

Bond Forming Initiation of "Charge-Transfer" Polymerizations and the Accompanying Cycloadditions

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Received August 6, 1996

Introduction and Background

The spontaneous reactions of electron-rich and electron-poor olefins and dienes take several forms. Cycloadditions, either [2 + 2], [4 + 2], or [2 + 4], as well as ene reactions can occur, while spontaneous polymerizations of these unsaturated compounds have also been reported. These polymerizations form either alternating copolymers or homopolymers (even mixtures). The spontaneous polymerizations belong to the family of "charge transfer" (CT) polymerizations, so called because a CT complex forms, as detected by the characteristic color. Even though the CT polymerizations in which we are interested proceed spontaneously, they can also be initiated. During the 1970s, CT polymerization was a very active field of research, and it has remained rather active over the years.¹ Ironically, CT complexes will be shown to play no generally significant role in either the polymerizations or the cycloadditions.

It has been our long-standing goal to correlate the results obtained in both organic and polymer chemistry with a common interpretation. We have reviewed our work in this area earlier, with an emphasis on the connection of these polymerizations with small molecules, i.e., organic chemistry.^{2–4} This report will be dedicated to a survey of our recent progress in this area.

Systematic Variation of Reactant Structure in Cycloadditions and Spontaneous Polymerizations (Scheme

H. K. Hall, Jr., was born in New York City in 1924. He received his undergraduate training at Brooklyn Polytech, a Master's degree at Pennsylvania State, and a Ph.D. from the University of Illinois in 1949. Postdoctoral work followed, with Prof. P. J. Flory at Cornell and with Profs. S. Winstein and W. G. Young at UCLA. After 17 years at DuPont, he moved in 1969 to the University of Arizona. He is the recipient of the 1996 ACS Polymer Chemistry Award. His research interests include the synthesis and polymerization of strained bicyclic systems, the initiation mechanism of spontaneous "charge-transfer" polymerizations, and the synthesis of high-technology polymers with nonlinear optical, photorefractive, conductive, or piezoelectric properties.

Anne B. Padias was born in Belgium in 1949. She completed both her undergraduate degree and Ph.D. (1975) at the University of Ghent in Belgium. Her Ph.D. thesis dealt with the cationic ring-opening polymerization of thietanes. She then joined Dr. Hall's research group at the University of Arizona as a postdoctoral associate, and has been his co-worker ever since, currently in a research scientist position. She is also the Laboratory Coordinator for the organic chemistry laboratories. Her research interests include the ring-opening polymerization of bicyclic acetals and ortho esters, the cycloaddition and polymerizations reactions of olefins, and the synthesis and design of high-technology polymers.

1). Although olefins of like polarity usually do not react when mixed, moderate disparity in electron density between two olefins can cause spontaneous free radical copolymerizations at slow, but reproducible, rates. A mixture of styrene (St) and methyl methacrylate (MMA) heated to 60 °C without added initiator forms a random copolymer, as described by Walling in 1949.⁵ The copolymerization is faster than either spontaneous homopolymerization.⁶ Similarly a mixture of St and acrylonitrile (AN) forms a random copolymer at 100 °C,⁷ a process used in industry. This initiation is not only due to self-initiation by styrene but is also caused by direct reaction of St and AN.⁸

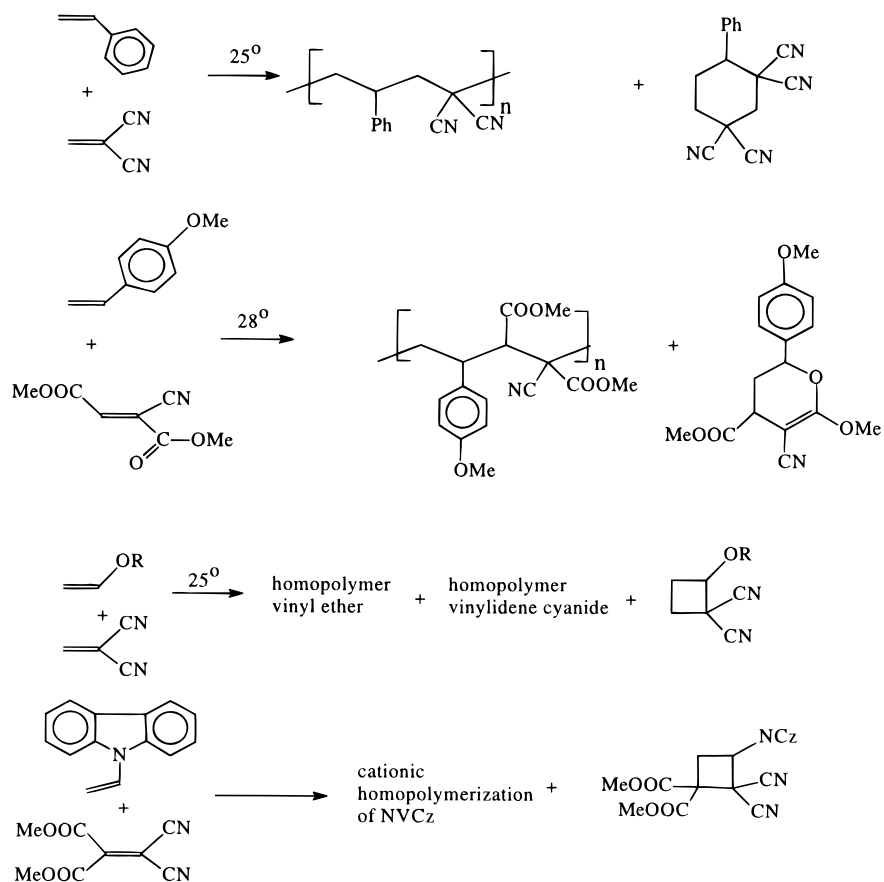
With a more electrophilic olefin such as vinylidene cyanide (VCN), St undergoes spontaneous copolymerization at room temperature and a strictly alternating copolymer, within NMR detection limits, is formed, along with 20% of a 2:1 VCN:St adduct.^{9,10} Another monomer pair in this category, which we have investigated in great detail, is the combination of *p*-methoxystyrene (MeOSt) and dimethyl cyanofumarate (CNF).¹¹ Here again an alternating copolymer forms spontaneously at room temperature along with a cycloadduct, and the rates are insensitive to solvent polarity.

