

Zwitterion and Diradical Tetramethylenes as Initiators of "Charge-Transfer" Polymerizations

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Early workers noticed that, upon mixing of certain electron-rich and electron-poor olefins, spontaneous polymerizations occurred without added initiator. For example, Trumbull and co-workers observed that a mixture of vinylidene cyanide and chloroprene, vinyl ether, or styrene led in each case to the formation of a copolymer and cycloadduct.¹ The case of vinylidene cyanide with a vinyl ether, in which homopolymerization of both monomers was observed, was further investigated by Stille and co-workers.² Many other examples of spontaneous polymerizations can be cited and have been reviewed extensively.³⁻⁶ Cycloadditions frequently accompanied these polymerizations.

Theories for these spontaneous polymerizations mostly center around the charge-transfer complexes (CT complexes).⁶ Mixing electron-rich olefins with electron-poor olefins almost always results in brightly colored solutions. The colors are due to the CT excitation ($h\nu_{CT}$) of the electron-donor-acceptor (EDA) complex. The EDA complex is a ground-state complex formed between the electron-rich (donor) and the electron-poor (acceptor) olefin, in which weak electron donation occurs from the donor to the acceptor. Mulliken used the term EDA complex, rather than CT complex, in his pioneering work on these complexes.⁷

The outcome of "charge-transfer" polymerizations has been systematized by Iwatsuki and Yamashita in their penetrating early review.⁸ They arrived at a correlation of polymerization behavior with the value of the EDA complex equilibrium constant, K_{eq} . With weak donor

K_{eq} , $M^{-1}L$	polymerization behavior	
	initiation	propagation
0-0.01	initiated free radical	random copolymerization
0.01-0.1	initiated free radical	alternating copolymerization
0.1-1.0	spontaneous free radical	alternating copolymerization
1.0-5.0	spontaneous ionic	homopolymerization
>5.0	single electron transfer to form stable complexes	

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. degree 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 Du Pont, he moved in 1969 to the University of Arizona. His research interests have included the synthesis and ring-opening polymerization mechanisms of strained bicyclic molecules, the mechanisms of reactions of donor with acceptor olefins, the synthesis and polymerization of imines, and the synthesis of electrically conductive, piezoelectric, and nonlinear optical polymers.

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and acceptor olefins, no spontaneous polymerization takes place, while the addition of radical initiator results in a random or an alternating copolymer depending on the value of K_{eq} . As the donor and acceptor strength of the olefins increases, spontaneous initiation rates for radical copolymerization increase; with even stronger donor and acceptor olefins, ionic homopolymerization takes place (cationic and/or anionic). As we shall see, this is qualitatively, although not quantitatively, correct.

The nature of the *initiation* of the spontaneous free-radical copolymerizations is still under discussion, and various initiating species have been proposed over the years: monomer cation and anion radicals, CT complexes, Diels-Alder adducts, dipolar (zwitterionic) intermediates.³⁻⁶ One specific mechanism proposes proton transfer from the cation radical to the anion radical, which leads to two distinct radicals. These radicals have been trapped by Otsu in the vinyl sulfide/maleic anhydride case.⁹ Kinetic studies of spontaneous free-radical polymerizations have been carried out first by Yamashita¹⁰ and, in recent years, more extensively by Nagai.¹¹ The latter derived a complete kinetic scheme for equal initial monomer concentrations. Spontaneous radical generation occurred, but no specific structure was assigned to the initiating species. Gaylord has proposed a novel polymerization by collapse of excited CT complexes directly to copolymer.¹² However, this mechanism has not received any support.

