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# Studies of end-groups in polystyrene using $^{1}$H NMR

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## Abstract

Studies have been made by 400 MHz $^{1}$H NMR of initiator fragments in polystyrene made by radical polymerization in solution at 60 °C. Azoisobutyronitrile, benzoyl peroxide and lauroyl peroxide have been used as initiators. The peaks arising from hydrogens in the end-groups have been recognized. They cause alterations in the ratio of “aromatic hydrogens” to “aliphatic hydrogens” for polystyrene.

*Keywords:* End-groups; Radical polymerization; Initiators; Polystyrene; $^{1}$H NMR

## 1. Introduction

Extensive use has been made of $^{13}$C NMR in studies involving $^{13}$C-enriched initiators in radical polymerizations, leading to detailed information about end-groups in polymers and copolymers [1]. The present report refers to application of $^{1}$H NMR to the examination of end-groups derived from initiators for the case of polystyrene (polySTY) made by radical polymerization in solution at 60 °C. The sources of radicals now considered are azoisobutyronitrile (AIBN), benzoyl peroxide (BPO) and lauroyl peroxide (LPO). It must be recognized that any $^{1}$H NMR signals derived from end-groups will be very much smaller than those derived from monomeric units unless the conditions for the polymerization are such as to lead to comparatively short kinetic chains so yielding polymer of quite low average molecular weight.

Generally the $^{1}$H NMR signals corresponding to “aliphatic hydrogens” can readily be distinguished from those due to “aromatic hydrogens”. Integration of a spectrum allows quantitative comparison of the numbers of the two types of hydrogen in a specimen. Samples of polySTY prepared using AIBN, BPO or LPO can be represented as $[CH_2 \cdot CHPh]_n[Me_2C \cdot CN]_1$, $[CH_2 \cdot CHPh]_n[Ph \cdot CO \cdot O \text{ or } Ph]_1$ or $[CH_2 \cdot CHPh]_n[C_{11}H_{23} \cdot CO \cdot O \text{ or } C_{11}H_{23}]_1$, respectively. The quantity (no. of aromatic hydrogens)/(no. of aliphatic hydrogens) is represented by the ratio “$r$”, expressed as $5n/(3n+6)$, $(5n+5)/3n$ or $5n/(3n+23)$ for the three cases considered above. With certain provisos, $n$ in each of the expressions is equal to the number-average kinetic chain length (KCL) in the appropriate polymerization. When this is so and if certain other

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readily accessible information is available, it becomes possible to deduce information about several aspects of the system including the rate of initiation for the polymerization, the rate at which the initiator furnishes "available" radicals, the number of initiator fragments in the average polymer molecule and the relative importances of combination and disproportionation in the termination process during the polymerization [1].

In studies of the type envisaged, it is essential that any NMR signals ascribed to initiator fragments incorporated in the polymer contain no contributions from occluded initiator or substances derived from it. Therefore stringent tests are required to check the efficiencies of procedures used to purify polymers. Previous work involving $^{14}$C-labelled initiators showed that all contamination by AIBN or BPO or by substances derived from them could be removed from polySTY by precipitations in methanol of polymers dissolved in benzene or toluene [1]. Similar tests could not be performed for LPO because $^{14}$C-labelled material was not available. Tests were made starting with mixtures of polySTY with unlabelled LPO and then examining by $^1$H NMR samples of polymer recovered after reprecipitations.

Studies of end-groups derived from LPO may be of particular significance because they contain sizeable hydrocarbon chains [2]. End-groups such as $CH_3 \cdot [CH_2]_{10}$– might confer upon certain polymers rather special physical properties. The polymers might be regarded as block copolymers of types AB or ABA according to the number of end-groups in the macromolecule.

## 2. Experimental

Materials were purified by standard procedures as used previously. Polymerizations of STY in toluene were performed under anaerobic conditions at 60 °C and were followed dilatometrically up to c.7% conversion. The volume of each reacting system was close to 2.4 ml. Polymers were recovered by precipitation in methanol (200 ml) containing $CaCl_2$ (c.40 mg) to assist coagulation; they were dried to constant weight in vacuum at c.20 °C. A sample of polymer to be reprecipitated was dissolved in toluene (5 ml). $^1$H NMR spectra were recorded at 400 MHz and ambient temperature with $CDCl_3$ as solvent, using a JEOL GSX400 spectrometer equipped with a 5 mm dedicated $^1$H-probe.

