Macromolecules **1997,** *30,* 3439−3446

Cationic Initiation of Vinyl Ether Polymerization Induced by $(4\text{-}R^1C_6H_4)(4\text{-}R^2C_6H_4)R^3CX$ in Conjunction with Silica: Producing Highly Head Group Functionalized Polymers

Ulrike Eismann and Stefan Spange*

Lehrstuhl fuer Polymerchemie, Technische Universitaet Chemnitz—Zwickau,
Strasse der Nationen 62, 09111 Chemnitz, Germany

Received November 19, 1996; Revised Manuscript Received March 31, 1997[⊗]

ABSTRACT: Addition of vinyl ethers to arylmethyl halides and silica at 0 and −78 °C results in the formation of polymers. The average molecular weight, the molecular weight distribution (MWD), and the head group functionality are strongly dependent on the structure of the arylmethyl halide and on the olefin/arylmethyl halide ratio. The heterogeneous induced polymerization depends not only on the temperature but also on the kind of silica used, e.g. Aerosil (Degussa) and Kieselgel 60 (KG 60) (Merck). We found that initiation with carbocations of the type $(4\text{-}R^1C_6H_4)(4\text{-}R^2C_6H_4)R^3C^+$ (R^1, R^2 = H, CH_3, OCH_3; R^3 = H, C_6H_5) with an electrophilicity in the range of $-5 > pK_{R+} > -9$ bearing a chloride counterion yields highly head group functionalized polymers. General mechanisms for the initiation and propagation step of the surface-mediated cationic vinyl ether polymerization considering the influence of the counterion and the initiating carbocation are discussed.

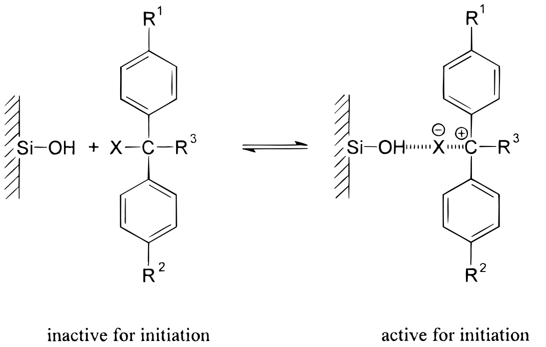
Introduction

During the last decades the cationic polymerization of vinyl ethers has been intensively studied because of the great importance of poly(vinyl ether)s in application and possible functionalization (see refs 1−3 and references cited therein). Up to 1995 all initiation processes of vinyl ethers resulting in functionalized polymers were generally of cationic nature. The greatest progress in living vinyl ether polymerization was made by introducing α-iodo ethers in combination with weak Lewis acids (e.g. ZnI_2), iodine, and other moderate acceptors[4−6] and of α-halogeno ethers in combination with tetraalkylammonium perchlorate[7−9] as initiator. In 1995, Baird and Wang were the first to report on a metallocene initiator, $(\eta^5\text{-}C_5Me_5)TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, for electron rich olefins like vinyl ethers[10] and isobutene.[11] The discussion of the polymerization mechanism induced by $(\eta^5\text{-}C_5Me_5)TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ is also based upon a carbocationically propagating species, the electrophilicity of which is controlled by the counterion $[(Me)B(C_6F_5)_3]^-$ (see Scheme 1 in ref 10). Thus, the effective control of the electrophilicity of the propagating carbocation is of great importance to guarantee optimal conditions for a long-lived cationic chain polymerization without transfer to the monomer. This principle was effectively demonstrated for alkoxy-substituted titanium(IV) chlorides as Lewis acidic activators for living cationic polymerization of isobutyl vinyl ether (IBVE) by Sawamoto et al.[12] The control of the Lewis acidity of the co-initiating system determines the nature of the polymerization reaction: not living, living, or long living.[12]

Recently, we have shown that covalent arylmethyl halides $(4\text{-}R^1C_6H_4)(4\text{-}R^2C_6H_4)R^3CX$ are ionized on the surface of silica particles,[13−15] as outlined in Scheme 1. The interaction mechanism of $(4\text{-}R^1C_6H_4)(4\text{-}R^2C_6H_4)R^3CX$ with the silica surface is attributed to the counterion-mediated contact of the highly polar and Lewis acidic silanol groups to the carbenium ion.

Analogous to well-known co-initiating systems for cationic polymerizable monomers, the silica surface serves as an activator like $B(C_6F_5)_3$ toward $(\eta^5\text{-}C_5Me_5)TiMe_3$[10] or alkoxytitanium chlorides toward α-chloro ethers.[12] As reported, $B(C_6F_5)_3$ can polymerize vinyl ethers alone without the metallocene component.[10] In contrast to this result, the bare silica surface is inactive as initiator for the cationic polymerization of *p*-methoxystyrene, vinyl ethers, cyclopentadiene, and *N*-vinylcarbazole within 12 h (see below). On the other hand, the covalent arylmethyl compound $(4\text{-}R^1C_6H_4)(4\text{-}R^2C_6H_4)R^3CX$ is inactive for the initiation of the cationic polymerization of vinyl ethers in hexane or aromatic solvents, and at concentrations below 2×10^{-3} mol^{-1} in halocarbons, too. Trityl chloride and trityl bromide are capable of the initiation of the cationic polymerization of vinyl ethers in solvents possessing acceptor properties, e.g. *m*-cresol[16] and liquid sulfur dioxide.[17] For nitroalkanes and solvent mixtures, see ref 18. Unfortunately, in these cases the monomer consumption is not complete, the MWD is very broad, and the structure of the polymer is not uniform due to isomerization and side reactions.[16−18] The initiation of vinyl ether polymerization in solution by completely ionized carbenium salts is by now a well-established method.[19,20]

Scheme 1. Heterolytic Dissociation of Arylmethyl Halides Induced by Silica Surface Silanol Groups



In 1991 we reported for the first time on the cationic polymerization of *p*-methoxystyrene as a model monomer using trityl halides (fluoride, chloride, and bromide) on the surface of Aerosil particles as initiator systems in 1,2-dichloroethane suspension at room temperature.[21] Due to the sterically hindered triphenylmethylium, the initiation occurs slower than the propagation reaction

