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MECHANISM OF THE INITIATION OF THE CATIONIC POLYMERIZATION OF STYRENES BY SILANES AND ACTIVATED COVALENT ESTERS

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Mechanism of the initiation of the cationic polymerization of styrenes by silanes and activated covalent species has been studied by NMR and SEC. Trimethylsilyl trifluoromethanesulfonate has been used as initiator for the cationic polymerization of styrene. It has been found that silyl triflate does not react directly with styrene but polymerization is initiated by the trace amount of the triflic acid formed by the hydrolysis of trimethylsilyl triflate. Polymer end groups do not contain silyl groups, polymerization is strongly inhibited by hindered pyridine and starts only after pyridine is completely consumed. Hexamethyldisiloxane has been found in the reaction products.

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Introduction

Polymers prepared in systems without transfer and termination, provided that initiation is fast, have narrow molecular weight distributions with degrees of polymerization corresponding to the ratio of reacted monomer to the used initiator. Such "living" systems have been known for 30 years in anionic polymerization[1], but only recently have well-defined polymers been prepared via cationic techniques. Living cationic polymerization has been first observed for heterocyclics[2] and later for vinyl monomers[3,4]. Carbenium ions, which are typical active centers in the cationic polymerization of alkenes, very easily participate in side reactions such as transfer, termination, or isomerization. This is, at least partially, due to hyperconjugation phenomena and high positive charge on β-H atoms. They are attacked by monomer and counterion leading to transfer processes. We have shown by simple semiempirical and *ab initio* calculations that up to 7% of charge is located on β-H atoms and 27% on C^+ atoms in 1-phenylethylium cations[5]. In the corresponding acetates (covalent species) a much stronger decrease of charge density on H-atoms (1%) relative to C-atoms (21%) was found. Thus, the covalent esters could react more selectively with alkenes, provided that they are reactive enough.

The direct reaction of covalent species with vinyl monomers has been first proposed by Plesch and Gandini[6]. Later, possibility of activation of a covalent ester by a cocatalyst has been recognized, not only for cationic[7], but also for anionic systems[8] (which are also known as group transfer processes). In these reactions the active centers have predominantly the covalent structure. However, the detailed spectral and kinetic experiments, as well as the molecular orbital considerations[9] suggest that polymerization could occur via ionic species which are present in very small amount, and which are in dynamic equilibria with dormant covalent centers.

Polymerization of monomers, which could be polymerized only via cationic mechanisms (vinyl ethers, isobutene), occurs with covalent species which are cocatalyzed by Lewis acids but which are not active alone. Styrenes are also polymerized by mixtures of different acetates and acids[10,11]. The resulting polymers have narrow molecular weight distributions. However, they are not strictly living, because termination has been observed after consecutive additions of monomer. We report below on the applications of different initiators in polymerization of styrenes and on the possible propagation mechanism.

Very recently polymerization of styrenes with trimethylsilyl trifluoromethansulfonate (1) has been reported [12]. We have been interested in the incorporation of silanes (and also polysilanes) into different polymers[13]. Therefore, we investigated the possibility of the direct reaction between 1 and styrenes in different solvents and found that initiation occurs via traces of acids formed by hydrolysis of 1.

Experimental

Styrenes and solvents were purified as described before[5,10]. 1-Arylethyl acetates were prepared from 1-arylethanol and the corresponding acids in the presence of carbodiimide. Commercial tertbutyl acetate was distilled before use. Reagents were transferred to NMR tubes or ampoules using a vacuum line. Solutions of monomer, ester, and hindered pyridines (2,6-di-tertbutyl-4-methylpyridine, or 2,6-di-tertbutylpyridine) were frozen in liquid nitrogen and the Lewis acid was distilled as the last reagent. Tubes or ampoules were then placed in the thermostated bath or directly into the NMR probe. NMR spectra were recorded at GE 300MHz, GPC traces were obtained using 10^3, 10^4, 10^5,10^6 (or linear ultrastyrogel), and 500 Å Waters columns.

