Determination of Tert-Butoxy Endgroups in Polymers: The Mode of Reaction of Tert-Butoxy Radicals with Methyl Methacrylate and Styrene

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ABSTRACT

A simple technique has been devised for the determination of
tert-butoxy endgroups in poly(methyl methacrylate) and poly-
styrene. The method is based on cleavage of the tert-butyl
ether with boron trichloride and analysis of the resulting
tert-butyl chloride by gas-liquid chromatography. In poly-
styrene, tert-butoxy endgroups were also determined by
dealkylation with trifluoroacetic acid, followed by reaction
of the resulting hydroxy endgroups with o-sulfobenzoic anhydride
and analysis for sulfonate by the dye-partition technique with
methylene blue reagent. From these analyses it was possible
to conclude that tert-butoxy radicals, derived from the decom-
position of di-tert-butyl peroxalate (DBPOX), initiated styrene
polymerization largely by direct addition, whereas in their
reaction with methyl methacrylate (MMA) both direct addition
and hydrogen abstraction from the monomer were important
processes. The extent of hydrogen abstraction was determined
from the yield of tert-butanol in the reaction of DBPOX with
MMA.

INTRODUCTION

Tert-butoxy radicals, available from a wide variety of sources
[1], have found extensive use as initiators of vinyl polymerization,
and it is somewhat surprising that relatively little effort has been
made to estimate this function as an endgroup or to delineate its
mode of polymer initiation. Notable exceptions are to be found in
the work of Allen and Bevington [2], who have used ^{14}C-labeled
di-tert-butyl peroxide to determine the extent of β-scission and
direct addition in the reaction of the tert-butoxy radical with styrene,
and the ESR investigation of Sato and Otsu [3], who have made use of
spin-trapping reagents to evaluate monomer reactivities and to show
that hydrogen abstraction from certain α-methylvinyl monomers is
an important reaction path for the tert-butoxy radical. Here, how-
ever, it should be emphasized that the ESR spectra of spin-trapped
propagating radicals generally gives little or no information about
the structure of the initiating radical. On the other hand, the
technique that makes use of radioactive initiators is particularly
tedious, requires syntheses of labelled materials and in some
cases allowances must be made for isotope effects [2].

In connection with our work on the polymerization of methyl
methacrylate (MMA) with the tert-butyl hydroperoxide-sulfuric acid
system [4, 5], we were interested in ascertaining whether or not
tert-butoxy radicals were involved in the initiation process. Before
this question could be answered it was necessary to gain an under-
standing of the mechanism by which a tert-butoxy radical, derived
from more conventional sources, initiates MMA polymerization and
to develop a method for the detection and quantitative determination
of the tert-butoxy endgroup. For this we chose to investigate poly-
(methyl methacrylate) (PMMA) and polystyrene obtained by initiation
of the corresponding monomers with di-tert-butyl peroxalate (DBPOX);
a substance known to decompose cleanly into tert-butoxy radicals
and carbon dioxide [6].

EXPERIMENTAL

Materials

Methyl methacrylate, styrene, and cumene were purified by passage
through alumina, followed by careful fractionation at reduced pressure.
Di-tert-butyl peroxalate was prepared from oxalyl chloride and tert-
butyl hydroperoxide [6]. Tert-butyl hydroperoxide was purified via
its sodium salt [7] and then fractionated at 20 mm pressure. Chloro-
benzene was distilled through a 40-cm packed column and before use

the fractions were checked for the absence of impurities that might interfere with the gas-liquid chromatographic determination of tert-butyl chloride. Pyridine was refluxed over barium oxide, fractionated and stored over potassium hydroxide pellets. Commercial o-sulfobenzoic anhydride (Fluka) was recrystallized from benzene.

