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Initiation of living polymerization of isobutyl vinyl ether by the "H_2O"/n-Bu_4NTiCl_5 system

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Summary

Living carbocationic polymerization (LC$^{\oplus}$Pzn) of isobutyl vinyl ether (IBuVE) is readily initiated by adventitious moisture ("H_2O") in the presence of n-Bu_4NTiCl_5 in CH_2Cl_2 solvent at -20 °C to yield high molecular weight polymers (up to 100,000 g/mole) with narrow molecular weight distributions ($\bar{M}_w/M_n \approx 1.1$). The number of macromolecules remains constant and reflects the number of "H_2O" molecules in the charge. The *de facto* initiator is most likely HCl formed *in situ* by the partial hydrolysis of n-Bu_4NTiCl_5. Surprisingly the overall polymerization rates obtained in the presence of purposely added initiator, MeCH(O*i*-Bu)Cl, were lower than in the absence of it, *i. e.*, with "initiator free" system. Experiments carried out in the presence of the proton trap, 2,6-di-*tert*-butylpyridine (D*t*BP), and alcohols were analyzed to explain the findings. The observed rates may be explained by reactions between "H_2O" and the various ingredients in the system prior to initiation.

Introduction

In the course of our investigations of living IBuVE polymerization induced by the MeCH(O*i*-Bu)Cl/n-Bu_4NTiCl_5 system (1), we have discovered that polymerization readily proceeds even in the absence of the MeCH(O*i*-Bu)Cl initiator, *i.e.*, in "initiator free" systems, and that, surprisingly, the overall rates obtained in the presence of purposely added initiator were lower than in the absence of it. These findings prompted us to carry out further experiments, described in this paper, which led us to the conclusion that in conventionally dried systems subanalytical quantities of moisture (or other protogenic impurities collectively indicated by the symbol "H_2O" (2)) are efficient initiators for the LC$^{\oplus}$Pzn of IBuVE, and that the relatively low rates obtained in the presence of MeCH(O*i*-Bu)Cl are most likely due to reaction products arising from "H_2O" plus ingredients in the charges.

Experimental

Chemicals. D*t*BP (Aldrich, 97%) was used as received. Poly(ethylene glycol) (PEG) (Aldrich, M.W.=6,800) and 2-phenyl-2-propanol (Aldrich, 97%) solutions in CH_2Cl_2 were dried by molecular sieves (Fisher, type 3A). The source and purity of other chemicals, together with the polymerization conditions and analytical techniques used have been described in our previous paper concerning the living polymerization of IBuVE (1).

Results and discussion

A) Initial Observations that Lead to Three Questions.

Table 1 and Figure 1 show the results of representative experiments in which IBuVE polymerizations were induced by adding the monomer to n-Bu_4NTiCl_5 solutions in CH_2Cl_2 at -20 °C under various conditions. In both sets of experiments, the molecular weight of the polymers increases linearly with the yield of polymer (W_p), and very high molecular weight

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Table 1. "Initiator-free" polymerization of IBVE by n-Bu_4NTiCl_5.
Solvent - CH_2Cl_2; -20 °C; V=10 mL.

[n-Bu_4NTiCl_5], mM	[IBuVE]$_0$, M	time, min	yield, %	$\overline{M}_n$, g/mole	$\overline{M}_w/\overline{M}_n$	[N], mM
		Individual Experiments				
5	1	160	22	18,000	1.08	1.2
10	1	160	80	74,000	1.08	1.1
40	1	160	98	94,000	1.29	1.0
20	1	20	41	45,000	1.14	0.9
20	1	80	89	92,000	1.12	1.0
Average						1.0 ± 0.2
		"All Monomer In" (AMI) Experiments				
20	0.5	180	98	20,700	1.05	2.4
20	1	180	98	42,000	1.11	2.3
20	2	180	101	70,000	1.09	2.9
20	3	180	101	101,000	1.07	3.0
Average						2.7 ± 0.4

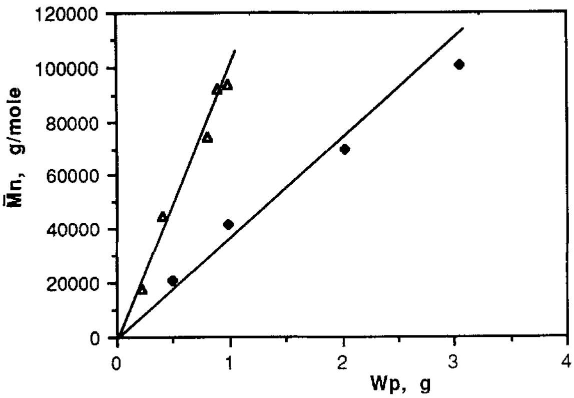

Figure 1. Molecular weight versus yield of polymer in IBuVE polymerization initiated by "H_2O"/n-Bu_4NTiCl_5.
△ - experiments carried out under various conditions (see the first set of five experiments in Table 1)
◆ - "All Monomer In" experiments. Solid lines were calculated assuming [N] = 1.0 and 2.7 mM, respectively. (see Table 1 for conditions)

