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Fast Living Polymerization and Helix-Sense-Selective Polymerization of Diazoacetates Using Air-Stable Palladium(II) Catalysts

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ABSTRACT. In this work, air-stable palladium(II) catalysts bearing bidentate phosphine ligands were designed and prepared, which could initiate fast and living polymerizations of various diazoacetate monomers under mild conditions. The polymerization afforded desired polymers in high yields with controlled molecular weights (M_ns) and narrow molecular weight distributions (M_w/M_ns). The M_ns of the isolated polymers were linearly correlated to the initial feed ratios of monomer to catalyst, confirming living/controlled manner of the polymerizations. The M_n also increased linearly to the monomer conversion, and all the isolated polymers showed narrow M_w/M_ns. The polymerization was relatively fast, and can be accomplished within several minutes. Such fast living polymerization method can be applied to a wide range of diazoacetates monomers in various organic solvents at room temperature under air. Taking advantage of the living nature, a series of block copolymers were facilely prepared through chain extension reactions. The amphiphilic block copolymers synthesized by this method exhibited interesting self-assembly properties. Moreover, polymerization of achiral bulky diazoacetate by Pd(II) catalysts bearing chiral bidentate phosphine ligand lead to the formation of polymers with high optical activity due to the formation of predominated one-handed helix of the main chain. The helix-sense of the polymers was determined by the chirality of the Pd(II) catalysts.

Introduction

It is well-known that the C-C main chain polymers are one of the most important classes of synthetic polymers and have been widely used in our modern life. These polymers are generally prepared via the polymerization of vinyl monomers. An alternating method is the polymerization of one carbon (C1) units such as isocyanide, dimethylsulfoxonium methylide and diazocarbonyl compounds.[1-5] The latter one is of particular interest because it can afford well-defined C-C main chain polymers bearing polar substituents at every main chain carbons, which cannot be accessed by Ziegler-Natta catalysts.[6,7] Thus, the diazoacetates polymerization seems an attractive route to prepare C-C main chain functional polymers. It can be argued that the radical polymerization of dialkyl fumarates or maleates can also produce polymers with similar structures.[8,9] However, the living/controlled polymerizations of these monomers have never been attained so far.

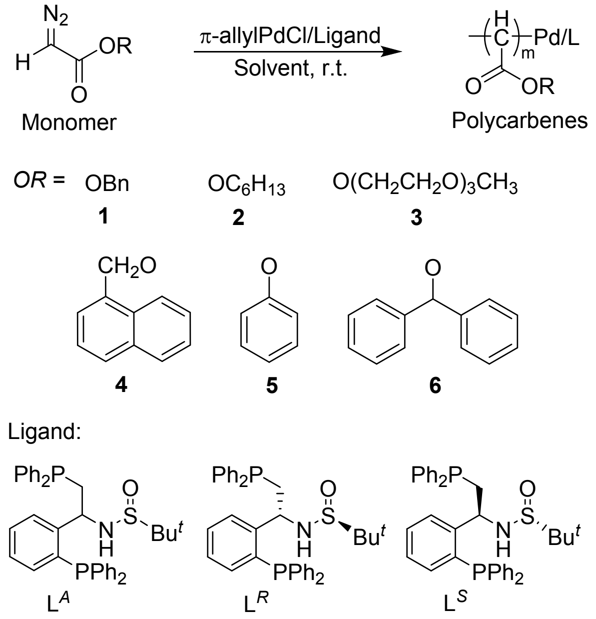
Recently, some organometallic compounds such as copper, palladium, and rhodium complexes have been reported to promote the polymerization of diazoacetates. Nevertheless, the Cu-mediated polymerizations can only generate low molecular weight oligomers.[10] The Rh-mediated polymerization of ethyl and benzyl diazoacetates yield syndiotactic polycarbenes with high molecular weights (M_ns).[11-14] While it is difficult to control the M_n and usually afford polymers with broad molecular weight distribution. Ihara and coworkers have reported a series of excellent π-allylPdCl based complexes that can promote the polymerization of various diazoacetates monomers, which made great contributions in this interesting research field.[15-17] In those pioneering works, they have proposed a possible mechanism for the Pd(II)-mediated diazoacetates polymerizations via detailed analyses of polymer chain end structures.[18] Moreover, high molecular weight polymers with moderate stereoregularity can also been obtained by using the Pd(II) catalyst.[19] However, living/control polymerization using the Pd(II) catalysts is still a great challenge. There is only one example on controlled polymerization of diazoacetate, in which a very specific diazoacetate monomer bearing a sterically bulky phosphazenes was employed.[20] Beside those disadvantages, most of the reported catalysts for the diazoacetate polymerization are sensitive to air, and the polymerizations have to be performed under an inert atmosphere except for some Rh-catalysts.[13,14] Additionally, the reported diazoacetates polymerizations usually require a quite long time because of the low activity of the catalysts. Therefore, developing air-stable catalysts for fast living polymerization of common diazoacetate monomers is of great desired.

The polymerization of diazoacetates afford polycarbenes comprised of C-C single bonds and carrying substituents on each main chain carbon. Introducing appropriate substituents on polycarbenes pendants may endow the polymer with a stable helical conformation due to the steric hindrance between the adjacent pendants.[21,22] De Bruin and coworkers have revealed that poly(ethylidene acetate) can adopt a flexible helical structure due to the steric repulsion between their ethyl side groups through computational molecular modeling.[23] As we know, helix is the central structure motif in biomacromolecules and plays important roles in living system including catalysis, recognition, replication, etc. Partially stimulated by the elegant helices in Mother Nature, fully synthetic helical polymers with controlled helix sense has attracted considerable research efforts in the past few decades.[24-27] Such research is not only just for mimicking the helices and functions in nature but also for developing new materials with novel functions and applications in asymmetric catalysis, chiral resolution, self-assembled nanomaterials, and electronic devices and so on.[28-32] Although great efforts have been devoted, the number and type of artificial helical polymers are still very limited, which strongly restricts the exploration on their structures and functions. Thus exploring novel helical polymers is of continuous and great interesting. Although the structure of polycarbenes is similar to helical polyisocyanide,[21] its helical conformation and the related chiroptical properties have rarely been explored to date.[23] Helix-sense-selective polymerization of achiral monomers can afford a helical polymers with controlled helicity, in which, a small amount of chiral catalyst, initiator or additives can produce a large amount of chiral materials.[33-41] The chirality of the afforded polymers is only come from the helicity of the main chain without containing any chiral pendants.

In this contribution, we report a family of air-stable Pd(II) complexes bearing a bulky bidentate phosphine ligand which can efficiently initiate fast living polymerizations of various diazoacetate monomers at room temperature under an air atmosphere. The polymerizations are relatively fast, and can be accomplished within several minutes. The living polymerizations lead to the formation of well-defined polycarbenes in high yields with controlled M_ns and narrow molecular weight distributions (M_w/M_ns) (Scheme 1). Taking advantage of this method, well-defined block copolymers can be facilely prepared. Moreover, the synthetic polycarbenes bearing bulky pendants was revealed to possess a stable helical conformation in solution. Helix-sense-selective polymerization of achiral diazoacetate monomers using a chiral Pd(II) catalyst afforded helical polycarbenes with high optical activity owing to the predominant of one-handed helix.

