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Cationic Polymerizability of 1-Substituted Vinyl Ethers and Styrenes

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SUMMARY:

To gain knowledge of the cationic polymerizability of 1,1-disubstituted ethylenes, homopolymerizations of 1-substituted vinyl ethers and styrenes, and also copolymerizations with the corresponding unsubstituted monomers are carried out. Methyl, ethyl, ethoxy, and phenyl groups are introduced in 1-position. Ethyl 1-methylvinyl ether and 1-methylstyrene produce homopolymers in contrast to ethyl 1-ethylvinyl ether, 1-ethylstyrene and 1-eth-, oxystyrene which do not furnish the homopolymers. In the copolymerization, all of these 1,1-disubstituted monomers are found to have greater reactivities for the unsubstituted propagating end than the corresponding unsubstituted monomers. It is concluded that 1,1-disubstituted ethylenes suffer from steric hindrance in the cationic polymerization more than the corresponding 1,2-disubstituted compounds, contrary to the situation in radical polymerizations. The change in reactivity of vinyl compounds with 1-methyl substitution in various reactions is discussed.

ZUSAMMENFASSUNG:

Um Kenntnis von der kationischen Polymerisierbarkeit von 1,1-disubstituierten Äthylenen zu erhalten, wurden Homopolymerisationen von 1-substituierten Vinyläthern und Styrolen sowie Copolymerisationen mit den entsprechenden nicht substituierten Monomeren durchgeführt. Methyl-, Äthyl-, Äthoxy- und Phenylgruppen wurden in 1-Stellung eingeführt. Äthyl-1-methylvinyläther und 1-Methylstyrol ergaben Homopolymere, nicht aber Äthyl-1-äthylvinyläther, 1-Äthylstyrol und 1-Äthoxystyrol. Bei der Copolymerisation wurde gefunden, daß all diese 1,1-disubstituierten Monomeren dem unsubstituierten wachsenden Kettenende gegenüber größere Reaktivitäten besitzen als die entsprechendenunsubstituierten Monomeren. Es wurde geschlossen, daß 1,1-disubstituierte Äthylene bei der kationischen Polymerisation – im Gegensatz zu Radikalpolymerisationen – einer stärkeren sterischen Hinderung unterliegen als die entsprechenden 1,2-disubstituierten Verbindungen. Die Änderung der Reaktivität von 1-substituierten Vinylverbindungen bei verschiedenen Reaktionen wird erörtert.

Introduction

In general, 1,2-disubstituted ethylenes cannot be polymerized by radicals, but many can be polymerized by cationic initiators. The influence of a 2-substituent on the cationic polymerizability of vinyl monomers has been studied, and the transition state of the propagation reaction has been discussed in detail on the basis of the electronic and steric effects of substitutents^{1,2}).

As for 1,1-disubstituted ethylenes, isobutene and 1-methylstyrene have great cationic polymerizabilities, so that the kinetics of polymerization of these monomers have been studied widely. However, there have been few works in which the cationic polymerizability of 1,1-disubstituted ethylenes has been compared with that of monosubstituted ethylenes. Therefore, it seems important at this stage to investigate how the introduction of 1-substituents affects reactivity, in order to obtain more information about the mechanism of cationic polymerization.

The present paper is concerned with the reactivity of several 1-substituted vinyl ethers and styrenes in cationic homopolymerization and copolymerization. The observed reactivities are discussed on the basis of the electronic and steric influences of 1-substituents. Moreover, the differences between the 1-methyl-substituent effects in the cationic polymerization of vinyl ethers and styrenes, and the differences in the 1-methylsubstituent effects in several electrophilic addition reactions are also discussed.

Experimental

Materials

Ethyl 1-methylvinyl ether (ethyl isopropenyl ether; E1MVE) was prepared by the dealcoholation of acetone diethyl ketal with sulfanilic acid as catalyst. Ethyl dimethylketal was prepared by HURD's method³⁾, bp 61°C, $n_D^{20} = 1,5301$, $d_4^{20} = 0,950$ (ref. bp 61,9°C, $n_D^{20} = 1,3927^{4}$).

