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From Nonconjugated Diynes to Conjugated Polyenes: Syntheses of Poly(1-phenyl-7-aryl-1,6-heptadiyne)s by Cyclopolymerizations of Asymmetrically α,ω-Disubstituted Alkadiynes

Charles C. W. Law, Jacky W. Y. Lam, Yuping Dong, Hui Tong, and Ben Zhong Tang*

Department of Chemistry, Center for Display Research,
The Hong Kong University of Science & Technology,
Clear Water Bay, Kowloon, Hong Kong, China

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1,6-Heptadiyne can be polymerized by $MoCl_5$-based catalysts into a polyene of cyclic structure.[1] The polymer is, however, insoluble in common solvents and sensitive to air oxidation. Introduction of substituents to the 4-position can help enhance the processability and stability of the polyene, and a large variety of (a)-symmetrically 4,4-disubstituted poly(1,6-heptadiyne)s have been synthesized (Supporting Information, Scheme S1), some of which have been found to show such functional properties as liquid crystallinity, photoconductivity, optical nonlinearity, and photorefractivity.[2,3] In contrast to the active research on the *internally* disubstituted polyenes, little work has been done on their *terminally* disubstituted congeners, mainly due to the involved synthetic difficulty. Among a few scattered reports in the area, polymerizations of 1,7-bis(trimethylsilyl)-4-oxa-1,6-heptadiyne gave insoluble powders with partially desilylated structural defects in very low yields ($\leq 13\%$),[2,4] and living polymerizations of diethyl 2,2-di(2-butynyl)malonate were catalyzed by delicate ternary mixtures of $MoOCl_4$ + organometallic cocatalysts + alcohols.[5]

If a "simple", effective polymerization system for terminally disubstituted diynes can be developed, it will be very rewarding. Chemically, it is easy to attach groups to the triple-bond terminals via versatile coupling reactions,[6] which will open a wide avenue to the creation of a great number of new functional polyenes. Substitution of the olefinic hydrogen in the backbone of the cyclic polyene by an aromatic ring will boost the polymer stability because it has been well understood in the linear polyene system that (1) the polymer stability increases with a decrease in the number of the active hydrogen atoms in the repeat unit: $-(RC{=}CR')_n- > -(RC{=}CH)_n- > -(HC{=}CH)_n-$ and (2) that, among the disubstituted polyenes, the polymers carrying aromatic pendants are more stable than those bearing alkyl ones: e.g., poly(1-phenyl-1-propyne) $-[(C_6H_5)C{=}C(CH_3)]_n-$ does not degrade after annealing at high temperatures (e.g., 160 °C) in air for 20 h, while poly(2-octyne) $-[(C_5H_{11})C{=}C(CH_3)]_n-$ decomposes to oligomeric species when heated at much lower temperatures (e.g., 100 °C).[7,8]

In this work, we designed and synthesized a group of α,ω-disubstituted alkadiynes with different aryl rings and spacer lengths [**1**(*m*)−**4**(3); Figure 1A). The polymerizability of the diyne is found to be very sensitive to its spacer length (*m*): only can the diynes with $m = 3$, viz., the 1,6-heptadiyne derivatives, be effectively polymerized. The terminally disubstituted 1,6-heptadiynes [**1**(3)−**4**(3)] show polymerization behaviors distinctly different from those of their internally disubstituted cousins: the former cannot be effectively polymerized by the Mo-based mixtures, which are good catalysts for the polymerizations of the latter. Delightfully, however, we find that $WCl_6{-}Ph_4Sn$, a simple metathesis catalyst, can convert the aryl-disubstituted diynes into high molecular weight, cyclic polyenes consisting of exclusively six-membered rings. The polyenes with their labile olefinic hydrogen atoms replaced by the stable aromatic rings are, as anticipated, processable and stable.