Results and Discussion

Scheme 1. Polymerization of Diazoacetates Using Air-Stable Pd(II) Catalysts



Fast Living Polymerizations. As shown in Scheme 1, benzyl diazoacetate (**1**) was first prepared and employed as a model monomer. It was polymerized by various Pd(II) catalysts to disclose the polymerization activity of the synthesized Pd(II) complexes. The Pd(II) catalysts bearing different ligands were simply prepared through the reaction of commercial available *π*-allylPdCl with the corresponding phosphine ligands in THF at room temperature. Initially, the ratio of phosphine atom to palladium was fixed at 2/1 ($[P]_0/[Pd]_0 = 2/1$). The resulting solution of Pd(II) catalyst was directly used for the diazoacetate polymerization without isolation and purification steps to minimize the decomposition of the complexes during the handling process. All the polymerizations of monomer **1** using the Pd(II) complexes were conducted in THF at room temperature under nitrogen atmosphere ($[\mathbf{1}]_0$ = 0.3 M, $[\mathbf{1}]_0/[\mathrm{Pd}]_0$ = 50). After 24 h, the polymerization solution was precipitated into a large amount of *n*-hexane. It was found that the ligand on the Pd(II) catalyst played important effect on the polymerization behaviors, although other experimental conditions were identical. White polymeric solid can only precipitated from the polymerization solutions using the Pd(II) catalysts bearing tri-*tert*-butylphosphane ($^t\mathrm{Bu}_3\mathrm{P}$) and bis(diphenylphosphino)-1,1'-binaphthalen (BINAP) ligands (run 1 and 4, Table 1). No polymeric materials could be isolated from the polymerizations using triphenylphosphine (PPh_3) and 1,3-bis(diphenylphosphino)propane (dppp) ligands on the Pd(II) catalysts (run 2-3, Table 1). The isolated polymers were first analyzed by size exclusion chromatography (SEC). The M_n and $M_\mathrm{w}/M_\mathrm{n}$ determined by SEC with equivalent to polystyrene standards were summarized in Table 1. All the isolated polymers exhibited molecular weight around 6~7 kDa, while the $M_\mathrm{w}/M_\mathrm{n}$ values are much different and depending on the ligand. It seems that increasing the steric hindrance of the alkyl phosphine ligand on the Pd(II) catalyst will decrease the $M_\mathrm{w}/M_\mathrm{n}$ value. Thus, we further synthesized a bulky bidentate phosphine ligand (*N*-[2-(diphenylphosphino)-1-[2-(diphenylphosphino)phenyl]ethyl]-2-methyl) (L^A) followed the reported procedure, and used as ligand in the Pd(II)-mediated diazoacetate polymerization.[42] The large size and relative rigid structure of L^A might promote the polymerization of diazoacetate under a living/controlled manner. To verify this hypothesis, the Pd(II)/L^A catalyst was prepared through the reaction of *π*-allylPdCl with the L^A in THF at 25 °C. The polymerization of **1** with Pd(II)/L^A was performed in THF at 25 °C ($[\mathbf{1}]_0$ = 0.3 M, $[\mathbf{1}]_0/[\mathrm{Pd}]_0$ = 50) followed the same experimental condition described above. To our delight, SEC trace of the isolated polymer showed a symmetrical and unimodal elution peak

(Figure 1a). The M_n of the isolated poly-$\mathbf{1}_{50}$ (the footnote indicates the initial feed ratio of monomer to catalyst) was determined to be 7.0 kDa, very close to the theoretical value (7.4 kDa). Most importantly, it showed a very narrow molecular weight distribution, and the M_w/M_n is only 1.16. This result suggested that the Pd(II)/L^A is a good catalyst for the polymerization of **1** and gives a polymer with expected M_n and narrow M_w/M_n.

Table 1. The Results for Polymerization of 1 Using Pd(II) Catalysts[a]

run	ligand	$[M]_0/[Pd]_0$ [b]	$[L]_0/[Pd]_0$ [c]	M_n [d] (kDa)	M_w/M_n [d]	yield[e] (%)
1	*t*BuP	50	2	6.8	1.47	62
2	PPh_3	50	2	-[f]	-[f]	-[f]
3	dppp	50	1	-[f]	-[f]	-[f]
4	Binap	50	1	5.8	1.57	64
5	L^A	50	1	7.0	1.16	81
6	L^A	75	1	8.3	1.17	80
7	L^A	100	1	10.1	1.17	83
8	L^A	125	1	11.9	1.16	85
9	L^A	150	1	13.7	1.18	81
10	L^A	175	1	14.8	1.19	82
11	L^A	200	1	16.9	1.19	82
12	L^A	50	0.5	6.8	1.34	76
13	L^A	50	2	6.9	1.29	78

[a] The polymerizations were carried in THF at 25 °C for 24 h according to Scheme 1. [b] The initial feed ratio of monomer to catalyst. [c] The feed ratio of phosphine ligand to π-allylPdCl. [d] The M_n and M_w/M_n values were determined by SEC with equivalent to polystyrene standards. [e] The isolated yields. [f] No polymer could be isolated.

The narrow M_w/M_n of the isolated poly-$\mathbf{1}_{50}$ indicated the polymerization may proceed in a living/controlled chain-growth manner. To verify this hypothesis, a series polymerizations of monomer **1** using Pd(II)/L^A as catalyst were conducted in THF at 25 °C, under the same experimental condition but in different initial feed ratios of monomer to catalyst. It was found that all the polymerizations were proceeded smoothly and yielded the expected polymers in high yields (yield > 80%, Table 1). As shown in Figure 1a, the SEC curves of the isolated polymers exhibited unimodal and symmetrical elution peaks, and continually shifted to higher M_n-region with the increased ratio of monomer to catalyst. The M_n and M_w/M_n values of the isolated polymers determined by SEC were summarized in Table 1. The M_n of the isolated polymers increased linearly and in proportion to the initial feed ratio of monomer **1** to the Pd(II) catalyst (Figure 1b). Moreover, all the isolated polymers showed narrow molecular weight distributions with M_w/M_n < 1.20. This result confirmed that the polymerization of **1** using Pd(II)/L^A as catalyst did proceed in a living/controlled manner. Taking advantage of this method, a variety of poly-$\mathbf{1}_m$s with controlled M_n and narrow M_w/M_n were facilely obtained in high yields (>80%) just through the variation on the initial feed ratio of monomer to catalyst (Table 1). It is worthy to note that variation on the feed ratio of L^A to the π-allylPdCl has strong influence on the results of the polymerization. The best ratio of the L^A to π-allylPdCl was determined to be 1 to 1 ($[L^A]_0/[\pi\text{-allylPdCl}]_0 = 1/1$). Further increase or decrease the ratio of L^A to π-allylPdCl in the catalysts, the M_w/M_n of the generated polymers became broad (run 12 and 13 in Table 1, and Figure S1 in Supporting Information). Thus the catalyst Pd(II)/L^A with $[Pd]_0/[L^A]_0 = 1/1$ was used in the following studies.

