

Living carbocationic polymerization of isobutylene with BCl_3 coininitiation in the presence of di-*tert*-butylpyridine as proton trap

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Summary

The living polymerization of isobutylene (IB) has been achieved with the 2,4,4-trimethylpentyl chloride (TMPCl) or cumyl chloride (CumCl)/ BCl_3 /(IB)/methyl chloride/-40° C system in the presence of proton trap 2,6-di-*tert*-butylpyridine (DTBP) in concentrations comparable to that of protic impurities. According to kinetic studies the polymerization is first order both in respect to monomer and BCl_3 . The polymerization rate is not effected by the excess DTBP which suggests that the livingness is not due to carbocation stabilization. Comparison of the results in the presence of DTBP and/or dimethyl sulfoxide (DMSO) demonstrated that the main function of the electron donor (ED) DMSO is to trap protic impurities. The assumption of carbocation stabilization is unnecessary, and reversible termination and the absence of chain transfer is sufficient to explain livingness. In the absence of proton trap or ED however, fast polymerization by the protic impurities occurs masking the much slower living polymerization and the monomer is consumed mainly by this process unless the protic impurities are scavenged.

Introduction

Recently we reported the living polymerization of IB with the 5-*tert*-butyl-1,3-dicumylchloride, or -methyl ether/ TiCl_4 /IB/methyl chloride-*n*-hexane (40/60 v/v)/-80° C system in the presence of the proton trap DTBP (1). Polymers with close to Poisson molecular weight distribution were obtained in the presence of proton trap in concentrations only slightly higher than the concentration of protic impurities in the system. The polymerization rate was found to be first-order of monomer, and not affected by the excess amount of DTBP

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which indicates that livingness is not due to carbocation stabilization. Comparison of the results with the two initiators did not corroborate the theory of carbocation stabilization by in situ electron donors (2,3). We suggested that the sole function of DTBP was to trap protogenic impurities in the polymerization system. Similarly we hypothesized that proton trapping is probably the main function of the externally added EDs.

We have extended our studies to BCl_3 coinitiated IB polymerizations and in the present publication we report on the results of polymerization studies with the TMPCl or $\text{CumCl}/\text{BCl}_3/\text{IB}/$ methyl chloride/ -40°C system in the presence of DTBP and/or DMSO supporting our hypothesis.

Experimental

The synthesis of CumCl and TMPCl have been described (5). Anhydrous DMSO (Aldrich) was used as received. Two methods were applied for the purification of polymer samples depending on their molecular weight: Polymers with $M_n > 1000$, were dissolved in hexanes and precipitated with excess of methanol. After evaporation of the hexanes, the methanol was decanted from the precipitated polymer, and this process was repeated three times. The $M_n < 1000$ samples were purified by column chromatography on ~ 10 g Silica Gel-60 (EM Science) by 100 mL hexanes as eluent. Other materials, polymerization procedures and characterization methods have been described elsewhere (1).

Results and Discussion

It has been reported (4) that the polymerization-inactive aliphatic tert-chlorine/ BCl_3 system becomes active and induces living IB polymerization in the presence of strong EDs. Thus living polymerization was achieved with the $\text{TMPCl}/\text{BCl}_3$ initiating system in the presence of DMSO or dimethylacetamide (DMA), while in their absence polymerization by protic impurities has occurred producing high molecular weight PIBs with broad molecular weight distribution (MWD). Importantly, in the presence of a strong ED polymerization was absent in the control runs, i. e., in the absence of TMPCl . The experimental observations were explained by assuming stabilization of carbocations arising from aliphatic tert-chlorides by strong EDs. Earlier polymerization studies (5) with the $\text{TMPCl}/\text{BCl}_3/\text{CH}_3\text{Cl}/-30^\circ\text{C}$ system which gave similar conversion and molecular weights in the presence and absence of TMPCl revealed that TMPCl is a very inefficient initiator relative to protogenic impurities. Consequently in order to evaluate its initiating activity protic initiation needs to be prevented. We have

already used DTBP, a hindered pyridine, to prevent protic initiation and to achieve living IB polymerization with TiCl_4 coinitiator. Thus we carried out polymerizations in the presence and absence of DTBP with the $\text{TMPCl}/\text{BCl}_3/\text{IB}/\text{CH}_2\text{Cl}_2/-40^\circ\text{C}$ system. Conversions were less than 5% in the control runs (i. e., in the absence of TMPCl and in the presence of DTBP) using polymerization times leading to complete conversions in the presence of TMPCl . According to the linear M_n versus conversion and $\ln [M_0/[M]]$ versus time plots, (Fig. 1.) the polymerization is living, although the rate of the polymerization is low by cationic standards.