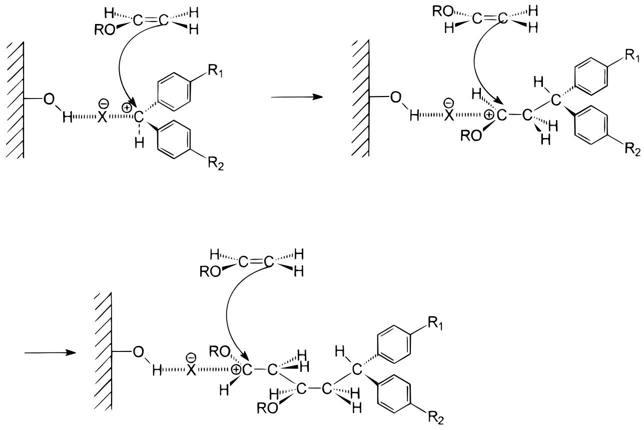
---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S0024-9297(96)01699-3 CCC: \$14.00

Scheme 2. Basic Mechanistic Concept of Ion Pair Propagation for Olefins Initiated by Diarylmethyl Chlorides on Silica Surfaces



on the surface, and initiation is entirely suppressed at −78 °C on Aerosil. In all cases, the monomer conversion was complete at higher temperatures, but only bromide as counterion yielded "living" systems on the particle surface.

At first, we suggested the following mechanistic concept for cationic polymerization on the surface of silica: the coordination of counterions, originally of stronger basic nature, such as chloride or bromide, on the particle surface with acceptor properties lowers the intrinsic basicity of the anion. Thus, these surface-coordinated anions cannot make a nucleophilic attack on a carbenium ion, but they can mediate a contact to an acceptor surface. The desorption process of the active cationic species from the surface into the surrounding liquid is accompanied by a cation−anion recombination, which is subject to diffusion control in the case of triphenylmethylium ions and halides in methylene chloride solution.[22] This means that the initiation and propagation can only take place at the surface of the acceptor particle, e.g. silica, because the reactivity of covalent carbon halide bonds, i.e. their electrophilicity, is not sufficient to insert into a nonactivated carbon−carbon double bond derived from vinyl ethers. Recently, we have shown that also disubstituted diarylmethyl halides can undergo ionization on silica, and that side reactions with surface groups can be suppressed by applying the surface species within 1 h after preparation.[23] Diarylmethylium species are highly reactive electrophiles which do react with strong π-nucleophiles, such as vinyl ethers, with a reaction rate constant of $k_2 = 10^6$ L mol^{-1} s^{-1} up to the diffusion limit of about 10^{10} L mol^{-1} s^{-1} [24] depending on the electrophilicity of the carbenium species.[25] Thus, an important condition for controlled polymerization should be met by these initiating carbenium ions: the initiating rate is effectively higher than the propagating rate. Scheme 2 represents the basic mechanistic concept of ion pair propagation for electron rich olefins initiated by $(4\text{-R}^1\text{C}_6\text{H}_4)(4\text{-R}^2\text{C}_6\text{H}_4)\text{CH}^+$ on the silica surface. It is expected that the diarylmethylium ion/surface complex is an excellent polymerization initiator for vinyl ethers.

In the following, a series of experiments to this effect will be described.

Experimental Part

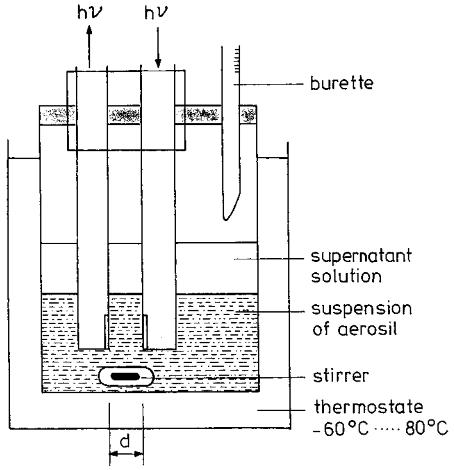


Figure 1. Equipment for UV/vis spectroscopy. Immersion cell with glass fiber optics.

Materials. The silicas used were commercially available products: Aerosil 300 (particle size circa 12 nm) from Degussa (Frankfurt/Main) and silica Kieselgel 60 (KG 60) (particle size 40−63 μm) from Merck (Darmstadt). Both silicas were dried carefully by heating under high vacuum at 250 °C for 12 h. The specific surface areas of Aerosil 300 and KG 60 were determined to 240 and 380 m^2/g, respectively, by the BET method.

1,2-Dichloroethane (and dichloromethane at −78 °C) were used as solvents for the UV measurements. The suspensions of Aerosil in these solvents are absolutely transparent, which allows us to take absorption and transmission spectra in the visible part of the spectrum by means of an immersion cell with glass fiber optics under inert conditions in a temperature range between +30 and −78 °C (Figure 1).

The equipment employed was a UV/vis spectrometer MCS 400 equipped with the immersion cuvette TS 5A (Zeiss). The immersion cell can be shifted vertically, which allows the comparison of both the spectra: that of the suspension and that of the supernatant solution.

1,2-Dichloroethane and methylene chloride were dried over CaH_2 and freshly distilled before use.

Isobutyl vinyl ether (IBVE) and ethyl vinyl ether (EVE) (Aldrich, >99%) were dried over CaH_2, distilled, and stored under argon.

The diphenylmethyl halides were prepared from diphenylmethyl alcohol and HCl_{gas}.[26] The materials are very air sensitive and must be carefully stored under dry argon.

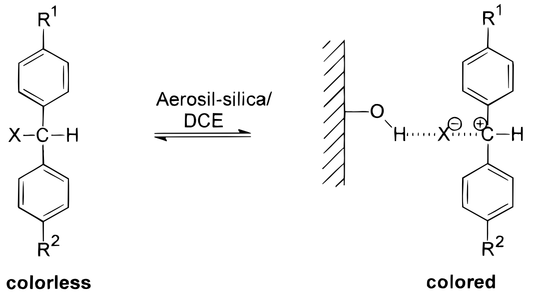
All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer, chemical shifts being determined by reference to residual ^{1}H and ^{13}C NMR solvent peaks, CDCl_3, respectively. Gel permeation chromatography (GPC) measurements of the polymers were carried out at room temperature using a Knauer model with ultrastyragel columns, THF as eluent, and polystyrene calibration.

The glass transition temperature was determined with a DSC 7 from Perkin-Elmer. Heating rates of 20, 10, and 5 K/min were used. The reported values were extrapolated according to a heating rate of 0 K.

