A new synthetic approach to macrocyclic molecules and main-chain polymers containing carbazole moieties

Yadong Zhang, Tatsuo Wada and Hiroyuki Sasabe

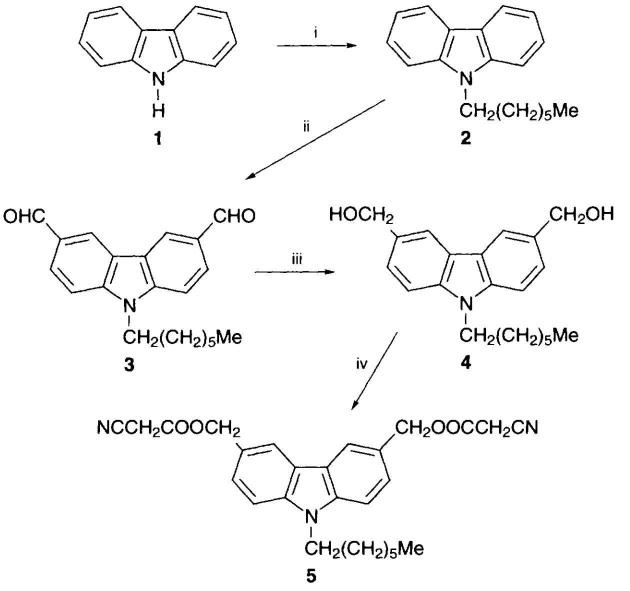
Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01 Japan

New macrocyclic molecules and main-chain polymers containing carbazole substituted with two acceptor groups are synthesized by the Knoevenagel condensation reaction.

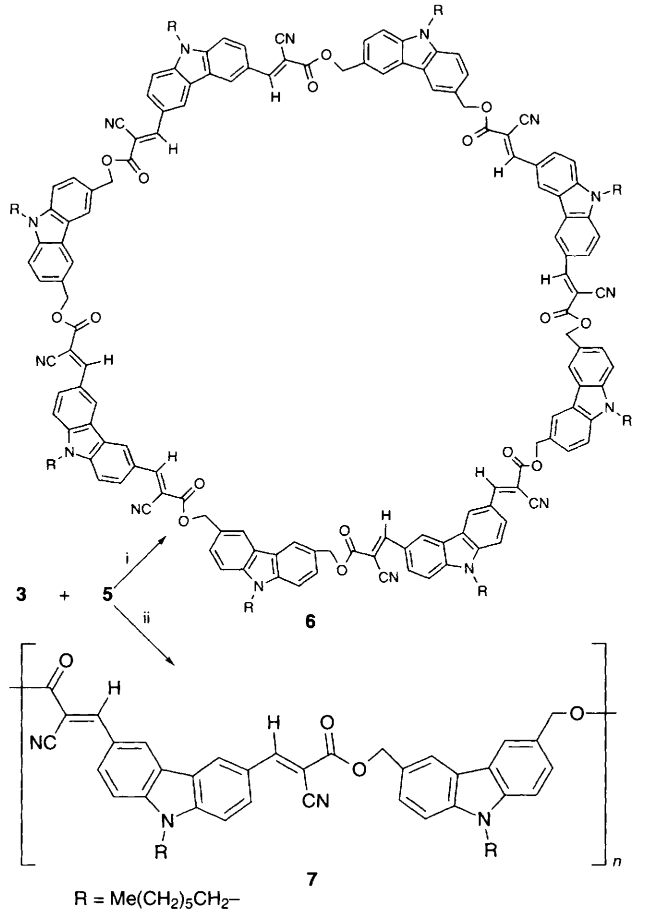
Functional macrocyclic compounds and polymers for nonlinear optics (NLO) and photorefraction have recently attracted attention due to their unique chemical structures and interesting physical properties.[1–10] While searching for building blocks for new functional materials, our attention was focused on carbazole compounds. It is well known that carbazole compounds have multifunctional properties, such as photoconductivity[11] and unique second-order nonlinear optical properties.[12–15] Carbazole components as NLO chromophores and photoconductive moieties have already played an important role in photorefractive materials.[16–19] In our laboratory, several types of carbazole main-chain and hyper-branched polymers have been obtained and showed good second-order nonlinear optical properties.[20–22] Based on carbazole bulding blocks, new monolithic photorefractive materials have also been synthesized and showed good photorefraction.[23] Recently we developed the dendritic supermolecular system with acceptor-substituted carbazoles for nonlinear optics. It was found that the second-order nonlinear optical effects of this system were large and stable.[24]

