Polymer Bulletin 26, 417–422 (1991)

Polymer Bulletin

Investigation of the mechanism of living cationic polymerization of isobutylene by B^{11} NMR spectroscopy

Miklós Zsuga, Tibor Kelen*, and János Borbély

Institute of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary

Summary

The living carbocationic polymerization of isobutylene initiated by tri-cumyl-ether (1)/BCl_3 and tricumyl-acetate(2)/BCl_3 was investigated by B^{11} NMR spectroscopy in the presence and absence of DMSO. With BCl_3, 1 yields tri-cumyl-chloride and BCl_2OMe due to fast exchange reaction, while 2 forms complexes. If the 1/BCl_3 mixture contains DMSO, well defined complexes can be detected, i.e., DMSO.BCl_3 and BCl_2OMe.DMSO. In the system 2/BCl_3/DMSO neutral complexes with broad NMR signals are formed. In the presence of isobutylene (real polymerization mixture) the same complexes can be detected.

Introduction

The t-ethers and t-acetates, in conjunction with BCl_3 [1,2] or $TiCl_4$ [3,4], are initiators of living carbocationic polymerization of olefinic monomers, such as isobutylene, styrene, etc. With the exception of the initiator 2,5-diacetoxy-2,5-dimethyl-hexene-3 [5], the resultant polymer has much broader molecular weight distribution (MWD) than it is expected when living polymerization takes place. Recent results [6,7,8] show, however, that in the presence of strong electron donors, e.g., dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAA) etc., the MWD narrows, due to the absence of slow initiation [7] and/or undesirable side reactions, e.g., indanyl skeleton formation [6] etc..

In our earlier paper [9] we showed that the B^{11} NMR was suitable to monitor the reactions in the t-ether BCl_3 system under exactly the same experimental conditions as required for a living polymerization.

In this work we have continued the investigation of reaction products and complexes in the tri-cumyl-ether/BCl_3 and tri-cumyl-acetate/BCl_3 systems, in the presence and absence of DMSO.

Experimental

Tri-cumyl-acetate was synthetized according to [10]. The source of all other materials, such as isobutylene, BCl_3, CH_2Cl_2, tri-cumyl-ether, DMSO has been published [9]. Polymerizations were carried out under dry nitrogen atmosphere in a dry-box.

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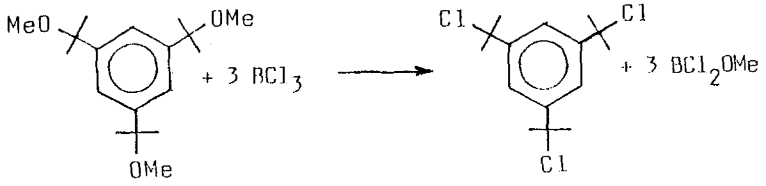
*To whom offprint requests should be sent

Procedures and NMR technique have been reported in detail [9].

Results and Discussion

As we have shown in our earlier publication [9], the reaction between BCl_3 and tri-cumyl-ether (1) yielded tri-cumyl-chloride and dichloroboronite.



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Accordingly, in the B^{11} spectrum of this system (Fig.1,a) we found the signals of the BCl_3 (δ=46.0-46.2 ppm) and of the dichloroboronite (δ=31.6-31.7 ppm)