Ethyl 1-ethylvinyl ether (E1EVE) was synthesized by the following reactions:

$$CH_{2}=CHOC_{2}H_{5} + Br_{2} \longrightarrow BrCH_{2} - CH - OC_{2}H_{5}$$

$$Br$$

$$Br$$

$$BrCH_{2} - CH - OC_{2}H_{5} + C_{2}H_{5}MgBr \longrightarrow BrCH_{2} - CH - OC_{2}H_{5}$$

$$C_{2}H_{5}$$

$$BrCH_{2} - CH - OC_{2}H_{5} \xrightarrow{KOH} CH_{2} = COC_{2}H_{5}$$

$$C_{2}H_{5}$$

1,2-Dibromoethyl vinyl ether was prepared by adding equimolar bromine to ethyl vinyl ether at 0°C slowly, so that the temp. did not rise. The second and third steps were carried out substantially in the manner of LAUER and SPIELMAN⁵). The dehydrobromination by refluxing an isopropanol solution was much more effective than that by distn. over potassium hydroxide, bp 86°C, $n_D^{20} = 1,3996$, $d_4^{20} = 0,7808$ (ref. bp 85–87°C, $n_D^{24,5} = 1,4011^{5}$).

Ethyl 1-phenylvinyl ether (E1PVE) was prepared in a similar manner to ethyl 1-ethylvinyl ether. bps 69°C, $n_{D}^{20} = 1,5301, d_4^{20} = 0,950$ (ref. bp₁₉ 96-98°C, $n_D^{26} = 1,5271^{5}$).

The synthesis of *1-ethylstyrene* (1ES) was done as follows: 2-phenyl-*n*-butanol was synthesized by reducing 2-phenyl-*n*-butyric acid with lithium aluminum hydride. Then it was dehydrated by the catalytic action of a 10:1 mixture of sodium and potassium hydroxides and the distillate at 70°C/15 mm Hg was collected. bp₁₅ 67°C, $n_D^{20} = 1,5285$, $d_4^{20} = 0,9579$, λ_{max} 241 nm, ε_{max} 1,03·10⁴ (ref. bp₃₀ 85-86°C, $n_D^{26,5} = 1,5260^{6}$).

1,1-Diphenylethylene (DPE) was synthesized from phenylmagnesium bromide and acetophenone, by a modification of ALLEN's method⁷), bp₅ 120 °C, $n_D^{20} = 1,6099, d_4^{20} = 1,0115$ (ref. bp₅ 123-125 °C, $n_D^{20} = 1,6085^{7}$).

The synthesized and commercial monomers (ethyl vinyl ether (EVE); styrene (ST)) were refined, care being taken to remove water. The catalysts and solvents used were purified as described elsewhere^{8, 9)}.

Procedures

The polymerization was carried out in an ERLENMEYER flask under a dry nitrogen atmosphere, the reagents being introduced with hypodermic syringes. The polymerization rate and relative reactivity were determined by measuring the consumption of monomers by gas chromatography. NMR spectra of polymers were measured in 10% solution in carbon tetrachloride at ambient temp. Monomer reactivity ratios were calculated by EZRIELEV's method¹⁰.

