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Reactivities of Carbocations and Carbanions

Dedicated to Professor *Henry K. Hall, Jr.*, on the occasion of his 80th birthday

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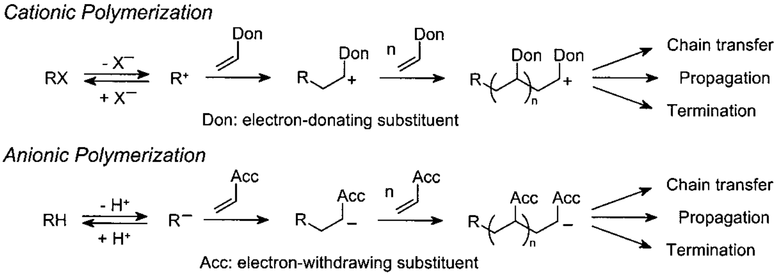
Summary: Initiation and propagation rate constants of carbocationic and carbanionic polymerizations can be predicted by the correlation equation $\log k_{20\,°\mathrm{C}} = s(N + E)$, where E characterizes the electrophilicity of carbocations and electron-deficient alkenes, and N characterizes the nucleophilicity of carbanions and electron-rich alkenes. Since the nucleophile-specific slope parameter s is generally close to 1, it can be neglected in a first approximation, and the two-dimensional representation in Figure 3 illustrates the gradual change from carbanionic to carbocationic polymerizations with Hall's "initiation by bond-formation" as the link connecting the two ranges. The value of model studies for understanding ionic polymerizations is illustrated.

Keywords: anionic polymerization; cationic polymerization; kinetics (polym.); reactivity scales; structure-reactivity relationships

Introduction

Carbocationic and carbanionic vinyl polymerizations follow closely related mechanisms (Scheme 1).[1] Initiators, which may be carbocations or carbanions, can reversibly or irreversibly be generated from alkyl halides or CH acidic compounds, respectively. In the next step, the carbocations add to electron-rich "nucleophilic" vinyl monomers while carbanions attack electron-deficient "electrophilic" vinyl monomers. In both cases



Scheme 1. Mechanisms of cationic and anionic polymerizations of vinyl monomers.

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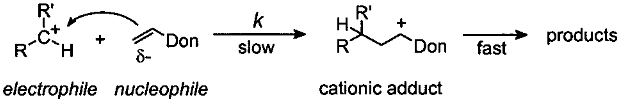
propagating ions are generated which may exist in equilibrium with dormant species. Chain transfer and termination processes compete with the propagation step and thus determine the molecular weight.[1]

In previous conferences of this series, we have reported about the kinetics of the reactions of carbocations with π-systems (Scheme 2).[2, 3]



Scheme 2. Reactions of π-nucleophiles with cationic electrophiles.

We have shown that the rates of the reactions of carbocations with alkenes, arenes, and other π-nucleophiles can be calculated by the equation

$$\log k_{20°\mathrm{C}} = s(N + E) \qquad (1)$$

where E represents the electrophilicity of the carbocations, N represents the nucleophilicity of the π-systems, and s (usually close to 1) is a nucleophile-specific slope parameter.[4–6] If very bulky systems, like tritylium ions, are excluded, equation 1 reproduces rate constants with an accuracy better than a factor of 10–10^2; this deviation includes ordinary steric, solvent, and counterion effects.

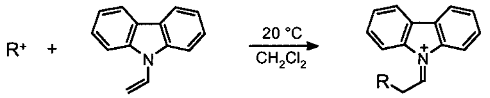
By using benzhydrylium ions as reference electrophiles,[5] we have derived the nucleophilicity parameters of a large variety of π-systems, which have been summarized in a recent review.[6] A small collection of data is summarized in Scheme 3 which allows one to directly compare the nucleophilicities of olefinic and aromatic π-systems.

Electrophilicity parameters of carbocations were analogously determined from the kinetics of their reactions with π-systems,[6] which have been defined as reference nucleophiles in 2001.[5] Scheme 4 shows the electrophilicity parameters of some carbocations determined in this way.

