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Synthesis of a New Carbazole Cyclic Dimer via Knoevenagel Condensation

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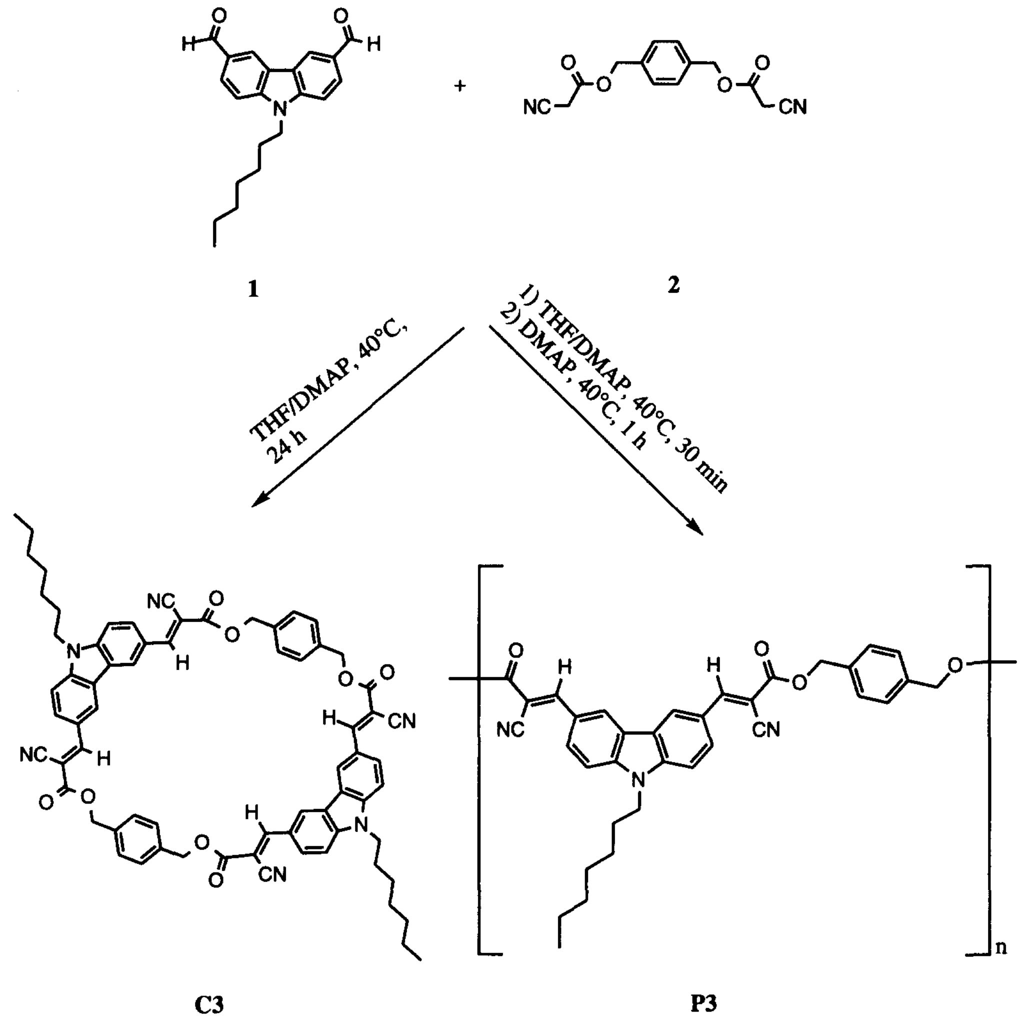
Abstract: The synthesis of a carbazole cyclic dimer and a main-chain polymer is reported. Knoevenagel condensation of 3,6-diformyl-9-heptylcarbazole and 1,4-bis(cyanoacetoxymethyl)-benzene using 4-(N,N-dimethylamino)pyridine as a base could yield a carbazole cyclic dimer or a carbazole main-chain polymer as a main product depending on the reaction conditions.

Knoevenagel condensation has been widely used for the synthesis of nonlinear optical (NLO) chromophores and polymers.[1] In our laboratory, several types of main-chain and hyperbranched polymers with carbazole moieties as a multifunctional material have been developed by Knoevenagel polycondensation and showed reasonable second-order NLO and photorefractive (PR) properties.[2] In the case of the synthesis of carbazole main-chain polymers, we found that Knoevenagel condensation of 3,6-diformyl-9-heptylcarbazole and 3,6-bis(cyanoacetoxymethyl)-9-heptylcarbazole using 4-(N,N-dimethylamino)pyridine (DMAP) as a base could give a carbazole cyclic tetramer in a high yield.[3] This result allows us to develop a new unique cyclic oligomer for NLO and PR applications. In this paper, we report Knoevenagel condensation of 3,6-diformylcarbazole and bis(cyanoacetate)s can yield the cyclic oligomers whose ring size can be determined by the bis(cyanoacetate) structures.

