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# Polymerisation of Isobutene by the Inifer Technique

## 3. The Effect of 2,6-di-t-Butyl Pyridine on the Polymerisation Using TCC + $BCl_3$*

**Stephen D. Pask and Oskar Nuyken**

Lehrstuhl für Makromolekulare Stoffe, TU München,
Lichtenbergstraße 4, D-8046 Garching, Federal Republic of Germany

## Introduction

Our attempts to produce low molecular weight polyisobutenes (PIB) using 1,3,5-(2-chloro-2-methyl ethyl)benzene (tricumyl chloride = TCC) and $BCl_3$ as an inifer system (KENNEDY and MARECHAL 1982) were not successful despite using the technique which we have shown to work with the dicumyl chloride + $BCl_3$ system (NUYKEN et al (b)). In order to see whether, using 2,6-di-t-butyl pyridine (DTBP) we could eliminate the production of broad molecular weight distributions and poor inclusion of aromatic nuclei in the polymer we made a series of experiments to test for the effect DTBP and monomer concentration and temperature on the reaction product. The results of these experiments are discussed in this paper.

## Experiments

The purification of 2-methyl propene (IB) and $CH_2Cl_2$ have been described (NUYKEN et al (b)). Both were freshly distilled for each experiment. TCC was synthesised by the method described by KENNEDY et al 1981, recrystallised *in vacuo* from $CH_2Cl_2$ and distributed into phials (PASK and PLESCH, 1981) as a solution in $CH_2Cl_2$. DTBP (EGA, 97 %) was distilled *in vacuo* from KOH into phials. Solutions of both $BCl_3$ and DTBP in $CH_2Cl_2$ were stored in phials ready for use. The reactor was a simple 26 mm Ø tube with a side arm which served as a phial magazine. The reactor was charged with the required phials and a Teflon "breaker", attached to the vacuum line and evacuated for at least 12 h before use. After distilling 20 ml $CH_2Cl_2$ and the required amount of IB into the reactor it was sealed off from the line and immersed in a constant temperature bath for 30min. The reaction was then started by breaking the phials; the $BCl_3$ phial was always the last. The Teflon "breaker" was used as a stirrer after the start of the reaction. Reaction time was invariably 10 min. Reactions were terminated by breaking the tube open under cold MeOH. The polymers were isolated by 2 x precipitating from MeOH.

*(Part 2, NUYKEN et al (a))

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| Exp. | -T<br>/°C | $[IB]_o$<br>mol $l^{-1}$ | $[TCC]_o$<br>x100 | $[BCl_3]_o$<br>x 10 | $[DTBP]_o$<br>x 100 | Yield<br>/% | $\bar{M}_w$<br>GPC<br>x$10^3$ | $\bar{M}_n$<br>VPO | $\bar{M}_n$<br>NMR | $f_{Cl}$ b) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 85 | 0.9 | 1.5 | 1.5 | 1.8 | 35 | 2.2 | 0.9 | 1.5 | 2.6 |
| 2 | 85 | 1.8 | 2.0 | 2.1 | 2.2 | 35 | 2.3 | 1.4 | 1.8 | 1.7 |
| 3 | 85 | 2.7 | 2.6 | 3.2 | 3.0 | 31 | 1.9 | 1.2 | 2.4 | 2.5 |
| 4 | 85 | 1.8 | 2.0 | 2.1 | --- | 60 | 10.9<br>5.1 | 1.5 | -- | -- |
| 5 | 85 | 1.8 | 2.0 | 2.1 | 4.1 | 27 | 1.6 | 1.2 | 1.5 | 1.2 |
| $6^{a)}$ | 85 | 0.7 | 0.7 | 0.7 | 2.3 | 35 | 3.0 | 1.7 | 2.2 | 3.0 |
| 7 | 75 | 0.9 | 1.5 | 1.5 | 1.6 | 45 | 2.5 | 1.5 | 1.8 | 1.5 |
| 8 | 75 | 2.3 | 2.1 | 2.5 | 2.4 | 29 | 1.0 | 1.0 | 1.4 | 2.6 |
| 9 | 75 | 1.8 | 2.0 | 2.4 | --- | 85 | 7.2<br>2.9 | 2.6 | 4.6 | -- |
| 10 | 75 | 1.8 | 2.2 | 2.3 | 4.8 | 38 | 1.2 | 0.9 | 1.5 | 2.0 |
| 11 | 60 | 0.9 | 1.6 | 1.6 | 2.0 | 70 | 3.0 | 1.8 | 2.1 | 2.9 |
| 12 | 60 | 1.8 | 1.6 | 2.5 | 1.8 | 50 | 2.1 | 2.0 | 2.1 | 2.4 |
| 13 | 60 | 2.7 | 2.2 | 2.6 | 2.7 | 24 | 2.0 | 1.3 | 1.1 | -- |
| 14 | 60 | 1.8 | 1.9 | 2.2 | --- | 50 | 6.4<br>2.4 | 2.4 | 3.2 | -- |
| 15 | 50 | 0.9 | 1.4 | 1.4 | 1.5 | 40 | 2.2 | 1.6 | 1.5 | -- |
| 16 | 50 | 1.8 | 1.8 | 2.2 | 2.0 | 44 | 2.6 | 1.9 | 2.3 | 2.2 |
| 17 | 50 | 2.7 | 2.1 | 2.2 | 2.4 | 25 | 1.5 | 1.5 | 1.3 | 1.5 |

a) The reaction was carried out under preparative conditions. i.e. Total volume = 200ml

b) $f_{Cl}$ = No. of Cl ends found / No. calculated using the $\bar{M}_n$ from NMR

## Results

The experimental results are given in the table. The details of the various analytical techniques used for polymer analysis have been described (NUYKEN et al (b)). To emphasise the effect of DTBP on the product the GPC traces of the polymers from reactions numbered 2 and 4 in the Table are shown in Fig. 1. It should be noted that the MeOH solutions from which the polymers had been precipitated always contained a small amount (5 % of total) of polymeric material and unreacted TCC in addition to DTBP (and its salts) and $BCl_3$ (and its hydrolysates).