Cationic Polymerization Procedure. Silica KG 60 (Merck) (1, 2, or 4 g) or 0.5 g of Aerosil (Degussa) was filled into a 100 mL Schlenk flask. The solids were dried by heating the flask at 250 °C for at least 12 h under vacuum (1 Torr). The flask was filled with dry argon and stoppered, and the contents were allowed to cool to 25 °C. A solution containing the arylmethyl halide initiator in 20 mL of CH_2Cl_2 or $\text{C}_2\text{H}_4\text{Cl}_2$ was then added. The resulting suspension was stirred for 5 min in an ice bath or for 10 min in a CO_2/acetone mixture (−78 °C), and the desired amount of cooled monomer was added by syringe over 10 s. After continuous stirring for the desired time, the suspension was filtered, and the filter residue was washed several times with portions of the solvent. If the reaction mixture had been sticky due to formed high molecular weight polymers, the suspension was diluted with 50 mL of the solvent before filtration.

In the case of polymerization of IBVE and EVE the organic fractions were combined and, after removing the solvent,

Table 1. Heterolytic Dissociation (Ionization) and Color Formation of Different Substituted Diarylmethyl halides on an Aerosil Surface



no.	R^1	R^2	pK_{R+}	λ_{max}/nm (Aerosil)
1	$-OCH_3$	$-OCH_3$	−5.71	512
2	$-OCH_3$	$-CH_3$	−7.36	484
3	$-OCH_3$	−H	−7.90	458
4	$-CH_3$	$-CH_3$	−9.35	colorless
5	$-CH_3$	−H	−11.6	colorless

dissolved in hexane and washed with a saturated solution of $NaHCO_3$ and one portion of distilled water. The organic fractions were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. After drying in high vacuum, the polymers are obtained as sticky materials.

In the case of polymerization of cyclohexyl vinyl ether (CyHVE) and *N*-vinylcarbazole (NVC) the combined organic fractions were concentrated by rotary evaporation to 25 mL. Then the polymer solution was poured into 250 mL of methanol. The precipitated polymers were filtered, washed with 20 mL of methanol, and dried in high vacuum.

Results

Initiators. We used isobutyl vinyl ether (IBVE) as the standard olefin to test various initiators of the (4-$R^1C_6H_4$)(4-$R^2C_6H_4$)CR^3X (R^1, R^2 = H, CH_3, OCH_3; R^3 = H, C_6H_5) type in the presence of silica. The structure of the (4-$R^1C_6H_4$)(4-$R^2C_6H_4$)CR^3X component was varied regarding both the electrophilicity of the carbocation (4-$R^1C_6H_4$)(4-$R^2C_6H_4$)$R^3C^+ = I^+$) and basicity of the counterion (X^-). The effects of varying I^+ on the degree of ionization of I−X on an Aerosil surface are shown in Table 1. The UV/vis spectra of the diarylmethyl halides in the presence of Aerosil were taken immediately after mixing the components at different temperatures in the suspension.

It can be seen that the degree of ionization on the Aerosil surface of I−X decreases with increasing electrophilicity of the initiating I^+. The same qualitative result is obtained with silica KG 60. In the case of silica KG 60, the diarylmethylium absorption appears in the supernatant solution at very low concentrations at room temperature. This effect is not observed at −78 °C.

The influence of the choice of silica, the temperature, and the solvent on the number average molecular weight and the molecular weight distribution (MWD) of selected polymer products is shown in Table 2. Our main result is that the chloride counterion yields colorless polymers with high head group functionality. The obtained sticky solutions are absolutely colorless and the head group functionality of the polymer is very high.

Unfortunately, in the case of bromide as counterion, the resulting polymers are yellow or brown and the MWDs are very broad (see Figure 2). Bromide forms weaker hydrogen bonds toward silanol than chloride. Therefore, we think it is likely in our case that the adsorbed bromide is more mobile than chloride and attacks the growing cation of the polymer chain via the Brønsted acidic β-hydrogen atom, as suggested in Scheme 3. In this case of bromide as counterion, the supernatant solution also becomes colored, where in the case of chloride as counterion the supernatant solution remains colorless.

Table 2. Effects of Varying Temperature and Choice of Silica Surfaces on the Number Average Weights of the Polymer Products[a]

no.	monomer	temp/°C	surface	$10^{-3}M_n$	M_w/M_n
1	IBVE	0	Aerosil 300	6.8	1.9
2	IBVE	0	KG 60	9.6	3.0
3	IBVE	−78	Aerosil 300		
4	IBVE	−78	KG 60	82.6	1.7
5	EVE	0	Aerosil 300	2.1	1.3
6	EVE	0	KG 60	4.6	4.1
7	EVE	−78	Aerosil 300		
8	EVE	−78	KG 60	58.4	2.7
9	CyHVE	−78	KG 60	16.2	2.9
10	NVC	−78	KG 60	200	2.4

[a] Initiator: bis(4-methoxyphenyl)methyl Chloride, $[I] = 4 \times 10^{-4}$ mol. [M] = 0.028 mol. [Aerosil] = 0.5 g; [KG60] = 1 g. Solvent: CH_2Cl_2.

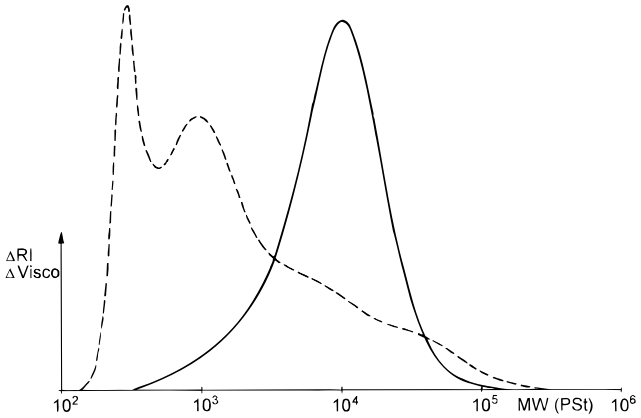
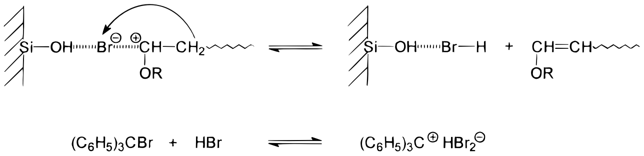


Figure 2. Influence of the counterion on the molecular weight and molecular weight distribution of polyIBVE on Aerosil at 0 °C; GPC diagrams of polyIBVE initiated with triphenylmethylchloride (—) and triphenylmethylbromide (− − −) $[I] = 2 \times 10^{-4}$ mol; $[M] = 8 \times 10^{-3}$ mol.

