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Initiation and Propagation Rate Constants for the Cationic Polymerization of *N*-Vinylcarbazole

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ABSTRACT: The kinetics of the reactions of benzhydryl cations with *N*-vinylcarbazole (**1**) and of the reactions of the *N*-ethylidenecarbazolium ion (**6**) with π-nucleophiles have been investigated to determine the nucleophilicity parameters *N* and *s* for **1** and the electrophilicity parameter *E* for **6**. These values were employed to predict potential initiators for the cationic polymerization of *N*-vinylcarbazole (**1**) and to calculate the propagation rate constant for this process.

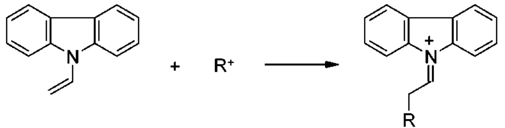
Introduction

Poly(*N*-vinylcarbazole) has attracted large interest because of its unique properties as dielectric material and photoconductor.[1] Recently, poly(*N*-vinylcarbazole) composites have been reported to show large photorefractivity[2] and electrochromic properties.[3] Among the various methods used for the polymerization of *N*-vinylcarbazole,[1] carbocationic polymerization is of particular importance.[4,5] In this study, we have investigated kinetic aspects of this process.

Extensive investigations have shown that the rates of the reactions of carbocations with π-systems can be calculated by eq 1, where *E* represents the electrophilicity parameter of the carbocations, and *N* and *s* represent the nucleophilicity and slope parameter of the π-systems, respectively.[6−9]

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

Since the charge distribution is only slightly altered during the course of ion−molecule reactions, solvent polarity has been observed to affect the rate constants only slightly.[6,10] Recently, the potential of eq 1 to derive rate constants relevant for carbocationic polymerizations has been summarized.[11]



1

(2)

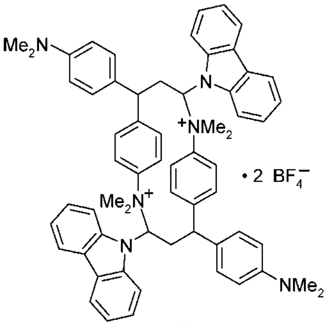
Equation 2 represents the initiation of the *N*-vinylcarbazole polymerization by the carbocation R^+. Knowledge of *N* and *s* for the monomer **1** would therefore allow the prediction of initiation rate constants by carbocations R^+ of known *E* parameters. If R^+ is the propagating cation, eq 2 corresponds to the propagation step. For the calculation of the propagation rate constants k_p, knowledge of the electrophilicity *E* of the propagating species is additionally needed.

Characterization of the Nucleophilic Properties of *N*-Vinylcarbazole

Benzhydryl cations have preferentially been used as reference electrophiles to determine the reactivity parameters *N* and *s* of π-systems.[9] Consequently, we have now employed the reactions with the benzhydryl cations **2a** and **2b** for characterizing the reactivity parameters *N* and *s* of *N*-vinylcarbazole (**1**) because the rate constants of these carbon−carbon bond-forming reactions are in a range that can easily be followed with our equipment (Scheme 1).

Since the cations **3a,b** can be expected to possess similar electrophilicity parameters as the *N*-ethylidenecarbazolium ion **6** ($E = 2.41$, see below), it is not surprising that the reaction of **2a** ($E = -4.72$)[9] with **1** does not terminate at the 1:1 product stage (**3a**). The iminium ion **3a** is more electrophilic than **2a**, and its reaction with the monomer **1** is faster than its formation from **2a** and **1**. As a consequence, *N*-vinylcarbazole (**1**) polymerizes while only a small percentage of the initiator **2a** is consumed.

Since the electrophilicity of **2b** ($E = -7.02$)[9] is even lower than that of **2a**, an analogous result was expected, and it was astonishing that the reaction of **2b** with **1** terminated at the 1:1 product stage **3b**. To account for the slow consecutive reaction of **3b** with **1** in dichloromethane, one has to postulate that the cation **3b** experiences some type of additional stabilization, e.g., by forming the dimer **5**. Because of the lower basicity of the triarylamino group, the absence of an analogous stabilization of **3a** may be explained. It should be emphasized, however, that there is not any proof for the intermediacy of **5**, and alternative explanations for the isolability of **3b** have to be considered.



