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Improved Procedure for Dye-Partition Analysis of Hydroxy Endgroups in Polymers

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ABSTRACT

Hydroxy radical-initiated poly(methyl methacrylate) and polystyrene have been reacted with *o*-sulfobenzoic anhydride to produce dye-active sulfonate groups and these were measured by a dye-partition technique with methylene blue. The important advantages over chlorosulfonic acid, previously employed in the dye-partition analysis for the conversion of hydroxy into sulfate groups, are that *o*-sulfobenzoic anhydride does not react at sites other than the hydroxy functionality and that it introduces the dye-active moiety (sulfonate) into the polymer via a hydrolytically more stable linkage.

INTRODUCTION

We became interested in endgroup analysis of polymers in relation to a study of the mechanism of the acid-induced free-radical decomposition of hydroperoxides and peroxides [1, 2]. In particular, we wished to identify the radical species involved in the initiation of vinyl polymerization by the *tert*-butyl hydroperoxide-sulfuric acid systems [2], and for this, analysis of the polymers for hydroxy

and tert-butoxy [3] endgroups seemed to be a reasonable starting point.

A convenient dye-partition technique, originally developed for the analysis of ionic surfactants (sulfates and sulfonates) [4], has been applied previously to the determination of hydroxy endgroups in poly(methyl methacrylate) (PMMA) following their conversion to sulfate endgroups with chlorosulfonic acid-pyridine at 85-90°C [5]. In our hands, this procedure was not entirely satisfactory, in that it produced dark reaction mixtures and subsequent loss of polymer in the purification step as a result of partial solubility of the product in methanol. This was an indication that undesirable side reactions were taking place, and it seemed appropriate to investigate the use of other reagents for the conversion of hydroxy groups to dye-sensitive functions. For this purpose, we now report the application of the commercially available *o*-sulfobenzoic anhydride on representative samples of hydroxy radical-initiated PMMA and polystyrene.

EXPERIMENTAL

Materials

Methyl methacrylate and styrene were purified by passage through alumina followed by fractionation through a 40 cm packed column at reduced pressure. Pyridine was refluxed over barium oxide, fractionated, and stored over potassium hydroxide pellets. Commercial *o*-sulfobenzoic anhydride (Fluka) was recrystallized from benzene. Sodium lauryl sulfate was "specially pure" grade; chloroform and methylene blue were of reagent grade and were used as such.

Preparation of Polymers

PMMA. A 2×10^{-4} M solution of ferrous ammonium sulfate containing methyl methacrylate (10 ml) in distilled water (1 liter) was deoxygenated by freezing and melting under vacuum and the flask was then filled with high purity nitrogen and sealed. To this was added deoxygenated 30% hydrogen peroxide (2.0 ml) through a rubber septum with the aid of a syringe and the solution stirred at room temperature (approx. 20°C) overnight. The polymer was collected by filtration washed thoroughly with distilled water and dried at the aspirator. It was then dissolved in acetone, filtered through a sintered-glass funnel, reprecipitated in a fine form by the slow

addition of the filtrate to water with vigorous stirring and again collected and washed first with distilled water and then with methanol and dried in a vacuum oven at 50°C. A final purification was performed by reprecipitation with benzene as the solvent and methanol as the precipitant and drying in a vacuum oven.

Polystyrene. Distilled water (200 ml) was acidified to pH 1 with concentrated hydrochloric acid; to it was added titanium trichloride (4 ml of a 15% solution). The solution was deoxygenated by bubbling high purity nitrogen through it for several hours, and the flask was then sealed with a rubber septum. An atmosphere of nitrogen at a slight positive pressure was maintained in the flask by a connection to the nitrogen line. To the above solution was added purified and deoxygenated styrene (20 ml). The mixture was stirred vigorously (efficient mechanical stirrer), while deoxygenated 3% hydrogen peroxide was added in tiny drops from a syringe until the purple color of Ti^{3+} was no longer discernible. The styrene layer was separated washed with water and dried and the polystyrene precipitated by slow addition to stirred methanol (200 ml). The polymer was then collected and purified by reprecipitation with the use of benzene as the solvent and methanol as the precipitant and dried at 50°C in a vacuum oven. The yield of polymer was only 0.4 g, but the aim of this method was to produce hydroxy radical-initiated polystyrene without contamination by emulsifying agents.

