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ScienceDirect
Mendeleev Commun., 2013, **23**, 274–276

Mendeleev Communications

Acetal-induced cationic polymerization of styrene and indene in hexafluoroisopropanol

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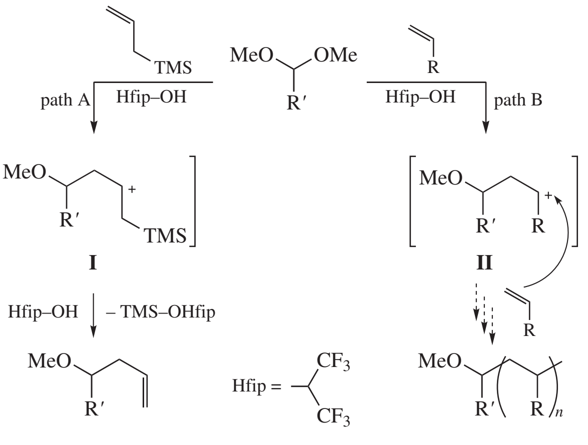
DOI: 10.1016/j.mencom.2013.09.012

Benzaldehyde and *p*-anisaldehyde dimethyl acetals in hexafluoroisopropanol initiate cationic polymerization of styrene and indene under essentially neutral conditions.

Recently,[1] an unprecedented ability of hexafluoroisopropanol (HFIP) to facilitate Hosomi–Sakurai reaction between dimethyl acetals and allylsilanes was disclosed by our team. Since HFIP has never been considered as a Lewis acid and its Brønsted acidity is quite low (pK_a = 9.3, *cf.* for acetylacetone pK_a = 9.0), the above fact was found to be rather surprising. It was suggested that the observed phenomenon is due to the capacity of HFIP to form a hydrogen bonded complex with acetal which reacts with a nucleophile through formation of a polar transition state stabilized within a conglomerate of several HFIP molecules (Scheme 1, path A).[1(b)]



Scheme 1

Here we present the results of our studies aimed at the employment of the above activating effect in the reactions of acetals with alkenes lacking silyl electrofuge. In this case an initially formed cationic species **II** (unlike intermediate **I**) should react with the next alkene molecule thus starting up the cationic polymerization (Scheme 1, path B).

It is relevant to note that according to earlier data β-pinene[2(a)] and *p*-methoxystyrene[2(b),(c)] readily undergo protonation in HFIP followed by the cationic polymerization in the absence of any other initiators. At the same time, for the less reactive styrene[2(b),(c)] and indene[2(c)] the addition of catalytic amounts of the fast-polymerizable alkene is required in order to achieve a reasonable rate of conversion. In this context, dimethyl acetals were considered to be the promising initiators of alkene polymerization in the HFIP medium.

We have chosen *p*-anisaldehyde dimethyl acetal **1** as the primary object for testing the possibility of acetal-initiated polymerization since it contains the electron-donating group which may stabilize the arising cationoid center and thus facilitate its formation under the mild reaction conditions. It was rewarding to find out that upon an addition of the catalytic amount of **1** to the solution of styrene in HFIP at ambient temperature an almost immediate formation of white precipitate is observed and after an additional stirring for 96 h the ^{1}H NMR data revealed that *ca.* 90% of styrene was converted into the respective polymer. After further evaporation of HFIP *in vacuo* polystyrene (M_n 10000, M_w/M_n 2.35) was isolated in 85% yield as a sole product.[†] Additional studies revealed that the variations in HFIP/styrene molar ratio may affect noticeably the rate of the polymerization and it is advisable to keep this value within the interval 5–9 : 1 (see Table 1, runs 2–4). ^{1}H NMR monitoring of reaction course indicated that neither M_n of the polymer nor its polydispersity reveal any trend in dependence on the conversion of the monomer (*e.g.*, data in run 3).[‡] However, since the reaction proceeds with the intensive formation of solid phase we found it rather problematic to carry out additional experiments in order to optimize the reaction conditions.

The above results could be contrasted to the data of the earlier studies[2(b),(c)] which attested to a nearly inertness of styrene toward attempts to perform its polymerization in HFIP in the absence of additional initiators. The observed dramatic acceleration of the styrene polymerization in HFIP caused by the addition of the catalytic amounts of acetal **1** (*cf.* runs 1 and 2) presents an unambiguous evidence showing that the latter plays actually a role of an efficient promoter of the polymerization as is shown in Scheme 2.

