bilization (general reactivity) of a resulting polymeric radical in cross propagation of the copolymerization. In other words, a rate-determining transition state in a conventional copolymerization should be much closer to a reaction product than a reacting species. This discrepancy in the reactivity order between the observed and calculated allows us to mention that a rate-determining transition state in an alternating copolymerization is different from that in a conventional radical copolymerization. In previous studies of alternating terpolymerizations among donor–donor–common acceptor monomers[23] and among acceptor–acceptor–common donor monomers,[24] it was pointed out that monomer reactivity is controlled much more by the polar effect of the monomer and much less by the general reactivity (resonance stabilization) effect than the corresponding one of a conventional random radical copolymerization and furthermore that the polar effect is reasonably related to an interaction somewhat equivalent to Coulomb force type of an interaction taking place between donor and acceptor monomers within the dative bond structure of the charge-transfer complex.[24] It may be concluded therefore in an alternating copolymerization that a rate-determining transition state is a state close to the reacting species in which a new covalent bond is not yet formed between a polymeric radical and a coming monomer, and a Coulomb type-like polar interaction between reacting species plays an important role in the rate determination even though its mechanism has not been demonstrated in a concrete form yet.

Anyway, when the extraordinary reactivity of PCA due to its high stabilization as the quinonoid form is taken into account, the relative reactivity of the acceptor monomers obtained in the terpolymerization experiments might be regarded as agreeing with their electron-accepting properties. It was concluded therefore that the reactivity in alternating copolymerization is controlled primarily by the polarity of the acceptor monomer. In the case of PCA, the general reactivity (resonance stabilization) of a monomer should be taken into consideration in alternating copolymerization, but the extent of its contribution is presumed to be much less than that in a conventional random radical copolymerization.

Registry No. CQM, 83928-83-0; MAnh, 108-31-6; PCA, 118-75-2; DDQ, 84-58-2; (CQM)(St) (copolymer), 107455-30-1; (CQM)(MeOSt) (copolymer), 107455-31-2; (CQM)(MAnh)(St) (copolymer), 107455-32-3; (CQM)(PCA)(St) (copolymer), 107455-33-4; (CQM)(DDQ)(St) (copolymer), 107455-34-5; St, 100-42-5; MeOSt, 637-69-4.

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Cationic Polymerization of Nitrogen-Containing Electron-Rich Vinyl Monomers by Electrophilic Olefins and Their Cyclobutane Cycloadducts

Mohamed Abdelkader, Anne Buyle Padias, and H. K. Hall, Jr.*

C. S. Marvel Laboratories, Chemistry Department, University of Arizona, Tuscon, Arizona 85721.

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ABSTRACT: The major pathways for the reactions of very electron-rich N-containing olefins with several electrophilic olefins were studied. *N*-Ethyl-3-vinylcarbazole (**1**), *N*-vinylcarbazole (**2**), and *p*-(dimethylamino)styrene (**3**) undergo kinetic cyclobutane formation with an electrophilic olefin without a leaving group, methyl β,β-dicyanoacrylate (**4**), and with one with a weak β-leaving group, tetracyanoethylene (**5**). The third electrophilic olefin, β,β-dicyanovinyl chloride (**6**), has a strong β-leaving group and readily initiates the cationic polymerization of **1** and **2** and oligomerization of **3**. If an excess of donor olefin is used, **4**, **5**, and **6** all initiate cationic homopolymerization of **1** and **2**, while **3** only leads to oligomers, as it does with conventional Brønsted initiators. Cationic initiation by their own cyclobutane adducts is observed for the very electron-rich monomers **1** and **2**. Postcyanovinylation of the formed polymers by the electrophilic olefins occurs. We can conclude that incorporation of a β-leaving group enhances the initiating ability of electrophilic olefins and that *N*-carbazyl and *N*-ethyl-3-carbazyl are overall the most effective donor substituents favoring cationic homopolymerization.

Introduction

In earlier work we showed that electrophilic olefins could be used to initiate cationic homopolymerization of electron-rich vinyl monomers.[1,2] Electrophilic tri- and tetrasubstituted olefins initiated cationic homopolymerization of very electron-rich vinyl monomers, in particular *N*-vinylcarbazole, through the intermediacy of zwitterionic tetramethylene intermediates.

