The Relationship of Cycloaddition Reactions to Spontaneous Vinyl Polymerizations

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To Professor *Rolf Huisgen* with grateful appreciation for his contributions to organic polymer chemistry!

The zwitterionic–biradical tetramethylene proposed by *Huisgen* as the key intermediate in stepwise [2+2] cycloaddition reactions has been shown to be the crucial intermediate in spontaneous vinyl polymerizations as well. Predominantly biradical tetramethylenes initiate free-radical copolymerizations, while predominantly zwitterionic tetramethylenes initiate cationic or anionic homopolymerizations. Stepwise cycloaddition is viewed as a spontaneous polymerization lacking a propagation step. These tendencies could be correlated in the form of an 'organic chemist's Periodic Table', which has recently been put on a quantitative basis.

Huisgen also showed experimentally that [4+2] *Woodward–Hoffman*-allowed cycloadditions are completely concerted. Spontaneous copolymerizations accompanying these cycloadditions, therefore, were ascribed to the s-*trans* diene form. This concept was given support by kinetics studies, as well as by exclusive cycloaddition from s-*cis* cyclopentadiene, and exclusive copolymerization from s-*trans* verbenene.

Introduction. – '*The great poet builds larger than he knows*'. This familiar saying also applies to great scientists. When *Rolf Huisgen* was studying the role of the tetramethylene intermediate in [2+2] cycloaddition reactions, surely the idea that this intermediate might play an important role in polymer chemistry never crossed his mind. Yet this has proven to be the case.

During the 1960s and 1970s, polymer chemists encountered various unexpected and perplexing observations in vinyl polymerizations. A tendency of the monomer units to alternate in the copolymer chain was observed. This was the case when electron-rich monomers, such as styrene or vinyl ethers, were copolymerized with electron-poor monomers, such as methyl acrylate or acrylonitrile. As the donor and acceptor character of the co-monomers increased, the alternation tendency grew stronger and stronger. Eventually, a new phenomenon set in, namely spontaneous polymerization. At first, spontaneous copolymerization occurred by a radical mechanism to form strictly alternating copolymers. With still stronger donor-substituted monomers, homopolymers of the donor monomer were found, which could only be formed by a spontaneous cationic homopolymerization.

Attempts by polymer chemists to understand these phenomena centered on the visible charge-transfer (CT) complexes formed by the two monomers. It was attractive to suppose that free-radical 'homopolymerization' of this CT complex would lead to the observed strictly alternating copolymers. But how this explained the cationic homopolymers or the CT complex initiated polymerizations, was not made clear.

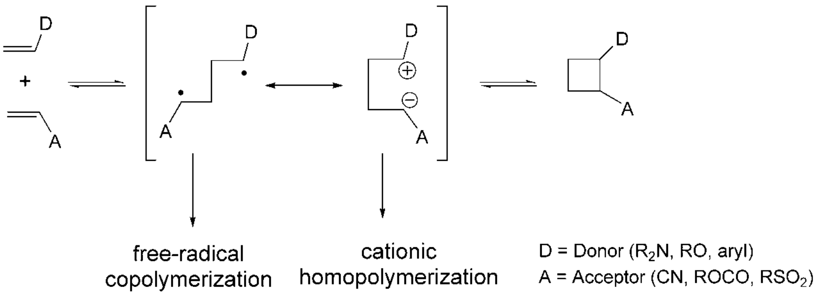
Nevertheless, hundreds of papers exist dealing with one or another aspect of these reactions, mostly focused on the propagation reaction.

During approximately the same time period, but on the organic chemistry side, *Huisgen* extensively studied the cycloaddition of vinyl ethers to tetracyanoethylene (=ethane-1,1,2,2-tetracarbonitrile) [1][2]. This remarkable electrophilic olefin had been introduced by researchers at the *DuPont* Central Research Department [3]. It was highly active in [2 + 2] cycloadditions with electron-rich olefins, and participated in a wide variety of other organic reactions. It stood alone in its unique reactivity.

