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Polymerisation of Isobutene by the Inifer Technique

2. Products Using Cumyl Chloride + BCl_3*

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Introduction

In our systematic studies aimed at elucidating the details of the inifer mechanism we have made a series of experiments using 2-chloro-2-methyl-ethylbenzene (Cumyl chloride = CC). The aim was to produce a polyisobutene (PIB) with a narrow molecular weight distribution (MWD), an aromatic ring at one end and a $C(CH_3)_2Cl$ group at the other.

Materials

The purification of 2-methylpropene (Isobutene = IB) (Linde), BCl_3 (Messer Griesheim 99.9%) and CH_2Cl_2 have been described (NUYKEN et al) CC was synthesised by the method described by OKAMOTO and BROWN (1957) 2,6 di-t-butyl pyridine (DTBP) was distilled in vacuo from KOH into phials.

Polymerisations

The polymerisations were carried out under vacuum in a flask with two side arms. One, a simple 26 mm Ø tube was charged with the BCl_3 phial and a breaker. The other was a break seal. This was used for the addition of pre-cooled methanol at the end of the reaction. The apparatus was evacuated for at least 12 h before starting the reaction by breaking the phials in the main flask, distilling in the CH_2Cl_2 and IB and finally, after temperature equilibration, breaking the phial of BCl_3.

Results

Experiments in which no DTBP was used produced three types of products. The GPC of a typical mixture is shown in Fig. 1. The major product is a PIB with a M considerably higher than expected on the basis of $[IB]_o/[CC]_o$. The low M products consisted of PIB which contained essentially one aromatic nucleus per molecule and a M close to the expected value. In addition a sharp peak at a M(PSty) of 200 - 300 was invariably present which had a relatively large absorption coefficient. In this set of experiments the ratio $[BCl_3]_o/[CC]_o$ was varied from 0.3 to 20 and the ratio $[IB]_o/[CC]_o$ was varied from 2 to 45 with no measurable reduction in the % of high M material.

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* part 1 (NUYKEN et al)

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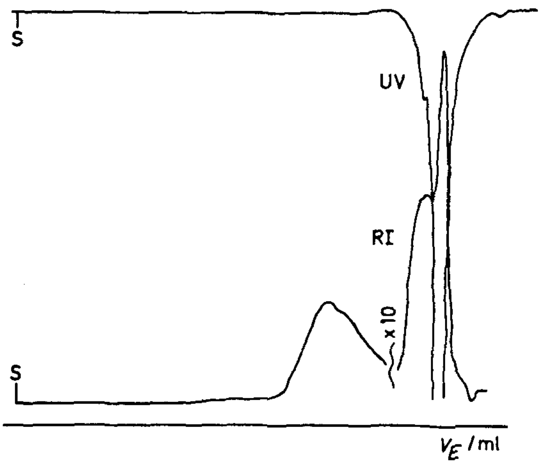


Fig. 1. GPC of PIB produced with CC + BCl_3 in CH_2Cl_2 without DTBP

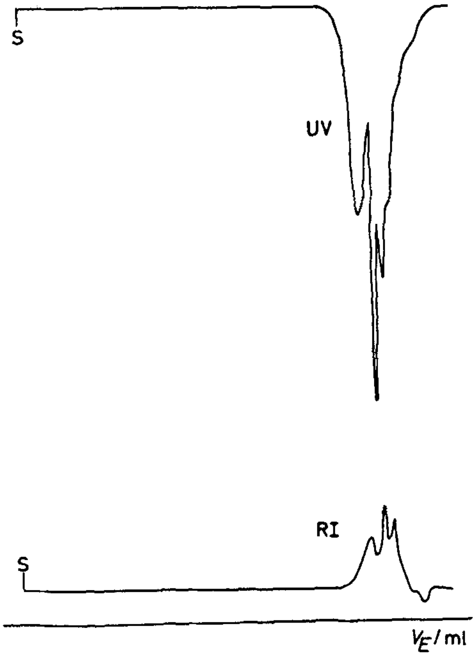


Fig. 2. GPC trace of products from BCl_3 + CC in CH_2Cl_2

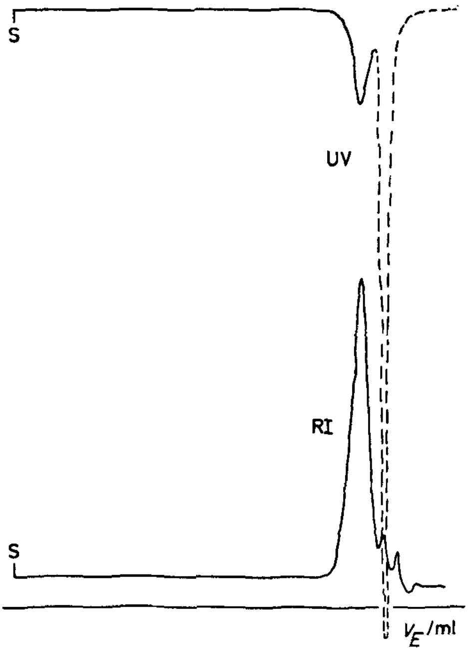
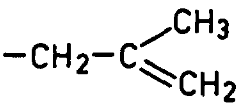


Fig. 3. GPC trace of PIB from an experiment with DTBP

An experiment in which no monomer was used, aimed at producing larger quantities of the lowest molecular weight material, gave a material for which the GPC trace is shown in Fig.2. Within the normal reaction time of 10 min CC reacts with BCl_3 to produce dimeric and oligomeric products. A normalised plot of UV/RI against M clearly demonstrated that the different oligomers contain different chromophores.