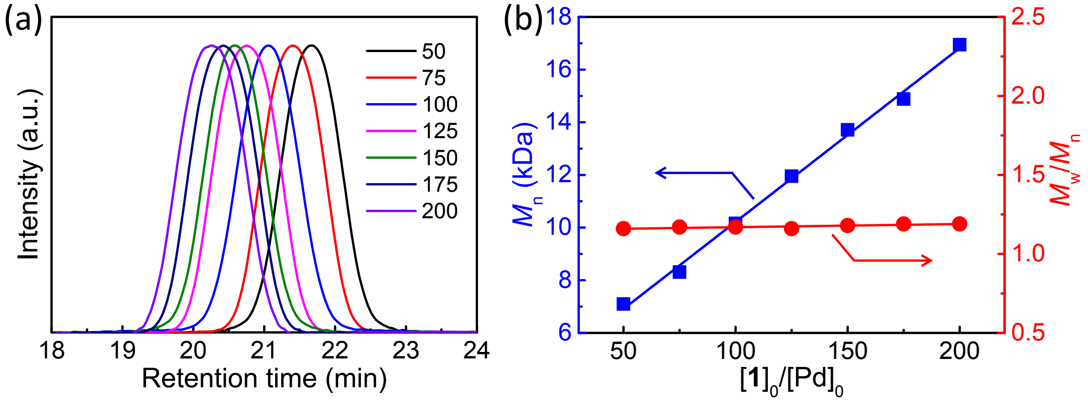


Figure 1. (a) Size exclusion chromatograms of poly-$\mathbf{1}_m$s prepared using the Pd(II)/L^{A}-mediated polymerization of **1** with different initial feed ratio of monomer to catalyst. (b) Plots of the M_n and M_w/M_n values of poly-$\mathbf{1}_m$s as a function of the initial feed ratios of **1** to the Pd(II)/L^{A}. The polymerizations were carried out in THF at 25 °C for 24 h. M_n and M_w/M_n were determined by SEC with polystyrene standards (SEC conditions: eluent = THF; temperature = 40 °C).

To get more details, the polymerization of **1** with Pd(II)/L^{A} was carried in THF at 25 °C with presence of dimethyl terephthalate as internal standard ($[\mathbf{1}]_0$ = 0.3 M, $[\mathbf{1}]_0/[\text{Pd}]_0$ = 100). The polymerization was followed by high performance liquid chromatography (HPLC) to estimate the monomer conversion as well as SEC to estimate the M_n and M_w/M_n values of the generated polymers at different polymerization stages. As outlined in Figure 2a, poly-$\mathbf{1}_m$s isolated at different stages showed unimodal and symmetric SEC traces, and continually shifted to shorter retention time region with the progress of the polymerization. Plots of the monomer conversion with M_n and M_w/M_n values of the isolated polymers were displayed in Figure 2b. The M_n of the generated polymer increased linearly and in proportion to the conversion of monomer **1**, while all the isolated polymers showed narrow molecular weight distribution with $M_w/M_n < 1.18$. This result further supports the living/controlled nature of the Pd(II)-mediated benzyl diazoacetate polymerization. Moreover, it was found that the polymerization was relatively fast, more than 90% of monomer was consumed within 10 min, suggesting the high activity of the Pd(II) catalyst (Figure 2c). Kinetic study revealed that the polymerization obey the first-order reaction rate law (Figure 2d). The appearance rate constant was estimated to be 0.41 s^{-1}, further confirms the fast living nature of the polymerization. It is worthy to note that the previously reported catalysts or initiators for the polymerization of diazoacetate monomers may require a long time, usually take more than ten hours and sometimes several days to accomplish the polymerizations.[13-18] The fast polymerization rate of this new catalyst suggests the presence of appropriate phosphine ligand on the Pd(II) catalyst not only endow the polymerization with excellent controllability but also enhance the activity of the catalyst, making the polymerization with fast living characters. The previously reported catalysts for the diazoacetates polymerizations usually require to be performed under inert atmosphere. In sharp contrast, the fast living polymerizations initiated by the Pd(II)/L^A here can be facilely performed under an air atmosphere, and yielded the desired polymers with expected M_n and narrow M_w/M_n (Table S1, Supporting Information). The influence of air on the polymerization using the Pd(II)/L^A catalyst is negligible. Probably the bulky and rigid ligand of L^A protected the living center of the Pd(II) units on the chain growth terminal, and suppressed the chain transfer and chain termination during the polymerization process. The accurate mechanism for this ligand promoted fast living polymerization is not very clear at the current stage. Ihara and coworkers have proposed an initiation and termination mechanism for the Pd(II)-mediated diazoacetates polymerization.[18] Since the polymerizations used the same π-allylPdCl as catalyst precursor, the Pd(II)/L^A catalyst may follow a similar mechanism. While other possible mechanisms cannot be completely excluded because the polymerization behaviors are different.

