

$(\text{CH}_3)_3\text{SiCl/TiCl}_4$ INITIATING SYSTEM FOR CATIONIC POLYMERIZATION OF 1,3-PENTADIENE*

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Abstract Cationic polymerizations of 1,3-pentadiene (PD) initiated by trimethylsilyl chloride (TMSCl) in combination with TiCl_4 were carried out in *n*-hexane at 30°C. The yield of polymer was greatly increased by the addition of TMSCl, indicating that the TMSCl/ TiCl_4 combination is an efficient initiating system for PD cationic polymerization. However, the introduction of TMSCl gave rise to a drop in the molecular weight of the polymer. Kinetic results demonstrated that the polymerization initiated by TMSCl/ TiCl_4 is 4.5 times faster than that induced by TiCl_4 alone. Various ethers were used to mediate the TMSCl/ TiCl_4 initiating system. Adding diphenyl ether could increase both the yield and molecular weight of the polymer. Structural evidence illustrates that the polymerization is indeed initiated by TiCl_4 in combination with HCl resulting from hydrolysis by adventitious water.

Keywords 1,3-Pentadiene, Cationic polymerization, TMSCl, TiCl_4

INTRODUCTION

In the past few years, trimethyl halide (TMSX) has been widely used as initiators for cationic polymerization due to the high reactivity of its combination with various Lewis acids. For example, the living cationic polymerization of isobutyl vinyl ether has been accomplished by using the TMSI/ZnI_2 initiating system^[1-4], and other TMSY/ZnX_2 (Y, X = Cl, Br, I) initiating systems have also been reported^[5, 6]. These investigations have gained much insight into cationic polymerization, particularly the initiation process. 1,3-pentadiene as an active monomer can be initiated by cationic polymerization. Recently, with the development of the petrochemical industry, the amount of 1,3-pentadiene as a fraction of the cracked C_5 in ethylene processing in China increased tremendously and will reach 1.7 million tons by the year 2000. But the basic and applied studies of 1,3-pentadiene are far behind that of developed countries. We recently reported that TMSCl/AlCl_3 is an efficient initiating system for the polymerization of 1,3-pentadiene (PD)^[7]. The introduction of TMSCl in the AlCl_3 initiated PD polymerization in *n*-hexane increases considerably both polymer yield and polymerization rate. However, the molecular weight of the polymers dropped with the introduction of TMSCl. In addition, the AlCl_3 initiated PD polymerization in *n*-hexane produces both soluble polymer and insoluble gel^[8-11], whereas the introduction of TMSCl fails to reduce the formation of gel^[7].

The present work describes PD polymerization in *n*-hexane induced by TMSCl/TiCl_4 initiating system. As TiCl_4 induced PD polymerization in *n*-hexane produces only soluble polymer, hence the effects of TMSCl on polymer yield, molecular weight and polymerization rate could be

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easily investigated and deduced.

EXPERIMENTAL

Materials

1,3-pentadiene (Fluka) and *n*-hexane were distilled over CaH_2 . TiCl_4 , TMSCl and 2,6-di-*tert*-butylpyridine (DtBP) from Aldrich were used as received. Ethers and ketones were purified by distillation over CaH_2 .

Polymerization

TiCl_4 was introduced into a three-necked-flask purged with dry nitrogen atmosphere. The solvent and TMSCl were added by syringe sampling and the mixture was stirred for 15 min. Polymerization was initiated by introducing PD by syringe sampling at the set temperature. After a given time, the polymerization was quenched by a solvent containing a small amount of methanol. The solution was washed with water, then dried to recover the soluble polymer by evaporating the solvent and unreacted monomer.

Measurements

The IR spectrum of the polymer was measured using a Nicolet MX-1 spectrometer and the ^1H -NMR spectrum was recorded using an AC-P300 spectrometer. The intrinsic viscosity of the polymers was determined with an Ubbelohde viscometer in toluene at 30°C .