## 3. Results and discussion

PolySTY (polymer-A) having $\overline{M}_n$ about 10,000 was made using monomer at 1.70 mol dm$^{-3}$ and AIBN at $1.35 \times 10^{-2}$ mol dm$^{-3}$. The $^1$H NMR spectrum of the reprecipitated polymer is shown as Fig. 1. A sharp peak at c.7.20 ppm was due to a very small amount of $CHCl_3$ in the $CDCl_3$ used as solvent; other sharp peaks at c.1.3 and 1.6 ppm resulted from unidentified contaminants and have been mentioned by other authors [3]. These sharp peaks make only very small contributions to the integrations of spectra; they are neglected and they have been removed from the spectra presented here. Integration of the spectrum in Fig. 1 gives "$r$" as 1.61; consideration of repeat recordings of the spectrum indicates that "$r$" should probably be quoted as 1.61 ± 0.03. The difference between the observed value of "$r$" and 1.67, the value expected for the monomeric units in polySTY, must be due to the "aliphatic hydrogens" of the $Me_2C(CN)$– end-groups in the polymer. The signals from these initiator fragments are small but clearly evident between 0.7 and 1.3 ppm, the spectral region expected for "methyl hydrogens".

Taking "$r$" as 1.61 and equal to $5n/(3n+6)$ gives $n$ as 57. The average polymer molecule is supposed to contain 1.8 initiator fragments, corresponding to 90% of the termination steps in the polymerization being by combination [4]; thus $\overline{M}_n$ of the polymer is found as 10,700.

The signals attributed to the hydrogens in $Me_2C(CN)$– end-groups are small compared with those arising from hydrogens in the monomeric units of the polymer so that the treatment which follows can be only approximate. Considering the

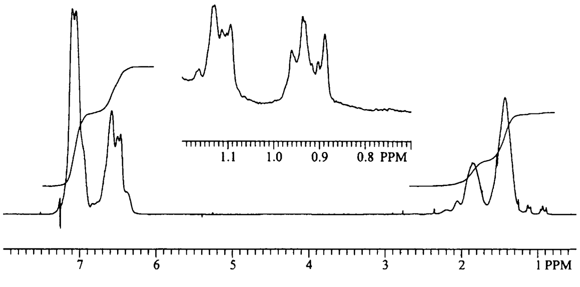

Fig. 1. 400 MHz $^1$H NMR spectrum of polystyrene (polymer-A) with inset of expansion of the region containing the signals assigned to the hydrogens in the methyl groups of $Me_2C(CN)$– end-groups derived from azoisobutyronitrile.

"aromatic hydrogens" of the STY units and the "aliphatic hydrogens" of the initiator fragments.

$5n/6 =$ (spectral area for 6.2–7.5 ppm)/(spectral area for 0.7–1.3 ppm). The ratio of areas is about 37 so that $n$ is about 44 and $\overline{M}_n$ about 8200. This value of $\overline{M}_n$ is in the same region as that deduced from comparison of the spectral areas for the "aromatic" and "aliphatic" hydrogens and that expected from the conditions prevailing in the original polymerization.

PolySTY (polymer-B) was obtained from a system in which [STY] and [BPO] were 1.70 and $2.36 \times 10^{-2}$ mol dm$^{-3}$, respectively; $\overline{M}_n$ of the polymer was expected to be about 10,000. The $^1$H NMR spectrum of the reprecipitated polymer is shown as Fig. 2; comments about some sharp peaks can be made as for Fig. 1. Integration of the spectrum leads to "$r$" as 1.71; it exceeds 1.67 because of the presence of "aromatic hydrogens" in the end-groups derived from BPO. About 80% of these end-groups are benzoate groups and the remainder are phenyl groups [5] but the two types are identical in their contents of "aromatic hydrogens". Taking "$r$" as $(5n+5)/3n$ gives $n$ as 38.5 and $\overline{M}_n$ as 7200, a value not very different from that expected for the polymer.

The $^1$H NMR spectrum of polymer-B contains rather small peaks between 7.3 and 7.9 ppm which persisted essentially unchanged after the polymer had been subjected to further purification. These peaks are not evident in the spectra of polymers made using AIBN or LPO instead of BPO; they are attributed therefore to initiator fragments derived from BPO but they are too small for any reasonable attempt to apply the treatment used in connection with the end-groups derived from AIBN. It must be concluded that signals from the initiator fragments are mostly buried amongst those from the "aromatic hydrogens" in the monomeric units.

