Polymer Bulletin 23, 335–340 (1990)

Polymer Bulletin

Investigation of 1,3,5-tris(2-metoxypropane)benzene/BCl_3 initiated living isobutylene polymerization by C^{13} and B^{11} NMR spectroscopy

Miklós Zsuga, Lajos Balogh, Tibor Kelen*, and János Borbély

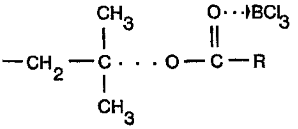
Department of Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary

Summary

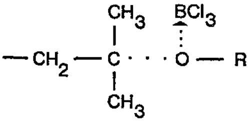
The living carbocationic polymerization of isobutylene initiated by 1,3,5-tris(2-methoxypropane)benzene (TriCumOMe)/BCl_3 system was investigated by C^{13} and B^{11} NMR spectroscopy. The reaction between the TriCumOMe and BCl_3 at -30°C in CH_2Cl_2 after 15 mins reaction time resulted in 1,3,5-tris(2-chloropropane)benzene (TriCumCl) and methyl-dichloroboronite (BCl_2OMe). The same system in the presence of isobutylene yielded three-arm star, chlorine terminated telechelic polyisobutylene and BCl_2OMe. No counterions, i.e., $BCl_3OMe^{\ominus}$, $BCl_4^{\ominus}$, or neutral boron complexes, e.g., TriCumOMe.3BCl_3 could be detected. The simultaneous measurement of static permittivity (direct monitoring method) showed different reaction rate patterns in the case of AMI method, and when the TriCumOMe+BCl_3 mixture was aged and the polymerization was started by isobutylene.

Introduction

The discovery of the living carbocationic polymerization of isobutylene was a milestone in the synthesis of well defined tert. chlorine capped telechelic polyisobutylenes (1). To explain the living character of the polymerization of isobutylene initiated by either tert. acetates/BCl_3 (2) or tert. ethers/BCl_3 (3), the so called insertion mechanism was proposed (2,3) involving neutral complexes with a higly polarized bond between the tertiary carbon and oxygen atoms:

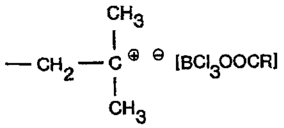


$$-CH_2-C(CH_3)_2\cdots O-\overset{O\cdots\rightarrow BCl_3}{\overset{\|}{C}}-R$$

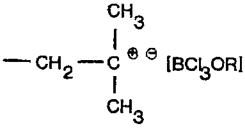


$$-CH_2-C(CH_3)_2\cdots\overset{BCl_3}{\overset{\vdots}{O}}-R$$

instead of ionpairs and/or free ions:



$$-CH_2-C^{\oplus}(CH_3)_2\ {}^{\ominus}[BCl_3OOCR]$$

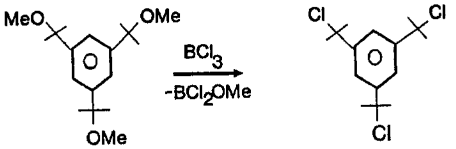


$$-CH_2-C^{\oplus}(CH_3)_2\ {}^{\ominus}[BCl_3OR]$$

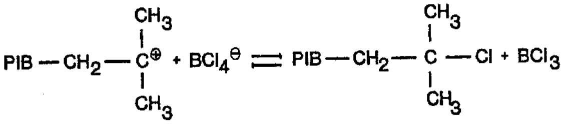
---

*To whom offprint requests should be sent

The use of strong nucleophiles as electron donors (with donor number higher than the donor number of $Cl^{\ominus}$) revealed another possibility of the mechanism, involving the primary chlorination of the initiator:



and higly stabilized carbonium cations by boron complexes with "in situ" and/or external electron donors (4), e.g., BCl_2OMe, $BCl_3.DMSO$ etc., and a reversible termination step:



$$\text{PIB}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^{\oplus}}} + BCl_4^{\ominus} \rightleftharpoons \text{PIB}-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl + BCl_3$$

The purpose of this work was to investigate the TriCumOMe $+BCl_3$ reaction in the presence and in the absence of monomer under the regular polymerization conditions by NMR spectroscopy to obtain information about the presence and absence of the compounds and complexes mentioned above.

Experimental

CH_2Cl_2 was washed with H_2O, dried over $MgSO_4$ and stored over KOH. The dry CH_2Cl_2 was refluxed over P_2O_5 for 24 hrs and distilled two times from fresh P_2O_5 just before use. The isobutylene (IB) (TIFO, Hungary, 99.99 %) was dried on a column filled with fresh $CaCl_2$ and condensed inside the dry-box. The TriCumOMe was synthetised according to (5) and purified by preparative column chromatography using silicagel (6). The BCl_3 was distilled under dry N_2 just before use.

