

Polycondensation of squaric acid with N-alkylcarbazoles

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Summary

1,2-Dihydroxycyclobutene-3,4-dione (squaric acid) was polycondensed with N-ethyl- and N-(1-butyl)carbazole in polyphosphoric acid to give polymers having 36-43% of 1,2-oriented squarate units. The polymers are insoluble in organic solvents or sulfuric acid. Condensation of 1,2-dichlorocyclobutene-3,4-dione (squaryl dichloride) with N-1-butylcarbazole in nitrobenzene gave 100% of 1,2-oriented squarate units. This polymer is soluble in most organic solvents, and the molecular weight (\bar{M}_w) is 1900 (DP = 6). The electrical conductivity was low, $<10^{-9}$ (ohm cm)⁻¹, and did not increase on treatment with iodine.

Introduction

1,2-Dihydroxycyclobutene-3,4-dione (squaric acid) is a member of the oxocarbon family (1). Knowledge of its chemical and physical properties has been developing rapidly since it is a new class of stabilized carbocyclic nonbenzenoid aromatic compound, and may have potential uses as dyes, organic semiconductors, and photographic materials (1-4).

The introduction of squaric acid as a constituent into polymers, for example, the poly(squaryl amides) (5-8) have been studied. Also, the structures of poly(squaryl amides) have been elucidated by using x-ray photoelectron spectroscopy (9,10).

In this work, we present the Friedel-Crafts polycondensation of squaric acid and squaryl dichloride with N-alkylcarbazoles. N-Alkylcarbazoles have previously been condensed with formaldehyde (11,12), chloromethyl methyl ether (13), methylene chloride (14), and iodine (15,16).

These carbazoles based polymers are expected to show high electrical conductivity and photoconductivity. Herein we report the synthesis and characterizations of the polymers containing both carbazole and squarate units.

Experimental

Materials - N-Ethylcarbazole and N-(1-butyl)carbazole were synthesized according to the procedure described in the literature (17).

Squaric acid and polyphosphoric acid (PPA) were obtained from Aldrich and were used as received. Squaric acid was also obtained from Chemische Werke Hüls, West Germany.

Squaryl dichloride was synthesized according to the literature (18).

Nitrobenzene was purified by distillation from CaH₂.

Trifluoroacetic acid was distilled from phosphorus pentoxide.

Measurements - The IR spectra were recorded on a Perkin-Elmer 983 spectrometer.

Thermogravimetric analyses were carried out by using a DuPont Model 951 under a nitrogen atmosphere.

Elemental analyses were performed by Micanal Laboratories of Tucson, Arizona.

The polymer molecular weights were determined by GPC using 50A (IBM 100-199 MW), PSM 60.5 (DuPont 10^2 - 10^4 MW), PSM 300.5 (DuPont 3×10^3 - 3×10^5 MW) columns with polystyrenes calibration.

Pellets have been pressed using an IR die and Electrodag 502 (Acheson Co.) was used to make the contacts. Conductivities have been measured at room temperature under air by four-point probe method.

Polycondensation of Squaric Acid and N-(1-Butyl)carbazole in Polyphosphoric acid (no. 3 in Table I). Into a three-necked flask (200 mL) was placed N-(1-butyl)carbazole (1,372 g, 6.15 mmol), squaric acid (0.708 g, 6.15 mmol) and polyphosphoric acid (12.30 g). The mixture was stirred mechanically under nitrogen. The temperature was raised from room temperature to 90°C within 30 min. Then the mixture was heated at 90°C for 5 h, at 130°C for 14 h, and at 160°C for 1 h. After the heating, the mixture was poured into water, and neutralized with NH_4OH solution. The polymer was filtered and washed with water. The polymer was extracted with refluxing water and ethyl alcohol for three days each. It was dried at 70-80°C for 4 h. Yield, 1.20 g (65%).