The object of this work was essentially to find the optimum conditions for the preparation of tristar PIB with $C(CH_3)_2Cl$ end groups and narrow molecular weight distributions. From the data in the table (especially the good agreement between the GPC, VPO and NMR determined molecular weights) it can be seen that all the polymers from reactions where DTBP was used were of very narrow distributions. In addition, for those reactions where DTBP was included the following observations can be made:

1) The temperature has little or no effect on the molecular weights or the yields.

2) The ratio $[IB]_o/[TCC]_o$ is the controlling factor for the molecular weight.

3) The yields were invaribly low and generally less than 50 %.

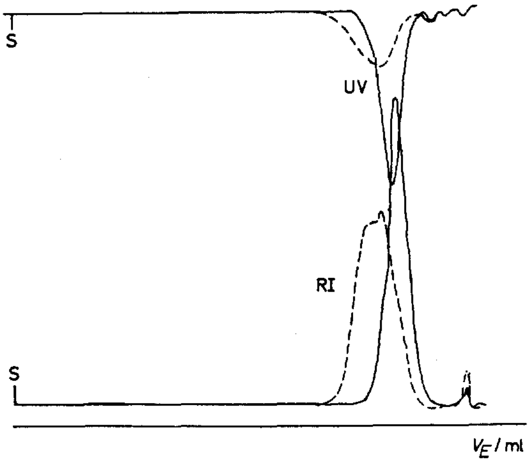

Fig. 1. GPC traces of the PIB from exp 2 (—) and 4 (---) (see table for exp. conditions)

Since the tri-star PIB are to be used as prepolymers for which a terminal double bond is an essential feature the nature of the end-groups is very important. From the IR and NMR spectra of the polymers it was established that where the $f_{Cl}$ was less than the theoretical value of three the other end-groups were essentially terminal double bonds ($C(CH_3)=CH_2$). Thus, although the low $f_{Cl}$ values of some of the products is unimportant from the point of view of the material it is interesting for a detailed understanding of the inifer mechanism. Although these preliminary experiments do not warrant a detailed discussion it is worth noting that the results suggest the following trends:

1) Where the ratio $[DTBP]_o/[TCC]_o$ was 2 $f_{Cl}$ is lower than when the ratio was 1.

2) The value of $f_{Cl}$ seems to be a function of $\overline{DP}_n$ (see Fig. 2). Thus, the lower the $\overline{DP}_n$ the greater the % of terminal double bonds.

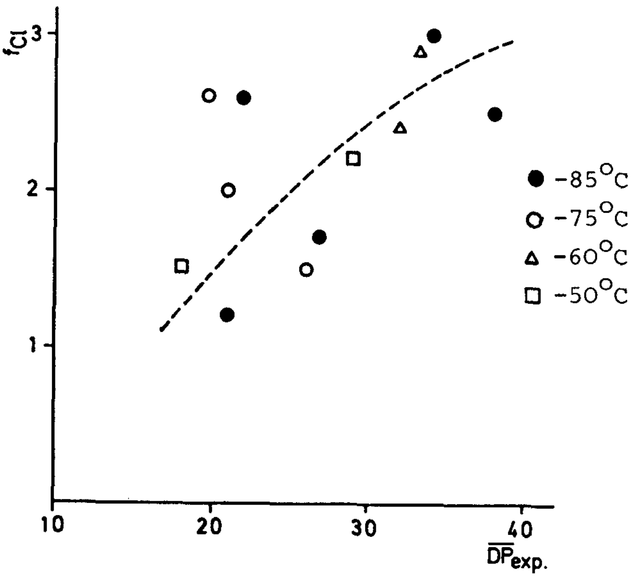

Fig. 2. Plot of $f_{Cl}$ vs. $\overline{DP}_n$(NMR)

The most important action of DTBP in this system is to hinder chain initiation by protons (either from a transfer reaction or impurities in the system) but it is obvious that DTBP also affects the chain termination reactions (and possibly also the rate of propagation). One possibility is that DTBP acts simply as a base and abstracts HCl from the ($C(CH_3)_2Cl$) capped chains. However, the reactions which included DTBP were observed to be pale yellow rather than the deep red colour of the reactions with no DTBP. This could indicate that the DTBP acts as a $\pi$ donor and complexes the growing ends. This would lead to slower polymerisations (as were visually observed), greater separation of the growing chain end and the gegenion and thus, possibly, a favouring of proton transfer from the growing end over collapse of the ion pair. That this effect seems to be molecular weight dependent could be explained in terms of competition between the monomer and the DTBP as complexing agents for the growing ends.

The details of the action of DTBP on the reaction of TCC + $BCl_3$ with IB are the subject of continuing research.

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