Carbocationic Vinyl Polymerizations

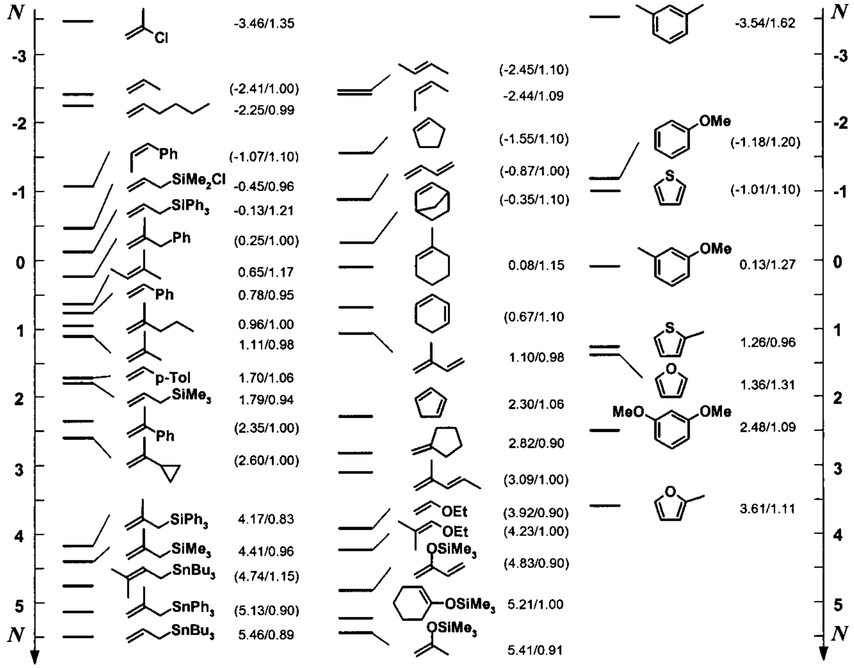
The E parameters of eventual inititators in Scheme 4 and the N parameters of eventual monomers in Scheme 3 can be combined to predict initiation rate constants. If the E

parameters of the propagating species and the *N* parameters of the monomers are available, one can also predict propagation rate constants, as shown for the cationic polymerization of *N*-vinylcarbazole.[7]