Greater electron disparity, such as between MeOSt and methyl β,β -dicyanoacrylate (DCA), still leads to spontaneous copolymerization along with formation of the cyclobutane and/or Diels–Alder adduct, depending on the solvent polarity.^{12–14}

When olefins with still greater electron disparity are used, ionic homopolymerizations dominate the outcome of the reactions and cycloadditions compete more effectively. Mixing VCN with an alkyl vinyl ether (VE) at room temperature results in the homopolymerization of both the VE and VCN, cationically and anionically, respectively.¹⁵ Moreover, as described by Stille, the cyclobutane adduct of the two olefins was isolated from the reaction mixture.¹⁶ In the presence of a radical initiator, a mixture of the alternating copolymer and the two

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- (5) Walling, C. J. *J. Am. Chem. Soc.* **1949**, *71*, 1930.
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- (10) Stille, J. K.; Chung, D. C. *Macromolecules* **1975**, *8*, 83.
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Scheme 1. Effect of Systematic Variation of Structure on Spontaneous Polymerization



homopolymers was formed along with the cyclobutane adduct, showing that the free radical mechanism is viable with this monomer pair and leads to a different polymer from the one obtained in the spontaneous system. In this laboratory, we investigated the reactions taking place in a mixture of *N*-vinylcarbazole (NVCz) with a tetrasubstituted electrophilic olefin. Cationic homopolymerization of NVCz takes place along with cyclobutane formation, and these reactions were highly sensitive to solvent polarity.¹⁷ Anionic homopolymerization from disparate olefin pairs has also been observed, e.g. by Hayashi in the reaction of nitroethylene with vinyl ether.¹⁸

This limited list of examples shows the change in mechanism as we progress from weak donor/acceptor olefin pairs to the strong donor/acceptor olefin pairs:

(1) Initiated free radical copolymerizations give copolymer with rather random structures.

(2) Initiated free radical copolymerizations give alternating copolymers.

(3) Spontaneous copolymerization and cycloaddition reactions occur upon heating.

(14) Srisiri, W.; Padias, A. B.; Hall, H. K., Jr. *J. Org. Chem.* **1993**, *58*, 4185.

(15) In the case of ionic homopolymerizations, two distinctive homopolymers are formed, one via anionic polymerization and the other cationic. The block copolymer is not formed because these systems go heterogeneous on a microscale, and phase separation occurs, with the anionic growing center surrounded with VCN molecules and the cationic center surrounded by vinyl ethers. In addition, chain transfer during propagation would prohibit the clean formation of these putative block copolymers.

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(4) Copolymers form spontaneously at room temperature and possess alternating structure.

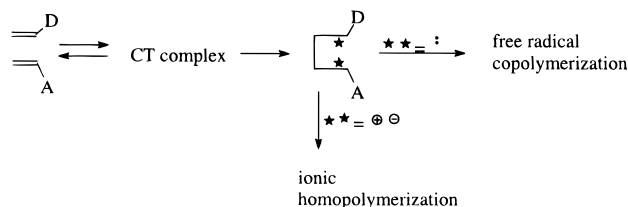
(5) Ionic homopolymerizations and [2 + 2] cycloadditions predominate.

The polarity difference between the reactants is of decisive importance in determining the nature of the spontaneous polymerizations, progressing from initiated free radical to spontaneous free radical copolymerizations and ultimately to spontaneous ionic homopolymerizations. The polarity difference is also crucial in accelerating both free radical and ionic reactions. This explains why spontaneous homopolymerizations of a single monomer have been very rare, perhaps restricted only to styrene, because the polarity difference is absent.

