

Study of the Interactions of Organic Sulfides with Active Species in the Cationic Polymerization of 1,3-Pentadiene

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Received: 10 October 2003/Revised version: 3 March 2004 / Accepted: 3 March 2004

Summary

Different alkyl sulfides (dimethylsulfide, ditertiobutylsulfide and diphenylsulfide) were investigated in the polymerization of 1,3-pentadiene initiated by aluminum trichloride in polar solvent in order to control the polymerization and to study the interaction between the electron donor and the active species. Thus, it was found that dimethylsulfide totally inhibited the polymerization, while thanks to its steric hindrance the polymerization occurred in the presence of ditertiobutylsulfide. However, for this electron donor, a transfer activity was evidenced at room temperature and at 0°C, which contributes to prevent the control of the polymerization. Diphenylsulfide stabilizes a little the active centers with nearly no transfer reaction. However in the studied experimental conditions, the stabilization was not sufficient to obtain a living polymerization.

Introduction

In the context of our studies on the cationic polymerization of 1,3-pentadiene, part of the research was devoted to the role of various electron donors in order to control the polymerization [3]. The work was interested in the understanding of the interactions between the electron donors and the active species. Most of the time, these studies are arduous because the lifetime of the active species is limited. In the case of the system 1,3-pentadiene-AlCl₃ in non polar medium studies revealed that the active species were long-lived despite numerous side reactions such as isomerization, cyclization, polymer grafting and cross-linking [4-5]. Preliminary studies showed that in a polar medium such as in CH₂Cl₂, the polymer was soluble which gave hopes of a simpler system, i.e. with less side reactions.

In the work published by Webster, it was demonstrated that alkyl sulfides were interesting Lewis bases to achieve controlled polymerization of isobutylvinylether [1]. As the sulfide concentration was increased, the rate of polymerization decreased and a nearly monodisperse polymer was obtained. Interestingly, when the bulkiness of the sulfide was increased, the rate of polymerization increased but the system deviated

from living behavior. The present study was aiming at determining whether the same kind of observation could be collected on the 1,3-pentadiene- $\text{AlCl}_3\text{-CH}_2\text{Cl}_2$ system.

Experimental part

Reactants

Methylene dichloride, pentane and 1,3-pentadiene were dried under vacuum by storage over calcium hydride. Aluminum trichloride (Aldrich) was used without purification and stored in a glove box under nitrogen. The sulfides, dimethylsulfide, ditertiobutylsulfide and diphenylsulfide (Aldrich), have been dried on molecular sieves.

Polymerizations

The polymerizations were carried out in a three necked reactor equipped with teflon magnet, and a rubber cap. After a nitrogen flush the reactor was introduced in the glove box equipped with a balance where aluminum trichloride was stored. After introduction of the required quantity of the Lewis acid, the reactor is connected to the vacuum line and placed in a liquid nitrogen bath. The solvent and the monomer are introduced by condensation under vacuum. The liquid additive is introduced by the rubber cap with a syringe. The reactor is rapidly brought to the required temperature and allowed to stand for the required time. The polymerizations are quenched by an injection of a few mL of butylamine.

Before workup, the cross-linked polymer was separated by filtration then dried under vacuum. The filtrate was washed with water, followed by evaporation of the solvent and remaining monomer under reduced pressure. The polymer samples can be purified several times by dissolution and precipitation in order to determine the extent of incorporation of the electron donor.

Results and discussion

It was interesting to compare the behavior of three sulfides : dimethylsulfide (SMe_2), diphenylsulfide (SPh_2) and ditertiobutylsulfide ($\text{S}(\text{t-Bu})_2$). They have been used in similar conditions to previous work so as to allow comparisons, i.e. a monomer concentration close to 1M and a Lewis acid concentration around 1.10^{-2}M . In these conditions, it has been shown that at room temperature in non polar medium the initiation reaction directly takes place on the Lewis acid, without the necessity of a proton donating species [2]. Operating in polar conditions (CH_2Cl_2) the results are similar to the ones in pentane, as shown in Table 1, except the above mentioned fact that the gel content is strongly decreased.

Whatever the solvent used, the polydispersity index of the soluble polymer was very high, higher than 10. It has been shown elsewhere that this situation is due to the reaction of the polymer with growing chain ends, leading to transfer [4]. It is known that such polymer transfer, when predominant over the other transfers and the reactions interrupting chain growth, leads to a polymer with the same average number molar mass as in the absence of transfer, but of course with an increased polydispersity index. It is noteworthy that, assuming that each aluminum atom is involved in the generation of one macromolecule, the \overline{M}_n of the three experiments carried out in CH_2Cl_2 (runs 2, 3 and 4) are close to the theoretical value (3300, 3900

and 4000 respectively). This observation is consistent with the assumption that the active species are long-lived during the polymerization time (2 hours). It is to be noticed that lowering the temperature at 0°C (run 1) does not strongly modified the overall yield, but induced an increase in the gel content.