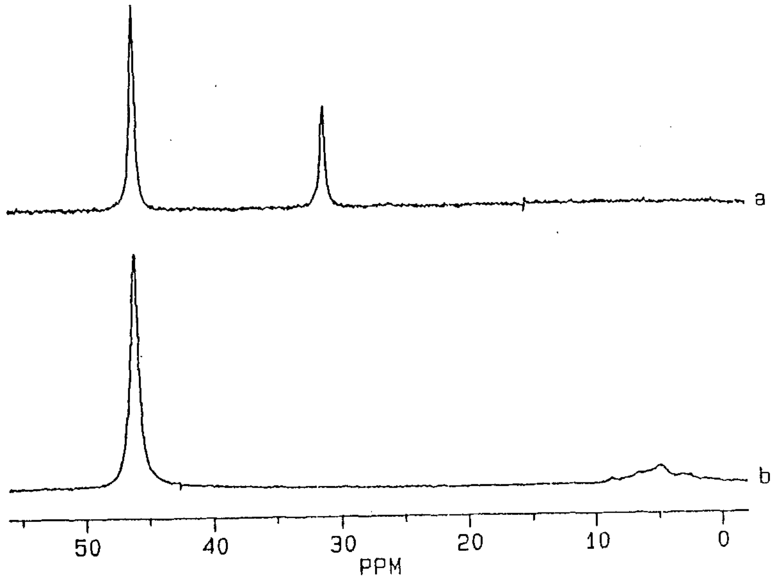
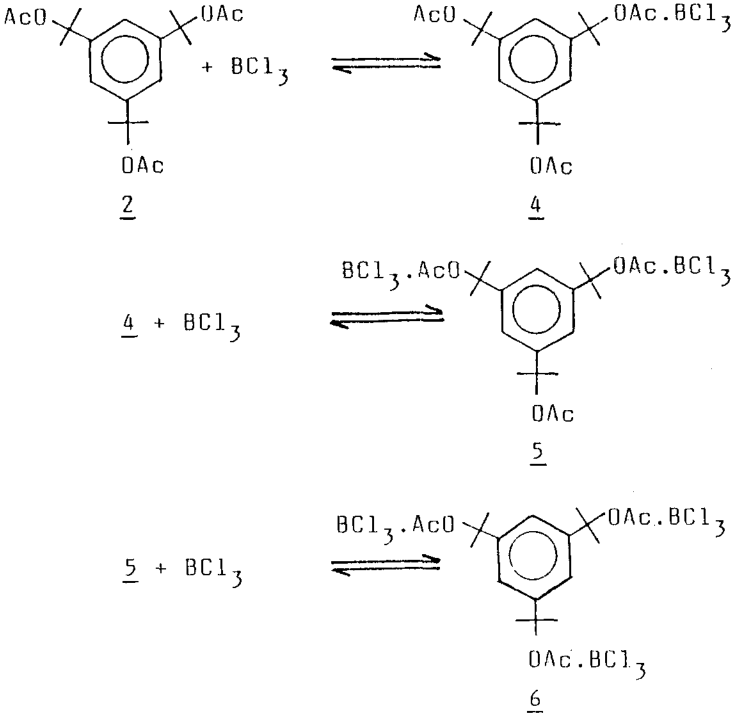


Fig.1: B^{11}-NMR spectra of the $\underline{1}/BCl_3$ (a) and $\underline{2}/BCl_3$ (b) systems at 243 K ($[\underline{1}]=[\underline{2}]$=0.0054 mole/L, $[BCl_3]$=0.05 mole/L, 15 mins, CH_2Cl_2)

In contrary, the tri-cumyl-acetate/BCl_3 system gives B^{11} signals in the region of δ=5.0-7.0 ppm (Fig.1,b) which is characteristic for molecular complexes [11].
The signal of BCl_3 is broader in the $\underline{2}/BCl_3$ system, indicating a fast dynamic equilibrium. The broadness of the not well

structured signal of the acetate.BCl_3 complexes hints to succesive complexation equilibria. In this system, we did not find the boronite-analog compound, BCl_2OAc (a peak around $\delta \sim 30$ ppm).

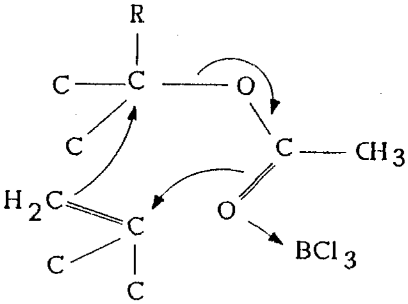


The lack of a signal around $\delta \sim 30$ ppm indicates that no exchange reaction takes place:

$$\underline{2} + 3\,BCl_3 \not\longleftrightarrow \underline{3} + 3\,BCl_2OAc.$$

In the presence of isobutylene we obtained essentially the same B^{11} spectra indicating that the sensitivity of B^{11} measurement is not high enough to detect the counter ions, i.e., CH_3OBCl_3, BCl_3OAc, BCl_4. This means that if ionic species are present, i.e., the polymerization proceeds via free ions, the concentration of ions is much lower than that of the neutral compounds. However, we were able to detect significant difference between the 1/BCl_3 and 2/BCl_3 initiating systems. While the 1/BCl. system yields 3 and a new Lewis acid., i.e., BCl_2OMe, the 2/BCl_3 forms molecular complexes, i.e., 4, 5 and 6. This means that we have to distinguish between two different mechanism for the two systems.

In case of the 1/BCl_3 system the propagation takes place in a quasi living manner, i.e. via termination-reinitiation steps, as reported by Kaszás et. al [6]. In contrary, the 2/BCl_3 system probably propagates via the cyclic intermedier 7 as reported by Faust and Kennedy [1].



In the presence of DMSO, additional complexes and exchange reactions have to be taken into account. Fig.2 shows the B^{11} NMR spectra of the systems BCl_3/DMSO, 1/BCl_3/DMSO and 2/BCl_3/DMSO.

