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$(CH_3)_3SiBr/AlCl_3$ induced cationic polymerization of 1,3-pentadiene

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SUMMARY

Cationic polymerizations of 1,3-pentadiene (PD) with $AlCl_3$ in n-hexane were carried out in the absence and presence of trimethylsilyl bromide (Me_3SiBr or TMSBr). Structural evidence and proton trap experiment demonstrate that in the TMSBr/$AlCl_3$ induced polymerization the real initiating system is the combination of $AlCl_3$ with HBr resulting from hydrolysis of TMSBr by adventitious water existing in the system. The conversion of the polymerization is greatly increased by adding TMSBr, but the introduction of TMSBr does not exert an effect on the formation of gel (crosslinked product). The molecular weight of the polymer prepared by TMSBr/$AlCl_3$ system shows a maximum in the range of $[TMSBr]/[AlCl_3] = 1$, and excessive TMSBr gives rise to a drop of the polymer molecular weight. Kinetic data show that $AlCl_3$ and TMSBr/$AlCl_3$ induced polymerizations have the comparable polymerization rates.

INTRODUCTION

In the past few years, trimethylsilyl 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 TMSI/ZnI_2 initiating system (1-4), and other TMSY/ZnX_2 (Y, X = Cl, Br, I) initiating systems have been also reported (5,6). We have recently found 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 increases considerably both polymer yield and polymerization rate. However, the molecular weight of the polymers shows a drop with adding TMSCl.

The present work describes the PD polymerization in n-hexane induced by TMSBr/$AlCl_3$ initiating system. The effects of TMSBr on polymer yield, molecular weight and polymerization rate will be discussed.

EXPERIMENTAL

Materials

1,3-Pentadiene (PD) from Fluka was dried with CaH_2 and distilled. *n*-Hexane was also dried with CaH_2 and distilled. $AlCl_3$ was purified by sublimation under reduced

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pressure. Trimethylsilyl bromide (TMSBr) and 2,6-di-*tert*-butylpyridine (D*t*BP), both from Aldrich, were used as received.

Polymerization

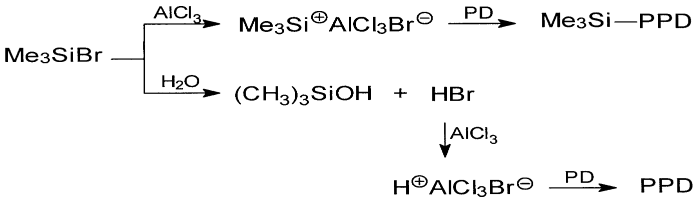
$AlCl_3$ was introduced in a three-necked-reactor in dry nitrogen atmosphere. The solvent and TMSBr were added by syringe and the mixture was stirred for 15 minutes. The polymerization was initiated by introduction of PD by syringe at the set temperature. After a given time, the polymerization was quenched with the solvent containing a small amount of methanol. The resulting solution was filtered to remove insoluble (crosslinked) gel. The filtrate was washed with water, then was dried to recover the soluble polymer by evaporating the solvent and unreacted monomer.

Measurements

The ^1H NMR spectrum of the polymer was recorded with an AC-P300 NMR spectrometer. Intrinsic viscosities of the polymers were determined with an Ubbelohde viscometer in toluene at 30°C.

RESULTS AND DISCUSSION

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 through hydrolysis by adventitious water (2). We have reported in the previous work that the polymerization of PD induced by TMSCl/$AlCl_3$ in n-hexane takes place through the latter process (7). As to the present polymerization system, we can also visualize the following two initiation processes:



We propose that the present TMSBr/$AlCl_3$ induced PD polymerization is also initiated through hydrolysis of TMSBr with adventitious water of the polymerization system. This consideration is supported by two experimental evidences as follows:

1) The ^1H NMR spectrum of polymer prepared by TMSBr/$AlCl_3$ does not show any signals of $(CH_3)_3Si$- groups, which should be resulted from "direct addition" initiation process. Therefore, we can exclude this path of initiation.

2) The polymerization initiated by TMSBr/$AlCl_3$ is considerably reduced by D*t*BP, a "proton trap", and is totally inhibited while [D*t*BP]/[TMSBr] reaches 1. This result indicates that the polymerization should be initiated by a proton process. It is worthy to note hat D*t*BP is hardly to inhibit $AlCl_3$ initiated polymerization (i.e. by "H_2O"/$AlCl_3$), indicating that initiation involving "H_2O"/$AlCl_3$ is a "concerted proton process" (8).

Based on these results, we conclude that in the TMSBr/$AlCl_3$ induced polymerization in *n*-hexane the real initiating system is the combination of $AlCl_3$ with HBr released by hydrolysis of TMSBr by adventitious water existing in the system.