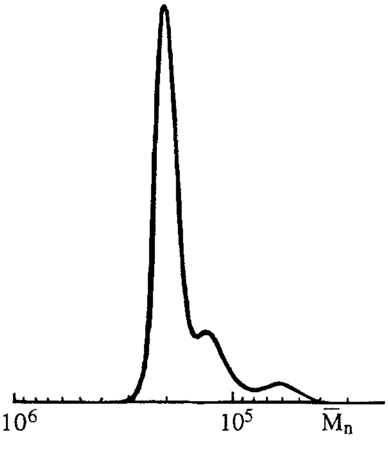

Figure 2. GPC trace of a polymer after the third incremental monomer addition in an "initiator-free" polymerization. [n-Bu_4NTiCl_5] = 20 mM;
solvent - CH_2Cl_2; -20 °C; V_0=10 mL;
increments - [IBuVE] = 1 M;
time between monomer additions 1.5 h;
total time 4.5 h.

(~100,000 g/mole) and narrow MWD ($\bar{M}_w/\bar{M}_n \approx 1.1$) products are readily obtained. Evidently these polymerizations are living.

The number of polymer molecules formed in these experiments ([N]=1-3 m*M*) reflects the number of "H_2O" molecules one usually finds in reasonably but not exhaustively dried systems (3). The fluctuation in N in the two sets of polymerizations is probably due to a fluctuation of ["H_2O"] in the charges as a result of the different purity levels of the solvent and reagents.

The results of experiments by the Incremental Monomer Addition (for a description of this so called IMA technique, see references (4-6)) showed multimodal MWDs, and the number of peaks in the GPC traces corresponded with the number of monomer increments added to the charges. Figure 2 shows a representative GPC trace obtained after three incremental monomer additions. The explanation of this phenomenon is given below.

It was observed that the rates of IBuVE polymerizations carried out with "initiator free" (*i.e.*, "H_2O"/*n*-Bu_4NTiCl_5) systems were higher than those carried out with purposely added initiator, *i.e.*, with the MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5 system. For example, the conversions obtained with the "H_2O" and MeCH(O*i*-Bu)Cl initiators were, respectively, 41 % and 20 % under the same conditions (compare the datum shown in the line 4 of Table 1 with that in the line 3 of Table 1 in ref.1). Evidently in the presence of the purposely added initiator, the rate was not proportional to [MeCH(O*i*-Bu)Cl] plus ["H_2O"], but was lower (!) than that obtained with "H_2O" alone.

The above observations prompted us to carry out experiments, specifically to answer three questions: 1) Is "H_2O" an initiator in the presence of MeCH(O*i*-Bu)Cl, and if so 2) How could the initiation by "H_2O" be rationalized; 3) Why is the rate of polymerization higher in an " initiator free" system than in the presence of MeCH(O*i*-Bu)Cl initiator? Below we proceed to develop answers to these questions.

B) Is "H_2O" an Initiator in the Presence of MeCH(Oi-Bu)Cl?

Proton traps are valuable tools in the investigation of the role of water in cationic polymerization (7,8). Thus, experiments were carried out with D*t*BP to elucidate the role of "H_2O" in the charges under investigation.

Table 2 shows the experimental design and summarizes the findings. The number of polymer molecules formed in the presence of D*t*BP is significantly lower than those obtained in the absence of this scavenging agent (compare N values in Table 2). Furthermore, the difference in N values obtained in experiments carried out in the presence and absence of MeCH(O*i*-Bu)Cl initiator (Δ[N] = 1.3, 1.4 m*M*) is virtually identical to the number of polymer molecules obtained with the control system "H_2O"/*n*-Bu_4NTiCl_5 (1.5, 1.7 m*M*). In line with the results of these experiments, we can answer the first question in the affirmative: "H_2O" is

Table 2. Influence of 2,6-di-*tert*-butylpyridine on IBuVE polymerization initiated by MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5. [*n*-Bu_4NTiCl_5] = 20 m*M*; [IBuVE]$_0$ = 1 *M*; Solvent - CH_2Cl_2; -20 °C; *V*=10 mL.; 5 hours.

