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Carbocationic polymerization in supercritical carbon dioxide

II. Synthesis of *tert*-Cl terminated polyisobutylene by mixed Friedel-Crafts acids

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Abstract

Polymerization of isobutylene (IB) in supercritical carbon dioxide (SC·CO_2) at 32.5°C and 140 bar by the use of 2-chloro-2,4,4-trimethyl-pentane (TMPCl) initiator in conjunction with a mixture of $TiCl_4$/BCl_3 leads to well-defined polyisobutylenes (PIB) capped by a t-Bu head group and a t-Cl tail group (*t*Bu-PIB-Cl^t) of $M_n \sim 1800$ g/mole and $M_w/M_n = 1.3$. The $TiCl_4$/BCl_3 mixture may be viewed a new Friedel-Crafts Acid that effects rapid initiation, essentially chaintransferless propagation and reversible termination. The mechanism of IB polymerization of $TiCl_4$/BCl_3 mixtures is discussed.

I. Introduction

As shown in the first paper of this series [1], IB can be polymerized by Friedel-Crafts acids, e.g., $TiCl_4$, BCl_3, $SnCl_4$, in SC·CO_2 at 32.5°C to reasonably high molecular weight products ($M_n \sim 2000$-2500, $M_w/M_n \sim 2.0$). The structures of these PIBs are essentially identical to those obtained in conventional (non-living) liquid-phase systems at cryogenic temperatures, i.e., they are capped by the usual mixture of exo- and endo-olefinic tail-groups, indicating that the main chain-breaking event is proton elimination (i.e., chain transfer to monomer).

Prompted by this discovery we set out to develop conditions for the high temperature synthesis of PIB in SC·CO_2 with the versatile -CH_2-$C(CH_3)Cl$ (tert-chlorine, -Cl^t) endgroup. This paper describes the road toward this objective, specifically the key prediction and subsequent demonstration that by the use of the mixed Friedel-Crafts acid system $TiCl_4$/BCl_3 well-defined PIBs with -Cl^t endgroups can be obtained in SC·CO_2 at 32.5°C.

II. Experimental

The source and purity of the chemicals, together with details of equipment, procedures and analytical methods have been described [1]. The polymerization were also effected as described [1] except in the present instances two coinitiators, $TiCl_4$ and BCl_3, were used. Two kinds of experiments were run: In one series the entire three-component initiating system TMPCl/$TiCl_4$/BCl_3 was charged in one glass ampoule (~ 7 mL), whereas in another series two ampoules were used: one charged with TMPCl/$TiCl_4$ and another with BCl_3. The ampoules were charged with the predetermined amounts of TMPCl and $TiCl_4$ in a dry box under dry nitrogen at room temperature. As described in our earlier paper [1] the TMPCl/$TiCl_4$ mixture is deep red at room temperature, however, the color rapidly changes to light yellow at -15°C. This color change is reversible. The TMPCl/($TiCl_4$/BCl_3) system was prepared by adding with a pipet liquified BCl_3 to precooled TMPCl/$TiCl_4$ at -50°C. The ampoule containing the three component mixture was closed by a rubber septum, cooled to -78°C, and sealed with a flame. Then the ampoule is stored for ~1 hour at room temperature under a hood to ascertain the absence of leakage. During this observation period the system slowly turns deep red. The sealed ampoules were stored (aged) at -15°C until use.

III. Results and Discussion

A. Polymerization of IB in SC·CO$_2$ by TMPCl in conjunction with TiCl$_4$/BCl$_3$ mixed coinitiators

Earlier research from our laboratories has shown [2] that living carbocationic polymerizations (LC$^{\oplus}$Pzn) of isobutylene, styrene and other olefins proceed by stabilized carbocations in the absence of dissociated "free" carbenium ions. LC$^{\oplus}$Pzn can be attained by several means, for example, by the use of internal or external electron donors, or by suppressing the concentration and/or life time of free carbocations (common ion effect) [2].