Copolymerizations of styrene with acceptors may in several instances follow the Mayo mechanism, originally proposed for the spontaneous homopolymerization of styrene.¹³⁻¹⁵ This mechanism involves hydrogen atom transfer from the [4 + 2] Diels-Alder adduct and has

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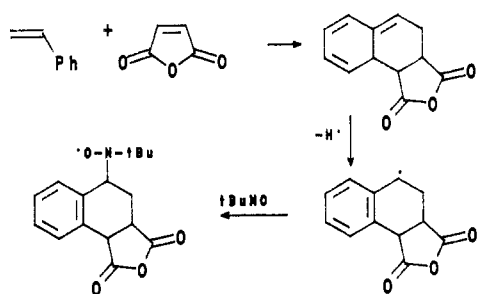
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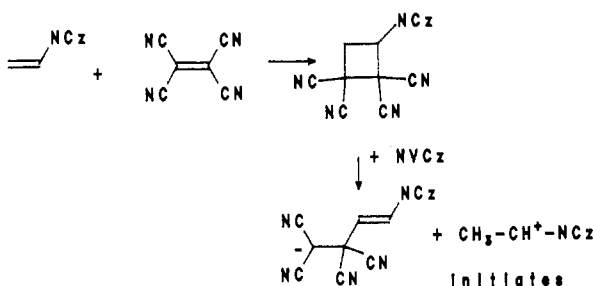
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been extended to spontaneous copolymerizations of styrene with, for example, maleic anhydride¹⁶ or acrylonitrile.¹⁷ Otsu has successfully trapped the initiating styrene radical in the former case.¹⁶



As far as spontaneous ionic homopolymerizations are concerned, ion radicals have also been mentioned as the initiating species.³ Zwitterionic initiators have been proposed in a few specific examples: *N*-vinylcarbazole (NVCz) and chloranil,^{3,18} *N*-vinylcarbazole and fumaronitrile,¹⁹ and vinyl ethers with dichlorodicyanobenzoquinone.²⁰ The cationic polymerization of *N*-vinylcarbazole (NVCz) in the presence of electrophilic olefins, such as tetracyanoethylene (TCNE), has been investigated by several research groups. Scott²¹ and Ellinger²² were the first to independently report this polymerization. Nakamura et al.²³ concluded that the cyclobutane adduct was the initiator by proton transfer to monomer, but Ledwith et al.²⁴ postulated initiation by the cation radical of NVCz.

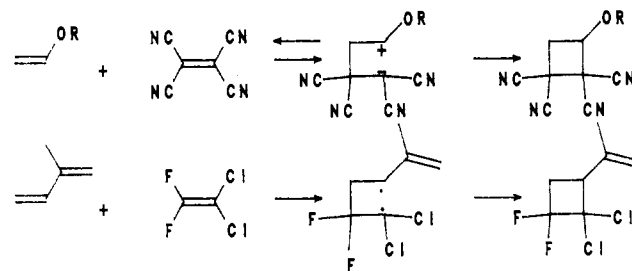


The propagation in the "charge-transfer" copolymerizations has also been thoroughly studied over the years. Two possibilities have been proposed to explain the strictly alternating character of many of these polymerizations: either the alternating monomer additions are governed by the polarity of the monomers, or the EDA complex itself acts as a monomer. Sophisticated kinetic schemes have been used to try to answer this question.²⁵⁻²⁸ Many excellent reviews in

the literature on specific monomer systems, such as styrene/maleic anhydride,²⁹ or in general^{3-6,29} discuss the mechanism of the propagation, and recently model studies have shed light on this problem.³⁰ However, the propagation reaction mechanism is not the subject of this Account.

Proposed Theory: Bond-Forming Initiation

From organic chemistry it is known that cycloaddition reactions between a donor olefin and an acceptor olefin leading to cyclobutanes are required to be stepwise reactions, according to the Woodward-Hoffmann rules.³¹ A bond is formed between the two olefins, leading to a tetramethylene intermediate (T). In a subsequent step, the second bond is formed, yielding the cycloadduct. Depending on the reactants, either zwitterionic or diradical tetramethylenes have been proposed as intermediates.^{32,33}



A unifying hypothesis for the observed organic chemistry was advanced by Huisgen,³² who suggested that all tetramethylenes lie on a continuous scale between zwitterionic and diradical structures and may be regarded as resonance hybrids of the two extreme forms. The predominant nature of the tetramethylene intermediate is determined by the terminal substituents, and the termini can interact with each other by through-bond interaction.^{32,34}

Our bond-forming initiation theory, originally proposed in 1983, extends the Huisgen hypothesis and proposes that these same tetramethylenes are the true initiators for the observed spontaneous polymerization, and that this concept is valid for both ionic and radical polymerizations. The tetramethylenes offer a lower energy pathway for initiation than ion radicals.