Starting from carbazole, 3,6-diformyl-9-heptylcarbazole **1** was synthesized in a two step procedure.[2a] 1,4-Bis(cyanoacetoxymethyl)benzene **2** was obtained by the reaction of 1,4-bis(hydroxymethyl)benzene with cyanoacetic acid in dichloromethane solution using N,N-dicyclohexylcarbodiimide (DCC) as a water acceptor. Monomers **1** and **2** were subjected to the conventional Knoevenagel condensation for NLO and PR main-chain polymers. Polycondensation carried out in THF solution could not yield carbazole main-chain polymer **P3**. In the case of condensation of **1** and **2** in THF solution, a yellow cyclic dimer **C3** was always obtained as a major product in 78% yield (as shown in Scheme 1). It was also found that the carbazole main-chain polymer **P3** could be obtained in 94% by a two-stage Knoevenagel polycondensation.[2a] The polycondensation of **1** and **2** carried out in THF solution for 30 min followed by a solid state polycondensation after removal of THF solvent could yield the carbazole main-chain polymer **P3** (as shown in Scheme 1).



Scheme 1. Synthesis of carbazole cyclic dimer **C3** and main-chain polymer **P3**

Gel permeation chromatography (GPC) analysis of **C3** shows monodispersion of molecular weight (as shown in Figure 1a). This result suggests that the only one kind of oilgomer was obtained from the polycondensation of **1** and **2** in THF solution. FAB-MS of oligomer **C3** exhibits the molecular ion M^+ (requires m/z 1115.3; found m/z 1115.4) which is corresponding to the cyclic dimer structure. This cyclic dimer was a little bit soluble in chloroform and showed absorption maximum at 421 nm. This absorption is attributed to carbazole moiety with two cyanocarboxyvinyl groups on 3, and 6 positions. GPC investigations on this polymer revealed a wide distribution (as shown in Figure 1b). The determined weight and number average molecular weight versus polystyrene standard are 3700000 and 120000, respectively. UV-vis absorption maximum of the polymer **P3** also appears at 421 nm due to the same carbazole moiety as the cyclic dimer. Differential scanning calorimeter (DSC) analysis indicated that the glass transition temperature (T_g) is about 156°C for the polymer **P3**. All the compounds have been characterized by ^1H NMR (except for **C3** due to its poor solubility in organic solvents) and IR spectroscopies, as well as elemental analysis.

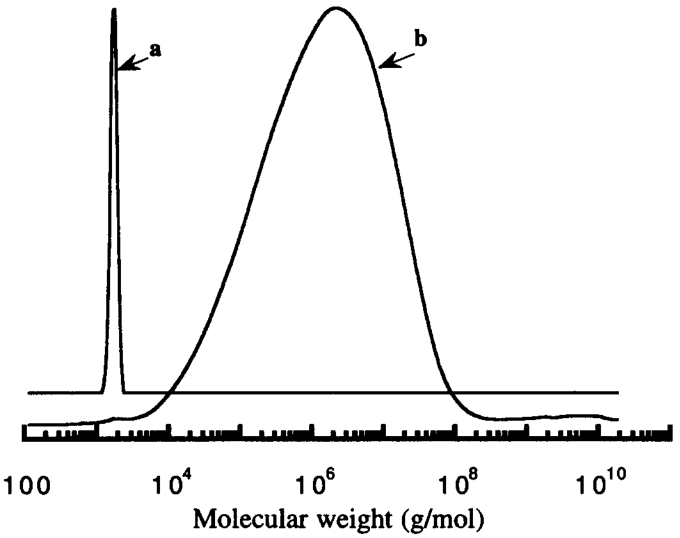
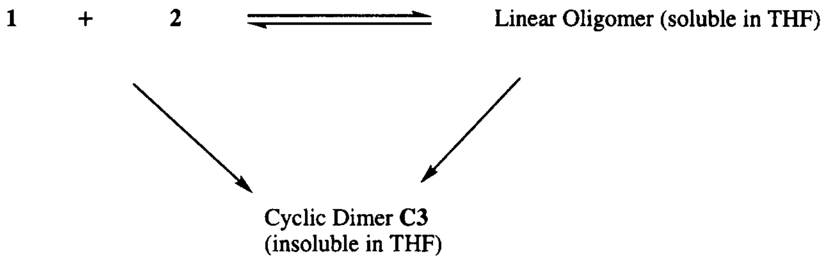


Figure 1. GPC traces of carbazole cyclic dimer **C3** (**a**) and main-chain polymer **P3** (**b**)

The monomers and linear oligomers yielded by the polycondensation are soluble in THF. This condensation is a reversible reaction in the presence of a base as shown in Scheme 2. This is the reason why we can not obtain carbazole main-chain polymer **P3** from the solution condensation. On the other hand, the cyclic dimer **C3** is insoluble in THF. Once the cyclic dimer was yielded, the cyclic dimer precipitated from the reaction solution. Therefore, the chemical equilibrium must be favorable for the formation of the cyclic dimer **C3** in THF solution. This is the reason why the cyclic dimer can be obtained in a high yield. In general, the production of high molecular weight polymers is often accompanied by the formation of cyclic oligomers with various ring sizes in polycondensation reaction.[4] However, in our case, only one size of cyclic oligomer, dimer, was obtained. Detail research work on the synthesis of carbazole cyclic oligomers from various bis(cyanoacetate)s is now in progress.



Scheme 2. The chemical equilibrium is favorable for cyclic dimer **C3** due to its insolubility in THF

We have demonstrated that Knoevenagel condensation of 3,6-diformylcarbazoles and bis(cyanoacetate)s is a unique approach to the synthesis of carbazole cyclic oligomers. These cyclic oligomers are expected to act as useful multifunctional chromophores for NLO and PR materials.

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