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Spontaneous Radical Polymerizations of 7,8-Bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane

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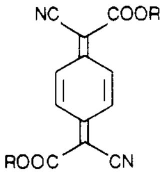
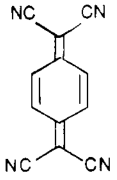
ABSTRACT: High molecular weight homopolymers of 7,8-bis(ethoxycarbonyl)-7,8-dicyanoquinodimethane (DEDCQ) or copolymers of DEDCQ-styrene (St) and DEDCQ-*p*-methoxystyrene (*p*-MeOSt) were formed spontaneously in chloroform containing acetic acid. All polymerizations occurred by a radical mechanism. High molecular weight polymers formed at low conversion. Radical homopolymerization of DEDCQ was promoted by ambient light or heat. DEDCQ-*p*-MeOSt copolymerizations yielded alternating copolymers, which formed rapidly relative to the DEDCQ homopolymerizations and copolymerizations with St which yielded copolymers rich in styrene. All of these polymerizations are thought to begin with a bond-forming mechanism and propagate by polyaddition.

Introduction

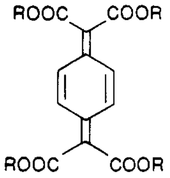
The diverse polymerization behavior of *p*-quinodimethanes bearing electron-withdrawing groups at all four 7- and 8-positions has attracted considerable interest.[1-4]



1a: R = Me
b: R = Et
c: R = Bu
bis(alkoxycarbonyl)dicyanoquinodimethanes



2
tetracyanoquinodimethane



3a: R = Me
b: R = Et
tetraalkoxycarbonylquinodimethanes

The most reactive monomers in this class are the bis(alkoxycarbonyl)dicyanoquinodimethanes (**1**). In early reports it was shown that 7,8-bis(methoxycarbonyl)-7,8-dicyanoquinodimethane (DMDCQ) (**1a**) and its ethyl ester analogue (DEDCQ) (**1b**) were highly reactive toward homopolymerization.[5,6] Homopolymerizations of DMDCQ and DEDCQ occurred instantly upon dissolution in acetonitrile, Me_2SO, and DMF. Polymerizations in CH_2Cl_2 proceeded more slowly but still resulted in significant conversions after 2-3 h. Anionic (and radical) initiators accelerated homopolymerizations in CH_2Cl_2. Iwatsuki et al. related the ability of a solvent to homopolymerize bis(butoxycarbonyl)dicyanoquinodimethane (DBDCQ) (**1c**) to its basicity.[4] On the basis of this correlation we may conclude that "spontaneous" solution polymerizations of bis(alkoxycarbonyl)dicyanoquinodimethanes are initiated by basic nucleophilic species, including solvent, and propagate via an anionic mechanism.

Attempts to initiate radical copolymerizations of DEDCQ and DMDCQ with donor olefins were unsuccessful because of this proclivity to homopolymerize.[5,6] However, Iwatsuki reported radical initiated copolymerizations of DBDCQ with styrene (St) and *p*-methoxystyrene (*p*-MeOSt) in the presence of acetic acid.[4] This result supports the assertion that the spontaneous homopolymerization of **1a-c** occurs by an anionic mechanism. Blocking this reaction pathway with a protic acid allowed radical reactivity in bis(butoxycarbonyl)dicyanoquinodimethane.

Iwatsuki's free radical initiated copolymerizations were directed toward determining the alternating vs random copolymerization nature of DBDCQ with the two styrenes. The experiments were run to low conversion, with variable monomer feed ratios. DBDCQ copolymerized alternatingly with *p*-MeOSt and randomly with St.

The literature also contains reports of spontaneous copolymerizations between electron-poor quinodimethanes and electron-rich olefins. Specifically, tetracyanoquinodimethane (**2**) copolymerizes spontaneously with styrene under heterogeneous conditions,[1] and tetrakis(methoxycarbonyl)quinodimethane (**3a**) copolymerizes spontaneously with isobutyl vinyl ether and *N*-vinylcarbazole.[2] We now describe the spontaneous homopolymerization of bis(ethoxycarbonyl)dicyanoquinodimethane (**1b**) and spontaneous copolymerizations of **1b** with St and *p*-MeOSt in acidified solution.