Table 1 . 1,3-pentadiene polymerization in CH₂Cl₂, 2 hours polymerization time.

Run	[M] ₀ mol/L	[AlCl ₃] ₀ mol/L	T °C	Total yield %	Insoluble Yield %	\bar{M}_n g/mol	\bar{M}_w/\bar{M}_n
1	1.6	2.3.10 ⁻²	0	75	16	2700	12.4
2	1.6	2.3.10 ⁻²	20	69	3	3300	19
3	1.6	2.3.10 ⁻²	20	83	3	2800	25.9
4	1.6	2.3.10 ⁻²	20	85	7	3700	18.5
5*	1.6	2.3.10 ⁻²	20	64	53	2200	10.2

*Experiment carried out in pentane

Initiation is assigned to direct initiation because it cannot be reasonable to assume that water concentration is at least equal to that of aluminum trichloride. This interpretation is in tune with previous observations on this system, since it has been shown that direct initiation is responsible for the production of active species in non polar solvent [2]. The detailed mechanism of direct initiation is not known, but did not constitute an objective of this research on the effect of thioethers as electron donors. However, it deserves a small comment. This is not the first time that a monomer possessing a conjugated double bond shows an initiation behavior which can be explained by direct initiation from the Lewis acid [6]. Similarly to the previous study carried out on 1,3-pentadiene in non polar solvent [2-5], Jordan and Mathieson examined the initiation of the polymerization of styrene and α -methylstyrene in the presence of aluminum trichloride in non polar medium at room temperature [7]. The reproducibility of the reactions and the absence of induction period were arguments in favor of the direct initiation mechanism [6-7]. In the present study, it is simply recognized that the concentration of the produced macromolecules seems to be fairly close to the theoretical concentration of aluminum atoms. This point will be dealt within further paper.

The effect of the introduction of diphenylsulfide and dimethylsulfide was investigated. Some results are shown on Table 2.

Table 2. Effect of the introduction of some organic sulfide in the 1,3-pentadiene polymerization in CH_2Cl_2 .

Run	$[\text{M}]_0$ mol/L	$[\text{AlCl}_3]_0$ mol/L	$[\text{SR}_2]_0$ mol/L	T °C	Time h	Total yield in %	Insoluble yield in %	\bar{M}_n g/mol	\bar{M}_w/\bar{M}_n
1	1.6	$2.3 \cdot 10^{-2}$	SMe_2 $2.3 \cdot 10^{-2}$	20	2	1	-	-	-
2	1.6	$2.3 \cdot 10^{-2}$	SPh_2 $2.3 \cdot 10^{-2}$	20	2	100	1	2400	6.3
3	1.0	$1.0 \cdot 10^{-2}$	0	0	1	76	3		
4	1.0	$1.0 \cdot 10^{-2}$	SPh_2 $0.25 \cdot 10^{-2}$	0	1	73	2	4400	4.2
5	1.0	$1.0 \cdot 10^{-2}$	SPh_2 $0.5 \cdot 10^{-2}$	0	1	79	1	4200	4.2
6	1.0	$1.0 \cdot 10^{-2}$	SPh_2 $2.1 \cdot 10^{-2}$	0	1	71	2	4000	2.9
7	1.0	$1.0 \cdot 10^{-2}$	SPh_2 $4.0 \cdot 10^{-2}$	0	1	56	1	3700	2.5

It is clear from the first experiment reported on the above Table 2 that dimethylsulfide does not allow polymerization, and according to the work of Webster, this is due to the high nucleophilicity of the molecule. The monomer molecules cannot compete with dimethylsulfide to react with the Lewis acid or with the active species. This is the reason why diphenylsulfide was tried. In this molecule, the two phenyl rings bring at the same time a way for the delocalization of the lone pairs of electron of the sulfur atom, and some steric hindrance which could decrease the reactivity towards the active species of the growing macromolecules. Indeed, the second experiment (run 2, Table 2) showed that with these reactant concentrations at room temperature and with two hours of polymerization time, the polymer yield was 100 %. Moreover, the polydispersity index of the polymer was much lower than the one of the polymerizations performed without electron donor (see Table 1) with a molar mass not too far, which means that SPh_2 stabilize a little the active species. If the concentrations are decreased, and lowering polymerization time and temperature, the yield was still high but incomplete, which showed that diphenylsulfide does not importantly give termination reaction. It is worth noting that the experiment without diphenylsulfide (run 3), carried in the same conditions as the experiments 4, 5, 6 and 7 gave a yield of 76 %, which shows that at relatively low concentration, the electron donor does not bring serious modifications to the polymer yield and molar mass. A fourfold excess of diphenylsulfide is necessary to observe a decreased activity of the polymerization system (run 7).