Results

Homopolymerizability

1-Substituted vinyl ethers

Ethyl 1-methylvinyl ether can be polymerized easily to produce a methanol-insoluble polymer at -78 °C in toluene or methylene chloride by various catalysts. Fig. 1 shows time-conversion curves for the poly-



Fig. 1. Time-conversion curves for the polymerization of E1MVE at -78° C ($[M]_0 = 1,0 \text{ mol/dm}^3$, $[C]_0 = 0,50 \text{ mmol/dm}^3$. Solvent and catalyst; \bullet : Toluene, I_2 ; \blacktriangle : Toluene, FeCl₃; \blacksquare : Toluene, CH₃COClO₄; \checkmark : Methylene chloride, I_2 ; \circ : Yield of methanolinsoluble polymer

merization with several catalysts. It was confirmed that the monomer consumed is converted quantitatively to a methanol-insoluble polymer. As unsubstituted vinyl ether polymerizes at 30 °C at a similar rate, ethyl 1-methylvinyl ether was estimated to have a large reactivity. The viscosity numbers of the polymers obtained ranged from 0,1--0,9 according to the catalyst, with ferric chloride giving the highest values (Fig. 2). All the polymers were found to have an exclusively syndiotactic structure, independent of the kind of catalyst and solvent, which is in fair accord



Fig. 2. Viscosity numbers of poly(E1MVE) obtained under various conditions (Polymerization conditions: $[M]_0 = 1,0 \text{ mol/dm}^3$, $[C]_0 = 0,50 \text{ mmol/dm}^3$, -78° C; Conditions of viscosity measurements: concn. 10 g/dm³ benzene, 30° C). Solvent and catalyst; \bullet : Toluene, I_2 ; \blacktriangle : Toluene, FeCl₃; \blacksquare : Toluene, CH₃COClO₄; \blacktriangledown : Methylene chloride, I_2

with the reported structure of poly(methyl 1-methylvinyl ether)¹¹). This result means that the steric structure of the polymer is not controlled by the counterion existing near the propagating end, but by the substituents of the monomer and of the propagating end.

Monomer	Catalyst	[Catalyst] /mmol·dm ⁻³	Time /h	% Cor Monomer consumption	version CH3OH-insol- uble polymer
EIEVE	I_2 PE O(C H -)-	1,0	1	0	0
150	$BF_{3}O(C_{2}\Pi_{5})_{2}$	- 10 - F 0	0,5	40	0
IES	BF ₃ O(C ₂ H ₅) ₂	5,0 10	20	0	0
EIPVE	CH ₃ COClO ₄	5,0	20	0	0
	BF ₃ O(C ₂ H ₅) ₂	10	20	0	0

Table 1. Attempts at homopolymerization of several 1,1-disubstituted monomers^{a)}

a) Polymerization conditions; solvent: Toluene; Temp.: -78°C, [M]₀ = 1,0 mol/l.

Next, the influence of substituents bulkier than the methyl group was studied. Ethyl 1-ethylvinyl ether reacts at -78 °C in toluene at a much smaller rate than ethyl 1-methylvinyl ether and does not form a methanolinsoluble polymer (Table 1). It is reported that ethyl 1-ethoxyvinyl ether (ketene diethyl acetal) can be polymerized by acids as weak as cadmium and zinc chlorides to a glassy polymer¹²). Ethyl 1-phenylvinyl ether is not consumed at all at -78 °C in toluene with various catalysts, though the system is colored red (Table 1). The color seems to be due to a stable carbenium ion formed from the monomer.

1-Substituted styrenes

As is well known, 1-methylstyrene gives easily a methanol-insoluble polymer with acidic catalysts. 1-Ethylstyrene was not consumed under mild conditions as shown in Table 1. Its dimerization, however, takes place without difficulty as reported by OVERBERGER⁶. 1-Ethoxystyrene (ethyl 1-phenylvinyl ether) has already been mentioned in the above section. EVANS has investigated the dimerization of 1,1-diphenylethylene which does not polymerize¹³. These results demonstrate that 1-substituted styrenes are, in general, difficult to polymerize by acidic catalysts because of steric hindrance.