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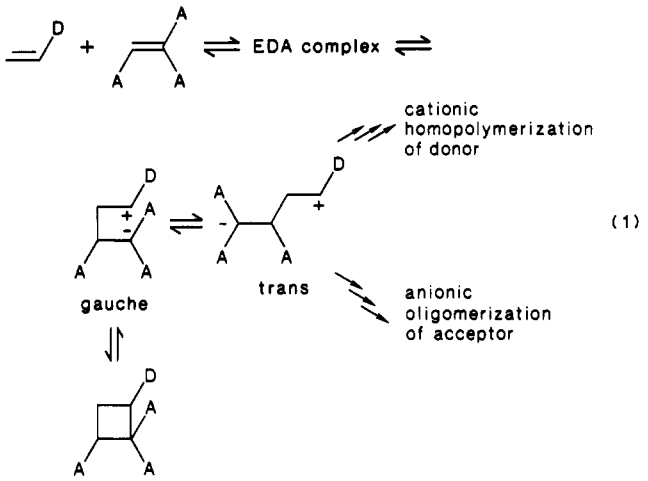
Table I
Reactions at Equal Initial Concentrations ("Organic Chemist's Conditions")[a]

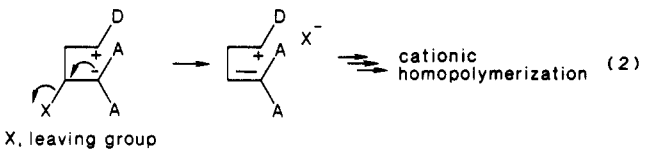
donor	concn, M	acceptor	concn, M	time	product[b]	yield, % (by NMR)
1	1.0	4	1.0	1 h	Cb 7	100
1	0.5	5	0.5	3 h[b]	Cb 8	100
1	1.0	6	2.0	10 min	homopoly-1[c]	100
2	0.52	4	0.50	30 min	Cb 9	100
2	0.05	5	0.05	40 s	Cb 10[d]	100
2	2.0	6	2.0	20 min	homopoly-2[e]	52
3	1.0	4	1.0	15 min	Cb 11 (2 isomers)	100
3	1.0	5	1.0	10 min	Cb 12	100
3	1.0	6	1.0	20 min	Bd 13	80
					oligo-3	20

[a] At 28 °C in $CDCl_3$. [b] Cb indicates cyclobutane derivative; Bd indicates 1,3-butadiene derivative. [c] Electrophile reacts with aromatic rings of homopoly-1 to give insoluble dicyanovinylated polymer when left for longer times. [d] Reference 2. [e] MW 130 000.



The delocalized carbanionic center, present at very low concentration, did not interfere significantly with the very stable propagating carbenium ion.

Later, we transformed the tetramethylene carbenium–carbanion zwitterion into an initiating carbenium ion–gegenion pair by incorporating a nucleofugic leaving group into the β-position[3]



When X was the triflate ion, high yields and high molecular weight were achieved for both *N*-vinylcarbazole and *p*-methoxystyrene.[3] When iodide or chloride were the leaving groups, *N*-vinylcarbazole polymerized well, but *p*-methoxystyrene only moderately so.[4] In the latter cases the halide ions compete nucleophilically with *p*-methoxystyrene to trap both the tetramethylene zwitterions and the growing chains.

Recently we carried out a thorough kinetic and mechanistic study of the reactions of *N*-vinylcarbazole (**2**) with tetracyanoethylene (**5**) (TCNE) and with dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate.[2] These facile reactions proceeded through an electron donor–acceptor (EDA) complex to a cis or gauche tetramethylene zwitterion held in this conformation by Coulombic attraction. Its easiest path is to collapse to cyclobutane as the kinetically favored product. The strained cyclobutane opens back to zwitterion, which can rotate to the trans conformer and initiate cationic homopolymerization of excess donor monomer to homopolymer. As implied by this scheme, the isolated cyclobutane was itself able to initiate the cationic polymerization of *N*-vinylcarbazole.