Scheme 3. Side Reactions in the Case of Bromide as Counterion



Thus, an unsaturated end group is formed, which rapidly undergoes further reaction with free HBr. Ether cleavage of −OR groups in the penultimate unit of the polymer chain finally leads to conjugated sequences, which cause the brown color of the polymer products. This side reaction is well-known for the IBVE polymerization with Brønsted acids.[27] Because of these undesirable side reactions, we used exclusively arylmethyl chlorides as surface initiators in our experiments. We believe that chloride coordinated to silanol keeps the balance between the surface and the propagating polyIBVE chain so that neither ion recombination nor β-hydrogen abstraction takes place. This also causes the polyIBVE to exhibit a high head group functionality of initiating groups. Figure 3 shows a ^1H NMR spectrum of a polyIBVE obtained by initiation with (4-$CH_3OC_6H_4$)$_2$CHCl on a silica surface. The GPC of the polyIBVE is shown in the inset of Figure 3.

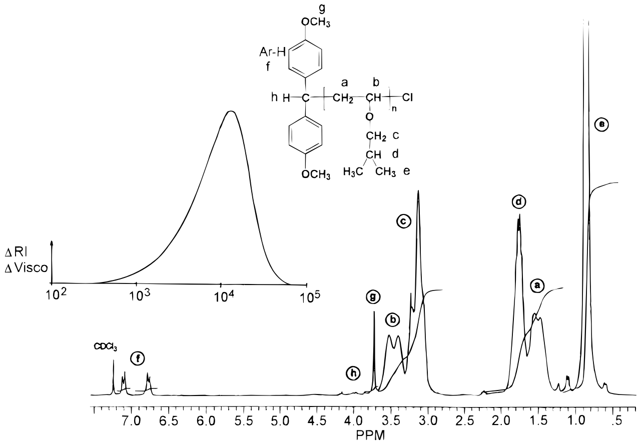


Figure 3. ^{1}H NMR spectrum of polyIBVE initiated with (4-$CH_3OC_6H_4)_2CHCl$ on a silica surface; Inset: GPC, $M_{nGPC} = 5710\ g\cdot mol^{-1}$, $M_{n\ calc.} = 5470\ g\cdot mol^{-1}$.

The addition of (4-$CH_3OC_6H_4)_2CH^+$ to the vinyl ether double bond can be easily detected by a characteristic triplet at 4.1 ppm (the former singlet of the initiator methine proton appears at 6.1 ppm). This derives from the coupling of the CH protons of the arylmethyl component with the CH_2 protons of the former olefin double bond of the vinyl ether component (see Table 3 for other end groups).

The head group functionality was determined by ^{1}H NMR spectroscopy. The number average molecular weight was calculated from the integrals of the methoxy protons of the initiator at 3.7 ppm, or of the protons of the aryl groups at $\delta = 6.77$ ppm and at $\delta = 7.15$ ppm, and the integrals of the methyl protons in the polymer chain at $\delta = 0.9$ ppm. Generally, the average molecular weight calculated (NMR analysis) and the molecular weight obtained by GPC agree excellently. The very high head group functionality was independently shown by conversion of the diarylmethyl head group into an diarylmethylium macroinitiator by hydride abstraction and its use for block copolymerization with *N*-vinylcarbazole. Surprisingly, the quantitative head group functionality is independent of the reaction temperature in the range of −78 to 0 °C. Therefore, we concluded that polymerization occurs without transfer to the monomer even at higher temperatures.

The head group functionality decreases in the presence of water traces on the silica surface. Thus, the product formation and the head group functionality are influenced significantly by the kind of silica preparation. The results are compiled in Table 4.

It may be stated that the presence of water in the system KG 60 leads to deactivation of the active species and thus inhibits the vinyl ether polymerization completely, whereas with Aerosil it is absolutely possible to obtain high molecular weight polyIBVE in the presence of water, though with a lower conversion and lower percentage of head group functionality.

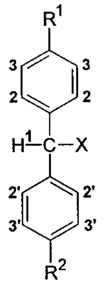
The end group functionality in the poly(vinyl ether)s obtained by initiation with (4-$CH_3OC_6H_4)_2CH^+$ in the case of chloride as counterion should be $-CH_2CHClOR$. The ^{1}H-signal of the $-CHClOR$ end group is expected at $\delta = 5.7$ ppm, according to refs 40,41. Unfortunately, the chloroacetal end groups rapidly undergo hydrolysis with residual water physisorbed on the surface or with hydroxyl groups on the surface itself. In these cases acetal end groups ($\delta = 4.6$ ppm, t) are found. The isolation of the polymer without washing the organic fractions with aqueous $NaHCO_3$ leads to yellow polymers bearing carbon double bonds in the chain (caused by HCl elimination). The hydrolysis of the $-CH_2CHClOR$ end group during the polymer isolation mainly yields aldehyde end groups ($-CH_{2\mathbf{b}}COH_{\mathbf{a}}$) detectable at $\delta_{\mathbf{a}} = 9.8$ ppm and $\delta_{\mathbf{b}} = 2.55$ ppm in the ^{1}H NMR spectrum. Direct evidence for $-CH_2CHClOR$ end groups was impossible to get by in situ solution state ^{1}H NMR spectroscopy of the suspension containing the immediately formed polymer in presence of the Aerosil nanoparticles, because the concentration of end groups is too low compared to the concentrations of monomer, polymer, and solvent. On the other hand, direct evidence for diarylmethyl chloride addition products to cationically polymerizable monomers such as styrene could be obtained. Due to the higher stability of this carbon−chlorine bond in the presence of silica,[23] the formation of these products is not surprising.

The influence of the electrophilicity of the initiating carbocation on the rate of polymerization and the average molecular weight follows the known behavior of cationic initiators in ionic equilibrium with the covalent nonactive and active species. With increasing electrophilicity of the initiating cation the reactivity of the initiating system involving the initiator and co-initiator reaches a maximum activity. Figure 4 shows the dependence of the average molecular weight of polyIBVE as function of the electrophilicity of the initiating carbenium for $R^1C_6H_4CHClC_6H_4R^2$/silica. The electrophilicity is expressed as pK_{R+}, which is defined for the reaction of carbenium with water; with $pK_{R+} = -\log [R_3COH][H^+]/[R_3C^+]$).[29] Graphs similar to those shown in Figure 4 were obtained by Kennedy[28] for isobutene polymerization induced by $RCl/AlEt_2Cl$. As discussed in the literature, the initiator/co-initiator combination works effectively if the reactivity of the initiating carbenium is similar to the electrophilicity of the propagating chain derived from the monomer. In addition, Mayr[29] reported on the equimolar reaction of $R^1C_6H_4CHClC_6H_4R^2/MtX_n$ with 2-methylpentene that both components (the electrophilicity of the carbocation $R^1C_6H_4CH^+C_6H_4R^2$ and the nature of the activator MtX_n) are responsible for the relative reactivity of the whole reaction. It seems that the electrophilicity of (4-$CH_3OC_6H_4)_2CH^+$ is similar to the electrophilicity of the propagating chain derived from isobutyl vinyl ether. This assumption is supported by results from model reactions: Mayr has also shown that methoxy-substituted diarylmethylium ions and oxycarbenium ions possess similar electrophilic strengths.[25]