Proposed Unifying Mechanism for Stepwise [2 + 2] Cycloaddition and Initiation of Polymerization. In earlier reviews²⁻⁴ we have indicated the fundamentals of the bond forming initiation theory to explain the spontaneous initiation of these polymerizations. Cyclobutanes often accompany the polymers. Concerted [2 + 2] cycloadditions are forbidden by the principle of conservation of orbital symmetry, as proposed by Woodward and Hoffmann in their famous communications in 1965.¹⁹ Accordingly, intermediates occur in these cyclobutane formations, namely tetramethylenes. These tetramethylenes form by coupling of the olefins at their β -positions and can be either singlet diradical or zwitterionic in nature depending on the terminal α -substituents. The actual structure is a resonance hybrid of these extremes, and the

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Scheme 2. Proposed Bond Forming Initiation



tetramethylene is stabilized by this resonance.²⁰ A tetramethylene is clearly energetically favored over a putative ion-radical pair by the energy of a new covalent bond.

The bond forming initiation theory, originally described in 1983,² proposes that these same tetramethylene intermediates are the true initiators of the observed spontaneous polymerizations, as shown in Scheme 2. *The weaker donor and acceptor olefins form a predominantly diradical tetramethylene intermediate which can initiate free radical copolymerization, while the more nucleophilic and more electrophilic olefins form a predominantly zwitterionic intermediate which can initiate ionic homopolymerization.* The polymer products offer a powerful diagnostic tool to characterize the tetramethylenes, in contrast to small molecules, such as cyclobutanes, which give only indirect information about the nature of the intermediate. The nature of the tetramethylene is also influenced by its geometry: zwitterionic tetramethylenes preferably adopt the *cis/gauche* conformation, as witnessed by the predominance of cyclobutane formation in these cases, while the diradical tetramethylenes adopt the *trans* conformation, preferentially initiating free radical polymerizations with very little or no cycloaddition present.²¹ In keeping with this concept, polar substituted cyclobutanes readily cleave to zwitterions but not to diradicals. Finally, solvent polarity also influences the nature of the tetramethylenes, with zwitterions being favored in more polar media, while diradicals are favored in nonpolar media.¹²

Charge-Transfer Complexes: Indicators of Electron Disparity. The reactions involving electron-rich and electron-poor compounds show visually transient colors ascribed to charge-transfer complexes and have become known as “charge-transfer” polymerizations. The intensity and color of the charge-transfer complex deepens and moves from yellow through red to blue as the electron disparity between the two reactants increases. This parallel with the general polymerization tendencies was described by Iwatsuki and Yamashita in their seminal paper in 1971.²² The obvious question is whether or not these CT complexes play a role in the mechanism of these polymerizations, be they initiated or spontaneous.

“Charge transfer” has frequently been confused with “electron transfer” (SET), but actually, these are totally different phenomena. “Charge transfer” is a weak interaction of electron-rich with electron-poor molecules. Detectable by UV or NMR spectroscopy, these complexes

have no chemistry. “Electron transfer” is an outright transfer of one electron from donor to acceptor, forming a pair of ion radicals. These ion radicals have totally different spectra, especially ESR, and a rich chemistry. To elucidate the role of CT or SET in the initiation of the observed “charge-transfer” polymerizations, we carried out the spontaneous reactions of the most electron-rich and electron-poor olefins, namely *N*-vinylcarbazole and tetracyanoethylene, or its equivalent dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate. Electron transfer was not involved in the initiation chemistry, even in these extremely favorable cases.¹⁷ The same conclusion as to the absence of electron transfer has been reached by Bauld in cycloaddition reactions of vinyl ethers with TCNE.²³ Electron transfer is possible only with extremely electron-rich dimethylamino-substituted olefins and dienes with TCNE.²⁴ Accordingly we regard charge-transfer complexes as merely indicators of electron disparity, which can lead to the phenomena listed above.

As to propagation, the alternating character often observed in these polymerizations led many researchers to postulate that CT complexes participate as “monomers” in the propagation step. Shirota calculated the contribution of the CT complex to the propagation from kinetics results.²⁵ More recently however, charge-transfer complex participation in copolymerizations has been excluded by Tirrell²⁶ and by Pittman.²⁷ The observed alternation is currently explained by considering the polarity of radicals and monomers: an electron-rich carbon radical will preferentially combine with an electron-poor monomer to give an electron-poor radical, while the latter will preferentially combine with an electron-rich monomer to form an electron-rich radical. This view has ample justification and support in small molecule organic chemistry.²⁸

Thermal Reactions

Donor Dienes and Acceptor Olefins. We wondered whether donor dienes would follow the same reaction patterns as the donor olefins and whether they could participate in bond-forming initiation reactions. Of course, in contrast to the olefin-olefin situation, a concerted [$\pi^4_s + \pi^2_s$] cycloaddition, namely the Diels-Alder reaction, can occur and will be favored over any spontaneous polymerization. The extensive organic chemistry literature on the Diels-Alder reaction contains almost no hint that polymerization can compete with cycloaddition, except that many Diels-Alder procedures include the addition

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(21) In the absence of chain transfer, initiation of free radical copolymerizations by diradical tetramethylenes will necessarily lead to polymer chains with a free radical growing center at each end. Termination by chain combination will lead to a larger polymer chain, still with two radical ends, therefore resulting in larger molecular weights. Suggestive indications for this point have been observed in the case of MeOST and CNF, but more study is warranted.