An analysis of polymerization mechanisms induced by various Friedel-Crafts acids, specifically by BCl$_3$ and TiCl$_4$ [3-5], led us to speculate that LC$^{\oplus}$Pzn of olefins could be achieved and well-defined -Cl^t terminated products could be obtained even at relatively high temperatures in conjunction with mixed TiCl$_4$/BCl$_3$ coinitiators, i.e., in polymerizations in which the beneficial characteristics of both TiCl$_4$ and BCl$_3$ would be combined. Specifically, we postulated that by the use of the TMPCl/(TiCl$_4$/BCl$_3$) mixed initiating system we will obtain controlled coinitiation by TiCl$_4$ and rapid reversible termination by BCl$_3$ (i.e., BCl$_4^{\ominus}$) leading to the well-defined tBu-headgroup and -Cl^t tailgroup, respectively, and thus will produce exclusively t-Bu-PIB-Cl^t (see Section III C for discussion of the mechanism).

Table 1 shows typical reaction conditions and results. In Expts. 1-3 the three-component initiating system TMPCl/(TiCl$_4$/BCl$_3$) was aged in one ampoule, whereas in Expts. 4-8 TMPCl/TiCl$_4$ and BCl$_3$ were placed in separate ampoules and combined by breaking the ampoules in the reactor. Expts. 7 and 8 are "controls": Expt. 7, carried out in the presence of only a relatively small quantity of CO$_2$ (20 bar, way below the critical pressure of CO$_2$), gave a very low amount (~5% conversion) of ill-defined (multimodal molecular weight distribution) product indicating that polymerization in liquid CO$_2$ (non SC·CO$_2$) lead to unacceptable results. Expt. 8, in which *n*-hexane was the solvent, gave practically no polymer (~0.5% conversion), suggesting, again that SC·CO$_2$ conditions are necessary to obtain satisfactory polymerizations. Expts. 4 and 5 were essentially duplicates (we do not think that the small difference in CO$_2$ pressure and/or aging time substantially affect the results).

Table 1. Polymerization of IB in SC·CO$_2$ initiated by the TMPCl/(TiCl$_4$/BCl$_3$) initiating system at 32.5°C*

	Conditions						Results		
Expt.	P bar	TiCl$_4$ mole	BCl$_3$ mole	Aging time, days	CH$_3$Cl mL	Time hours	Conv.** %	M$_n$ g/mole	M$_w$/M$_n$
TMPCl/TiCl$_4$/BCl$_3$: The three components aged in the ampoule									
1	140	0.036	0.027	1	30	3.0	~42	1800	1.4
2	140	0.036	0.030	0.5	30	3.0	~40	1800	1.4
3	140	0.036	0.040	0.1	30	3.0	~35	1700	1.3
TMPCl/TiCl$_4$ aged in one ampoule; BCl$_3$ in second ampoule									
4	129	0.036	0.027	16	14	4.0	~45	2400	1.5
5	140	0.036	0.027	9	15	4.0	~40	2000	1.4
6	140	0.036	0.054	14	15	3.6	~36	2000	1.3
7	20	0.036	0.027	4	15	3.8	~5	2000	broad, multimodal
8***	-	0.036	0.027	5	15	4.0	~0.5	-	-

* [TMPCl] = 0.001 mole, [IB] = 0.36 mole, total volume = 300 mL

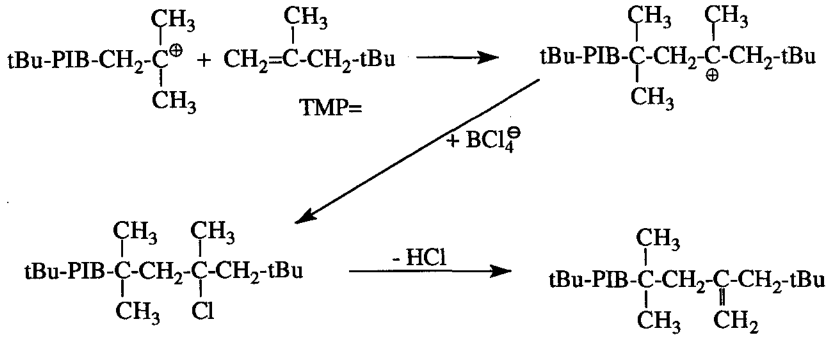
** Minimum values; some loses due to incomplete recovery of PIB from the reactor

*** 220 mL n-hexane was used as solvent

In Expt. 3 and 6 the BCl_3 concentration was increased and the narrowing of the molecular weight distribution to $M_w/M_n = 1.3$ may be due to this change.

