The Use of 2,6-Di-tert-Butyl-4-Methylpyridine to Distinguish Between Different Modes of Initiation in Cationic Polymerisation

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SUMMARY. 2,6-Di-tert-butyl-4-methylpyridine (DBMP) effectively
discriminates between the two major initiation mechanisms encoun-
tered in cationic polymerisation. Whenever a protonic acid is
involved in the formation of chain carriers, directly or through
cocatalysis, addition of equivalent amounts of DBMP inhibits the
process. If however direct electrophilic addition of a Lewis
acid to the monomer is the source of active species, the hindered
base cannot intervene to alter its course. When both pathways
are operative DBMP only quenches the former and provides a means
of assessing the relative importance of each. Examples are
given of the three situations. The simplicity of the method is
emphasised.

INTRODUCTION

The initiation mechanism in the cationic polymerisation of alkenyl
and heterocyclic monomers promoted by Lewis acids is still a
source of controversy for many systems. Two major routes are pos-
sible, viz. direct initiation or intervention of a cocatalyst
(water, alcohols, hydrogen halides, carboxylic acids...) which
acts as a proton source (1,2). In several instances the occur-
rence of either or both mechanisms has been clearly demonstrated
(1), but considerable experimental difficulties make such under-
takings long and tedious. Moreover, any conclusion reached on a
given system cannot be extrapolated to another, however similar,
since the behaviour of a cationic polymerisation can vary drast-
ically with even minor changes in its chemical or physical para-
meters. Therefore the study of the initiation mechanism(s) must
be carried out for every specific situation. Recently we were
faced with a problem of this nature in the context of the discov-
ery of a new class of initiators of cationic polymerisation, i.e.
some metal salts of strong acids (3,4). Work in progress in our
laboratory on the synthesis of telechelic isobutene oligomers
through cationic initiation (5) also required a better understand-
ing of the mechanism(s) leading to the formation of chain carriers.

In 1953 Brown and Kanner (6) first reported "a simple method of
distinguishing between protonic and Lewis acids" which involved
the use of 2,6-di-tert-butylpyridine (DBP), a sterically hindered
base incapable of reacting with electrophiles other than protonic

acids. These authors showed (6,7) that the bulky substituents at the 2,6-positions impeded the addition of such compounds as CH_3I, SO_3, Br_2 and BF_3 onto the nucleophilic nitrogen atom of DBP, but not that of HCl and chloroauric acid, although the equilibrium formation of $HDBP^+$ in 50% ethanol-water indicated an abnormally low pK_a for that base due to steric crowding. More recent studies on 2,6-di-_tert_-butyl-4-methylpyridine (DBMP) confirmed this discriminating property (8,9). Indeed this base does not react with the highly electrophilic agent $CF_3COSO_3CF_3$, but can be used as a proton sponge in its acylating reactions since it readily neutralises the triflic acid formed (9).

On the basis of the above considerations we decided to use DBMP in various cationic polymerisations to test the nature of their initiating mechanisms, and report here a preliminary account of its usefulness and potential.

EXPERIMENTAL

Monomers and solvents were purified and dried following standard procedures. Catalysts were used as received, except for the metal salts which were prepared and vacuum baked as already described (3). DBMP (Fluka) was purified by vacuum sublimation and stored thereafter under nitrogen in the dark. Its purity was checked by thin-layer chromatography (single spot after sublimation). Reactions were carried out in vacuo or under nitrogen in stirred vessels provided with a temperature sensor.

RESULTS AND DISCUSSION

Three types of responses were observed when DBMP was added to typical cationic systems, depending on their nature.

1. Inhibition by DBMP. The first system studied was styrene/triflic acid/CH_2Cl_2 at room temperature. With $[DBMP]/[CF_3SO_3H] \geqslant 1$ no polymerisation occurred either when the acid solution was added to the styrene-DBMP mixture or when the monomer was added to the acid-DBMP mixture. When the DBMP solution was added after mixing monomer and catalyst, a limited yield was obtained which was the higher the longer the time elapsed before the introduction of the base. With $[DBMP]/[CF_3SO_3H] < 1$ polymerisations were the slower the higher the concentration of the base. These experiments were conducted with acid concentrations of about 10^{-4}M and in the absence of DBMP 100% yields of polystyrene were obtained within several minutes. These results clearly show that DBMP rapidly neutralises an equivalent amount of triflic acid in methylene chloride. The resulting salt $HDBMP^+$ $CF_3SO_3^-$ was also prepared by mixing equimolar quantities of triflic acid and DBMP and characterised by NMR spectroscopy (CH_2Cl_2): DBMP δ 1.33 (s,18H), 2.32 (s,3H) and 6.83 (s,2H); $HDBMP^+$ δ 1.57 (s,18H), 2.67 (s,3H) and 7.63 (s,2H); note that the corresponding values given by Anderson and Stang in CCl_4 (8) were probably inverted by mistake. The inhibiting effect of DBMP added after mixing monomer and acid is best interpreted as arising from the rapid neutralisation of

the triflic acid continuously regenerated by proton expulsion from the active species, i.e. the first step of a spontaneous transfer process.