Experimental Section

Materials. The preparation of DEDCQ by oxidation of 7,8-bis(diethoxycarbonyl)-7,8-dicyano-*p*-xylene has been previously described.[5,6] This reaction was typically run on a 2-g scale. Crude DEDCQ was dissolved at room temperature in a minimum amount of chloroform containing a few drops of acetic acid. Recrystallization was allowed to proceed overnight at -40 °C. The precipitate was rapidly filtered from solution by using a coarse glass filter and strong aspirator vacuum. The purified DEDCQ was then crushed to a fine powder during continued application of vacuum to facilitate rapid removal of solvent. Yields were consistently around 35%. Monomer was protected from heat during subsequent handling and was always used immediately upon preparation. *p*-MeOSt and St were purchased from Aldrich Chemical Co. and purified by conventional methods. $CHCl_3$ was freed of ethanol preservative by washing with H_2SO_4, H_2O, 10% NaOH, and again with H_2O. It was dried over CaH_2 and distilled. Reagent grade acetic acid was used as received.

Polymerization Procedure. Prior to isolation of DEDCQ, 4.0 mL of $CHCl_3$ was distilled directly into a flamed ampule equipped with a stir bar. Acetic acid, 80 μL, was added. DEDCQ was added, with stirring to aid dissolution, followed by donor monomer for copolymerizations. The polymerization mixture was immediately frozen, then degassed by the freeze-thaw method, sealed, and stirred under the desired conditions. Isolation of polymeric products was achieved by precipitating the reaction mixture into 150 mL of vigorously stirred acetic acid methanol (a 1:1 by volume mixture completely removed unreacted DEDCQ). The precipitated polymer was concentrated by centrifuge and then filtered. Further purification was achieved by redissolving the polymer product in CH_2Cl_2, reprecipitation in a small volume of CH_3OH, filtration, and drying to constant weight.

Instrumentation. Size exclusion chromatography employed a Shodex A-805 GPC column which, using polystyrene standards,

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Table I
Spontaneous (Co)polymerizations of DEDCQ and *p*-MeOSt or St in Dark and Ambient Light[a]

run no.	DEDCQ, mg	comonomer	comonomer, mg	DEDCQ in feed, %	temp, °C	time, h	yield, %	% N	% copoly DEDCQ	$10^6 M_n$	η_{inh},[b] dL/g
				Reactions under Dark Conditions[c]							
1	125	...		100	4	43	...				
2	117	St	47.3	47	4	28	7	8.11	69	1.1	
3	116	St	47.4	47	4	44	11	8.00	65	1.5	
4	117	*p*-MeOSt	55.5	49	4	7	12	6.05	45	1.3	
5	120	*p*-MeOSt	57.1	49	4	10	18	6.20	47	1.3	1.97
6	125	*p*-MeOSt	58.5	49	4	17	28	6.18	47	1.2	2.16
7	121	*p*-MeOSt	56.5	49	4	28	42	6.14	46	1.2	2.23
8	112	...		100	25	25	...				
9	117	...		100	25	45	13			1.4	
10	116	St	41.8	49	25	13	9	8.82	83	1.0	
11	117	St	41.7	50	25	21	20	8.38	74	1.6	2.69
12	115	St	41.4	49	25	42	30	8.53	78	1.2	2.10
13	117	*p*-MeOSt	56.5	47	25	5	20	6.29	48	1.3	
14	116	*p*-MeOSt	54.8	49	25	7	25	6.21	47	1.3	
15	118	*p*-MeOSt	53.5	50	25	9	33	6.31	48	1.2	2.19
16	113	*p*-MeOSt	52.0	49	25	17	41	6.21	47	1.2	2.14
17	105	*p*-MeOSt	51.5	48	25	29	28	6.44	50	1.2	2.22
				Reaction in (Fluorescent) Ambient Light							
18	115	...		100	25	24	15			1.5	
19	120	...		100	25	45	55			1.5	
20[d]	69.0	...		100	25	72	...				
21	112	St	42.7	48	25	30	30	8.20	71	1.4	2.14
22	112	St	44.1	47	25	45	38	8.46	76	1.3	2.19
23	115	*p*-MeOSt	55.7	48	25	5	17	6.53	51	1.2	
24	116	*p*-MeOSt	55.1	49	25	7	35	6.51	51	1.2	2.24
25	113	*p*-MeOSt	50.7	50	25	16	42	6.51	51	1.2	1.95

