Communications to the Editor

The Spontaneous, Simultaneous Homopolymerization of Vinylidene Cyanide and Cyclic Ethers on Mixing the Two Monomers at 25°

Vinylidene cyanide reacts with vinyl ethers in solution (benzene) at 25° essentially to produce good yields of homopolymers of the vinyl ethers and polymers containing high contents of vinylidene cyanide,[1] regardless of the molar ratio of the vinyl ether to the vinylidene cyanide charged (5:1 to 1:5[2]). These results and the information[1] that the addition of trihydroxyethylamine or phosphorus pentoxide inhibits the polymerization of the vinyl ethers and vinylidene cyanide, respectively, suggests simultaneous cationic and anionic polymerizations. These extraordinary results prompted us to explore the possibility that other monomers which are both electron donors and are susceptible to polymerization *via* cationic mechanisms, such as the cyclic ethers, would also lead to the formation of homopolymers of each type of monomer (vinylidene cyanide and cylic ether) when the two were mixed.

The reaction of vinylidene cyanide with polymerizable cyclic ethers in toluene at 25° gave an insoluble fraction of polymer which precipitated immediately, and a soluble polymer fraction which was produced more slowly (Table I). The insoluble fraction, as it was obtained from the reaction without further fractionation was essentially a homopolymer of vinylidene cyanide; the polymer remaining in solution, when obtained, was essentially homopolymer of the cyclic ether. Room temperature appeared to be approximately the threshold temperature for polymerization, since no polymer of either monomer was formed at 0°.

The ethers which were studied can be divided into three categories: (1) those which induced the polymerization of vinylidene cyanide and polymerized themselves—tetrahydrofuran, oxetane, 2,2-dimethyloxirane, epichlorohydrin, and styrene oxide. Of these, only tetrahydrofuran and oxetane reproducibly gave high yields of polyether, regardless of the monomer ratio; (2) those which induce the polymerization of vinylidene cyanide but do not polymerize themselves—trioxane, 3,3-bischloromethyloxetane, and oxirane; (3) those which do not polymerize vinylidene cyanide (not given in Table I)—1,3-dioxolane, tetrahydropyran, and diethyl ether. In this category, neither the 1,3-dioxolane nor the vinylidene cyanide polymerized.

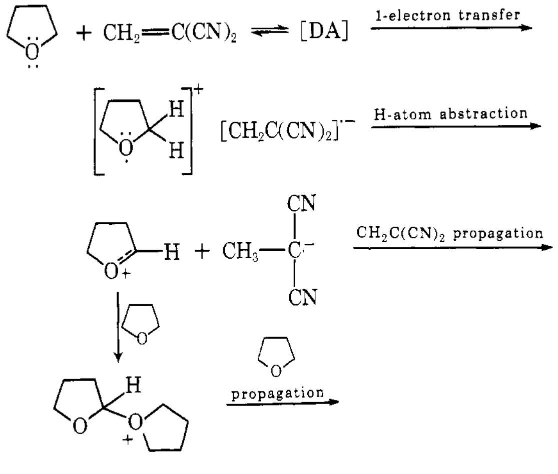
Styrene oxide and ethylene oxide are the only two of these cyclic ethers which also are known to afford polymer by anionic catalysis. In both cases, however, dioxane derivatives were isolated from the polymerization mixture containing polyether and poly(vinylidene cyanide); dioxane was obtained from the ethylene oxide polymerization and four diphenyldioxanes (*cis*-2,6-, *cis*-2,5-, *trans*-2,6-, and *trans*-2,5-diphenyl-1,4-dioxane) were obtained from the styrene oxide polymerization. These products are characteristic of cationic polymerizations of these monomers.[3] When vinylidene cyanide and ethylene oxide were polymerized in a 1:10 ratio in bulk, a small amount of block polymer was formed, presumably by the anionic initiation of ethylene oxide by poly(vinylidene cyanide) anion.

