

Cationic polymerization of 1,3-pentadiene with $(\text{CH}_3)_3\text{SiCl}/\text{AlCl}_3$

Y.X. Peng*, W.M. Shi

Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences,
P.O. Box 415, Chengdu 610041, People's Republic of China

Received: 13 February 1996/Revised version: 3 April 1996/Accepted: 8 April 1996

Summary

Cationic polymerizations of 1,3-pentadiene (PD) with AlCl_3 in *n*-hexane was carried out in the absence and presence of trimethylsilyl chloride (TMSCl). The polymer yield is greatly increased by the addition of TMSCl, indicating that the TMSCl/ AlCl_3 combination is an efficient initiating system for PD cationic polymerization. The polymerization rate induced by TMSCl/ AlCl_3 is 10 times greater than that by AlCl_3 alone. The introduction of TMSCl does not exert an effect on the crosslinking reaction. The molecular weight of the polymer decreases with the addition of TMSCl to a extent and then remains constant. Structural evidences demonstrate that the polymerization is indeed initiated by AlCl_3 in combination with HCl resulting from hydrolysis of TMSCl by adventitious water.

Introduction

Recently, trimethylsilyl halide (TMSX) has been widely used for initiators in the cationic polymerization due to the high reactivity of its combination with various Lewis acids towards cationically polymerizable monomers. 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). These investigations have achieved an amount of insight into the cationic polymerization process.

The present work describes the cationic polymerization of 1,3-pentadiene (PD) initiated by trimethylsilyl chloride (TMSCl) in combination with AlCl_3 . It is known that cationic polymerization of PD (like other dienes) is difficult compared to other active monomers such as isobutylene, vinyl ethers and styrene, and that the initiation process of PD needs strong acidic initiators (7). We expect that the TMSCl/ AlCl_3 combination could provide an novel strongly acidic initiating system for the PD polymerization.

Experimental

Materials

1,3-Pentadiene from Fluka and *n*-hexane were distilled over CaH_2 . AlCl_3 was purified by sublimation in vacuum. TMSCl from Fluka was used as received.

* Corresponding author

Polymerization

AlCl_3 was introduced in a three-necked-reactor in dry nitrogen atmosphere. The solvent and TMSCl were added by syringe and the mixture was stirred for 15 minutes. The polymerization was initiated by introduction of PD by syringe. 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) product. The filtrate was washed with water and dried by evaporation to recover the soluble polymer.

Measurements

The ^1H NMR spectrum of the polymer was recorded by a AC-P300 spectrometer. Intrinsic viscosities of the polymers were 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 by $\text{TMSCl}/\text{AlCl}_3$ at different ratios. The addition of TMSCl exerts an obvious enhancing effect on the AlCl_3 -induced polymerization. The yield is greatly increased by adding TMSCl and a complete conversion is obtained while $\text{TMSCl}/\text{AlCl}_3$ ratio reaches 2. This result indicates an involvement of TMSCl in the initiation process.

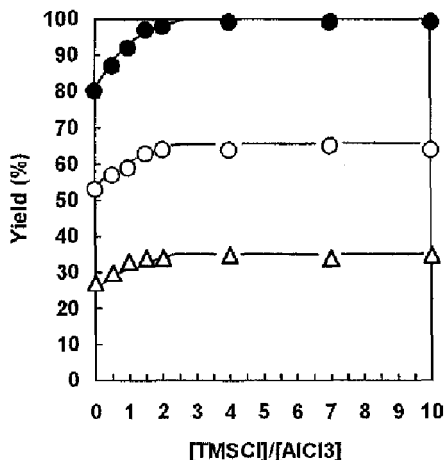


Figure 1. Effect of $\text{TMSCl}/\text{AlCl}_3$ ratio on yield. $[\text{M}]_0 = 2.0 \text{ mol/L}$; $[\text{AlCl}_3] = 2.0 \times 10^{-2} \text{ mol/L}$; Solvent: *n*-hexane; Temp: 30°C ; Time: 4h. ● Total yield; △ soluble; ○ crosslinked.