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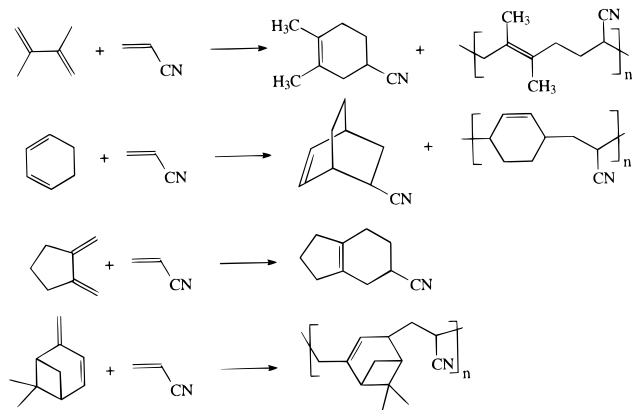
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Scheme 3. Spontaneous Reactions of Various Dienes with Acrylonitrile



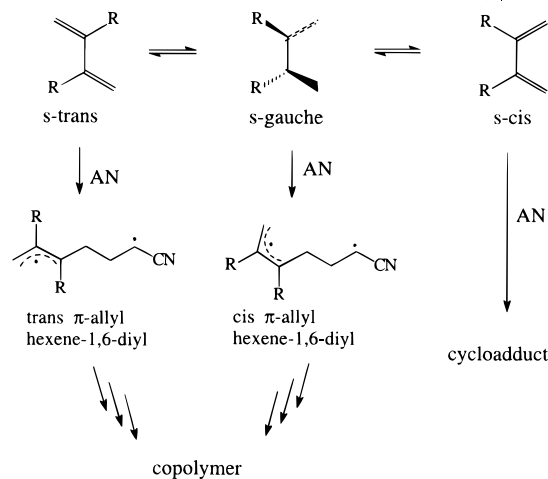
of free radical inhibitor.²⁹ However, there are numerous examples of initiated “charge-transfer” polymerizations of dienes in the polymer chemistry literature, wherein cycloadducts accompany the copolymers.^{1a}

We quote Professor Huisgen in mentioning that concerted cycloaddition reactions are dominant due to “the magic of the symmetry-allowed concerted cycloaddition”.³⁰ The importance of diene conformation for Diels–Alder reactions has been thoroughly investigated by Sustmann in the reactions of various dienes with TCNE.³¹ Dienes in the *s-cis* conformation react substantially faster with the dienophile than dienes that prefer the *s-trans* conformation.

We determined that spontaneous polymerizations indeed do occur in mixtures of dienes with electrophilic olefins.³² These polymerizations are reproducible and not due to impurities. They lead to extremely high molecular weight polymers. If the diene and dienophile are able to copolymerize by deliberately adding free radical initiators, then spontaneous copolymer formation accompanying the Diels–Alder reaction is evidence for the presence of initiating (di)radicals in the reaction mixture.

A series of alka-1,3-dienes was reacted with acrylonitrile (AN)³² (Scheme 3). The dienes were divided into different groups according to their conformational equilibria. The dienes that exist in a *s-cis/s-trans* equilibrium include 2,3-dimethyl-1,3-butadiene (DMB), isoprene, and (*E*)-1,3-pentadiene. In the reactions of DMB with AN, alternating copolymers are obtained along with the expected Diels–Alder cycloadduct at 80 and 100 °C. The copolymerization and the cycloaddition proceed as two *independent* second-order reactions. The proposed free radical initiating species is a *trans*-2-hexene 1,6-diradical formed by reaction of the *s-trans* conformer of the diene with AN, while the *s-cis* conformation undergoes the concerted cycloaddition (Scheme 4). Even though the spontaneous polymerization is evidence for the presence of a 2-hexene 1,6-diradical in the reaction mixture, we do not propose any contribution of a stepwise mechanism to the observed [4 + 2]-cycloadditions.

Scheme 4. Proposed Initiation Mechanism for the Spontaneous Polymerization of Dienes and Acrylonitrile



1,3-Cyclohexadiene (CHD) has a cyclic structure, which excludes the *s-trans* conformer. Therefore, we were surprised to find a literature report that thermal reactions of CHD with AN lead to a mixture of copolymer and cycloadduct.³³ We confirmed this finding and again found independent second-order kinetics for both the copolymerization and the cycloaddition.³² This indicates that the nonplanar “*s-gauche*” conformer of the diene can also form a *cis* π -allyl initiating diradical. The competing concerted [4 + 2]-cycloaddition takes place from the *s-cis* form of the diene.