According to spectroscopic structure analysis (see Section III B) the PIBs obtained in all SC·CO_2 experiments (Expts. 1-6) contained the expected -Cl^t tailgroup and revealed no detectable evidence of terminal unsaturation. Importantly, the tBu-/-Cl^t (i.e., headgroup/tailgroup) ratios of PIBs obtained in Expts. 1-3 were within experimental error of unity indicating the "clean" synthesis of the target tBu-PIB-Cl^t.

In contrast to the theoretical values obtained in the first series of experiments in which the three initiator components were aged in the same ampoule, the tBu-/-Cl^t ratios were higher than unity (e.g., ~1.4) in products obtained in Expts. 4-6, i.e., when the TMPCl/$TiCl_4$ and BCl_3 were in separate ampoules. The higher than unity tBu-/-Cl^t ratio can be readily explained by postulating that the TMPCl lost HCl in the presence of $TiCl_4$ during aging, and that the 2,4,4-trimethyl-1-pentene (TMP=) so formed reacted with propagating carbocations. Scheme 1 outlines the sequence of steps giving rise to a product with tBu-/-Cl^t = 2.0. The "buried" carbocation formed from the propagating carbenium ion plus TMP= (Step 1) cannot sustain further propagation because of steric hindrance [6,7] and will undergo termination by chloride capture (Step 2). This large tert-chloride may under forcing conditions (in the presence of $TiCl_4$ at the relatively high temperature of 32.5°C) lose HCl and give rise to a large exo-olefin which, in turn, may also start to compete for active carbocations (the likelihood for this reaction is, however, slight).



Scheme 1

To substantiate the possibility of the above side reaction, the structure of the product formed in Expt. 5 was identified (structural analysis involved dehydrochlorination by tBuOK [8] and subsequent ^1H NMR spectroscopic analysis; see Section III B). Gratifyingly, this exercise showed the presence of the =CH_2 group (resonances at 4.71 and 4.75 ppm) in the dehydrochlorinated product, which we regard proof positive for the existence of the corresponding tert-chloride precursor, shown in Scheme 1.

B. The Structure of PIBs Produced by Friedel-Crafts Acids in SC·CO_2

The microstructure of representative PIBs obtained by various Friedel-Crafts acids in SC·CO_2 under different conditions have been determined by ^1H NMR spectroscopy. Figure 1a and 1b show the olefinic regions of the ^1H NMR spectra of PIBs obtained with TMPCl/$TiCl_4$ and TMPCl/$SnCl_4$ respectively (Expts. 1 and 8 in Table 2 of [1]). The singlets at 5.1 ppm are characteristic of the -CH= protons of the internal terminal olefin group, whereas the doublets at 4.61 and 4.82 ppm are associated with the CH_2= protons of the external terminal unsaturations [9]. Further resonances appearing at 4.77, 4.78, 4.85 and 5.14 ppm in Figures 1a and b are attributed to various non-terminal CH_2= and -CH= protons arising by various isomerization/deprotonation reactions proceeding at the relatively high polymerization temperature. According to this evidence the products prepared by $TiCl_4$ and $SnCl_4$ contain a variety of ill-defined olefinic endgroups.

Figure 1c shows the olefinic region of the ^1H NMR spectrum of a representative product obtained with the mixed $TiCl_4/BCl_3$ coinitiator system (Expt. 5, Table 1). Significantly the spectrum does not show any evidence of unsaturation. The absence of olefinic endgroups indicates the absence of proton loss, i.e., chain transfer to monomer, during the polymerization.