Tests on the removal of uncombined LPO from polySTY were made with a polymer prepared using AIBN and having $\overline{M}_n$ about 5000; "$r$" for the polymer was $1.54 \pm 0.03$. The polymer (206 mg) was dissolved in toluene (25 ml) containing LPO (44 mg); for the mixture of polymer and LPO, "$r$" would have been 0.85. Samples of the polymer taken after 1, 2 or 3 precipitations were found to have values of "$r$" of 1.57, 1.51 and 1.55, respectively, suggesting successful removal of LPO from the polymer.

Polymer-C was prepared using STY at 1.52 mol dm$^{-3}$ and LPO at $2.22 \times 10^{-2}$ mol dm$^{-3}$; for polymer-D, [STY] and [LPO] were 1.90 and $2.29 \times 10^{-2}$ mol dm$^{-3}$, respectively. The $^1$H NMR spectrum of the twice reprecipitated polymer-C is shown as Fig. 3, the sharp peaks due to contaminants of low molecular weight having been removed; an almost identical spectrum was obtained for polymer-D. Values of "$r$" are 1.37 and 1.38 for polymer-C and -D, respectively; application of the expression $5n/(3n+23)$ for "$r$" gives values of $n$ of 35 and 37 and of $\overline{M}_n$ of 6600 and 6900 which are similar to those expected from the conditions for the polymerizations.

The spectra contain a structured signal at c.0.9 ppm attributed to the hydrogens of the methyl groups of the incorporated initiator fragments and also a fairly sharp signal at c.1.25 ppm assigned to the hydrogens in their chains of methylene groups. As stated in connection with polymer-A, only an approximate treatment can be applied to the comparison of the spectral areas for the "aromatic hydrogens" in the monomeric units with those for the "methyl hydrogens" in the initiator fragments. For both polymers, $5n/3$ is approximately 60 so that in each case $n$ is roughly 36 and $\overline{M}_n$ is about 6700.

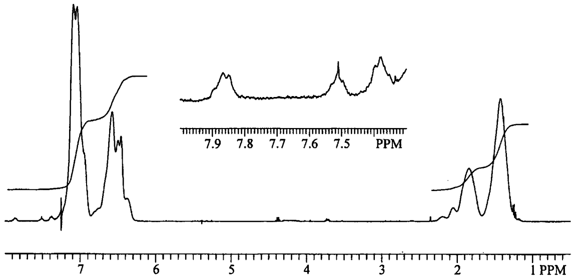

Fig. 2. 400 MHz $^1$H NMR spectrum of polystyrene (polymer-B) with inset of region containing some of the signals arising from the hydrogens in phenyl groups in end-groups derived from benzoylperoxide.

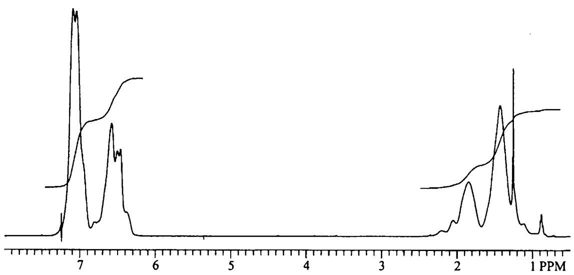

Fig. 3. 400 MHz $^1$H NMR spectrum of polystyrene (polymer-C) prepared using lauroyl peroxide as initiator.

It is believed that almost all the lauroyloxy radicals derived by thermal dissociation of LPO undergo very rapid decarboxylation [6] so that, in polymerizing systems, the peroxide gives rise predominantly to $CH_3 \cdot [CH_2]_{10}$– end-groups. It is expected that $^1$H NMR signals due to "methyl hydrogens" in $CH_3 \cdot [CH_2]_{10}$– end-groups would hardly differ from those due to any $CH_3 \cdot [CH_2]_{10} \cdot CO \cdot O$– end-groups because of the presence of the chain of ten methylene groups.

There is a very noticeable difference between the $^1$H NMR signals associated with the two methyl groups in $Me_2C(CN)$– end-groups and those found for the single methyl group in end-groups derived from LPO. The $Me_2C(CN)$– groups give rise to two separated and structured peaks because of stereochemical relationships between the methyl groups and the phenyl groups in adjacent STY units in the polymer chains. The "methyl hydrogens" in the end-groups formed from LPO give a single although structured $^1$H NMR peak because the presence of the chain of methylene groups between the methyl group and the monomeric units largely precludes effects of stereochemistry. It can be noted that stereochemcial relationships between end-groups and monomeric units lead to complexities in the $^{13}$C-NMR spectra of polymers made using AIBN enriched in the methyl groups with carbon-13 [7].

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