We confirmed these conclusions by using either planar *s-cis*-locked or *s-trans*-locked dienes. The former include 1,3-cyclopentadiene and 1,2-dimethylenecyclopentane, which react with AN only to undergo concerted cycloaddition. It also finds support in the essential lack of polymerization induced by an isoelectronic 1,3-dipolarophile, which is planar by definition.³⁴ In contrast, *s-trans*-locked dienes, such as 2,5-dimethyl-2,4-hexadiene and verbenene (2-methylene-6,6-dimethylbicyclo[3.1.1]hept-3-ene), give exclusively copolymers in reactions with AN, still following the second-order kinetics and with comparable rate constants.

Studies with 1-methoxy-1,3-butadiene showed that, as the electrophilicity of the acceptor olefin increases, the rates increased as expected. The products went from predominantly alternating copolymer to predominantly [4 + 2]-cycloadduct.³⁵ Sustmann noticed the same shift from copolymers to cycloadducts in the reactions of 1,1-dimethoxy-1,3-butadiene with increasingly electrophilic dienophiles.³⁶

Electrophilic Quinodimethanes and Donor Olefins.

The interesting electron-poor molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) forms charge-transfer complexes with moderately electron-rich molecules and, by single electron transfer, ion–radical salts with very electron-

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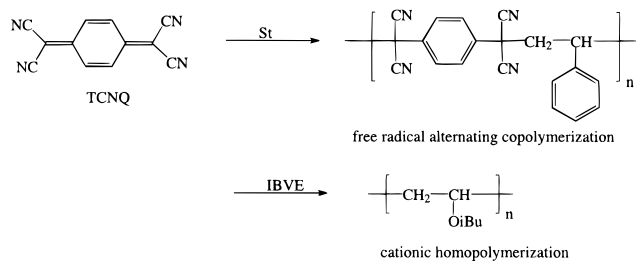
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Scheme 5. Polymerization Behavior of TCNQ

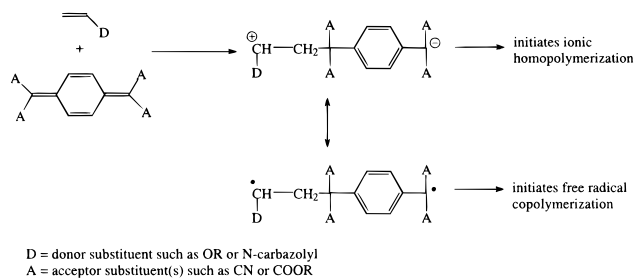


rich molecules. TCNQ does not homopolymerize. However, Iwatsuki discovered that mixing the rather insoluble TCNQ with styrene at room-temperature gave spontaneous alternating copolymerization after a few hours.³⁷ α -Methylstyrene and 1,1-diphenylethylene also copolymerized spontaneously with TCNQ, as did various dienes.³⁸ In contrast, the very electron-rich monomers, IBVE and NVCz, gave only homopolymers by spontaneous cationic polymerization caused by TCNQ (Scheme 5). Reaction of TCNQ with 1-methoxycyclohexene led to an oligomer of the latter, formed by cationic oligomerization with a TCNQ end group.³⁹

The polymer chemistry of an extensive series of electrophilic 7,7,8,8-tetrasubstituted quinodimethanes was investigated both at the Mie and the Tucson laboratories, in which the 7,7,8,8-substituents became progressively less electron-attracting: CN > COOR > C₆H₅.⁴⁰ Replacing cyano groups by ester substituents and also phenyl groups shifted the products from spontaneous alternating copolymers to random copolymers, and eventually, the polymerizations had to be initiated. To illustrate this point, 7,8-dicyano-7,8-dicarboalkoxyquinodimethane spontaneously formed a random copolymer with styrene and an alternating copolymer with MeOSt, in contrast to the behavior of TCNQ which formed an alternating copolymer with both. The even less electrophilic 7,7,8,8-tetracarboalkoxyquinodimethane copolymerized spontaneously only with the more nucleophilic olefins IBVE and NVCz.

We suggested that these spontaneous polymerization could be explained by an extension of the bond-forming initiation theory.⁴¹ Combination of an electron-rich monomer with an electrophilic quinodimethane by bond formation between the terminal carbons leads to a *p*-phenylenetetramethylene (Scheme 6). As in the olefin-olefin case, the zwitterionic or diradical nature of this intermediate depends on the terminal substituents.⁴¹ A clear change in mechanism from diradical to zwitterionic is evident as one proceeds toward stronger donors and acceptors and the rates of the reactions increase. In comparison to the olefin-olefin case, the presence of the phenyl ring in the *p*-phenylenetetramethylene intermediate shifts the transition from diradical to zwitterionic to stronger donors and

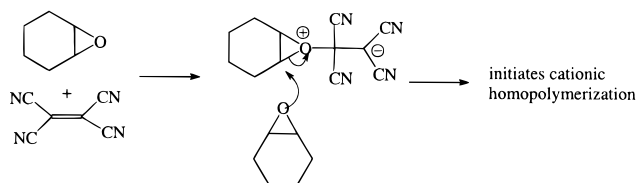
Scheme 6. Proposed Mechanism for Spontaneous Polymerizations Involving Quinodimethanes



acceptors. In other words, a combination of substituents which would lead to a zwitterionic intermediate in the olefin-olefin reactions shows up as a diradical in the quinomethane-olefin reaction. For example, the reaction of MeOSt and TCNE, leading to a cyclobutane adduct, clearly proceeds through a zwitterionic tetramethylene, while the reaction of TCNQ with MeOSt yields an alternating copolymer, initiated with the diradical *p*-phenylenetetramethylene. This shift is due to the preference of the phenyl group in the latter to stabilize a diradical intermediate.

