Polyethers

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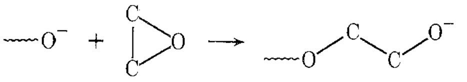
Several inherent characteristics of the ether linkage have stimulated extensive research and development of linear polymers with ether links in the polymer backbone.[1,2] The ether linkage has low polarity and low van der Waals interaction characteristics (ΔH_{vap} = 87.5 cal/g for pentane *vs.* 83.9 cal/g for diethyl ether). The carbon–oxygen bond has a lower barrier to rotation than the carbon–carbon bond (2.7 kcal/mol for dimethyl ether *vs.* 3.3 kcal/mol for propane) and thus provides a lower barrier to coiling and uncoiling of chains. The ether oxygen has an even lower excluded volume than a methylene group (van der Waals radii of 1.4 Å *vs.* 2.1 Å) and thus, of all backbone units, has the smallest "excluded volume." This also is a factor which permits greater chain flexibility. The carbon–oxygen bond has as great a bond energy (85 kcal/mol) as a carbon–carbon bond (82 kcal/mol) and much greater hydrolytic resistance than ester, acetal, or amide links.

All these useful characteristics have, in the past two decades, led to extensive commercial development and use of a variety of polyethers. Poly(propylene oxide) has become the basis of the large scale, world-wide development of "one-shot" polyurethan foam rubber, for mattresses, furniture, cushions, and rug padding. Poly(tetrahydrofuran) has been an important component of Corfam synthetic leather substitute and of elastic fibers. Linear poly(2,6-xylenol) is made on a large scale as an engineering plastic with an important combination of properties, such as high glass transition temperature, good thermal stability, good electrical properties, excellent adhesion, and ready solubility in common organic solvents. In each of these polyethers, the ether link is part of the "backbone" of the polymer chain. In each, the ether linkage makes an important contribution to the physical properties and chemical stability on which the utility is based.

The chemistry of the generation of polyethers is notably different from that of the classical vinyl polymerization processes. Many investigators have been involved in studying the mechanism, stereochemistry, and other aspects of polyether formation. It is our purpose here to present some of the results of these studies for those polyether systems in which we have been particularly interested, the polyepoxides, the poly(*p*-phenylene ethers), and the alternating poly(*p*-phenylene–methylene ethers).

Polyepoxides

Epoxide polymerization can be described in terms of three different mechanisms: (1) anionic (base catalyzed), (2) cationic (acid catalyzed), and (3) coordinate. The third actually combines features of the first two extremes, since it involves coordination of the monomer oxygen at a Lewis acid catalyst site (L), followed by attack on the thus-activated monomer by an alkoxide already bound to the site.



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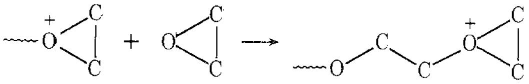

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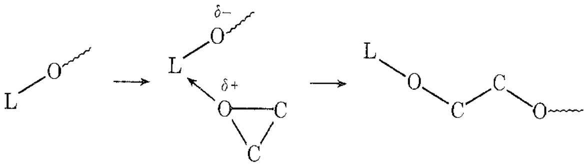

(3)

The ring-opening step in each case is a nucleophilic substitution and, in every case where the stereochemistry has been established, has been shown to occur with inversion of configuration at the carbon atom undergoing nucleophilic attack.[3,4] The ether-like oxygen in the strained three-membered ring thus behaves like a good "leaving" group. In the monomer itself, a strong nucleophile such as alkoxide ion, is required for SN2 attack. However, when the epoxide is converted to an oxonium state, as in the cationic process, it becomes such a good "leaving" group that even the weakly nucleophilic oxygen of the monomer is able to attack effectively.

The characterization of the epoxide oxygen as a good "leaving" group is supported by the fact that it not only can undergo SN2 displacement but E2 elimination. For example, tetramethylethylene oxide, on treatment with a catalytic amount of a base such as potassium *tert*-butoxide, undergoes "elimination" almost quantitatively.[5]

Anionic. Because of the intervention of the E2 process, only ethylene oxide is readily converted to

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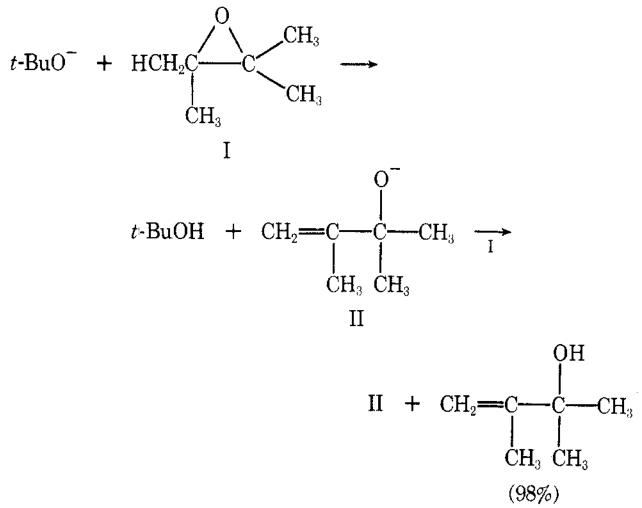
(1) National Research Council–Quartermaster Corps Arctic Rubber Conference, Washington, D. C., Jan 30–Feb 2, 1949.

(2) Quartermaster Corps High Temperature Rubber Conference, Washington, D. C., Nov 3-4, 1953.

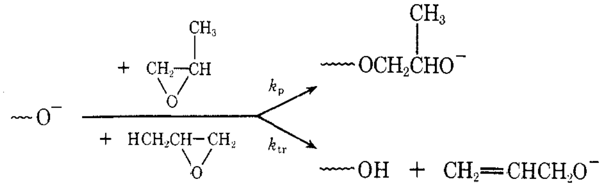
(3) E. J. Vandenberg, *J. Amer. Chem. Soc.*, **83**, 3538 (1961); *J. Polym. Sci., Part B*, **2**, 1085 (1964).

(4) C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **88**, 4171 (1966).