Polycondensation of Squaryl Dichloride with N-(1-Butyl)carbazole in Nitrobenzene (no. 5 in Table I). Into a three-necked flask (100 mL) was placed N-(1-butyl)carbazole (1.858 g, 8.32 mmol) 1,2-dichlorocyclobutene-3, 4-dione (1.259 g, 8.32 mmol), and nitrobenzene (15 mL), and this solution was heated at 130°C for 18 h and at 180°C for 5 h under nitrogen. After heating, the solution was poured into methanol (1 L) to precipitate the polymer. The polymer was filtered and reprecipitated from DMF-methanol three times. The polymer was then collected and dried at 50°C for 2 h under vacuum. Yield, 0.64 g (25%).

Results and Discussion

Polycondensation of squaric acid with N-alkylcarbazoles were carried out in equimolar quantities using polyphosphoric acid (PPA) as a solvent. The yields of the polymers depend on the heating conditions (Table I). Heating at 120°C for 15 h and at 150°C for 4.5 h gives 89% of polymer (no. 5). However, heating at 90°C for 28 h (no. 2) or at 160°C for 1 h (no. 1) only gives 53% and 36% yields. The polymers (nos. 1, 3, 4) are insoluble in any solvent tried, and the color of these polymers are black. But the color of polymer no. 2 is green, and it is soluble in DMF, DMSO, and concentrated sulfuric acid. The inherent viscosity of this polymer is $0.79 \text{ g}^{-1} \cdot \text{dL}$.

Condensation of squaryl dichloride and N-(1-butyl)carbazole was carried out in nitrobenzene (no. 6) to give 25% yield. This polymer has brown color and dissolves in CHCl_3 , acetone, DMF, and sulfuric acid. The molecular weight (M_w) is 1900 (D.P. = 6) determined by gel permeation chromatography.

Table I

| No. | Wt. of (a) substrate, g | Wt. of (b) N-Alkylcarbazole, g | Solvent | Temp (°C) | Time (h) | Yield (%) | Inherent viscosity g-1.dL | Elemental (d) Analysis (Found) C. H. N. | % of 1,2-orientation unit |
|------|----------------------------|-----------------------------------|------------------------|----------------|----------|-----------|---------------------------|---|---------------------------|
| 1 | 0.350 | 0.600 | PPA, 9.55g | 160 | 1 | 36 | - | 72.34 4.10 5.21 | 36 |
| 2 | 0.350 | 0.600 | PPA, 23.44g | 90 | 28 | 53 | 0.79 | 76.42 4.63 5.52 | 42 |
| 3 | 0.350 | 0.600 | PPA, 7.25g | 90/150 | 4/20 | 81 | - | 75.69 4.10 5.11 | 43 |
| 4 | 0.708 | 1.372 | PPA, 12.30g | 90/130/ 160 | 5/14/1 | 65 | - | 77.09 5.30 4.65 | 36 |
| 5 | 2.800 | 5.427 | PPA, 54.40g | 120/150 | 15/4.5 | 89 | - | 72.67 5.42 4.05 | 37 |
| 6 | 1.259 | 1.858 | nitrobenzene 15 mL. | 130/180 180 | 18/5 | 25 | 0.79 | 76.09 4.60 4.42 | 100 |
| 7(e) | 1.994 | 2.942 | nitrobenzene 15 mL. | 70/100/ 180 | 4/15/8 | 62 | - | 78.64 5.49 5.00 | 99 |

a) Substrates used, Nos 1-5, squaric acid, Nos 6-7, squaryl dichloride.