The degree of ionization of I−X depends not only on the nature of I^+ and X^- but also on the concentration of the activator, i.e. the silica surface. The results shown in Table 5 demonstrate that the effective surface area for the activation of I−X plays a very important role. Effective conditions are [I−X]/silica ratios of about $3.6 \times 10^{-4}\ mmol\cdot m^{-2}$. Table 5 shows the influence of the surface area on the conversion of IBVE and the yield of polymer products at −78 and 0 °C. However, the maximum of catalytic activity as a function of the electrophilicity of the initiating carbenium does not depend on the activator concentration. Due to the presence of nonionized arylmethyl halide (see Scheme 1), transfer to initiator I−X (inifering) (see Scheme 5), was observed.

Aside from the heterogeneity of the system, the inifer hypothesis also explains the increase of molecular weight distribution in comparison to homogeneous

Table 3. ^{1}H NMR Characterization of the Initiators and End Group Functionalized PolyIBVE



no.	R^1	R^2	F_p/°C (X = Cl)	δ/ppm X = Cl	δ/ppm X = polyIBVE
1	$-OCH_3$	$-OCH_3$	84	3.79 (s, 6H, OCH_3), 6.12 (s, 1H, H-1), 6.86 (d, 4H, H-3,3′), 7.32 (d, 4H, H-2,2′)	3.71 (s, 6H,OCH_3), 4.10 (t, 1H, H-1), 6.75 (d, 4H, H-3,3′), 7.11 (d, 4H, H-2,2′)
2	$-OCH_3$	$-CH_3$	47	2.32 (s, 3H, CH_3), 3.77 (s, 3H,OCH_3), 6.08 (*s*, 1H, H-1), 6.84 (d, 2H, H-3), 7.12 (d, 2H, H-3′), 7.25−7.31 (m, 4H, H-2,2′)	2.19 (s, 3H, CH_3), 3.65 (s, 3H,OCH_3), 4.00 (*t*, 1H, H-1), 6.71 (d, 2H, H-3), 6.92 (d, 2H, H-3′), 7.10 (m, 4H, H-2,2′)
3	$-OCH_3$	−H	62	3.79 (s, 3H, OCH_3), 6.10 (*s*, 1H, H-1), 6.84 (d, 2H, H-3), 7.14−7.40 (m, 7H, Ar-H)	3.71 (s, 3H, OCH_3), 4.10 (*t*, 1H, H-1), 6.77 (d, 2H, H-3), 7.08−7.3 (m, 7H, Ar-H)
4	$-CH_3$	$-CH_3$	45	2.30 (s, 6H, CH_3), 6.06 (*s*, 1H, H-1), 7.10 (d, 4H, H-3,3′), 7.13 (d, 4H, H-2,2′)	2.25 (s, 6H, CH_3), 3.85 (*t*, 1H, H-1), 7.05 (d, 4H, H-3,3′), 7.17 (d, 4H, H-2,2′)
5	$-CH_3$	−H	136[a]	2.42 (s, 3H, CH_3), 6.20 (*s*, 1H, H-1), 7.22−7.53 (m, 9H, Ar−H)	2.24 (s, 3H, CH_3), 3.78 (*t*, 1H, H-1), 7.04−7.35 (m, 9H, Ar−H)

[a] K_p (0.4 mm).

Table 4. Influence of the Pretreatment of the Silica Gels on the Properties of the Polymers[a]

surface/pretreatment	$\bar{M}_n$	$\bar{M}_w\bar{M}_n$	head group functionality/%[b]
Aerosil/not dried	7500	2.1	50
Aerosil/dried (8 h; 300 °C; vacuum)	7500	1.9	100
KG 60/not dried	720	1.8	
KG 60/dried (2 h; 300 °C)	13400	broad	≈60
KG 60/dried (8 h; 300 °C; vacuum)	10100	3.4	100

[a] Initiator: bis(methoxyphenyl)methyl chloride. $T = 0$ °C. $n_1 = 10^{-4}$ mol. $n_M = 7 \times 10^{-3}$ mol. $m_{Aerosil} = 0.5$ g; $m_{KG} = 1.0$ g. [b] Determined via ^{1}H NMR specroscopy.

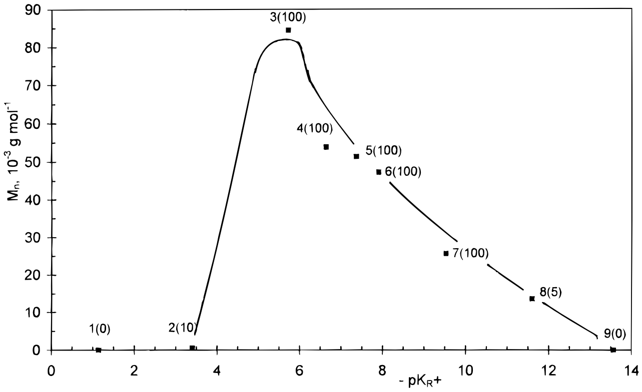


Figure 4. Obtained effective average molecular weight (M_n) of polyIBVE as a function of the electrophilicity of I^+ by initiating IBVE with different arylmethyl chlorides (I-Cl) at KG 60 at −78 °C. (The values in parentheses under the plots indicate the yield of polyIBVE.) [KG 60] = 4 g, [I-X] = 4 × 10^{-4} mol, [IBVE] = 0.028 mol. 1: $(4\text{-}CH_3OC_6H_4)_2(C_6H_5)CCl$. 2: $(4\text{-}CH_3OC_6H_4)(C_6H_5)_2CCl$. 3: $(4\text{-}CH_3OC_6H_4)_2CHCl$. 4: $(C_6H_5)_3CCl$. 5: $(4\text{-}CH_3OC_6H_4)(4\text{-}CH_3C_6H_4)CHCl$. 6: $(4\text{-}CH_3OC_6H_4)(C_6H_5)CHCl$. 7: $(4\text{-}CH_3C_6H_4)_2CHCl$. 8: $(4\text{-}CH_3C_6H_4)(C_6H_5)CHCl$. 9: $(C_6H_5)_2CHCl$.