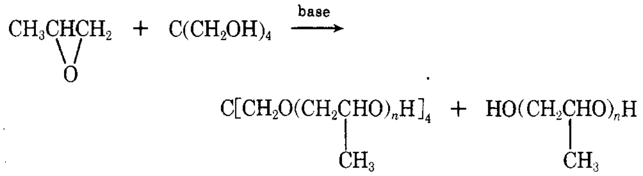
(5) C. C. Price and D. D. Carmelite, *J. Amer. Chem. Soc.*, **88**, 4039 (1966).



high polymer by base catalysis. The polymerization can be carried out so that one polymer molecule forms for each catalyst molecule added.[5] With propylene oxide, however, the E2 reaction intervenes and serves, in effect, as a chain-transfer process. The alkoxide ion formed by elimination is, of course, capable of initiating a new chain, now capped at one end by an allyl ether group.[6] The maximum molecular weight of base-catalyzed propylene oxide polymer is limited by the ratio of the rates of propagation (k_p) to transfer (k_{tr}); since at operable temperatures $k_p/k_{tr} \leq 100$, this is 6000 awu.

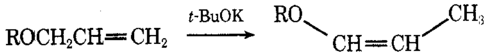


It was this molecular-weight-limiting chain transfer which led us to seek synthetic approaches to building a cross-linked rubber structure from poly(propylene oxide) chains. This was successfully accomplished in 1949 by building branched-chain liquid polymer, followed by conversion into a rubber network structure by reaction with diisocyanates.[7]



$$CH_3CHCH_2 + C(CH_2OH)_4 \xrightarrow{\text{base}} C[CH_2O(CH_2CHO)_nH]_4 + HO(CH_2CHO)_nH$$

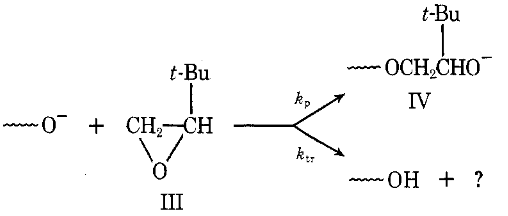
The allyl ether end group is preserved only under mild conditions of polymerization. Studies on its disappearance under more vigorous conditions led to discovery of the base-catalyzed rearrangement of allyl to *cis*-propenyl ethers[8-11] and postulation of a transition complex involving oxygen–potassium coordination to explain the cis stereospecificity. This



rearrangement was also found to extend to allyl amines, although without cis stereospecificity.[12]

$$R_2NCH_2CH{=}CH_2 \xrightarrow{t\text{-BuOK}} R_2NCH{=}CHCH_3$$

tert-Butylethylene oxide was studied in the hope that a structure not permitting E2 elimination to an allyl oxide would lead to high molecular weight polymer.[5] However, the SN2 displacement is also much slower in this monomer, presumably due to steric hindrance. Under the more vigorous conditions necessary for polymerization, another chain-transfer process must occur, although its exact nature has not yet been established. In any event, the limiting molecular weight for poly(*tert*-butylethylene oxide) is about 2000. It is of interest to note that *tert*-butoxide ion adds to III more readily than does IV, a neopentyl-type alkoxide.[5]



(4)

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One of the unexpected discoveries in studying base-catalyzed polymerization of III was that, in bulk, it gives a stereoregular, crystalline polymer shown to be different by melting point, X-ray diffraction pattern, and solution nmr from the crystalline isotactic polymer. The first guess[13] that it must be syndiotactic was proven to be incorrect and it was shown to be instead regularly alternating isotactic and syndiotactic sequences (abridged to "isosyn").[14] Such a sequence can be explained by a propagation step in which the configuration of the incoming monomer must be opposite to that of the *penultimate* unit. An hypothesis, illustrated below, was proposed to account for such an unexpected selectivity factor. The main feature of the proposal is the importance of chelation of the ion-paired cation (K^+) with at least the last and next-to-last ether oxygens. The geometry of this chelate is mainly dictated by the requirement that the penultimate *tert*-butyl group be in an equatorial conformation. A few reasonable postulates about the preferred geometry of the transition state[14] then indicate the necessary preference for the configuration of the incoming epoxide to be opposite to that of the penultimate unit.

The importance of this particular chelation is supgroups in determining the stereoselection is supported by observation on the polymerization of several substituted phenyl glycidyl ethers.[14] In this case the stereoselection is for all isotactic rather than alternating isosyn sequences. This can be accommodated in transition state V* by the assumption that, in

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(6) C. C. Price and L. E. St. Pierre, *J. Amer. Chem. Soc.*, **78**, 3432 (1956).

(7) C. C. Price, U. S. Patent 2,866,744 (Dec. 30 1958); *Chemist*, **38**, 1 (1961).

(8) G. C. Dege, R. L. Harris, and H. S. MacKenzie, *J. Amer. Chem. Soc.*, **81**, 3374 (1959).

(9) D. M. Simons and J. J. Verbanc, *J. Polym. Sci.*, **44**, 303 (1960).

(10) T. S. Prosser, *J. Amer. Chem. Soc.*, **83**, 1701 (1961).

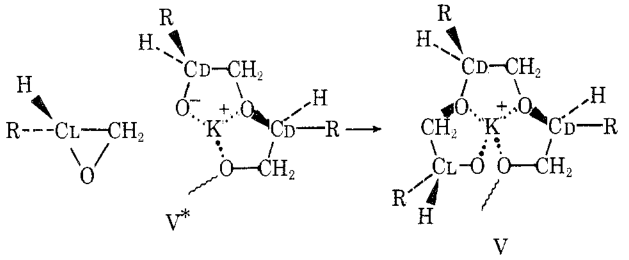
(11) W. H. Snyder and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1773 (1961).

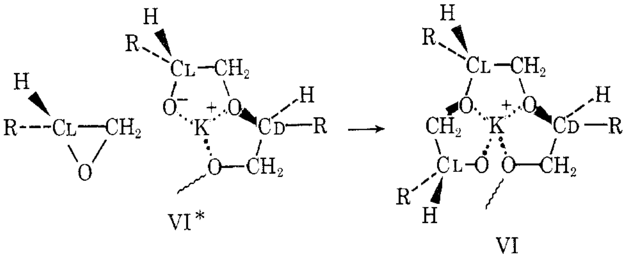
(12) C. C. Price and W. H. Snyder, *Tetrahedron Lett.*, 69 (1962).