b) Nos. 1-3, N-ethyl carbazole, Nos. 4-7, N-(1-butyl)carbazole

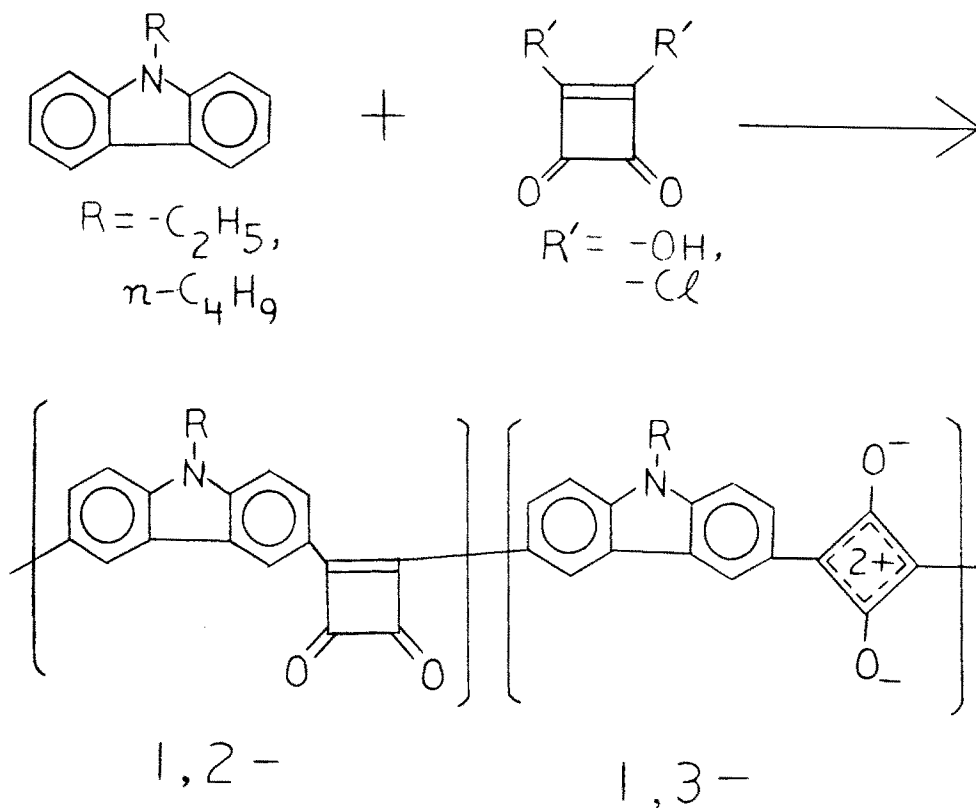
c) 0.5% (W/V) at 30°C in 98% H₂SO₄.

d) Calcd. for Nos. 1-3, C, 78.58; H, 4.76; N, 5.09.
Calcd. for Nos. 4-7, C, 79.72; H, 5.30; N, 4.65.

e) equivalent amount of trifluoroacetic acid was added.

Acid catalyzed condensation of squaryl dichloride and N-(n-butyl)carbazole with equivalent amount of trifluoroacetic acid in nitrobenzene (no. 7) gave 62% yield of brown polymer with a molecular weight (\bar{M}_w) of 2500 (D.P. = 8). This polymer also has good solubility in CHCl_3 and DMF.

The polycondensation of squaric acid (or squaryl dichloride) with N-alkylcarbazole can be expressed as follows:



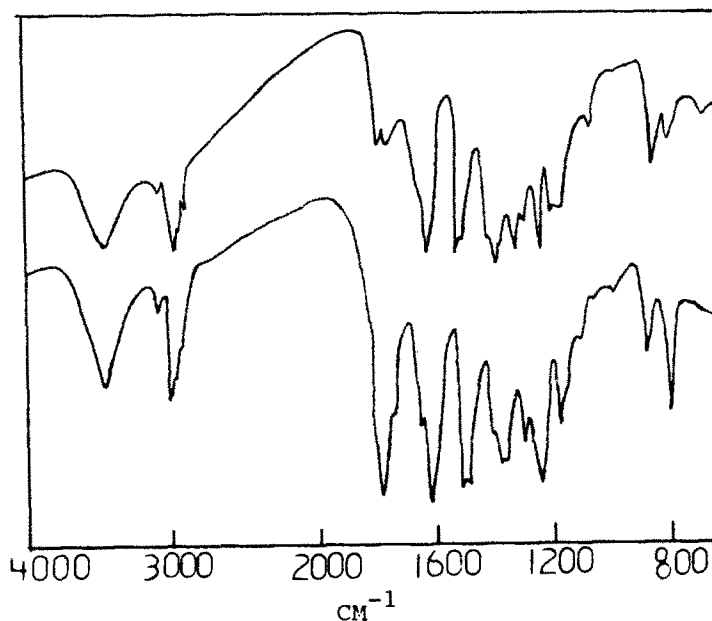


Fig. 1 IR spectra of polymers, no. 4, above, and no. 6, below.

