

7,7,8,8-Tetra-(Methoxycarbonyl)-Quinodimethane, a Reactive Electrophilic Monomer

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Abstract

7,7,8,8-Tetra-(methoxycarbonyl)-quinodimethane, TMQ, was synthesized in improved yield from tetramethyl p-phenylenedimalonate by forming the dianion of the latter with potassium hydride and oxidizing it with iodine. Free radical and anionic initiators gave homopolymer quantitatively. The homopolymer, m.p. 295-315°, was insoluble in all solvents except for the strong acids, sulfuric, chlorosulfonic, and trifluoromethanesulfonic acid, in which it exhibited polyelectrolyte viscosity behavior.

Free radical copolymerization with styrene using excess or equivalent TMQ in the feed gave only 1:1 alternating copolymer, but excess styrene gave copolymers richer in styrene. Other electron-rich comonomers: p-chlorostyrene, 2-vinylnaphthalene, p-methoxystyrene, N-vinylcarbazole, and isobutyl vinyl ether also gave alternating copolymers with TMQ, the latter two without added initiator. Less electron-rich vinyl compounds did not copolymerize.

TMQ possesses less electron affinity than TCNQ, as established by cyclic voltammetry and tests with donor molecules.

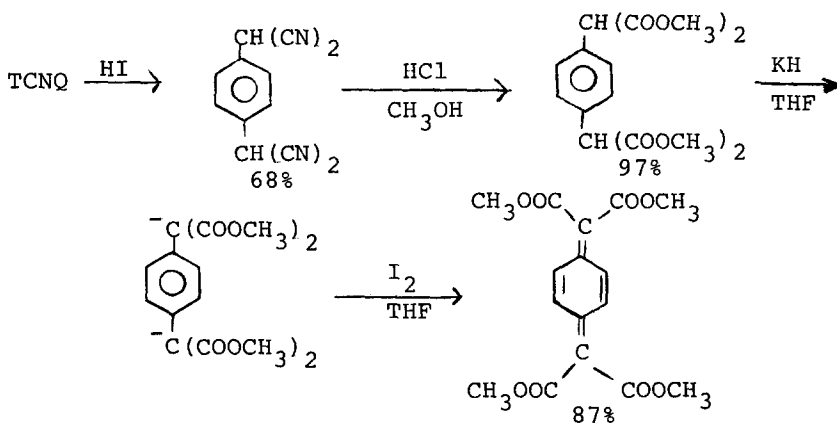
Introduction

7,7,8,8-Tetra(methoxycarbonylquinodimethane) (TMQ) was originally synthesized by Acker and Hertler, who

briefly described its properties (ACKER et al., 1962). In particular, they noted that it oligomerized on heating. Here we describe a more intensive study of the synthesis and polymerization behavior of TMQ.

Results

Synthesis. -Following the literature (ACKER et al., 1962), TCNQ was reduced to p-phenylenedimalononitrile and methanolized to tetramethyl p-phenylenedimalonate. Difficulty in converting this to dianion with sodium methoxide in methanol was overcome by using potassium hydride in tetrahydrofuran. Oxidation with iodine gave TMQ in 87% yield [27%(ACKER et al., 1962)].



Properties. - TMQ is a canary-yellow solid which can be recrystallized from toluene-pentane in presence of inhibitors, and can be stored at 3° for extended periods. It is readily soluble in common organic solvents. It melts at 142° but begins to polymerize immediately thereafter.

Homopolymerization. - TMQ homopolymerizes with great facility. The monomer polymerizes even at room temperature in diffuse light. Heating in the range 142-180° brings about complete polymerization.

With AIBN in THF, TMQ polymerizes, again in quantitative yield. Finally, addition of n-BuLi to a

solution of TMQ in benzene-THF brings about instant polymerization.

The polymer melted at approximately 300° and was insoluble in all common solvents tested, including hexafluorisopropanol. The intractability of poly-TMQ made it difficult to obtain meaningful molecular weight data. It was soluble in sulfuric, chlorosulfonic, and trifluoromethanesulfonic acids, evidently by forming carboxonium poly-salt. This was shown by the viscosity-concentration curve (Fig. 1), where poly-electrolyte behavior is evident. Extrapolation of the linear portion gave an intrinsic value of about 0.93 dl. g.⁻¹.