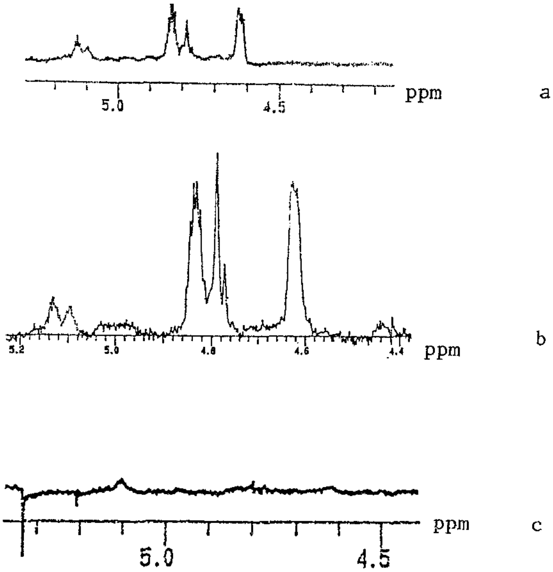


Figure 1. The olefinic regions of ^1H NMR spectra of PIBs obtained in SC·CO_2 with
a) TMPCl/$SnCl_4$ (Expt. 8 of Table 2 in [1])
b) TMPCl/$TiCl_4$ (Expt. 1 of Table 2 in [1]).
c) TMPCl/($TiCl_4/BCl_3$) (Expt. 5 of Table 1, this work). Amplification ~100x; see text for assignments

We then proceeded to determine directly the tBu-/-Cl^t ratio in our products. Figure 2a shows the aliphatic region of the ^1H NMR spectrum of PIB obtained with the TMPCl/($TiCl_4/BCl_3$) system (Expt. 3, Table 1). Integration of the resonance at 0.96 ppm due to the 9 protons of the tBu- headgroup (#5 in Figure 2a) relative to that at 1.66 ppm due to the 6 protons of the $-C(CH_3)_2Cl$ groups (#1 in Figure 2a) gave close to the expected theoretical value; however, the accuracy of this analysis (computer and manual integration) was judged to be low because of the uncertainty in the area of the 0.96 ppm resonance. The latter small resonance is too close to the large resonance at 1.08 ppm due to the numerous $-CH_3$ groups in the PIB repeat unit, and this overlap could adversely affect quantitation. To enhance our analytical accuracy, we turned to our well-established method for the quantitive determination of terminal -Cl^t in PIB [8]. Thus, the product obtained in Expt. 3 was dehydrochlorinated and the $CH_2=$ group of the olefin so obtained was quantitated by ^1H NMR spectroscopy. Figure 2b shows the spectrum. According to the resonances at 4.61 and 4.82 ppm the dehydrochlorinated product contains only the expected terminal $CH_2=$ unsaturation which proves the existence of the -Cl^t tailgroup in the product of Expt. 3. In addition, one can see the expected shifts in the positions of the resonances associated with the CH_3- and $-CH_2$- groups caused by the appearance of the terminal $CH_2=$ group.

A further quantitative structure proof can be obtained by molecular weight determination by ^1H NMR spectroscopy. Thus, area integration of the readily identifiable two terminal olefinic protons ($CH_2=$ at 4.61 and 4.82 ppm) relative to all the protons in the product, gave molecular weights (M_n) within experimental error (10-15%) obtained by GPC. This analytical method indicates that every molecules contains one $CH_2=$ terminus.

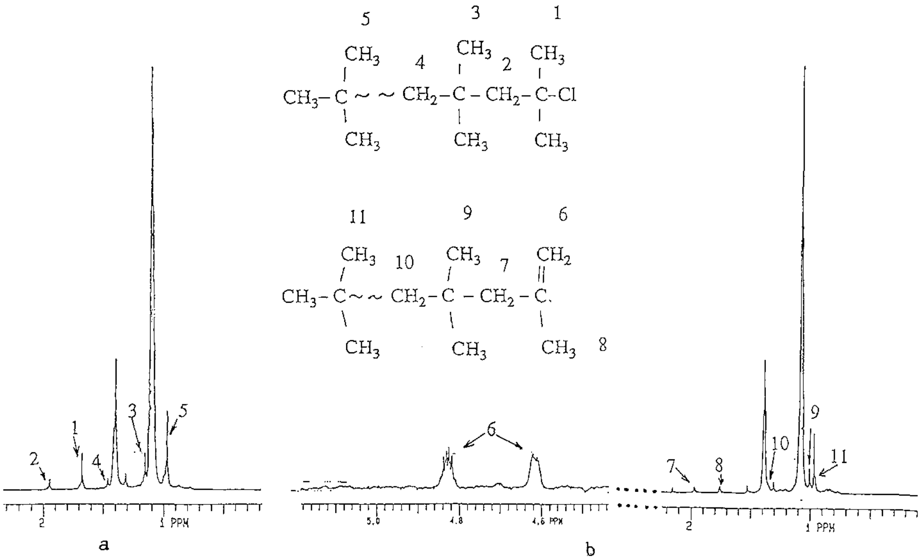


Figure 2. ^1H NMR spectra of the products obtained in Expt. 3 of Table 1
a) before and b) after dehydrochlorination

