

Synthesis of Deuterated Poly(4-acetoxystyrene) by a Polymer-analogous Reaction Sequence

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Abstract

This study describes a new simple method for preparing deuterated poly(4-acetoxystyrene). The new method offers cost-effective and alternative route to preparing deuterated polymers that otherwise have to be prepared from the deuterated monomers. Deuterated poly(4-acetylstyrene) (ACPS- d_4) and poly(4-acetoxystyrene) (APS- d_4) were synthesised from deuterated polystyrene under thermal reactions. The polystyrene- d_5 (PS- d_5) was acetylated using cyclohexane as solvent instead of carbon disulfide (a highly toxic and flammable solvent) and acetyl chloride as the acetylating agent. Using commercially available reagents, the acetyl group was converted to an acetoxy group by Baeyer-Villiger oxidation. The oxidation of ACPS was carried out with various agents and reaction conditions. The oxidation kinetics with peracetic acid was followed by FT-IR spectroscopy. The deuterated polymers were characterised by nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FTIR). The optimised procedure will make future work using neutron scattering possible.

Keywords: *polystyrene- d_5 , thermal reactions, Baeyer-Villiger oxidation*

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1. Introduction

Recently, deuterated polymers have aroused interest not only for use in neutron scattering studies but also as materials for applications in optical communication due to their transparency in the infrared, particularly the region between 500 and 800 cm^{-1} .^{1, 2} Although a wide variety of deuterated polymers are commercially available, they can be quite expensive and viable synthetic routes to such polymers are desirable. The synthesis of deuterated polymers is accomplished by the polymerisation of a deuterated monomer or by H/D isotope exchange of a non-deuterated polymer. For example, the N-H protons in polyamides are readily exchangeable with deuterium oxide,³ whereas partial H-D exchange on the

aromatic ring of polystyrene is usually performed under hydrothermal conditions in the presence of a deuterium source and with the assistance of a Lewis acid catalyst.² A number of works concerning H/D exchange of polycyclic aromatic hydrocarbons have been reported in literature.⁴⁻⁷ In addition, the preparation of deuterium-labelled compounds has been aided recently by the development of microwave-assisted techniques.⁸⁻¹⁴ This study describes a successful preparation of deuterated polymers starting with deuterated PS. However, to the best of our knowledge, no attempts have been made, so far, for the synthesis of deuterated polymers, such as poly(4-acetylstyrene) and poly(4-acetoxystyrene) starting with deuterated PS under conventional conditions. This methodology offers several advantages over low-temperature anionic polymerisation or free-radical polymerisation of the protected monomer.

2. Experimental

2.1 Reagents

PS-*d*₅ (degree of deuteration ~85%) was prepared according to literature producer.¹⁵ acetyl chloride (CH₃COCl), acetic anhydride (>99.5%), hydrochloric acid (HCl, 36%), cyclohexane, aluminium chloride (AlCl₃, 99%), were purchased from Aldrich. hydrogen peroxide (35% w/w) and sulphuric acid (H₂SO₄, >95%), tetrahydrofuran (THF) were supplied by BDH.

2.2 Characterisation techniques

2.2.1 Nuclear magnetic resonance (NMR)

NMR analyses were performed with Bruker spectrometers at 300 MHz. NMR spectra were recorded for every sample prepared in order to confirm that no solvent or other impurities were present. NMR samples were prepared by dissolving 15-20 mg of material in 1 mL of CDCl₃ or DMSO-*d*₆

2.2.2 Fourier transform infrared spectroscopy (FTIR)

IR measurements were performed with a Perkin Elmer RX Fourier transform infrared spectrometer. KBr discs made from solid powder were used to overcome solubility problems.

2.3 Synthesis of deuterated poly(4-acetylstyrene) (ACPS-*d*₄)

Polystyrene-*d*₅ (2.60 g, 24.04 mmol) was dissolved in 25 mL cyclohexane. A three-necked round-bottom flask equipped with a condenser, dropping funnel, and magnetic bar for stirring was placed in hot bath at 55 °C. AlCl₃ (6.7 g, 0.05 mol) and 25 mL cyclohexane were added and the mixture was stirred vigorously. To this solution (3.5 mL, 3.86 g, 0.05 mol) acetyl chloride (CH₃COCl) was added dropwise. The reaction mixture turned yellow, with the evolution of hydrogen chloride (HCl) gas during the addition. The reaction was continued for 7 hours until the evolution of hydrogen chloride ceased. The reaction was stopped, and cyclohexane was removed by rotary evaporation. The residue obtained had a light yellow colour; air dried overnight and transferred into a beaker containing 100 g crushed ice and 5 mL of