Copolymerizability

1-Methyl substitution

In Fig. 3 are shown the copolymer composition curves for the copolymerization of ethyl vinyl ether (M_1) with ethyl 1-methylvinyl ether (M_2) and of styrene (M_1) with 1-methylstyrene (M_2) . In both systems the 1-substituted monomers have a considerably larger reactivity than the



Fig. 3. 1-Methyl substitution effect in copolymerizations in methylene chloride at -78 °C, $[M]_0 = 0.50 \text{ mol/dm}^3$. \bullet : EVE-E1MVE $\{BF_3O(C_2H_5)_2\}$; \blacksquare : ST-1MS (SnCl₄·TCA)

unsubstituted ones. The reactivity l/r_1 of 1-methylvinyl ether relative to vinyl ether for the vinyl ether propagating end, is about 8 (see Table 2). For the styrene system $1/r_1$ is about 4, and thus smaller than for the vinyl ether system.

Mono- mer 1	Mono- mer 2	Catalyst	Solvent	r ₁	\mathbf{r}_2	1/r1	r ₁ • r ₂
EVE	EIMVE	BF ₃ O(C ₂ H ₅) ₂	CH ₂ Cl ₂	$\textbf{0,}13\pm\textbf{0,}04$	$\textbf{29,3} \pm \textbf{3,5}$	7,7	3,8
EVE	E1EVE	BF ₃ O(C ₂ H ₅) ₂	CH ₂ Cl ₂	$\textbf{0,}11 \pm \textbf{0,}05$	$\textbf{13,8} \pm \textbf{1,6}$	9,0	1,5
EVE	E1PVE	BF ₃ O(C ₂ H ₅) ₂	$C_6H_5CH_3$	$(r_1 = r'_1) 0,5^{a}$	$(r_2')\approx 20^{a)}$	≈ 2	
ST	1 MS	SnCl ₄ ·TCA	CH ₂ Cl ₂	$0,\!25\pm0,\!08$	$\textbf{20,6} \pm \textbf{3,5}$	4,0	5,2
ST	1ES	SnCl ₄ ·TCA	CH ₂ Cl ₂	$\textbf{0,53} \pm \textbf{0,17}$	$3,2\pm0,5$	1,9	1,7
ST	DPE	SnCl ₄ ·TCA	CH ₂ Cl ₂	$\textbf{0,88} \pm \textbf{0,08}$	$0,03\pm0,03$	1,1	0,0

Table 2. Monomer reactivity ratios for copolymerizations between unsubstituted and 1-substituted monomers. Polymerization temp.: -78 °C

a) Assumed the penultimate model and $r_2 = 0$, $r_1 = r'_1$.

1-Ethyl substitution

Fig. 4 shows the copolymer composition curves of 1-substituted (M_2) and unsubstituted (M_1) monomers, and the monomer reactivity ratios are given in Table 2. In the copolymerization of ethyl vinyl ether (M_1) and ethyl 1-ethylvinyl ether (M_2) , r_1 is 0,11 and r_2 13,8. The reactivity is



Fig. 4. 1-Ethyl substitution effect in copolymerizations in methylene chloride at -78 °C, $[M]_0 = 3,0 \text{ mol/dm}^3$. •: EVE-E1EVE $\{BF_3O(C_2H_5)_2\}; \blacksquare: ST-1ES (SnCl_4 \cdot TCA)$

not enhanced as strongly by 1-ethyl substitution as by 1-methyl substitution. This may be due to the steric effect of the ethyl group, because the ethyl group is more electron-donating and so enhances reactivity electronically more than the methyl group. In the copolymerization of styrene with 1-ethylstyrene in methylene chloride, dimerization also proceeds during polymerization when the 1-ethylstyrene content in the feed is large. Accordingly, r_2 is only apparent, since M_2 does not homopolymerize. On the other hand, l/r_1 conforms to the copolymerization theory, and the value of l/r_1 indicates that 1-ethyl substitution increases the reactivity only by factor of two.