5

A different behavior of **2a** and **2b** was also observed in the kinetic experiments, which were performed under pseudo-first-order conditions with 10−300 equiv of **1** with respect to **2**. While the decay of **2b**, which was

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Scheme 1

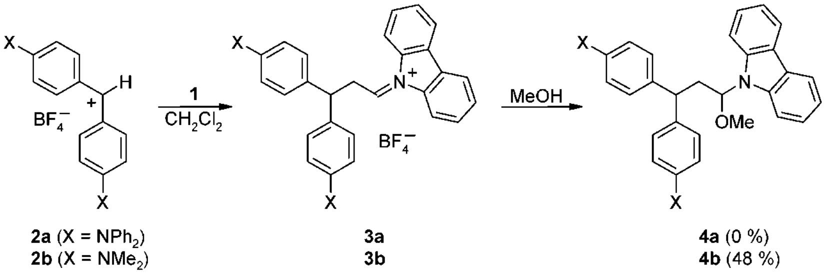


Table 1. Rate Constants for the Reactions of 1 with the Benzhydrylium Tetrafluoroborates 2a,b (in CH_2Cl_2, at 20 °C)

electrophile	*E*	*k*, L mol^{-1} s^{-1}	log *k*
2a	-4.72^a	1.93 ± 0.22	0.286
2b	-7.02^a	$(1.35 \pm 0.03) \times 10^{-2}$	-1.87

[a] From ref 9.

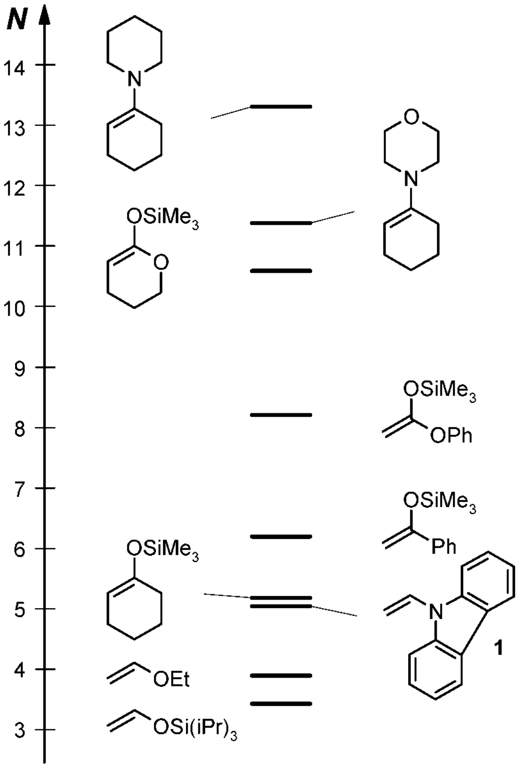


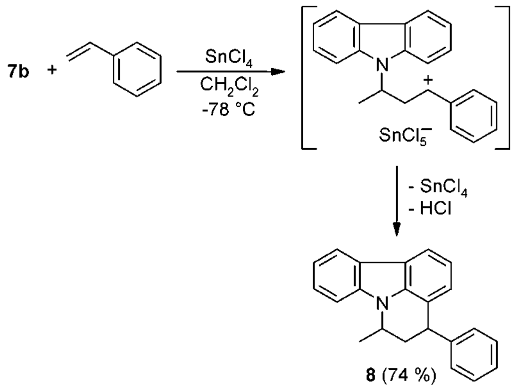
Figure 1. Comparison of the nucleophilicity of *N*-vinylcarbazole (**1**) with that of other π-systems.[6,9]

monitored photometrically, followed pseudo-first-order kinetics over more than 50% conversion, only the initial period of the reaction of **1** with **2a** (5–17%) could be evaluated for determining the rate constants (Table 1). Substitution of the values given in Table 1 into eq 1 yields $N(\mathbf{1}) = 5.02$ and $s(\mathbf{1}) = 0.94$.

As observed for other substituted ethylenes,[6,9] including enol ethers,[12] the slope parameter *s* closely resembles unity. The nucleophilicity of **1** ($N = 5.02$) is somewhat higher than that of alkoxy-substituted ethylenes but considerably lower than that of ordinary enamines (Figure 1). Since the lone pair of the nitrogen is part of the aromatic π-system of carbazole, it does not increase the electron density at the ethylenic π-bond to a similar extent as in ordinary enamines.