concentrated hydrochloric acid. The precipitate was filtered, dried in vacuum oven at 80 °C for 2h (aluminium chloride decomposed and polymer was obtained as a yellow precipitate) and then dissolved in 6.5 mL acetone, and precipitated in water. The suspension was dissolved in 5.5 mL THF and then precipitated in methanol. Yield: 2.80 g (77.7%). ¹H NMR (300 MHz, CDCl₃): δ 1.3-1.6 (m, CH₂ and CH-Ar), 2.50 (s, CH₃-CO), 6.2 - 7.5 IR spectrum ν (cm⁻¹): 2923, 2845 alkyl (C-H), 2272 (C-D aromatic), 1670 (C=O) and 1576 (Ar-C=C).

2.4 Synthesis of deuterated poly(4-acetoxystyrene) (APS-d₄)

Poly(4-acetylstyrene)-d₄ (1.0 g, 6.66 mmol) was dissolved in 25mL of CHCl₃. This was added to an oxidizing solution consisting of 5 mL of acetic anhydride, 5 mL of 30% H₂O₂, and trace amounts of concentrated H₂SO₄ (as the catalyst) and refluxed for 142 h at 85°C. At the end of every 12 h, 2.5 mL of acetic anhydride and 2.5 mL of H₂O₂ were added. After 142 hours the reaction was stopped, the organic layer was separated with a separating funnel and precipitated into 20 times methanol. The precipitated polymer was filtered and dried under vacuum. Yield : 1.3 g (63%). ¹H NMR (300 MHz, CDCl₃): δ 1.3 (br, s, CH₂) 1.7 (br, s, CH-Ar), 2.25 (s, CH₃-COO), 6.3- 6.8 (m, Ar-C-H). IR spectrum ν (cm⁻¹): 3024(Ar- C-H), 2923, 2845 alkyl (C-H), 1750 (O-C=O), 2272 (C-D aromatic).

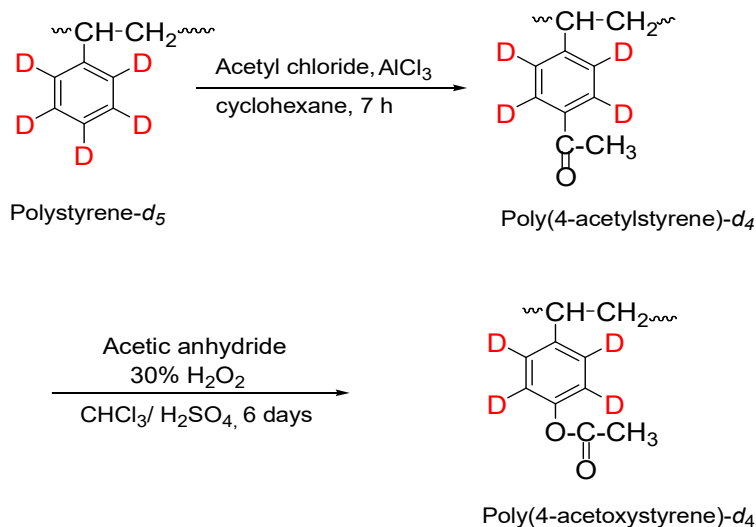


Fig. 1 Reaction scheme for synthesis of deuterated APS-d₄ form PS-d₅

3. Result and Discussion

3.1 Synthesis of deuterated poly(4-acetylstyrene) (ACPS-d₄)

The acetylation of PS-d₅ (degree of deuteration ~85%) was conducted using cyclohexane (instead of the toxic and flammable carbon disulfide proposed in the literature)¹⁶ as the solvent and acetyl chloride as the acylation agent (**Figure 1**). The mono-substituted aromatic rings in the polymer side chain were acylated at the *para* position because of the large steric requirement of the attacking reagent. It should be noted

that acylation reactions conducted in non-polar solvent such as cyclohexane are faster than acylation reactions in halogenated solvents.