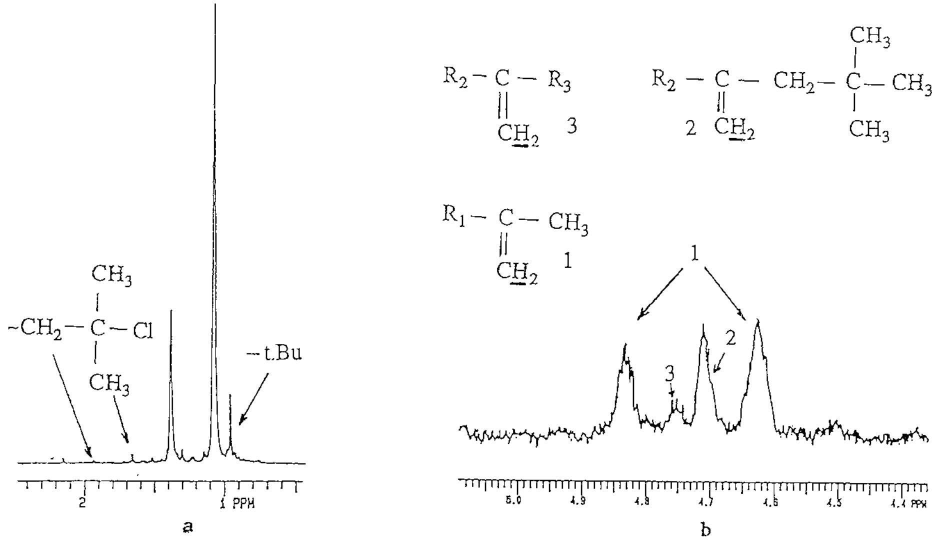


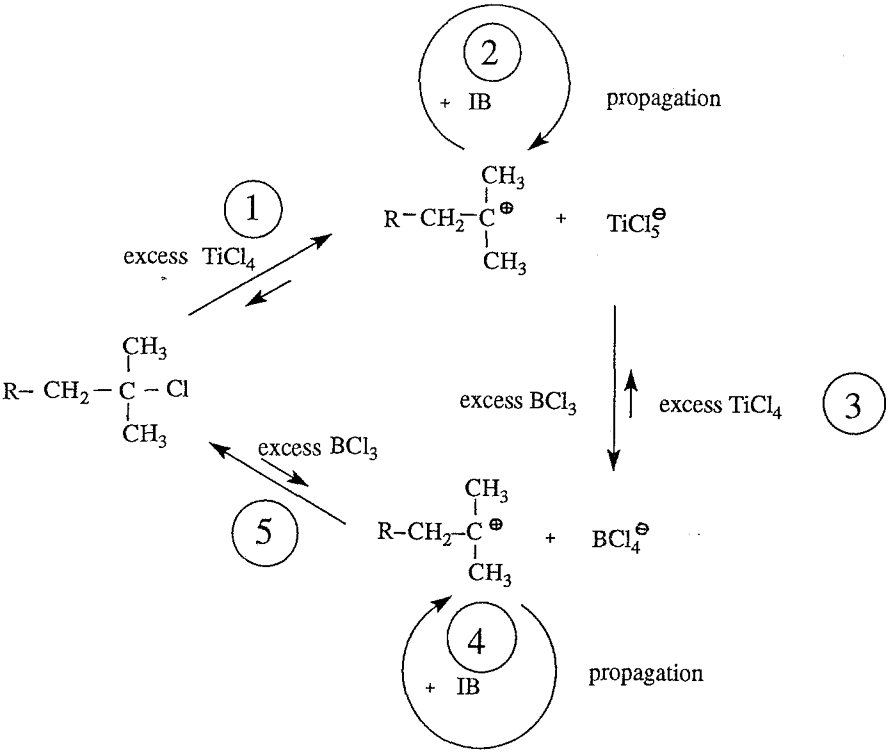
Figure 3. ^1H NMR spectra of the product obtained in Expt. 5 of Table 1
a) aliphatic region before and b) olefinic region after dehydrochlorination