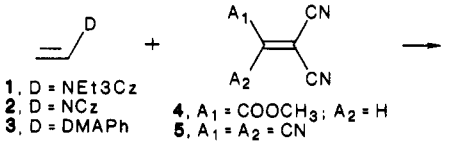
Because the zwitterion is partitioned between first-order cyclization and second-order initiation, the outcome was determined in part by the relative concentrations of the reagents. We therefore distinguished between "organic chemist's conditions", namely, equivalent concentrations, and "polymer chemist's conditions", namely, a large excess of polymerizable monomer.

In the present work we extend these studies to the very electron-rich monomers *N*-ethyl-3-vinylcarbazole (**1**) and *p*-(dimethylamino)styrene (**3**) and provide additional information on the reactions of *N*-vinylcarbazole (**2**). The electrophilic ethylenes of the present study represent three types, one with no leaving group, methyl β,β-dicyanoacrylate (**4**), one with a weak leaving group, CN, TCNE (**5**), and one with a strong leaving group, Cl, β,β-dicyanovinyl chloride (**6**).

We shall also comment on the effects of donor substituents on cationic polymerizability of vinyl monomers.

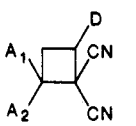
Results

Reactions at Equal Initial Concentrations: "Organic Chemist's Conditions" (Table I). Reactions of donor olefins **1**, **2**, and **3** with acceptors **4** and **5** gave cyclobutanes in quantitative yields. The reactions proceeded at 28 °C over 10–30 min and were faster in more polar solvents. From benzene, the cyclobutanes precipitated as formed.



1, D = NEt3Cz
2, D = NCz
3, D = DMAPh

4, A_1 = $COOCH_3$; A_2 = H
5, A_1 = A_2 = CN

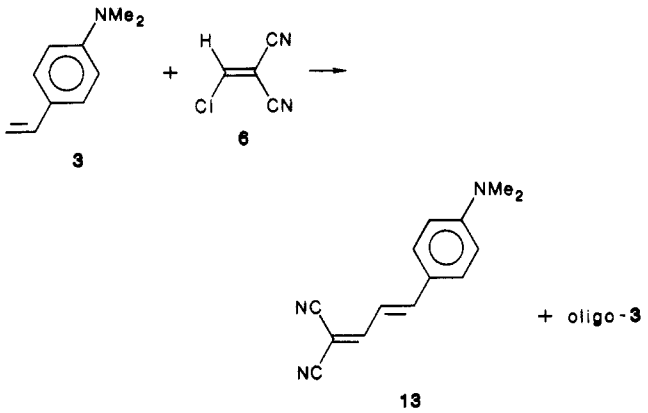


7, D = NEt3Cz; A_1 = $COOCH_3$; A_2 = H
8, D = NEt3Cz; A_1 = A_2 = CN
9, D = NCz; A_1 = $COOCH_3$; A_2 = H
10, D = NCz; A_1 = A_2 = CN
11, D = DMAPh; A_1 = $COOCH_3$; A_2 = H
12, D = DMAPh; A_1 = A_2 = CN

Reactions of **6** proceeded differently. In the presence of an equivalent amount of **6**, **1** and **2** gave high yields of high molecular weight cationic homopolymer, while **3** gave cationic oligomers and the red butadiene derivative **13**.

Intensely colored EDA complexes were observed in all of these reactions. Those from **4** and **6** were red, while those with **5** were intense blue, indicating that the latter (TCNE) forms stronger complexes.

Reactions with Excess Donor: "Polymer Chemist's Conditions" (Table II). Excess **1** mixed with electrophiles **4** and **5** gave high MW homopoly-**1**. Similarly excess **2** in the presence **5** gave high MW poly-**2**,[2] but in the



3 6 13

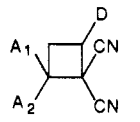
presence of 4 only a trace of polymer is obtained. Monomer 3 gave only oligomers under these conditions. Excess 1 and 2 in the presence of 6 homopolymerized, while excess 3 with 6 gave again the butadiene derivative 13, which is the same result as observed above. The same colored EDA complexes were observed as in the reactions with equal initial concentrations.