Procedures

The reactions and polymerizations were carried out in a dry box under dry nitrogen atmosphere. Large test tubes served as reactors. To a 25 ml solvent (i.e., $CDCl_3$ for C^{13} and CH_2Cl_2 for B^{11} measurements), the initiator and, in some cases, monomer were added and the reaction was started by fast introduction of bulk BCl_3 into the mixed solution at -30°C. For the NMR investigations, 2 mL samples were taken out and transferred into 10 mm NMR test tubes. For B^{11} NMR measurements, 0.2 ml $CDCl_3$ was added to maintain deuterium for locking. The NMR tube was put immediately into a cooling bath to keep the temperature constant.

The NMR spectra were recorded after 15 mins reaction time by a Bruker 200 instrument equipped with a multinuclear head. The temperature of the head was adjusted by liquid nitrogen to the reaction temperature. The method and instrumentation of the direct monitoring procedure will be published in the next paper (7).

Results and Discussion

For the investigation of the complex reaction, TriCumOMe was selected as initiator to obtain relatively high concentration of species expected to form during the reactions.
In addition, to obtain well-defined C^{13} NMR spectra, the concentrations of TriCumOMe and BCl_3 were maintained higher than regular in case of isobutylene polymerization.
The C^{13} NMR spectra of TriCumOMe/BCl_3/$CDCl_3$ mixture showed a chlorination of the initiator, i.e., the peaks characteristic for the benzylic (δ =77.0 ppm) and CH_3 carbon atoms adjacent to the CH_3O-group (δ = 28.03 ppm) and the peak characteristic for the carbon atom of CH_3O-group (δ =50.45 ppm) are shifted to δ=69.49 ppm, δ=34.34 ppm and δ=56.85 ppm positions, respectively, in the presence of BCl_3 (Figure 1).

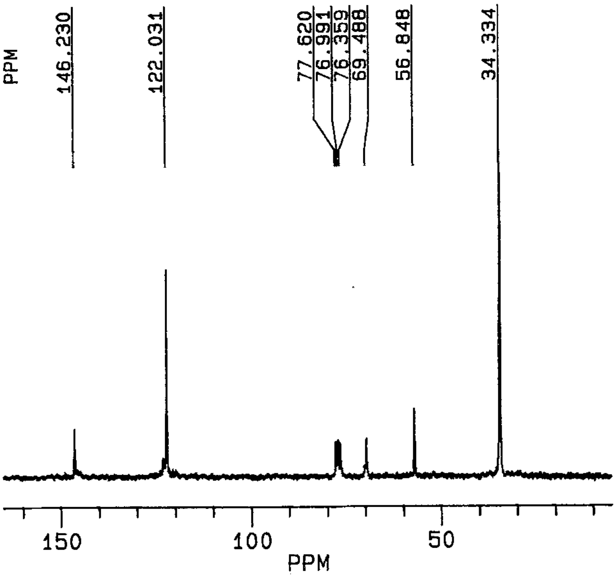


Figure 1. C^{13} NMR spectrum of TriCumOMe/BCl_3 system at -30°C in $CDCl_3$. ([TriCumOMe] =0.022 mole/L, $[BCl_3]$=0.77 mole/L, t=15 mins)

Since the natural abundance of B^{11} isotope is relatively high it allowed us to run experiments under real polymerization conditions (Table 1).

Figure 2 shows the B^{11} NMR spectra of systems A,B and C. The B^{11} NMR spectrum of system A gives the chemical shift of BCl_3 in CH_2Cl_2 from the standard of $BF_3.Et_2O$.

Table 1

Reaction conditions for B^{11} NMR investigation at -30°C in 25 mL CH_2Cl_2 ($[BCl_3]$ =0.05 mole/L, t=15 mins)

	[IB] (mole/L)	[TriCumOMe] 10^3 mole/L	Observation
A	-	-	no color
B	-	5.38	wine red
C	0.23	5.38	pale yellow

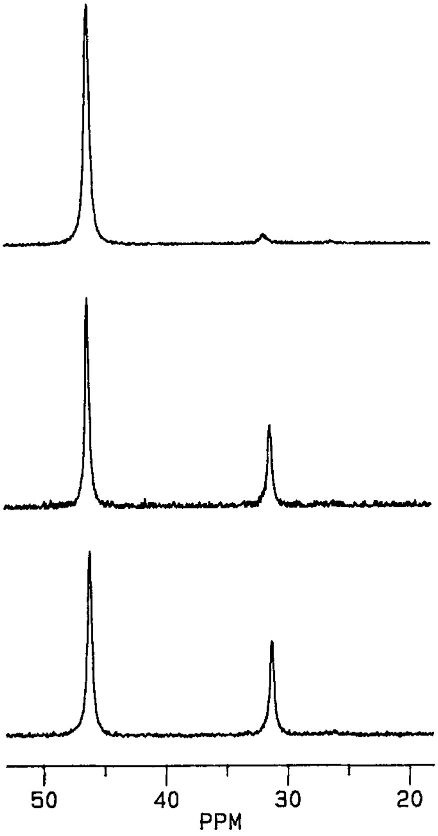
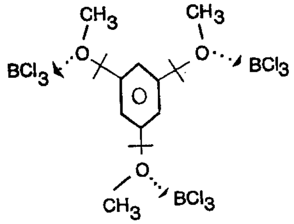