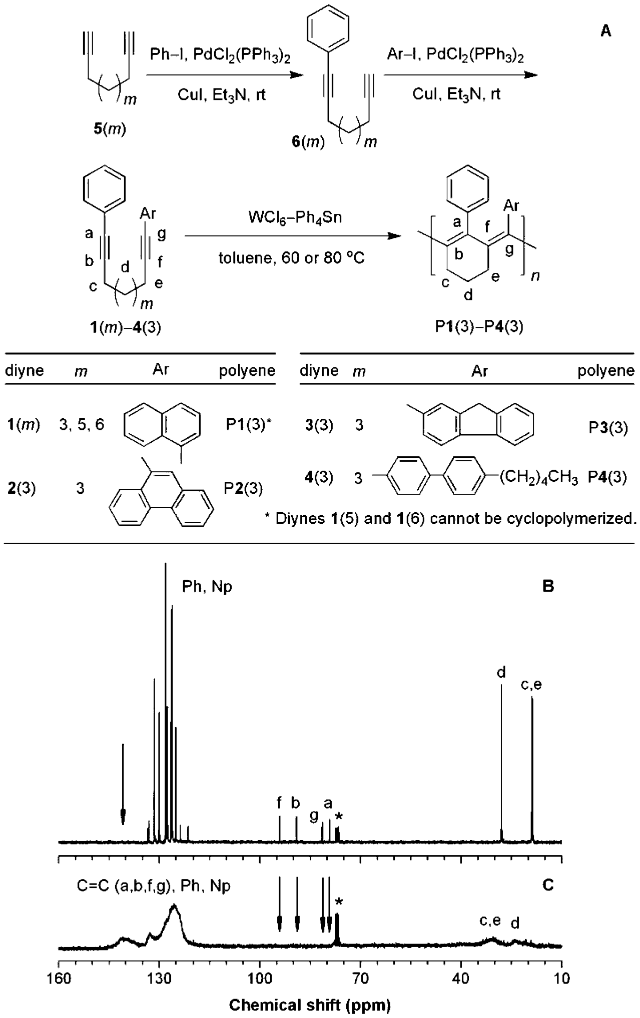

Figure 1. (A) Syntheses of poly(1-phenyl-7-aryl-1,6-heptadiyne)s **P1**(3)−**P4**(3) and ^{13}C NMR spectra of chloroform-*d* solutions of (B) monomer **1**(3) and (C) its polymer **P1**(3) (sample taken from Table 1, no. 2). The solvent peaks are marked with asterisks (∗).

The alkadiynes (**1**−**4**) were prepared by a synthetic route involving consecutive palladium-catalyzed cross-coupling reactions[9] (Figure 1A) and all the products give satisfactory analysis data (see Supporting Information for details). Whereas many internally disubstituted 1,6-heptadiynes can be effectively cyclopolymerized by the $MoCl_5$-based catalysts, the Mo-catalyzed reaction of **1**(3),

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* Corresponding author. Telephone: +852-2358-7375. Fax: +852-2358-1594. E-mail: tangbenz@ust.hk.

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Table 1. Polymerizations of 1-Phenyl-7-aryl-1,6-heptadiynes[a]

no.	catalyst	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
1-Phenyl-7-(1-naphthyl)-1,6-heptadiyne [**1**(3)]					
1	$MoCl_5-Ph_4Sn$	60	10.1	12 600	1.8
2	WCl_6-Ph_4Sn	60	99.0	60 900	2.3
3	WCl_6-Ph_4Sn	80	99.0	56 300	2.7
1-Phenyl-7-(9-phenanthryl)-1,6-heptadiyne [**2**(3)]					
4	WCl_6-Ph_4Sn	60	82.0	16 000	2.5
5	WCl_6-Ph_4Sn	80	68.2	14 100	2.0
1-Phenyl-7-(2-fluorenyl)-1,6-heptadiyne [**3**(3)]					
6	WCl_6-Ph_4Sn	60	40.0	23 000	2.0
1-Phenyl-7-[(4-pentyl-4′-biphenylyl)]-1,6-heptadiyne [4(3)]					
7	WCl_6-Ph_4Sn	60	95.0	83 500	3.1

[a] Carried out under nitrogen in toluene for 24 h; $[M]_0 = 0.2$ M, [cat.] = [cocat.] = 10 mM. [b] Determined by GPC in THF on the basis of a polystyrene calibration.

a terminally disubstituted 1,6-heptadiyne, proceeds sluggishly, giving a polymeric product in a low yield (~10%; Table 1, no. 1). The monomer can, however, be nicely polymerized by WCl_6-Ph_4Sn, producing a completely soluble polymer with a high molecular weight in a practically quantitative yield.