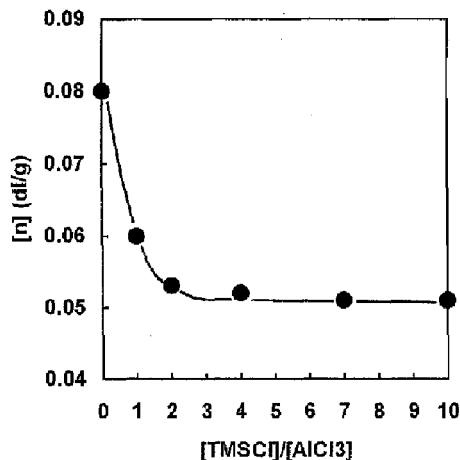


Figure 2. Effect of $\text{TMSCl}/\text{AlCl}_3$ ratio on the intrinsic viscosity of soluble polymers. $[\text{M}]_0 = 2.0 \text{ mol/L}$; $[\text{AlCl}_3] = 2.0 \times 10^{-2} \text{ mol/L}$; Solvent: *n*-hexane; Temp: 30°C ; Time: 4h.

We have previously shown that polymerization of PD initiated by AlCl_3 in *n*-hexane generates both soluble polymer and insoluble product resulting from crosslinking reactions (8,9). Figure 1 shows that the addition of TMSCl does not exert an effect on the crosslinking reaction, i.e., TMSCl increases the yields of both soluble polymer and insoluble product.

Figure 2 shows the effect of the $\text{TMSCl}/\text{AlCl}_3$ ratio on the intrinsic viscosity of the polymer. The introduction of TMSCl reduces the molecular weight of the polymer. In a precedent work (9) we showed that *tert*-butyl chloride (*t*-BuCl) reduces molecular weight in the PD polymerization initiated by AlCl_3 through chain transfer and the molecular weight decreases gradually with the concentration of *t*-BuCl. However, the effect of TMSCl falls out of this scenario, as shown in Figure 2. The molecular weight decreases in the first stage to a extent and then remains unchanged at a constant value.

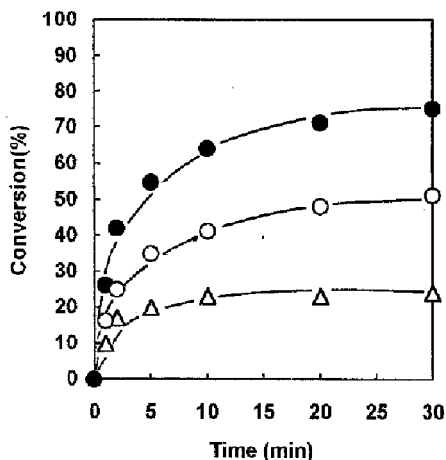


Figure 3. Time-conversion curve for the polymerization of PD initiated by AlCl_3 alone. $[\text{M}]_0 = 2.0 \text{ mol/L}$; $[\text{AlCl}_3] = 2.0 \times 10^{-2} \text{ mol/L}$; Solvent: *n*-hexane; Temp: 30°C . ● Total conversion; △ soluble; ○ crosslinked.

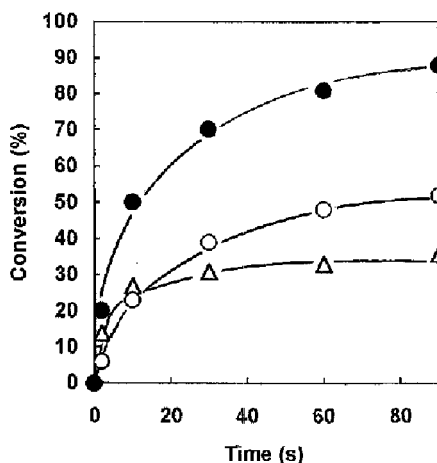


Figure 4. Time-conversion curve for $\text{TMSCl}/\text{AlCl}_3$ initiated polymerization. $[\text{M}]_0 = 2.0 \text{ mol/L}$; $[\text{AlCl}_3] = 2.0 \times 10^{-2} \text{ mol/L}$; $[\text{TMSCl}]/[\text{AlCl}_3] = 2$; Solvent: *n*-hexane; Temp: 30°C . ● Total conversion; △ soluble; ○ crosslinked.