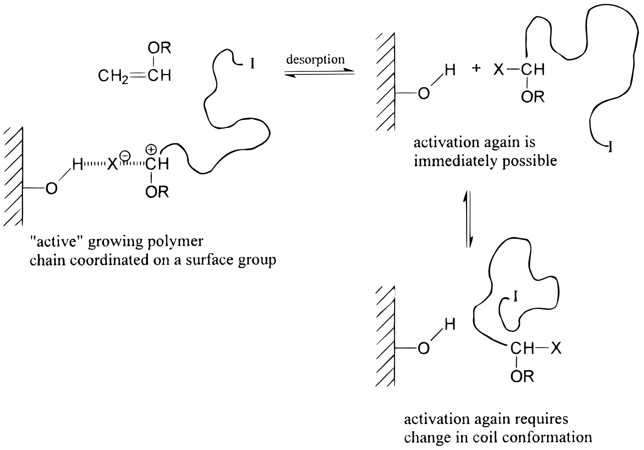
systems and the graphs shown in Figure 4. This agrees with the high headgroup functionality, too. In every case, $(4\text{-}CH_3OC_6H_4)_2CH^+$ as initiating species provides the best results regarding the yield of polymer and the average molecular weight.

Table 5. Yield of PolyIBVE for Different Initiator/Co-initiator (Arylmethyl Halide/Silica) Ratios at Two Different Reaction Temperatures

initiator (I) no.[a]	yield % [I]/KG 60 = 0.4 mmol/1120 m^2 (*T* = −78 °C)	yield % [I]/KG 60 = 0.4 mmol/1120 m^2 (*T* = 0 °C)	yield % [I]/KG 60 = 0.4 mmol/280m^2 (*T* = −78 °C)
1	100	100	100
2	100	57	80
3	100	61	4 (oligomers)
4	100	50	3 (oligomers)
5	5	20	3 (oligomers)

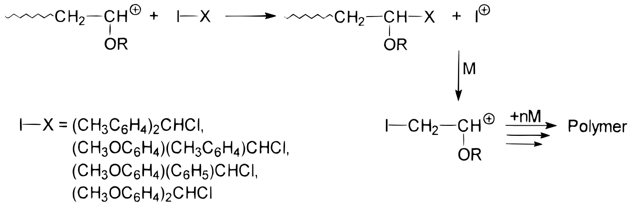
[a] According to no. from Table 3.

Scheme 4



The results show that it is possible to synthesize highly head group functionalized polyIBVE and polyEVE at −78 °C (KG 60) and at 0 °C (Aerosil 300) by heterogeneously catalyzed cationic polymerization. The M_n of the polymers is determined by the electrophilicity of the initiating cation and by the [monomer]/[initiator] ratio. The independence of the head group functionality from the reaction temperature in this case of cationic vinyl polymerization seems surprising because the k_p/k_{trM} ratio is strongly dependent on the reaction temperature.[30] Therefore, we conclude that the surface

Scheme 5. Inifer Mechanism for the Initiation with Strong Electrophilic Carbocations



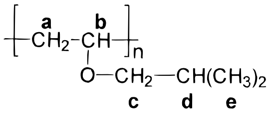
polymerization of polyVE is nearly free of transfer reactions to the monomer. This means that the dependence of the average molecular weight on the reaction temperature is caused by a different mechanistic feature.

We suggest the following hypothetical model. The desorption of the generated polymer from the surface is faster at higher temperatures. High molecular weight leads to coil formation in solution. Thus, the end group, which is capable of the activation is covered and immediate reactivation does not seem possible (Scheme 5).

Variation of the Monomer. Polymerization of Isobutyl Vinyl Ether (IBVE). From Figure 4 it is apparent that IBVE can be polymerized best by the carbocation $(4\text{-}CH_3OC_6H_4)_2CH^+$ to high molecular weights. We found that the obtained molecular weights strongly depend on the choice of silica and the temperature. While with silica KG 60 polyIBVE with $M_n \approx 10^5$ can be synthesized at −78 °C, on Aerosil 300 only polyIBVE with $M_n \approx 1500$ is obtained at this temperature and the monomer consumption amounts to only 5−10%. That means that the surface of Aerosil is largely inactive at −78 °C (see Table 2). At higher temperatures (0 °C) high head group functionalized polymers with M_n up to 6000 are prepared at the Aerosil surface. Up to now, we have no rational explanation for this effect.

The molecular weights can be controlled by the ratio of monomer concentration to initiator concentration up to $[M]/[I] \leq 40$. Unfortunately, it is impossible to calculate the molecular weight according to the equation $M_n = [M]_0/[I]_0 M_{monomer}$, because the exact concentration of initiating carbocations at the surface is unknown. The rate of the propagation reaction is rather small compared with those observed in homogeneous systems. Complete monomer consumption was achieved in about 24 h.

Characteristics. ^1H NMR (298 K in $CDCl_3$): δ/ppm



3.3−3.5 (d, 1H, b), 3.0−3.2 (m, 2H, c), 1.6−1.9 (m, 1H, d), 1.4−1.9 (m, 2H, a), 0.87 (d, 6H, e). ^{13}C NMR (298 K in $CDCl_3$): δ/ppm 75.7 (b), 73.7 (c), 41.4 + 39.5 − 39.9 (a), 28.9 (d), 19.6 (e).

The fractions of isotactic, syndiotactic, and atactic polymers were determined from the signal of the CH_2 resonance (^{13}C NMR).[31] The results are summarized in Table 6. PolyIBVE prepared at −78 °C shows a high content of syndiotactic structures. With increasing reaction temperature, the fraction of syndiotactic structures decreases in favor of atactic fractions. The content of isotactic structures remains constant over the chosen temperature range.

Table 6. Tacticities of Poly(vinyl ether)s Obtained at Various Temperatures with Diarylmethyl Halides as Initiators on Aerosil and KG 60, Respectively

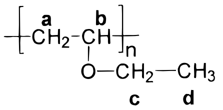
		tetrads obs (^{13}C NMR)/%		
olefin	T/°C	rr	mr	mm
IBVE	−78	40	36	24
IBVE	0	30	47	23
EVE	−78	42	36	22

[a] mm values were calculated by means of the equation: mm = mmm ± mmr.