RESULTS AND DISCUSSION

Figure 1 shows the polymerization of PD in *n*-hexane at 30°C initiated by the $\text{TMSCl}/\text{TiCl}_4$ initiating system at different $[\text{TMSCl}]/[\text{TiCl}_4]$ ratios. The addition of TMSCl exerts an obvious enhancing effect on the TiCl_4 -induced polymerization. The polymer yield is greatly increased by raising the $[\text{TMSCl}]/[\text{TiCl}_4]$ ratio and hits a plateau when $[\text{TMSCl}]/[\text{TiCl}_4]$ reaches 0.5. This result indicates an involvement of TMSCl in the initiation process.

Figure 2 shows the effect of the $[\text{TMSCl}]/[\text{TiCl}_4]$ ratio on the intrinsic viscosity of the polymer. It can be observed that the introduction of TMSCl reduces the molecular weight of the polymer. The molecular weight decreases in the first stage to a certain extent and then remains unchanged at a constant value in the range of $[\text{TMSCl}]/[\text{TiCl}_4] > 1$.

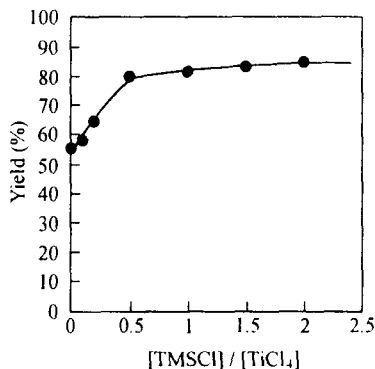


Fig. 1 Effect of $[\text{TMSCl}]/[\text{TiCl}_4]$ ratio on polymer yield
 $[\text{M}]_0 = 2.0 \text{ mol/L}$, $[\text{TiCl}_4] = 2.0 \times 10^{-2} \text{ mol/L}$,
 solvent: *n*-hexane; $T = 30^\circ\text{C}$, $t = 5 \text{ h}$

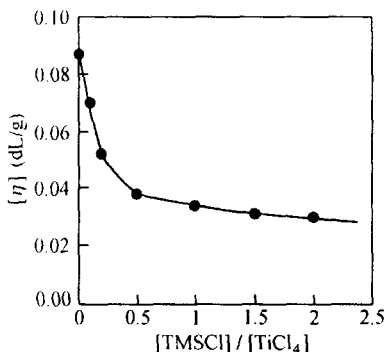


Fig. 2 Dependence of the intrinsic viscosity of the PD polymer on the $[\text{TMSCl}]/[\text{TiCl}_4]$ ratio
 See Fig. 1 for reaction conditions

The enhancing effects of TMSCl on the polymerization of PD induced by TiCl_4 alone and $\text{TMSCl}/\text{TiCl}_4$ respectively are further demonstrated by Fig. 3 and Fig. 4. Figure 3 gives the

conversion-time curves for polymerizations initiated by TiCl₄ and TMSCL/TiCl₄. It is observed that the TMSCL/TiCl₄ induced polymerization is much faster than that initiated by TiCl₄ alone. We used the first order equations to describe the kinetic data and obtained a plot of $\ln[M]_0/[M]$ versus reaction time, as shown in Fig. 4. From the slope of the lines we obtained the value of two constants (i.e. noted k_1 and k_2 for TiCl₄ and TMSCL/TiCl₄, respectively). The result of $k_2/k_1 = 4.5$ reveals that TMSCL/TiCl₄ will initiate the polymerization 4.5 times faster than that induced by TiCl₄ alone.

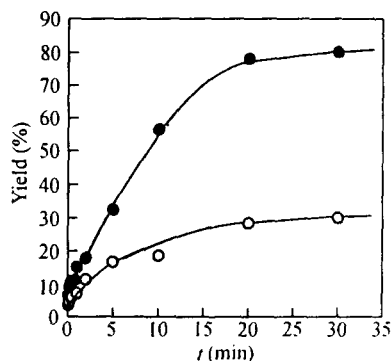


Fig. 3 Time-conversion curves for the polymerizations initiated by TiCl₄ (○) and [TMSCL]/[TiCl₄] (●) [TiCl₄] = [TMSCL] = 2.0×10^{-2} mol/L, see Fig. 1 for reaction condition