Oxacycles and Acceptor Olefins. We extended our work to reactions of electrophilic olefins with *n*-donors, namely oxacyclic monomers. Work on the cycloaddition and polymerization reactions of oxacycles with vinylidene cyanide had already been published by Stille, who showed that epoxides underwent cationic homopolymerization when mixed with vinylidene cyanide, the latter simultaneously underwent anionic homopolymerization.⁴² Again the reaction rapidly became heterogeneous. Trioxane caused the vinylidene cyanide to polymerize but did not itself polymerize. Okamoto studied the polymerization of TCNE and THF under high pressure and suggested that the alternating copolymer arose by copolymerization of THF with a cyano group of TCNE.⁴³

In a systematic study of the initiation of cationic polymerization of oxacycles and aldehydes by electrophilic olefins, we found that these reactions were rather slow.⁴⁴ TCNE with cyclohexene oxide (CHO) at 90° gave modest conversion to polymers. Other electrophilic olefins, such as methyl β,β -dicyanoacrylate, with CHO gave a low yield of polycyclohexene oxide and oligomers of both components, while dimethyl cyanofumarate was oligomerized by CHO. The initiation of the polymerization of oxacycles with electrophilic olefins is feasible; however, the rates are too slow to be practical.



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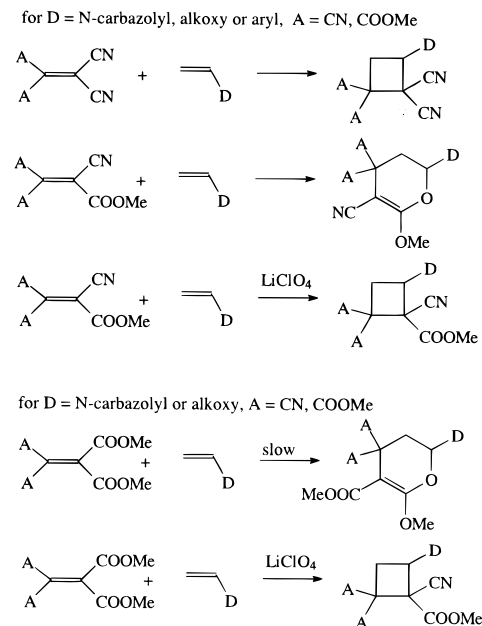
Lewis-Acid-Catalyzed Reactions

Donor Olefins and Acceptor Olefins. The electrophilic character of the acceptor olefins can be increased by putting in additional cyano or ester substituents or substituting ester groups by cyano. Another way to increase the electrophilic character is to use Lewis acids. When the donors are hydrocarbons, the Lewis acid complexes readily to the cyano or carbomethoxy groups of the electrophilic olefin and increases the latter's electrophilic character. We have used two Lewis acids, namely 5 M ethereal LiClO_4 and anhydrous ZnCl_2 .^{14,45} We avoided the use of alkylaluminum chlorides because these are prone to react with oxygen at the alkyl to aluminum bond, thereby providing an extraneous source of free radicals.

Lewis acids are well-known to affect the *propagation* step of initiated vinyl copolymerizations to give alternating copolymers.⁴⁶ We felt that the same factor leading to alternating copolymerization, namely increased electrophilic character of the acceptor olefin, should also give rise to spontaneous *initiation* of free radical polymerizations. Only brief mentions of such spontaneous initiations were found in the literature.⁴⁷ In our studies, St reacted spontaneously with AN in the presence of ZnCl_2 to form alternating copolymer at temperatures well below those at which spontaneous radical initiation from styrene itself can occur.⁴⁵ The rates increased as the concentration of ZnCl_2 went up. In the same conditions, pMeSt reacted much faster than St, as expected due to its greater electron-rich character. Attempts to extend these studies to still more electron-rich monomers, such as MeOSt and IBVE, led to complications. First, cationic polymerization of the donor monomer in presence of the ZnCl_2 occurred. We could exclude this by using *N*-ethyl-diisopropylamine as inhibitor of cationic polymerization, or by using 2,5-dimethyltetrahydrofuran as solvent. The sterically hindered amine can terminate propagating carbocations, while its crowded steric nature prevents it from deactivating the ZnCl_2 . Although this trapping of adventitious carbocations was successful, the results with both MeOSt and IBVE in the presence of AN and ZnCl_2 were still inconclusive. We traced the difficulties to the presence of the oxygen lone-pair electrons of the donor olefin, which competitively complexed the ZnCl_2 , thus deactivating the donor monomer and competing with the complexation of AN.