(13) C. C. Price and H. Fukutani, *J. Polym. Chem., Part A-1*, **6**, 2653 (1968).

(14) C. C. Price, M. K. Akkapeddi, B. T. deBona, and B. C. Furie, *J. Amer. Chem. Soc.*, **94**, 3964 (1972).

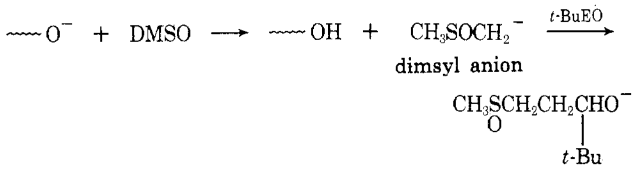
contrast to R = *t*-Bu, where R prefers to be as far from K^+ as possible, for R = $ArOCH_2$, the oxygen will seek to coordinate to K^+ in the transition state. This will require the incoming monomer to have the D configuration in V* for R = $ArOCH_2$.


V* V


VI* VI

The importance of this particular chelation is supported by the observations that *p*-methoxy and *p*-methyl groups increase the yield of crystalline isotactic polymer, while *p*-chloro or 2,6-dimethyl groups decrease the isotactic fraction.[14] The general importance of the chelation in establishing stereochemistry is supported by the observations that additions of dicyclohexyl-18-crown-6 ether in an amount equivalent to catalyst, or of solvents coordinating strongly with K^+, such as dimethyl sulfoxide or hexamethylphosphortriamide (HMPT), markedly decrease the crystalline polymer from either *tert*-butylethylene oxide or phenyl glycidyl ether.[14]

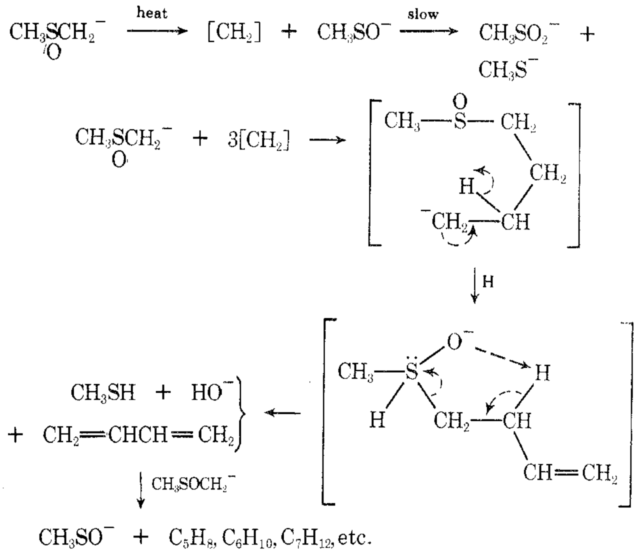
Incidentally, our part in the discovery of the remarkable utility of DMSO as a solvent for base-catalyzed reactions[5,11,15] was stimulated by our desire to find a solvent suitable for study of base-catalyzed epoxide polymerization under homogeneous conditions. DMSO has one drawback in that it can participate in chain transfer. This decreases the molecular weight (as compared to comparable conditions in HMPT) and incorporates sulfoxide groups in the polymer from the following transfer process.[5]



$$\sim\!O^- + \text{DMSO} \longrightarrow \sim\!OH + \underset{\text{dimsyl anion}}{CH_3SOCH_2^-} \xrightarrow{t\text{-BuEO}} CH_3\underset{O}{S}CH_2CH_2\underset{t\text{-Bu}}{CHO^-}$$

This process then can compete with the unidentified transfer reaction to monomer (reaction 5).

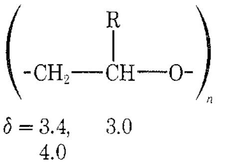
The use of DMSO also led us to a study of the decomposition of dimsyl ion at elevated temperatures. The identification of methyl mercaptide, methylsulfenate, and methylsulfinate ions and a number of methylated butadienes was accounted for by the following scheme.[16]



$$CH_3\underset{O}{S}CH_2^- \xrightarrow{\text{heat}} [CH_2] + CH_3SO^- \xrightarrow{\text{slow}} CH_3SO_2^- + CH_3S^-$$

$CH_3SH + HO^- + CH_2{=}CHCH{=}CH_2 \xrightarrow{CH_3SOCH_2^-} CH_3SO^- + C_5H_8, C_6H_{10}, C_7H_{12}$, etc.

An interesting and unexpected sidelight of our studies of *tert*-butylethylene oxide arose from the demonstration by Tani[17] that, in the nmr spectrum, the upfield of the three backbone hydrogens in the polymer is the tertiary hydrogen, contrary to normal expectation.[13] In isotactic polymer, these three hydrogens appear as double doublets at δ = 3.0, 3.4, and 4.0 ppm. Our assumption that the downfield hydrogen (δ = 4.0 ppm) was the methine[13] was proven incorrect by Tani.[17] When he replaced this H by D, it was the upfield absorbance (δ = 3.0) which disappeared, leaving the other two as doublets. A year earlier, a similar unexpected upfield nmr shift had been reported for the methylene group in neopentyl methyl ether and neopentyldimethylamine.[18] This led us to the proposal that this "neopentyl effect" was due to a preferred conformation of the neopentyl methylene hydrogens as far as possible from the lone pairs on oxygen and nitrogen.[19] This idea was also shown to explain the downfield chemical shift of methyl ethers, sulfides, selenides, amines, phosphines, arsines, fluoride, chloride, and bromide without any "electronegativity" factor but only the very simple postulate that there is no downfield shift of hydrogen by an adjacent lone pair trans to a proton, but by a fixed amount for a lone pair in the skew (or gauche) conformation to the adjacent hydrogen.[20]



$$\left(\underset{\delta = 3.4,\ 4.0}{-CH_2}-\underset{3.0}{\overset{R}{\overset{|}{CH}}}-O-\right)_n$$

Cationic Polymerization. While alkyl substitutions on the ethylene oxide ring are detrimental to the anionic polymerization process, they are beneficial to the cationic process. Ethylene oxide itself gives only low-molecular-weight oils by the usual strong Lewis acid catalysts such as BF_3 or $AlCl_3$. On

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[15] D. J. Cram, B. Rickborn, and G. R. Knox, *J. Amer. Chem. Soc.*, **82**, 6412 (1960).