For reference, the electrophilic initiator trifluoroacetic acid in 1,2-dichloroethane with 3 also gave only oligo-3 in quantitative yield.

The possible initiation by acid (HCl or HCN) has been excluded by other workers.[2,3]

Initiation by Isolated Cyclobutane Cycloadducts. Our scheme implies that the isolated cyclobutane adducts should be capable of reverting to tetramethylene zwitterion and initiating cationic polymerization of donor monomer.

The kinetically formed cyclobutanes 7–12 were thermodynamically unstable. Left in solution at 28 °C for extended periods, they led in each case to poly-1, poly-2, and oligo-3. These products then underwent post-reaction with the electrophile. Cycloadducts from *p*-methoxystyrene or vinyl ether 14–16 were much more thermally stable and required heating to 86 °C to cause them to open.



14, D = $pCH_3OC_6H_4$; $A_1 = A_2 = COOCH_3$
15, D = p-$CH_3OC_6H_4$; $A_1 = A_2 = CN$
16, D = i-C_4H_9O; $A_1 = A_2 = CN$

In order to test the initiating ability of these cycloadducts, they were mixed with excess donor. The cyclobutane adducts 8 and 10 of respectively 1 and 2 with 5 (TCNE) can initiate the cationic polymerization of 1 and 2 at 28 °C. These cyclobutanes were, however, incapable of initiating *p*-methoxystyrene or vinyl ether polymerization.

We also tried to use the cyclobutane adducts 14–16 to initiate cationic polymerization of our electron-rich monomers 1 and 2, but no reaction occurred at 28 °C. At the higher temperature required to cause ring-opening of the cyclobutanes, thermal free-radical polymerization of monomer obscured the results.

Postreactions. The homopolymer of 1 and 2 and the oligomers of 3 react with 5 via further blue EDA complexes to give black insoluble polymers. The carbazyl substituents of poly-1 and poly-2 and the aromatic rings of the oligo-3 undergo electrophilic aromatic substitution (multicyanovinylation)[5,6] with the electrophilic initiators. The oligomer of monomer 3 on the other hand does initiate the anionic oligomerization of olefins 4 and 5.

The reaction of *N*,*N*-dimethylaniline (DMA) with TCNE 5 has been thoroughly studied in the literature.[6,7]

Table II
Reactions Involving Excess Donor ("Polymer Chemist's Conditions")[a]

donor	concn, M	acceptor	concn, M	time, h	product[b]
1	0.50	4	0.05	21	55% polymer, MW 1 500 000
1	0.25	5	0.0125	18	19% polymer, MW > 1 000 000
1	0.5	6	0.05	21	80% polymer, MW 48 000 15% oligomer, MW 1500
2	0.51	4	0.033	20	trace homopolymer
2	0.22	5	0.01	5	60% polymer[c]
2	0.25	6	0.0375	21	27% polymer, MW 24 000 12% polymer, MW 2300
3	0.5	4	0.044	110	no polymer, trace oligomers
3	0.5	5	0.047	110	no polymer, trace oligomers
3	0.5	6	0.053	110	no polymer

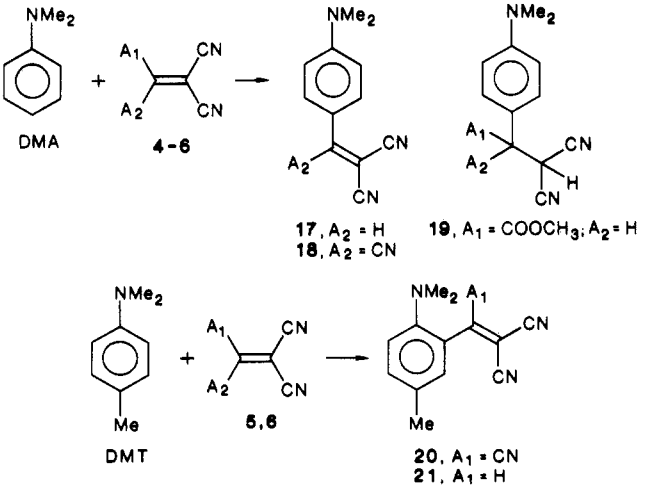
[a] In CH_2Cl_2 at 28 °C except as noted. [b] Molecular weights by SEC. [c] Reference 2.