We systematically studied other electrophilic tri- and tetrasubstituted olefins, in which the substituents were CN and MeOOC groups [4][5]. Our thought was that, by systematic structure variation, trends in reactivity and course of reaction could find rational interpretation. Tetracyanoethylene itself does not copolymerize, contrary to the hopes and expectations of its discoverers. However, similar electrophilic, *trisubstituted* olefins do copolymerize with electron-rich olefins [4][5]. The rates of these reactions are much faster than those found in the literature and, so, drew our attention to the general problem outlined above. Nevertheless, for a while, like the other polymer chemists in the field, we floundered around for an interpretation.

The *Huisgen* Tetramethylene Intermediate. – In 1977, *Rolf Huisgen* published his seminal papers in Accounts of *Chemical Research* on tetramethylene intermediates [1][2]. The crucial line can be quoted in full: '*Their relative weights are determined by the substituents at the terminal centers; they decide where a given tetramethylene species has to be located on the continuous scale between biradical and zwitterion*'. This concept, namely that the polarity of the tetramethylene might be high, yet preserve the radical rather than solely zwitterionic character, was the *Ariadne*'s thread, which was to lead us out of the labyrinth. Briefly, copolymerization, occurring by a radical mechanism, would be induced by a polar biradical tetramethylene; homopolymerization, which could be cationic or anionic, would be induced by a zwitterionic tetramethylene. With this concept of *bond-forming initiation*, as illustrated in *Scheme 1*, we were able to interpret hitherto inexplicable behavior [6]. For example, it rationalized the observation that some combinations of polar monomers gave facile spontaneous initiation of free-radical copolymerizations, while still more-polar monomers readily gave ionic homopolymerization.

Scheme 1. *Tetramethylene Intermediates Initiating Spontaneous Polymerizations*

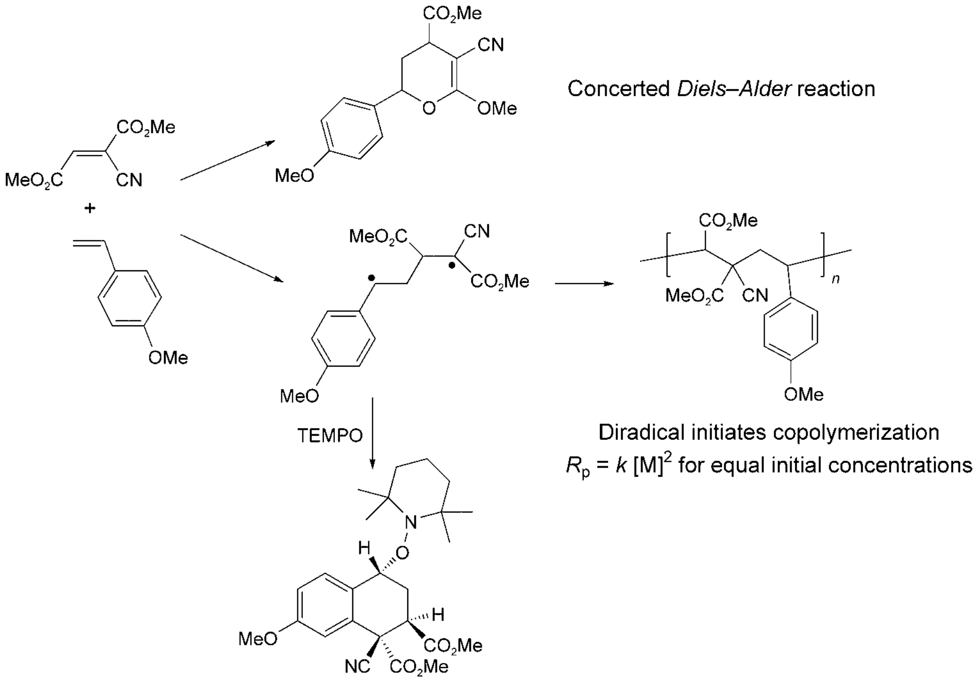


D = Donor (R_2N, RO, aryl)
A = Acceptor (CN, ROCO, RSO_2)

As far as propagation is concerned, the alternation aspect of the free-radical copolymerizations can be understood based on recent work on the polarity of radicals. Here, an electron-poor radical will preferentially react with an electron-rich substrate. *Fischer* and *Radom* have established quantitative measurements for this effect [7], providing fundamental physical-organic-chemistry data for this postulate.

