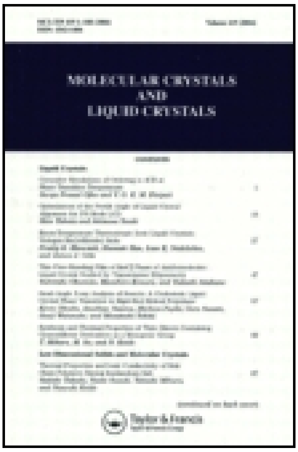

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Molecular Design of Novel Main-Chain Biscarbazolyl Polymers for Nonlinear Optics

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MOLECULAR DESIGN OF NOVEL MAIN-CHAIN BISCARBAZOLYL POLYMERS FOR NONLINEAR OPTICS

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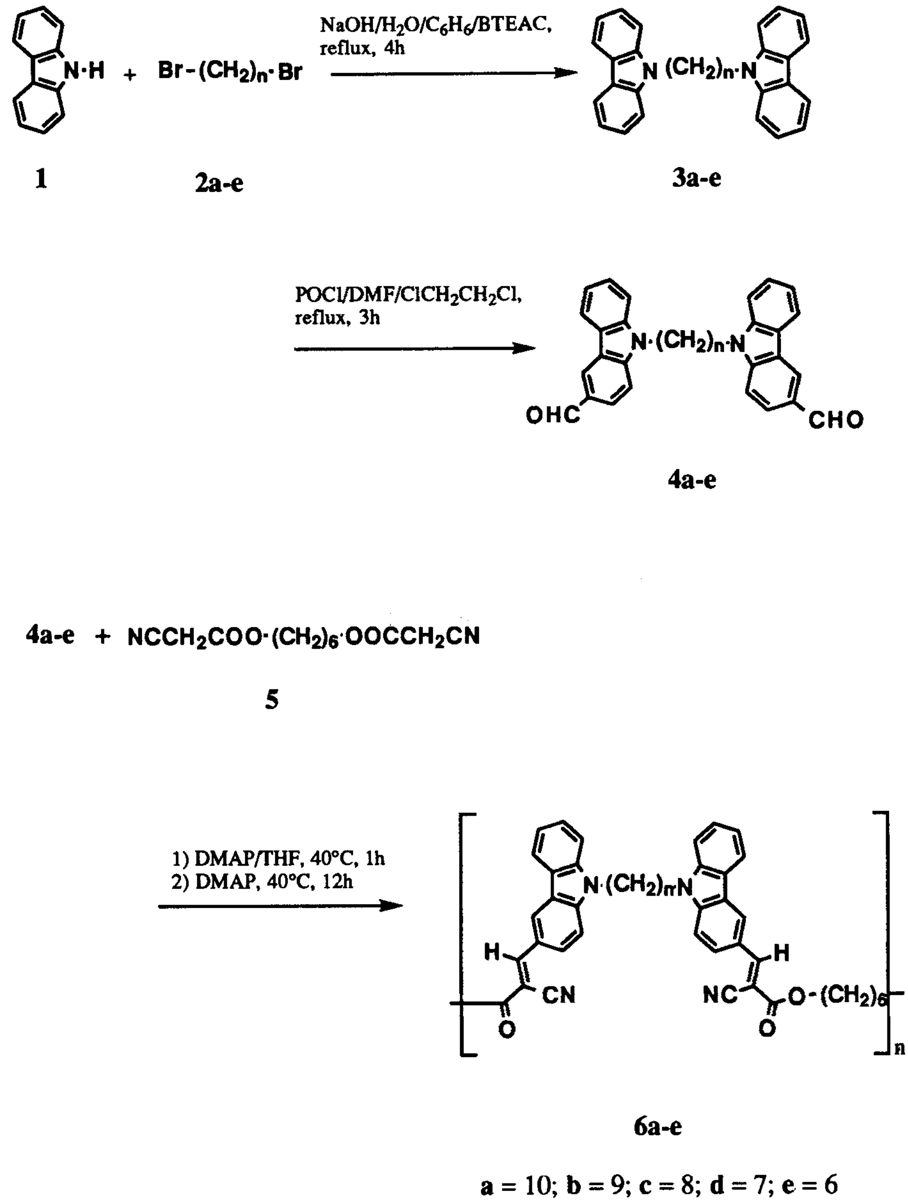
Abstract A series of α,ω-bis[(3-formyl)carbazolyl]alkane monomers have been prepared and copolymerized with bis(cyanoacetate) to provide novel accordion-type carbazole main-chain polymers. These main-chain polymers are soluble in common organic solvents, and have glass transition temperatures in the range of 94-117°C and molecular weight 25000-72000.