Table III
Cyclobutane-Initiated Polymerizations[a]

monomer	cyclobutane deriv	time, h	yield	MW[b]
1	8	19	3	
	10	19	32.6	460 000
	15	23	0	
2	8	19	18	240 000
	8	47	63.2	135 000[c]
	10	19	88.4	160 000
	14–16	23	0	

[a] Monomer, 0.5 M; cyclobutane, 16 mg; solvent, 2 mL of dichloromethane; temperature, 28 °C. [b] Determined by SEC. [c] Broader MW distribution, maximum shift to lower MW with increasing yield.

As models for the observed postreactions, the reactions of DMA, *N*,*N*-dimethyltoluidine (DMT), and *N*-ethylcarbazole with olefins 4–6 were investigated (Table IV).



17, A_2 = H
18, A_2 = CN
19, A_1 = $COOCH_3$; A_2 = H
20, A_1 = CN
21, A_1 = H

DMA with olefins 4–6 yielded the trans addition products 17–19, in accordance with the literature data. Partial anionic oligomerization of 4 is observed in the presence of DMA. DMT with olefins 5 and 6 also led to the addition products 20 and 21, but 4 underwent total oligomerization

Table IV
Model Studies of Polymer Postreactions[a]

aromatic amine	electrophile	time	product	NMR data[b]
DMA	4	15 h	oligo-4 and 19	δ 2.8, 2.9 (s, 6 H, NCH_3), 3.7 (s, 3 H, OCH_3), 3.8–4.4 (m, 2 H, $CHCOOCH_3$ and $CH(CN)_2$), 6.5–6.7 (d, 2 H, aromatic), 7–7.15 (d, 2 H, aromatic)
	5	15 h	17	δ 3.2 (s, 6 H, NCH_3), 6.6–6.8 (d, 2 H, aromatic), 7.9–8.1 (d, 2 H, aromatic)
	6	15 h	18 (cryst)	δ 3.21 (s, 6 H, NCH_3), 6.7–6.8 (d, 2 H, aromatic), 7.5 (s, 1 H, CH=C), 7.8–8.0 (d, 2 H, aromatic)
DMT	4	7 days	oligo-4	
	5	7 days	20	δ 2.28, 2.38 (s, 3 H, $ArCH_3$), 2.85, 2.9 (s, 6 H, NCH_3), 3.65 (s), 4.08 (s), 6.5–7.28 (m, 3 H, ArH)
	6	7 days	21	δ 2.3 (s, 3 H, $ArCH_3$), 2.7 (s, 3 H, NCH_3), 3.0 (s, NCH_3), 6.9–7.9 (m, 4 H, aromatic and HC= at 7.12)

[a] 1 mmole of each in 0.5 mL of $CDCl_3$ at 28 °C. [b] NMR: $CDCl_3$, 60 MHz.

in the presence of DMT. This is in agreement with the observed anionic oligomerization of 4 in the presence of oligo-3.

The reactions of *N*-ethylcarbazole with 5 and 6 were also investigated by NMR. With TCNE 5 only a different splitting pattern for the aromatic protons is observed. With 6 there is additional evidence that reaction takes place, because the olefinic proton of 6 shifts from δ 8.0 to 7.08 in the adduct.

Discussion

We shall discuss all these results in terms of our bond-forming initiating theory (eq 1 and 2). Briefly, cationic homopolymer and cyclobutane formation are favored as the respective electrophilic and nucleophilic character of the olefins increases.[1] Exclusive cationic homopolymerization of the donor olefin occurs if an electrophilic olefin with a strongly nucleofugic leaving group is used.[3,4] Cyano, a weak leaving group, is an intermediate case.

