Base-promoted Condensation Polymerization of Aminoesters with Diphenylacetylene and *trans*-Stilbene Backbones

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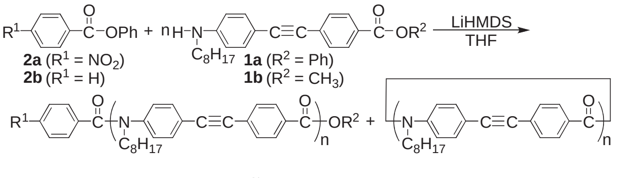
Polymerization of diphenylacetylene and *trans*-stilbene monomers bearing 4-alkylamino and 4′-phenoxy- or 4′-alkoxycarbonyl groups was carried out with an initiator in the presence of lithium 1,1,1,3,3,3-hexamethyldisilazide. Chain-growth polymerization afforded corresponding polyamides, whereas step-growth polymerization resulted in the formation of cyclic oligoamides.



Scheme 1.

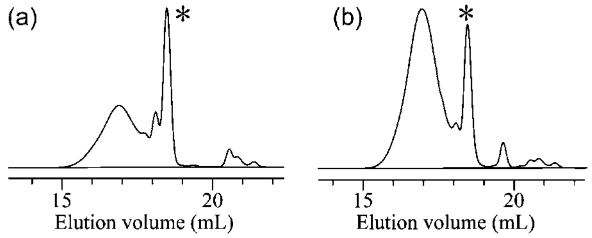
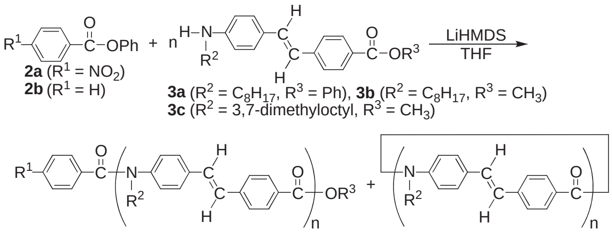


Figure 1. GPC profiles of the reaction products obtained by the polymerization of (a) **1a** for 20 min and (b) **1b** for 2 h with 10 mol % of **2a** in the presence of LiHMDS at −30 °C. The sharp peaks marked with an asterisk are thought to be due to cyclic oligomers.

Diphenylacetylenes bearing amino and alkoxycarbonyl groups at the 4 and 4′ positions, respectively, are known as "push–pull" alkynes,[1] and exhibit interesting features, such as nonlinear optical properties.[2–4] Imai and co-workers synthesized diphenylacetylene-containing polyamide via Pd-catalyzed coupling reaction,[5] but polymerization via amide-forming condensation reaction has not been reported. The *trans*-stilbene counterparts correspond to "push–pull" alkenes,[6] and polymers having a 4-(dimethylamino)-4′-stilbenecarboxylic acid ester unit at the end of the side chains showed liquid-crystalline phases[7,8] and nonlinear optical properties.[9]

In the course of our study of chain-growth condensation polymerization for the synthesis of well-defined aramides,[10] we have investigated the polycondensation of monomers consisting of two benzene units. When (octylamino)benzoic acid dimer phenyl esters were treated with a base, the reaction afforded cyclic oligomers and/or linear polyamides depending on the relative orientation of the amino and carbonyl groups of the monomers.[11,12] The formation of the cycles was probably due to the bending cis conformation of the *N*-alkyl amide linkage.[13,14] On the other hand, diphenylacetylenes and *trans*-stilbenes possessing alkylamino and alkoxycarbonyl groups at the 4 and 4′ positions have rigid and linear structures, and the electron-donating effect of the 4-amino group of these compounds is thought to transfer to the 4′-alkoxycarbonyl group by resonance, as in the case of 4-(alkylamino)benzoic acid esters,[15] which can be polymerized in a chain-growth polymerization manner even in the absence of any initiator.[16] Considering the structural and electronic analogy to 4-(alkylamino)benzoic acid esters, we expected that the diphenylacetylene and *trans*-stilbene monomers would also show chain-growth polymerization nature. In this communication, we describe the base-promoted condensation of the diphenylacetylene and *trans*-stilbene monomers, and show that the chain-growth polymerization tendency of these monomers is greater than that of (alkylamino)benzoic acid dimer esters.

We first studied the polymerization of diphenylacetylene monomer **1a** having octylamino and phenoxycarbonyl groups in the presence of 10 mol % of phenyl 4-nitrobenzoate (**2a**) as an initiator in THF (Scheme 1). If perfect chain-growth condensation polymerization occurs from the initiator, the M_n value of the obtained polymer is calculated to be 3560. When the polymerization was carried out under conditions similar to those used for the chain-growth condensation polymerization of 4-(alkylamino)benzoic acid esters,[17] with 1.1 equiv. of lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) as a base at −30 °C,[18] the monomer **1a** was consumed in 20 min. Gel permeation chromatography (GPC) analysis of the crude product showed $M_n = 3000$ relative to polystyrene standards and $M_w/M_n = 1.55$. The GPC elution curve was accompanied with a sharp peak at the lower molecular weight region, as in the case of the condensation of (octylamino)benzoic acid dimer phenyl esters,[11,12] suggesting the formation of cyclic oligomers (Figure 1a). Indeed, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry revealed that the product contained the liner oligomer with/without initiator unit, as well as cycles such as cyclic dimer, trimer, and tetramer. Polymerization at lower temperature such as −50 and −78 °C afforded similar results, and the use of different bases, such as lithium diisopropylamide (LDA) or the $(C_2H_5)_3SiN(C_8H_{17})$-C_6H_5/18-crown-6/CsF system,[15] resulted in slow and incomplete conversion of the monomer. We thought that the high reactivity of the phenyl ester moiety induced self-condensation of the monomer, leading to the formation of the cycles, and therefore we examined the reaction of methyl ester monomer **1b**. Polymerization of **1b** with 10 mol % of **2a** in the presence of 1.1 equiv. of LiHMDS in THF at −30 °C went to completion in 2 h to afford a polymer with $M_n = 3130$ and $M_w/M_n = 1.43$. The GPC elution curve of the product was similar to that obtained by the polymer-