INTRODUCTION

Recently nonlinear optical (NLO) polymers have attracted a great deal of interest for their potential applications in integrated optics[1] because the synthetic polymers can be tuned to meet specific requirements in devices fabrication and application. Various guest-host systems,[2,3] side-chain[4,5] and main-chain polymers[6] have been developed as NLO materials. Among them, a very unique approach is the incorporation of the NLO chromophores directly in the polymer main chain to utilize their higher order structure.[7-9] We have selected carbazole moieties as an NLO active chromophore and synthesized several types of main-chain polymers besides side-chain polymers.[10-14] In this paper, we describe the synthesis and characterization of a series of novel head-to-head carbazole main-chain polymers as second-order NLO materials.

EXPERIMENTAL

Synthesis route is summarized in Scheme I.



SCHEME I Synthesis of diformylcarbazole monomer **4** and polymer **6**.

Monomer Synthesis

The α,ω-bis[(3-formyl)carbazolyl]alkane monomers **4** were synthesized in two steps: formation of α,ω-bis(carbazolyl)alkanes **3** starting from carbazole **1** and Vilsmeyer formylation reaction. α,ω-Bis(carbazolyl)alkanes **3** were obtained by nuclieaphilic substitution reaction on α,ω-dibromoalkane **2** using carbazole **1** as a nucleaphile, soduim hydroxide as a base and benzytriethylammonium chloride as a phase transfer catalyst. In order to obtain the soluble monomers and polymers, the flexible long alkane chain (n=6-10) were introduced to between two carbazole rings. The bis(cyanoacetate) monomer **5**[7] was prepared by the transesterification reaction of the 1,6-hexanediol with an excess of ethyl cyanoacetate in the presence of a catalytic amount of $Ti(OC_4H_9)_4$.

Two-stage Knoevenagel Polycondensation

Wright and his co-workers have reported the synthesis of main-chain polymers by the Knoevenagel polycondensation technique.[3] In our case, carbazole main-chain polymers were also synthesized from diformyl-substituted carbazole monomers and bis(cyanoacetate) by the Knoevenagel polycondensation using DMAP as a base. The Knoevenagel copolymerization involved the two-stages, firstly the copolymerization of **4** and **5** was carried out in tetrahydrofuran solution, and then the copolymerization was let be going in solid-state after removal of solvent to give accordion carbazole main-chain copolymers **6** with high molecular weight in high yield.

RESULTS AND DISCUSSION

Molecular Design

Nonlinear optical properties of several organic charge-transfer (CT) complex systems have been studied and recently photorefractive effects have been observed in CT complex crystal and poled photoconductive polymers. These poled polymers consist of three components: the nonlinear optically active chromophore to provide the electro-optic response, a hole transporting molecule and a photosensitizer which exhibit photoconductive properties.[14] Carbazole compounds are well-known to exhibit good hole transporting properties and their photocarrier generation efficiency can be sensitized by formation of CT complexes.[15]

In searching for multifunctional chromophores we selected acceptor-substituted carbazole derivatives which possess both photoconductivity and second-order nonlinear optical response. Based on the carbazole building blocks, we have synthesized head-to-tail,[11] shoulder-to-shoulder, head-to-head,[10] and crossliking main-chain polymers (general structure as shown in Figure 1) which have mono-acceptor-substituted or di-acceptor-substituted carbazole chromophores. It has been found that these main-chain polymers show reasonable second-order nonlinear optical responses. Hyperbranched polymers, supramolecules and dendrimers[16] with substituted carbazole chromophores have been also developed as an important new concept in molecular design for three-dimensional multifunctional materials with unique properties for nonlinear optics.