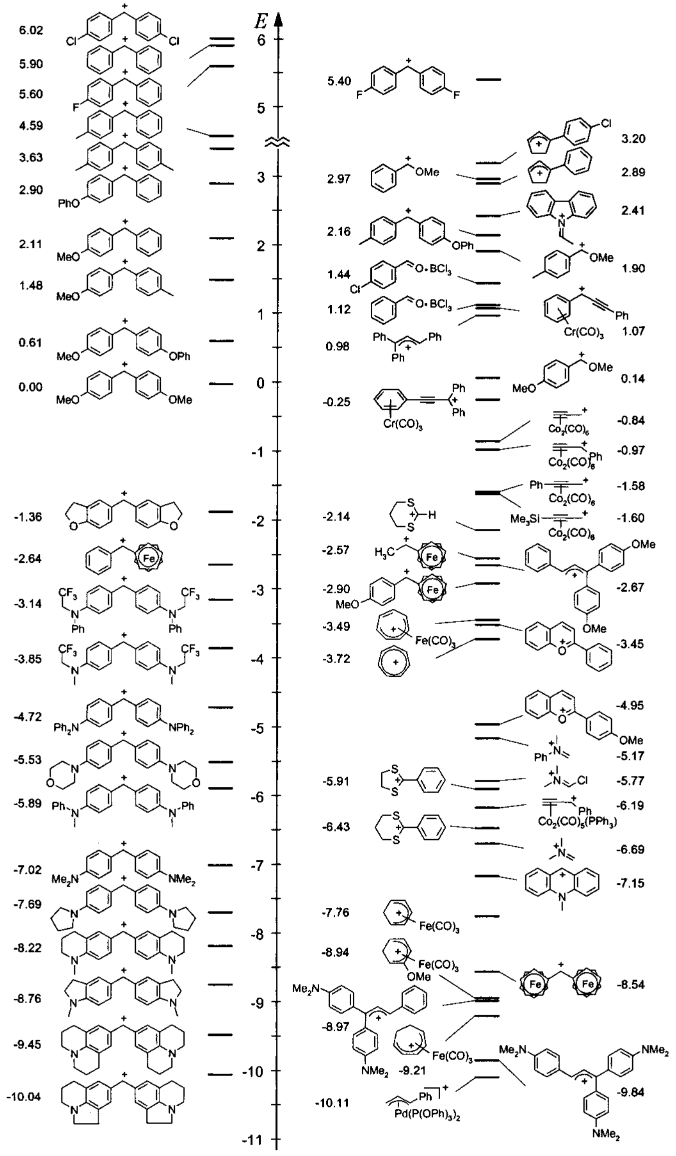


(2)

Equation 2 shows the initiation of the polymerization of *N*-vinylcarbazole by the carbocation R^+. Knowledge of *N* and *s* for *N*-vinylcarbazole would therefore allow the prediction of the rate constants of the reactions of *N*-vinylcarbazole with any carbocations R^+ of known *E* parameters. If R^+ is the propagating cation, equation 2 corresponds to the propagation step.

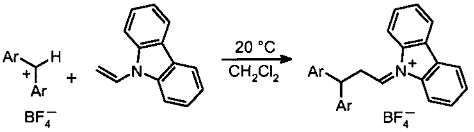


Scheme 3. Nucleophilicity and slope parameters *N*/*s* for π-nucleophiles (parentheses indicate estimated values of *s*).[6]



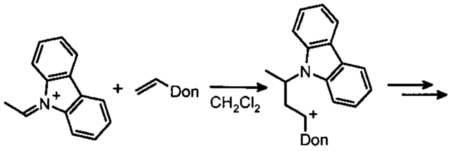
Scheme 4. Electrophilicity parameters *E* for carbocationic electrophiles derived from reactions with reference π-nucleophiles.[6]

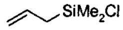
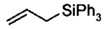
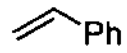
Determination of the nucleophilicity parameters of N-vinylcarbazole:



Ar	*E*	k / M^{-1} s^{-1}
p-(Ph_2N)-C_6H_4	-4.72	1.93
p-(Me_2N)-C_6H_4	-7.02	1.35×10^{-2}

Determination of the electrophilicity parameter of the propagating species:



nucleophile	*N*	*s*	k(20°C) / M^{-1} s^{-1}
	-0.45	0.96	197
	-0.13	1.21	500
	0.78	0.95	475

Scheme 5. Model reactions for the prediction of rate constants relevant for the carbocationic polymerization of *N*-vinylcarbazole.[7]

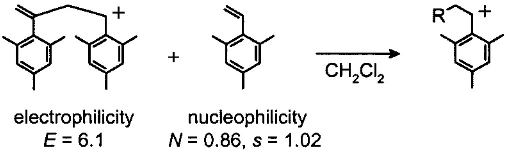
As shown in Scheme 5, the kinetics of the reactions of *N*-vinylcarbazole with benzhydryl cations Ar_2CH^+ have been investigated in order to determine the nucleophilicity parameters *N* and *s* of *N*-vinylcarbazole ($N = 5.02$, $s = 0.94$). The *N*-ethylidenecarbazolium ion has been used as a model for the cationically propagating *N*-vinylcarbazole chain (Scheme 5). From the rate constants of its reactions with three reference π-nucleophiles an electrophilicity parameter $E = 2.41$ has been derived.[7]

With equation 1, a rate constant of $k(20\ °C) = 9.6 \times 10^6\ M^{-1}\ s^{-1}$ can be calculated for the reaction of the *N*-ethylidenecarbazolium ion with *N*-vinylcarbazole which can be considered to be close to the propagation rate constant k_p for the cationic polymerization of *N*-vinylcarbazole. Comparison with the values determined calorimetrically[8–10] in polymerization experiments at 0 and 20 °C[9, 10] indicates agreement within a factor of 10^2, the error limit postulated for predictions of rate constants by equation 1. The consistency obtained for this propagation rate constant by completely different methods (Table 1) confirms the fidelity of the rate constant as well as the validity of the different methods used for its determination.