The purpose of this Account is to describe our results, which support our early proposal of the "bond-forming initiation" theory.

Experimental Design

To accentuate the spontaneous reactions, we have chosen strong donor and acceptor substituents for the electron-rich and electron-poor olefins used in this study. In this way, reactions proceed readily at room temperature. The chosen olefins can undergo small-

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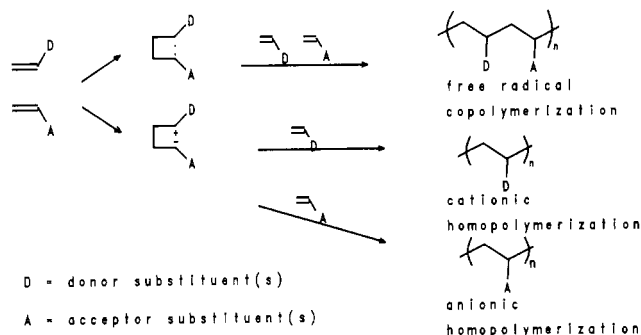
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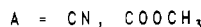
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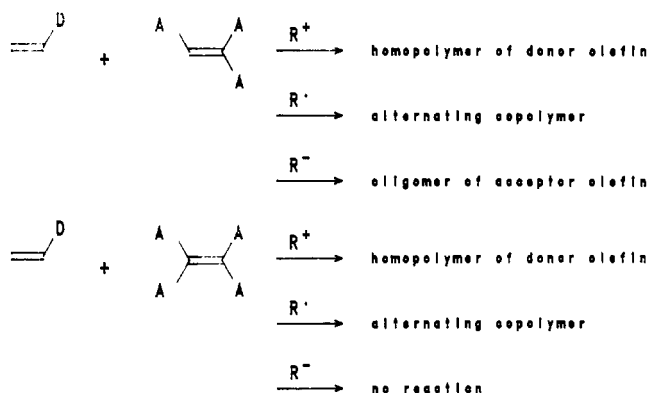
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molecule reactions, such as cycloadditions, and are also able to polymerize. As electron-rich olefins, *p*-methoxystyrene, vinyl ethers, and *N*-vinylcarbazole have been used. As electron-poor olefins, the whole range of tri- and tetrasubstituted ethylenes containing combinations of ester (weaker acceptor) and cyano (stronger acceptor) groups were synthesized.³⁶⁻⁴⁴ Rational



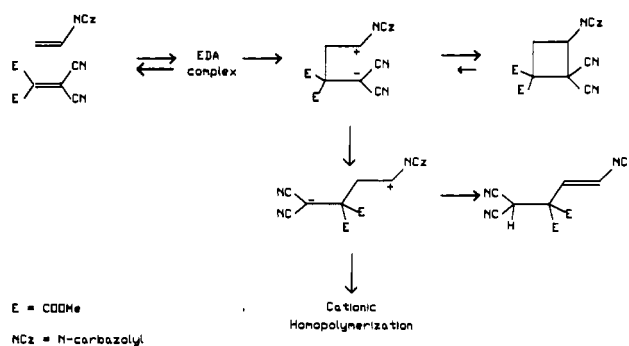
structure-reactivity relationships become possible by progressive replacement of ester groups by cyano groups. Reactions were run in two sets of conditions: organic chemist's conditions involve high dilution and equimolar amounts, while polymer chemist's conditions involve high concentrations and an excess of one reactant (in the case of possible homopolymerizations). We needed to know what propagations were possible for our novel olefin combinations. After subjecting various pairs to known initiators, the following generalizations can be made:



The nature of the polymer is *diagnostic* of the nature of the initiating intermediate. The homopolymer of the donor olefin in the presence of an acceptor monomer

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Scheme I



can only be obtained by a cationic propagation mechanism, and not by a free-radical mechanism. Correspondingly, the homopolymer of the acceptor olefin in the presence of a donor monomer can only be obtained by an anionic mechanism. In contrast, the free-radical propagation leads to copolymerization with a strong tendency to alternate.