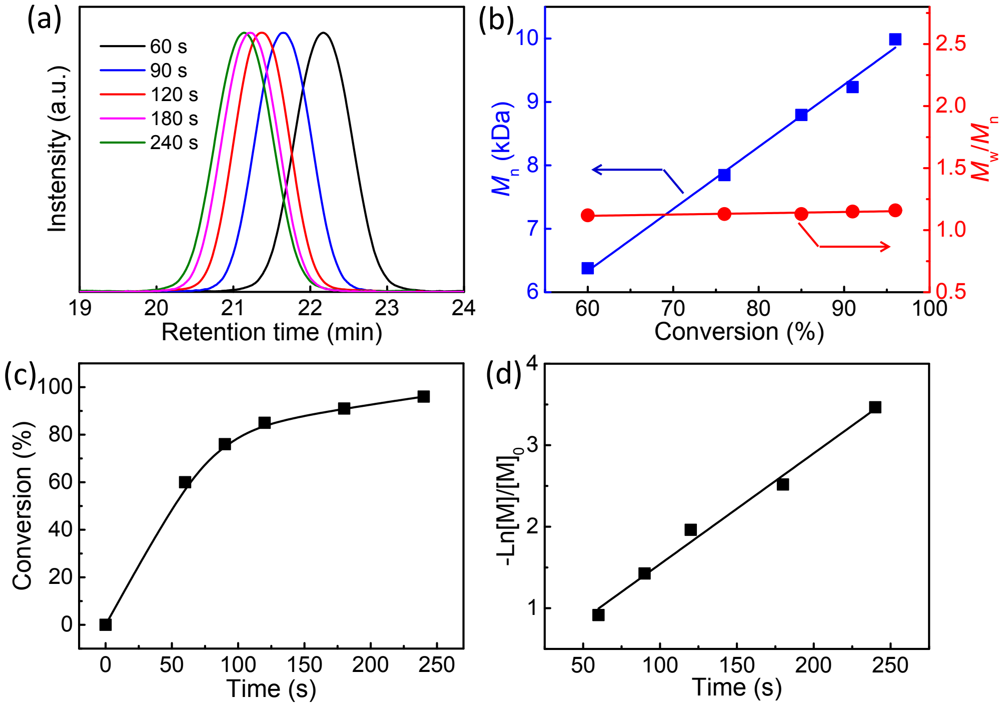


Figure 2. (a) Time-dependent SEC chromatograms for Pd(II)/L^A initiated living polymerization of **1**. (b) Plots of M_n and M_w/M_n values as a function of the conversion of monomer **1**. (c) Plot of the conversion of monomer **1** with polymerization time. (d) First-order kinetic plot for the polymerization of **1** initiated by Pd(II)/L^A. The polymerization of **1** using Pd(II)/L^A catalyst was performed in THF at 25 °C with [**1**]$_0$ = 0.3 M, and [**1**]$_0$/[Pd]$_0$ = 100.

The fast living polymerization of **1** using the Pd(II)/L^A as catalyst was then attempted be performed in various organic solvents with different polarity (Table S2, Supporting Information). It was found that the polymerization could be facilely performed in toluene, chloroform, dichloromethane, and chlorobenzene at room temperature. All the polymerizations led to the formation of well-defined poly-**1**$_m$s in high yields. Although the M_w/M_n became broad when the polymerizations were performed in dichloromethane and chlorobenzene. The broad polydispersity is likely due to the presence of ethanol stabilizer in the solvents that acted as a chain-transfer agent.[43] The polymerizations performed in *n*-hexane and methanol were failed because of the poor solubility of the generated polymers in these solvents. These results indicated the polymerization can be carried out in various organic solvents, while the THF is the best.

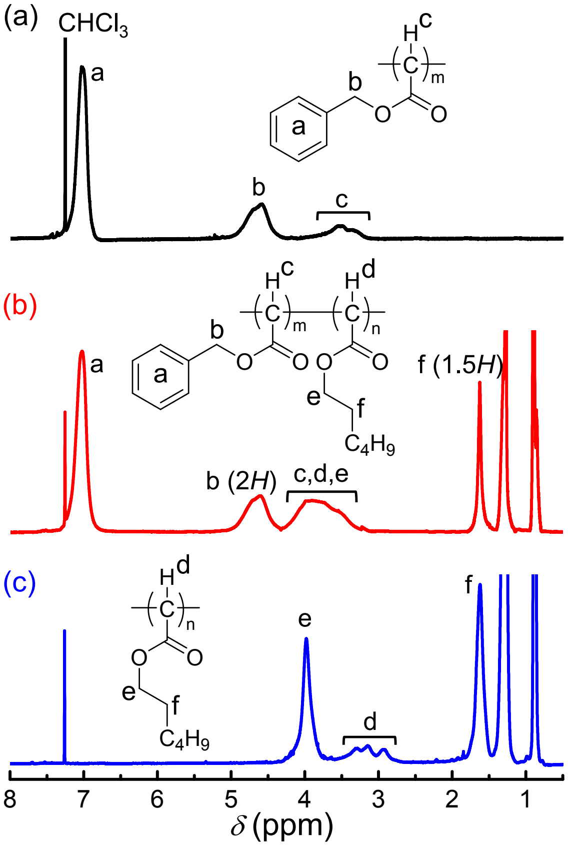


Figure 3. ^{1}H NMR (600 MHz) spectra of poly-**1**$_{50}$, poly(**1**$_{100}$-*b*-**2**$_{75}$), and poly-**2**$_{100}$ recorded in $CDCl_3$ at 25 °C.

In addition to SEC, the formation of the well-defined polymers were further characterized by ^{1}H, ^{13}C, and ^{31}P NMR, and FT-IR analyses (Figure S2-S5, Supporting Information). The ^{1}H NMR spectrum of poly-$\mathbf{1}_{50}$ showed intense resonance at 7.48–6.69 and 5.21–4.28 ppm, which were attributed to the protons of phenyl ring and benzyl methylene, respectively (Figure 3a). The resonance of the main chain C*H* proton was located at 3.86–3.21 ppm and splitted into doublet. ^{13}C NMR spectrum also confirmed the chemical structure of the isolated polycarbene (Figure S2, Supporting Information). The resonance of the main chain carbon of poly-$\mathbf{1}_{50}$ was splitted into two peaks located at 45.0 and 46.5 ppm, consist to the ^{1}H NMR analysis.[16] Note that the main chain carbon of a fully atactic polycarbene usually showed multiple resonances from 43-48 ppm on ^{13}C NMR, suggesting the yielded poly-$\mathbf{1}_{50}$ may possess some content of stereoregularity.[16,17] The ^{13}C resonances of the carbonyl carbon of poly-$\mathbf{1}_{50}$ showed a major signal at 170.0 ppm accompanied with minor signal at 171.1 ppm. On the basis of the pioneering works of Ihara and de Bruin, the resonance at 171.1 ppm can be ascribed to the syndiotactic polycarbene.[12,13,16,19] Thus, the isolated poly-$\mathbf{1}_{50}$ may contains a rather enhanced isotactic sequence. Interestingly, ^{31}P NMR spectrum of poly-$\mathbf{1}_{50}$ showed two broad signals at 15.89 and 16.82 ppm, indicating the Pd(II) unit was quite stable and was maintained at the living chain-end after the post polymerization treatments (Figure S3, Supporting Information). FT-IR spectrum of the poly-$\mathbf{1}_{50}$ showed characteristic vibration of C=O at 1730 cm^{-1}, corresponding to the ester pendants (Figure S4, Supporting Information). Collectively, these studies confirmed the formation of expected polycarbenes.

