESI†). Figure S1 shows the ^{1}H NMR spectrum of the crude product which was obtained by merely evaporating the solvent after reaction. The proton resonance of formed trisubstituted benzene was observed at δ 7.78 as singlet peak, which belongs to the typical 1,3,5-trisubstituted benzene core. Meanwhile, no 1,2,4-triphenylbenzene was found in the product as no peak was observed below δ 7.2. These results clearly demonstrate that 1,3,5-triphenylbenzene was exclusively formed and the reaction is regioselective.

Encouraged by these exciting results, we applied it for the polymerization of diynes. To test the universality, we designed and synthesized both of aliphatic and aromatic diyne monomers (**1a-1d**) (Schemes 1 and S2-S5, ESI†). We first used **1a** to investigate the catalytic performance of anhydride InCl$_3$ and its tetrahydrate (InCl$_3$•4H$_2$O) because both of them are commercially available. Table 1 summarized the polymerization results. The anhydride InCl$_3$/2-iodophenol catalyzed PCT of **1a** in chlorobenzene at 130 ^{o}C for 24 h under nitrogen readily produced hyperbranched polyarylene with weight-average molecular weight (M_w) of 13200 in excellent yield of 94.0%. Meanwhile, the InCl$_3$•4H$_2$O/2-iodophenol catalytic system performed almost the same, polymer with similar M_w (13500)

Scheme 1. Syntheses of regioregular hyperbranched polyarylenes by InCl$_3$/2-iodophenol catalyzed polycyclotrimerization of diynes.
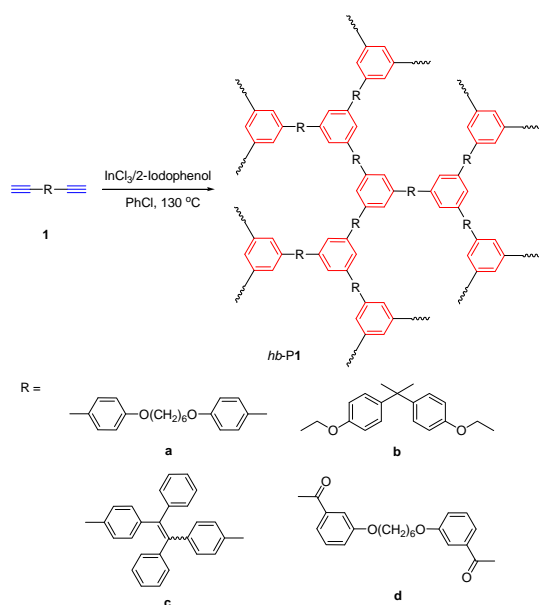

Table 1. Effect of Catalyst on Polycyclotrimerization of Diyne 1a^a

entry	catalyst	yield (%)	$M_w{}^b$	PDI^b
1	InCl$_3$	94.0	13200	2.46
2	InCl$_3$•4H$_2$O	91.0	13500	2.47

^{a} Carried out under nitrogen at 130 ^{o}C in chlorobenzene for 24h; [**1a**] = 0.15 M; [In] = 0.015 M; [2-iodophenol] = 0.10 M. ^{b} Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; PDI = polydispersity index.

was produced in similar yield (91.0%), indicating that the trace amount of water in the reaction system exerts little influence on this polymerization. Moreover, the ^{1}H NMR measurements of these two products indicate that they possess exact same structures (Figure S2, ESI†). Thus, taking the cost saving and industrial potential into account, InCl$_3$•4H$_2$O was adopted in our following study.

After selecting the catalyst, we systematically investigated the PCT conditions using **1a** as model diyne monomer. We first followed the time-course of the polymerization in chlorobenzene at 130 ^{o}C with a monomer concentration of 0.15 M. The experimental results showed that the M_w values of the products increased from 6700 to 13200 and the yields enhanced from 20.0 to 94.1% when the reaction time prolonged from 1 to 5 h (Table S1, ESI†). Afterward, the products became partially soluble in commonly used organic solvents such as THF and dichloromethane (DCM). So, 5 h was chosen as the preferable reaction time.

Next, we examined the effect of solvents on the polymerization of **1a**. As reported, the Indium catalysts display activity only at elevated temperature. Thus, we carried out the polymerizations in the solvents with boiling point higher than 100 ^{o}C. As indicated in Table S2 (ESI†), trace amount of polymeric products were obtained from the reaction carried out in toluene and DMF, while, polymers with lower M_w values and yields were produced in *o*-xylene and 1,2-dichlorobenzene than that in chlorobenzene. Thus, we chose chlorobenzene as polymerization solvent.