Results and Discussion

Initiation with Silanes. Several parameters such as solvent, temperature, structures of a counterion, the activating Lewis acid, monomer, and the structure of electrophilic initiator R_1 can influence the extent of transfer and termination as well as the rate of initiation:

$$R_1\text{-A} + CH_2{=}CH(Ar) \xrightarrow{LA} R_1\text{-}CH_2\text{-}CH(Ar)\text{-A} \xrightarrow{(n\text{-}1)\cdot M} R_1\text{-}[CH_2\text{-}CH(Ar)]_n\text{-A}$$

The structure R_1 should be chosen in such a way that the rate of initiation should be at least as fast as the rate of propagation and that the reactivity of the first addition product should be at least similar to that of the growing macromolecular species. Trimethylsilyl group has been reported to increase the stability of β-carbenium ions which means that the reactivity of the esters should be enhanced by the β-SiR_3 group.

1 was used as the initiator of polymerization of styrene and 4-methylstyrene in the presence of small amount of 2,6-di-t-butyl pyridine (hindered pyridine) which is known to react with protonic acids but not with bulkier electrophiles such as trimethylsilyl group or carbenium ions. In the NMR tubes, sealed off under vacuum, no polymerization was observed after more than 1 month at low as well as at ambient temperatures. In the NMR tubes which were closed with septa, polymerization started after the hindered pyridine was completely consumed by the acid. This clearly indicates that the real initiator in these systems is triflic acid and not trimethylsilyl triflate. The NMR spectra of the precipitated polymers do not show presence of trimethylsilyl group. 1 was slowly hydrolysed to hexamethyldisiloxane and the acid which was immediately trapped by the hindered pyridine. The ^1H NMR spectrum which is shown on Fig. 1 reveals the presence of unreacted styrene (methylene protons at 5.20 and 5.80 ppm, methine proton at 6.75 ppm and aromatic protons at above 7.2 ppm), two singlets of the tert-butyl group of the unreacted 2,6-di-tert-butylpyridine (1.34 ppm) and protonated pyridine at 1.58 ppm, unreacted trimethylsilyl triflate at 0.52 ppm and hexamethyldisiloxane at 0.07 ppm. At longer reaction times increase of the proportion of hexamethyldisiloxane along with the complete disappearance of pyridine was found. At that stage styrene started to polymerize. Identical phenomena were observed for 4-methylstyrene. The dipole-dipole reaction of trimethylsilyl triflate with styrenes could be

accelarated in solvents with higher dielectric constants. However, even in most polar nitromethane similar behavior was observed. It seems that affinity of silicon towards oxygen is sufficient to induce the formation of silyl ketene acetals and cleavage of esters and some ethers[14], but the affinity towards carbon is too low to observe the addition of the most reactive 1 to styrene and 4-methylstyrene even in nitromethane solutions.

Other Alkylating Reagents . The structure of the alkylating reagent R_1 (shown in eq.1) should influence the relative ratio of initiation and propagation. We have investigated the influence of the structure of different acetates activated by Lewis acids (mostly BCl_3) on the properties of prepared polystyrenes. Slow initiation leads to broadening of the molecular weight distribution and incomplete initiation to molecular weights higher than predicted from $[M]_0/[I]_0$ ratios. On the other hand the "too good" initiator may also lead to incomplete initiation because it would decompose prior to addition to monomer.

The primary, secondary, and tertiary esters (mostly different acetates) were used as initiators in polymerization of styrenes. None of peralkyl esters (even tert-butyl acetate) when activated by Lewis acid initiated polymerization of styrenes. The initiation started with secondary esters bearing α-phenyl group. 1-Phenylethyl acetate which is the closest model of propagating species in polymerization of styrene gave polymers with relatively narrow molecular weight distribution ($M_w/M_n<2.$). Better results were found with esters of stronger acids such as halogenated acetates, for which polydispersities lower than ($M_w/M_n<1.3$) were found.

We have observed the interactions between growing carbenium ions and penultimate aromatic rings[15]. These interactions increase reactivity of dimeric and trimeric species in comparison with the 1-phenylethyl moiety. Thus, initiation might be slower than propagation for these systems. We have increased reactivity of initiators by incorporation of the p-methoxy groups into aromatic rings. These esters are much more active. Complexes between 1-(4-methoxyphenyl)ethyl acetate and BCl_3 decompose rapidly at -78^0 C in the absence of monomers. Under similar conditions complexes of 1-phenyl acetate and BCl_3 were stable up to -30^0 C [11]. Tertiary acetates with a phenyl group ionize in CH_2Cl_2 with different Lewis acids including SbF_5 and BCl_3 (strong UV absorption at 333 nm). Thus, the initiation with the latter esters involves ionic species. The addition of alkene to tertiary esters via multicenter rearrangement is impossible for steric reasons.