A third set of experiments using DTBP produced materials which included no high polymer (see Fig.3). In addition, the PIB showed a sharper MWD close to the theoretical value of 2. The lowest molecular weight material was not separated from the PIB by the usual precipitation procedure but was removed by filtering the product through a 10 cm Al_2O_3 column using n-pentane as the solvent. By varying the $[DTBP]_o/[CC]_o$ ratio from 0 to 2 it was evident that at least a ratio of 1 was necessary to synthesise products with a MWD suitable for further use.

Analysis of the polymers produced, where $[DTBP]_o/[CC]_o$ = 2, by NMR showed that the end groups of the polymers comprised c.50% structure I and c. 50% structure II. As the ratio $[DTBP]_o/[CC]_o$ decreased the MWD became broader and the detectable % of structure I end groups decreased.



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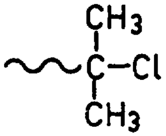
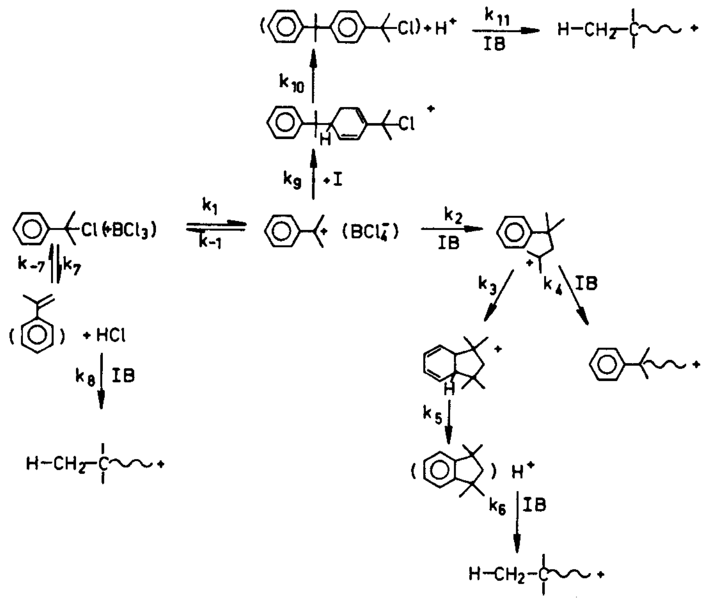


II

With these experiments we have shown that it is possible to produce low M monofunctional PIB using CC and BCl_3 as the initiating system providing that DTBP is included in the reaction mixture and that the ratio $[DTBP]_o/[CC]_o > 1$.

However, the presence of DTBP in the reaction mixture tends to lead to a reduction in the number of the desired, $C(CH_3)_2Cl$ end groups. Although this is of little importance for the further use to which these polymers are put it raises the interesting question as to the detailed effect of DTBP on the course of the reaction.

We envisage the following reaction scheme:



(It should be noted that reactions with rate constants k_6, k_8 and k_{11} are essentially identical and that the formation of an indane can either take place with one unit of IB (as shown: k_2, k_3, k_5) or with one unit of α-methyl styrene (from reaction 7). (NGUYEN and KENNEDY, 1981))

KENNEDY and CHOU (1979) have suggested that the sole action of DTBP in the polymerisation of α-Me-styrene is to hinder the transfer of a proton from the growing end to monomer. However, MOULIS et al. (1980) have shown that an important action of DTBP is the exclusion of initiation by protonic acids. The results of the experiments described here suggest that DTBP certainly acts as a blocking agent for steps 6, 8 and 11 in the scheme. These steps are the probable reactions which produce the high M PIB when DTBP is not included in the reaction mixture. This is, however, not the only action of DTBP. It appears that the proportion of the material with a M of c.200-300 is reduced in the presence of DTBP. This is perhaps explained in terms of a stabilization of the growing cation by DTBP which favours monomer addition rather than intramolecular cyclisation (Reaction 3 in the scheme). A further action of DTBP is to increase the % of double bond end groups in the product. This could be effected either by proton abstraction from the growing end or by the simple HCl abstraction from the already terminated polymers, a typical and well established reaction between pyridines and alkyl halides.

Although we have shown how the desired low molecular weight, monofunctional PIB can be produced this study has raised a number of interesting questions with respect to the detailed mechanism. These questions are the subject of our further research.

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