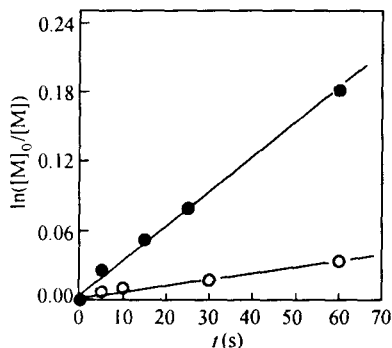
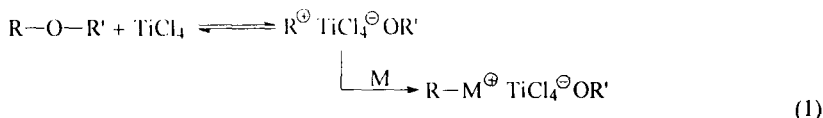


Fig. 4 Plots of $\ln([M]_0/[M])$ versus reaction time for polymerization of PD initiated by TiCl₄ (○) and [TMSCL]/[TiCl₄] (●) See Fig. 1 and Fig. 3 for reaction conditions

Electron donors (EDs) capable of changing the nature of the active species, such as ethers and ketones, have often been used to mediate the cationic polymerization induced by TMSX initiating systems^[2, 3]. They produce the effect in two ways. Firstly, they can act on initiator of the initiating system to initiate the polymerization. This can be described in Eq. (1).



Secondly, EDs may also react with growing propagating cationic carbon to stabilize it with counter anions. This reaction can be expressed in Eq. (2).

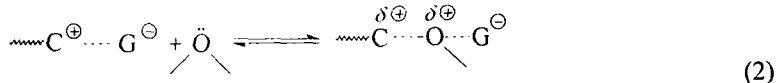


Table 1 Effect of ethers on the PD polymerization initiated TMSCL/TiCl₄*

Ether	Yield(%)	$[\eta]$ (dL/g)
None	81.5	0.035
THF	6.5	-
Dioxane	11	-
Diethyl ether	60.0	0.016
Phenyl methyl ether	81.0	0.032
Diisopropyl ether	82.5	0.024
Diphenyl ether	89.5	0.060

* $[M]_0 = 2.0$ mol/L, $[\text{ROR}'] = [\text{TMSCL}] = [\text{TiCl}_4] = 2.0 \times 10^{-2}$ mol/L, solvent: *n*-hexane, $T = 30^\circ\text{C}$, $t = 5$ h

We studied the effect of different ethers on the PD polymerization initiated by TMSCL/TiCl₄ (1:1) and the results are given in Table 1. Diethyl ether, tetrahydrofuran (THF) and dioxane

decrease the polymer yield. Phenyl methyl ether and diisopropyl ether do not affect the yield much. On the contrary, diphenyl ether increased the polymer yield. The molecular weight of the polymer is reduced by adding ethers (except for diphenyl ether). These results indicated that the nucleophilicity of ethers, which is determined by their steric hindrance, is the most important factor affecting polymer yield and molecular weight. For example, dethyl ether decreases polymer yield and molecular weight, diisopropyl ether does not affect the yield but decreases the molecular weight, and diphenyl ether increases both polymer yield and molecular weight.

In order to obtain further information about the effects of diisopropyl ether (*i*-Pr₂O) and diphenyl ether (Ph₂O) on the polymerization initiated by TMSCl/TiCl₄, the dependence of polymer yield and molecular weight on [ROR']/[TMSCl] ratio, was studied and the results are shown in Fig. 5 and Fig. 6. It was noted that the nature of the interactions of *i*-Pr₂O and Ph₂O with the initiating system is quite different. *i*-Pr₂O with stronger nucleophilicity reduces the activity of carbonocations and therefore hinders propagation reaction to some extent. As a result, the polymer yield is not affected and the molecular weight is reduced by adding *i*-Pr₂O, which could act as a chain transfer agent. On the other hand, the steric hindrance of bulky phenyl groups prohibits the interaction between Ph₂O and the carboncation so that Ph₂O shows less nucleophilic interactive with active species. Therefore, the polymer yield and molecular weight are increased by the introduction of Ph₂O. The IR spectra of polymer Fig. 7 indicate that the polymer has phenyl groups (690 cm⁻¹, 760 cm⁻¹). This result demonstrated that the diphenyl ether has an effect on the initiating process.