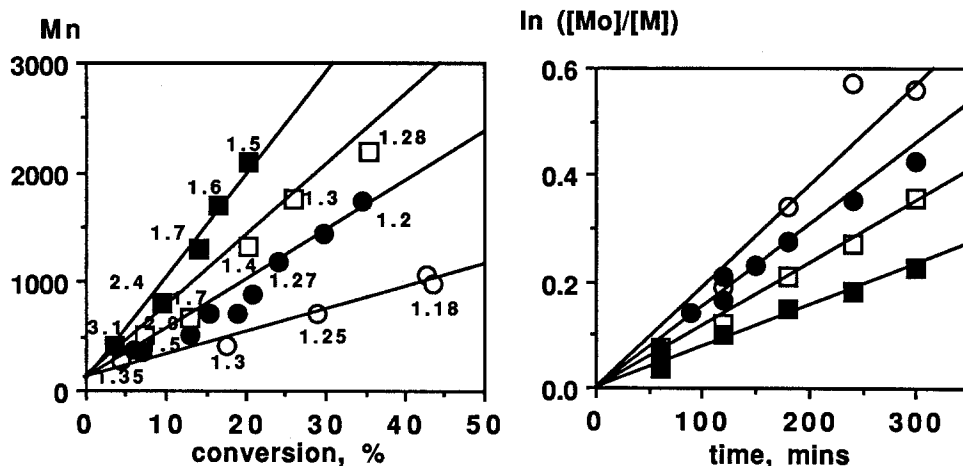


Figure 1.: Polymerization of IB initiated with TMPCl in the presence of DTBP at -40°C in methyl chloride. $[\text{TMPCl}] = 1.16 \times 10^{-2}\text{ M}$, $[\text{BCl}_3] = 0.24\text{ M}$, $[\text{DTBP}] = 2.01 \times 10^{-3}\text{ M}$, $[\text{IB}]_0$: $\circ = 0.48\text{ M}$, $\bullet = 0.96\text{ M}$, $\square = 1.44\text{ M}$, $\blacksquare = 1.91\text{ M}$. The numbers are M_w/M_n values in the Figure.

Essentially the same results were obtained with CumCl (Fig. 2.). According to the apparent propagation rate constants the polymerization is very sensitive to solvent polarity, i. e., by increasing the monomer concentration over 1 M (8 % v/v) decreased the rate constants, presumably by decreasing the solvent polarity. The molecular weight distributions are narrow but increase somewhat with increasing monomer concentration. With 1.44 and 1.91 M monomer bimodal molecular weight distributions were observed at low conversions.

Importantly, polymerization rates remained unchanged in the $[\text{DTBP}] = 1.0\text{--}8.6 \times 10^{-3}\text{ M}$ range (Fig. 3.), which demonstrates that the

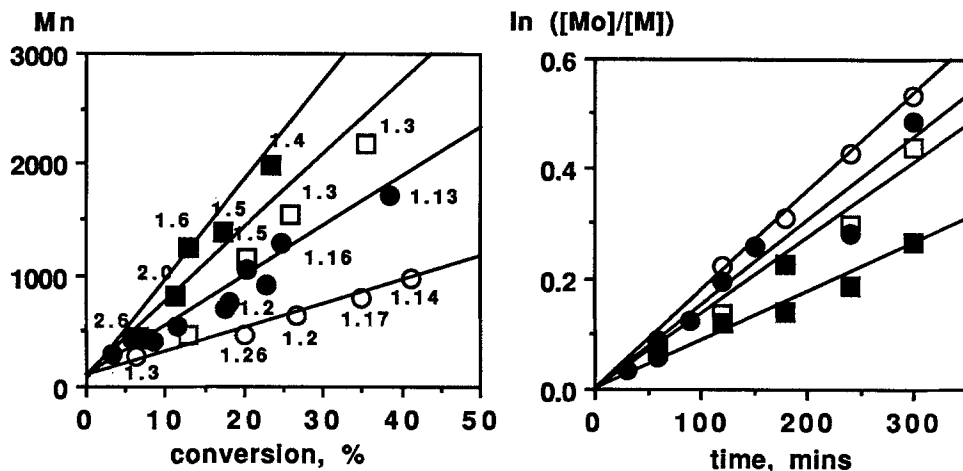


Figure 2.: Polymerization of IB initiated with CumCl in the presence of DTBP at -40°C in methyl chloride. The numbers are M_w/M_n values. $[\text{CumCl}] = 1.16 \times 10^{-2}\text{ M}$, $[\text{BCl}_3] = 0.24\text{ M}$, $[\text{DTBP}] = 2.01 \times 10^{-3}\text{ M}$. $[\text{IB}]_0$: $\circ = 0.48\text{ M}$, $\bullet = 0.96\text{ M}$, $\square = 1.44\text{ M}$, $\blacksquare = 1.91\text{ M}$