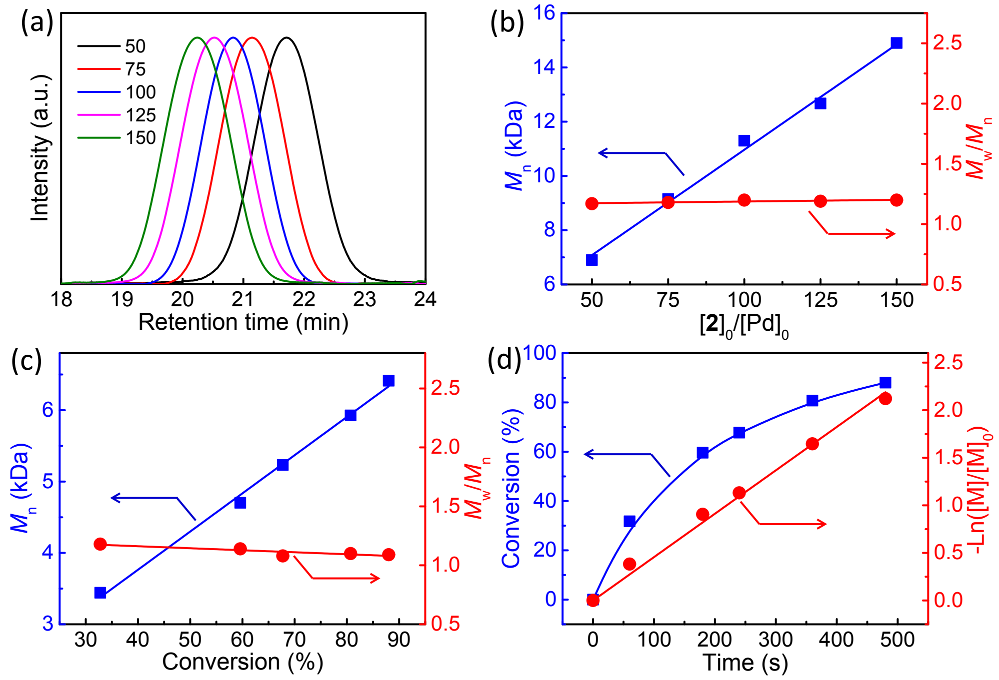


Figure 4. (a) Size exclusion chromatograms of poly-**2**$_m$s prepared from the Pd(II)/L^A-catalyzed polymerization of **2** in THF at 25 °C with different initial feed ratio of monomer to catalyst. (b) Plotted of M_n and M_w/M_n values of poly-**2**$_m$s as a function of the initial feed ratio of **2** to Pd(II) /L^A catalyst. (c) Plots of M_n and M_w/M_n values as a function of the conversion of monomer **2** catalyzed by Pd(II)/L^A in THF at 25 °C. (d) Plot of monomer conversion as a function of the polymerization time and first-order kinetic plot for the polymerization of **2** initiated by Pd(II)/L^A.

The established fast living polymerization method using Pd(II)/L^A catalyst was then applied to various diazoacetates monomers with different substituents to disclose the monomer scope. As shown in Scheme 1, monomer **2** bearing less steric *n*-hexyl ester was polymerized in THF at 25 °C by using Pd(II)/L^A catalyst ([**2**]$_0$ = 0.3 M, [**2**]$_0$/[Pd]$_0$ = 50), followed the procedure described above. SEC analyses revealed the polymerization was succeeded, the isolated poly-**2**$_{50}$ showed unimodal and symmetrical elution peak on SEC curve (Figure 4a). The M_n and M_w/M_n were determined to be 6.9 kDa and 1.17, respectively. Further studies suggested the polymerization was also proceeded in a living/controlled manner because the M_n of the produced poly-$\mathbf{2}_m$s increased linearly to the initial feed ratio of monomer to catalyst (Figure 4b). All the isolated poly-$\mathbf{2}_m$s showed narrow molecular weight distribution with $M_w/M_n < 1.20$. To get more details, the polymerization of **2** with the Pd(II)/L^A catalyst was followed by SEC and HPLC to disclose the relationship between monomer conversion with reaction time, M_n and M_w/M_n values of the produced polymers. As shown in Figure 4c, the M_n of the poly-$\mathbf{2}_m$s isolated at different polymerization stages was linearly correlated to the conversion of monomer **2**, while the M_w/M_n kept narrow ($M_w/M_n < 1.20$). It was found that the polymerization was relatively fast, more than 80% of monomer **2** was consumed within 10 min (Figure 4d). These studies further revealed the polymerization of less steric alkyl diazoacate monomer using the Pd(II)/L^A as catalyst was also proceeded in a fast living fashion, efficiently afforded the desired polycarbenes in high yields with controlled M_n and narrow M_w/M_n. The chemical structure of poly-$\mathbf{2}_m$ was further confirmed by ^{1}H, ^{13}C NMR and FT-IR (Figure 3c, and Figure S6-S7 in Supporting Information). ^{1}H NMR spectrum of poly-$\mathbf{2}_{100}$ showed characteristic resonances at 4.22–3.81 and 3.61–2.85 ppm, respectively corresponding to the OCH_2 of pendants and CH of the main chain (Figure 3c).

Table 2. **Polymerizations of Various Diazoacetates by Pd(II)/L^A in THF at 25 °C**[a]

run	monomer	$[M]_0/[Pd]_0$[b]	time (h)	M_n[c] (kDa)	M_w/M_n[c]	yield[d] (%)
1	**2**	50	0.5	6.9	1.17	79
2	**2**	100	0.5	11.3	1.20	84
3	**2**	150	0.5	14.9	1.20	76
4	**3**	50	12	6.2	1.20	55
5	**3**	100	12	8.5	1.19	60
6	**4**	50	8	6.1	1.18	78
7	**4**	100	8	9.9	1.19	81
8	**4**	150	8	12.2	1.20	82
9	**5**	50	12	6.2	1.17	75
10	**5**	100	12	7.4	1.20	76
11	**5**	150	12	8.7	1.18	81
12	**6**	50	24	3.1	1.13	43
13	**6**	100	24	3.5	1.15	34
14	**6**	150	24	4.1	1.14	35

[a]The polymers were prepared according to Scheme 1. [b]The initial feed ratio of monomer to catalyst. [c]The M_n and M_w/M_n values were determined by SEC with equivalent to polystyrene standards. [d]The isolated yields.

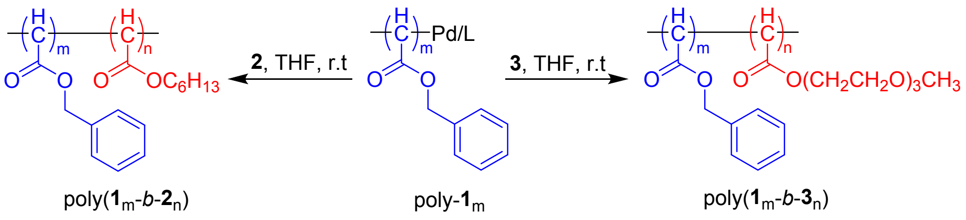
The fast living polymerization method using Pd(II)/L^A catalyst was then applied to other diazoacetate monomers including 2-(2-(2-methoxyethoxy)ethoxy)ethyl 2-diazoacetate (**3**), 1-naphthalenylmethyl ester diazoacetate (**4**), phenyl ester diazoacetate(**5**), and diphenylmethyl ester diazoacetate (**6**) (Scheme 1). The polymerizations were performed in THF at room temperature, followed the same procedure to that of monomer **1** and **2**. As expected, all the polymerizations afforded desired polymers with controlled M_n and narrow M_w/M_n (Table 2, and Figure S8-S18 in

Supporting Information). Thus, it can be concluded that the established fast living polymerization method using Pd(II)/L^{A} as catalyst can be applied to a variety of diazoacetate monomers.