Kinetics of Spontaneous Copolymerization. – Although free-radical copolymerization is ordinarily too complicated to be studied kinetically, it proved possible to carry out a kinetic analysis of the *p*-methoxystyrene/dimethyl cyanofumarate reaction (*Scheme 2*) [8]. The copolymerization was first-order in each compound, consistent with formation of a polar biradical tetramethylene. The molecular weight of the copolymer increased through the reaction, consistent with biradical termination. Although a bright yellow CT complex was visible in solution, the kinetics excluded its participation in either initiation or propagation. The rate constant was insensitive to solvent polarity. No cyclobutane adduct was formed, but an inverse *Diels–Alder* cycloadduct was formed concertedly. The presence of the initiating biradical was further reinforced by our more-recent spin-trapping experiments [9]. In these experiments, the 1,4-diradical was shown to lead to a different formal [4+2] cycloadduct, thereby affirming the concerted nature of the *Diels–Alder* cycloaddition.

Scheme 2



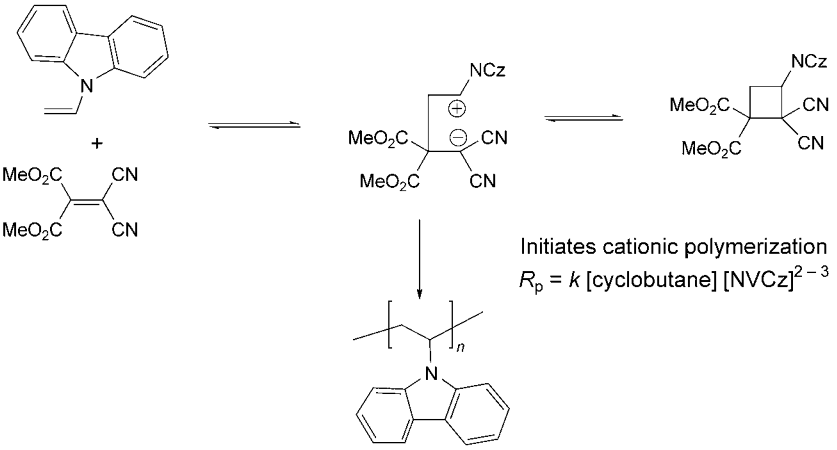
Concerted *Diels–Alder* reaction

Diradical initiates copolymerization

$R_p = k\,[M]^2$ for equal initial concentrations

Kinetics of Cationic Homopolymerization. – Completely different results were obtained in the reaction of *N*-vinyl-9*H*-carbazole with dimethyl (dicyanomethylidene)malonate (*Scheme 3*) [10]. Here, a cyclobutane was formed as the kinetically favored product. When left in solution with excess *N*-vinyl-9*H*-carbazole, it reversibly opened to the zwitterionic tetramethylene, initiating cationic homopolymerization. The observed kinetics were consistent with initiation by the zwitterionic intermediate. This reaction was very sensitive to solvent polarity.

Scheme 3



Anionic Homopolymerization. – Reaction of isobutyl vinyl ether with nitroethene gave the homopolymer of the latter, consistent with initiation of the anionic homopolymerization by a tetramethylene zwitterion [11]. In this case, inverse *Diels–Alder* reaction, allowed to be concerted, occurred competitively as well.