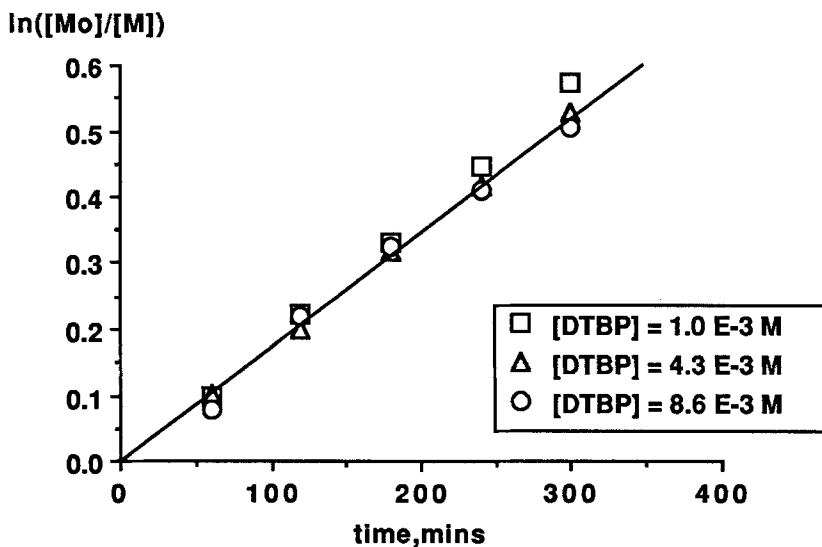


Figure 3.: Polymerization of IB initiated with TMPCl in the presence of increasing amounts of DTBP at -40°C in methyl chloride. $[\text{IB}]_0 = 0.96\text{ M}$, $[\text{TMPCl}] = 1.16 \times 10^{-2}\text{ M}$, $[\text{BCl}_3] = 0.24\text{ M}$

living nature of the polymerization is not due to carbocation stabilization.

Polymerization rates measured at different BCl_3 concentrations are plotted as $\ln(k_p[M_n^+])$ versus $\ln[\text{BCl}_3]$ in Fig. 4.

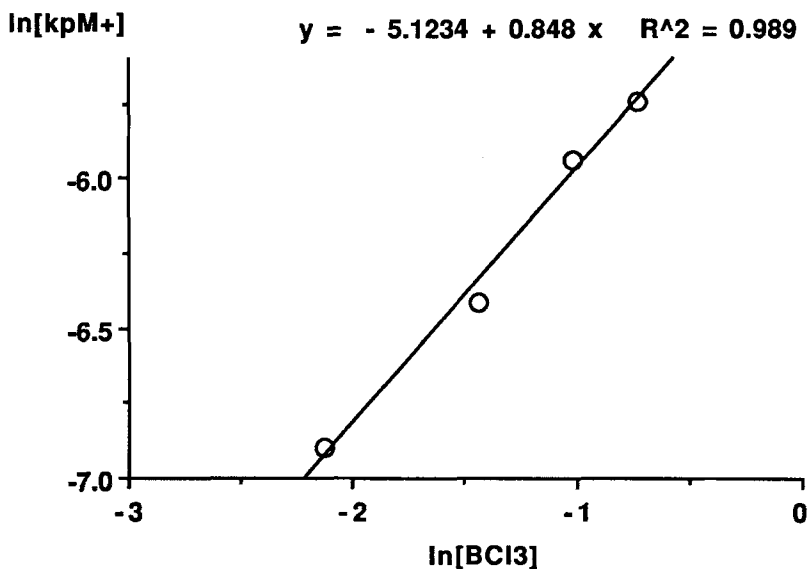


Figure 4.: Reaction order of BCl_3 in the polymerization of IB with TMPCl in the presence of DTBP at -40°C in methyl chloride.