Chain Extension Reactions. To further confirm the living nature of the polymerization and also to reveal the activity of the Pd(II) complex on the chain end, chain extension reaction of the isolated poly-$\mathbf{1}_{\mathrm{m}}$ with a new feed of diazoacetate monomer was then performed. By this method, well-defined block copolymers may be facilely obtained. The Rh-catalyst also showed living character and has been used in the synthesis of block polycarbenes although some random segments may contained.[44-46] While well-defined block polycarbenes have rarely been reported.[20] As shown in Scheme 2, the isolated poly-$\mathbf{1}_{100}$ (M_{n} = 10.1 kDa, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.18) was treated with monomer **2** in THF at 25 °C ($[\mathbf{2}]_0$ = 0.3 M, $[\mathbf{2}]_0/[\mathrm{Pd}]_0$ = 75). SEC analysis indicated the block copolymerization did take place because the elution peak of the resulting polymer shifted to the high-M_{n} region, while it still remained symmetric and unimodal (Figure 5a). The M_{n} of the isolated block copolymer poly($\mathbf{1}_{100}$-*b*-$\mathbf{2}_{75}$) was estimated to be 18.6 kDa, remarkably larger than that of the precursor poly-$\mathbf{1}_{100}$ (M_{n} = 10.1 kDa, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.18), while the distribution kept narrow with $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.20 (Table 3). ^{1}H NMR spectra also supported the formation of the expected block copolymer poly($\mathbf{1}_{100}$-*b*-$\mathbf{2}_{75}$). As displayed in Figure 3b, ^{1}H NMR spectrum of poly($\mathbf{1}_{100}$-*b*-$\mathbf{2}_{75}$) recorded in $CDCl_3$ at 25 °C is almost the superposition of the respective two homopolymers of poly-$\mathbf{1}_{\mathrm{m}}$ and poly-$\mathbf{2}_{\mathrm{n}}$. The resonances come from the two blocks could be clearly observed. Moreover, the block ratio deduced from the integral analyses of the resonances at 5.21–4.23 ppm of poly-$\mathbf{1}_{100}$ segment and at 1.82–1.58 ppm of the poly-$\mathbf{2}_{75}$ segment is ca. 4:3, which agree with the initial feed ratio of the two monomers used in the block copolymerization. Note that the random copolymerization of the two diazocarbonyl monomers usually showed the shifted resonances of the two repeating units.[20,44] Combined with FT-IR and differential scanning calorimetry (DSC) analyses (Figure

S19 and S20, Supporting Information), these studies confirmed the formation of expected block copolymer, and further supported the living nature of the polymerization of diazoacate monomers using Pd(II)/L^{A} as catalyst. It is worthy to point out that the living chain end of the polymers can maintained for quite a long time even in solution, because the solution of poly-**1**$_{100}$ in THF stored at room temperature for one week can still chain extended with a new feed of monomer. Taking advantage of this method, a variety of block copolymers with tunable compositions, controlled M_n and narrow M_w/M_n was facilely prepared just through the variation on the initial feed ratios of the two monomers to the Pd(II) catalyst (Table 3).

Scheme 2. Chain Extension Reaction of Poly-1$_m$ with Monomer 2 and 3



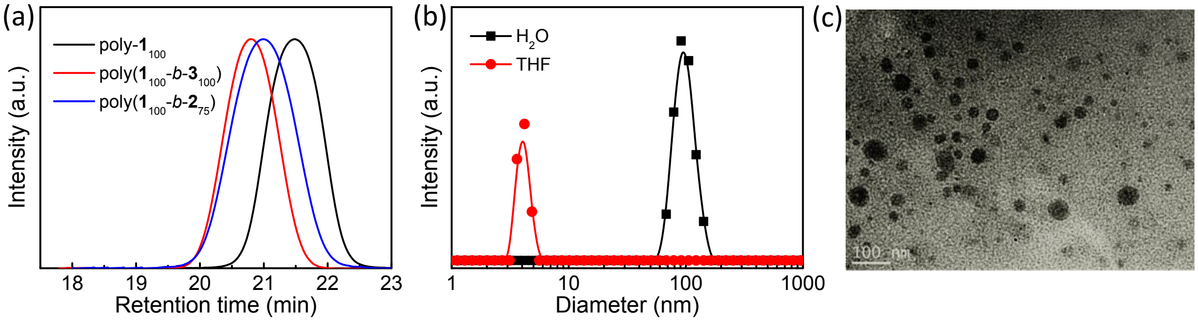


Figure 5. (a) SEC curves of chain extension reactions. (b) DLS of amphiphilic block copolymer poly(**1**$_{100}$-*b*-**3**$_{100}$) measured in THF and water. (c) TEM image of the self-assembled structure formed from poly(**1**$_{100}$-*b*-**3**$_{100}$) in water.

After the block copolymerization was established, amphiphilic block copolymer was facilely prepared through the copolymerization of poly-**1**$_{100}$ with monomer **3** which bearing a triethylene glycol monomethyl ether chain to provide the block copolymer with amphiphilic character (Table 3). The structure of poly(**1**$_{100}$-*b*-**3**$_{100}$) block copolymer was confirmed by SEC (Figure 5a), ^{1}H NMR, and FT-IR (Figure S21 and S22, Supporting Information). Because of the amphiphilic feature, the block copolymer has good solubility in most common organic solvents including THF, chloroform, dichloromethane, and in water as well. To further support the formation of amphiphilic block copolymer, the self-assembly property of poly(**1**$_{100}$-*b*-**3**$_{100}$) in selective solvents was investigated. Dynamic light scattering (DLS) study revealed the hydrodynamic diameter of poly(**1**$_{100}$-*b*-**3**$_{100}$) in THF was smaller than 10 nm, indicating it was molecularly dissolved (Figure 5b). However, when the solvent was changed from THF to water, a good solvent for poly-**3**$_{100}$ but a poor solvent for poly-**1**$_{100}$ segment, the diameter of poly(**1**$_{100}$-*b*-**3**$_{100}$) increased to ca. 95 nm. The increased size was probably due to the self-assembly of the amphiphilic block copolymer into supramolecular micelles in water. The critical aggregation concentration of poly(**1**$_{100}$-*b*-**3**$_{100}$) block copolymer was determined to be 0.087 mg/mL (Figure S23, Supporting Information). The morphology of the self-assembled supramolecular structure was further investigated by transmission electron microscopy (TEM). As shown in Figure 5c, spherical nanoparticles with ca. 85 nm diameter were clearly observed on the TEM images of poly(**1**$_{100}$-*b*-**3**$_{100}$) casted from the water solution. All these studies confirmed the formation of amphiphilic block copolymer, and further supported the living nature of the polymerization of diazoacetate monomers using the Pd(II) catalyst.