Table 1. Propagation rate constants k_p (in CH_2Cl_2) for the cationic polymerization of *N*-vinylcarbazole.

laboratories	methods	k_p / M^{-1} s^{-1}	*T* / °C	ref.
Rooney	calorimetry	$(1.0 ... 2.4) \times 10^4$	-40	8
Ledwith et al.	calorimetry	$(2.2 ... 4.6) \times 10^5$	0	9
Rodriguez & León	calorimetry	9.5×10^5	20	10
Mayr et al.	linear free energy relationship (equation 1)	9.6×10^6	20	7

In an earlier contribution to this conference, J.-P. Vairon compared the propagation rate constants for the carbocationic polymerization of 2,4,6-trimethylstyrene determined by different methods.[11, 12] This system polymerizes via stabilized benzyl cations and cannot undergo indanic cyclizations, and the directly measured k_p values are in perfect agreement with those determined by the competition method by Faust.[13] They deviate by less than a factor of 10^2 from the value calculated by equation 1[14] (Scheme 6).



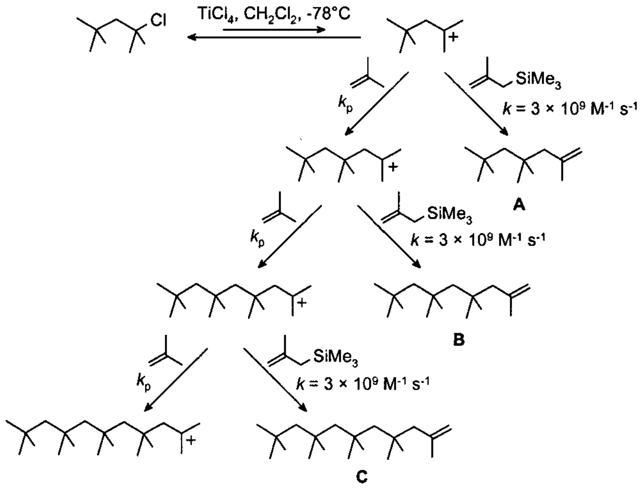
laboratories	methods	$k_p(20°C)$ / M^{-1} s^{-1}
Vairon et al.	polymerization (ln $[M_0]/[M]$) vs t)	3.5×10^5 [a]
Faust et al.	competitive capping	5.9×10^5 [a]
Mayr et al.	linear free energy relationship (equation 1)	1.3×10^7

[a] Extrapolated from rate constants at –70 °C.

Scheme 6. Reactivity parameters for the cationic polymerization of 2,4,6-trimethylstyrene.

While equation 1 is an excellent tool for predicting the approximate magnitude of the rate constants of any initiation and propagation reaction as well as of the relative reactivities of vinyl monomers in copolymerization reactions within an accuracy of factor 10–100, in many cases more precise values are needed.

For that purpose we have introduced the diffusion clock method in 1995[15] which has the additional advantage that it avoids the generation of persistent carbocations. This method, which is a modification of the azide clock method by Richard and Jencks,[16] determines the degree of oligomerization of a vinyl monomer in the presence of a trapping agent, which reacts with diffusion control. Scheme 7 illustrates the 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ initiated oligomerization of isobutylene in the presence of trimethyl(2-methylallyl)silane. The transient *tert.*-alkyl cations $R\text{-}CH_2\text{-}C(CH_3)_2^+$ either propagate by reaction with isobutylene or are irreversibly trapped by the diffusion-controlled reaction with the organosilicon compound. Since diffusion controlled rate constants are known to be in the order of $(3 \pm 1) \times 10^9$ M^{-1} s^{-1} in typical organic solvents,[17] the ratio **A**:**B**:**C** allows one to calculate a propagation rate constant of $k_p = 6 \times 10^8$ M^{-1} s^{-1} for the cationic polymerization of isobutylene.[18]