[a] In 4.0 mL of $CHCl_3$ containing 80 μL of CH_3COOH. [b] 0.2–0.4% chloroform solutions ca. 24.5 °C. [c] Polymerization ampule was wrapped in aluminum foil prior to addition of DEDCQ. [d] In 3.0 mL of $CHCl_3$ containing 60 μL of CH_3COOH and 20 mg of tetramethylpiperidinyl oxide (TEMPO).

gave a linear calibration curve over the range MW = 2×10^5 to 2×10^6. Sample molecular weight values were assigned by using this curve and were uncorrected. The standards and samples were eluted with $CHCl_3$ and detected by using a Spectra Physics UV detector (254 nm). NMR spectra were recorded on a Bruker WM-250 MHz spectrometer. Viscosity values were obtained by using a Ubbelohde viscometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Results

Homopolymerizations. At 4 °C in the dark no DEDCQ polymerization occurred after 2 days. Slow homopolymerizations occurred at room temperature and were accelerated by exposure to ambient fluorescent light. Addition of the radical trap tetramethylpiperidinyl oxide (TEMPO) prevented the formation of any polymer as evidenced by GPC analysis of the polymerization mixture after 3 days.

Copolymerizations. Addition of donor monomers resulted in spontaneous copolymerizations. These polymerizations were more rapid than the homopolymerizations of DEDCQ and proceeded even in the dark, at 4 °C. DEDCQ–*p*-MeOSt copolymerizations became noticeably viscous after 4 h at room temperature. As polymerization proceeded, yields and viscosities increased and the red charge-transfer color faded. ^{13}C NMR analysis of the polymeric products shows them to be highly alternating in nature. In each case the DEDCQ carbon resonances in the copolymer spectrum appear as more complex signals than in the homopolymer spectrum. None of the copolymer signals show a peak at the homopolymer resonance frequencies. All the DEDCQ–*p*-MeOSt copolymers were shown to be close to 1:1 by nitrogen analyses that were reproducible to within 0.1%. There is a small trend in the DEDCQ–*p*-MeOSt copolymer compositions. As the copolymerization conditions become more favorable to DEDCQ homopolymerization (higher temperature, light), the copolymers become slightly richer in DEDCQ. Copolymerizations with St proceeded slower than those with *p*-MeOSt and gave copolymers rich in DEDCQ. At room temperature, exposure to light had no discernible effect on the rate of copolymerization.

Polymer Molecular Weights. The molecular weight of the (co)polymers produced was consistently high once the protocol for monomer preparation, detailed in the Experimental Section, was implemented. Deviation from the outlined procedures resulted in molecular weight, around (2–4) × 10^5. These lower molecular weight polymers did not form isolable precipitates in the methanol–acetic acid precipitation mixture and are not included in our results. At every point in the polymerization the only species present were monomers, some small molecules and high polymer. The molecular weight of the polymer did not increase with conversion.