Since the Indium catalyst is sensitive to the temperature, we performed the experiments to study the effect of temperature on the polymerization results. We selected three temperatures of 110, 120 and 130 ^{o}C to polymerize **1a**. The results display that both of M_w values and yields of the products decreased with lowering down the temperature (Table S3, ESI†). Thus, 130 ^{o}C is the optimal temperature.

Finally, the component's concentrations were optimized. When keeping other reaction parameters unchanged, the M_w values and yields of the resulting polymers have a tendency of climbing along with increase of the concentration of **1a** from 0.10 to 0.18 M (Table S4, ESI†). However, when **1a** reached 0.18 M, the product became partially soluble. Thus, 0.15 M was regarded as the proper concentration for polymerization. Interestingly, the concentration of InCl$_3$•4H$_2$O exerts less effect on the polymerization results especially on the M_w (Table S5, ESI†). When the catalyst concentration increased to 0.015 M, the polydispersity index (PDI) of product broadened to 3.12, which is much higher than that with concentration of 0.011 M. Hence, the latter was considered as the optimal concentration.

At last, as an additive component of the catalyst system, the mass of 2-iodophenol was also tested (Table S6, ESI†). It turns out that pronounced effect on the yields of products was observed upon varying the additive concentration. More additive has led to higher yield, whereas, the M_w and PDI of the products has no direct relationship with the additive concentration. When the concentration of 2-iodophenol is 0.13 M, the produced polymer became partially soluble. So, the additive with concentration of 0.10 M is the best.

With the optimal reaction conditions in hand, we first tried to investigate the catalytic mechanism of PCT. Besides the InCl$_3$/2-iodophenol system, we also used InCl$_3$/ iodobenzene, InCl$_3$/phenol or InCl$_3$ to catalyze the reactions. The results showed that the InCl$_3$/2-iodophenol system could catalyze the PCT of **1a** to produce polymer with M_w of 17200, which is 2.5 and 2.8 times higher than those catalyzed by InCl$_3$/iodobenzene and InCl$_3$, respectively (Table S7, ESI†). Furthermore, the additive of phenol displays negative

effect on the PCT. By combining the reported hypothetic mechanism, we propose that the 2-iodophenol could act as an oxidant to cleave C-In δ-bonds to generate regioregular benzene-cored polymers and active $InCl_3$ although additional proofs should be collected.[14]

Then, we performed the PCT of diynes **1b**, **1c**, and **1d** (Scheme 1 and Table 2, ESI†) with those optimized conditions. The aliphatic diyne of **1b** could be polymerized to produce polymer P**1b** with M_w of 27400 after 5 h, but the solubility is poor probably due to the high reactivity of **1b**. Delightfully, shortening the reaction time to 2 h could furnish soluble polymer with satisfactory M_w of 12200 in good yield (82.8%). Similarly, when the aromatic **1c** was polycyclotrimerized for 2 h instead of 5 h but keeping other conditions unchanged, soluble P**1c** with M_w of 10000 could be obtained in high yield (87.8%). However, the carbonyl connected terminal diyne **1d**, a kind of activated alkyne, was hard to get completely soluble product due to its high reactivity as proven in our previous work.[10a,b] The M_w of soluble part of P**1d** was measured by gel permeation chromatography (GPC) to be 5400 after **1d** was polymerized for 1 h. It should be noted that the GPC calibrated by linear polystyrene standards can significantly underestimate M_w values of hyperbranched polymers.[15] Deffieux et al., for example, found that the relative molecular weights of their hyperbranched polystyrenes estimated by GPC were normally ~7-fold, sometimes even ~30-fold, lower than the absolute values.[16] These results demonstrate not only the universality but also the fidelity of $InCl_3 \cdot 4H_2O$/2-iodophenol for catalyzing the PCTs of different type of diynes.

Table 2. Polycyclotrimerizations of Diynes 1a-1d^a

entry	monomer	polymer	yield (%)	$M_w{}^b$	PDI^b
1^c	**1a**	P**1a**	94.1	12600	2.68
2	**1b**	P**1b**	82.8	12200	1.54
3	**1c**	P**1c**	87.8	10000	1.56
4^d	**1d**	P**1d**	50.0	5400^e	1.64

^{a} Carried out in chlorobenzene at 130 ^{o}C under nitrogen for 2 h; [M]$_0$ = 0.15 M; [In] = 0.011 M; [2-iodophenol] = 0.10 M. ^{b} Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; PDI = polydispersity index. ^{c} The reaction time is 5 h. ^{d} The reaction time is 1 h. ^{e}Soluble part.