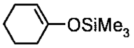
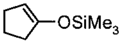
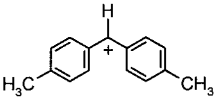
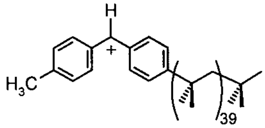
Scheme 7. Determination of the propagation rate constant k_p in the cationic polymerization of isobutylene by the diffusion clock method.[18]

Though this value is in good agreement with kinetic models by Puskas,[19] and the diffusion clock method has successfully been employed for other cationic vinyl polymerizations by Faust,[13, 20] the reliability of our approach has been questioned, because the rate constant determined by us was considerably larger than previously accepted values.[21, 22]

Previously, it had already been shown that the rates of attack of carbocations at π-nucleophiles are independent of the complex counterions,[6] and recent UV-Vis and NMR investigations allowed us to conclude that free and paired carbocations with closely similar spectroscopic properties also exhibit similar reactivities.[23, 24] Finally, different reactivities of low molecular weight and polymeric carbocations had to be excluded.

In a trinational collaboration it was recently shown that structurally analogous carbocations with M = 195 g mol^{-1} and $M_n \approx 2400$ g mol^{-1} exhibit the same reactivities towards weak nucleophiles (slow reactions) as well as towards strong nucleophiles (fast reactions) as illustrated in Table 2.[25] In this way, it has unequivocally been demonstrated that the conclusions derived from low-molecular weight model compounds can directly be transferred to polymerizing systems.[26]

Table 2. Rate constants ($M^{-1}\ s^{-1}$) for the reactions of benzhydrylium ions with π-systems.[25]

electrophiles	nucleophiles			
				
	25.6[a]	385[a]	1.60×10^{8} [b]	4.62×10^{8} [b]
 39	24.6[a]	391[a]	1.26×10^{8} [b]	3.56×10^{8} [b]

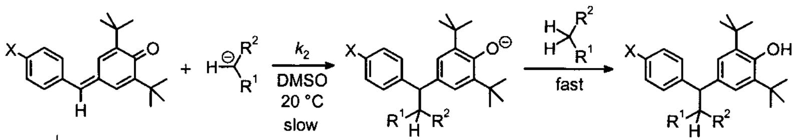
[a] Conventional UV-vis kinetic measurements in dichloromethane at −70 °C.
[b] Laser flash kinetics in acetonitrile/dichloromethane mixtures (1:3, v/v) at 20 °C.

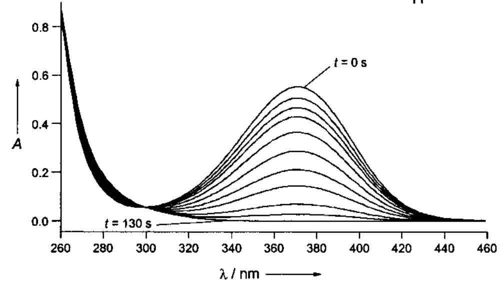
Anionic Vinyl Polymerizations

Recently, we have shown that simple second-order kinetics can also be observed for the additions of stabilized carbanions to acceptor substituted ethylene derivatives.[27] When quinone methides, structural analogues of the previously investigated benzhydrylium ions, were used as reference electrophiles, rate determining CC-bond formation by addition of the carbanions $R^1R^2CH^-$ to the electron deficient CC-double bond could be achieved in the presence of an excess of its conjugate acid $R^1R^2CH_2$ which almost quantitatively protonates phenolates in DMSO (Scheme 8).