Initiation. Olefin–olefin spontaneous polymerizations occur via tetramethylene intermediates, formed by collapse of EDA complexes, as the true initiating species. Strong donors and acceptors, able to stabilize charge, cause a tetramethylene to be zwitterionic. Its carbenium center is able to initiate cationic homopolymerization (eq 1). However, this route has limitations. The carbanion center may interfere with the propagating carbenium ion or it may initiate anionic oligomerization of the electrophile.

The departure of a nucleofugic leaving group from a tetramethylene must confer carbenium ion character to the remaining terminus (eq 2). Every electrophilic ethylene with a leaving group, regardless of the nature of the donor and acceptor substituents, initiates only homopolymerization or, in certain cases, butadiene formation. Thus they are upgraded to more effective initiators for cationic polymerization, limited only by the stability of the gegenion to the propagating carbenium ion.

Propagation and Transfer/Termination. The π-electrons of monomer must compete effectively with the anionic center, whether this is the resonance-stabilized carbanion terminal or the nucleofugic gegenion, in order to obtain high molecular weight homopolymer. Our results show that *N*-ethyl-3-vinylcarbazole (1) and *N*-vinylcarbazole (2) compete effectively with any of these anionic centers.

Cyclobutane Initiation. The cyclobutanes derived from *N*-ethyl-3-vinylcarbazole (1) and *N*-vinylcarbazole (2), left in solution with excess parent donor monomer, were able to initiate the polymerization of these monomers. However other electron-rich monomers were not polymerized by these cyclobutanes, because this would require that a stable carbenium ion must generate a less stable one. Moreover cyclobutanes 14–16 from these other monomers (*p*-methoxystyrene and vinyl ethers) were too stable to initiate cationic polymerization of 1 or 2 at 28 °C. Therefore, cyclobutane initiation of cationic polymerization is limited to very electron-rich monomers.[2]

Postreaction. Finally, postreaction with electron-rich aromatic rings by electrophilic aromatic substitution may consume the initiator. Although possible for the carbazole-containing polymers, it appears to be controllable by minimizing contact time and temperature. For *p*-(dimethylamino)styrene (3) it becomes a major reaction, as confirmed by model studies.

Oligomerization of Electrophilic Olefin. Another factor in the use of certain electrophilic olefins as initiators is their possible anionic oligomerization. This effect is shown in the present studies by methyl β,β-dicyanoacrylate (4), which undergoes slow postoligomerization.

Nucleophilicity/Basicity of Substituents Limits Cationic Polymerizability. Gandini and Cheradame[8] have cited another factor that can limit homopolymer yields and molecular weights. If the donor substituent becomes too basic/nucleophilic, it will itself react with initiator and/or propagating carbenium ions to prevent polymerization. This effect is seen in the behavior of *p*-(dimethylamino)styrene (3). Neither our electrophilic initiators nor conventional Brønsted acids (trifluoroacetic acid and trichloroacetic acid[9]) give high polymer from this monomer because of the rather strong amino group. It appears that the *N*-carbazyl and *N*-ethyl-3-carbazyl groups are the strongest donor substituents that can be used to facilitate cationic polymerization.

Experimental Section

Instrumentation. NMR spectra are recorded with an EM-360 Varian 60-MHz nuclear magnetic resonance spectrometer. The infrared data are obtained from a Perkin-Elmer Model 983 infrared spectrometer. Melting points are measured with a Thomas–Hoover capillary melting apparatus without any correction. Chemical analyses are performed by MicAnal, Tucson, AR.

Size-exclusion chromatography was carried out with three columns, Du Pont Zorbax PSM 300S, PSM 60S and IBM GPC/SEC pore type A columns calibrated with polystyrene standards, and with chloroform as eluent and a Spectra Physics detector at 254 nm.

Reactants. Deuteriated solvents from Aldrich are used without any purification. Dichloromethane and benzene were treated with sulfuric acid until colorless, washed with water, 3% sodium carbonate, and water, and dried over calcium chloride. Then dichloromethane, benzene, and acetonitrile were distilled from calcium hydride and stored under nitrogen in the presence of molecular sieves.

N-Ethyl-3-vinylcarbazole (1) is synthesized according to literature procedure[10] and recrystallized 3 times from ethanol (treated with carbon black): mp 67–68 °C.