Correlation by an Organic-Polymer-Chemist's 'Periodic Table'. – We amassed a large body of results with varying donor and acceptor-substituted monomers. It was reasonable to attempt to correlate them. Casting about for methods to do so, we arrived back at the oldest correlation in chemistry: the Periodic Table [12]! This can be viewed as a correlation of the reaction of donor elements as ordinate with acceptor elements as abscissa. We arranged our donor–acceptor olefin results analogously. Donor character, measured by *Hammett para-σ* constants, increased down the ordinate; acceptor character, measured similarly, increased along the abscissa (*Figure*). We were pleased to discover a well-defined mechanism change, when proceeding diagonally downward from biradical (analogous to covalent) to zwitterionic (analogous to ionic) tetramethylene (T). Even further down, we encountered a change from covalent to ionic products, with outright single-electronic transfer only occurring in extreme cases. Now, we finally had predictive power. Specifying the substituents then led to prediction of approximate rates, kinetic laws, response to solvent polarity, and presence or absence of cyclobutane adducts.

In a recent remarkable and far-reaching development, *Ofial* and *Mayr* placed the 'Periodic Table' on a quantitative basis [13]. Initiation- and propagation-rate constants

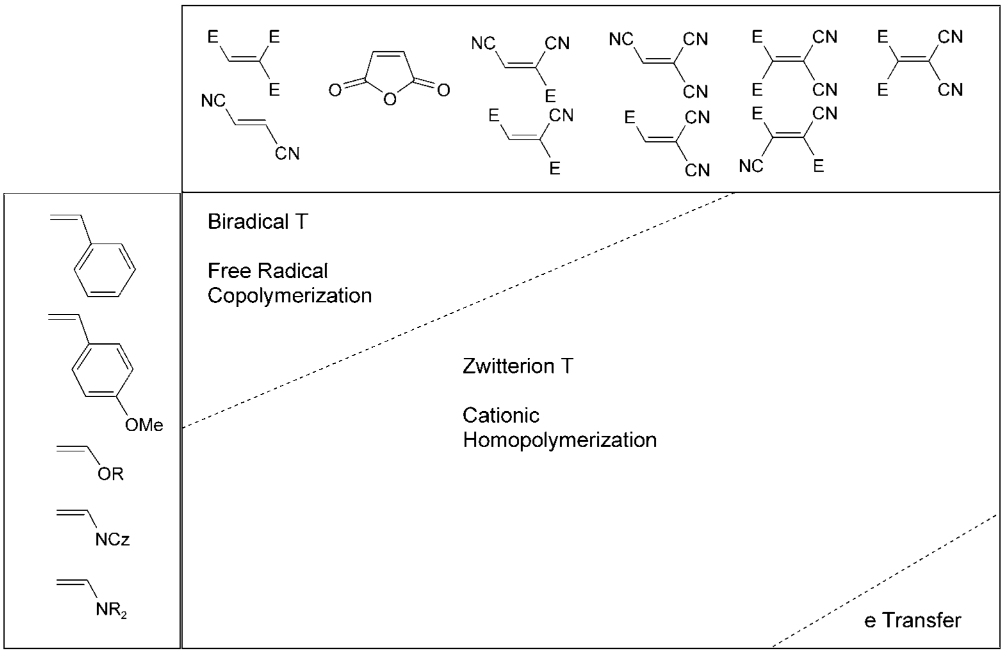


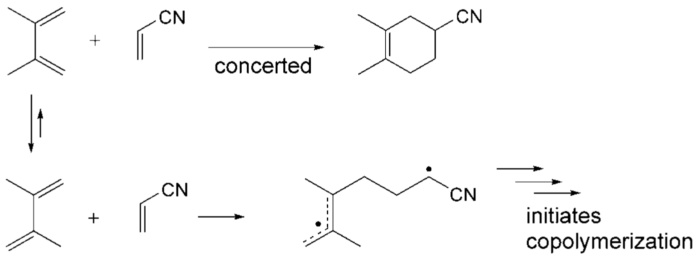
Figure. *An organic polymer chemist's 'Periodic Table'.* T = Tetramethylene intermediate.

of carbocationic and carbanionic polymerizations could be predicted by means of a quantitative scale for the electrophilicity of carbocations and electron-poor olefins, and the nucleophilicity of carbanions and electron-rich olefins. *Bond-forming initiation* mechanistically bridges carbocationic and carbanionic polymerizations.