The mechanism of the reaction can be described by Friedel-Crafts acylation reaction of benzene as illustrated in **Figure 2**.¹⁷ The extent of the acylation of long chain molecules, such as polystyrene-*d*₅ presents difficulty in the accessibility of a particular reaction site due to conformational complexity. For this reason, the acetylation of polystyrene, like so many polymer-analogous reactions, was not quantitative. The progress of acetylation in benzene and other lower mass analogues such as toluene and so on depends on catalyst, acyl component, solvent, and the ratio of the catalyst to acyl component.¹⁶

In general, the dependence of the extent of acetylation of non-deuterated polystyrene could be easily monitored by the reduction in FT-IR peak at 700 cm⁻¹ which is characteristic of monosubstituted benzene. However, this peak was absent and had shifted to 511-540 cm⁻¹ in the deuterated polystyrene. Furthermore, the reaction was monitored by the reduction in ¹H NMR signal at 7.15 ppm; there was also a new signal at 7.55 ppm which is characteristic the protons *ortho* to the acetyl group. The structure of the product was confirmed by ¹H NMR and FT-IR spectroscopy. The ¹H NMR spectra of PS-*d*₅ and ACPS-*d*₄ are shown in **[Figure 3 (a and b)]**. The ¹H NMR spectrum of ACPS-*d*₄, when compared to PS-*d*₅ shows a new signal at 2.50 ppm which is due to the methyl (CH₃) protons of acetyl moiety and a new signal due to the protons *ortho* to the acetyl group appears around 7.55 ppm whereas, in the aromatic region, the intensity of the broad signal at 7.15 ppm is reduced. The FTIR spectrum of ACPS-*d*₄ is displayed in **Figure 4**. The presence of a C=O stretching at 1670 cm⁻¹ and C-O stretch at 1240 cm⁻¹ confirms that the acetylation had indeed occurred.

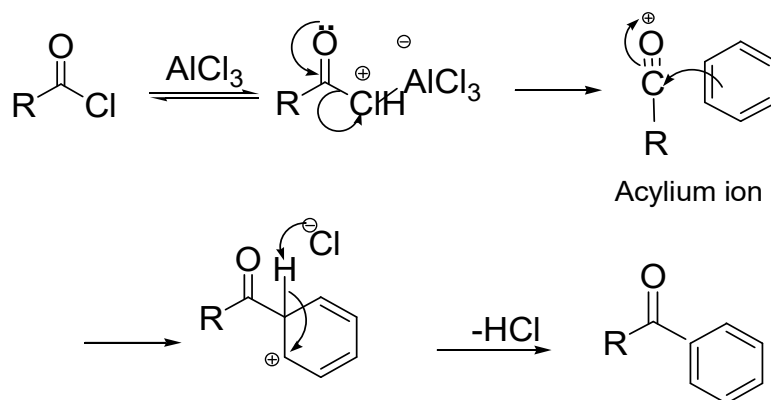


Fig. 2 The mechanism of Friedel-Crafts acylation reaction of benzene.¹⁷

3. 2 Synthesis of deuterated poly(4-acetoxystyrene) (APS-*d*₄)

Poly(4-acetoxystyrene) can be prepared from poly(4-acetylstyrene) by Baeyer-Villiger oxidations of aromatic ketones to esters. In this study, several peroxy acids were tested as reagents to convert ACPS-

d_4 to APS- d_4 in a Baeyer-Villiger oxidation: potassium persulphate,¹⁸ sodium perborate in acetic acid, and peracetic acid¹⁹ with chloroform as the solvent. The mechanism of the Baeyer-Villiger reaction may be demonstrated in four steps as shown in **Figure 5**.²⁰ In this reaction, the reactivity of the carbonyl group is increased by protonation at the carbonyl group; addition of the peroxide to the carbonyl carbon yields a hydroperoxide to afford the Criegee intermediate. The subsequent migration of R₂ or R₁ onto the neighbouring carbon is accompanied by cleavage of the peroxy O-O bond and loss of a proton in the last step to afford the ester in the usual way.