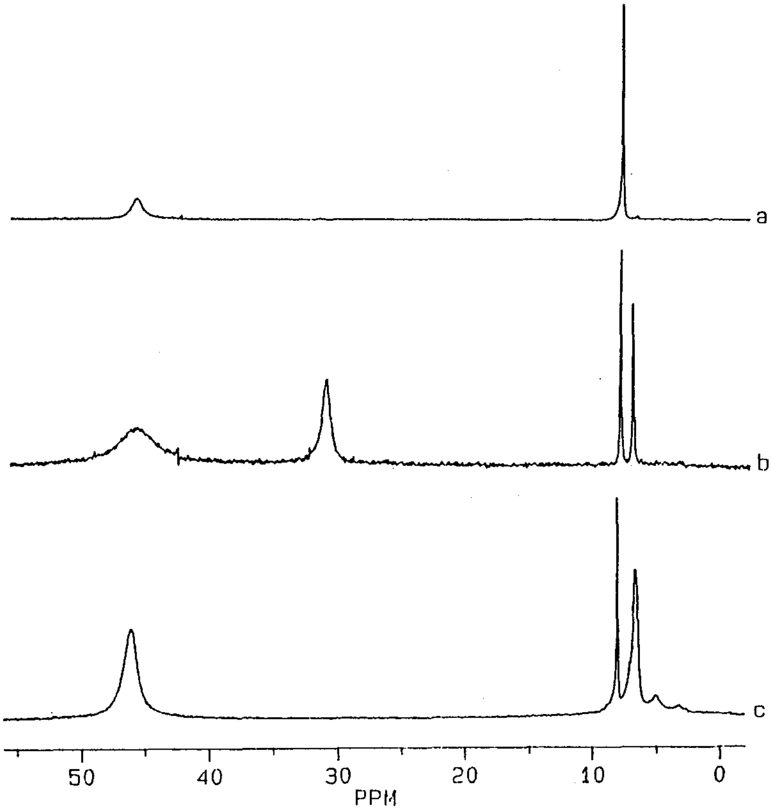


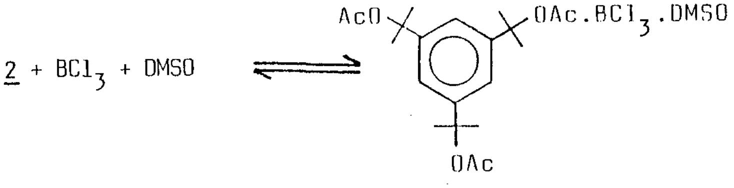
Fig.2: B^{11}-NMR spectra of the BCl_3/DMSO (a), 1/BCl_3/DMSO (b) and 2/BCl_3/DMSO (c) systems at 243 K ([1]=[2]=0.0054 mole/L, [DMSO] =0.015 mole/L [BCl_3] =0.05 mole/L, 15 mins, CH_2Cl_2)

The assignment for the 1/BCl_3/DMSO system is as follows: $\delta = 46.1$ ppm: BCl_3. $\delta = 31.6-31.7$ ppm: BCl_2OH (impurities). $\delta = 31.1-31.2$ ppm: BCl_2OMe. $\delta = 8.0-8.1$ ppm: $BCl_3.DMSO$. $\delta = 7.1-7.2$ ppm: BCl_2OMe DMSO. This means that if the reaction mixture contains DMSO, a strong electron donor, both Lewis acids, i.e., BCl_3 and BCl_2OMe form complexes with DMSO.

$$BCl_3 + DMSO \rightleftharpoons BCl_3.DMSO$$

$$BCl_2OMe + DMSO \rightleftharpoons BCl_2OMe.DMSO$$

The B^{11} spectrum of the 2/BCl_3/DMSO system indicates significant differences. No peak can be found around $\delta \sim 30.0$ ppm, but an additional structured peak appears arround $\delta = 6.6$ ppm. The fine structure of this peak indicates three overlapped signals which can be assigned to the succesively formed complexes (8, 9 and 10) of 2 and BCl_3.DMSO:



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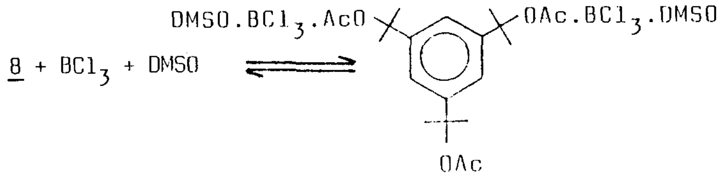

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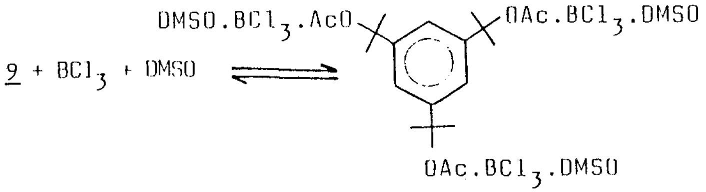

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Of course, also mixed complexes, i.e., conbinations of different Lewis acids as complexing agents in the same acetate molecule, may simultaneously occur in the system.
The narrow peak at $\delta = 8.0-8.1$ ppm belongs to BCl_3.DMSO. The small broad peaks at $\delta = 3.0-5.2$ ppm probably belong to 5 and 6 (see Fig.1).

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Accepted April 9, 1991 C