A second instance of inhibition by DBMP was encountered with the system isobutene/BF_3-H_2O/EtCl at about -40°C. In these experiments no extra care was taken to insure maximum dryness, and the residual moisture acted as a cocatalytic agent. In the absence of DBMP polymerisations were fast and complete ($[M] = 1.0M$, $[BF_3] = 0.01 - 0.1 M$). Addition of DBMP up to concentrations of $(2 - 3) \times 10^{-3}$ M still gave 100% yields, but progressively more slowly and with considerable reduction in the DP's of the polymers. With $[DBMP] > 3 \times 10^{-3}$ M no polymerisation occurred even at the highest BF_3 concentrations. These "dormant" solutions could however be reactivated by the addition of small amounts of water or methanol which produced fast and complete polymerisation. Strong evidence was thus obtained in favour of an initiation mechanism in which BF_3 can only operate in the presence of a protogenic substance, i.e. classical cocatalysis. Whatever the details of this mechanism (1), a Brønsted-type acid must form at some stage (e.g. HBF_3OH) and be neutralised by an excess of the added base. With DBMP concentrations lower than that of the residual moisture, polymerisations can still take place, though more slowly, since some of the cocatalyst remains available. The critical concentration of DBMP above which the system was inhibited must therefore reflect the level of water concentration present in our solutions. From the inactivity of very high concentrations of BF_3 with $[DBMP] > [DBMP]_c$ it can be concluded that this Lewis acid cannot induce the direct initiation of isobutene polymerisation under the conditions tested.

The study of the above two systems shows that if the only initiating species is a protonic acid, added as such or formed through cocatalysis, the introduction of sufficient amounts of DBMP will inhibit the polymerisation by neutralising the initiator.

2. Discrimination by DBMP. With the system ⍺-methylstyrene/$TiCl_4$-H_2O/CH_2Cl_2 the phenomenology following the addition of DBMP was different. In these experiments particular care was taken to minimise the residual moisture level which was probably well below 10^{-3} M. The following table gives some of the results obtained for reactions stopped after 7 minutes. The main conclusion therefrom is that two different initiation mechanisms occur simultaneously in this system, one involving water cocatalysis, predominant at the higher temperatures and quenched by the added base, and the other involving direct initiation, more important at the lower temperatures and not affected by DBMP. GPC analysis of the products obtained at -30°C showed that the presence of DBMP induced the suppression of the low-DP tail of the initially broad spectrum, but did not alter the position of its maximum. This is further evidence of the existence of two types of mechanisms (and chain carriers), one of which, viz. that giving the lower molecular weights through cocatalysis, is quenched by DBMP. At the lower temperatures such an analysis was not possible due to the

lack of information on the different activation energies for the chain-breaking processes of both mechanisms.

TABLE

No	$\dfrac{[\text{MeSt}]}{M}$	$\dfrac{[\text{TiCl}_4]}{10^{-3}M}$	$T/°C$	$\dfrac{[\text{DBMP}]}{10^{-3}M}$	$\dfrac{\text{Yield}}{\%}$	$\overline{M}_v$
B2	0.30	2.99	-68	0	84	310000
B'2	0.30	2.99	-70	1.0	61	238000
B3	0.30	2.70	-43	0	80	31000
B'3	0.31	2.72	-45	1.0	17	32500
B4	0.31	3.00	-30	0	55	12000
B'4	0.31	3.00	-30	1.0	16	19000

Experiments with DBMP concentrations higher than that used for the runs shown in the table did not alter the features of those polymerisations thereby demonstrating that the concentration of residual water in these systems was lower than 10^{-3}M. Another series of polymerisations was carried out at -45°C, $[\text{TiCl}_4]$ = 9.1 x 10^{-3}M, $[\text{MeSt}]$ = 0.82 M and DBMP concentrations up to 0.01 M. They all yielded 100% conversion indicating that in these conditions direct initiation gave a sufficient concentration of chain carriers to assure a rapid and complete polymerisation. The reaction of DBMP with $TiCl_4$ in "wet" CH_2Cl_2 was investigated by NMR spectroscopy. The percentage of base converted into $HDBMP^+$ was found to decrease as drying improved, and no evidence was detected of any interaction between the Lewis acid and DBMP. The overall reaction leading to the protonated base is probably

$$TiCl_4 + H_2O + DBMP \longrightarrow HDBMP^+ \; TiCl_4OH^-,$$
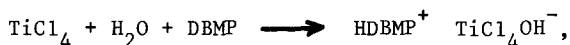
although the exact nature of the anion remains to be proved and is under investigation.