Considering the weak efficiency of diphenylsulfide to decrease the polymerization rate, it was of interest to investigate the possible effects of di-*t*-butylsulfide. Some results are shown on Table 3.

Table 3. Effect of the introduction of di-*t*-butylsulfide in the 1,3-pentadiene polymerization at 20°C in CH₂Cl₂.

Run	[M] ₀ mol/L	[AlCl ₃] ₀ mol/L	[<i>t</i> -Bu ₂ S] ₀ mol/L	Time h	Total yield in %	Insoluble yield in%	\bar{M}_n g/mol	\bar{M}_w/\bar{M}_n
1	1.6	2.3·10 ⁻²	0	2	83	3	2800	25.9
2	1.6	2.3·10 ⁻²	0	2	85	7	3700	18.5
3	1.6	2.3·10 ⁻²	1.15·10 ⁻²	2	85	6	1200	4.2
4	1.6	2.3·10 ⁻²	2.3·10 ⁻²	2	90	2	1100	3.4
5	1.6	2.3·10 ⁻²	4.6·10 ⁻²	2	83	2	800	2.6
6	1.6	1.15·10 ⁻²	1.15·10 ⁻²	2	68	1	1000	3.6

The comparison of runs 3, 4 and 5 shows that at 20°C the yield was as high as in the experiments carried out without electron donor (runs 1 and 2), but the molar mass was lower which indicates that transfer is operating. If the concentrations of the Lewis acid and di-*t*-butylsulfide are divided by a factor of 2, as shown by the comparison of runs 4 and 6, it can be seen that the yield is decreased, but the molar mass does not change appreciably. Consequently, in order to decrease the transfer efficiency of the electron donor and to try to improve the yield, the polymerizations were carried out at 0°C. The results of some kinetic experiments are shown on Table 4.

Table 4. Effect of the introduction of di-*t*-butylsulfide in the 1,3-pentadiene polymerization at 0°C in CH₂Cl₂.

Run	[M] ₀ mol/L	[AlCl ₃] ₀ mol/L	[<i>t</i> -Bu ₂ S] ₀ mol/L	Time h	Total yield in %	Insoluble yield in %	\bar{M}_n g/mol	\bar{M}_w/\bar{M}_n
1	1.6	2.3·10 ⁻²	2.3·10 ⁻²	2.25	55	2	1100	3.5
2	1.6	2.3·10 ⁻²	2.3·10 ⁻²	4	59	1	1100	3.5
3	1.6	2.3·10 ⁻²	2.3·10 ⁻²	5	68	1	1000	3.9
4	1.6	2.3·10 ⁻²	2.3·10 ⁻²	24	92	18	1000	4.1
5	1.0	1.0·10 ⁻²	1.0·10 ⁻²	1	38	0	1900	1.7*
6	1.0	1.0·10 ⁻²	1.0·10 ⁻²	3	59	0	2500	2.1*
7	1.0	1.0·10 ⁻²	1.0·10 ⁻²	5	62	0	2200	1.8*
8	1.0	1.0·10 ⁻²	1.0·10 ⁻²	7	70	1	2300	1.9*
9	1.0	1.0·10 ⁻²	2.0·10 ⁻²	3	35	0	1650	1.5*
10	1.0	1.0·10 ⁻²	2.0·10 ⁻²	5	48	0	1700	1.6*
11	1.0	1.0·10 ⁻²	2.0·10 ⁻²	7	48	0	1800	1.6*