The high dielectric constant $\varepsilon = 46.45$ of DMSO[28] is responsible for the fact that in 10^{-4} to 10^{-3} M solutions ion-pairing is unimportant as indicated by the equal reactivities of potassium and tetrabutylammonium salts and the independence of the rate constants of the presence of crown ethers or cryptands (Scheme 8).[27]

Since we have also succeeded to directly measure the rates of the reactions of stabilized carbanions with stabilized benzhydrylium ions in DMSO,[29] it was feasible to link the two sets of data: Carbocations + neutral nucleophiles on one side and carbanions + neutral electrophiles on the other side. As shown by Figure 1, there is no noticeable break in the linear correlations as the solvent is changed from dichloromethane on the left of Figure 1 to DMSO on the right. It thus became possible to develop a single nucleophilicity scale ranging from toluene, the weakest nucleophile in the series to nitroethyl anion, the strongest





Counterion	k / M^{-1} s^{-1}
K^+	335 ± 8
K^+ / 18-crown-6	325 ± 9
K^+ / cryptofix 222	329 ± 7
NBu_4^+	349 ± 5

Scheme 8. Irreversible reactions of quinone methides with carbanions $R^1R^2CH^-$ in the presence of the conjugate CH acid $R^1R^2CH_2$. The UV-vis spectra and the rate constants refer to the reaction with X = CH_3, R^1 = CO_2Et, and R^2 = CN.[27]

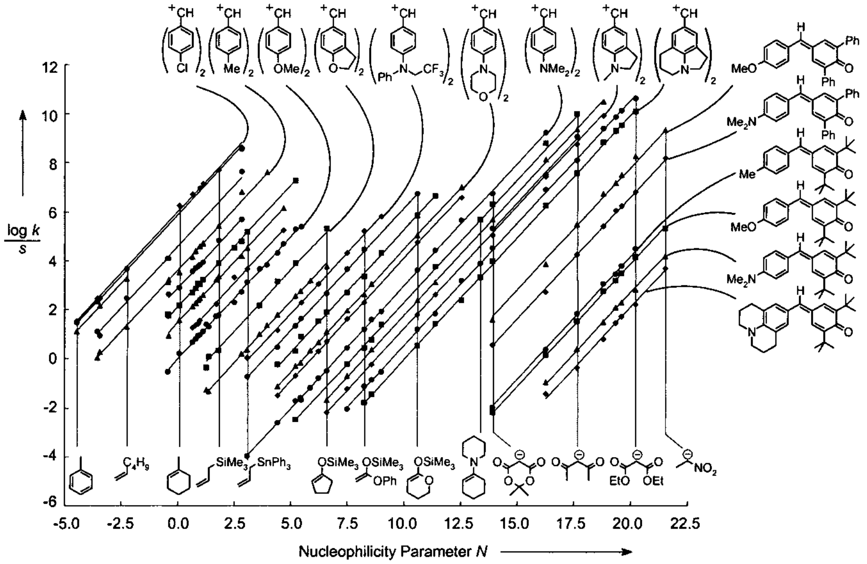


Figure 1. Plot of (log k)/s versus the nucleophilicity parameter N for the reactions of benzhydryl cations or quinone methides with π-nucleophiles or carbanions.[29]

nucleophile. The 26 orders of magnitude covered by these nucleophiles correspond to relative reactivities of 1 min to 10^{20} years.

For the parametrization, the electrophilicity parameters E according to equation 1 have been defined as solvent-independent quantities. Extensive investigations of the solvent dependence of the kinetics have shown that the rates of the reactions of carbocations with neutral π-systems and hydride donors are almost independent of the solvent.[4c, 6, 30, 31] Since the nucleophilicities of amines, alcohols, and carbanions are strongly affected by the solvents,[32–34] their N parameters have to be specified with respect to a certain solvent.

The reactivity parameters N and s derived from the reactions of the corresponding nucleophiles with benzhydrylium ions and structurally analogous quinone methides can only be considered as useful parameters if they are also applicable to reactions with other types of electrophiles. This has repeatedly been demonstrated for other types of carbocations[4–6] and recently also for neutral Michael acceptors. Figure 2 shows that the relative reactivities of carbanions which have been observed versus benzhydrylium ions and quinone methides are also observed with respect to arylidenemalodinitriles.[35]