IR spectra of the polymers (Fig. 1) show characteristic of 1,2,4-trisubstitution on an aromatic ring at ca. 800 and 880 cm^{-1} . Thus, the polymerization proceeds mainly via a 3,6-substitution in carbazoles.

Condensation of squaric acid can give 1,2- and 1,3-oriented polymer. In order to evaluate quantitatively the contents of 1,2- or 1,3-units, we condensed squaryl dichloride with N-(1-butyl)carbazole (nos. 6,7, Table I) to give the polymer considered to be predominantly of 1,2-oriented unit. Accordingly, the percentage of 1,2- and 1,3-oriented units can be tentatively determined by IR spectra (7). That is, with comparing the ratio of the absorbance of the asym carbonyl stretching peak near 1750 cm^{-1} to that of the out-of-plane phenyl-ring C-H deformation band near 805 cm^{-1} , we can determine the percentage of 1,2-oriented unit in the polymers. The polymers (nos. 1-5, Table 1) prepared in PPA have 36-43% of 1,2-oriented unit.

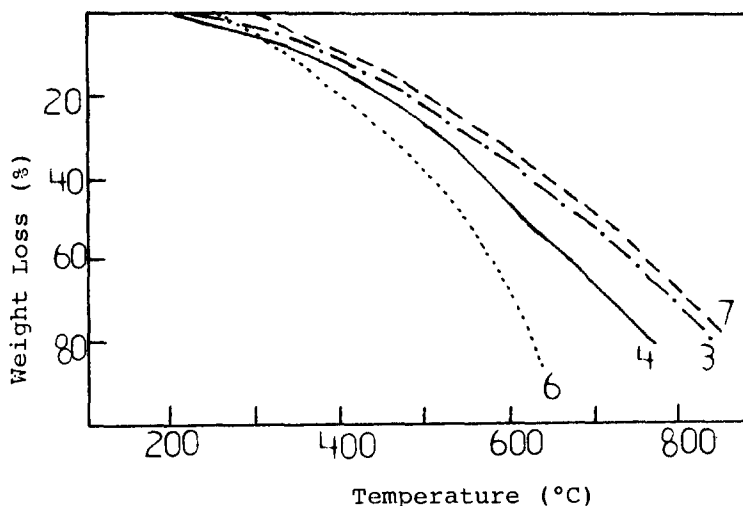


Fig. 2 TGA curves in nitrogen at 10°C/min for polymers nos. 3, 4, 6, and 7 in Tab. 1.

The heat stability of polymers was investigated by thermogravimetric analysis (TGA). TGA curves (Fig. 2) show the initial decomposition temperatures for polymers nos. 3,4,6,7 (Table I) are 200, 210, 225, and 287°C, respectively. The half (50%) weight loss temperatures are 700 (no. 3), 650 (no. 4), 560 (no. 6), and 710 °C (no. 7). For 1,2-oriented polymers (nos. 6,7), polymer having a higher molecular weight (no. 7) appears to have a better thermal stability. Also, polymer having predominantly 1,2-oriented unit (no. 7) displays a higher thermal stability than those containing both 1,2- and 1,3-oriented polymers (nos. 3,4).

Measurements on compacted pellets of nondoped polymers show conductivities of $<10^{-9} (\Omega\text{cm})^{-1}$. After doping polymers in vapor (no. 5, %C=61.26; %H=3.55; %N=4.06; %I=19.62) or in DMF (no. 7, %C=65.50; %H=4.39; %N=3.94; %I=19.62) with iodine, no significant changes in conductivities can be observed.

Acknowledgment

We are deeply indebted to the Office of Naval Research for partial support of this work, and to Chemische Werke Hüls AG for a generous gift of squaric acid. We also thank Dr. T. Ogawa and Dr. G. Burillo for TGA measurements.

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Accepted September 29, 1986 K