Lewis acids are also well-known to catalyze cycloaddition reactions, in particular Diels–Alder reactions, as witnessed by many reports in the literature.⁴⁸ We studied a wide variety of [2 + 2]-cycloaddition reactions of cyano- and/or ester-substituted olefins in the presence of Lewis acids.¹⁴ The cycloaddition reaction is increasingly favored over spontaneous copolymerization as the electron disparity increases. This is in keeping with greater zwitter-

Scheme 7. Effect of Lewis Acids on Olefin–Olefin Reactions



ionic character in the tetramethylene intermediate, which favors the *gauche* or *cis* conformation by Coulombic interaction and therefore favors cycloaddition. The terminal substituents on the electrophilic olefin have a decisive influence on the reaction sequence, as illustrated in Scheme 7. Upon mixing highly electrophilic olefins with *gem*-dicyano groups with donor olefins, [2 + 2]-cycloadditions occur at room temperature. With olefins containing one cyano and one carbomethoxy group on the same carbon, inverse electron demand Diels–Alder cycloaddition involving the ester substituent dominates. However, in the presence of Lewis acids, the cyclobutane adducts can be obtained quantitatively in reactions with the most nucleophilic olefins. With olefins with two carbomethoxy substituents on the same carbon, the reactions are much slower, and [2 + 4]-cycloaddition dominates with the most reactive donor olefins, while the [2 + 2]-cycloadduct can be obtained only in the presence of Lewis acid. With several weaker acceptor olefins, free radical copolymerizations compete with the cycloadditions when reacted with the least reactive donor olefins.

Dienes and Acceptor Olefins. To study the effect of Lewis acids on the spontaneous reactions of electron-rich dienes and acceptor olefins, AN was reacted with 1,3-dienes in the presence of various amounts of ZnCl_2 .⁴⁹ Again, the spontaneous reactions were accelerated in the presence of ZnCl_2 . Alternating copolymers and [4 + 2] cycloadducts formed. The structure of the diene and its electron-rich character control the product distribution. In the reaction of DMB (2,3-dimethylbutadiene) and AN, raising the temperature and increasing the ZnCl_2 concentration enhances the cycloaddition process, while the maximum yield of copolymer is obtained at 45 °C. With 4-methyl-1,3-pentadiene, only copolymer is formed because the two terminal methyl groups preclude the concerted [4 + 2]-cycloaddition. Isoprene (IP) is less reactive than DMB, and the overall yields are lower. These

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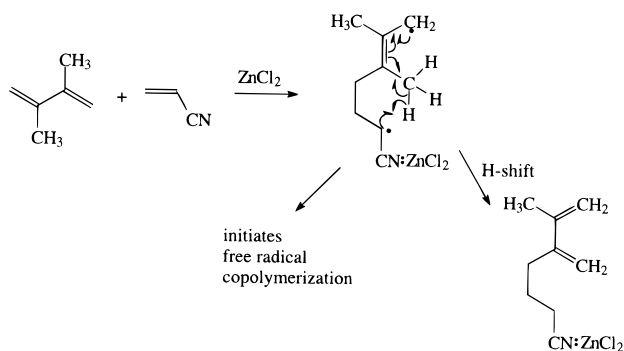
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Scheme 8. Proposed Mechanism for 1,3-Diene/Acrylonitrile in the Presence of a Lewis Acid



results are in agreement with a postulated mechanism involving competition between a π -allyl 2-hexene 1,6-diradical and concerted cycloaddition, as shown in Scheme 8. At higher temperatures, lower polymer yields were observed for the DMB/AN and IP/AN olefin pairs and a mechanism involving a H-transfer in the diradical intermediate is suggested to explain this unexpected behavior.

Importance of Experimental Conditions

Although the fields of organic chemistry and polymer chemistry are often considered to be separate disciplines, they are really different sides of the same coin. The organic molecules used in both disciplines behave by a single set of rules, and the same mechanistic laws apply independent of the intent of the individual researcher. The results observed in each discipline, however, do depend greatly on the reaction conditions to which "charge-transfer" polymerizations are particularly susceptible. The perceived discontinuity between the two disciplines, based solely on the different size of the molecules, has resulted in an incomplete literature view of the chemistry on hand.

Polymer chemists set up their experiments differently from organic chemists, and they work them up differently as well. *To a major extent these artifacts dictate the outcome of the experiments.* Polymer chemists prefer concentrated solutions, even bulk monomers, to optimize the yield of polymer. An initiator is routinely added, even before the presence or absence of a spontaneous thermal polymerization has been established. The ratio of reactants (i.e., monomers/initiator) is kept very high (>100:1) to obtain high molecular weights. Order of addition of reagents can possibly play a role in determining the outcome when extremely reactive monomers are being used. The product is isolated by pouring into a large volume of nonsolvent, filtering, and drying. In this way, cycloadducts and other small molecules, if present, are lost in the filtrates. Organic chemists, on the other hand, prefer dilute and equimolar solutions and routinely add free radical inhibitor to prevent any spontaneous polymerizations. The product is often isolated by filtering and discarding any polymeric materials and evaporating the filtrate. So polymer chemists and organic chemists have much in common: *each group throws away the other's product!*

Either process can be enhanced at the discretion of the researcher. Polymerization can be favored by deliberately adding initiator. Small molecules, in contrast, are favored

when inhibitors are deliberately added. Still other complications arise if adventitious trace impurities are present which may initiate or inhibit chain polymerization reactions. Over the years the purity of monomers, particularly industrial ones, has increased so greatly that adventitious impurities can generally be excluded as influencing the results.