Table 3. Results for the Block Copolymerization Using Poly-$\mathbf{1_m}$ as the Macroinitiator[a]

		homopolymer		block copolymer		
run	polymer	M_n[b] (kDa)	M_w/M_n[b]	M_n[b] (kDa)	M_w/M_n[b]	Yield[c] (%)
1	poly($\mathbf{1}_{50}$-*b*-$\mathbf{2}_{50}$)	7.0	1.15	14.2	1.19	80
2	poly($\mathbf{1}_{100}$-*b*-$\mathbf{2}_{75}$)	10.1	1.18	18.6	1.20	84
3	poly($\mathbf{1}_{50}$-*b*-$\mathbf{3}_{50}$)	7.1	1.16	14.0	1.20	68
4	poly($\mathbf{1}_{100}$-*b*-$\mathbf{3}_{100}$)	10.3	1.18	21.5	1.21	67

[a] The block copolymerizations were performed in THF at 25 °C for 8 h according to Scheme 1. [b] The M_n and M_w/M_n values were determined by SEC with equivalent to polystyrene standards. [c] The isolated yields.

Helix-Sense Selective Polymerization. The backbone of polycarbenes was constituted by C-C single bonds and carrying pendant on each main chain carbon. Thus it may form a helical conformation if the pendants are bulky enough, similar to that of the helical polyisocyanide.[21-23] However, to the best of our knowledge, the helical conformation and the related chiroptical properties of polycarbenes have rarely been disclosed to date. To address this challenge, two chiral catalysts Pd(II)/L^R and Pd(II)/L^S bearing *R*- or *S*-ligand, analogue to Pd(II)/L^A were prepared and employed in the polymerization of monomer **1** (Scheme 1).[42] Firstly, monomer **1** was polymerized by chiral Pd(II)/L^R catalyst in THF at 25 °C under the same experimental conditions described above, afforded the expected *R*-poly-$\mathbf{1}_m$ in high yield (>80%) with expected M_n and narrow M_w/M_n (Figure S24, Supporting Information). The ^{1}H NMR, FT-IR and UV-vis spectrum of *R*-poly-$\mathbf{1}_{50}$ were almost the same to that of poly-$\mathbf{1}_{50}$ prepared using the achiral catalyst Pd(II)/L^A, indicating the same chemical structure of the two polymers (Figure S25-S27, Supporting Information). The optical activity of *R*-poly-$\mathbf{1}_{100}$ was investigated by CD and UV-vis spectra recorded in THF at 25

°C. To out delight, intense positive CD was observed at the absorption region around 205–230 nm, corresponding to the absorption of the *R*-poly-$\mathbf{1}_{100}$ backbone (Figure 6a). Since there are no chiral substituents on the polymer backbone or on the pendants, the optical activity was reasonably ascribed to the predominated one-handed helical conformation of the polymer backbone induced by the chiral catalyst during the process of the helix-sense-selective polymerization. However, the CD intensity of *R*-poly-$\mathbf{1}_{100}$ was not stable, it gradually decreased in solution even at low temperature (–10 °C), and almost no CD could be discerned after 5 h (Figure 6b, and Figure S28 in Supporting Information). In contrast, almost no changes could be observed on the absorption spectrum of *R*-poly-$\mathbf{1}_{100}$ during the course of CD decrease. Thus, it can be speculated that the polycarbene bearing benzyl benzoate did form a helical conformation in solution, while it is unstable and quickly transferred to random coil. It is worthy to note that the helix of the polymer is come from the twist of the C-C main chain. The arrangement of the pendants, the tacticity may has significant influence on the helix formation. The partial stereoregular segments of the generated *R*-poly-$\mathbf{1}_{\mathrm{m}}$ synthesized by using this new method may play important roles on the helix formation.

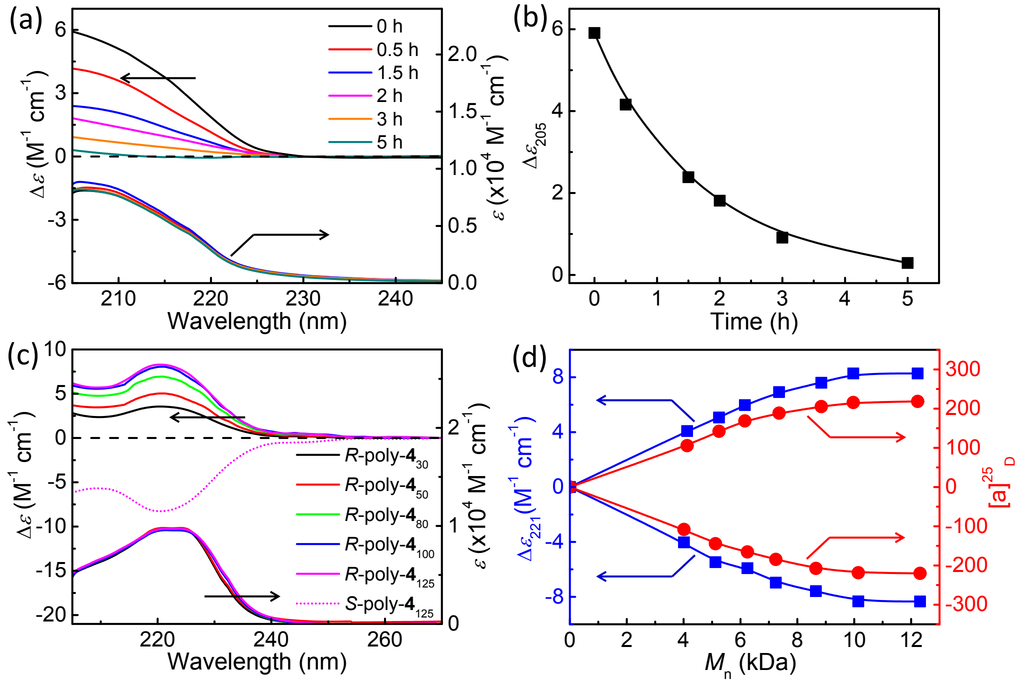


Figure 6. (a) Time-dependent CD and UV-vis spectra of *R*-poly-**1**$_{100}$ in THF at 25 °C. (b) plotted of CD intensity at 205 nm of *R*-poly-**1**$_{100}$ with time. (c) CD and UV-vis spectra of *R*-poly-**4**$_m$ and *S*-poly-**4**$_m$ with different M_n. (d) Plots of CD and optical rotation values of *R*-poly-**4**$_m$ and *S*-poly-**4**$_m$ with M_n.