[16] C. C. Price and Toshio Yukuta, *J. Org. Chem.*, **34**, 2503 (1969).

[17] H. Tani and N. Oguni, *Polym. Lett.*, **2**, 803 (1969).

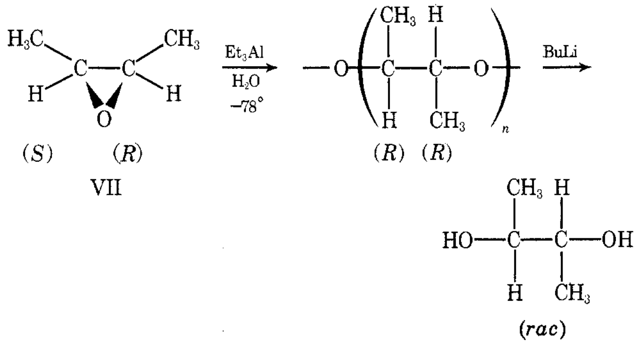
[18] S. I. Goldberg, F.-L. Lam, and J. E. Davis, *J. Org. Chem.*, **32**, 1658 (1967).

[19] C. C. Price, *Tetrahedron Lett.*, 4527 (1971).

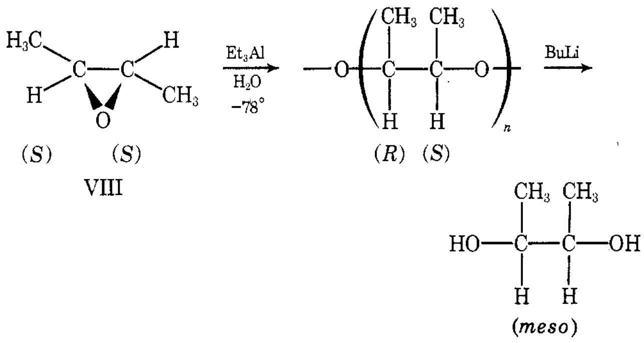
[20] C. C. Price, *J. Org. Chem.*, **38**, 615 (1973).

the other hand, tetramethylethylene oxide, which gives no polymer by base, is readily converted by BF_3 to a solid polymer decomposing above 300° and insoluble in all common solvents.[21] This material must be of at least moderately high molecular weight to exhibit these properties, but its insolubility has so far prevented a molecular weight determination.

The activating effect of electron donor groups, such as methyl groups, is also shown by the polymerization of *cis*- and *trans*-2-butene oxides. Vandenberg used these monomers to offer the first proof that the ring-opening reaction in cationic polymerization proceeded with clean inversion of configuration.[22]



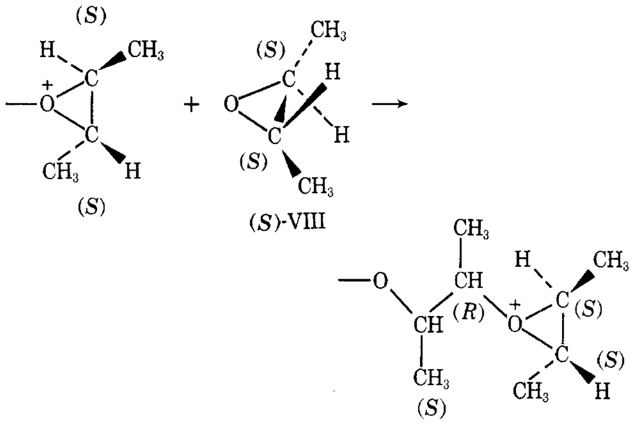
VII



VIII

This same stereochemistry for ring opening has been shown for the case of *cis*- and *trans*-1,2-dideuterioethylene oxide for cationic, anionic, and coordination polymerization.[4,23]

Vandenberg's studies with VII and VIII led to the interesting discovery that, whereas VII gave amorphous polymer, VIII gave a crystalline polymer, mp $\sim$160°, in 97% yield, even when *rac*-VIII was used as starting material. Thus one concludes that, for VII, ring opening of the oxonium intermediate can occur equally readily at the *S* carbon (to give an *RR* unit) or the *R* carbon (to give an *SS* unit). In the polymerization of *rac*-VIII, however, the formation of crystalline polymer must mean that the reactive oxonium intermediate from an *S* unit reacts highly preferentially with (*S*)-VIII. This appears to be an excellent example of "chain-end" stereoselection.[22] When an (*S*)-VIII approaches an oxonium intermediate derived from (*S*)-VIII, as illustrated, with the two three-membered rings in a favorable right angled orientation, an H in VIII confronts a methyl in the oxonium ring and *vice versa*. If the approaching monomer were (*R*)-VIII, then there would be two highly unfavorable methyl–methyl confrontations. Thus the stereochemistry of the growing chain end dictates the stereochemistry of the incoming monomer.



Coordination Polymerization. Stereoselective polymerizations of epoxides have played an important role in developing the mechanistic concepts for this major development in polymer chemistry. The first report by Natta of isotactic polypropylene[24] appeared a few months before the Pruitt and Baggett patent issued on the preparation of isotactic polypropylene oxide.[25] Undoubtedly, the work of Pruitt and Baggett antedated that of Natta, although it was a year after Natta's first paper before our work appeared showing that the Pruitt–Baggett polymer was indeed isotactic.[26]

The chirality (asymmetry) of the methine carbon in propylene oxide and in its polymer has provided many extra experimental parameters to use in studies of the mechanism of stereoselective polymerization by coordination catalysts. The first proposal of the coordination polymerization scheme to explain stereoselective α-olefin and olefin oxide polymerization arose from the propylene oxide studies.[26,27]

There are many effective catalyst systems, such as $FeCl_3$–propylene oxide, diethylzinc–water, and trialkylaluminum–water–acetylacetone reaction products. For none is the exact structure of the catalyst site established. For all, the number of polymer molecules formed is small compared to the metal atoms used to make the catalyst. This suggests that the fraction of metal atoms at cataylst sites must be at least as small.