Besides the diagnostic nature of the polymer, the other advantage of these systems is *amplification*: a low concentration of an intermediate initiates a polymerization, a chain reaction, and leads to an easily detected and isolated amount of product. Thus, polymerization is a very effective trapping method compared to trapping as small-molecule products.

Zwitterionic tetramethylenes had previously been trapped by small molecule products by several investigators. Huisgen used methanol, acetone, or acetonitrile to trap the zwitterionic tetramethylenes in the reactions of vinyl ethers with TCNE.⁴⁶ In our own work, the zwitterionic tetramethylene in the reaction of *N*-vinylcarbazole with tetrasubstituted electrophilic olefins could be trapped very efficiently with methanol.⁴³

A further kind of trapping is observed when 2:1 adducts are obtained. This was observed in the reactions of enamines.^{40,47,48} The cyclohexane derivatives ($\pi^2 + \pi^2 + \pi^2$ adducts) from two molecules of one olefin and one of the other can be explained by addition of one monomer to the tetramethylene, followed by ring closure. Their formation then implies that the molecule involved twice should be readily ionically polymerizable, as recognized by Brannock.⁴⁷

Zwitterionic Tetramethylenes as Initiators of Cationic Homopolymerization

The spontaneous cationic homopolymerization of *N*-vinylcarbazole was reinvestigated, taking into account the known organic chemistry.⁴³ Previous researchers had already commented on the role of the cyclobutane adduct in the initiation (see above); however, the proposed proton transfer did not fit in with the data known from organic chemistry. Moreover, *N*-vinylcarbazole and TCNE are at the extremes of the electron-rich and electron-poor scales, respectively. Therefore, if ion radicals are part of a viable mechanism, they should occur in this system.

Our seven tetrasubstituted olefins possessing various combinations of cyano and carbomethoxy substituents

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were reacted with *N*-vinylcarbazole. The products were to a great extent determined by the reaction conditions. When equimolar amounts of reactants were used, the reaction proceeded in the following sequence: instantaneous formation of the EDA complex as witnessed by the bright colors and subsequent formation of the cyclobutane adduct (Scheme I). The reaction rates were determined by the electron-withdrawing capacity of the substituents of the electrophilic olefin. If the reaction was run in methanol, the zwitterionic tetramethylene (T) was trapped. The proposed mechanism involves bond formation to the zwitterionic tetramethylene, which closes reversibly to the cyclobutane adduct. Stronger conditions (higher temperatures, more polar solvents) led to isomerization of the gauche T to trans T; the latter can undergo intramolecular proton transfer to form the 1-butene derivative.

The polymerization of excess NVCz in the presence of dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate was studied in great detail (Scheme I). The cationic homopolymerization of NVCz could be initiated by adding either the electrophilic olefin or the cyclobutane adduct, in agreement with Nakamura's TCNE study.²³ When the polymerization is initiated by the cyclobutane adduct, the color of the EDA complex is never observed, showing that this cyclobutane adduct does not revert back to the free olefins. We postulate that the initiation occurs when a monomer unit attacks the trans form of the tetramethylene. Thus, the polymerization occurs in a competitive reaction with the isomerization to the 1-butene derivative, and the rate law for the polymerization is as follows:

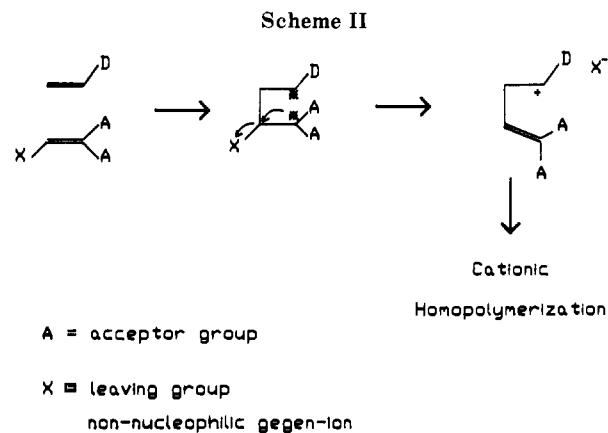
$$R_p^\circ = k[\text{cyclobutane}][\text{NVCz}]^{2-3}$$

The initial propagation rate R_p° is first order in cyclobutane concentration and varies from second to third order in NVCz depending on the NVCz concentration.

Our results demonstrate conclusively that neither the EDA complex nor the ion radical pair has anything to do with initiation. Polymerization is proceeding at its maximum rate long after the EDA complex concentration has diminished to 0. If ion radicals were formed in this system, the cation radical of NVCz would react with another NVCz molecule to form the homodimer;²² no homodimer was ever detected in these systems.

Subsequently, we extended this initiating system to other electron-rich olefins. *N*-Ethyl-3-vinylcarbazole is as effective as NVCz in the spontaneous polymerizations.⁵⁰ However, if the donor substituent becomes more nucleophilic, it will itself react with the electrophilic olefin or with the propagating carbenium ion and, thus, prevent polymerization. This was found to be the case for *p*-(dimethylamino)styrene.⁵⁰ On the other hand, for vinyl ethers with our electrophilic olefins, cycloaddition is preferred.⁵⁰ If even less electron rich olefins are used, such as *p*-methoxystyrene, a change in mechanism is observed: radical copolymerization takes place initiated by a diradical tetramethylene⁴⁹ (see below).

Highly effective cationic initiators are obtained by incorporating a β leaving group in the acceptor olefin⁵⁰⁻⁵³ (Scheme II). Expulsion of the leaving group



from the zwitterionic tetramethylene results in a more efficient cationic initiator, in which the carbanion has been replaced by a less nucleophilic counterion which allows propagation to proceed. In this category, β,β -dicyanovinyl-*p*-toluenesulfonate (tosylate) and β -cyano- β -carbomethoxyvinyl tosylate were the most effective.⁵³

Zwitterionic Tetramethylenes as Initiators of Anionic Polymerization

In our studies of the reactions of electron-rich with electron-poor olefins, the emphasis has mostly been on the highly substituted electron-poor olefins. Therefore, the great majority of polymerizations observed in these ionic systems have been cationic. However, the tetramethylene intermediates are also capable of initiating anionic polymerizations.

In some cases, anionic oligomerization of trisubstituted olefins has been observed, if the cationic polymerization is inhibited, for example, in the reaction of *p*-(dimethylamino)styrene with dimethyl cyanofumarate.⁵⁰ The 1,1-disubstituted electrophilic olefin methyl α -cyanoacrylate polymerizes via an anionic mechanism in the presence of *n*-butyl vinyl ether.⁵⁴ On the other hand, with *p*-methoxystyrene or styrene, radical copolymerization is observed. Hayashi describes the reaction of isobutyl vinyl ether and nitroethylene, which leads to an unstable cyclobutane adduct; this adduct is capable of initiating the anionic polymerization of excess nitroethylene, as well as the cationic polymerization of added NVCz.⁵⁵

Diradical Tetramethylenes as Initiators of Radical Polymerizations

In analogy with the ionic polymerizations, the bond-forming initiation theory proposed that the initiating species for spontaneous free-radical copolymerization is the diradical tetramethylene. Trapping a diradical as a small-molecule product is not common, because diradicals are much less stable and more short-lived than zwitterions. Radical traps, such as nitroxyl radicals, can be used, but polymerization is the preferred trapping method. Trapping monoradicals by polym-