The enhancing effect of TMSCl on the polymerization of PD induced by AlCl_3 is further demonstrated by Figures 3 and 4, conversion-time curves for the polymerizations initiated by AlCl_3 alone and $\text{TMSCl}/\text{AlCl}_3$ respectively. The $\text{TMSCl}/\text{AlCl}_3$ -induced polymerization is much faster than that initiated by AlCl_3 . It is noteworthy that in both the polymerization systems the soluble polymer and crosslinked insoluble product are generated in different rates. Soluble polymers are formed faster and reach a plateau while insoluble products are steadily produced at a relatively low rate.

In order to quantitatively obtain further information about the enhancing effect of TMSCl on the AlCl_3 -initiated polymerization of PD, we obtained the dependence of the monomer concentration on the reaction time for the polymerizations initiated by AlCl_3 alone and $\text{TMSCl}/\text{AlCl}_3$ respectively, as shown in Figure 5. We used the following first order kinetic equations to describe these data:

$$-\frac{d[M]}{dt} = k[M]$$

or

$$\text{Log} \frac{[M]_0}{[M]} = kt$$

Figure 6 plots $\log([M]_0/[M])$ versus reaction time t for the two polymerization systems initiated by AlCl_3 and $\text{TMSCl}/\text{AlCl}_3$. From the slopes of the plots we obtained two values of constant k (noted k_1 and k_2 for AlCl_3 and $\text{TMSCl}/\text{AlCl}_3$ respectively). The result of $k_2/k_1 = 10$ reveals that the $\text{TMSCl}/\text{AlCl}_3$ -initiated polymerization is 10 times faster than that induced by AlCl_3 .

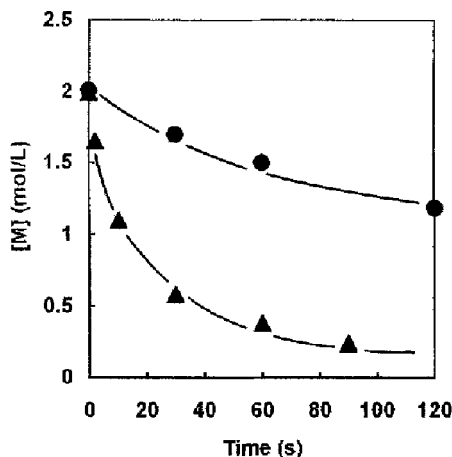


Figure 5. Dependence of monomer concentration on reaction time for polymerizations by AlCl_3 (\bullet) and $\text{TMSCl}/\text{AlCl}_3$ (\blacktriangle). See Figures 3 and 4 for reaction conditions.

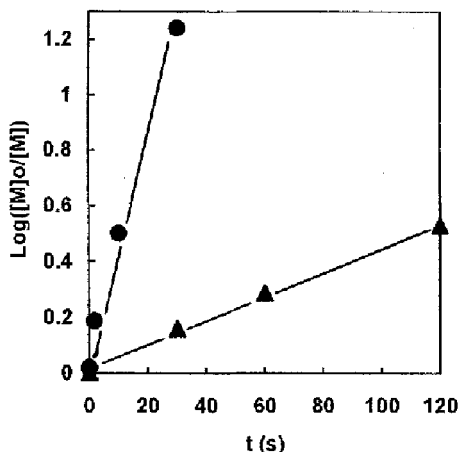
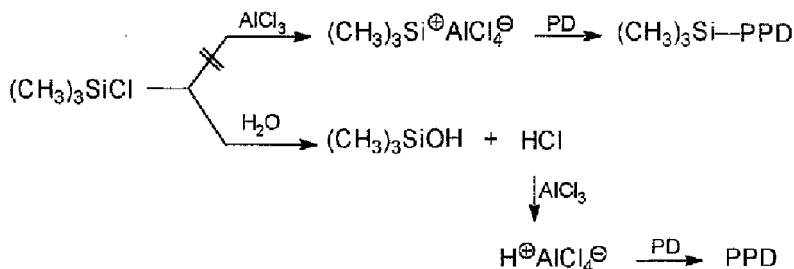