Switching from **1** to benzaldehyde dimethyl acetal **2** did not cause a noticeable change in the polymerization rate (*cf.* runs 2 and 5). Hence one may conclude that the presence of an electron-donating group is not a necessary prerequisite for the promoter efficiency. At the same time, it was found that the parent *p*-anisal-

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[†] *Typical preparative procedure*. The initiator was introduced to a 25 ml pre-dried vial filled with argon and containing solution of monomer in HFIP (the reagents were distilled over calcium hydride) *via* microsyringe under stirring at room temperature. Polymerization progress was monitored by ^{1}H NMR by withdrawing *ca.* 0.05 ml of liquid phase from the reaction mixture and placing it to NMR tube containing $CDCl_3$ (*ca.* 0.4 ml). Stirring was continued until the ratio [HFIP]/[monomer] became constant. If conversion was less than 75% the residue was additionally refluxed in ethanol (*ca.* 10 ml) in order to remove traces of monomer and oligomeric material. The solvent evaporation followed by vacuum-drying (70 °C/0.5 Torr) furnished the respective products as white solids.

[‡] These observations obviously indicated a non-living nature of the styrene polymerization[3] under the elaborated conditions.

Table 1 Polymerization of styrene in HFIP medium at room temperature.

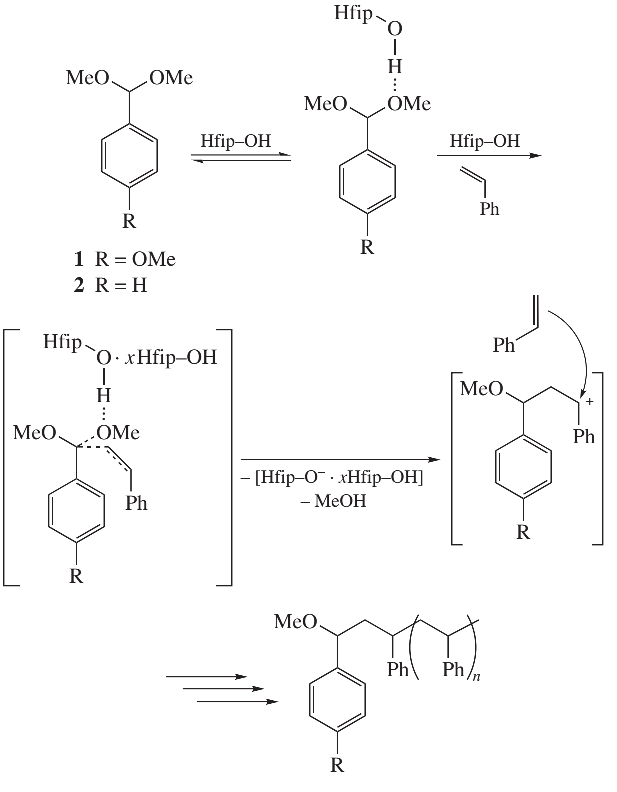
Run	Initiator	[Initiator]/[styrene]	[HFIP]/[styrene]	*t*/h	Conversion (%)[a]	Yield (%)	M_n/g mol^{-1}[b]	M_w/M_n[b]
1	–	–	5.0	170	5	3	28300	1.81
2	$4\text{-MeOC}_6\text{H}_4\text{CH(OMe)}_2$	0.02	5.0	96	90	85	10000	2.35
3	$4\text{-MeOC}_6\text{H}_4\text{CH(OMe)}_2$	0.02	8.7	24	75	73	12400	1.98
				96	85	80	7700	2.27
4	$4\text{-MeOC}_6\text{H}_4\text{CH(OMe)}_2$	0.02	15.7	96	65	60	8200	2.30
5	PhCH(OMe)_2	0.02	8.4	96	90	83	8800	2.58
6	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	0.02	8.6	96	10	5	14300	2.03

[a] Determined by ^{1}H NMR. Conversion was calculated from the ratio of intensities of characteristic proton signals in styrene and HFIP. [b] Determined by SEC using PS standards.

Table 2 Polymerization of indene in HFIP medium at room temperature.