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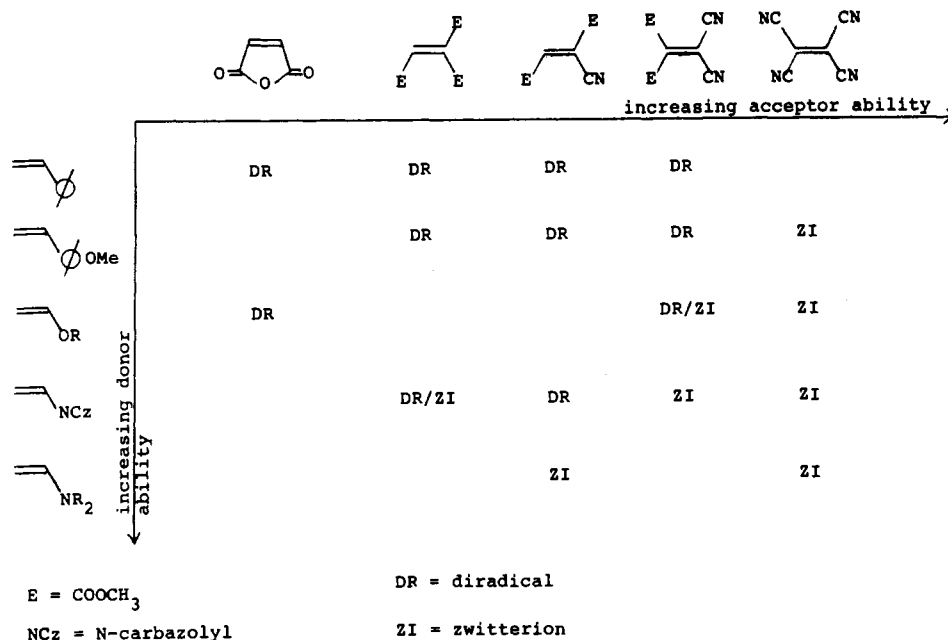


Figure 1. An organic chemist's periodic table.

erization is already familiar, for example, Todres used the polymerization of styrene as a detection method for phenylthiyl radicals,⁴⁵ but so far no report has described the trapping of diradicals by polymerization.

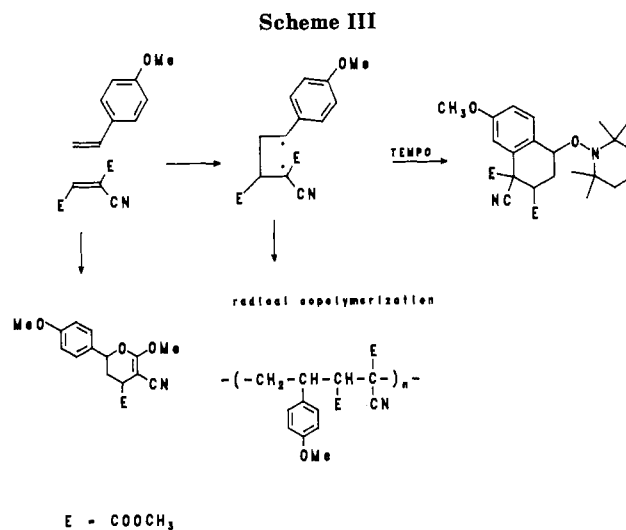
We carried out a thorough study of the spontaneous copolymerization of *p*-methoxystyrene and dimethyl cyanofumarate⁴⁹ (Scheme III). In this system at very low concentrations, an inverse electron-demand [2 + 4] cycloaddition is favored; at high concentration, only alternating copolymerization is observed. The kinetic scheme was derived on the following assumptions: (1) the initiating species is a diradical tetramethylene; (2) propagation occurs through either alternating additions of the free monomers or addition of EDA complex as monomer; (3) termination occurs only through recombination of two different terminal radicals; and (4) a steady state is obtained in which the initiation rate is equal to the termination rate. For equimolar initial concentrations, the following rate law is derived:

$$R_p = -2d[D]/dt = YK^{1/2}[D]^2 + ZK^{3/2}[D]^3$$

in which R_p is the propagation rate, Y and Z are composite rate constants, K is the EDA complex equilibrium constant, and $[D]$ is the concentration of donor olefin. Because the polymerization is strictly alternating, donor and acceptor olefin concentrations are always equal. In the rate law, the first term describes the contribution of free-monomer propagation (second order in donor, or first order in each monomer), while the second refers to the propagation by EDA complex (third order in donor).