Figure 6. Plots of $\text{Log}([M]_0/[M])$ versus reaction time for polymerizations by AlCl_3 (\blacktriangle) and $\text{TMSCl}/\text{AlCl}_3$ (\bullet). Data from Figure 5. See Figures 3 and 4 for reaction conditions.

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:



As shown in the above scheme, TMSCl can react with AlCl_3 directly to form a complex capable of initiating the monomer by "direct addition", or react with adventitious water existing always in the system to give HCl , of which the combination with AlCl_3 is an efficient initiating system. We have conducted a 300Mz ^1H NMR analysis of the polymer

prepared by $\text{TMSCl}/\text{AlCl}_3$, and the spectrum does not show any signals of $(\text{CH}_3)_3\text{Si}$ -groups. This result strongly evidences that the "direct addition" resulting in trimethylsilyl headgroups does not occur under our conditions, and the polymerization is quite likely to take place through the hydrolysis of TMSCl with adventitious water (2).

In addition to TMS halides, cationic initiations through the hydrolysis of other TMS compounds such as TMS esters have also been reported, e.g., polymerizations of THF and p-methoxystyrene by TMS methanesulfonate and TMS diphenyl phosphate (10), polymerization of styrene by TMS trifluoromethanesulfonate (triflate) (11) and polymerization of isobutyl vinyl ether by TMS triflate (12).

Therefore, we propose that in our polymerization system the real initiating system is the combination of AlCl_3 with HCl released by hydrolysis of TMSCl . As HCl is much more reactive than H_2O towards AlCl_3 , hence the polymerization of PD initiated by AlCl_3 (i.e. by " $\text{H}_2\text{O}/\text{AlCl}_3$ " initiating system) is greatly accelerated by adding TMSCl . However, the molecular weight of the polymer prepared by $\text{TMSCl}/\text{AlCl}_3$ is lower than that induced by AlCl_3 alone, as shown in Figure 2. This is probably due to the difference between the natures of counteranions AlCl_4^\ominus and $\text{AlCl}_3(\text{OH})^\ominus$ derived from the two initiating systems $\text{TMSCl}/\text{AlCl}_3$ and " $\text{H}_2\text{O}/\text{AlCl}_3$ " respectively.

Acknowledgement

The National Natural Science Foundation of China is gratefully acknowledged for financial support.

References

1. Sawamoto M, Kamigaito M, Higashimura T (1988) *Polym Bull* 19: 359
2. Kamigaito M, Sawamoto M, Higashimura T (1990) *Macromolecules* 23: 4896
3. Meirvenne DV, Haucourt N, Goethals EJ (1990) *Polym Bull* 23: 185
4. Goethals EJ, Haucourt N, Peng LB (1994) *Makromol Chem, Macromol Symp* 85: 97
5. Kamigaito M, Sawamoto M, Higashimura T (1991) *J Polym Sci, Polym Chem* 29:1909
6. Kamigaito M, Sawamoto M, Higashimura T (1993) *Makromol Chem* 194: 727
7. Peng YX, Nguyen HA, Macedo A, Cheradame H (1994) *Eur Polym J* 30: 69
8. Peng YX, Liu JL, Dai HS, Cun LF (1995) *Polym Bull* 35: 393
9. Peng YX, Liu JL, Dai HS, Cun LF (1995) *J Polym Sci, Polym Chem Ed* 33: 2087
10. Hall HK, Padias AB, Atsumi M, Way ATF (1990) *Macromolecules* 23: 678
11. Lin CH, Matyjaszewski K (1990) *J Polym Sci, Polym Chem Ed* 28: 1771
12. Cho CG, Feit BA, Webster OW (1992) *Macromolecules* 25: 2081