When phosphorus pentoxide was present in the tetrahydrofuran or oxetane polymerizations, no poly(vinylidene cyanide) was formed; when pyridine or water was present, no polyether was obtained.[4] In the case of the tetrahydrofuran polymerization, benzoyl peroxide and oxygen affected neither the yield nor the composition of the vinylidene cyanide polymer but both effectively inhibited the formation of polytetrahydrofuran. No transient color was observed in these very rapid polymerization of vinylidene cyanide.

With the exception that propylene sulfide is polymerized by various acceptors,[5] these results are without precedent. Oxetane will polymerize in tetranitromethane in the presence of an electron donor olefin, but the initiator for its polymerization is the acid, trinitromethane.[6,7]

Our data clearly implies anionic homopolymerization of vinylidene cyanide and cationic homopolymerization of

Scheme I



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[1] H. Gilbert, F. F. Miller, S. J. Averill, E. H. Carlson, V. L., Folt, H. J. Heller, F. D. Steward, R. F. Schmidt, and H. L. Trumbull, *J. Amer. Chem. Soc.*, **78**, 1669 (1956).

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[3] A. M. Eastham in "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, p 403.

[4] H. Gilbert, F. F. Miller, S. J. Averill, R. F. Schmidt, F. D. Stewart, and H. L. Trumbull, *J. Amer. Chem. Soc.*, **76**, 1074 (1954).

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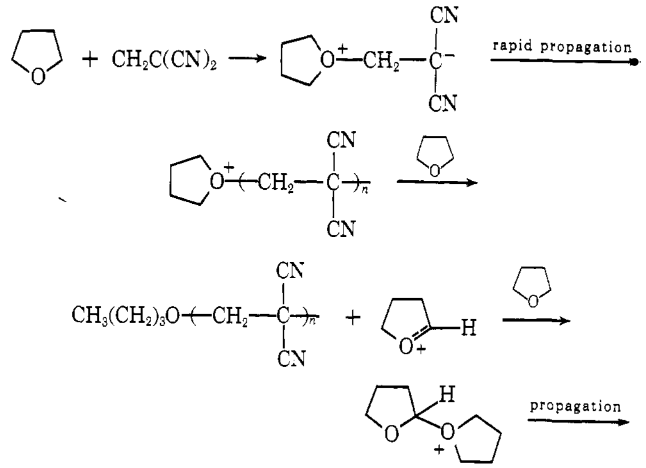
Table I
Polymerization of Vinylidene Cyanide (VC) and Cyclic Esters at 25° [a]

Cyclic Ether	Mol Ratio VC:Ether	Solvent	Insoluble Fraction Composition % VC	Insoluble Fraction Composition % Conv	Soluble Fraction Composition % Ether	Soluble Fraction Composition % Conv
Trioxane	1:1	CH_2Cl_2 [b]	86	62		0
	5:1	CH_2Cl_2 [b]	86	32		0
Tetrahydrofuran	1:10	Bulk[c]		Trace	86[d]	25
	1:1	Bulk[c]	92	54	93[d]	65
	5:1	Bulk[c]	93	36	95[d]	100
Oxetane	1:5	Toluene	68	37	97[e]	79
	1:1	Toluene	78	64	95[e]	100
	5:1	Toluene	90	33	94[e]	100
3,3-Bis(chloromethyl)-oxetane	1:5	Toluene	86	34		0
	1:1	Toluene	86	56		0
	1:1	Acetonitrile	88	56		0
2,2-Dimethyloxirane	1:5	Toluene	87	100	90	3
	1:1	Toluene	90	84	88	7
	5:1	Toluene	85	61	70	44
2-Chloromethyloxirane (epichlorohydrin)	1:10	Toluene	86	73		2
	1:1	Toluene	92	94	80	69
	10:1	Toluene	94	79		4
2-Phenyloxirane (styrene oxide)	1:5	Toluene	79	100	91	3[f]
	1:1	Toluene	87	100	83	45[f]
	5:1	Toluene	99	54	80	67[f]
Oxirane (ethylene oxide)	1:5	Toluene	87	16		1[g]
	1:1.5	Toluene	93	100		5[g]
	2.5:1	Toluene	92	84		2.5[g]
	1:10	Bulk	82	90	51[h]	1.5[g]