Polymerization of Ethyl Vinyl Ether (EVE). Polymerization of EVE was investigated at −78 and 0 °C, using Aerosil 300 and KG 60 as cocatalysts. As shown with IBVE, products with higher molecular weights are formed at the lower temperature. The degree of polymerization and the values of M_w/M_n agree well with those of the polyIBVE formed at various temperatures.

Also arylmethyliums with lower reactivities than tritylium ionizing more strongly at the silica surface can initiate the polymerization of EVE. We believe that the smaller molecular size of EVE compared to IBVE is the cause of this. The EVE molecules can interact better with the active groups on the silica surface. PolyEVE with molecular weights (M_n) up to 5000 and values of M_w/M_n from 1.2 to 1.8 are obtained by initiation with 4-methoxytrityl chloride/Aerosil at 0 °C. The samples of polyEVE are also very sticky, completely colorless materials.

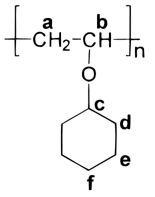
Characteristics. ^1H NMR (298 K in $CDCl_3$): δ/ppm



3.3−3.6 (m, 3H, b + c), 1.4−1.8 (m, 2H, a), 1.05−1.15 (t, 3H, d). ^{13}C NMR (298 K in $CDCl_3$): δ/ppm 73.6 (b), 64.2 (c), 39.4 + 41.1 (a), 15.6 (d).

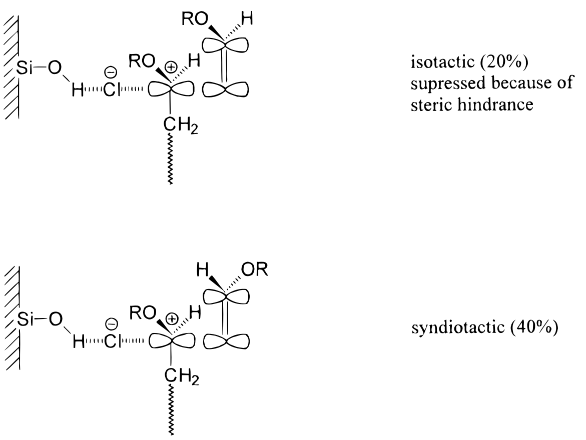
Polymerization of Cyclohexyl Vinyl Ether (CyHVE). Among the very often used alkyl vinyl ethers also CyHVE was included in these experiments, because of the interest in studying the reaction of sterically hindered monomers in the surface-mediated polymerization. In contrast to IBVE and EVE, CyHVE shows decreased reactivity caused by a reduced resonance stability of the double bond. This is a consequence of the interference of concurring groups of the sterically demanding substituent.[32−34] However, CyHVE is not very suitable for surface polymerization. It is true that it is possible to synthesize completely end group functionalized polymers, but complete conversion of monomer could not be achieved and fractionation into a polymer- and an oligomer part was observed. The part of polyCyHVE (see Table 2) amounted to 20% relating to $[M]_0$. Obviously, the CyHVE molecule is sterically too demanding to react with all the carbocationic active centers at the silica surface. PolyCyHVE is a white, solid material that was precipitated from methanol.

Characteristics. ^1H NMR (298 K in $CDCl_3$): δ/ppm



3.52 (m, 1H, b), 3.25 (m, 1H, c), 1.85 (m, 2H, a), 1.69

Chart 1



(m, 4H, d), 1.51 (m, 2H, f), 1.18 (m, 4H, e). ^{13}C NMR (298 K in CDCl$_3$): δ/ppm 75.0 (b), 71.2−71.5 (c), 42.4 (a), 33.4 (d), 25.8 (f), 24.2 (e).

Unfortunately, it was impossible to determine the tacticity of polyCyHVE from ^{13}C NMR, because the signal of the backbone methylene carbons at ≈40 ppm was not sufficiently resolved.

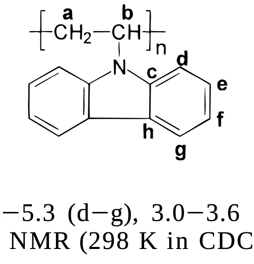
Polymerization of *N*-Vinylcarbazole (NVC). Because of its interesting photoconductivity properties, the polymerization of NVC with suitable cationic initiators has been investigated recently. In comparison to alkyl vinyl ethers only a few initiating systems have been discovered for “living” polymerization of NVC[35−38] so far.

We investigated the polymerization of NVC at 0 and −78 °C with various arylmethyl cations on KG 60. We found that reactive initiating carbocations are not suitable to control the polymerization of NVC at higher temperatures. At 0 °C we obtained polyNVC with number average weights of $\approx 10^5$ and very broad molecular weight distributions. Using initiators with lower carbocationic reactivity, the polymerization becomes controllable even at 0 °C.

Polymerization of NVC with bis(4-methoxyphenyl)methyl chloride at −78 °C yields a white, solid material precipitating from methanol. It has a high glass transition temperature (T_g = 216 °C). The syndiotactic fraction X_s was 60%, determined according to the equation $(T_g - 399)(1 - X_S) + (T_g - 549)X_S = 0$.[39]

This means that the syndiotactic fraction of polyNVC is higher than that of the poly(vinyl ether)s. Probably, the bulky volume of the NVC monomer is responsible for the favorite propagation according to a syndiotactic attack of the monomer at the surface-mediated propagating chain end. This result is also very close to the properties of polyNVC obtained by Wang and Baird.[10]

The values of M_n for this polyNVC are high (see Table 2) and the molecular weight distributions are small compared to many other initiators.[42−44]



Characteristics. ^{1}H NMR (298 K in CDCl$_3$): δ/ppm 5.8−7.9 and 4.4−5.3 (d−g), 3.0−3.6 and 2.2−2.8 (b), 0.8−1.9 (a). ^{13}C NMR (298 K in CDCl$_3$): δ/ppm 140.0 + 137.8 (c), 125.0 (g), 123.7 + 122.0 (h), 120.1 (e), 118.7 (f), 110.6 + 108.0 (d), 48.2−50.0 (b), 32−37 (a).

Final Conclusions and Outlook

Thus, our mechanistic explanation for the arylmethyl halide/silica induced vinyl ether polymerization is similar to the results obtained by Wang and Baird[10] for the metallocene-like initiation, because very similar tacticity triads are found. According to this and to the fact that the proportion of isotactic polymer is about 20%, an ion pair species should be responsible for the propagation reaction. In contrast, for the living polymerization of vinyl ethers in solution mainly isotactic polymer fractions are observed.[45]

The monomer can attack the growing chain from both sides, leading to syndiotactic or atactic sequences with equal probability. The isotactic attack is suppressed due to steric hindrance by the oxygen atoms of the vinyl ether component (Chart 1).