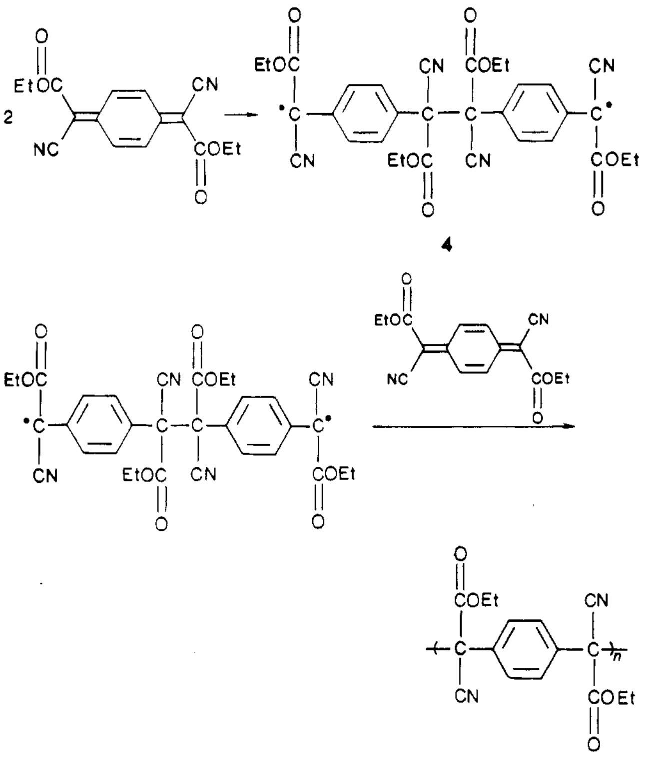
Discussion

Homopolymerizations. The inhibiting effect of TEMPO on DEDCQ homopolymerization and the fact that DEDCQ copolymerized with the donor olefins indicate that spontaneous DEDCQ anionic homopolymerization has been effectively inhibited by adding acid, and that slower spontaneous radical polymerizations have taken its place.

The degree of polymerization of the DEDCQ homopolymers (MW = 1.5×10^6) is approximately 60000. The efficiency of this polymerization and its reproducibility support a spontaneous initiation mechanism as opposed to initiation by impurity. If adventitious impurities were responsible for initiation, we would expect that in some instances no polymerization would occur and the molecular weight of the polymers produced would be low and variable.

We believe the spontaneous homopolymerization of DEDCQ in acidified solution begins with formation of a dimer diradical, 4 (Scheme I). Although it is possible that polymerization is initiated by the diradical form of the

Scheme I



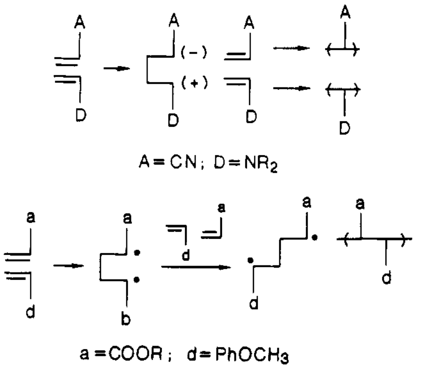
quinodimethane, we feel this is unlikely. For example, spectroscopic studies of several quinodimethanes reveal no measurable diradical content.[7,8] Furthermore the thermodynamics of DEDCQ dimerization are quite favorable. In addition to the energy gained by bond formation, dimerization results in the aromatization of two rings. Finally the resulting radicals are highly stabilized by the substituents at their centers. Room temperatures or light are required for the formation of the dimer diradical 4. It initiates chain propagation to form high polymer.

Propagation by radical coupling is also a possibility; however, this would result in an increase in molecular weight with time. Furthermore it is reasonable to expect that coupling between two tertiary centers is a much slower process than chain addition of monomer that results in ring aromatization.