Preparation of Polymers and Molecular Weight Determinations

Poly(methyl methacrylate) and polystyrene were prepared as follows. The cold (4°C) monomers were added to DBPOX, the solutions were deoxygenated by repeated freezing and thawing on a vacuum line, sealed under purified nitrogen, and allowed to react to less than 5% conversion in a thermostatted bath at either 30°C or 60°C. The polymers were precipitated by slow addition of the solutions to a large excess of stirred methanol, collected by filtration and washed thoroughly with methanol. They were then purified by reprecipitation using benzene as the solvent and methanol as the precipitant and dried at 50°C in a vacuum oven.

Viscosity measurements were made on benzene solutions of the polymers at 30 ± 0.1°C by using a Ubbelohde viscometer. Molecular weights were calculated from the intrinsic viscosities $[\eta]$ by using the relations:

$$\overline{M}_n = 2.22 \times 10^5 \, [\eta]^{1.32}$$

for PMMA [8, 9] and

$$\overline{M}_n = 1.84 \times 10^5 \, [\eta]^{1.40}$$

for polystyrene [10].

Cleavage of Tert-Butoxy Endgroup and Dye-partition Analysis

Polystyrene (0.5 g) (from DBPOX initiation at 30°C) in benzene (10 ml) was treated with trifluoroacetic acid (1 ml) and kept at room temperature overnight under nitrogen. The polymer was precipitated with methanol, collected by filtration, washed with methanol and partially dried by suction. In order to hydrolyze any trifluoroacetate derivative of the hydroxy-containing polymer, it was redissolved in dioxane (10 ml), treated with triethylamine (1 ml) and water (0.5 ml),

stirred at room temperature for 6 hr, recovered as above, and then dried in a vacuum oven at 50°C.

This polymer (0.2 g) was dissolved in dry pyridine (5 ml), o-sulfobenzoic anhydride [11] (0.3 g) was added, and the mixture was stirred at room temperature under nitrogen overnight. The mixture was filtered through a sintered funnel into stirred methanol (150 ml), the polymer collected, washed thoroughly with methanol, and purified further by reprecipitation with benzene as the solvent and methanol as the precipitant, and finally dried in a vacuum oven at 50°C.

A 0.031% chloroform solution of this polymer of number-average molecular weight 80,700 attained an optical density at 655 nm equivalent to that of 7.28×10^{-6} N sodium lauryl sulfate when subjected to the dye-partition test with methylene blue reagent [11, 12]. From this it can be calculated that the polymer contained 1.9 sulfonate endgroups per chain, and this would correspond to the number of tert-butoxy endgroups in the original polymer sample.

Cleavage of Tert-Butoxy Endgroups with BCl_3 and Analysis for Tert-Butyl Chloride

Polystyrene. A sample of polystyrene (0.435 g) prepared by DBPOX initiation at 30°C, of number-average molecular weight 67,000, was dissolved in purified chlorobenzene (10 ml) in a dry 25 ml round-bottomed flask protected from moisture by a $CaCl_2$ drying-tube. The solution was cooled to -78°C, BCl_3 (0.2 ml) was added to it dropwise through a rubber septum with the aid of a dry syringe, and the mixture was stirred at room temperature for 3 hr. The solution was cooled to 0°C, and the excess BCl_3 was decomposed by the careful addition of a few drops of water with vigorous stirring. The HCl that remained in solution was removed by addition of solid sodium bicarbonate and the flask was attached to a distillation apparatus consisting of a short fractionating column, a short air condenser and a graduated test tube-shaped receiver. The polymer solution was frozen in liquid nitrogen and the system evacuated at approximately 10 mm pressure and sealed off. A portion of the volatiles (5.10 ml) was then distilled (fractionation) by gentle heating of the reaction vessel with a warm-air blower while keeping the receiver immersed in liquid nitrogen. This distillate was found to contain 0.00106 g of tert-butyl chloride, corresponding to an average of 1.77 tert-butoxy endgroups per polystyrene chain. Further distillation failed to recover any more tert-butyl chloride.