Table 1. Effect of D*t*BP on polymerizations initiated by $AlCl_3$ and $TMSBr/AlCl_3$ [a)]

Initiating system	[D*t*BP]/[$AlCl_3$] ratio	Conversion (%)		
		Soluble polymer	Gel	Total
$AlCl_3$	0	30	50	80
	0.5	25	47	72
	1	22	43	65
$TMSBr/AlCl_3$[b)]	0	38	60	98
	0.5	21	14	35
	1	4	~1	5

[a)] $[M]_0 = 2.0$ mol/L; $[AlCl_3] = 3.0\times10^{-2}$ mol/L; Solvent: *n*-hexane; Temp: 30°C; Time: 4h.
[b)] $[AlCl_3] = [TMSBr] = 3.0 \times 10^{-2}$ mol/L;

We have shown that the $AlCl_3$ induced PD polymerization in *n*-hexane produces both soluble polymer as well as insoluble product resulting from crosslinking reactions (9-11). Figure 1 shows the polymerization of PD in *n*-hexane at 30°C by $TMSBr/AlCl_3$ at different $[TMSBr]/[AlCl_3]$ ratios. We found that the addition of TMSBr exerts an obvious enhancing effect on the $AlCl_3$ induced PD polymerization. The total conversion is greatly increased by adding TMSBr and a complete conversion is obtained while $[TMSBr]/[AlCl_3]$ ratio reaches ~1, indicating an involvement of TMSBr in the initiation process. We suggest that the increase of conversion of $AlCl_3$ system by adding TMSBr is due to an higher reactivity of HBr than H_2O in complexation with $AlCl_3$. Figure 1 shows also that the addition of TMSBr does not exert an effect on the crosslinking reaction, i.e., TMSBr increases conversions of both soluble polymer and gel (insoluble product).

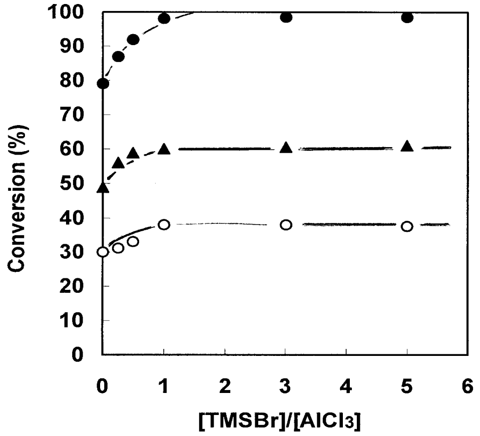


Figure 1. Effect of $[TMSBr]/[AlCl_3]$ ratio on conversions. ● total conversion; O soluble polymer; ▲ gel. $[M]_0 = 2.0$ mol/L; $[AlCl_3] = 3.0\text{x}10^{-2}$ mol/L; Solvent: *n*-hexane; Temp: 30°C; Time: 4h.

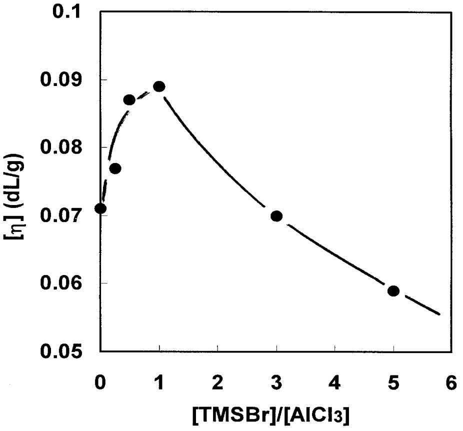


Figure 2. Effect of $[TMSBr]/[AlCl_3]$ ratio on the intrinic viscosity of soluble polymers. $[M]_0 = 2.0$ mol/L; $[AlCl_3] = 3.0 \text{ x } 10^{-2}$ mol/L; Solvent: *n*-hexane; Temp: 30°C; Time: 4h.

Figure 2 shows the effect of the [TMSBr]/[$AlCl_3$] ratio on the intrinsic viscosity of the soluble polymer. The molecular weight of the polymer increases and attains maximum at [TMSBr]/[$AlCl_3$]=1, then gradually decreases with augmentation of TMSBr. These observations illustrate that the molecular weight of the polymer prepared by TMSBr/$AlCl_3$ in the range of [TMSBr]/[$AlCl_3$]=0-1 is higher than that produced by $AlCl_3$ alone. This is probably due to the difference between the natures of two counteranions. It is well known that both the increase of active specie concentration and the chain transfer reaction can reduce the molecular weight of the polymer. As the molecular weight decreases just while [TMSBr]/[$AlCl_3$]>1, hence we suggest that the excessive HBr arising from TMSBr probably results in drop of the molecular weight through chain transfer (12). In addition, we have shown in the previous work (7) that the introduction of TMSCl reduces the molecular weight of the polymer. Therefore, TMSBr and TMSCl show different effects on the polymer molecular weight.

Figure 3 shows the kinetic results of PD polymerization initiated by TMSBr/$AlCl_3$. It is observed that the conversions of soluble polymer and insoluble gel increase simultaneously, indicating that the crosslinking reaction occurs during polymerization. To obtain a comparison between reaction rates of $AlCl_3$ and TMSBr/$AlCl_3$ polymerization ystems. Figure 4 gives the polymerization time-total conversion curves for PD polymerizations initiated by $AlCl_3$ and by TMSBr/ $AlCl_3$, respectively. We noted that the introduction of TMSBr in the polymerization system initiated by $AlCl_3$ does not considerably increase the polymerization rate.