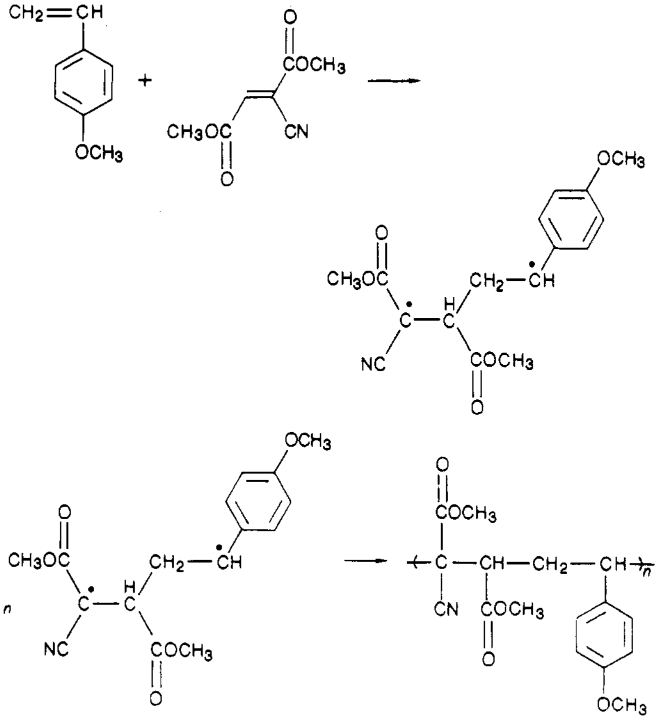
Copolymerizations. The fact that spontaneous copolymerizations of DEDCQ and donor monomers proceed more rapidly than homopolymerization, and do not require light and ambient temperatures, points toward the existence of a more efficient initiation mechanism under these conditions. Bond formation in the spontaneous reactions of olefins bearing electron-accepting substituents with those bearing withdrawing substituents has been studied extensively by Hall and his colleagues[9] (Scheme II). The radical or zwitterionic nature of the resulting tetramethylenes depends on the substituents. When the donor terminus bears a *p*-methoxyphenyl group and the acceptor terminus cyano and ester substituents as in the case of *p*-MeOSt–dimethyldicyanofumarate, the tetramethylene is highly diradical in nature.[10] The *p*-MeOSt–dicyanofumarate system copolymerized spontaneously to give alternating copolymers (Scheme III). The molecular weight of the copolymers increased with conversion, indicating that in this case propagation was occuring by diradical coupling.

Analogous bond formation between DEDCQ and the styrene comonomers would lead to formation of a "*p*-phenylene tetramethylene" which would have at its radical centers the same substituents as the *p*-MeOSt–cyanofumarate tetramethylene (Scheme IV). Here the radical at the acceptor end of the phenylene tetramethylene is further stabilized by resonance with the benzene ring. It is therefore reasonable to assume that such a species forms and that it initiates the spontaneous copolymerizations of DEDCQ and *p*-MeOSt and St. Our observation that *p*-MeOSt copolymerizations are faster than St copolymerizations is consistent with tetramethylene initiation because the stronger donor is able to impart greater polar push–pull stabilization to the diradical intermediate.

Scheme II



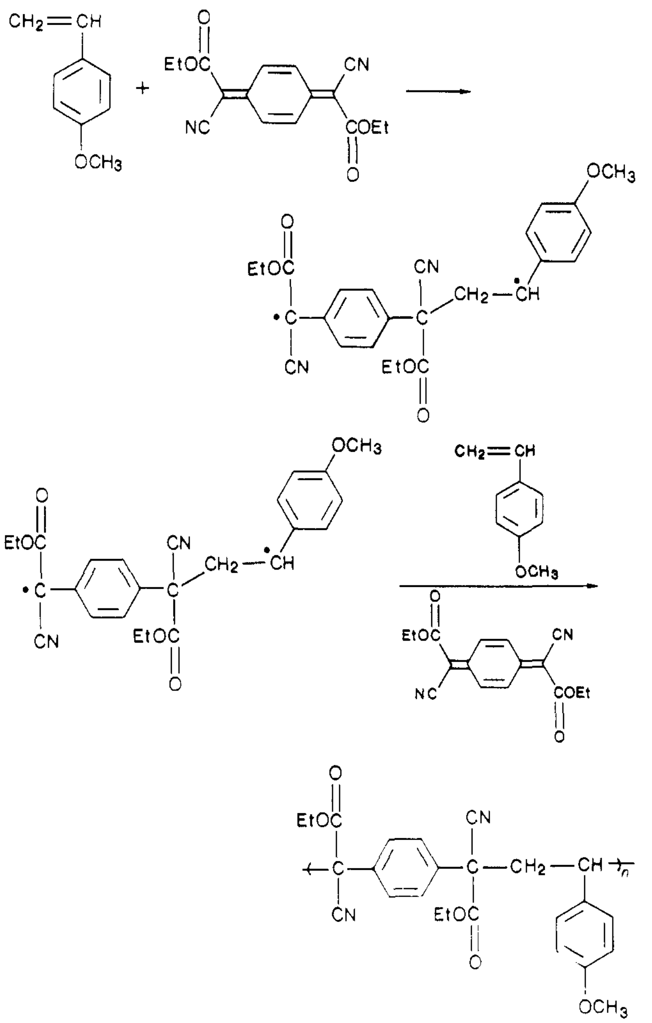
Scheme III



Electron donor–acceptor complexes are considered to be precursors to the tetramethylene intermediate and may also add to the growing chain.