The tert-butyl chloride was determined on a Perkin-Elmer 900 gas chromatograph by use of a SCOT column (length 50 m, ID 0.5 mm) coated with SE30 on Chromosorb R (deactivated by silylation) and operated at 55°C. Quantitative determinations were made with the

aid of an Autolab Minigrator by comparison of peak areas with those of standard solutions of tert-butyl chloride in chlorobenzene. The identity of the tert-butyl chloride from the BCl_3 dealkylation experiments was firmly established by comparison of the fragmentation pattern with that of an authentic sample, both recorded on a Finnigan 3300 gas chromatograph-mass spectrometer.

Poly(methyl Methacrylate). The procedure for the determination of tert-butoxy endgroups in PMMA was essentially the same as for polystyrene, except that a longer time (overnight at 5°C followed by 3 hr at room temperature) was allowed for the reaction with BCl_3. For example, PMMA (1.0 g) prepared by DBPOX initiation at 30°C, of number-average molecular weight 107,800, produced 0.00056 g of tert-butyl chloride, from which it can be estimated that the sample contained an average of 0.65 tert-butyoxy endgroups per polymer chain.

Hydrogen Abstraction by the Tert-Butoxy Radical from MMA and Cumene

DBPOX (0.0083 g) was dissolved in cold (0°C) freshly purified MMA (90 ml) in a 100 ml round-bottomed flask. The solution was degassed by repeated freezing and melting under vacuum. The flask was then filled with high purity nitrogen and placed in a thermostatted bath at 60°C for 2 hr. In this period of time the decomposition of the DBPOX should be essentially complete as its half life in solution at 60°C has been shown to be of the order of 7 min [6].

A portion of the volatiles (50.0 ml) was separated from the polymer by fractional distillation at reduced pressure in a closed system (see isolation of tert-butyl chloride above). This was found to contain 0.00210 g of tert-butyl alcohol (0.80 mole/mole DBPOX) by a gas chromatographic analysis; the same system and conditions were used as for the determination of tert-butyl chloride (see above), but with the use of standard solutions of tert-butyl alcohol in MMA for comparison. Acetone was not detected. A second portion of distillate (20 ml) was found to be free of tert-butyl alcohol.

As a check on the validity of the above procedure at these very low concentrations, DBPOX was decomposed in purified and deoxygenated cumene under the exact conditions used for the decomposition in MMA. In this case it was found that tert-butyl alcohol was formed at the rate of 1.81 mole/mole of perester, in close agreement with a previously reported value of 1.77 determined at much higher concentrations [6]. The amount of acetone formed was estimated to be less than 0.05 mole/mole of perester.
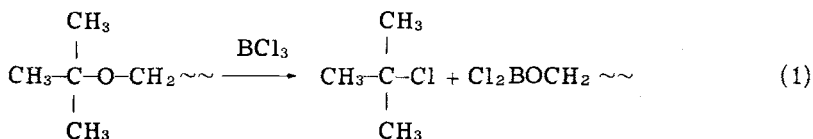
RESULTS AND DISCUSSION

The expected ease of dealkylation of tert-butyl ethers [13] and
our success with the determination of hydroxy endgroups [11]
suggested a method for the estimation of the tert-butoxy function.
This would involve cleavage of the ether linkage with a suitable
reagent to give the corresponding hydroxy-containing polymer, con-
version of the hydroxy group to a dye-sensitive function with o-
sulfobenzoic anhydride [11] and analysis for sulfonate endgroups
by the dye-partition method described previously [11, 12].

Polystyrene (obtained by DBPOX initiation at 30°C) was found
to be quite amenable to this technique. Thus cleavage of the ether
with trifluoroacetic acid at room temperature and subsequent
analysis as outlined above led us to conclude that the polymer con-
tained an average of approximately 1.9 tert-butoxy endgroups per
chain.