1-Phenyl substitution

In the copolymerization of 1-phenyl-substituted monomers with unsubstituted ones, unusual copolymer composition curves are obtained because of the bulkiness of the substituents (see Fig. 5). The copolymers



Fig. 5. 1-Phenyl substitution effect in copolymerizations at -78°C, [M]₀ = 3,0 mol/dm³
●: EVE/E1PVE (Toluene, CH₃COClO₄);
■: ST/DPE (Methylene chloride, SnCl₄·TCA);
○, □: Copolymer composition analysis by NMR)

of ethyl vinyl ether and ethyl 1-phenylvinyl ether always contain more than 33 mol-% of ethyl vinyl ether, as was expected by Lüssi¹⁴. When the vinyl ether content in the feed, is less than 20 mol-% the copolymer formed is expected to have a regular structure consisting of

$$\dots (M_1 M_2 M_2)_{\overline{n}} \dots$$

sequences. The monomer reactivity ratios were obtained by a curvefitting method assuming the penultimate model and $r_2 = 0$, $r_1 = r'_1$. When the catalyst was added the reaction mixture became red and the colour was discharged when the polymerization was stopped with methanol.

In the styrene/diphenylethylene copolymerization, the steric effect becomes even more pronounced and a 1:1 alternating copolymer is obtained when the styrene content in the feed is less than 20 mol-%. The copolymer compositions were determined by NMR spectroscopy. The value of l/r_1 is about unity which means that the relative reactivity of both monomers for a styrene propagating end is about equal. The polymerization system was colored red.

Discussion

The above-mentioned results are summarized in Table 3. 1-Methyl and 1-ethoxyvinyl ethers homopolymerize, but 1-ethyl- and 1-phenyl-substituted ones do not. 1-Substituted styrenes, except 1-methylstyrene, cannot

 Table 3. The cationic polymerizability of 1-substituted vinyl ethers and styrenes relative to unsubstituted monomers

	Vinyl	ether	Styrene		
1-Substituent	Homopoly- merizability	Copoly- merizability ^{a)}	Homopoly- merizability	Copoly- merizabilitv ^{a)}	
CH3	≫l	7,7	≫l	4,0	
C_2H_5	0	9,0	0	1,9	
OC_2H_5	≫1 ^{b)}	≫ 1 b)	0	≫ 1	
C_6H_5	0	≈ 2	0	1,1	

a) $1/r_1$ (M₁: unsubstituted monomer) is used as the measure.

b) Expected from the data in ref. 12).

produce homopolymers. These results mean that steric effects are very important in the cationic homopolymerization of 1,1-disubstituted ethylenes. The extent of steric hindrance by the 1-substituents is greater in styrene than in vinyl ether, as is clear from the homopolymerization of 1-ethoxy-substituted monomers and from copolymerization of 1-phenylsubstituted monomers (see Table 3).

The relative reactivity of vinyl monomers is increased considerably by methyl and ethoxy 1-substitution, but less so by ethyl and phenyl 1-substitution. The increase in reactivity by substitution due to electronic effects might be expected to lie in the order of $C_2H_5O > C_6H_5 > CH_3 \simeq C_2H_5$, but the actual changes in reactivity are the net result of opposing electronic and steric effects.

When the methyl group is introduced in the 2-position, the reactivity in cationic polymerization of vinyl ethers becomes 1-4 times greater and that of styrene about 0, 1-0, 7 times. Comparing this with our results for 1-methyl substitution, it is clear that 1-substitution by the methyl group enhances the reactivity more than 2-substitution in cationic polymerization.