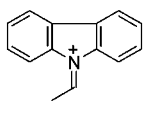
With the *N* and *s* parameters of **1** given above, one can now derive potential initiating systems. Let us consider a second-order rate constant of 10^{-2} L mol^{-1} s^{-1} at −70 °C, corresponding to a half-life of 1 min (for $[\mathbf{1}]_0 = 1$ mol L^{-1}), to be the lower limit for a fast initiation reaction. Assuming a typical activation entropy of $\Delta S^{\ddagger} = -100$ J mol^{-1} K^{-1},[9] this value corresponds to $k = 11.1$ L mol^{-1} s^{-1} at +20 °C. This rate constant can be expected for the reaction of **1** with a carbocation of $E = -3.9$ according to eq 1. Consequently, carbocations with $E > -4$ can be expected to initiate the polymerization of *N*-vinylcarbazole at −70 °C.

Scheme 2

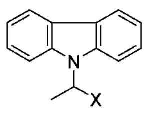


Characterization of the Electrophilicity of the *N*-Ethylidenecarbazolium Ion (6)

In contrast to other iminium ions,[13] the *N*-ethylidenecarbazolium ion (**6**), which is considered as a model for the cationically propagating chain of poly(*N*-vinylcarbazole), could not be isolated as a salt at room temperature. Treatment of a solution of **7a**[14] in diethyl ether with trimethylsilyl triflate (TMSOTf) at room temperature yielded poorly soluble blue precipitates. Since decolorization of the inhomogeneous mixture takes place when treated with methanol or with 1-methoxy-2-methyl-1-(trimethylsiloxy)propene, these precipitates are probably salts of organic cations, but we did not succeed in isolating properly defined products under these conditions.



6



7a (X = OMe)
7b (X = OAc)

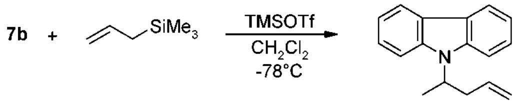
Solutions of **6** were accessible, however, when **7b**[15] was treated with $SnCl_4$ in dichloromethane at −70 to −30 °C. Successive addition of styrene gave the cyclized product **8** (Scheme 2).[16] Purification by column chromatography yielded a single diastereoisomer, the stereochemistry of which has not been elucidated.

Table 2. Activation Parameters and Rate Constants for the Reactions of the Ethylidenecarbazolium Ion (6) with π-Nucleophiles (in CH_2Cl_2, 20 °C)

nucleophile	N	s	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J mol^{-1} K^{-1}	k, L mol^{-1} s^{-1}	log k	E_{calc}
allylchlorodimethylsilane	-0.45^a	0.96^a	23.5 ± 1.6	-120.9 ± 7.2	197	2.29	2.84
allyltriphenylsilane	-0.13^a	1.21^a	33.2 ± 0.4	-79.8 ± 2.0	500	2.70	2.36
styrene	0.78^a	0.95^a	31.4 ± 0.9	-86.5 ± 4.1	475	2.68	2.04
							$E(\mathbf{6})^b = 2.41$

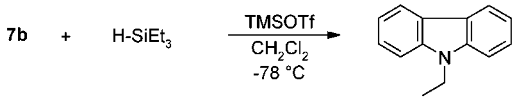
[a] From ref 9. [b] $E(\mathbf{6})$ was obtained by minimizing $\Delta^2 = \Sigma(\log k_i - s_i(E + N_i))^2$.

Analogous reactions of **7b** with trimethylsilyl triflate and allyltrimethylsilane (eq 3) or triethylsilane (eq 4) gave the carbazole derivatives **9** and **10**, respectively. Cyclopentene and 1,4-cyclohexadiene did not react under these conditions, as indicated by the isolation of carbazole, the hydrolysis product of **6** after aqueous workup.



9 (89 %)

(3)



10 (82 %)

(4)

For kinetic studies, solutions of $\mathbf{6}$-$SnCl_5^-$ or $\mathbf{6}$-BCl_4^- were treated with allylchlorodimethylsilane, allyltriphenylsilane, or styrene. Covalent products were formed, and the rates of the reactions could be followed by conductometry as described previously.[10] All reactions were studied under pseudo-first-order conditions (10−50 equiv of π-nucleophile). The observation of well-behaved Eyring plots (see Experimental Section) from experiments with different nucleophile concentrations proves the operation of a second-order rate law. The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ derived from experiments in the range of −70 to −30 °C allow us to calculate k(20 °C) values as shown in Table 2.