N-Vinylcarbazole (2) (Polysciences) in hexane is passed through a layer of charcoal and recrystallized in the same solvent at −50 °C. The process was repeated twice.[11]

p-(Dimethylamino)styrene (**3**) is synthesized according to literature procedure[12] and stored under nitrogen in the dark at −50 °C.

Methyl β,β-dicyanoacrylate (**4**) is synthesized as follows: In a round-bottom flask (100 mL), equipped with a Soxhlet extraction containing activated molecular sieves, are placed methyl glyoxylate methyl hemiacetal (24 g, 0.4 mol, distilled) and malononitrile (66 g, 0.1 mol) in acetonitrile (50 mL). The reaction mixture is refluxed for 3 h, the solvent evaporated, and the oil distilled at 62–63 °C (0.1 mmHg):[13] yield, 6 g (45%). The product is stored under nitrogen in the dark at −50 °C: NMR δ ($CDCl_3$) 3.94 (s, 3 H), 7.2 (s, 1 H). Anal. Calcd. 52.94; H 2.94; N, 20.58. Found: C, 52.09; H, 2.87; N, 19.82.

Tetracyanoethylene (**5**) was purchased from Fluka, recrystallized from 1,2-dichloroethane, sublimed twice through a layer of activated carbon black, and stored at −10 °C: mp 198–200 °C.

β,β-Dicyanovinylchloride (**6**) is synthesized according to literature procedure,[14] distilled, and stored under nitrogen in the dark at −50 °C.

General Procedure. In deuteriated solvent the two monomers are mixed in an NMR tube and the reaction is monitored.

When a nondeuteriated solvent is used, the reactants are placed each in one arm of a Y polymerization tube, and solvent is added to both arms. The reaction mixture is placed at −78 °C and degassed, and the vessel is filled with nitrogen gas. The procedure is repeated. The tube is then placed at 28 °C and the two solutions are mixed. From benzene solutions the cyclobutanes could be filtered after the reactions were complete. Homopolymer is precipitated in ether or methanol and washed with acetone. The homopolymer is identified by NMR and IR, and the average molecular weight is determined by size-exclusion chromatography using polystyrene as standard.

Reactions of Cyclobutanes in Solution. The reactions were followed by NMR and SEC. Faint EDA colors were observed when the cyclobutanes were left in solution. The NMR spectra of the polymers initially formed showed that homopoly-**1** and -**2** were formed and then underwent cyanovinylation postreaction. NMR showed this clearly in the aromatic region by comparing them with the spectra of model compounds from *N*,*N*-dimethylaniline and *N*,*N*-dimethyl-*p*-toluidine.

Poly-1. NMR ($CDCl_3$) δ 0.52–2.8 (broad, 6 H), 3.4–4.32 (broad, 2 H), 5.9–8 (broad, 7 H); IR (KBr) 3061 (w), 2968 (w), 1624 (w), 1596 (m), 1482 (s), 1453 cm^{-1} (s).

Poly-2. NMR ($CDCl_3$) δ 0.6–3.8 (3 broad peaks, 3 H), 4.42–5.4 (broad, 1 H), 5.6–8.1 (broad, 7 H); IR (KBr) 3050, 1621, 1482, 1451, 1351, 1156, 743 cm^{-1}.

Cyclobutane Synthesis and Identification. The two olefins, 1 mmol each, are mixed in 10 mL of benzene under a nitrogen atmosphere. After 5 h the solution is added to 100 mL of hexane and placed at −45 °C. The crystals are washed with benzene.

Cyclobutane **7** (70% yield) is purified by crystallization from dichloromethane–hexane (1:20): mp 121 °C (turns red); NMR ($CDCl_3$) δ 1.28 (t, 3 H), 2–3.5 (m, 3 H), 3.68, 3.72 (s, 3 H), 4.05 (q, 2 H), 4.5 (m 1 H) 6.8–8.2 (m, 7 H). It was unstable when left at room temperature in solution. IR (KBr) 3048 (w), 2951 (m), 2246 (w), 1747 (s), 1598 cm^{-1} (m).