Run	Initiator	[Initiator]/[indene]	[HFIP]/[indene]	*t*/h	Conversion (%)[a]	Yield (%)	M_n/g mol^{-1}[b]	M_w/M_n[b]
1	–	–	5.5	360	15	15	22000	2.15
2	$4\text{-MeOC}_6\text{H}_4\text{CH(OMe)}_2$	0.100	5.0	2	95	90	11500	3.05
3	$4\text{-MeOC}_6\text{H}_4\text{CH(OMe)}_2$	0.025	5.3	2	95	92	26000	1.97
4	PhCH(OMe)_2	0.025	5.0	2	95	90	29200	1.89
5	$4\text{-MeOC}_6\text{H}_4\text{CHO}$	0.025	5.0	240	15	10	20900	2.60

[a] Determined by ^{1}H NMR. [b] Determined by SEC using PS standards.



Scheme 2

dehyde reveals a much lower initiating activity than acetal **1** (*cf.* runs 2 and 6).

In order to evaluate the generality of the disclosed capacity of the acetal/HFIP system to promote the cationic polymerization we turned our attention to indene since its cationic polymerization is well-investigated and the respective polymer may find a number of practically useful applications.[3,4]

The results of the experiments with indene are presented in Table 2.

In close analogy to styrene, indene exhibits a rather slow rate of polymerization when mixed with a neat HFIP or with HFIP/*p*-anisaldehyde system (runs 1 and 5). At the same time in the presence of acetals **1** or **2** a rather fast and nearly quantitative polymerization took place (runs 2–4). Noteworthy, a decreasing of the amount of initiator leads to the expected increase of the molecular weight (*cf.* runs 2 and 3). Higher reactivity in comparison with that of styrene (*cf.* Tables 1 and 2) could be explained by the presence of electron-donating alkyl substituent[3(c)] and the impossibility of chain transfer *via* an intramolecular Friedel–Crafts alkylation.[3(a),(b)]

Representative polystyrene and polyindene samples were analyzed by ^{19}F NMR spectroscopy which revealed the absence of any fluorine atoms. This observation indicates that termination involving the attack of hexafluoroisopropyl anion across the cationic active center apparently does not occur; therefore, chain ends are most likely formed by standard chain transfer reactions like β-proton elimination and Friedel–Crafts alkylations.[3,§]

A large number of classical procedures for the cationic polymerization of indene[4] and styrene[5] are known which involve the usage of initiating systems containing Lewis acids [*e.g.* TMPCl/TiCl_4[4(c),5(d)], cumyl chloride/SnCl_4,[4(d)] cumyl methyl ether/TiCl_4,[4(e)] 1-(*p*-methylphenyl)ethyl acetate/BCl_3,[5(c)] 1-phenylethyl chloride/$\text{TiCl}_3(\text{OPr}^i)$[5(e)]]. Interestingly, adducts of HCl with vinyl ethers in conjunction with SnCl_4 and Bu_4NCl were also employed as initiators for the synthesis of α-functionalized polystyrenes.[5(f)]

In a striking contrast to all these well-elaborated methods, the initial generation of carbocationic species under our conditions occurs in the absence of any Lewis or strong Brønsted acidic compounds since HFIP provides an electrophilic activation of acetals due to its outstanding hydrogen bond donating capacity in conjunction with a number of other properties such as the propensity to stabilize cationoid intermediates well described in the literature.[6]

In conclusion, the data in the present work demonstrate the interesting capability of dimethyl acetals of aromatic aldehydes in HFIP medium to serve as the initiators for the styrene and indene cationic polymerization under the acid-free conditions. This novel protocol is experimentally simple, ecologically benign and furnishes the respective polymers in excellent yields.[¶]

[§] Unfortunately, we were not able to prove this assumption because ^{1}H NMR signals which could be possibly assigned to end-group protons have too small intensities (at the level of trace impurities).

[¶] The obtained polymers reveal MWD characteristics comparable to those for the products of the conventional non-living cationic polymerization of indene[4(a),(b)] and styrene.[5(a)–(c)] ^{1}H and ^{13}C NMR spectra of the prepared polymers corroborated with the data found in the literature for polyindenes[4(c),(e)] and polystyrenes.[5(e),(f)]

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Received: 29th April 2013; Com. 13/4114