The hyperbranched polyarylenes P**1a**-P**1d** were characterized spectroscopically, and all of the polymers gave analysis data corresponding to their expected molecular structures (see Experimental Section and Figures S3-S12, ESI† for details). Example of the IR spectrum of P**1a** is shown in Figure S3 (ESI†). For comparison, its monomer of **1a** is also presented. The diyne monomer shows absorption bands at 3305 and 2102 cm^{-1} due to ≡C-H and C≡C stretching, respectively. These bonds are absent in the spectrum of P**1a**, revealing that the triple bonds have been converted to the benzene rings or formed the macrocycles by the PCT. Similar results were observed in the IR spectra of P**1b**-P**1d**. (Figures S4-S6, ESI†)

The ^{1}H NMR spectrum of model compound has proven that solely 1,3,5-regioregular benzene derivate was produced. Similar conclusions could be drawn from the ^{1}H NMR spectra of hyperbranched polyarylenes. Figure 1 shows the ^{1}H NMR spectra of

P**1a** and its monomer of **1a**. The acetylene proton of its monomer **1a** absorbs at δ 2.90, which almost disappeared after PCT. While, such peaks only become weaker in the ^{1}H NMR spectra of P**1b**-P**1d** (Figures S7-S9, ESI†), implying that the macrocycles may be formed during the PCT of **1a** due to its relative flexible structure. Meanwhile, the typical peaks of the protons in the newly formed 1,3,5-trisubstituted benzene rings of P**1a**-P**1d** could be clearly identified in the downfield, manifesting the regioselectivity of the $InCl_3 \cdot 4H_2O$/2-iodophenol catalyze PCT. The ^{13}C NMR spectra of these polymers further substance the conclusions drawn from the ^{1}H NMR spectra (Figures S10-S12, ESI†). The important parameter for hyperbranched polymers, i.e. degree of branching, is difficult to calculate due to the severe overlapping of the resonances in the ^{1}H NMR spectra of the polymers.

Thanks to the formed benzene rings, the hyperbranched polyarylenes P**1a**-P**1d** are thermally stable, of which the temperatures for 5% weight loss are all higher than 295 ^{o}C (Figure S13, ESI†).
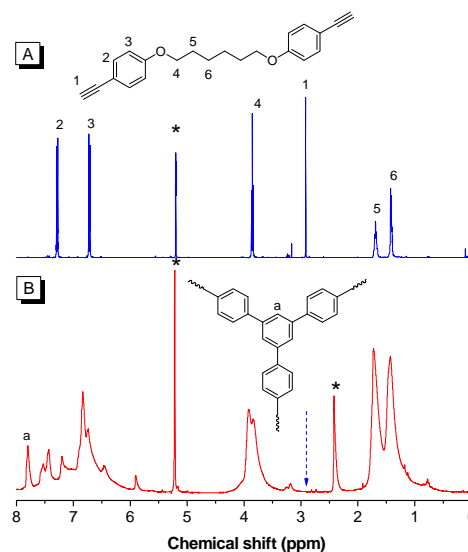

Figure 1. ^{1}H NMR spectra of monomers (A) **1a** and (B) polymer P**1a** in DCM-d_2. The solvent peaks are marked with asterisks.

Conclusions

A new and facile $InCl_3$/2-iodophenol catalyzed PCT of diynes were successfully developed and solely 1,3,5-trisubstituted benzene-cored hyperbranched polyarylenes with high M_w were obtained in good yields. The commercial hydrate $InCl_3$ could be used to efficiently catalyze this polymerization. Compared to the reported catalytic systems for the PCT of diynes, our reported one is cheaper and could catalyze the polymerization in regioselective fashion. Moreover, the moisture-tolerance ability of this polymerization makes it promising for wide application in preparing functional hyperbranched polymers, which is the on-going project in our group.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed synthetic routes to monomer **1a** and P**1a**; Characterization data of P**1a**-P**1d**; Schematic synthetic routes to **1a-1d**; ^{1}H NMR spectra of model compound; IR, ^{1}H and ^{13}C NMR spectra of P**1a**-P**1d**; tabulate data of optimization of polymerization conditions. See DOI: 10.1039/c000000x/

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The facile and efficient InCl$_3$/2-iodophenol-catalyzed polycyclotrimerization of diynes to generate regioregular hyperbranched polyarylenes was successfully established.