[MeCH(O*i*-Bu)Cl]$_0$, m*M*	[DTBP], m*M*	yield, %	$\bar{M}_n$, g/mole	[N], m*M*	Δ[N], m*M*
5.0	-	103	18,500	5.6	→ 1.3
5.0	10	98	23,000	4.3	
2.5	-	102	28,500	3.6	→ 1.4
2.5	10	89	41,000	2.2	
-	-	108	74,000	1.5	
-	-	94	56,000	1.7	

indeed an initiator for the LC$^{\oplus}$Pzn of IBuVE in the presence of MeCH(Oi-Bu)Cl. At this point the question immediately arises:

C) How Can Initiation by "H_2O" be Rationalized?

A possible answer could be given by assuming partial hydrolysis of n-Bu_4NTiCl_5:
"H_2O" + n-$Bu_4NTiCl_5 \longrightarrow HCl + n$-$Bu_4NTiCl_4OH \dashrightarrow HCl + n$-$Bu_4NTiCl_3O$
and initiation by the *in situ* formed HCl:
$HCl + CH_2{=}CH(Oi$-$Bu) \longrightarrow MeCH(Oi$-$Bu)Cl \longrightarrow$ polymerization
The exact course of the hydrolysis of n-Bu_4NTiCl_5 may be quite complex (9) and may be similar to that of $TiCl_4$ (10). Thus the composition of hydrolysis products has not been determined and the formulas shown are hypothetical.

The conclusion in regard to "H_2O" as the cationogen has been substantiated by experiments in which alcohols were used as initiators. We assumed that similarly to "H_2O", alcohols would also give rise to HCl by alcoholysis of n-Bu_4NTiCl_5:
$ROH + n$-$Bu_4NTiCl_5 \longrightarrow HCl + n$-$Bu_4NTiCl_4OR$
so that polymerizations would be initiated by alcohols, however, the polymers formed would not contain alcohol residues. To facilitate our analytical task we selected an aromatic alcohol, $PhMe_2COH$, and a relatively high molecular weight PEG as initiators. We theorized that if HCl would be the initiator, the PIBuVE formed would contain neither the aromatic moiety from $PhMe_2COH$ nor the PEG block from PEG. The presence of the aromatic residue could be detected by UV spectroscopy, and PEG could be traced by GPC.

Table 3 shows the experimental conditions and results. To avoid hydrolysis of the expected acetals upon quenching with MeOH (containing ~2%vol. of NH_4OH), the systems were rapidly evaporated, the products dissolved in THF, filtered, and analyzed. The polymer obtained with 2-phenyl-2-propanol did not show UV activity by the UV detector of the GPC instrument. In case of initiation by similar aromatic alcohols of isobutylene polymerization, the aromatic head-group is easily detectable by UV spectroscopy even if the molecular weights are quite high (11). In the case of PEG initiator, the resulting product exhibited bimodal MWD by the RI detector of the GPC instrument: One of the peaks was due to the PIBuVE formed, the other to the (practically) unchanged PEG, indicating that the two polymer segments were independent of each other and that PEG did not get incorporated into the PIBuVE formed.

According to these results, the two alcohols examined induced polymerization, however, the alcohol residues did not become attached to the polymer. Significantly, the number of macromolecules formed in these experiments was equal to the number of OH groups employed (see Table 3). In line with these results, we postulate that ROH/n-Bu_4NTiCl_5 combinations induce IBuVE polymerization and that the true initiating entity is HCl formed by alcoholysis of the complex salt. By implication, these facts also support our proposition that initiation by "H_2O" occurs by HCl formed by hydrolysis of n-Bu_4NTiCl_5.

Table 3. IBuVE polymerization initiated by alcohol/n-Bu_4NTiCl_5.
$[OH]_0 = 10$ mM; $[n$-$Bu_4NTiCl_5] = 20$ mM; $[IBuVE]_0 = 1$ M; Solvent - CH_2Cl_2; -20 °C; V=10 mL.; 5 hours.

alcohol	yield, %	M_n, g/mole	[N], mM	remarks
$PhMe_2COH$	30	2,800	10.7	UV inactive product
H-$(OCH_2CH_2)_n$-OH (M_n~ 6800)	11	1,100[1]	10.0	Bimodal product

[1] The peak of poly(isobutyl vinyl ether) in the bimodal GPC trace (see text).

D) Rates of Polymerizations in "H_2O" and MeCH(Oi-Bu)Cl Initiated Systems.