The congeners of **1**(3) with longer alkyl spacers, that is **1**(5) and **1**(6), cannot be polymerized by the Mo and W catalysts (Supporting Information, Table S1), due to the difficulty in forming larger alkenyl rings. On the other hand, the cousins of **1**(3) with the same length of alkyl spacer, viz., **2**(3)−**4**(3), can all be polymerized by the W catalyst under the similar reaction conditions (Table 1, nos. 4−7), confirming the key role the spacer length plays in determining the stability of the alkenyl rings and hence the ease of their formation in the diyne cyclopolymerization. The result of the polymerization of **4**(3) is especially impressive: a polymer with a high molecular weight (M_w 83500) is produced in a very high yield (95%).

All the polymers readily dissolve in common organic solvents such as toluene, THF, and chloroform, enabling structural characterizations by various spectroscopic methods. An example of the IR spectrum of P**1**(3), along with that of its monomer **1**(3), is given in Figure S1. The C≡C stretching band observed at ~2224 cm^{-1} in the spectrum of **1**(3)[10] is absent in that of P**1**(3), indicating that the polymer contains no triple bonds in its repeat unit. The ^{1}H NMR spectrum of P**1**(3) is composed of two very broad peaks centered at δ ~7.1 and ~1.6, which are assignable to the resonances of the protons of the aromatic rings and alkyl spacer, respectively. No information about the cyclic polyene structure can be obtained from the ^{1}H NMR analysis, because the polymer is a disubstituted polyene that contains no olefinic protons.

The ^{13}C NMR spectra are more informative. Again, no resonance peaks of acetylenic triple bonds are observable in the spectrum of P**1**(3), although they are clearly seen in that of its monomer **1**(3) in the chemical shift region of $\delta = 94.2-79.3$ (Figure 1). A new broad peak appears in the spectrum of P**1**(3) at $\delta \sim 140$, which is assignable to the resonance of the olefinic carbon in the polyene backbone, taking into account that many internally disubstituted poly(1,6-heptadiyne)s bearing no aromatic pendants resonate in this chemical shift region ($\delta \sim 138-142$).[3,5,11] This spectroscopically confirms the conversion of the triple bonds in **1**(3) to the double bonds in **P1**(3) by the W-catalyzed diyne cyclopolymerization.

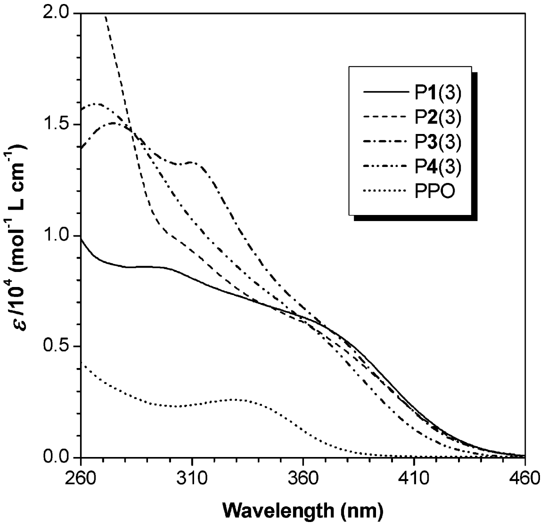

Figure 2. UV spectra of THF solutions of polymers P**1**(3) (sample taken from Table 1, no. 2), P**2**(3) (Table 1, no. 4), P**3**(3) (Table 1, no. 6), P**4**(3) (Table 1, no. 7), and poly(1-phenyl-1-octyne) (PPO).

Accompanying the yne-ene transformation, the carbon atoms of the methylene groups at α (c, e) and β positions (d) shift up- and downfield, respectively (Figure 1C). In the cyclopolymerizations of some internally disubstituted 1,6-heptadiynes, both six- and five-membered alkenyl rings are formed.[2] The resonances of the methylene carbon atoms of the former occur in the higher chemical shift region (downfield) than those of the latter,[3a,5] due to the ring strain involved in the smaller pentenyl ring. The α-methylene carbon atoms in the five-membered ring of P**1**(3), if formed, are expected to resonate at $\delta \sim 35-40$. No resonance peaks are, however, observed in this chemical shift region in the spectrum of P**1**(3), revealing that the five-membered rings are not formed in the W-catalyzed cyclopolymerization of **1**(3). In other words, P**1**(3) are comprised of exclusively six-membered rings.