The N, s, and k values listed in Table 2 can be substituted into eq 1 to yield the E parameter for the cation **6** (Table 2, right column). The close similarity of E_{calc}, obtained from reactions with different nucleophiles, indicates that eq 1 is applicable to these reactions and that the electrophilicity of **6** is well represented by $E(\mathbf{6}) = 2.41$. The reliability of this E parameter is further corroborated by the observation that the rate constant observed for the reaction of **6** with triphenylsilane ($\Delta H^\ddagger = 33.8$ kJ mol^{-1}, $\Delta S^\ddagger = -71.7$ J mol^{-1} K^{-1}, k(20 °C) $= 1040$ L mol^{-1} s^{-1}) is almost identical to $k = 1095$ L mol^{-1} s^{-1} calculated from eq 1 with $E(\mathbf{6}) = 2.41$, $N(HSiPh_3) = 2.06$,[9] and $s(HSiPh_3) = 0.68$.[9]

As shown in Figure 2, **6** is a considerably stronger electrophile than the N-methyl-N-phenylmethyleneammonium ion (**11**), the Vilsmeier ion (**12**), or the N,N-dimethylmethyleneammonium ion (**13**).[17] It is a stronger electrophile than the tropylium or the dianisylcarbenium ion, comparable to the methoxy(p-tolyl)carbenium ion.[9] The same factors that reduce the nucleophilicity of N-vinylcarbazole (**1**) relative to ordinary enamines also operate to increase the electrophilicity of **6** with respect to typical iminium ions.[17,18]

The high electrophilicity of **6** implies that propagation is faster than initiation when carbocation salts with E < 2 are used as initiators. In such cases, controlled polymerization (i.e., initiation faster than propagation) can only be achieved if conditions of incomplete ionization are employed.[11]

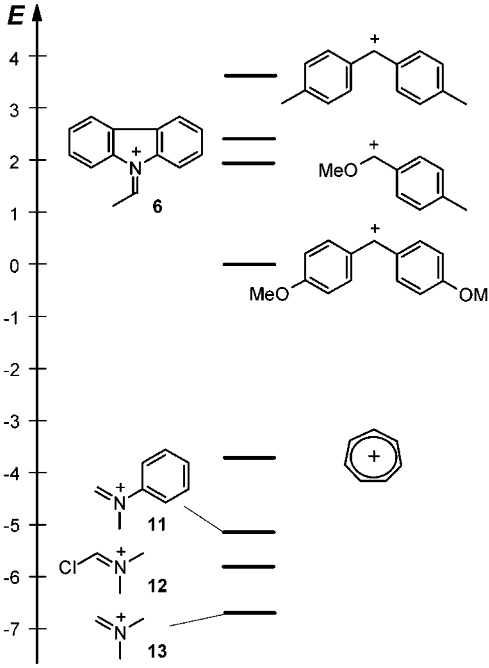


Figure 2. Comparison of the electrophilicity of the N-ethylidenecarbazolium ion (**6**) with that of other carbocations.

Table 3. Propagation Rate Constants k_p for the Cationic Polymerization of N-Vinylcarbazole (1) Determined by Calorimetry (in Dichloromethane)

author	k_p, L mol^{-1} s^{-1}	T, °C	ref
Rooney	$(1.0-2.4) \times 10^4$	−40	19
Ledwith et al.	$(2.2-4.6) \times 10^5$	0	20
Leon and Rodriguez	9.5×10^5	20	21

Propagation Rate Constant for N-Vinylcarbazole Polymerization

Equation 1 can now be used to calculate $k = 1 \times 10^7$ L mol^{-1} s^{-1} (20 °C) for the reaction of **6** ($E = 2.41$) with N-vinylcarbazole **1** ($N = 5.02$, $s = 0.94$). Since **6** is a model for the cationically propagating N-vinylcarbazole chain, this rate constant can be considered to reflect the propagation rate constant k_p for the cationic polymerization of **1**. Comparison with the values determined calorimetrically[19−21] in polymerization experiments at 0 and 20 °C[20,21] (Table 3, entries 2 and 3) indicates agreement within a factor of 10^2, the error limit postulated for predictions of rate constants by eq 1.[9] The consistency obtained for this propagation rate constant by completely different methods confirms the fidelity of the rate constant as well as the validity of the different methods used for its determination.