In contrast, a number of reagents and conditions (p-toluene-
sulfonic acid [13], trifluoroacetic acid [13], trimethylsilyl iodide
[14]) which had proved so useful to the organic chemist in selectively
dealkylating tert-butyl ethers, failed to liberate hydroxy endgroups
to any appreciable extent when applied to PMMA prepared by DBPOX
initiation. The possibility that the ether was indeed cleaved and that
the hydroxy groups were subsequently masked by transesterification
with PMMA was excluded by the fact that the molecular weight of
the polymer did not increase. Although intramolecular transesteri-
fication (lactone formation) remains a possibility we prefer to
attribute the failure to the difficulty in dealkylating a tert-butyl
ether endgroup in PMMA under mild conditions as a result of the
considerable steric hindrance and appreciable basicity inherent in
PMMA. Here, the ester groups would tend to reduce the effective-
ness of the acidic dealkylating agents by mutual coordination.
Forcing conditions for the dealkylation step were not applicable
as these caused excessive demethylation of the ester groups giving
a polymer with unsuitable solubility properties for dye-partition
analysis.

An alternative approach to the determination of tert-butoxy
endgroups could make use of a reagent capable of cleaving the ether
linkage and yielding the tert-butyl moiety as a stable, clearly defined
and easily analyzable substance, irrespective of its action on the
remainder of the polymer molecule. These conditions were fulfilled
by boron trichloride [15]. This reagent cleaves tert-butyl alkyl
ethers with exclusive formation of tert-butyl chloride and the alkyl
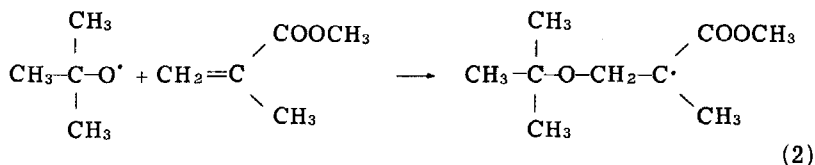dichloroboronite [reaction (1)].

The volatile tert-butyl chloride (b. p. 51°C) is separated easily
and quantitatively from the polymer by codistillation (in a closed
system) with the solvent of the reaction medium and it can then be

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3\text{--}C\text{--}O\text{--}CH_2 \sim\sim \\
| \\
CH_3
\end{array}
\quad \xrightarrow{\quad BCl_3 \quad} \quad
\begin{array}{c}
CH_3 \\
| \\
CH_3\text{--}C\text{--}Cl \\
| \\
CH_3
\end{array}
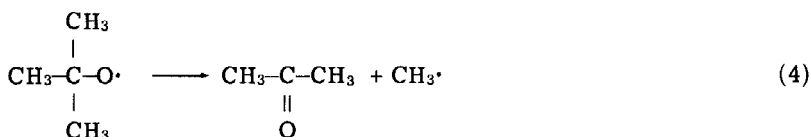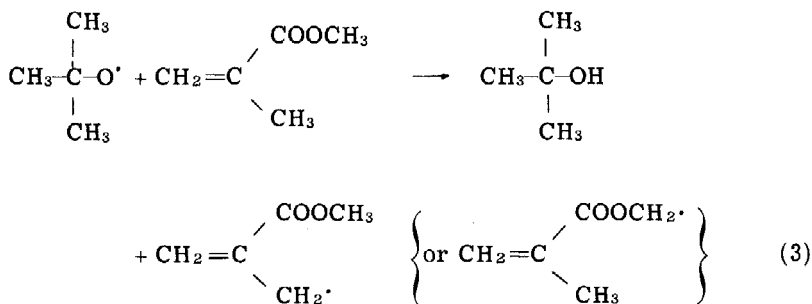+ Cl_2 BOCH_2 \sim\sim
\qquad (1)
$$

estimated accurately by taking advantage of the high sensitivity of gas-liquid chromatography. A suitable high boiling solvent (e. g. chlorobenzene) as the medium for the dealkylation reaction can be used to advantage in that it allows the concentration of tert-butyl chloride to be increased by fractionation during co-distillation. This then permits estimation of tert-butoxy endgroups even in polymers of very high molecular weight. For example, as much as 2-3 g of high molecular weight polymer (PMMA or polystyrene) can be dissolved in 20-25 ml of chlorobenzene, and subsequent to reaction with BCl_3 all the tert-butyl chloride can be secured in the first few millileters of distillate. Methyl chloride resulting from partial demethylation of the ester groups in PMMA does not interfere with the gas-liquid chromatographic analysis of tert-butyl chloride.