From the slope (0.848) close to first order behavior was obtained for BCl_3 in CH_3Cl at -40°C . This is in contrast to the $\text{TiCl}_4/\text{CH}_3\text{Cl};n\text{-hexane}$ (40/60 v/v)/ -80°C system where the order in TiCl_4 was close to two, due to bimolecular aggregates (or bimolecular complex gegenions) of TiCl_4 (1).

We acknowledge that our results contradict a report with the $\text{CumCl}/\text{BCl}_3/\text{DTBP}/\text{CH}_2\text{Cl}_2/-50^\circ\text{C}$ system according to which DTPB is able to abstract a proton from the propagating $\sim\text{C}^+(\text{CH}_3)_2$ center thereby lowering conversions and molecular weights (6). Our ^1H NMR measurements verified that the products are ω -chloro PIBs and unsaturation is absent.

We have compared the polymerization of IB with the $\text{TMPCl}/\text{BCl}_3/\text{CH}_3\text{Cl}/-40^\circ\text{C}$ system using DMSO or DTBP . Polymerization rates, molecular weights and molecular weight distributions are practically the same (Fig. 5 and 6.). Although the polymerization rate in the presence of DMSO is somewhat lower than reported under the same conditions (4), molecular weights and molecular weight distributions are similar at comparable conversions.

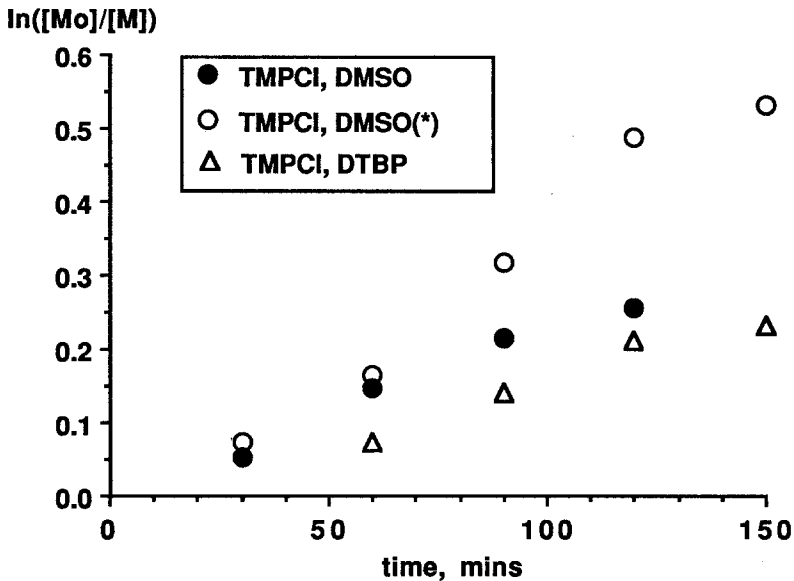


Figure 5.: Comparison of rates of IB polymerizations initiated by the TMPCl/DMSO or DTBP/ $\text{BCl}_3/\text{CH}_3\text{Cl}/-40^\circ\text{C}$ system. $[\text{IB}]_0=0.96\text{ M}$, $[\text{TMPCl}]=1.16\times 10^{-2}\text{ M}$, $[\text{BCl}_3]=0.24\text{ M}$, $[\text{DTBP}]=1.25\times 10^{-3}\text{ M}$ or $[\text{DMSO}]=1.13\times 10^{-2}\text{ M}$. $[\text{DMSO}^*]=1.16\times 10^{-2}\text{ M}$, Ref. (4)