[a] Polymerizations were carried out in the absence of light in sealed evacuated tubes using vacuum line techniques. Generally, 2 ml of solvent with about 0.25 to 1 g of the monomer present in the lower molar ratio was used. All polymerizations were carried out using dry, carefully purified monomers and solvents, and were allowed to run for 24 hr in most cases. Solution polymerization of vinylidene cyanide took place immediately; polymerization of the cyclic ether was slower. Conversions are calculated on the basis of the respective monomer charged. [b] Cyclic ether insoluble in toluene. [c] Polymerization of cyclic ether in toluene takes place only very slowly (weeks). [d] η_{inh} = 1.28 (1:10), 0.74 (1:1), 0.27 (5:1) in benzene at 25°. [e] η_{inh} = 1.22 (1:5), 0.24 (1:1), 0.10 (5:1) in benzene at 25°. [f] A mixture of four diphenyl-1,4-dioxane isomers was obtained in each example. [g] In each case, 1,4-dioxane was obtained from the reaction. [h] Block copolymer as evidenced by its nmr and solubility in toluene. The nmr spectrum was identical with that of the two homopolymers.

Scheme II



the cyclic ethers, all in the same reaction medium. The rate of propagation of vinylidene cyanide is extremely rapid[4] and apparently virtually complete before appreciable cyclic ether polymerization, which has a relatively slow propagation rate,[8] has taken place. This could explain the cationic and anionic propagations in the same medium, but little information as to the mechanism of initiation is provided. Poly(vinylidene cyanide) does not initiate the polymerization of tetrahydrofuran or oxetane under the reaction conditions.

One possible mechanism consistent with these results is illustrated with tetrahydrofuran (Scheme I).

Polymerizations which are initiated *via* donor-acceptor complexes have been observed with a strong donor monomer (*N*-vinylcarbazole) and a weak acceptor monomer (methyl methacrylate or acrylonitrile).[9,10] In these cases little or no color was observed. Tetrahydrofuran forms a complex with maleic anhydride, a weak acceptor, but undergoes the one-electron transfer only on irradiation.[11] Under these conditions certain cyclic ethers will undergo ring-opening polymerization.[12] In the polymerization of vinylidene cyanide with the cyclic ethers, weak donors[13]

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(11) C. E. H. Bawn, A. Ledwith, and A. Perry, *Chem. Commun.*, 490 (1965); A. Ledwith and M. Sambhi, *ibid.*, 64 (1965).

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(13) The ionization potentials (electron impact) of cyclic ethers such as tetrahydrofuran, oxetane, and oxirane are 10.1, 9.85, and 10.65 eV, and are weaker donors, for example, than methyl vinyl ether, 8.9 eV: V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," St. Martin's Press, New York, N. Y., 1966.

and a strong electron acceptor are involved, but any slight color may be obscured by the rapid precipitation of poly(vinylidene cyanide). This mechanism is not consistent, however, with the observation that all our attempts to initiate polymerization of oxetane or tetrahydrofuran with the strong acceptors dichlorodicyano-*p*-benzoquinone, tetracyanoethylene, and tetracyanoquinodimethane produced only a trace of polymer. A "polar-mechanism" similar to that proposed for the polymerization of donor monomers with weak acceptors[9,10] may be responsible for the initiation. Another possible initiation mechanism relies on the rapid rate of propagation of vinylidene cyanide compared to the cyclization of the zwitterion (Scheme II). The further elucidation of the mechanism of initiation is under investigation.

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