In the syntheses of the main-chain polymers containing carbazole substituted with two acceptor groups, we unexpectedly found that 9-heptyl-3,6-diformylcarbazole reacted with 9-heptyl-3,6-bis(cyanoacetoxymethyl)carbazole using DMAP as base to yield a main-chain polymer or a macrocyclic compound. It is noteworthy that the main products could be obtained in a polymer or a macrocyclic compound by controlling the reaction conditions. Here we report the synthesis and characterization of a new macrocyclic compound **6** and main-chain polymer **7**.

Carbazole **1** was treated with heptyl bromide in a two phase system of 50% aqueous sodium hydroxide and benzene using benzyltriethylammonium chloride as a phase-transfer catalyst at 40 °C to yield 9-heptylcarbazole **2** (Scheme 1). 9-Heptyl-3,6-diformylcarbazole **3** was synthesized by the Vilsmeier formylation from *N*-heptylcarbazole **2**. Treatment of **3** with sodium borohydride in ethanol at room temperature afforded 9-heptyl-3,6-di(hydroxymethyl)carbazole **4**. 9-Heptyl-3,6-bis(cyanoacetoxymethyl)carbazole **5** was obtained by the treat-



Scheme 1 *Reagents and conditions*: i, $Me(CH_2)_5CH_2Br$, NaOH, $H_2O–C_6H_6$, 40, 94%; ii, DMF–$POCl_3$, $ClCH_2CH_2Cl$, 90 °C, 48 h, 46%; iii, $NaBH_4$–NaOH, ethanol, room temp., 2 h, 89%; iv, $NCCH_2COOH$–DCC, pyridine, >5 °C, 8 h, 87%.



Scheme 2 *Reagents and conditions*: i, DMAP, THF, 40 °C, 18 h, 67%; ii, Polycondensation was first carried out in THF for 20 min at 40 °C using DMAP as a base. After removal of THF under vacuum, polycondensation in the solid state for 6 h at 40 °C yielded the carbazole main-chain polymer **7** in 95% yield.

ment of **4** with cyanoacetic acid in dichloromethane using DCC as a water acceptor.

The carbazoles **3** and **5** were subjected to the conventional Knoevenagel polycondensation (Scheme 2). Unexpectedly, this polycondensation carried out in THF yielded the main-chain polymer **7** in very low yield. Attempts to improve the yield of the polymer **7** using different reaction temperatures and concentrations of **3** and **5** were unsuccessful. In these cases a yellow compound, to which the macrocyclic structure **6** was assigned,† was always obtained as a major component in high yields. However, it was found that the carbazole main-chain polymer **7** with very large molecular weight could be obtained in high yield by a two-stage Knoevenagel polycondensation. The polycondensation of **3** and **5** in THF for 20 min followed by solid state polycondensation after removal of THF yielded the polymer **7** as a main product (Scheme 2).