* polymers purified by precipitation

In the first series of experiments carried out with the highest concentrations (runs 1 to 4), it can be seen that the polymer yield is increasing with time. However, the average number molar mass does not change which again indicates transfer. The \bar{M}_n are lower than in the absence of electron donor (run 1, Table 1) which also supports the transfer effect of the di-*t*-butylsulfide. When the concentrations are decreased, keeping constant and equal to 1 the ratio of the concentrations of sulfide and aluminum trichloride, (runs 5 to 8), the same behavior seems to be observed. The yields being uncomplete, the question of the presence of active species at the end of the polymerization can be solved introducing after a required time a new monomer charge and measuring the new polymer yield. This has been done for experiment 9 after three

hours and in a separated experiment adding twice the same monomer charge as the initial one after three and six hours. It was observed that if active species are still present after three hours of polymerization time, they are no more active after 6 hours in these conditions. This result is in agreement with the constant yield obtained for experiments 10 and 11. Doubling the sulfide concentration (runs 9, 10 and 11) showed that the yield is lower. The average number molar mass does not change with yield, which again indicates transfer. The comparison of the experiments carried out with a ratio $[DE]/[AlCl_3] = 1$ (runs 5 to 8) with the last three runs of Table 3 for the same ratio = 2, shows the transfer effect of an increased concentration of the di-*t*-butylsulfide. Since the yield is decreasing with increasing sulfide concentration and since the active species are killed after 5 hours, it can be assumed that besides the transfer effect, the sulfide has a termination effect or at least an effect of complexation with the active species.

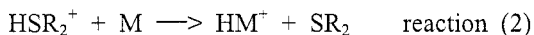
However, the fact that the molar mass remains approximately constant as a function of the yield deserves some comments. If the average number polymerization degree is expressed as the number of monomer units in the sample divided by the number of macromolecules, one obtains:

$$\overline{DP}_n = ([M]_0 - [M])/N$$

where $[M]_0$ and $[M]$ are respectively the initial monomer concentration and the monomer concentration at the time t , and N the concentration of macromolecules. Introducing the expression giving the yield Y :

$$\overline{DP}_n = [M]_0 \cdot Y/N$$

The fact that \overline{DP}_n is constant whatever the yield simply means that the number of macromolecules increases proportionally to the yield. Since the polymerization rate is proportional to the first power of the monomer concentration, it follows that the number of macromolecules generated by transfer is also proportional to the monomer concentration. This is precisely the characteristic of monomer transfer. This last characteristic must be combined with the fact that the transfer efficiency depends on the di-*t*-butylsulfide concentration, since in the absence of the electron donor, monomer transfer is negligible. This discussion leads to the system:



in which P^+ is a growing chain, M the monomer and SR_2 the sulfide. In other words, this is a transfer to monomer assisted by the sulfide. Obviously, the equilibrium (1) is the same kind of equilibrium demonstrated by Webster for the polymerization of isobutylvinylether in the presence of sulfide, and the rate of reaction (2) must be low enough (rate determining) to give rise to a number of new macromolecules proportionally to monomer concentration.

Conclusion

This work shows that, according to the work of Webster, the dimethylsulfide cannot be used as an electron donor capable of control of the long-lived polymerization of 1,3-pentadiene initiated by aluminum trichloride in methylene dichloride. In the context of non polar medium, this electron donor was used in order to quench the active species of this system characterizing them under the form of sulfonium ions [8]. Decreasing the donicity of the electron donor and increasing the

steric hindrance as in the case of diphenylsulfide does not open a way to control this polymerization in the studied experimental conditions. In the case of di-*t*-butylsulfide at room temperature, it is clear that the electron donor is a transfer agent. If the reaction temperature is decreased in order to minimize this effect, besides some termination, the transfer activity is still noticed. These observations give some informations on the interactions between electron donors and the active species. Indeed di-*t*-butylsulfide is at least as nucleophilic as dimethylsulfide and should give the same termination reaction as dimethylsulfide. The difference lies in the steric hindrance which is important in the case of di-*t*-butylsulfide. Since the termination activity of the di-*t*-butylsulfide is sufficiently decreased so as to allow polymerization, a transfer activity is evidenced which contributes to prevent the control of the polymerization. When the sulfide is prevented to react with the electrophilic center of the active species, it reacts with hydrogen atoms at the alpha position of the active species giving most probably a conjugated system of two double bonds. This conjugated system can compete with the monomer, which explains the occurrence of equilibrium (1). The differences between the present system and the system studied by Webster are the consequence of the electrophilicity of the active species in the cationic polymerization of 1,3-pentadiene higher than that of the active species of the vinyl ethers. This study illustrates that in cationic polymerization transfer agents are specific to each system. Contrary to strong nucleophiles such as dimethylsulfide which completely inhibit polymerization (too strong interaction), when the latter were less strong and used in excess to the initiator (Lewis acid) it is difficult to choose among the different mechanistic steps proposed in the literature in the presence of electron donor [9].

Acknowledgements. The Association Franco-Chinoise de Recherche Scientifique et Technique (AFCRST) is gratefully acknowledged for a support.

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