Table 4. Rate Constants for the Reactions of 1 with the Benzhydrylium Tetrafluoroborates 2a,b (in CH_2Cl_2, 20 °C)

electrophile	[**2**]$_0$, mol L^{-1}	[**1**]$_0$, mol L^{-1}	conv, %	k_2, L mol^{-1} s^{-1}
2a	5.54×10^{-5}	5.90×10^{-4}	5	1.92
	2.96×10^{-5}	6.32×10^{-3}	10	2.04
	5.86×10^{-5}	6.25×10^{-3}	8	2.04
	3.09×10^{-5}	4.13×10^{-3}	17	1.51
	5.06×10^{-5}	1.69×10^{-3}	6	2.12
2b	6.62×10^{-5}	6.51×10^{-3}	54	1.37×10^{-2}
	3.19×10^{-5}	1.47×10^{-2}	55	1.31×10^{-2}
	4.02×10^{-5}	4.63×10^{-3}	45	1.38×10^{-2}

Experimental Section

General. All reactions were carried out under dry, oxygen-free nitrogen and with carefully dried solvents. ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane as internal standard (δ_H 0.00) or to the solvent signal (δ_C 77.0), respectively. DEPT-135 experiments were used to obtain information about the multiplicities of ^{13}C resonances.

***N*-(3,3-Bis(4-dimethylaminophenyl)-1-methoxyprop-1-yl)carbazole (4b).** A solution of **2b** (340 mg, 1.00 mmol) in a mixture of dichloromethane (45 mL) and methanol (0.40 mL) was prepared. Then a solution of **1** (193 mg, 1.00 mmol) in dichloromethane (2 mL) was added dropwise, and the mixture was stirred for 4 h. Aqueous ammonia (40 mL) was added, the phases were separated, and the aqueous phase was extracted with diethyl ether (20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification of the crude product by column chromatography (basic alumina, activity grade IV, eluent: toluene/dichloromethane 10:1) yielded **4b** (230 mg, 48%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.60−2.75 (m, 1 H, $^1/_2 \times CH_2$), 2.85 (s, 12 H, $2 \times NMe_2$), 2.95−3.08 (m, 1 H, $^1/_2 \times CH_2$), 3.09 (s, 3 H, OMe), 3.88 (t, $J = 7.0$ Hz, 1 H, NCH), 5.50 (t, $J = 7.0$ Hz, 1 H, Ar_2CH), 6.64−8.08 (m, 16 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.9 (t, CH_2), 40.7 (q, NMe_2), 45.1 (d, Ar_2CH), 55.7 (q, OMe), 86.1 (d, NCH), 110.1, 112.9, 119.3, 120.1 (4 d, Ar), 123.5 (s, Ar), 125.6, 128.2 (2 d, Ar), 132.7, 139.5, 149.1 (3 s, Ar). MS (70 eV): *m/z* (%) 478 (8), 477 (23) [M$^+$], 254 (20), 253 (100), 237 (14). Anal. Calcd for $C_{32}H_{35}N_3O$ (477.65): C, 80.47; H, 7.39; N, 8.80. Found: C, 80.57; H, 7.32; N, 8.81.

Compound **4b** was also isolated when the reaction of **2b** with **1** was carried out in pure dichloromethane, and methanol was added after 3 h reaction time.

6-Methyl-4-phenyl-5,6-dihydro-4*H*-pyrido[3,2,1-*jk*]carbazole (8). A solution of **7b**[15] (253 mg, 1.00 mmol) in dichloromethane (50 mL) was cooled to −78 °C, and $SnCl_4$ (521 mg, 2.00 mmol) was added. After the dropwise addition of a solution of styrene (208 mg, 2.00 mmol) in dichloromethane (5 mL), the mixture was stirred for 1 h. Then aqueous ammonia (10 mL) was added, and the mixture was filtered through Celite. The organic layer was separated, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography (neutral alumina, activity III, eluent: CH_2Cl_2) to yield **8** (220 mg, 74%) as pale yellow crystals. Only the signals of the major diastereomer are given here. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (d, $J = 6.7$ Hz, 3 H, 6-CH_3), 2.42−2.56 (m, 2 H, 5-H_2), 4.44 (t, $J = 6.0$ Hz, 1 H, 4-H), 4.63 (m$_c$, 1 H, 6-H), 6.96−7.42 (m, 10 H, ArH), 7.90−7.92, 8.06−8.08 (2 m, 2×1 H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 20.7 (q, 6-CH_3), 39.3 (t, C-5), 40.6 (d, C-4), 48.5 (d, C-6), 109.8, 118.3, 118.6, 118.9, 120.9 (5 d, Ar), 121.0, 122.6, 123.5 (3 s, Ar), 124.2, 125.3, 126.4, 128.41, 128.43 (5 d, Ar), 137.9, 139.6, 144.6 (3 s, Ar). Signal assignments are based on gHSQC and gHMBC experiments. MS (70 eV): *m/z* (%) 298 (22), 297 (100) [M$^+$], 283 (19), 282 (87), 204 (22), 167 (12). Anal. Calcd for $C_{22}H_{19}N$ (297.40): C, 88.85; H, 6.44; N, 4.71. Found: C, 88.54; H, 6.64; N, 4.43.