While the detailed structure of a catalyst site remains to be elucidated, several important features of these catalysts are now known. Perhaps the most important feature was established by Tsuruta,[28] who proved that the stereoselectivity was not a feature of the chirality of the growing end but was built into the catalyst site itself ("catalyst-site" control). The normal catalyst preparation gives an equal number of *R* and *S* chiral catalyst sites which selectively coordinate with *R* and *S* monomer, respectively. This was demonstrated by starting with 75% *R* and

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(21) T. L. Cairns and R. M. Joyce, Jr., *U. S. Patent* 2,445,912 (1948); S. Ishida, *Bull. Chem. Soc. Jap.*, 33, 924 (1960).

(22) E. J. Vandenberg, *J. Polym. Sci.*, 47, 489 (1960).

(23) J. M. Yokoyama, H. Ochi, H. Tadokoro, and C. C. Price, *Macromolecules*, 5, 690 (1972).

(24) G. Natta, *J. Polym. Sci.*, 16, 143 (1955).

(25) M. E. Pruitt and J. M. Baggett, U. S. Patent 2,706,182 (April 12, 1955).

(26) C. C. Price and M. Osgan, *J. Amer. Chem. Soc.*, 78, 690, 4787 (1956).

(27) C. C. Price and M. Osgan, *J. Polym. Sci.*, 34, 153 (1959).

(28) T. Tsuruta, S. Inoue, N. Yoshida and Y. Yokota, *Makromol. Chem.*, 81, 191 (1965); see also T. Tsuruta, *J. Polym. Sci., Part D*, 180 (1972).

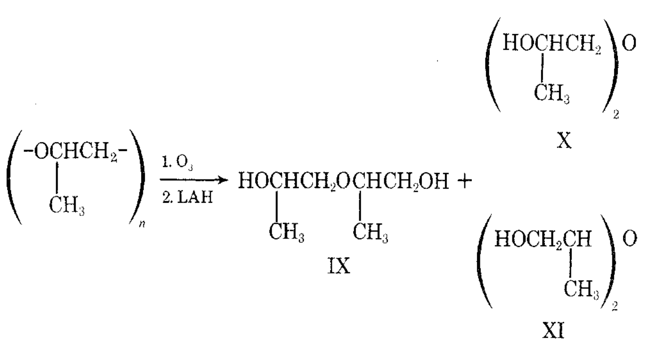
25% *S* monomer. After extensive polymerization, the recovered monomer was of unchanged optical purity. If the chirality of the catalyst site were due to the chirality of the growing chain ("chain-end" control) one would expect that the growing chains would assume a 75:25 ratio. The preferential reactivity for *R* monomer would then be 9:1 (rather than the experimentally observed 3:1) and the recovered monomer should tend toward a 50:50 mixture with increasing conversion.

The chirality of the catalyst sites can be influenced in some cases. For example, Tsuruta[29] has shown that the catalyst made from (*R*)-borneol and diethylzinc is stereoelective, *i.e.*, it will polymerize (*RS*)-propylene oxide, giving isotactic polymer with an excess of *R* monomer units and leaving the unreacted monomer rich in the *S* isomer. This behavior can be accounted for by assuming that (*R*)-borneol produces the two chiral catalyst sites in unequal numbers. A number of other chiral alcohols and *R* monomer failed to give stereoelective catalyst, *i.e.*, they gave catalyst which behaved as though it had equal numbers of *R* and *S* sites.[29,30] One possible explanation which has been offered[31] is that the more hindered bornyl group prevents it from migrating from the catalyst site L in the propagation step (reaction 3). Other simpler groups are known to migrate, becoming end groups in the polymer.[29,32]

Another effective stereoelective catalyst for both epoxide and episulfide polymerization is the reaction product of (*R*)- (or (*S*)-) *tert*-butylethylene glycol with diethylzinc.[33]

One of the key features of the stereoselective coordination catalysts for propylene oxide polymerization is that, while they can give isotactic polymer with a very high ratio of isotactic to syndiotactic sequences (*e.g.*, >370)[34], in the same reaction mixture a large part of the polymer is amorphous.[35] Even when (*R*)-propylene oxide is used as starting material, much of the product is amorphous polymer of low optical rotation containing many (*S*)-propylene oxide units.[30]

This amorphous polymer has been shown to contain head-to-head units as the imperfections in structure. This was shown by degradation and isolation of the dimer glycols.[36,37]



$$\left(-\text{O}\underset{\text{CH}_3}{\text{CH}}\text{CH}_2-\right)_n \xrightarrow[\text{2. LAH}]{\text{1. O}_3} \text{HO}\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{O}\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH} + \left(\text{HO}\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\right)_2\text{O} \quad \left(\text{HOCH}_2\underset{\text{CH}_3}{\text{CH}}\right)_2\text{O}$$

IX X XI

The diprimary (XI) and disecondary (X) dimer glycols will arise only from head-to-head units in the polymer. Fortunately, the three isomeric glycols can be separated by glc. For isotactic polymer or amorphous polymer made by base catalysis of *RS* monomer, little if any X and XI was found. The amorphous polymer separated from isotactic polymer prepared from a variety of coordination catalysts gave 25–40% of X and XI. Furthermore, the correlation of the head-to-head content from such degradative studies with the optical activity of the amorphous fraction using *R* monomer with the same catalyst shows that for every head-to-head unit there is one *R* monomer converted to an *S* polymer unit. This proves that, at the coordination site giving amorphous polymer, the abnormal ring opening which occurs at the secondary carbon, to give the head-to-head unit, has done so with inversion of configuration.

A more recent similar study of amorphous polymer accompanying isotactic polymer in the polymerization of (*RS*)-*tert*-butylethylene oxide by coordination catalysts has shown that it also contains head-to-head units.[14] In this case, the primary–secondary dimer glycol, which was only 30–40% of the dimer mixture, could be separated into its erythro and threo isomers by glc. The isotactic polymer gave, as expected, almost exclusively the erythro isomer, while the amorphous fractions gave only 40–45% erythro and 55–60% threo.