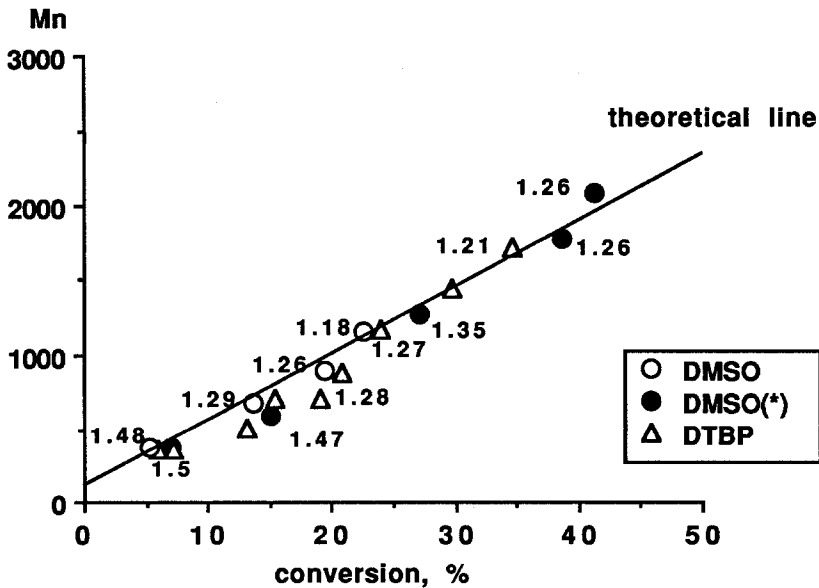


Figure 6.: Living polymerization of IB initiated by the TMPCl/DMSO or DTBP/ $\text{BCl}_3/\text{CH}_3\text{Cl}/-40^\circ\text{C}$ system. Concentrations as on Fig. 5.

The similar rate in the presence of DTBP which is unable to stabilize the growing centers (1,7) and in the presence of DMSO suggests that DMSO may serve only as a proton trap.

An experiment was carried out measuring polymerization rates by adding increasing amounts of DMSO to polymerization systems already containing DTBP.

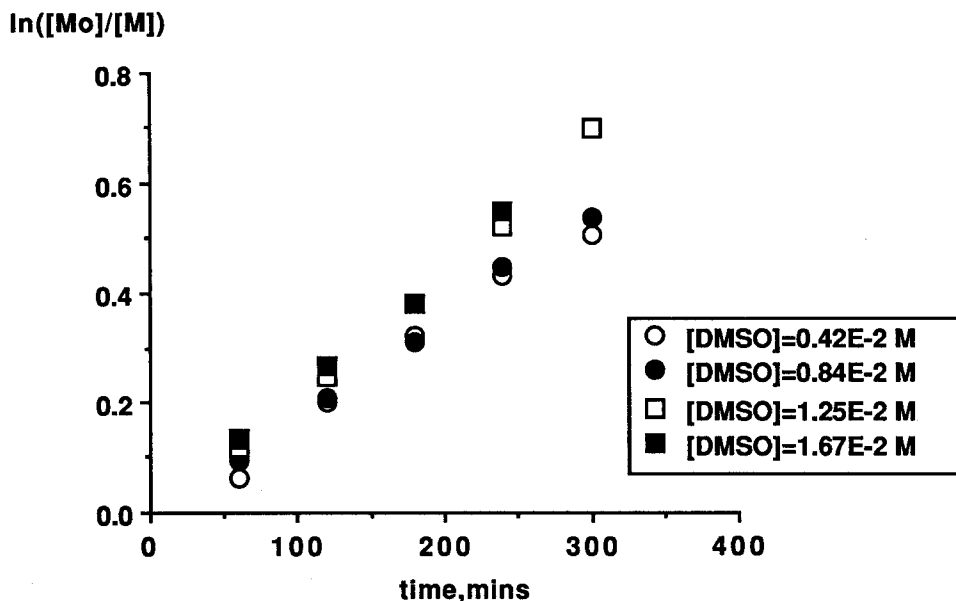


Figure 7.: First order plots of IB polymerization initiated by the TMPCl/DMSO and DTBP/ BCl_3 / CH_3Cl /-40 °C system. $[\text{IB}]_0=0.96$ M, $[\text{TMPCl}]=1.16 \times 10^{-2}$ M, $[\text{BCl}_3]=0.48$ M, $[\text{DTBP}]=4.2 \times 10^{-3}$ M $[\text{DMSO}]=4.2 \times 10^{-3}$, 8.4×10^{-3} , 1.25×10^{-2} and 1.67×10^{-2} M respectively.

We have demonstrated that the sole function of DTBP is to trap protic impurities in the system. If DMSO stabilizes the growing carbocations we should have observed decreased rates in its presence. In fact, increasing the DMSO concentration to 1.67×10^{-2} M (well above the concentration used in Ref. 4. to obtain living polymerization) gave only a slight rate increase, possibly due to increased polarity (Fig. 7.), verifying that carbocation stabilization is absent.

Conclusion

We have demonstrated that living polymerization of IB can be achieved by the TMPCl or CumCl/BCl₃ initiating system in the presence of proton trap in concentrations comparable to that of protic impurities in the system. We have confirmed that the living nature of the polymerization using electron donors in place of the proton trap is not due to carbocation stabilization. We propose that the polymerization is living due to the absence of chain transfer and reversible termination; in the absence of proton trap or EDs however fast polymerization by protic impurities occurs masking the much slower living polymerization and the monomer is essentially consumed by the former process unless the protic impurities are scavenged.

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