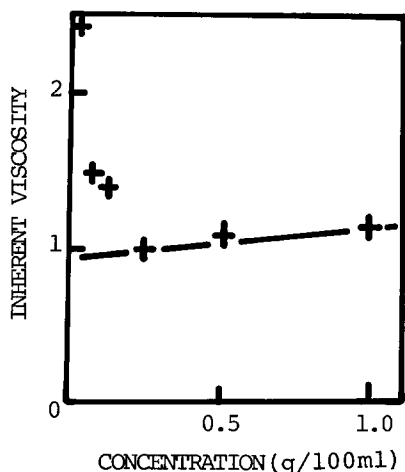


Fig. 1.

TMQ Homopolymer Viscosity Plot.

Conditions: (1) Trifluoromethane Sulfonic Acid Solvent; (2) 30°C; (3) Large Bore Canon-Fenske Tube.

Copolymerization. TMQ copolymerized readily under free radical conditions with various electron-rich vinyl monomers to give alternating copolymers in good conversion (Table I). Spontaneous reactions were observed with N-vinylcarbazole or p-methoxystyrene. Vinyl acetate or more electrophilic vinyl monomers did not copolymerize.

Depolymerization. - De Jongh and et al., (1973) established that compounds such as $C_6H_5CE_2CE_2C_6H_5$ ($E=COOCH_3$) undergo facile homolysis when heated. It was reasonable to expect that, on heating, poly TMQ

Table 1. TMQ Copolymerizations with Vinyl Monomers^a

Comonomer	Comonomer Weight, (mg)	TMQ Weight, (mg)	Molar Ratio TMQ: Comonomer	Polymer Weight, mg (%)	Inherent Viscosity ^c	TMQ, Mole Percent in Polymer ^d
Styrene	160	500	1:1	560 (85)	0.32	51.7
p-Methoxystyrene	200	500	1:1 ^{e,f}	350 (50)	0.34	53.9
N-Vinylcarbazole	180	500	1.61:1 ^{e,f}	80 (10)	0.16	60.3
N-Vinylcarbazole	290	500	1:1 ^f	330 (42)	0.19	54.4
9-Vinylanthracene	300	500	1:1	200 (25)	0.19	60.8
2-Vinylnaphthalene	230	500	1:1	560 (77)	0.35	54.0
4-Chlorostyrene	210	500	1:1	580 (82)	0.41	52.3
Styrene	160	1,000	2:1	330 (28)	0.23	51.1
Styrene	320	500	1:2	330 (40)	0.43	41.0
Isobutyl vinyl ether ^b	50	200	1:1	17 (7)	--	45.0
Vinyl acetate ^b	43	200	1:1	198 (81)	--	100

a. All polymerizations, except as noted, used 10 mL sulfolane, 5 mg AIBN, 57°, 72 hr.

b. Sulfolane 4 mL, AIBN, 2 mg.

c. Sulfolane, 0.1%, 30°C.

d. Based on percentage of carbon in elemental analysis.

e. Spontaneous reaction occurred.

f. Red color observed.

would undergo homolysis and depolymerize. In fact, heating poly TMQ at 150° and 0.1 Torr caused sublimation of TMQ in 10%-15% yield.

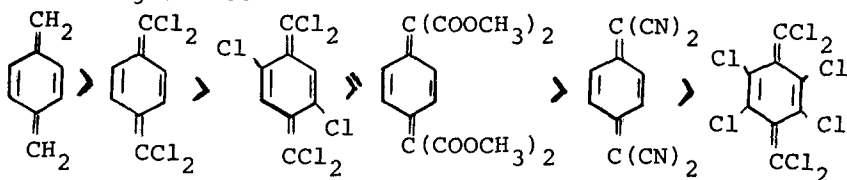
Electron-Accepting Ability

It was of interest to compare the electron-accepting ability of TMQ with that of TCNQ. The cyclic voltammetric reduction potential for TMQ in acetonitrile using a silver-silver nitrate electrode was -0.83 V. (irreversible); that of TCNQ was -0.2 V. (reversible). TMQ in tetrahydrofuran or acetonitrile gave no indication of salt formation with tetrathiofulvalene, but with N,N,N',N'-tetramethyl-p-phenylenediamine in acetonitrile gave the characteristic deep blue Würster cation radical.

Discussion

TMQ is now readily available. It homopolymerizes readily under thermal, radical, and anionic conditions. It copolymerizes readily with nucleophilic monomers, but not with electrophilic ones, to form alternating copolymers.

Iwatsuki et al. (1974) arranged the known quino-dimethanes in order of their ability to homopolymerize and to copolymerize with styrene. Combining their results with TCNQ (IWATSUKI et al., 1978 and 1979) and the present results with TMQ, we can propose the following series:



Finally, TMQ possesses less electron affinity than TCNQ.