These data combined indicate that a typical coordination catalyst, such as Et_2Zn-H_2O, contains *isotactic* catalyst sites and *amorphous* catalyst sites. The isotactic sites are highly selective in coordinating with either *R* (or *S*) monomer (reaction 3, step 1) and highly selective in propagating by ring opening only at the primary carbon of the epoxide ring (reaction 3, step 2). The amorphous catalyst site can coordinate equally well with *R* or *S* monomer in step 1, and has very little preference for attack at the primary or secondary carbon in the ring-opening propagation step.

Not much quantitative information is available on the relative reactivities of epoxides in copolymerization. With base in DMSO, phenyl glycidyl ether is seven times more reactive than propylene oxide, presumably due to the inductive electron-withdrawing effect of the phenoxy group.[38] A *p*-chloro substituent enhances the reactivity of PGE while a *p*-methoxy group diminishes it. That coordination catalysts exhibit properties closer to cationic than anionic catalysts is indicated by the opposite influence of *p*-chloro and *p*-methoxy groups in phenyl glycidyl ether, the latter now being the more reactive.[39] Furthermore, propylene oxide is 50% more reactive than phenyl glycidyl ether and epichlorohydrin 33% less reactive using Et_3Al-H_2O as a catalyst.

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(31) C. C. Price in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967.

(32) P. E. Ebert and C. C. Price, *J. Polym. Sci.*, **34**, 157 (1959).

(33) M. Sepulchre, N. Spassky, and P. Sigwalt, *Macromolecules*, **5**, 92 (1972).

(34) C. C. Price and A. L. Tumolo, *J. Polym. Sci., Part A-1*, **5**, 175 (1967).

(35) The crystalline isotactic poly(propylene oxide) is readily separated from the amorphous soluble polymer by chilling an acetone solution of the mixture to −35°.

(36) C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **87**, 2069 (1965).

(37) C. C. Price and A. L. Tumolo, *J. Polym. Sci., Part A-1*, **5**, 407 (1967).

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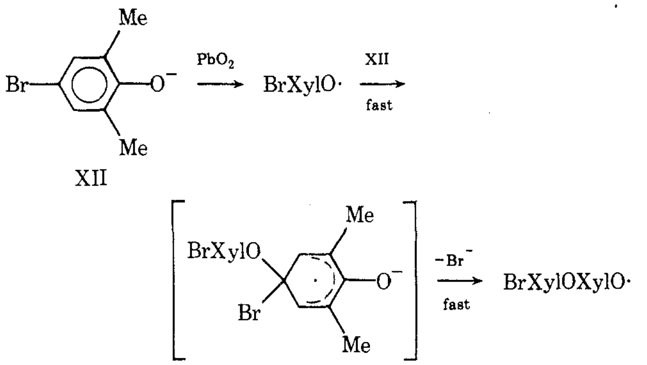
Polyphenylene Oxides

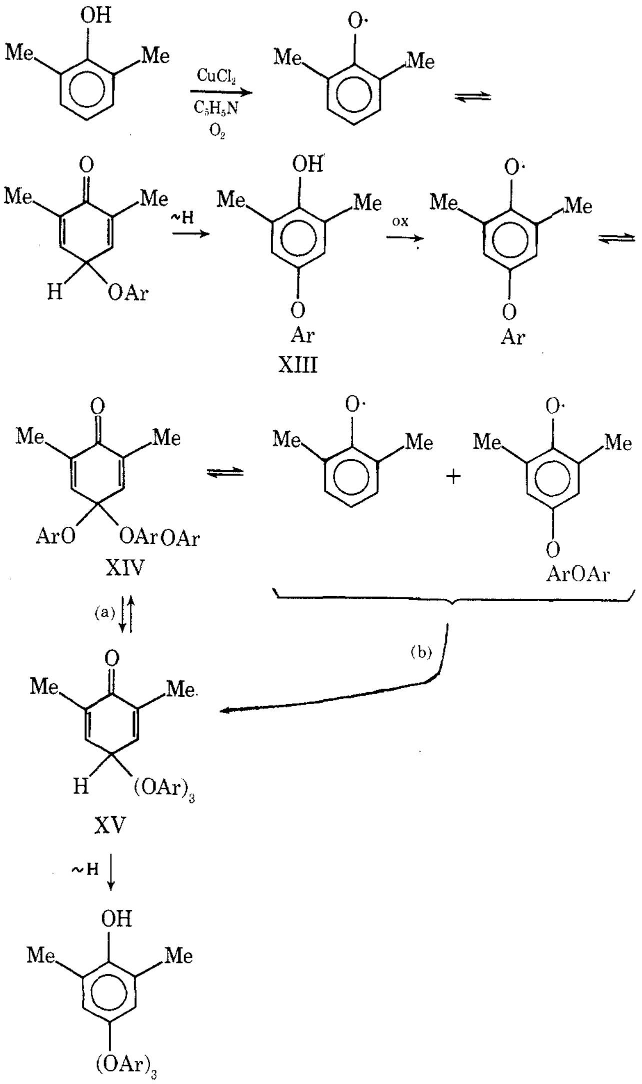
The thermal and chemical stability of diphenyl ether has long been recognized as suggesting interesting and useful properties for high polymers built with this structural unit.[2] The development of successful methods for preparing such structures has been a challenge to the synthetic chemist. The remarkable chemistry of the processes discovered has also led to significant new facts and hypotheses about the behavior of phenoxy radicals.

The investigations in our laboratory were originally inspired by the work of Hunter and his students.[40] They concluded that the amorphous products formed from trihalophenols on treatment with various oxidizing agents were low-molecular weight polymers formed by loss of a halogen atom in either the 2 or the 4 position. We decided to investigate this reaction further, but with 4-halo-2,6-xylenols as monomers.