Macrocycle **6** was soluble in chloroform to give a yellow solution and showed λ_{max} at 421 nm. The chemical structure of this macrocycle has been proposed on the basis of FTIR, ^{1}H NMR and FAB-MS spectroscopy, as well as elemental analysis.† The proton resonance signals of the terminal groups, such as the proton of the formyl group (C*H*O) and the proton of cyanoacetate ($\mathrm{NCC}H_2\mathrm{COO}$), were not observed in the ^{1}H NMR spectrum. This result suggest that compound **6** has a cyclic structure. On the basis of the FABMS spectrum, the structure of **6** was assigned to a cyclic tetramer. The FTIR spectrum shows the signals of CN, C=O, the carbazole ring and the flexible long chain. This data is in accord with the cyclic tetramer structure for **6**. Attempts to obtain an X-ray crystal structure have not yet been successful. Gel permeation chromatography (GPC) of **6** shows a sharp peak (Fig. 1). This means only one kind of macrocycle was obtained from the Knoevenagel cyclic condensation reaction.

The main-chain polymer **7** was soluble in both chloroform and THF. The chemical structure of this polymer has also been confirmed by FTIR and ^{1}H NMR.† GPC of the polymer **7** revealed a multi-model distribution (Fig. 1). The determined weight and number average molecular weight *vs.* polystyrene were 3 400 000 and 100 000 g mol^{-1}, respectively. The GPC behaviour of the polymer **7** is much different from that of the cyclic compound **6** (Fig. 1). Differential scanning calorimetry (DSC) measurements demonstrated the amorphous nature of the polymer **7**. A glass transition was observed at about 134 °C.

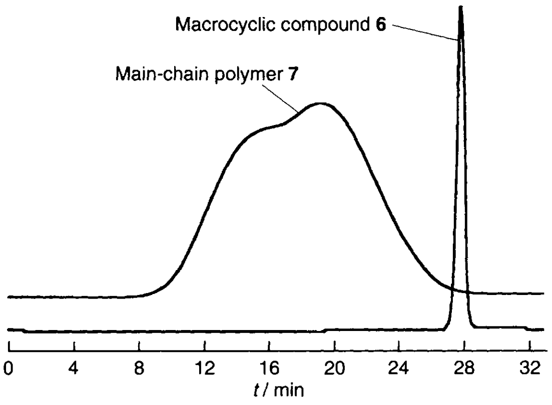


Fig. 1 GPC traces of macrocycle **6** and the carbazole main-chain polymer **7**

Footnote

† Selected spectroscopic data for the macrocycle **6** ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.53 (s, 2 H), 8.37 (s, 2 H), 8.28 (d, 2 H), 8.27 (s, 2 H), 7.59 (d, 2 H), 7.44 (s, 2 H), 7.41 (s, 2 H), 5.57 (s, 4 H), 4.28 (m, 4 H), 1.86 (m, 4 H), 1.26 (m, 16 H) and 0.85 (m, 6 H), FTIR (KBr) ν/cm^{-1} 2955, 2220, 1700, 1631, 1501, 1493, 1388, 1255, 1232, 1201, 1161 and 806. FABMS $C_{192}H_{192}N_{16}O_{16}$ requires *m/z* 2979.4767 (M^+), found 2979.466 (M^+); $C_{96}H_{96}N_8O_8$ requires *m/z* 1489.7383 ($M^+/2$), found 1489.750 ($M^+/2$); $C_{48}H_{48}N_4O_4$ requires *m/z* 745.3708 ($M^+/4$); found 745.400 ($M^+/4$). Satisfactory spectroscopic data and elemental analyses for all new compounds **3**, **4** and **5** were obtained. For the polymer **7**: ^{1}H NMR (270 MHz; $CDCl_3$) δ 8.47 (s, br, 2 H), 8.30 (m, br, 6 H), 7.58 (d, br, 2 H), 7.30 (m, br, 4 H), 5.50 (s, br, 4 H), 4.19 (m, br, 4 H), 1.70 (m, br, 4 H), 1.19 (m, br, 16 H) and 0.80 (m, br, 6 H). FTIR (KBr) ν/cm^{-1} 2953, 2220, 1710, 1631, 1501, 1493, 1388, 1257, 1232, 1196, 1161 and 806.

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