The slight and highly reproducible enrichment of DEDCQ–*p*-MeOSt copolymers in DEDCQ as conditions become more favorable to spontaneous DEDCQ homopolymerization supports our assertion that a DEDCQ dimer diradical initiates the spontaneous homopolymerization of DEDCQ. At 4 °C in the absence of light DEDCQ does not homopolymerize spontaneously and the molar fraction of DEDCQ in the *p*-MeOSt copolymer was at most 46%. At room temperature under ambient light where spontaneous polymerization of DEDCQ does occur the DEDCQ mole fraction is consistently 51%. This enrichment may be explained by a small amount DEDCQ

Scheme IV



dimer diradical formation under ambient conditions. Subsequent incorporation of the dimeric DEDCQ diradical in the growing chain results in DEDCQ chain enrichment. If spontaneous DEDCQ homopolymerizations are initiated by a monomeric diradical under ambient conditions, no such chain enrichment will occur.

Finally as we would expect, DEDCQ-*p*-MeOSt copolymerizations proceed faster than those between the olefinic analogue of DEDCQ, diethyl dicyanofumarate, and *p*-MeOSt due to the reactivity of the quinodimethane nucleus.[11]

Molecular Weights. As with the spontaneous homopolymerizations of DEDCQ the spontaneous copolymerizations produced high molecular weight copolymer at low conversion and the molecular weight remained constant thereafter. It is reasonable to expect that at any instant in time the growing chain has at its end a highly stabilized DEDCQ radical (addition of DEDCQ to a styrene radical is very fast). Therefore, propagation by radical combination would again require coupling between two sterically congested centers. For these reasons we conclude that the copolymers also propagate by chain addition.

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Registry No. (DEDCQ)(*p*-MeOSt) (alternating copolymer), 114379-07-6; (DEDCQ)(St) (copolymer), 114379-08-7; (*p*-MeOSt)(dimethyldicyanofumarate) (copolymer), 637-69-4; DEDCQ (homopolymer), 114379-06-5; DEDCQ, 114379-00-9.

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Thermal Polymerization of a 2-(Carboxyalkyl)-2-oxazoline

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ABSTRACT: A 2-(carboxyalkyl)-2-oxazoline was synthesized by the addition of 3-mercaptopropionic acid (MPA) to 2-isopropenyl-2-oxazoline (IPO). Thermal polymerization of 3-[(2-[2-oxazolin-2-yl]propyl)thio]propionic acid yielded a branched polymer with (1-oxa-2,8-dioxo-5-thia-9-aza-7-methyl-1,9-nonanediyl)ethylene as the repeat unit as identified by ^{1}H and ^{13}C NMR and IR. Vapor pressure osmometry (VPO) showed number-average molecular weight to be in the range 1050–3370. Hydrolysis of the polymer and analysis of the products by high-performance liquid chromatography (HPLC) and NMR spectroscopy identified the branch site structure as [(1,7-dioxo-8-oxa-4-thia-2-methyl-1-octanyl)imino]ethylene. Various end groups (carboxyl, methacrylamido, acryloyl, and (2-hydroxyethyl)amino) were identified by NMR. The mechanism proposed for the polymerization describes the reactions that result in branching and termination.

Introduction

We recently reported the thermal polymerization of 2-(mercaptoalkyl)-2-oxazolines that proceeds by ring-opening nucleophilic attack of sulfur on the CH_2–O (5-position) of the oxazoline ring.[1] This paper involves an extension of this work to the polymerization of a 2-(carboxyalkyl)-2-oxazoline. We report the synthesis of 3-[(2-[2-oxazolin-2-yl]propyl)thio]propionic acid (III) by the

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