***N*-(Pent-4-en-2-yl)carbazole (9).** A solution of **7b**[15] (253 mg, 1.00 mmol) and allyltrimethylsilane (228 mg, 2.00 mmol) in dichloromethane (50 mL) was cooled to −78 °C. Trimethylsilyl triflate (222 mg, 1.00 mmol) was added, and the mixture was stirred at −78 °C for 1 h. Then aqueous ammonia (15 mL) was added, and the stirred mixture was allowed to warm to ambient temperature. The phases were separated, and the aqueous phase was extracted with diethyl ether (20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (neutral alumina, activity I, eluent: dichloromethane) to give **9** (210 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.58 (d, $J = 6.8$ Hz, 3 H, CH_3), 2.60−2.68, 2.86−

Table 5. Kinetics of the Reactions of Ethylidenecarbazolium Ion (6)[a] with Nucleophiles (in CH_2Cl_2, Determined Conductometrically[b])

T, °C	[**7b**]$_0$, mol L^{-1}	Lewis acid	[Lewis acid]$_0$, mol L^{-1}	[Nuc]$_0$, mol L^{-1}	conv, %	*k*, L mol^{-1} s^{-1}
			Nuc = Allylchlorodimethylsilane			
−70.4	6.68×10^{-5}	$SnCl_4$	1.35×10^{-2}	1.35×10^{-3}	41	1.75
−61.0	8.09×10^{-5}	$SnCl_4$	1.26×10^{-2}	2.51×10^{-3}	45	3.55
−50.4	6.42×10^{-5}	$SnCl_4$	1.18×10^{-2}	1.76×10^{-3}	51	8.00
−41.3	4.27×10^{-5}	$SnCl_4$	1.24×10^{-2}	1.23×10^{-3}	52	1.35×10^{1}
−30.6	5.98×10^{-5}	$SnCl_4$	1.19×10^{-2}	5.93×10^{-4}	40	1.91×10^{1}
			Nuc = Allyltriphenylsilane			
−70.0	5.50×10^{-5}	BCl_3	5.82×10^{-2}	3.59×10^{-4}	23	7.98×10^{-1}
−61.0	4.31×10^{-5}	BCl_3	3.25×10^{-2}	8.02×10^{-4}	20	2.05
−51.3	5.30×10^{-5}	BCl_3	2.81×10^{-2}	8.64×10^{-4}	40	4.86
−41.1	8.39×10^{-5}	BCl_3	5.92×10^{-2}	1.82×10^{-3}	30	1.09×10^{1}
−31.2	6.54×10^{-5}	BCl_3	5.77×10^{-2}	7.11×10^{-4}	41	2.26×10^{1}
			Nuc = Styrene			
−70.7	5.19×10^{-5}	$SnCl_4$	1.29×10^{-2}	4.49×10^{-4}	79	1.07
−60.5	8.12×10^{-5}	$SnCl_4$	1.34×10^{-2}	1.17×10^{-3}	77	2.48
−51.2	5.73×10^{-5}	$SnCl_4$	1.19×10^{-2}	8.26×10^{-4}	84	6.02
−41.5	8.25×10^{-5}	$SnCl_4$	2.56×10^{-2}	8.92×10^{-4}	90	1.15×10^{1}
−31.5	3.93×10^{-5}	$SnCl_4$	1.22×10^{-2}	4.24×10^{-4}	75	2.65×10^{1}
			Nuc = Triphenylsilane			
−70.9	6.90×10^{-5}	BCl_3	3.23×10^{-2}	2.72×10^{-4}	84	1.43
−70.8	7.34×10^{-5}	BCl_3	2.84×10^{-2}	7.70×10^{-4}	67	1.40
−60.7	3.78×10^{-5}	BCl_3	3.10×10^{-2}	9.22×10^{-4}	73	3.95
−50.9	7.67×10^{-5}	BCl_3	3.27×10^{-2}	4.58×10^{-4}	83	9.07
−41.2	6.56×10^{-5}	BCl_3	2.87×10^{-2}	5.82×10^{-4}	83	2.12×10^{1}
−31.5	4.47×10^{-5}	BCl_3	2.93×10^{-2}	4.76×10^{-4}	74	4.52×10^{1}