Cyclobutane **8** is recrystallized from ether–dichloromethane–hexane (2:1:6): mp: 100 °C (turns yellow), 155 °C (forms red crystals), 169–170 °C (red crystals melt). The red crystals are presumably the butadiene derivative. NMR ($CDCl_3$) δ 1.4 (t, 3 H, J = 6 Hz, CH_3), 2.85–3.72 (m, 2 H, ring CH_2) 4.2 (q, 2 H, J = 6 Hz, NCH_2), 4.6 (dd, 1 H, J = 8 Hz, 12 Hz) 7–7.65 (m, 5 H, aromatic), 7.85–8.2 (m, 2 H). IR (KBr) 3051 (w), 293 (m), 2249 (w), 1598 (sharp), 1496 (sharp), 1236 (sharp), 749 cm^{-1} (sharp). Anal. Calcd: C, 75.63; H, 4.33; N, 20.05. Found: C, 75.51; H, 4.24; N, 19.41.

Cyclobutane **9** (30% yield) is characterized as follows: mp 123 °C (turns red); NMR ($CDCl_3$) δ 2.5–3.1 (m, 1 H, CH_2), 3.2–3.7 (m, 1 H, CH_2) 3.92–4.45 (m, 1 H, CH–E), 5.28–5.68 (dd, 1 H, CH–N), 7.82 (m, 8 H, aromatic); IR (KBr) 3061 (m), 2955 (m), 2247 (m), 1745 (s), 1597 cm^{-1} (sharp). Anal. Calcd: C, 72.93; H, 4.59; N, 12.76. Found: C 72.59; H, 4.35; N, 12.86.

Cyclobutane **11** is not stable and gives oligomers upon attempted isolation. A mixture of two isomers is formed according to NMR (trans/cis ratio = 70/30): NMR ($CDCl_3$) δ 2.1–3.2 (m, 2 H), 2.95 (s, 6 H), 3.7 (m, 1 H), 3.8, 3.82 (s, 3 H), 3.8–4.4 (m, 1 H), 6.7–7.2 (2d, 4 H); IR (KBr) 2954, 1741, 1613 cm^{-1}.

Cyclobutane **12** is unstable: NMR ($CDCl_3$) δ 2.1–3.7 (m, 2 H, CH_2), 3.0 (s, 6 H, N–CH_3), 4.5 (t, 1 H, $J_1 = J_2$ = 11 Hz, CHar), 6.68–6.82 (d, 2 H, aromatic), 7.18–7.3 (d, 2 H, aromatic).

Butadiene **13** is recrystallized from dichloromethane: mp 141–142 °C; NMR ($CDCl_3$) δ 3.08 (s, 6 H, NCH_3), 6.52–6.68 (d, 1 H, J = 9 Hz, aromatic), 6.52–7.50 (m, 3 H, HC=), 7.4–7.5 (d, 1 H, J = 6 Hz, aromatic); IR (KBr), 2923, 2210, 1590, 1522 cm^{-1}. Anal. Calcd: C, 75.31; H, 5.8; N, 18.82. Found: C, 74.51; H, 5.42; N, 17.93.

Cyclobutane **14** is precipitated in methanol: mp 100–102 °C; NMR ($CDCl_3$) δ 2.6–3.5 (ddd, J = 9 Hz, 12 Hz, 9 Hz, 2 H, CH_2), 3.9–4.1 (3s, 9 H, CH_3), 4.5 (dd, J = 9 Hz, 12 Hz, 1 H, CH), 6.8–7.4 (9, 4 H, aromatic).

Cyclobutane **15** is characterized: NMR (Me_2SO-d_6) δ 3.1–3.6 (m, 2 H, CH_2), 3.8 (s, 3 H, OCH_3), 4.8–5.1 (m, 1 H, CH), 7–7.5 (dd, 4 H, aromatic).

Cyclobutane **16** is characterized: NMR ($CDCl_3$) δ 0.93 (d, 6 H, CH_3), 1.6–2.1 (m, 1 H, CH), 2.9–3.7 (m, 4 H, CH_2–O and CH_2), 4.7 (m, 1 H, (H–O).

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