The structure of the products obtained in experiments where the two coinitiators were in separate ampoules have also been characterized. Figure 3a shows the aliphatic region of the spectrum of the products obtained in Expt. 5. As discussed above the polymer contains more than one tBu- group per chain. The position of the -Cl^t group becomes apparent upon examining the olefinic region after dehydrochlorination (Figure 3b). The doublet at 4.62 and 4.82 (#1 in Figure 3b) is due to the terminal CH_2= groups while the resonances at 4.71 and 4.75 ppm (#2 and 3, respectively) are associated with various non-terminal CH_2= groups arising by dehydrochlorination of internal -Cl^t groups.

These evidences clearly indicate termination by chlorination and the virtual absence of chain transfer and/or isomerization even at high temperatures in IB polymerization coinitiated by $TiCl_4/BCl_3$ mixtures.

C. Speculation on the Mechanism of IB polymerization by $TiCl_4/BCl_3$ mixtures

The experimental observations may be explained in terms of the following scheme (The R = tBu during initiation by TMPCl and/or PIB chain during propagation):



Scheme 2

The polymerization starts by ion generation from TMPCl mainly by $TiCl_4$ (1 in the Scheme) which is a far more efficient coinitiator with tert-chlorides than BCl_3 [3,4]. The reason for the surprising fact that BCl_3, a stronger acid than $TiCl_4$, is nonetheless a very low efficiency coinitiator with TMPCl in nonpolar solvents (like SC•CO_2), is because the $BCl_4^{\ominus}$ counterion is very unstable and rapidly reverts to BCl_3 (i.e., $TMP^{\oplus}BCl_4^{\ominus} \rightarrow TMPCl + BCl_3$) [3,4]. The $TMP^{\oplus}TiCl_5^{\ominus}$ ion pair sustains propagation as indicated by the top loop 2 in the Scheme.

Our key proposition is rapid counter anion exchange which occurs in the presence of excess BCl_3:

$$TiCl_5^{\ominus} + BCl_3 \rightleftharpoons TiCl_4 + BCl_4^{\ominus}$$

This equilibrium is shifted to the right because of the stronger acidity of BCl_3 relative to $TiCl_4$. The $PIB^{\oplus}$ (or $TMP^{\oplus}$ during initiation) $BCl_4^{\ominus}$ ion pair may propagate (bottom loop 4 in Scheme) but more likely it will collapse to RCl^t + BCl_3 before deprotonation (i.e., chain transfer) can take place [3,4].

The main route to tBu-PIB-Cl^t leads via 1 - 2 - 3 - 4 - 5 - along the long arrows. The critical counterion exchange 3 may be viewed as a "buffer" equilibrium which rapidly converts the $PIB^{\oplus}TiCl_5^{\ominus}$ ionpair into the desirable $PIB^{\oplus}BCl_4^{\ominus}$ ion pair, which in turn rapidly (prior to proton elimination) leads to the product tBu-PIB-Cl^t. The role of BCl_3 is essential: It suppresses the existence of the relatively stable long-lived $PIB^{\oplus}TiCl_5^{\ominus}$ ion pair which, if allowed to prevail, would surely lead to chain transfer.

The effect of BCl_3 can also be seen by comparing the structures of the products obtained in the two kinds of experiments: a) with TMPCl/($TiCl_4$/BCl_3) Expts. 1-3, and b) with TMPCl/$TiCl_4$/BCl_3 Expts. 4-6. Unadulterated tBu-PIB-Cl^t was obtained only in the first series when TMPCl was aged in the presence of both $TiCl_4$ and BCl_3 coinitiators. In contrast, when TMPCl/$TiCl_4$ was aged in the absence of BCl_3, the undesirable side reaction TMPCl + $TiCl_4$ $\rightarrow$ $TMP^{=}$ + $H^{\oplus}TiCl_5^{\ominus}$ could proceed and mixed products were obtained because the $TMP^{=}$ entered the polymerization reaction. In the presence of BCl_3 this cannot happen because the $BCl_4^{\ominus}$ formed suppresses $TMP^{=}$ formation by the mechanism shown in Scheme 2 (in the case R = tBu), and "clean" tBu-PIB-Cl^t is obtained.

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