This proved successful when catalysts were used which Cook[41] found useful in converting 2,4,6-tri-*tert*-butylphenol to its stable blue free radical. Under these conditions, 4-bromo-2,6-xylenol can be converted to a high-molecular weight polymer in seconds, liberating the bromine as bromide ion. In the absence of oxidant catalyst, no bromide ion is liberated even after months. The polymerization is thus obviously not a nucleophilic displacement. Furthermore, it has the characteristics of a chain reaction, since polymer formed even at only 5% conversion is of high molecular weight.[42] While the polymer has a very low brittle temperature (−150°), its high glass transition temperature (>200°) makes it very hard to crystallize. The polymer is normally amorphous and soluble in the usual organic solvents, such as benzene. By heating a solution in α-pinene overnight, it separates as crystalline polymer, mp 275°.[43]

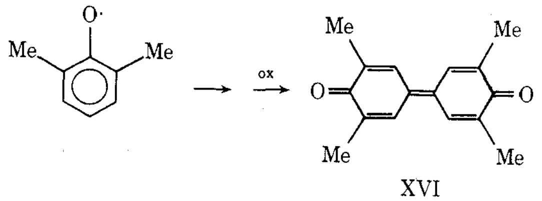


The commercial synthesis of polyxylenol (sometimes referred to as PPO, *p*oly(*p*henylene *o*xide)) is carried out by the oxidative coupling of 2,6-xylenol. This remarkable reaction was discovered by Hay and his coworkers.[44] One intriguing feature of this polymerization is that it is a stepwise condensation. The product at 50% conversion is a low-molecular-weight oil. The dimer (XIII) and trimer in this material are as easily polymerizable as the monomer. The accepted mechanism involves coupling of aryloxy intermediates to give quinone ketals.[45-47]



The Dutch workers in particular studied many simple models to determine what structural factors and conditions favored conversion of XIV to XV by direct rearrangement (a) or through dissociation and recombination (b).

One of the intriguing features of the oxidative coupling is the question of the features dictating C–O coupling to give dimer XIII *vs.* C–C coupling to give the diphenoquinone XVI. For oxidation by Ag_2O[48] or MnO_2,[47] excess oxidant gives polyxylenol, while ex-



XVI

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(40) W. H. Hunter and M. A. Dahlen, *J. Amer. Chem. Soc.*, **54**, 2456 (1932).

(41) C. D. Cook, *et al.*, *J. Org. Chem.*, **18**, 261 (1953); *J. Amer. Chem. Soc.*, **78**, 2002, 3797, 4159 (1956).

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(45) G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *J. Amer. Chem. Soc.*, **87**, 3996 (1965).

(46) W. J. Mijs, O. E. van Lohuizen, J. Bussink and L. Vollbracht, *Tetrahedron*, **23**, 2253 (1967).

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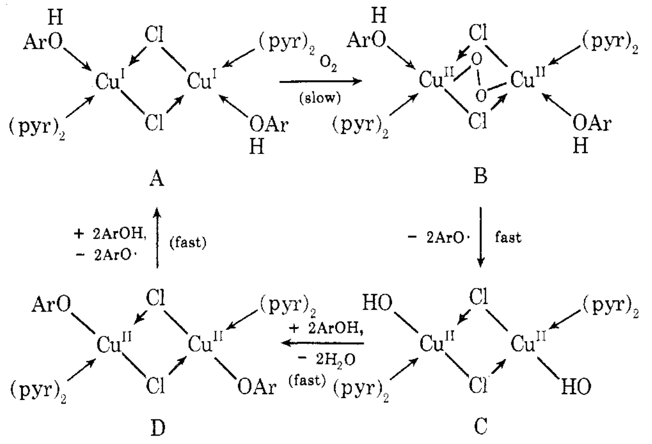
(48) B. O. Lindgren, *Acta Chem. Scand.*, **14**, 1203 (1960).

cess xylenol gives XVI. Even under the Hay conditions, replacement of one methyl by *tert*-butyl or both by *i*-Pr led to the diphenoquinone as the main product.

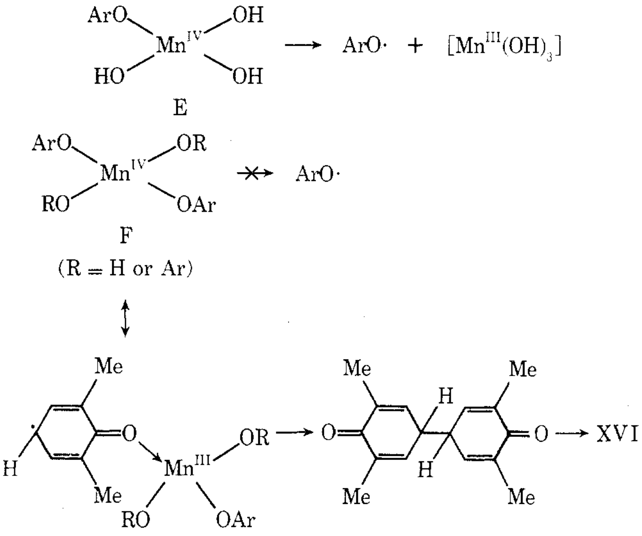
The rate of phenol oxidation under the Hay conditions is first order in catalyst, first order in O_2 pressure, and zero order in phenol, although the magnitude of the rate is quite sensitive to substitutions in the phenol ring, being favored by electron-releasing groups.[49] We have suggested Scheme I to account for these observations. The dimer XIII could arise either by coupling of two *free* free radicals or by attack of a radical, liberated in the transformation from B to C in Scheme I to remove ArC· from D.

Scheme I



Decreased base coordination on Cu (by ligand concentration, ligand hindrance, or ortho hindrance in the phenol) favors C–C coupling.[50] We have proposed the modified Scheme II to explain this behavior. The essential feature is that decreased base coordination at Cu increases the affinity of the Cu for the oxygen of the incipient ArO· radical. Since the incipient radical remains bound to Cu at oxygen, it couples at the exposed C-4.

The behavior of Ag_2O and freshly prepared MnO_2 can also be fit into this scheme. Using MnO_2 as an example, for excess oxidant there might be only one phenol coordinated on manganese (E), while for excess phenol, two (or more) (F).