[a] Generated in situ by ionization of **7b** with $SnCl_4$ or BCl_3. [b] The conductometrical kinetic measurements were performed and analyzed as described in ref 10.

2.98 (2 m, 2 × 1 H, CH$_2$), 4.66−4.71 (m, 1 H, NCH), 4.79−4.96 (m, 2 H, CH=C*H*$_2$), 5.57−5.71 (m, 1 H, C*H*=CH$_2$), 7.14−7.43 (m, 6 H, ArH), 8.04−8.06 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 18.7 (q, CH$_3$), 39.1 (t, CH$_2$), 51.1 (d, NCH), 110.0 (br d, Ar), 117.3 (t, CH=*C*H$_2$), 118.6, 120.2 (2 d, Ar), 123.2 (s, Ar), 125.3 (d, Ar), 134.8 (d, *C*H=CH$_2$), 139.6 (s, Ar). MS (70 eV): *m*/*z* (%) 235 (14) [M$^+$], 195 (12), 194 (100), 167 (18).

***N*-Ethylcarbazole (10).** As described above for the formation of **9**, a mixture of **7b**[15] (253 mg, 1.00 mmol), triethylsilane (232 mg, 2.00 mmol), and trimethylsilyl triflate (222 mg, 1.00 mmol) in dichloromethane reacted to yield **10** (160 mg, 0.82 mmol, 82%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.25 (t, J = 6.0 Hz, 3 H, CH$_3$), 4.14 (q, J = 6.0 Hz, 2 H, CH$_2$), 7.14−7.38 (m, 6 H, Ar), 8.02−8.05 (m, 2 H, ArH).[22]

Kinetics. The employed methods for the kinetic measurements are described in ref 10. Colored solutions of the benzhydrylium tetrafluoroborates **2a,b**[9,12] in dichloromethane with concentrations of (3−7) × 10^{-5} mol L^{-1} were prepared. An excess (10−300 equiv) of **1** was added, and the reactions were followed by measuring the decay of absorption. Results are summarized in Table 4.

Solutions of the iminium salts **6**-SnCl$_5^-$ or **6**-BCl$_4^-$ were prepared by adding **7b** to cooled solutions of BCl$_3$ or SnCl$_4$ in dichloromethane. An excess of the nucleophilic reaction partner was added, and the reactions were followed by measuring the decay of conductivity. Results are summarized in Table 5.

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References and Notes

(1) Pearson, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. C., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, pp 257−294.

(2) Reviews: (a) Wang, Q.; Wang, L.; Yu, L. *Macromol. Rapid Commun.* **2000**, *21*, 723−745. (b) Kippelen, B.; Golemme, A.; Hendrickx, E.; Wang, J. F.; Marder, S. R.; Peyghambarian, N. In *Field Responsive Polymers*; ACS Symposium Series; American Chemical Society: Washington, DC, 1999; Vol. 726, pp 204−225. (c) Kippelen, B.; Meerholz, K.; Peyghambarian, N. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; pp 465−513. (d) Kippelen, B.; Sandalphon; Volodin, B. L.; Meerholz, K.; Peyghambarian, N. In *Photonic and Optoelectronic Polymers*; ACS Symposium Series; American Chemical Society: Washington, DC, 1997; Vol. 672, pp 218−235.