Transformation of Hydroxyl Endgroups to Sulfonate Endgroups

A solution of the polymer (PMMA or polystyrene) (0.2 g) in dry pyridine (5-8 ml) was treated with *o*-sulfobenzoic anhydride (0.2-0.3 g) and stirred in a sealed flask at room temperature under nitrogen for 24 hr. The mixture was filtered through a sintered-glass funnel into stirred methanol (150 ml), and stirring was continued for 2 hr in order to convert the excess *o*-sulfobenzoic anhydride to the more soluble pyridinium salt of 2-carbomethoxybenzenesulfonic acid. The polymer was then collected, washed several times with methanol, 10-15 min contact time being allowed with each fresh portion of methanol while stirring, and dried at the aspirator. It was purified further by reprecipitation into methanol from a benzene solution and dried in a vacuum oven at 50°C.

Molecular Weight Determinations

The number-average molecular weight M_n of the polymers was calculated from intrinsic viscosities $[\eta]$ by using the relations:

$\bar{M}_n = 2.22 \times 10^5 [\eta]^{1.32}$ for PMMA [6, 7] and $\bar{M}_n = 1.84 \times 10^5 [\eta]^{1.40}$ for polystyrene [8]. Viscosity measurements were made on benzene solutions of the polymers at $30 \pm 0.01^\circ\text{C}$ by using a Ubbelohde viscometer.

Dye-Partition Analysis

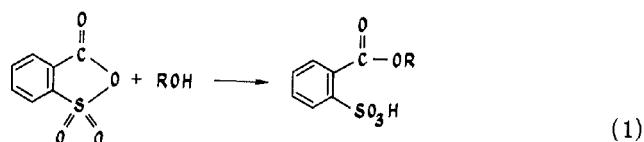
A calibration plot of sulfate concentration versus optical density was constructed as follows: Aqueous solutions (5.0 ml) of sodium lauryl sulfate (NaLS) containing amounts ranging from 0.010 to 0.050 mg were each added to separate 10.0 ml portions of methylene blue reagent (prepared by dissolving 20.0 mg of methylene blue dye in 1 liter of aqueous 0.02 M hydrochloric acid) in 35 ml test tubes with ground glass stoppers. To each was added chloroform (10.0 ml), the contents were shaken thoroughly, the layers were allowed to separate, and the optical density of the chloroform solutions was measured at 655 nm on a Unicam SP1700 spectrophotometer. A plot of NaLS concentration versus optical density gave a straight line passing through the origin.

For the estimation of the sulfonate content in the polymers 10.0 ml of polymer solution of known concentration in chloroform was shaken with the same methylene blue reagent (10.0 ml) and distilled water (5.0 ml). The optical density of the chloroform layer was then translated into the equivalent of NaLS concentration with the aid of the previously established calibration plot. For example, it was found that 18.7 mg of the PMMA ($\bar{M}_n = 175,500$) and 1.25 mg of the polystyrene ($\bar{M}_n = 26,100$) described above, produced optical densities equivalent to those of 0.0296 mg and 0.0282 mg of NaLS (MW = 288.38), respectively. From this it can be deduced that the original PMMA contained 0.96 hydroxy endgroups per chain and the polystyrene 2.04 hydroxy endgroups per chain.

DISCUSSION

o-Sulfobenzoyl anhydride is known to react rapidly and quantitatively with alcohols with the exclusive formation of carboxylic acid esters and liberating a sulfonate group [9].