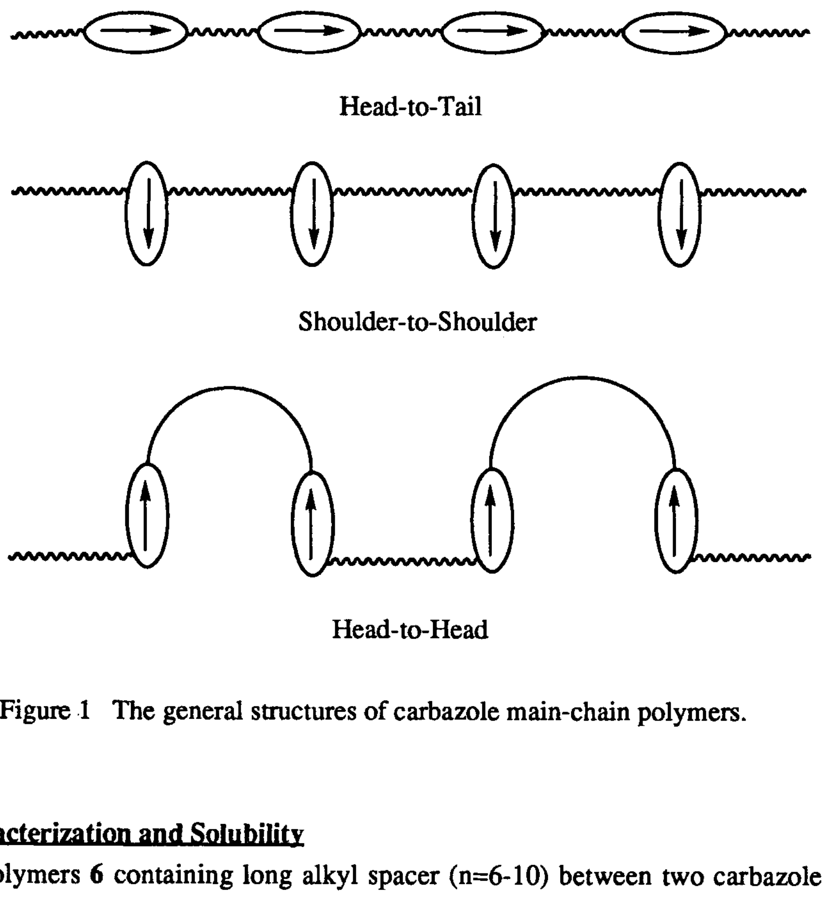


Figure 1 The general structures of carbazole main-chain polymers.

Characterization and Solubility

All polymers **6** containing long alkyl spacer (n=6-10) between two carbazole rings exhibit good solubility in common organic solvents. The thin films of the polymers with good optical quality can be easily obtained by spin-coating method from chloroform solution for optical measurements. In elemental analysis for the intermediate compounds, monomers and polymers agree very well with calculated values. The IR and NMR spectra of polymer **6** are in accordance with their chemical structures. Gel permeation chromatography (GPC) investigations on these main-chain polymers show the average molecular weight in the range of 25000-72000.

TABLE I Yields and Elemental Analysis for Main-chain Polymer **6**.

Polymer	Yield (%)[a]	Elemental analysis[b] Found (Calc.) (%)		
		C	H	N
6a	86	76.70 (77.42)	6.51 (6.45)	7.27 (7.53)
6b	77	76.75 (77.26)	6.34 (6.30)	7.37 (7.67)
6c	84	76.77 (77.09)	6.19 (6.15)	7.88 (7.82)
6d	72	76.39 (76.92)	6.04 (5.98)	7.73 (7.98)
6e	83	76.28 (76.74)	5.80 (5.81)	8.00 (8.14)

a. Isolated yields.
b. Performed at Microanalytical Laboratory in RIKEN.

TABLE II Molecular Weight and Glass Transition Temperature of Main-chain Polymer **6**.

Polymer	n	M_w[a]	M_n[a]	T_g (°C)[b]
6a	10	53569	33540	94.5
6b	9	40199	14548	96.4
6c	8	72808	10232	96.7
6d	7	25065	7118	107.8
6e	6	36209	9754	117.7

a. Determined by GPC relative to polystyrene standards.
b. Obtained by Perkin-Elmer DSC-7.

Differential scanning calorimetry (DSC) analysis shows that the polymer **6** have glass transition temperatures (Tg) without feature of melting. Tg values range from 94.5 to 117.7°C depending on the length of spacer between the two carbazole rings.

CONCLUSIONS

A series of new carbazole main-chain polymer **6** with high molecular weight have been prepared by the two-stage Knoevenagel polycondensation for nonlinear optics. All these polymers are soluble in common organic solvents. The polymer thin films with good optical quality could be obtained by spin-coating method. The details of nonlinear optical research work on theses carbazole main-chain polymers is now progressing.

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