(3) For some recent reports, see: (a) Brotherston, I. D.; Mudigonda, D. S. K.; Osborn, J. M.; Belk, J.; Chen, J.; Loveday, D. C.; Boehme, J. L.; Ferraris, J. P.; Meeker, D. L. *Electrochim. Acta* **1999**, *44*, 2993−3004. (b) Meeker, D. L.; Mudigonda, D. S. K.; Osborn, J. M.; Loveday, D. C.; Ferraris, J. P. *Macromolecules* **1998**, *31*, 2943−2946. (c) Geissler, U.; Hallensleben, M.; Toppare, L. *Synth. Met.* **1993**, *55*, 1662−1667. (d) Desbene-Monvernay, A.; Lacaze, P. C.; Dubois, J. E.; Desbene, P. L. *J. Electroanal. Chem.* **1983**, *152*, 87−96. (e) Lacaze, P. C.; Dubois, J. E.; Desbene-Monvernay, A.; Desbene, P. L.; Basselier, J. J.; Richard, D. *J. Electroanal. Chem.* **1983**, *147*, 107−121.

(4) (a) Rooney, J. M. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 3, pp 697−704. (b) For reviews on carbocationic polymerizations, see references cited in: Baird, M. C. *Chem. Rev.* **2000**, *100*, 1471−1478.

(5) For cationic grafting polymerizations of *N*-vinylcarbazole (**1**) as method for surface modification of inorganic solid materials, see: (a) Spange, S.; Gräser, A.; Müller, H.; Zimmermann, Y.; Rehak, P.; Jäger, C.; Fuess, H.; Baehtz, C. *Chem. Mater.* **2001**, *13*, 3698−3708. (b) Spange, S.; Gräser, A.; Huwe, A.; Kremer, F.; Tintemann, C.; Behrens, P. *Chem. Eur. J.* **2001**, *7*, 3722−3728. (c) Review: Spange, S. *Prog. Polym. Sci.* **2000**, *25*, 781−849.

(6) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990−1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957.

(7) Mayr, H.; Kuhn, O.; Gotta, M. F.; Patz, M. *J. Phys. Org. Chem.* **1998**, *11*, 642−654.

(8) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993−2000.

(9) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512.

(10) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

(11) (a) Mayr, H. In *Ionic Polymerizations and Related Processes*; Puskas, J. E., Michel, A., Barghi, S., Paulo, C., Eds.; NATO Sci. Ser. E Applied Sciences; Kluwer Academic Publishers: Dordrecht, 1999; Vol. 359, pp 99−115. (b) Mayr, H. In *Cationic Polymerization: Mechanisms, Synthesis and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 51−136.

(12) Burfeindt, J.; Patz, M.; Müller, M.; Mayr, H. *J. Am. Chem. Soc.* **1998**, *120*, 3629−3634.

(13) (a) *Iminium Salts in Organic Chemistry (Adv. Org. Chem. Vol. 9)*; Böhme, H., Viehe, H. G., Eds.; Interscience: New York, 1976. (b) Mayr, H.; Ofial, A. R.; Würthwein, E.-U.; Aust, N. C. *J. Am. Chem. Soc.* **1997**, *119*, 12727−12733 and references therein.

(14) A gas−solid reaction of *N*-vinylcarbazole (**1**) with HCl gas and subsequent addition of methanol was performed at −78 °C to obtain **7a** (83%). For analogous reactions, see: (a) Kaupp, G.; Matthies, D. *Chem. Ber.* **1987**, *120*, 1897−1903. (b) Kaup, G.; Matthies, D. *Mol. Cryst. Liq. Cryst.* **1988**, *161*, 119−143.

(15) Kricka, L. J.; Ledwith, A. *J. Org. Chem.* **1973**, *38*, 2240−2241.

(16) For analogous reactions, see: Katritzky, A. R.; Zhang, G.; Qi, M.; Xie, L. *Tetrahedron Lett.* **1997**, *38*, 6959−6960.

(17) Mayr, H.; Ofial, A. R. *Tetrahedron Lett.* **1997**, *38*, 3503−3506.

(18) Böttger, G. M.; Fröhlich, R.; Würthwein, E.-U. *Eur. J. Org. Chem.* **2000**, 1589−1593.

(19) Rooney, J. M. *Makromol. Chem.* **1978**, *179*, 165−171.

(20) Bowyer, P. M.; Ledwith, A.; Sherrington, D. C. *Polymer* **1971**, *12*, 509−520.

(21) Rodriguez, M.; León, L. M. *Eur. Polym. J.* **1983**, *19*, 585−588.

(22) Flo, C.; Pindur, U. *Liebigs Ann. Chem.* **1987**, 509−513.

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