The feasibility of using this reagent for the conversion of hydroxy endgroups to sulfonate endgroups in polymers was tested on PMMA and polystyrene initiated by the systems $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ and $\text{Ti}^{3+}\text{-H}_2\text{O}_2$, respectively. In both cases, *o*-sulfobenzoyl anhydride in pyridine at room temperature gave rise to clean reactions and the polymers



could then be recovered quantitatively by precipitation with methanol. Subsequent purification by reprecipitation and analysis by the dye-partition method with methylene blue reagent [10] indicated that the content of sulfonate endgroups was approximately 1 for PMMA and approximately 2 for polystyrene (see Experimental Section). Identical treatment of samples of PMMA and polystyrene prepared by initiation with azobisisobutyronitrile gave clear blanks, confirming that *o*-sulfobenzoyl anhydride does not react with the backbone of the polymers. This reagent then, offers a clear advantage over chlorosulfonic acid which has been found to introduce sulfonate groups into the polymer backbone during the conversion of hydroxy to sulfate endgroups [5]. Although sulfates and sulfonates can be easily distinguished by their large difference in hydrolyzability, the necessary correction complicates the procedure and introduces a further source of error [5]. In fact, the ease of hydrolysis of the sulfate group raises a further objection to the functionalization of hydroxy groups by the chlorosulfonic acid-pyridine procedure in that considerable care is required in the purification of the sulfate-containing polymers prior to the dye-partition test [10]. With *o*-sulfobenzoyl anhydride on the other hand, the dye-active and nonhydrolyzable sulfonate moiety is attached to the polymer via a carboxylic acid ester; a function of considerably greater stability to hydrolysis than a sulfate.

The measurements of sulfonate in the present investigation were made with the aid of a calibration plot using sodium lauryl sulfate (NaLS) as the reference compound, and here we made the generally accepted assumptions that the molar extinction coefficients for a methylene blue-sulfonate ion pair is the same as that for a methylene blue-sulfate ion pair [10], and that at most only small errors are involved in the use of a short-chain surfactant (NaLS) as a standard for the determination of the anionic groups SO_3^- and OSO_3^- in polymers of high molecular weight. These assumptions and the applicability of *o*-sulfobenzoyl anhydride in the dye-partition analysis for hydroxy endgroups seem to be substantiated by our results.

For polystyrene, our finding is in accord with the generally accepted view of exclusive combination in the termination mechanism of the polystyryl radicals; a process which results in the incorporation of two initiating radicals per polymer chain [11].

In the case of PMMA it might be predicted that the OH content should

be somewhat greater than one per polymer chain since it is widely agreed that both disproportionation and combination play a part in the termination of the poly(methyl methacrylate)yl radicals. For example, in PMMA initiated by AIBN, values of the order 1.1-1.2 primary radicals per polymer chain have been established [11, 12]. Our finding of approximately 1 OH group per PMMA chain is in fair agreement with this view and corresponds closely to the values determined by Palit and co-workers [13] using a dye-interaction technique, if we make allowance for the discrepancy in the methods of calculation of the number-average molecular weight (\bar{M}_n) of the polymers. For PMMA initiated by $\text{Fe}^{2+}\text{-H}_2\text{O}_2$ (at concentrations similar to those used in the present work) they report values of about 1.2 OH per polymer chain, calculated by the use of \bar{M}_n derived from the relation, $\bar{M}_n = 2.81 \times 10^5 [\eta]^{1.32}$. The relation $\bar{M}_n = 2.22 \times 10^5 [\eta]^{1.32}$, used in the present investigation, is considered to be the more accurate [6, 7] and yields values for \bar{M}_n in close agreement with those obtained by GPC analysis [14].

A possible reason for the lower than expected number of OH groups in OH radical initiated PMMA, might be that these radicals participate in hydrogen abstraction processes from MMA, analogous to those of the tert-butoxy radicals [3]. If this is the case, polymer chains could be initiated by species other than OH radicals.

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