It has been reported that introducing of bulky substituents onto a polymer pendants can stabilized the helical conformation of a synthetic polymer due to steric hindrance between the adjacent repeating units.[21-24] Thus, to make polycarbenes with more stable helical conformation, a series of *R*-poly-**4**$_m$s with different M_ns and narrow M_w/M_ns were facilely prepared just by varying the initial feed ratio of monomer to the Pd(II)/L^R catalyst (Table 4, and Figure S29-S31 in Supporting Information), followed the procedure described above. Because of more bulky of the pendants, they may possess stable helical conformation in solution. As expected, all the isolated

R-poly-$\mathbf{4}_{\mathrm{m}}$s polymers with different M_{n}s showed intense positive CD at the absorption region of the polymer backbone, indicating the formation of predominated one-handed helix. To our delight, the helical conformation of the main chain was quite stable, no discernable change could be observed on the CD and UV-vis spectra in THF solution at the temperature range from –10 to 55 °C for 24 h (Figure S32, Supporting Information). The helical conformation could be maintained in various solvents with different polarity at 25 °C, including THF, chloroform and dichloromethane, suggesting the solvents have no significant influence on the helical structure (Figure S33, Supporting Information). Moreover, the optical activity of *R*-poly-$\mathbf{4}_{100}$ showed a linear correlation with its concentration at the range of 0.05–0.30 mg/mL in THF at 25 °C (Figure S34 and S35, Supporting Information), confirming the optical activity was come from its helical backbone, not the supramolecular aggregation. To disclose the CD was come from the polymer backbone other than the residual L^{R} ligand, the CD and UV-vis spectra of Pd(II)/L^{R} were recorded in THF at 25 °C. As anticipated, it showed intense CD at 205–220 nm, while the CD and UV-vis patterns were completely different to those of the *R*-poly-$\mathbf{4}_{100}$ (Figure S36, Supporting Information). Moreover, no CD could detected on Pd(II)/L^{R} at the same concentration as that on the chain end of *R*-poly-$\mathbf{4}_{100}$. When the optically active L^{R} ligand was completely removed by treated *R*-poly-$\mathbf{4}_{100}$ with $NaBH_4$, the isolated polymer showed almost the same CD and UV-vis patterns ($\Delta\varepsilon_{221} = 8.32$, Figure S37 in Supporting Information), and the optical rotation was also maintained ($[\alpha]^{25}_{\mathrm{D}} = 216.54$). Thus it can be safely concluded that the optical activity of *R*-poly-$\mathbf{4}_{100}$ was not come from the Pd(II)/L^{R} group of the chain end, but the *R*-poly-$\mathbf{4}_{\mathrm{m}}$ backbone itself. Since the repeating units of the *R*-poly-$\mathbf{4}_{\mathrm{m}}$ were achiral, the CD was ascribed to the helical conformation of the main chain with predominated one-handed helix.

Table 4. Polymerizations of 4 in THF at Room Temperature Using Chiral Catalysts[a]

run	polymer	$[M]_0/[Pd]_0$[b]	M_n[c] (kDa)	M_w/M_n[c]	yield[d] (%)	$\Delta\varepsilon_{221}$[e]	$[\alpha]^{25}_D$[f]
1	*S*-poly-$\mathbf{4}_{20}$	20	4.0	1.16	78	–4.03	–108.12
2	*S*-poly-$\mathbf{4}_{30}$	30	5.1	1.17	83	–5.47	–144.54
3	*S*-poly-$\mathbf{4}_{40}$	40	6.2	1.17	75	–5.91	–165.54
4	*S*-poly-$\mathbf{4}_{50}$	50	7.2	1.19	72	–6.96	–184.50
5	*S*-poly-$\mathbf{4}_{60}$	60	8.6	1.20	74	–7.58	–207.58
6	*S*-poly-$\mathbf{4}_{80}$	80	10.1	1.19	73	–8.33	–218.54
7	*S*-poly-$\mathbf{4}_{100}$	100	12.1	1.20	75	–8.33	–220.14
8	*R*-poly-$\mathbf{4}_{40}$	40	6.1	1.18	82	5.96	168.66
9	*R*-poly-$\mathbf{4}_{50}$	50	7.3	1.20	78	6.91	188.54
10	*R*-poly-$\mathbf{4}_{60}$	60	8.8	1.20	73	7.59	205.12
11	*R*-poly-$\mathbf{4}_{80}$	80	9.9	1.18	71	8.27	215.68
12	*R*-poly-$\mathbf{4}_{100}$	100	11.9	1.18	72	8.27	217.45

[a]The polymers were prepared in THF at 25 °C for 8 h using Pd(II)/L^R and Pd(II)/L^S as the catalyst. [b]The initial feed ratio of monomer to catalyst. [c]The M_n and M_w/M_n values were determined by SEC using polystyrene standards. [d]Isolated yields. [e]The optical rotations were recorded in THF at 25 °C. [f]The molar circular dichroisms at 221 nm were measured in THF at 25 °C.

Further studies revealed the CD intensity of *R*-poly-$\mathbf{4}_m$s was dependent on the M_n (Figure 6c). Increasing the M_n lead to the increase of the ellipticity (θ) until it became constant when the M_n reached to 10.1 kDa (Figure 6d). The optical rotation of *R*-poly-$\mathbf{4}_m$ showed similar relationship with M_n (Figure 6d). This study indicated that the optical activity was indeed resulted from the helical polycarbene backbone and became stable when the degree of the polymerization reached to ca. 80. To get more details, monomer **4** was then polymerized by Pd(II)/L^S catalyst, the enantiomeric antipode of Pd(II)/L^R, under the same experimental conditions. As anticipated, the isolated *S*-poly-$\mathbf{4}_{125}$ showed an intense negative CD at the absorption region of the backbone, and was almost the mirror image to that of the *R*-poly-$\mathbf{4}_{125}$. While the UV-vis spectra of the two polymers were almost the same (Figure 6c). The CD intensity and optical rotations of *S*-poly-$\mathbf{4}_{\mathrm{m}}$ also increased with the increase of the M_{n} until the value of M_{n} reached to 9.9 kDa, similar to that of *R*-poly-$\mathbf{4}_{\mathrm{m}}$ (Figure 6d). Collectively, these studies revealed that the polycarbenes bearing bulky pendants can possessing a stable helical conformation in solution. This is the first study that disclosed the helicity and the chiroptical properties of polycarbene backbone.

Conclusions

In summary, we have developed a family of novel Pd(II)-based catalysts, which could promote a fast living polymerization of various diazoacetates under mild conditions under air. The polymerization was very fast, and can be accomplished within several minutes, afforded polycarbenes in high yields with controlled M_{n} and narrow $M_{\mathrm{w}}/M_{\mathrm{n}}$. Taking advantage of this method, a variety of block copolymers were facilely prepared through chain extension reaction. Moreover, fast living polymerization of diazoacetates bearing bulky substituents by chiral Pd(II) catalysts afforded well-defined polycarbenes with high optical activity due to the formation of predominated one-handed helix. The present study provides not only a novel method for fast living polymerization of various diazoacetates under mild conditions, but also for the first time revealed the helical conformation of polycarbene, which may have great potentials in many fields including chiral recognition, enantiomer separation and asymmetric catalyst, and so on.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental procedure, and additional spectra of the polymers, monomers and the related mediates.

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Notes

The authors declare no completing financial interest.

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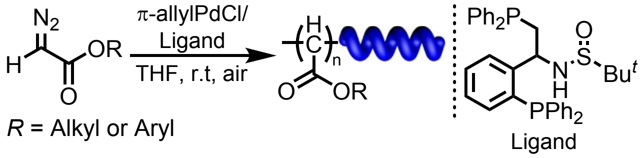

Fast living polymerization
Controlled M_n & narrow M_w/M_n
Optically active helical polymer