Figure 2. The B^{11} NMR spectra of systems A, B and C. (Experimental details in Table 1)

The small peak at δ =31.71 ppm comes from the impurities of the system. In the presence of TriCumOMe (System B) we found two significant peaks at δ=46.15 ppm and at δ =31.19 ppm which are characteristic for the uncomplexed BCl_3 and BCl_2OMe (8), respectively. Surprisingly, using AMI technique (2) when monomer was present (System C), we obtained similar B^{11} NMR spectrum.

Unfortunately, under these measuring conditions, we were not able to detect the possible counter ions, i.e., $CH_3OBCl_3^{\ominus}$ and/or $BCl_4^{\ominus}$ or the complexed initiator, i.e.,



This fact indicates that the major elementary events of the polymerization take place at very low concentrations of the active species. This was the reason why we tried to get more information by using the direct monitoring method (7). Figure 3 demonstrates the characteristic change of the static permittivity of the polymerization mixtures in cases of AMI technique and aging (premixing) (9) of TriCumOMe plus BCl_3:

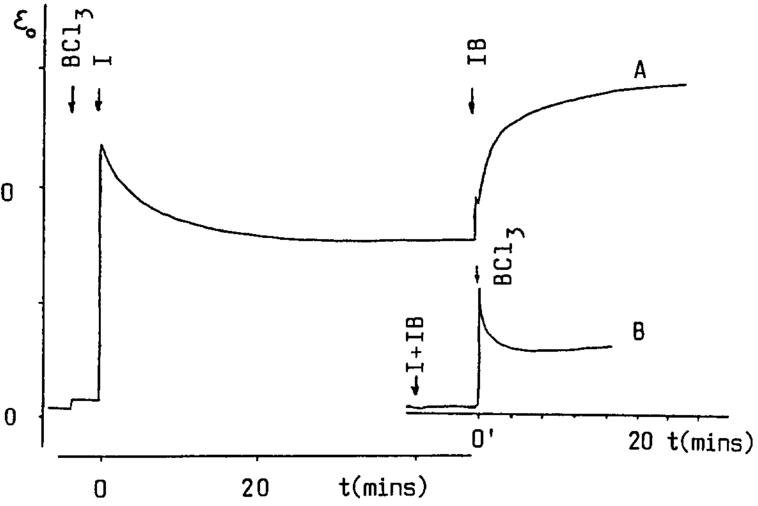


Figure 3. Change of the static permittivity of a polymerization mixture in case of aging (A) and AMI technique (B) at -30°C in CH_2Cl_2. In both cases the polymerizations were started at 0' min as shown by the scale in the inset. ([TriCumOMe]=3.62 10^{-3} mole/L, [BCl_3]=7 10^{-2} mole/L, [IB]=0.13 mole/L)

The change in static permittivity in these two cases shows completely different reaction rate pattern. The difference between the results is immediately apparent. If the primary chlorination of TriCumOMe would be the basic elementary step in both cases, no difference could be expected between the results obtained by AMI and aging methods. The details and explanation of the experimental results obtained by the direct monitoring method concerning the mechanism of the living polymerization of isobutylene initiated by TriCumOMe/BCl_3 system is discussed in our next paper (7).

Acknowledgement:
The athors would like to express their thanks to Dr I. Majoros for providing the pure TriCumOMe.

References

1. R. Faust and J.P. Kennedy, Polym. Bull. 15, 317 (1986)
2. R. Faust and J.P. Kennedy, J. Polym. Sci., Polym. Chem.Ed. 25(A), 1847 (1987)
3. M.K. Mishra and J.P. Kennedy, J. Macromol. Sci., Chem. A 24(8), 933 (1987)
4. G. Kaszás, J.E. Puskás, C.C. Chen and J.P. Kennedy, Polym. Bull. 20, 413 (1988)
5. M.K. Mishra, B. Wang and J.P. Kennedy, Polym. Bull. 17, 307 (1987)
6. I. Majoros, L. Sipos, L. Balogh and T. Kelen, to be published
7. L. Balogh, L. Fábián, I. Majoros and T. Kelen, Polym. Bull. the next paper in this issue
8. H. Nöth and H. Vahrenkamp, Chem. Ber. 99 1049 (1966)
9. L. Toman, S. Pokorny, J. Spevacek and J. Danhelka, Polymer 27, 1121 (1986)

Accepted December 29, 1989 C