Our experimental results indicate that the propagation rate is second order in donor concentration: no propagation occurs via the EDA complex. Moreover, the diradical tetramethylene as the initiating species is consistent with the kinetic results. A substantial increase in the molecular weight during the polymerization was also observed due to termination by successive recombinations of polymer chains with two radical ends.

We were able to trap the diradical tetramethylene with TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl),



and the 1:1:1 adduct could be isolated (Scheme III). Similar adducts have been described in the literature to prove the Mayo mechanism (see above). However, in the *p*-methoxystyrene/dimethyl cyanofumarate case, an inverse Diels–Alder adduct is formed. In any reaction, there can be only one possible Diels–Alder adduct, thereby excluding a Mayo adduct in our system. The trapping in conjunction with the kinetics and the increase in molecular weight observed during the polymerization provide powerful evidence for bond-forming initiation in radical copolymerization.

A Polymer Chemist's Periodic Table

Huisgen stated that the nature of donor and acceptor substituents determined the nature of the tetramethylene.³² We cast about for a convenient, stimulating format. The periodic table might be regarded as the oldest correlation for donors and acceptors in chemistry. Accordingly, we have presented existing data in this form (Figure 1).³⁵ The donors are listed in a generally accepted sequence of increasing nucleophilicity and the acceptors in order of increasing electrophilicity, based on physical organic values such as Hammett values and ionization potentials. In this pe-

riodic table format, our own and existing organic and polymer literature data can be correlated; a clear distinction can be made between the diradical and zwitterionic nature of the tetramethylenes. This corresponds to the occurrence of spontaneous alternating copolymerizations versus ionic homopolymerizations. Moreover, for the first time, predictive power is achieved.

From our experience, the delineation of mechanism change from radical to ionic polymerization does not strictly depend on the K_{eq} of the EDA complex, as had been proposed by Iwatsuki and Yamashita.⁸ In the case of *p*-methoxystyrene/dimethyl cyanofumarate, alternating copolymerization takes place and $K_{eq} = 0.16 \text{ mol}^{-1} \text{ L}$,⁴⁹ while *N*-vinylcarbazole undergoes cationic homopolymerization in the presence of dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate with $K_{eq} = 0.20 \text{ mol}^{-1} \text{ L}$.⁴³ The general outline of their scheme is correct, but the areas of mechanism change are not clearly defined by the value of K_{eq} .

Confirmation of the assignments of predominant diradical and zwitterionic tetramethylenes comes from a completely independent approach. Using theoretical SINDO1 calculations, Jug showed good agreement between the predicted nature of tetramethylenes with selected terminal substituents and the experimental data based on the periodic table.⁵⁶

The nature of the tetramethylene can be varied from nonpolar diradical to polar diradical and finally to zwitterionic. The nonpolar diradicals have been thoroughly described by Bartlett³³ while the zwitterions were investigated by Huisgen.³² However, in between these two extremes are borderline cases: polar diradicals or schizophrenic tetramethylenes.

If one terminal substituent favors a zwitterion and the other a diradical, we have a schizophrenic borderline case. An early example was that of Stille, using vinylidene cyanide and styrene.²⁰ The cyclohexane had the structure expected from a zwitterion, but an alternating copolymer also formed. These schizophrenic tetramethylenes will be on the continuous scale between zwitterions and diradicals.