Conclusions

TMQ readily homopolymerizes and copolymerizes with

selected vinyl monomers. It possesses modest electron-accepting capabilities.

Experimental

NMR spectra were obtained using Varian T-60. Infrared spectra were determined on a Perkin-Elmer 337 grating infrared spectrophotometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona or by the University Analytical Center, Department of Chemistry, University of Arizona, Tucson. All of the melting points were determined in °C in a Thomas-Hoover melting point apparatus and are uncorrected.

7,7,8,8-Tetra(methoxycarbonyl)quinodimethane, TMQ.- Potassium hydride, 5.6 g (70 mmoles) of a 50% suspension in mineral oil (Alfa Inorganics), was cleaned by three washes with pentane and covered with 350 mL of purified tetrahydrofuran containing 0.1 g of di-t-butyl catechol. Tetramethyl p-phenylenedimalonate (ACKER et al., 1962), 10.00g (30 mmole), was added, and the mixture was stirred at 51-54°C in a nitrogen atmosphere for 92 hr. Iodine, 15.2g (60 mmol), dissolved in 55 ml of tetrahydrofuran, was added with stirring. Most of the tetrahydrofuran was removed by evaporation under nitrogen, and the dark, moist solid was stirred with a solution of 10g of potassium iodide and 10g of sodium bisulfite in 300 ml of water to decolorize it. The yellow solid was filtered, washed with water, and dried. It was dissolved in the minimum volume of hot toluene containing di-t-butylcatechol, twice the volume of pentane was added and allowed crystallize at -10°C. Filtration gave 8.72g (87%) of TMQ as a canary-yellow solid.

NMR (acetone-d₆): δ =7.5 (s, 4H), 3.85 (s, 12H) ppm.

Ir(KBr): 1725 (s), 1580, 1470, 1250 (br.) cm⁻¹.

M.p. 142°, immediately followed by resolidification.

Homopolymerizations. - All homopolymerization recipes, whether thermal, free radical, or anionic, gave quantitative yields of polymer.

Heating TMQ, 0.5 g, in 10 mL of tetrahydrofuran, with 5 mg of benzoyl peroxide, at 90° in a sealed vial for 18 hours under nitrogen gave a quantitative yield of polymer, m.p. \sim 300°.

Thermal polymerization in bulk could be carried out in the range of 140°-180°, and gave a quantitative yield of polymer, m.p. 290-310°.

To a solution of TMQ in 1:1 tetrahydrofuranbenzene was added at 28° one drop of n-butyllithium solution in hexane. Polymerization occurred instantly, and a quantitative yield of polymer, m.p. 317°, was isolated.

NMR (H_2SO_4): δ =4.6 - 3.8 (broad, protonated ester functions), 4.2 (s, free ester groups) ppm. The peak due to the phenyl protons is not observed due to a large time.

Ir(KBr): 3000, 2960, 2780, 1635(s), 1520, 1430, 1240(s), 1020 cm^{-1} .

Anal: Calc'd for: C, 57.1; H, 4.8.

Found: C, 56.8; H, 4.8.

Heating this polymer under vacuum at 150° for 2 hours caused depolymerization to occur. About a 10% yield of monomer is obtained. Further heating, however, gave no further monomer.

Copolymerizations. - In a typical copolymerization, TMQ, 0.5 g, comonomer, 10 mL of purified sulfolane, and 5 mg of AIBN were heated under nitrogen at 57° for 72 hours. The solution was precipitated into 200 mL of methanol and filtered. The precipitate was redissolved in 1:1 tetrahydrofuran-acetone and refluxed under air for 15 minutes. Any unreacted TMQ homopolymerized under these conditions, and was filtered. Precipitation into 200 mL of methanol, filtration, and vacuum drying gave the copolymers.

Inherent viscosities of copolymers were done at 30°C in sulfolane.

Electrochemical Measurements. - Spectrograde acetonitrile was used directly without purification. Sample preparation and electrochemical measurements were carried out under nitrogen atmosphere. A three compartment electrochemical cell with a main compartment of 100 mL capacity was used for voltammetric studies. The side arms contained a reference electrode (0.1 M AgNO₃ in MeCN and a silver wire) and a platinum counter electrode respectively. The Pt working electrode was a 1.16 cm flag and was cleaned in nitric acid, oven dried and heated in a flame to incandescence prior to each run. A Princeton Applied Research Model 173 potentiostat and Hewlett Packard Model 7001 A x-y recorder used for electrochemical measurements.

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