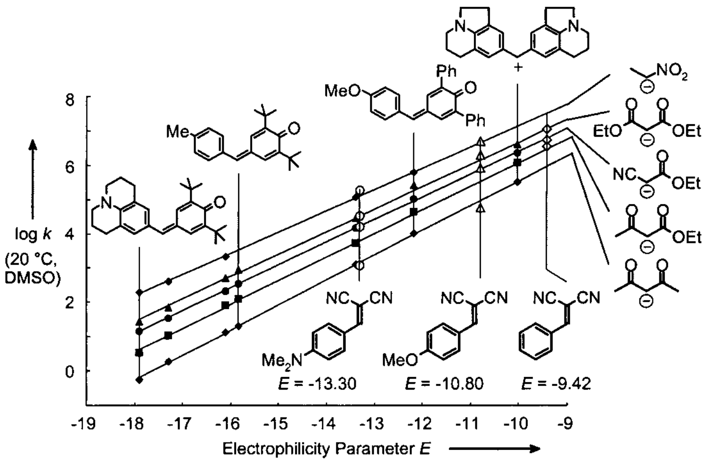


Figure 2. Determination of the electrophilicity parameters E of benzylidenemalodinitriles.[35]

While Figures 1 and 2 show that initiation and propagation rate constants of carbanionic polymerizations can also be predicted by equation 1 if ion-pairing is avoided, this approach can definitely not be employed for analyzing alkyllithium initiated polymerizations of styrenes, dienes, etc. which do not proceed via free carbanions. In these cases, the dependence of the spectral properties of the organometallics on metal, solvent, and concentration is also reflected by the different reactivities.[1]

A Framework for Describing Reactivities of Carbocations and Carbanions

Since the s parameters of π-nucleophiles, which correspond to the slopes of log k vs E correlations (e.g., in Figure 2), are generally close to 1,[6] an alternative representation of electrophile nucleophile combinations becomes possible. In Figure 3, nucleophiles are ordered according to increasing N parameters from top to bottom, and electrophiles are arranged according to increasing reactivity from left to right. The diagonal from bottom left to top right corresponds to $E + N = 0$ which implies a rate constant of 1 M^{-1} s^{-1} according to Equation 1. Starting from this diagonal, one can move upwards (towards weaker nucleophiles) or left (towards weaker electrophiles) and arrive in the sector where electrophile nucleophile combinations are predicted to be so slow that reactions cannot be expected. Moving from this diagonal downwards or to the right one gets into the diffusion controlled sector where selectivities often become low. We have discussed that most synthetically used organic reactions are found in the activation controlled corridor jacketing the drawn diagonal ($10^{-6} < k < 10^{10}$ M^{-1} s^{-1}).[29]

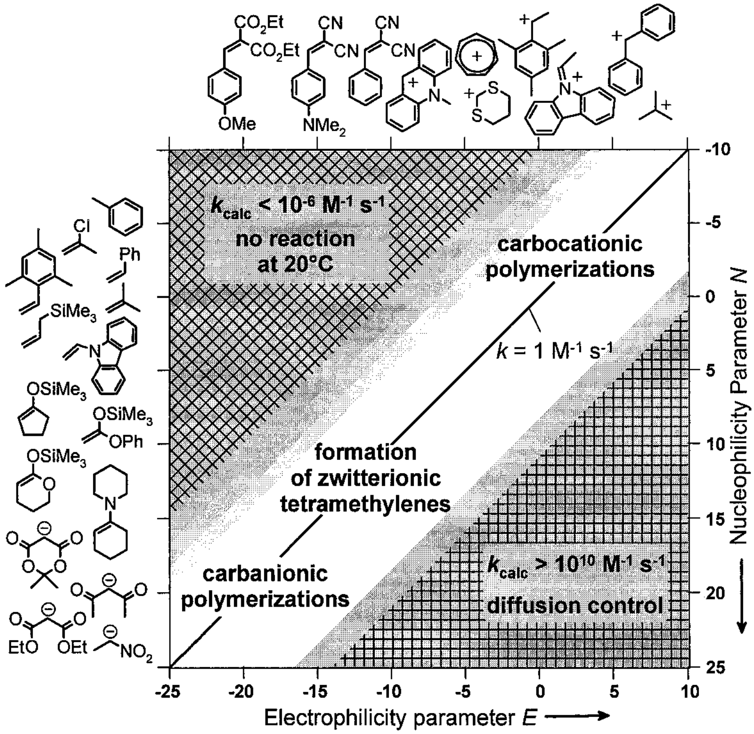
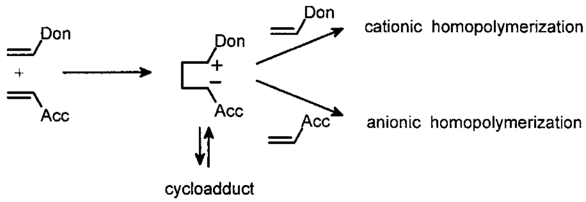