In Table 4 are listed the changes in reactivity with 1-methyl substitution of ethyl vinyl ether and styrene in several reactions. Protonation reactions (hydrolysis, hydration and alcoholations) are accelerated 10^2-10^4

Reactant	Reaction	Ratio ^{a)} of k or K	Reaction conditions	Ref.
Ethyl vinyl ether	Hydrolysis	1,9.104	25°C, HClO ₄ , dioxan/H ₂ O (80 : 20)	15)
	Hydrolysis	1,3.104	25 °C, HCl, dioxan/H2O (80 : 20)	16)
	Bromination	3,0	0°C, CCl ₄	17)
	Bromination	3,2	0°C, CH ₂ Cl ₂	17)
	Polymerization	9,1	78°C, BF3O(C2H5)2 CH2Cl2	this work
	Argentation	(K) 1,0	10°C, (CH ₂ OH) ₂	18)
Styrene	Hydration ^{b)}	$1, 1 \cdot 10^2$	25°C, HClO ₄ , H ₂ O	19)
	Alcoholation	6,2.102	60°C (extrapolated), H ₂ SO4, CH ₃ OH	20)
	Alcoholation	9,1·10 ²	60°C (extrapolated), H ₂ SO4, C ₂ H ₅ OH	20)
	Bromination	12,6	0°C, CCl ₄	17)
	Bromination	4,8	0°C, CH ₂ Cl ₂	17)
	Polymerization	4,0	–78°C, SnCl ₄ ·TCA, CH ₂ Cl ₂	this work
	Argentation	(K ₁) 0,41 (K ₂) 0,92	0°C, H ₂ O	21)
	$\pi ext{-Complexation}$ with I_2	(ΣK _i) 0,53 i	room temp., isooctane	22)

Table 4. 1-Methyl substitution effect on the reactivity of vinyl ethers and styrenes in various cationic and related reactions

a) The ratio of rate or equilibrium constant (k or K) of 1-methyl-substituted reactants to that of 1-unsubstituted ones.
 b) Reactant: p-methoxystyrene.

times by 1-methyl substitution. On the contrary, the acceleration is no more than 3-13 times in the bromination and in cationic polymerization. Further, the equilibrium constants of complex formation with silver ion or iodine molecule hardly change or become smaller when an 1-methyl group is introduced. This tendency suggests that the smaller and the harder the electrophilic reagent, the greater the relative reactivity of the 1-methyl-substituted reactant. This is explained as follows: by substituting the 1-proton by the methyl group, the electron density at the 2-carbon in a double bond increases and that at the 1-carbon decreases, that is, the introduction of the methyl group induces an imbalance of electron density distribution in the double bond. Then the olefin will be more susceptible to attack by a hard acid such as a proton, since the acid will act selectively only on the 2-carbon of the double bond. The effect will not be so great in the case of a soft acid like silver ion or iodine because the acid attacks both carbons of a double bond at an early stage of the ratedetermining step. It can be said that the substituent effects in cationic polymerization and bromination are intermediate between those in protonations and in complexations with silver ion or iodine. This is further confirmed by the effect of 2-methyl substitution in cationic polymerization as described in our previous paper²³.

This study shows that ethyl 1-phenylvinyl ether (1-ethoxy-1-phenylethylene) does not produce a homopolymer under cationic conditions and ethyl 2-phenylvinyl ether (1-ethoxy-2-phenylethylene) does homopolymerize cationically²⁴⁾. Therefore, it may be concluded that the 1,1-disubstituted ethylene suffers more steric hindrance than does the 1.2-disubstituted one. On the other hand, many 1,1-disubstituted ethylenes form homopolymers by radical polymerization, but the corresponding 1,2disubstituted ethylenes do not, with the exception of those in which fluorine is the substituent. This leads one to suppose that the configuration in the transition state of cationic polymerization differs from that of radical polymerizations. It appears that the formation of the transition state complex between a carbenium ion and a double bond is constrained in such a way that an 1,1-disubstituted ethylene approaches the active species with more difficulty than the corresponding 1,2-disubstituted ethylene does. Accordingly, in cationic polymerization a 1-substituent may hinder the reaction more than a 2-substituent. On the other hand, as a radical attacks the 2-carbon directly, so a 2-substituent of a monomer hinders the approach of the active species more than an 1-substituent does. Therefore, the situation is reversed in radical polymerizations.

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