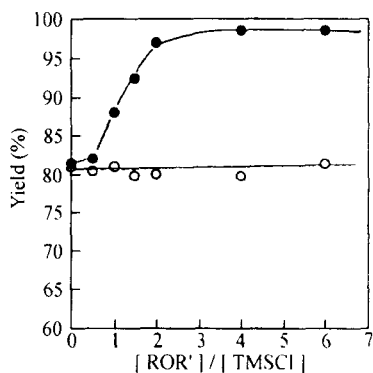


Fig. 5 Effect of [ROR']/[TMSCl] ratio on polymer yield
ROR': Ph₂O (●), *i*-Pr₂O (○); [TiCl₄] = [TMSCl] = 2.0×10^{-2} mol/L; see Fig. 1 for other reaction conditions

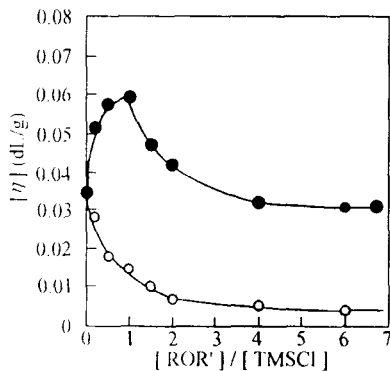


Fig. 6 Effect of [ROR']/[TMSCl] ratio on the intrinsic viscosity of the polymers
ROR': Ph₂O (●), *i*-Pr₂O (○); see Fig. 5 for other reaction conditions

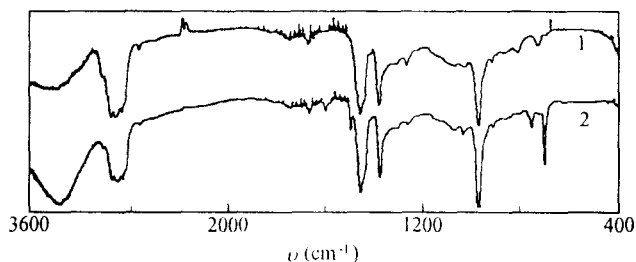


Fig. 7 IR spectra of PPD prepared in *n*-hexane
1) TMSCl/TiCl₄, 2) TMSCl/TiCl₄/Ph₂O

Figure 8 is the GPC chromatogram of polymers initiated by TiCl_4 , $\text{TMSCl}/\text{TiCl}_4$, $\text{TMSCl}/\text{TiCl}_4/i\text{-Pr}_2\text{O}$ and $\text{TMSCl}/\text{TiCl}_4/\text{Ph}_2\text{O}$ initiating systems. These results demonstrated that molecular weight decreased by adding TMSCl , and that Ph_2O could increase the molecular weight of the polymer. All these results coincided with the earlier conclusion.

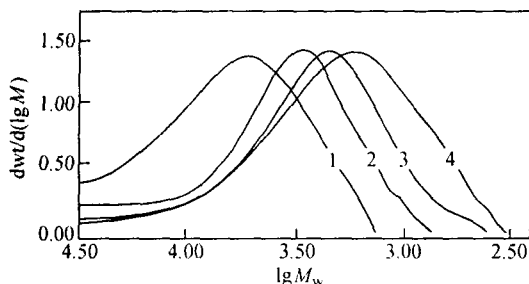


Fig. 8 GPC Chromatograms of polymer initiated by $\text{TMSCl}/\text{TiCl}_4$ initiating system

- 1) TiCl_4 , 2) $\text{TMSCl}/\text{TiCl}_4/\text{Ph}_2\text{O}$, 3) $\text{TMSCl}/\text{TiCl}_4$,
4) $\text{TMSCl}/\text{TiCl}_4/i\text{-Pr}_2\text{O}$

It is well known that trimethylsilyl halides are involved in the initiation process of the cationic polymerization mainly through two paths, i.e. through "direct addition"^[5] or hydrolysis by adventitious water^[2]. In the present polymerization system, we can visualize the following two reaction paths:

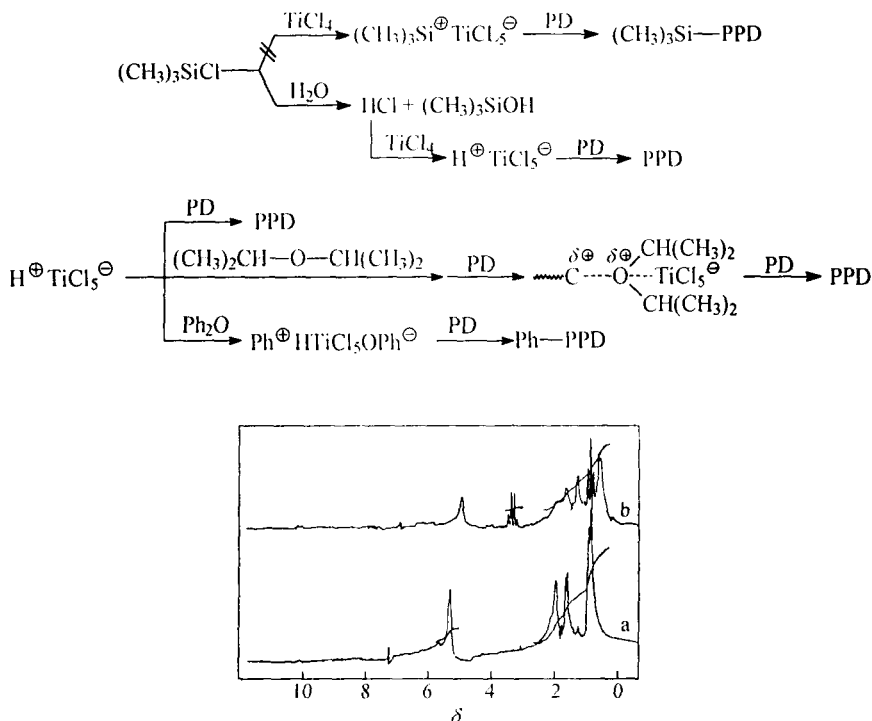


Fig. 9 The ^1H -NMR spectra of polymer initiated by $\text{TMSCl}/\text{TiCl}_4$ initiating system
a) $\text{TMSCl}/\text{TiCl}_4$, b) $\text{TMSCl}/\text{TiCl}_4/\text{Ph}_2\text{O}$

As shown in the above scheme, TMSCl can react with TiCl_4 directly to form a complex which is capable of initiating the monomer by "direct addition", or can react with adventitious water that

exists always in the system to give HCl. The combination of HCl with TiCl_4 is an efficient initiating system. We have conducted a ^1H -NMR analysis of the polymer prepared by $\text{TMSCl}/\text{TiCl}_4$ and the spectrum does not show any signals of $(\text{CH}_3)_3\text{Si}-$ groups (Fig. 9). These results strongly prove that the "direct addition" resulting in terminal trimethylsilyl group does not occur under our conditions, and the polymerization quite likely takes place through the hydrolysis of TMSCl with adventitious water. In order to demonstrate this mechanism, we added proton trap 2,6-di-tert-butyl-pyridine (DtBP), which interacts neither with TMSCl nor with growing cation. However, hindered pyridine irreversibly traps protons. When the ratio of $[\text{DtBP}]/[\text{TMSCl}]$ was ≥ 1 , no polymerization was observed for a few days.

Therefore, we propose that in our polymerization system the real initiating system is the combination of TiCl_4 with HCl released by hydrolysis of TMSCl . As HCl is much more reactive than H_2O towards TiCl_4 , hence the polymerization of PD initiated by TiCl_4 (e.g. by the $\text{H}_2\text{O}/\text{TiCl}_4$ initiating system) is greatly accelerated by adding TMSCl . However, the molecular weight of the polymer prepared by $\text{TMSCl}/\text{TiCl}_4$ is lower than that induced by TiCl_4 alone, as shown in Fig. 2. This is probably due to the difference between the natures of counter anions TiCl_5^- and $\text{TiCl}_4(\text{OH})^-$ derived from the two initiating systems $\text{TMSCl}/\text{TiCl}_4$ and " H_2O "/ TiCl_4 , respectively. In the polymerization system initiated by $\text{TMSCl}/\text{TiCl}_4$ in the presence of diphenyl ether, Ph_2O is involved in initiation process by stabilizing the growing species and hence high molecular weight polymers could be produced.

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