Figure 3. The continuum of ionic polymerizations.

Applying this model to ionic vinyl polymerizations, one can see that carbocationic polymerizations are found in the upper right part of this corridor while carbanionic polymerizations are found in the lower left part. In the center of this diagram, one can find strong neutral nucleophiles and strong neutral electrophiles, which are predicted by Equation 1 to give 1,4-zwitterions with reasonable rates.

Twenty years ago, H. K. Hall Jr. summarized polymerizations of alkenes initiated by bond formations (Scheme 9).[36] Using chemical experience, the reactivities of alkenes have been arranged in the form of a periodic table.[36a, 36b] Thus, Figure 4 arranges nucleophilic alkenes according to increasing donor ability from top to bottom; electrophilic alkenes are arranged from left to right with increasing acceptor ability.



Scheme 9. Initiation of cationic and anionic homopolymerizations by bond formation according to Hall.[36]

Strong donors (on the bottom) spontaneously react with strong acceptors (on the right) to yield zwitterionic tetramethylenes which then are able to act as initiators for the homopolymerization of the corresponding olefins (Scheme 9).[36]

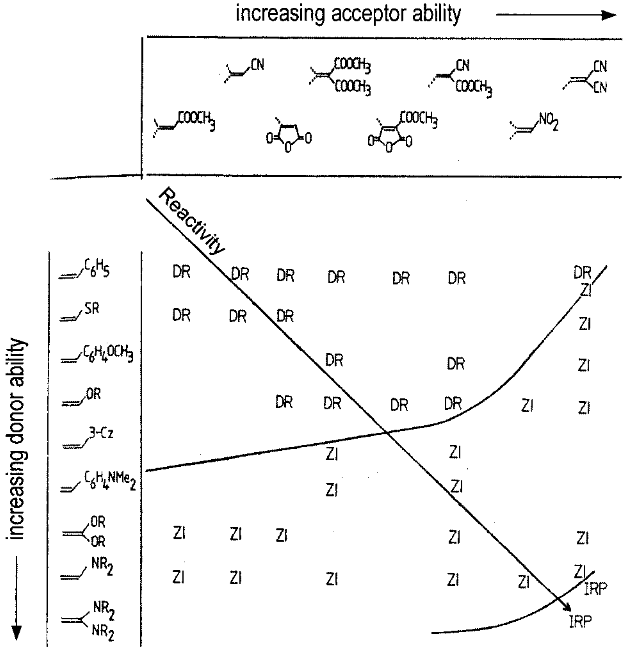


Figure 4. The sector of Hall's "periodic table of alkenes" where mechanistic changes are observed on variation of the donor and/or acceptor ability of the alkenes (DR: diradical formation, ZI: zwitterion formation, IRP: ion-radical pair formation).[36a, 36b]

Initiation by bond formation as proposed by Hall thus is the link between carbocation and carbanion initiated polymerizations,[36] and our electrophilicity and nucleophilicity scales[5, 6, 29] provide the quantitative basis for Hall's concept. In recent work we have shown that the whole range of polar organic reactions, from Friedel-Crafts alkylations (typical acid catalyzed reactions) to Michael additions (typical base catalyzed reactions) can be described by a single set of reactivity parameters.[29] We now demonstrated that the same concept can also be employed for ordering ionic polymerizations.

Acknowledgement

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