Another theoretical study on the effect of solvent on tetramethylenes by Jug predicted that a borderline diradical could switch to a zwitterion in polar solvents.⁵⁷ A unique experimental case of a polar diradical was found in the reactions of *p*-methoxystyrene and methyl β,β -dicyanoacrylate, which led to different products, depending on the polarity of the solvent.⁵⁸

Extensions of the Bond-Forming Initiation Theory

In a recent article on "Geometric and Topological Thinking in Organic Chemistry", Turro points out that problems can be solved more easily if the chemist can determine into which "topology" that particular problem fits.⁵⁹ It seems to us that many topics in organic and polymer chemistry fit in the same topology of knowledge as the reactions of electron-rich and electron-poor olefins. This topology comprises several concepts, such as donor, acceptor, EDA complex, bond

formation, diradical/zwitterion, cycloadducts, and polymers.

The reactions of *electrophilic quinodimethanes* with electron-rich olefins very clearly fit the same framework as the reactions described in this Account. EDA complexes form upon mixing, and spontaneous polymerizations, radical or ionic depending on the nature of the reactants, occur. A detailed analysis of these systems shows the great parallelism between the reactions of the electrophilic quinodimethanes with electron-rich olefins and the reactions of the electrophilic olefins with those same electron-rich olefins.⁶⁰

The reactions of double bonds other than C=C also can fit the same topology. Reactions of *carbonyl compounds* with olefins can lead to hetero tetramethylenes. Carbonyl compounds such as hexafluoroacetone have been used as π -acceptors in cycloadditions⁶¹ or even as initiators of polymerization.⁶² The chemistry of carbonyl cyanide exactly parallels that of TCNE.⁶³ The carbonyl component can also act as a π -donor. A remarkable example is the hexafluoroacetone-initiated polymerization of formaldehyde and its copolymerizations with acetone.⁶⁴

The bond-forming initiation theory is not limited to the reaction of π -donors with π -acceptors, but can be extended to *n-donors*. A case of bond-forming initiation between an *n*-donor and a π -acceptor had previously been described in the literature: when tetrahydrofuran is mixed with vinylidene cyanide, both cationic homopolymerization of the former and anionic homopolymerization of the latter are observed.⁶⁵ In a systematic study of the initiation of cationic polymerization of aldehydes and oxacycles by electrophilic olefins, we found that these reactions are rather slow.⁶⁶ Better results are obtained with electrophilic olefins with a β leaving group.⁵⁰

Complexation of the electron-poor olefin with *Lewis acids* enhances its electrophilic character. These systems also fit the same topology as long as the Lewis acid does not cause unrelated reactions, such as direct initiation of the donor olefin.^{67,68} An excellent example of the effect of Lewis acid complexation is the spontaneous copolymerization of vinyl acetate with acrylonitrile in the presence of zinc chloride.⁶⁹

Electrophilic *bicyclobutanes* are also known to spontaneously copolymerize with electron-rich olefins. In this case, a single carbon-carbon bond is broken to form a diradical, which can initiate the polymerization.⁷⁰ A similar argument can be made for the observed spontaneous polymerization of a bridged [1.1.1]pro-

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pellane with acrylonitrile.⁷¹

Diene-olefin reactions also fit the same topology. Nagai has described the competition between cycloadditions and spontaneous copolymerizations in systems involving cyclic dienes and α -chloroacrylonitrile.⁷² We have started to investigate the reactions of common donor dienes with moderately electrophilic olefins. Early indications are that the spontaneous reaction of, for example, 1,3-pentadiene with acrylonitrile leads to a copolymer, presumably initiated by a diradical.⁷³ In order to obtain the expected cycloadduct, a dilute solution of the reactants has to be heated to a high temperature in the presence of an inhibitor.

We have also extended the study of the reactions of donor and acceptor olefins to their *photochemical* reactions.^{74,75} In this case again, the cycloaddition

products can give vital information about the initiating species of the observed polymerizations. In this work, we are trying to unify the photochemical and thermal reactions of donor and acceptor olefins by examining the possible role of tetramethylene intermediates.

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