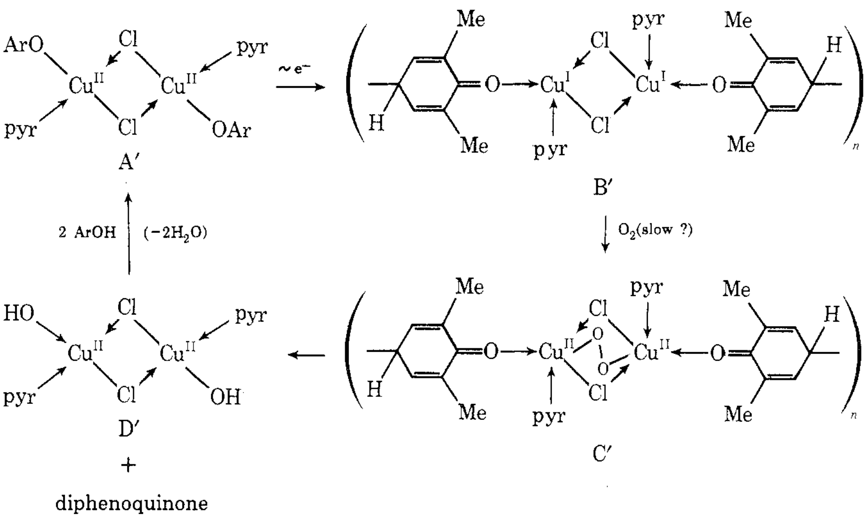


The manganese in E, as compared to F, would be more "neutralized" by hydroxyl groups, would thus be a weaker Lewis acid, and could thus more readily liberate a free aryloxy radical, envisaged as necessary for C–O coupling. In F, the manganese would be a stronger Lewis acid and, like A′, would form a stronger bond to the aryl oxygen, would not liberate the free aryloxy radical, and would therefore give C–C coupling.

Arylene–Alkylene Copolymers

Dewar has reported that 2,6-dihalo-1,4-diazooxides can be converted by photolysis to poly(2,6-dihalophenylene oxides).[51,52] He has proposed that the role of X = halogen is to promote singlet to triplet interconversion for the intermediate after loss of N_2.[52]

Scheme II



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(50) A. S. Hay, *Fortschr. Hochpolym.-Forsch.*, 496 (1967).
(51) M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 917 (1958).
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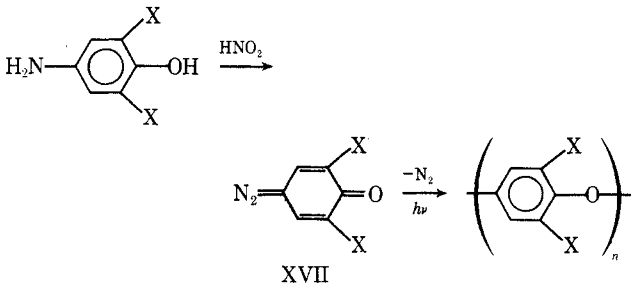


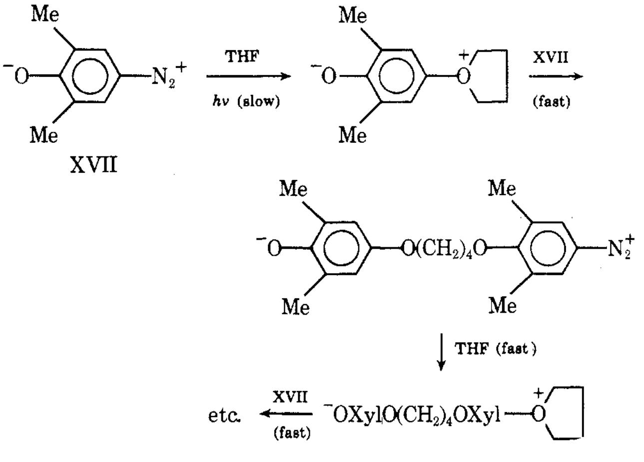
XVII

When this reaction was attempted with X = CH_3, no polymer was obtained, unless the reaction was carried out in THF or dioxane. Stille[53] and we[54] discovered concurrently and independently[55] that this polymerization involves incorporation of the cyclic ether solvent.

Scheme III does account for the regular alternating 1:1 polymer obtained. Most of the polymers obtained were low molecular weight, low melting, and soluble. Only a small amount (*ca.* 5%) of high-molecular-weight crystalline polymer was obtained, and that was deposited as a film on the glass surface of the reaction vessel.

In conclusion, while it is evident that much has been learned about reactions producing polyethers and important factors which affect them, there remain intriguing unanswered questions. Although there has been much speculation, it is not clear that we know in any detail the structural features of stereoselective and stereoelective coordination catalysts for epoxide polymerization.

Scheme III



For oxidative coupling of 2,6-xylenol, there has also been much speculation about the nature of the catalyst, but again there is much yet to be learned. In both cases, it seems clear that the central structural questions revolve around the nature of reactive groups coordinated around one or more metal atoms.

In the case of the polymerization of 4-bromo-2,6-xylenol, the free-radical chain-reaction hypothesis rests on relatively slender evidence. We are in the process of attempting to study the reaction under homogeneous conditions which may provide more substantial evidence for the mechanism involved.

I express my appreciation to the many coworkers who have been involved in our studies of polyethers. I also acknowledge the financial support of the General Tire and Rubber Company and of the U. S. Army Quartermaster Corps.

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[55] The last two references would have appeared together were it not for an oversight in editorial handling of the manuscripts.

Applications of Sodamide-Containing "Complex Bases" in Organic Synthesis

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Heterogeneous reactions, in which a solid substance reacts with something dissolved in a liquid solvent, often serve the chemist well. Yet they have idiosyncrasies, and may be a source of vexation.

It is sometimes found that a solid reactant will participate satisfactorily in such a reaction in one solvent but not in another which, *a priori*, would seem equally attractive. Sometimes seemingly minor changes in the solid reactant—such as changing the cation which accompanies a reactive anion, or adding some nonparticipating substance to the system—will be the means of converting failure to success.

In general terms, one can appreciate some of the factors that must be important in heterogeneous reactions. If the actual reaction occurs in the liquid phase, anything that alters the (slight) solubility of the solid reactant is of obvious importance. If reaction occurs at the surface of the solid phase, changing the ionic make-up of the solid reactant (if it is

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