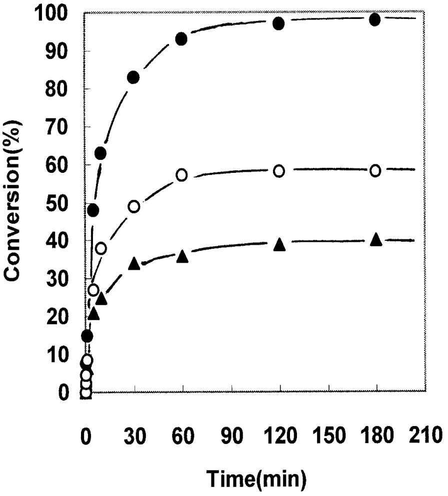


Figure 3. Time-conversion curves for PD polymerization initiated by TMSBr/$AlCl_3$. • Total conversion; ▲ soluble polymer; O gel. $[M]_0$ = 2.0 mol/L; [$AlCl_3$] = [TMSBr] = 3.0 x 10^{-2} mol/L; Solvent: *n*-hexane; Temperature: 30ºC.

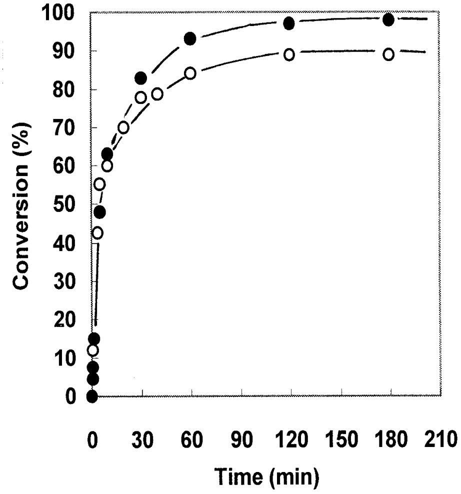


Figure 4. Time-total conversion curves for PD polymerizations initiated by $AlCl_3$ (O) and TMSBr/$AlCl_3$ (•). $[M]_0$ = 2.0 mol/L; [$AlCl_3$] = 3.0x10^{-2} mol/L; [TMSBr] = 3.0 x 10^{-2} mol/L; Solvent: *n*-hexane; Temperature: 30ºC.

We used the first order kinetic equation to describe reaction time-monomer concentration data given by Figure 5 and obtained the plots Ln($[M]_0$/[M]) versus reaction time for the two polymerization systems initiated by $AlCl_3$ and TMSBr/$AlCl_3$, as shown in Figure 6. From the slopes of the plots we obtained the value of two constant *k* (noted k_1 and k_2 for $AlCl_3$ and TMSBr/$AlCl_3$ respectively). The result of k_2/k_1 = 1.05 reveals that the TMSBr/$AlCl_3$-initiated polymerization has a reaction rate comparable to that induced by $AlCl_3$. We have reported (7) that the TMSCl/$AlCl_3$-induced polymerization is much faster than that initiated by $AlCl_3$. We conclude hence that TMSBr and TMSCl exert different effects on reaction rate of $AlCl_3$ initiated PD polymerization.

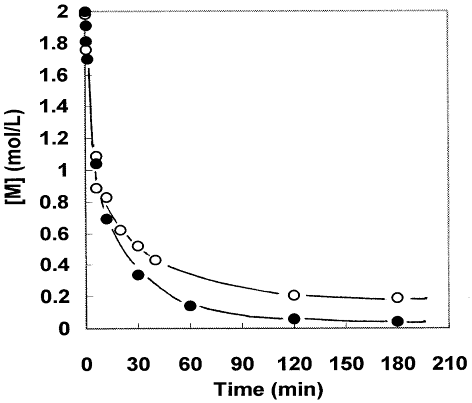


Figure 5. Time-monomer concentration curves for PD polymerizations initiated by $AlCl_3$ (O) and TMSBr/$AlCl_3$ (•). See Figure 4 for reaction conditions.

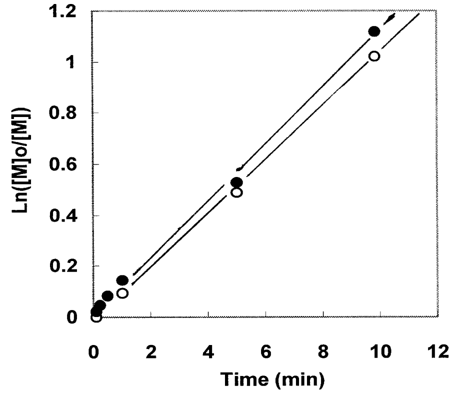


Figure 6. Plot of Ln($[M]_0$/[M]) versus reaction time for PD polymerizations by $AlCl_3$ (O) and TMSBr/$AlCl_3$ (•). See Figure 4 for reaction conditions.

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