The occurrence of both direct initiation and cocatalysis in the polymerisation of α-methylstyrene by $TiCl_4$ in methylene chloride is not surprising, since it had been previously postulated (10, 11) on the basis however of less straightforward evidence than that obtained here.

Kennedy and Chou (12) recently studied the effect of DBP on the cationic polymerisation of α-methylstyrene by BCl_3-H_2O in methylene chloride at different temperatures and concluded that its role consisted in scavenging transient protons arising from

monomer transfer reactions. They made no mention of the possible
intervention of this base in the initiation processes. With high
concentrations of DBP their results followed the same trend as
those reported in the table, i.e. a yield reduction increasing
with decreasing temperature. The effect of DBP concentration,
studied at -60°C, clearly showed the existence of a critical
value, $[DBP]_c \sim 10^{-3}M$, below which 100% conversion was always rea-
ched and above which polymerisations gave a constant limited
yield independent of the excess of DBP added. Both $\overline{M}_n$ and $\overline{M}_w$
increased with $[DBP]$ for $[DBP] < [DBP]_c$, but remained practically
constant for $[DBP] > [DBP]_c$. Finally, the ratio $\overline{M}_w/\overline{M}_n$ decreased
from 3.4 for a polymer prepared without DBP to about 1.5 for one
obtained with $[DBP]_c$; with DBP concentrations above the critical
value that ratio remained around 1.5. The striking similarity
between Kennedy and Chou's results and those involving $TiCl_4$
suggests that the former system must also be characterised by
the occurrence of two modes of initiation, one sensitive to DBP,
i.e. water cocatalysis, and the other insensitive to it, i.e.
direct initiation by BCl_3. Polymer formed by cocatalysis posse-
sed lower DP's than that generated by direct initiation and the
progressive suppression of the former by the addition of increas-
ing quantities of DBP up to $[DBP]_c$ produced the observed increase
in $\overline{M}_w$ and $\overline{M}_n$ and the corresponding decrease in their ratio.
$[DBP]_c$ corresponds, as discussed above, to the residual water
concentration in Kennedy and Chou's system. Addition of base
above that critical concentration did not bring about any further
changes in polymer yield or molecular weight because the only
process generating active species at that point was one insensit-
ive to the presence of DBP, viz. direct initiation.

The systems analysed in this section showed that whenever cocat-
alysis and direct initiation operate simultaneously, the addition
of a hindered pyridine in sufficient concentration readily gives
an answer as to the relative contribution of each mechanism and
their respective DP's.

3. Inefectiveness of DBMP. As we recently reported(3,4) certain
metal salts of strong acids are powerful initiators of cationic
polymerisation both in heterogeneous and homogeneous conditions.
Addition of DBMP to these systems in concentrations as high as
those of the initiators did not cause any appreciable change in
the phenomenology of the ensuing polymerisation. This was ver-
ified in particular for the homogeneous and heterogeneous action
of aluminium triflate on isobutene (3,4) and for the homogeneous
polymerisation of that monomer with $(CF_3SO_3)_2Al^+ SbF_6^-$ (4).
The lack of inhibition or retardation by excess DBMP proves that
these salts initiate via direct addition onto the monomer double
bond and rules out such alternative mechanisms for the generation
of active species as protonation by Brønsted-acid impurities in
the salts or cocatalysis by residual moisture.

The system isobutene/$EtAlC_2$/EtCl at -60°C was also found to be
insensitive to DBMP. In the absence of that base polymerisa-
tions were fast but reached a limiting yield, as already reported

in previous similar studies (13,14). Addition of DBMP up to 6×10^{-3} M did not produce any change in behaviour except for a small decrease in the limiting yield which was probably within experimental error. Thus direct initiation predominates in this polymerisation, the present brief study confirming previous speculations (13,14).

The examples given in this section clearly reflect the inability of DBMP to quench any initiation mechanism involving non-protonic addition prossesses. This peculiarity of hindered pyridines can therefore be readily exploited to detect the occurrence of direct initiation in systems where this mode of activation prevails.

CONCLUSIONS

The exceptional potential of Brown's original study of hindered pyridines nearly thirty years ago seems to have escaped the attention of researchers in the field of cationic polymerisation. The examples given in this paper clearly show that DBMP is an excellent discriminating substance for the unravelling of initiation mechanisms, due to its inhibiting power towards any reaction involving a protonic acid coupled with its incapacity to add Lewis acids, i.e. metal halides, electrophilic reagents, carbenium ions, etc. This reagent is available comercially and its use does not involve elaborate techniques. Further work is in progress to extend the present findings and to study the role of DBMP on transfer reactions.

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