A deeper insight into the mechanism of the surface-mediated cationic polymerization of vinyl ethers will be reported soon. The occurrence of controlled cationic vinyl ether polymerization on the surface of inorganic substrates (silica particles or flat surface of glass) offers the introduced method for a lot of further applications in material research. We will report on this subject in following papers.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Bonn, for financial support of these investigations, Degussa, Frankfurt/Main, for provision of Aerosil, and BASF AG, Ludwigshafen, for providing vinyl monomers.

References and Notes

(1) Higashimura, T.; Sawamoto, M. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, New York, Beijing, Frankfurt, São Paulo, Syndey, Tokyo, and Toronto, 1989; Vol. 3, p 673.
(2) Cho, C.; Feit, B. A.; Webster, O. W. U.S. Patent 5,196,491, March 23, 1993 (to E. I. du Pont de Nemours, and Co.).
(3) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1982.
(4) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265.
(5) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1989**, *22*, 1552.
(6) (a) Schappacher, M.; Deffieux, A. *Macromolecules* **1991**, *24*, 2140. (b) Schappacher, M.; Deffieux, A. *Macromolecules* **1991**, *24*, 4221.
(7) Nuyken, O.; Kröner, H.; Aechtner, S. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 671.
(8) Nuyken, O.; Kröner, H.; Aechtner, S. *Makromol. Chem., Makromol. Symp.* **1990**, *32*, 181−197.
(9) Nuyken, O.; Kröner, H. *Makromol. Chem.* **1990**, *191*, 1−16.
(10) Wang, Q.; Baird, M. C. *Macromolecules* **1995**, *28*, 8021−8027.
(11) (a) Quyoum, R.; Wang, Q.; Tudoret, M. J.; Baird, M. C.; Gillis, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 6435. (b) Jeremic, D.; Wang, Q.; Quyoum, R.; Baird, M. C. *J. Organomet. Chem.* **1995**, *197*, 143. (c) Barsan, F.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1995**, 1065.
(12) Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 5671−5675.
(13) Spange, S.; Walther, R. *Org. Reactivity (Tartu)* **1995**, *29*, 45−48.
(14) Spange, S. *Vysokomol. Soedin., Ser. A & B* **1993**, *35*, 1873−1877.
(15) Spange, S.; Fandrei, D.; Simon, F.; Jacobasch, H. J. *Colloid Polym. Sci.* **1994**, *272*, 99−107.
(16) Eley, D. D.; Richards, A. W. *Trans. Faraday Soc.* **1949**, *45*, 436.
(17) Bauerfeind, D.; Wondraczeck, R.; Heublein, G. *Polym. Bull.* **1983**, *10*, 70−72.
(18) Spange, S.; Dreier, R.; Opitz, G.; Heublein, G. *Acta Polym.* **1989**, *40*, 55.
(19) Ledwith, A. *Makromol. Chem.* **1974**, *175*, 1117−1138.

(20) (a) Kunitake, T.; Matsuguma, Y.; Aso, C. *Polym. J.* **1971**, *2*, 345. (b) Kunitake, T. *J. Macromol. Sci., Chem.* **1975**, *A9*, 797−816.
(21) (a) Spange, S.; Heublein, G.; Simon, F. *J. Macromol. Sci., Chem.* **1991**, *A28*, 373−396. (b) Spange, S.; Heublein, B. *J. Macromol. Sci., Chem.* **1992**, *A29*, 987−996. (c) Spange, S.; Simon, F.; Schütz, H.; Schramm, A.; Winkelmann, H. *J. Macromol. Sci., Chem.* **1992**, *A29*, 997−1006.
(22) Dorfmann, L. M.; Sujdak, R. J.; Jones, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 4875.
(23) Spange, S.; Walther, R. *Angew. Chem.*, in preparation.
(24) Mayr, H. In: *Cationic Polymerizations*, Matyjaszewski, K., Ed.; Marcel Dekker, Inc.: New York, Basel, Hong Kong, 1996; pp 51−136.
(25) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990−1010.
(26) Strauss, F.; Duetzmann, A. *J. Prakt. Chem.* **1922**, *103*, 47.
(27) Aoshima, S.; Higashimura, T. *Polym. J.* **1984**, *16*, 249−258.
(28) Kennedy, J. P.; Ivan, B. In *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser Publishers: Munich, Vienna, New York, Barcelona, 1992; p 25.
(29) Mayr H. In *Control of Electrophilicity in Aliphatic Friedel-Crafts-Reactions*; Schinzer, D., Ed.; NATO ASI series C; Kluwer: Dordrecht, The Netherlands, 1989; Vol. 289, pp 21−36.
(30) Sigwalt, P.; Polton, A.; Tardi, M. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 953−968.
(31) Hatada, K.; Kitayama, T.; Matsuo, N.; Yuki, H. *Polym. J.* **1983**, *15*, 719−725.
(32) Plesch, P. H. *The Chemistry of Cationic Polymerization*; Pergamon Press: New York, 1963; p 378.
(33) Yuki, H.; Hatada, K.; Takeshita, M. *J. Polym. Sci., Part A* **1969**, *7*, 667.
(34) Feeney, F.; Ledwith, A.; Sutcliff, L. H. *J. Chem. Soc.* **1962**, *1962*, 2021.
(35) Higashimura, T.; Tearanski, H.; Sawamoto, M. *Polym. J.* **1980**, *12*, 393.
(36) Higashimura, T.; Deng, Y. X.; Sawamoto, M. *Polym. J.* **1983**, *15*, 385.
(37) Sawamoto, M.; Fujimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916.
(38) Nuyken, O.; Riess, G.; Loontjens, J. A. *Macromol. Rep.* **1995**, *A32*, 25−38.
(39) Terrell, D.; Evers, F. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2529−2543.
(40) Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 1643−1649.
(41) Katayama, H.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 3747−3755.
(42) Yoshida, E.; Nakamura, K.; Takata, T.; Endo, T. *J. Polym. Sci., Part A* **1993**, *31*, 1505.
(43) Sawamoto, M.; Fujimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916.
(44) Gonzalez, M.; Rodriguez, M.; Leon, L. M. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32*, 1773−1780.
(45) Sawamoto, M. *Macromol. Symp.* **1994**, *85*, 33−43.

MA961699P