Application of this procedure to PMMA derived from bulk polymerization of MMA with DBPOX as the initiator at 30°C and at 60°C indicated that the polymers contained an average of 0.65 and 0.60 tert-butyl endgroups per chain respectively.

If we are to accept these values, then pathways other than direct addition of the tert-butoxy radicals to MMA must play a part in the initiation process since incorporation of initiating radicals in PMMA is expected to be in the order of at least 1.1 per polymer chain [16, 17]. Consideration of the known chemistry of the tert-butoxy radical [1] suggests that three main reaction pathways should be taken into account in any attempt to define the species involved in the initiation process of a particular vinyl monomer by this radical. These are (using MMA as the example): direct addition of the tert-butoxy radical to the monomer [reaction (2)], hydrogen abstraction from the monomer (or solvent if any) followed by initiation by the newly formed radicals [reaction (3)], and fragmentation of the tert-butoxy radical with subsequent initiation of polymerization by the methyl radical [reaction (4)].

$$
\begin{array}{c}
CH_3 \\
| \\
CH_3\text{--}C\text{--}O^{\bullet} \\
| \\
CH_3
\end{array}
+ CH_2\!\!=\!\!C
\begin{array}{l}
\diagup COOCH_3 \\
\diagdown CH_3
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
CH_3 \\
| \\
CH_3\text{--}C\text{--}O\text{--}CH_2\text{--}C^{\bullet} \\
| \\
CH_3
\end{array}
\begin{array}{l}
\diagup COOCH_3 \\
\diagdown CH_3
\end{array}
$$

$$(2)$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^{\cdot} + CH_2=C\overset{\diagup COOCH_3}{\diagdown CH_3} \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

$$+ CH_2=C\overset{\diagup COOCH_3}{\diagdown CH_2^{\cdot}} \left\{ \text{or } CH_2=C\overset{\diagup COOCH_2^{\cdot}}{\diagdown CH_3} \right\} \qquad (3)$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^{\cdot} \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3^{\cdot} \qquad (4)$$

The extent of reactions (3) and (4) was estimated by a gas-liquid chromatographic analysis for tert-butanol and acetone following the complete reaction of DBPOX at a suitable concentration in MMA and separation of the volatiles from polymer. Complete reaction of DBPOX avoids the difficulties in determining the exact amount consumed [6] which need to be sufficiently small so as not to produce an excessive amount of polymer and thereby an unmanageable reaction mixture.

At 60°C, we find that 0.80 mole equivalent of tert-butanol is formed per mole equivalent of DBPOX (this accounts for 40% of DBPOX consumed) while acetone was not detected at the sensitivity of our experiments. This then clearly defines the importance of reactions (3) and (4) and lends considerable credibility to our finding of 0.60-0.65 tert-butoxy endgroups per PMMA chain in that we can now account for approximately one initiating radical per PMMA chain by processes (2) and (3) if we make the reasonable assumption that the radicals resulting from hydrogen abstraction [reaction (3)] do in fact initiate MMA polymerization efficiently.

For polystyrene, prepared by DBPOX initiation at 30°C, we find an average of 1.77 tert-butoxy endgroups per polymer chain using the ether cleavage procedure with BCl$_3$ described above. This result is in agreement with the view that polystyryl radicals terminate largely by combination but is not inconsistent with the possibility that a small proportion of chain termination takes place by disproportionation, as reported recently [18, 19]. Here, it might be predicted that initiation should take place largely by direct addition

of the tert-butoxy radical, as hydrogen abstraction from styrene would be highly unfavorable, while prior fragmentation of the tert-butoxy radical [reaction (4)] has been shown to be of little importance in the bulk monomer, even at more elevated temperatures [2].

The ether cleavage technique we have described is quite simple, sensitive, and versatile, and it should find wide application in the detection and estimation of the ubiquitous tert-butoxy endgroup, especially in polymers of high molecular weight where more direct methods such as NMR spectroscopy are not applicable.

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