Scheme 2.

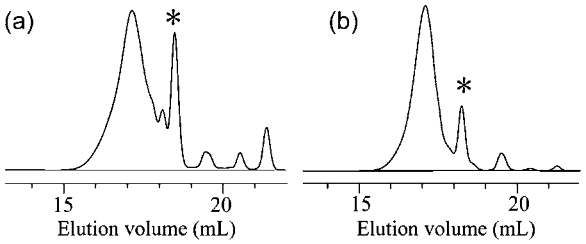


Figure 2. GPC profiles of the reaction products obtained by the polymerization of (a) **3a** with 11 mol % of **2a** for 30 min and (b) **3c** with 10 mol % of **2b** for 5 h in the presence of LiHMDS at −30 °C. The sharp peaks marked with asterisk are thought to be due to cyclic oligomers.

ization of **1a**, but the formation of the cyclic oligomers was decreased compared with the case of **1a** (Figure 1b). Polymerization at −50 °C gave similar results, but reaction at 0 °C afforded products with larger molecular weight and broader molecular weight distribution. Therefore, we thought polymerization of **1b** at −30 °C would be best, and analyzed the polymerization in more detail. When the polymerization was carried out with 10 mol % of **2a**, the M_n value of the polymeric product, appearing at the higher molecular weight region of the GPC elution curve than the cycles, increased with increasing conversion of the monomer at the late stage of the polymerization.[18,19] Although complete control of the molecular weight was difficult due to the formation of the cycles, polymerization of **1b** with 5 and 20 mol % of **2b** resulted in the formation of higher and lower molecular weight polymers, respectively, than polymerization with 10 mol % of the initiator.[18] These results suggest that the main part of the reaction proceeded in a chain-growth polymerization manner, accompanied to some degree with step-growth polymerization.

We next studied the polymerization of *trans*-stilbene monomer **3** under conditions similar to those used for **1** (Scheme 2). When the phenyl ester monomer **3a** bearing an *N*-octyl side chain was polymerized with 11 mol % of **2a** at −30 °C, the increase of viscosity made it difficult to stir the reaction mixture, but the monomer was consumed completely in 0.5 h. The GPC elution curve of the product ($M_n = 3570$ and $M_w/M_n = 1.35$) was similar to that obtained by the polymerization of **1**; a sharp peak at the lower molecular weight region suggested the formation of cyclic oligoamides (Figure 2a). Polymerization with 10 mol % of **2a** at higher temperature also resulted in thickening of the reaction mixture and incomplete consumption of the monomer (conversion of **3a** was 82% at 0 °C in 0.4 h and 62% at room temperature in 1 h), and the molecular weight distributions were broadened (0 °C: $M_n = 2600$ and $M_w/M_n = 2.25$, room temperature: $M_n = 3870$ and $M_w/M_n = 2.17$). Polymerization of the methyl ester monomer **3b** at −30 °C proceeded in a manner similar to that of **3a** to yield a polymer with $M_n = 3710$ and $M_w/M_n = 1.36$.

In order to control the polymerization of the *trans*-stilbene monomer, the solubility of the polymer was increased by using a 3,7-dimethyloctyl group as the side chain instead of the octyl group. Polymerization of **3c** in the presence of 10 mol % of **2b** at −30 °C went to completion in 5 h to give the polymer with $M_n = 3710$ and $M_w/M_n = 1.22$. The GPC profile of the product showed that the formation of cyclic oligomers and other low molecular weight by-products was decreased compared with the case of **3a** and **3b** (Figure 2b). This result indicates that the polymerization of **3c** was better controlled than that of **3a** and **3b**. Detailed analysis of the polymerization revealed that, in spite of the formation of the cyclic oligomers, the M_n values of the polymer increased in proportion to the conversion of the monomer,[18] suggesting the involvement of chain-growth polymerization.

In conclusion, we have demonstrated that base-promoted condensation polymerization of the diphenylacetylene monomer **1** and *trans*-stilbene monomer **3** shows chain-growth polymerization characteristics, but step-growth polymerization also occurs to afford cyclic oligomers. The strong tendency for the monomers to cyclize may be utilized as a novel method to construct macrocycles. Experiments along this line are in progress.

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18 A typical polymerization procedure, conversion–M_n plots for the polymerization of **1b** and **3c**, and the effect of feed ratio of **2b** to **1b** on the M_n value of the polymer are given in the Supporting Information, available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
19 We could not analyze the first nor middle stage of the polymerization due to the rapid conversion of the monomer.

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