Structure of the Leaving Group. Too low nucleophilicity of the leaving group leads to the formation of ionic species with life times sufficient for complete dissociation and, subsequently, for transfer reactions[16]. Anions such as trifluoromethanesulfonate and perchlorate can serve as examples. More nucleophilic anions form covalent species which are not active *per sc* and require additional activation by either Lewis or protonic acids. We have studied polymerization of styrene, 4-methylstyrene, and 2,4,6-trimethylstyrene with acetates, chloroacetates and trifluoroacetates; we also used 1-methoxy-1-phenylethane as initiator with the methoxy leaving group. For the latter system no six-membered transition state could be drawn for the potential multicenter rearrangement reaction. In the experiments presented in Table 1, quantitative conversions were found. Polydispersities were quite low, which indicates that transfer was suppressed. Nevertheless, these systems are not living, since the termination by formation of chlorides was observed. Esters (or ethers) ionize reversibly in the presence of activating Lewis acids. However, once in a while they collapse back to chlorides. This is irreversible termination since 1-phenylethyl chlorides could not initiate polymerization of styrenes.

Mechanistic considerations. Polymerization of styrenes with counterions capable of forming covalent bonds may involve either ionic are covalent species. Typical cationic polymerization is accompanied by transfer reactions and is never living. Results discussed in these papers as well as the evidence coming from other systems indicate suppression of transfer and termination. How could this be achieved? Via covalent process (multicenter rearrangement) or via short living ionic species? Can the assumed ions behave in a special way, can they dissociate more weakly and be less susceptible to transfer? Some results support the presence of ionic species with very short life-times which reversibly form dormant covalent centers. The ionization of the latter might occur in the solvent cage, in which they could react once in a while with a monomer and immediately collapse back. Under these conditions dissociation could be negligible. Better results in less polar solvents and in the presence of salts with common ion might indicate that the ionic species can dissociate to "free" ions and participate in the usual side reactions. One important general feature of the systems with suppressed transfer is the use of anions which are stronger nucleophiles than bases. Therefore they preferentially coordinate with C^+-atoms rather than abstract β– H-atoms.

Eventually, the orbital symmetry theory and parity rules forbid the rearrangement within the four membered transition state and allow only the six membered transition state[9]. Some initiators such as ethers could not form six memebered transition states but they behave in the way similar to acetates. Thus, in these systems (and probably others, too) the only possible mechanism comprises ionic species. We have recently demonstrated that 1-phenylethyl trifluoroacetate is activated by trifluoroacetic acid [11]. However, the experiments with optically active acetate revealed that racemization of the ester is faster than its incorporation. This also confirms ionic mechanism of propagation. Some recent kinetic results suggest that group transfer polymerization also involves ionic intermediates. Thus, the suppresion of side reactions in all systems with covalent species can indicate the formation of short living ionic species and propagation which might occur within solvent cage without complete dissociation.

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Table 1

Molecular Weights and Polydispersities of Polystyrenes Prepared at -75^0 C in CH_2Cl_2 with Activated Covalent Initiators.

no	M	$[M]_0$	I	$[I]_0$	$[BCl_3]_0$	$[Py]_0$	M_n^T	M_n	M_w/M_n
1	1	2.8	11	.16	.19	.07	3310	2990	1.7
2	1	2.25	16	.019	.033	.001	12016	8400	1.3
3	1	1.0	15	.016	.020	.004	6500	6450	1.8
4	1	3.5	15	.39	.31	.48	1176	970	1.15
5	1	3.0	14	.26	.27	.10	1200	6500	1.7
6	1	1.45	17	.017	.010	-	8700	50000	1.6
7	2	0.81	12	.019	.023	.004	5030	5100	1.46
8	3	.65	11	.106	.12	.044	896	25200	1.16
9	3	.71	15	.016	.02	.004	648	5850	1.70
10	3	.66	12	.018	.024	.004	5353	5970	1.37

M: 1 (styrene), 2 (4-methylstyrene), 3 (2,4,6-trimethylstyrene)

I: 11 (1-phenylethyl acetate), 12 (1-phenylethyl methyl ether), 14(1-phenylethylchloroacetate), 15(1-phenylethyl trichloroacet-ate), 16(1-phenylethyl trifluoroacetate), 17(1-(4-methoxy)phe-nylethyl acetate)

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