The UV spectra of the polyenes are shown in Figure 2. Since none of their monomers absorbs at $\lambda > 300$ nm, the peaks of the polymers in the visible spectral region thus must be due to the absorptions of their polyene backbones. The molar absorptivities are larger and the band edges are redder than those of poly(1-phenyl-1-octyne) (PPO), a linear cousin of the cyclic polyenes, revealing that the backbones of P**1**(3)−P**4**(3) are more electronically conjugated. The twisting of the alternating double bonds is hampered by the alkenyl rings, enabling the polyene backbone to take a more planar conformation. While PPO emits strong blue light,[7] all the cyclic polyenes are weak fluorophores, whose fluorescence quantum yields (Φ_F) are low, ranging from 0.04% to 0.23% (Supporting Information, Figure S2; cf., $\Phi_{F,PPO} = 43\%$[12]). This once again proves that the backbones of the cyclic polyenes are more π-conjugated than that of the linear PPO, considering that polyacetylene, a linear polyene with an extended π-conjugation, is totally nonluminescent.[7]

The polymers are not only soluble but also stable. None of them loses any weight when heated to ~350 °C under nitrogen (Figure 3). Polymer P**1**(3) retains ~95% of its original weight at ~390 °C, and the 5% weight loss for P**2**(3) occurs at ~400 °C, thanks to its “bigger” phenanthryl pendant. Even when the polymer is heated to 500 °C, still more than half of its weight

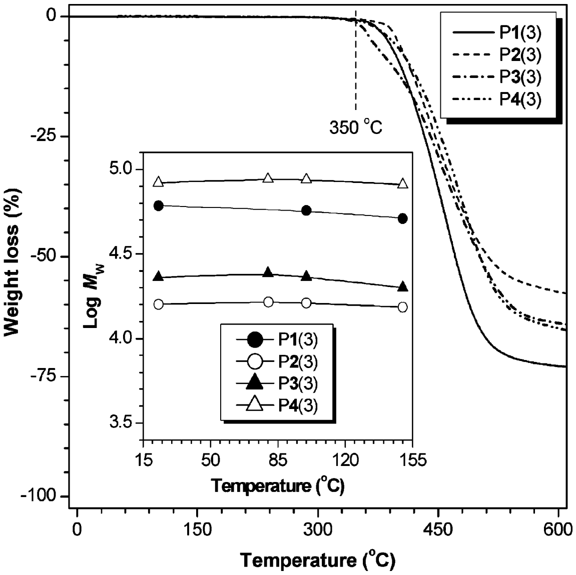

Figure 3. TGA thermograms of polymers P**1**(3) (sample taken from Table 1, no. 2), P**2**(3) (Table 1, no. 4), P**3**(3) (Table 1, no. 6), and P**4**(3) (Table 1, no. 7) recorded under nitrogen at a heating rate of 20 °C/min. Inset: Changes in molecular weights of P**1**(3)−P**4**(3) after heating in air for 2 h.

(∼53%) is retained. Its high stability is due to the "jacket effect" of the bulky and stable aromatic pendants,[7,12] which wrap the labile polyene backbone and shield it from the attack by thermolytic species. Since polymeric materials are normally used in air, it is of importance to check the resistance of the cyclic polyenes to oxidative degradation. After P**1**(3) was annealed at 100 and 150 °C in air for 2 h, neither cross-linking nor chain scission occur to a significant extent, as verified by the hardly changed GPC traces given in Figure S3 (Supporting Information) and the almost flat M_w−T plot shown in the inset of Figure 3. The M_w−T plots for other polyenes are similar, that is, all the polymers are resistant to the oxidative thermolysis.

In summary, in this work, we succeeded in converting a group of terminally aryl-disubstituted diynes into cyclic polyenes of high molecular weights in high yields by the cyclopolymerization catalyzed by a simple catalyst system. Our structural design paid off: the replacement of the active olefinic hydrogen atoms by the bulky and stable aromatic rings endowed the polyenes with processability and stability. Following the versatile synthetic route developed in this study, we are now working on the preparations of cyclic poly(1,6-heptadiyne)s (a)symmetrically α,ω-disubstituted by various functional groups, in an effort to add useful functionalities to the processable and stable polyenes.

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Supporting Information Available: Text describing detailed synthetic procedures and analytical data of the monomers [**1**(*m*)−**4**(3)] and polymers [P**1**(3)−P**4**(3)], Table S1, listing the results of the attempted polymerizations of **1**(5) and **1**(6), Scheme S1, showing the reactions, and Figures S1, S2, and S3, showing the IR spectra of **1**(3) and P**1**(3), the PL spectra of P**1**(3)−P**4**(3), and the GPC chromatograms of the annealed P**1**(3), respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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