As mentioned above, IBuVE can be efficiently initiated both by "H_2O"/*n*-Bu_4NTiCl_5 (*i. e.*, "initiator free") systems and by MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5 combinations, and the rate of polymerizations is higher in the former systems than in the latter ones. The question arises: How come that the polymerization rate in the presence of purposely introduced initiator, MeCH(O*i*-Bu)Cl, is lower than in its absence?

These at the first glance strange findings can be readily accounted for by assuming that first, "H_2O" hydrolyses the initiator:
"H_2O" + MeCH(O*i*-Bu)Cl ⟶ HCl + MeCH(O*i*-Bu)OH
and the hemiacetal so formed may react with the coinitiator *n*-Bu_4NTiCl_5 (similarly to the alcoholysis of $TiCl_4$):
MeCH(O*i*-Bu)OH + *n*-Bu_4NTiCl_5 ⟶ HCl + *n*-Bu_4NTiCl_4OCH(O*i*-Bu)Me
yielding the *de facto* initiator HCl plus a species *n*-Bu_4NTiCl_4OCH(O*i*-Bu)Me that causes retardation. The exact mechanism of retardation is obscure.

The results obtained with alcohol initiators are in line with this proposition: The structure of the complex acetal *n*-Bu_4NTiCl_4OCH(O*i*-Bu)Me formed in the above reaction and the complex alkoxide *n*-Bu_4NTiCl_4OR formed from alcohols are similar, and the addition of increasing amounts of alcohols reduces the rate of polymerization (compare the complete conversion of monomer in the presence of MeCH(O*i*-Bu)Cl (Table 2) with the 11% and 30% yields obtained in the presence of alcohols (Table 3) under the same conditions).

Conclusions

The observations described in this paper may be rationalized by the reactions summarized in Scheme 1.

Scheme 1.

Initiation by "H_2O"
n-Bu_4NTiCl_5 is hydrolyzed by "H_2O":
"H_2O" + *n*-Bu_4NTiCl_5 ⟶ HCl + *n*-Bu_4NTiCl_4OH ⟶ HCl + *n*-Bu_4NTiCl_3O
and the *in situ* formed HCl yields the *de facto* initiator:
HCl + CH_2=CH(O*i*-Bu) ⟶ MeCH(O*i*-Bu)Cl ⟶ polymerization.
The coinitiator is most likely a mixture of *n*-Bu_4NTiCl_5 and products of its hydrolysis, the structures of which are uncertain.

Initiation by MeCH(O*i*-Bu)Cl in the presence of "H_2O"
"H_2O" may hydrolyze purposely added initiator:
"H_2O" + MeCH(O*i*-Bu)Cl ⟶ HCl + MeCH(O*i*-Bu)OH
and the hemiacetal formed goes on to react with the coinitiator *n*-Bu_4NTiCl_5:
MeCH(O*i*-Bu)OH + *n*-Bu_4NTiCl_5 ⟶ HCl + *n*-Bu_4NTiCl_4OCH(O*i*-Bu)Me.
These reactions yield the *de facto* initiator HCl:
HCl + CH_2=CH(O*i*-Bu) ⟶ MeCH(O*i*-Bu)Cl ⟶ polymerization
plus acetals which may function as retarders. The coinitiator is probably a mixture of *n*-Bu_4NTiCl_5 and other reaction products including *n*-Bu_4NTiCl_4OCH(O*i*-Bu)Me.

Initiation by alcohols in the presence of "H_2O"
Alcoholysis of *n*-Bu_4NTiCl_5
ROH + *n*-Bu_4NTiCl_5 ⟶ HCl + *n*-Bu_4NTiCl_4OR
yields HCl which triggers the polymerization:
HCl + CH_2=CH(O*i*-Bu) ⟶ MeCH(O*i*-Bu)Cl ⟶ polymerization.
Initiation by "H_2O" may also occur. The coinitiator in this case is likely a complex mixture of *n*-Bu_4NTiCl_5, *n*-Bu_4NTiCl_4OR, *n*-Bu_4NTiCl_3O, *etc.*

Scheme 1 also explains why the AMI experiments produce uniform polymers with very high molecular weights and narrow MWDs (Table 1), while IMA experiments yield polymers with multimodal MWDs (Figure 2): Under AMI conditions all "H_2O" in the charge is consumed in the first step giving rise to uniform products with monomodal MWDs; in contrast, in IMA experiments each fresh monomer increment is tantamount to the introduction of a fresh aliquot of "H_2O", which may hydrolyze n-Bu_4NTiCl_5 and thus yield HCl *in situ* which in turn gives multimodal product.

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