As to time, i.e., kinetics versus thermodynamics, cycloadducts may cyclorevert and lead to either polymers or other adducts, including linear dimers and cyclic trimers. Temperature is a two-edged sword in this chemistry. Higher temperatures are often required to bring the initiation of the spontaneous polymerizations up to acceptable rates. On the other hand, one must work below the ceiling temperature if polymer is to be formed. The ceiling temperature becomes lower with more substituents and in dilute solution.⁵⁰

Valuable information is available from both the small molecules and the polymer. A cyclobutane, for example, is the signature of a tetramethylene intermediate in thermal reactions, whereas the type of polymer gives clues as to the nature of the spontaneously formed initiating intermediate, whether zwitterionic or diradical. A particularly significant aspect of the trapping of an intermediate by initiating a polymerization is the enormous amplification that is involved. An initiating species formed in a vanishingly small amount can still lead to a substantial quantity of polymer that is easily isolated and identified.

All of the above factors need to be carefully weighed in designing experiments in this fascinating area.

Future Directions

Many aspects of spontaneous cycloaddition/polymerizations remain to be established. Anionic initiation has not been emphasized in our work, as we have routinely used highly substituted electrophilic olefins. Yet the early work of Hayashi on polymerization of nitroethylene by a cyclobutane adduct is very encouraging preliminary information.¹⁸ Switching to less substituted electrophilic olefins in reactions with highly substituted donor olefins should lead to spontaneous anionic polymerizations. We have also begun the study of the electron-rich/electron-poor olefin systems in photochemical conditions, and these preliminary results show that these reactions are in agreement with our theory.⁵¹⁻⁵⁴

The use of tetramethylene intermediates to initiate a third monomer represents an appealing direction. Earlier attempts have failed because monomers forming the tetramethylenes are swept out by terpolymerization, and so initiation comes to a halt. Our studies to establish whether or not tetramethylene diradicals can be generated from strained small ring compounds have been encourag-

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ing but not conclusive.⁵⁵ Ionic polymerizations, generating the tetramethylene zwitterion from cyclobutanes can indeed be carried out,¹⁷ but attempts to do the same for diradical tetramethylenes have not yet been successful.

Although in the past much effort has been expended in looking for spontaneous thermal homopolymerization of vinyl monomers, only styrene has been unequivocally shown to do so, largely by the Mayo mechanism.⁴ Of course no polarity difference is involved in such reactions. Rather the area to look for spontaneous initiations is copolymerizations, as was early appreciated by Walling.⁵

Conclusions

A major outcome of this work is the widespread importance and applicability of bond-forming initiation reactions. We have come to the conclusion that charge-transfer complexes between donor and acceptor molecules serve only as indicators of electron disparity. No experimental information requires their presence in either propagation or cycloaddition. Of course, the CT complexes may be on the path leading to the tetramethylene, but in general, there is no way to prove such a postulate. Nevertheless, Kochi has assembled powerful evidence about the ubiquity of charge-transfer complexes on the road to both outer-sphere and inner-sphere reactions.⁵⁶

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The zwitterionic or diradical nature of the tetramethylene is dictated by the terminal substituents, the conformation, and the solvent polarity.

Finally, organic and polymer chemistries form a seamless continuous whole. Seeming differences are traceable to differences in experimental protocols, notably in the mode in which the reaction is carried out and, very importantly, in how it is worked up. A satisfactory description of systems leading to spontaneous copolymerizations and cycloadditions requires a satisfactory mass balance which accounts for the major products, both small molecules and polymers.

We are deeply indebted to the National Science Foundation, Division of Materials Research, for generous funding of this work. Partial support also came from the donors of the Petroleum Research Fund, administered by the American Chemical Society, DuPont, and Allied-Signal. The authors acknowledge the work of their numerous able co-workers who have worked on this project over the years: Drs. Gerry Noren, Bob Daly, Pierre Ykman, Husam Rasoul, Mohammed Abdelkader, Jim Rhoades, Bob Sentman, Mark Glogowski, Tetsuya Gotoh, Ashish Pandya, Hitoshi Tanaka, Cherylyn Lee, Guangyi Wang, Hester Clever, Tun Fun Way, Stacy Evans, Warunee Srisiri, Jacques Penelle, Yufei Li, Michael Mikhael, Tong Li, Guobei Chu, Hua Wang, and Takahito Itoh. They also acknowledge numerous discussions with Professors R. Huisgen, R. Sustmann, K. Houk, E. Mash, and S. Iwatsuki and with Dr. Firestone.

AR950222F