Diene–Dienophile Reactions. – *Huisgen* and his colleagues made another important contribution to organic polymer chemistry. The classic rules of *Woodward* and *Hoffman* postulate that the $[\pi 4_s + \pi 2_s]$ *Diels–Alder* cycloaddition is completely concerted. *Huisgen* and co-workers painstakingly subjected various *Diels–Alder* reactions to scrupulous examination, and provided experimental confirmation that the reaction was indeed concerted [14]. The classical physical-organic test of stereochemistry preservation, insensitivity to solvent polarity, and inability to trap intermediates supported this conclusion. This demonstration of the complete concertedness of $[\pi 4_s + \pi 2_s]$ cycloadditions at first seemed at variance with sporadic literature reports of polymerizations accompanying *Diels–Alder* reactions. Free-radical inhibitors are often added by organic chemists to forestall such adventitious polymerizations. When polymerization occurs during the cycloaddition, a biradical intermediate has to exist at some point in time, and then can be intercepted by a polymerizable monomer. The amplification provided by polymerization makes this a very sensitive test. How could these results be reconciled?

Yufei Li in this laboratory meticulously examined the reaction of 2,3-dimethylbuta-1,3-diene with acrylonitrile (*Scheme 4*) [14]. Alternating copolymers always accompanied the cycloaddition in a systematic and reproducible yield, with a rate maximum at a 1:1 reactant ratio. Therefore, an intermediate must exist that initiates the free-radical copolymerization in the presence of a concerted cycloaddition. We postulated that the s-*cis*/s-*trans* conformational diene equilibrium was the key: the s-*cis* diene underwent completely concerted $[\pi4_s + \pi2_s]$ cycloaddition, while the s-*trans* diene reacted by '*bond-forming initiation*' to the polar 1,6-biradical (*Scheme 4*). The latter was responsible for initiation of the observed copolymerizations, but did not cyclize.

Scheme 4. *Competition between Concerted Diels–Alder Reaction and Initiation of Copolymerization with Dienes*



An obvious test of this concept was to use conformationally fixed dienes. In the reaction of s-*cis*-fixed cyclopentadiene with acrylonitrile, only the *Diels–Alder* adduct forms. In sharp contrast, the s-*trans*-fixed diene verbenene¹) reacted with acrylonitrile to form only copolymers [15]. Both reactions proceed *via* second-order kinetics. Similar results were obtained from the investigations of the spontaneous reactions of 2-methyl-2,4-pentadiene ('1,1-dimethylbuta-1,3diene') and of 1-methoxybuta-1,3-diene with electrophilic olefins, respectively [16][17].

Our work has been summarized in several review articles [6][12][18–20].

Conclusions. – Professor *Huisgen*'s research has played a guiding role in the two main areas of spontaneous polymerizations that we have investigated over the years [18–20]. First, in the case of the olefin–olefin systems, his description of the tetramethylene intermediate as two resonance forms, *i.e.*, zwitterionic and diradical, led to the elucidation of the observed ionic and free-radical polymerizations. The relationship of stepwise cycloadditions to spontaneous vinyl polymerizations is now clear: *A stepwise cycloaddition is a spontaneous vinyl polymerization that lacks a propagation step!* Second, in the reactions of dienes with dienophiles, *Huisgen*'s insistence on the concertedness of the *Woodward–Hoffman*-allowed reaction required the existence of another pathway, the reaction of an s-*trans* diene with an electron-poor olefin. The basic principles are the same for organic and for polymer chemistry, and they form a seamless whole.

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¹) Trivial name for 6,6-dimethyl-4-methylidenebicyclo[3.1.1]hept-2-ene.

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