The results for the oxidation of acetyl polystyrene- d_4 to acetoxy polystyrene- d_4 are summarised in **Table 1**. Potassium persulphate gave no reaction at all. Sodium perborate in acetic acid resulted in partial hydrolysis so that the final product was mixture of poly(4-hydroxystyrene-co-acetoxystyrene). The best result was obtained when the Baeyer-Villiger oxidation was conducted in the presence of peracetic acid after 142 h. therefore, were conducted with it. The oxidation kinetics with peracetic acid was followed by FT-IR. The transformation of acetyl group to acetoxy was completed after 142 h of oxidation. The FTIR spectrum showed the appearance of a new peak at 1750 cm⁻¹ due the new ester C=O stretch (for the acetoxy group), whereas the aromatic ketone C=O stretch of the acetyl group at 1670 cm⁻¹ disappeared suggest that the expected functional group transformation took place. The ¹H NMR spectrum supported the FT-IR findings (**Figure 4**). The acetyl signal at 2.50 ppm was replaced gradually with time by an acetoxy methyl at 2.25 ppm. In addition, the residual aromatic signal at 7.5 ppm also gradually shifted upfield to 6.80 ppm as a result of the oxidation [**Figure 3 (b and c)**]. This was attributed to the loss of the deshielding of the protons ortho to the acetoxy group that previously were deshielded as a result of the presence of an acetyl group. After 142 h the oxidation was complete as evident from the appearance of signals at 2.25 and 6.80 ppm and the disappearance of the signals at 2.50 and 7.50 ppm.

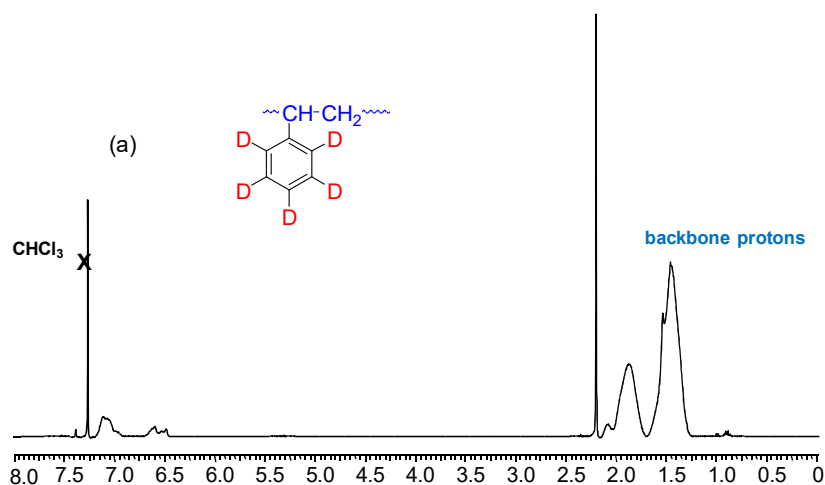


Fig. 3. ¹H NMR spectra (300 MHz, CDCl₃) of (a) PS- d_5 (80% deuteration), (b) ACPS- d_4 and (c) PAS- d_4 . Solvent and water signals are marked by X.

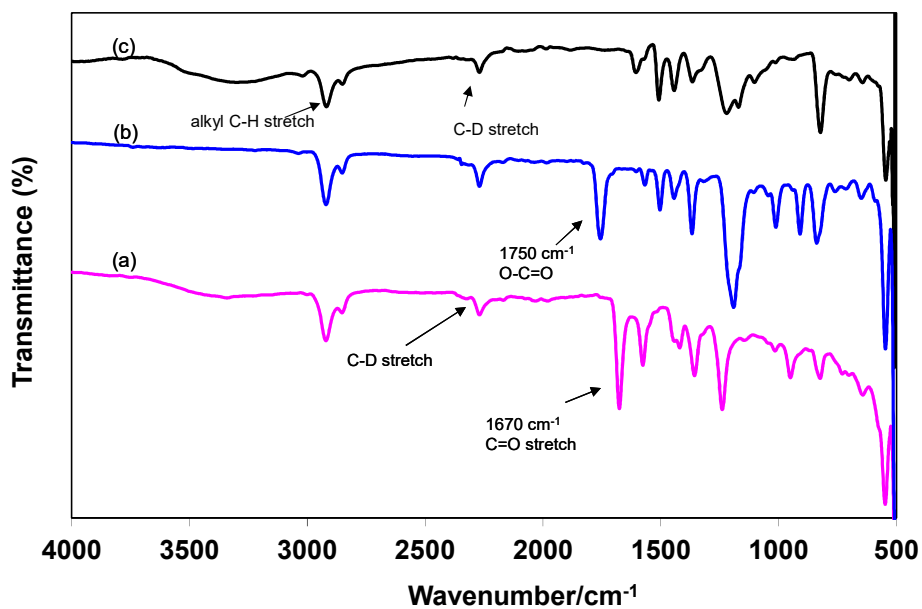
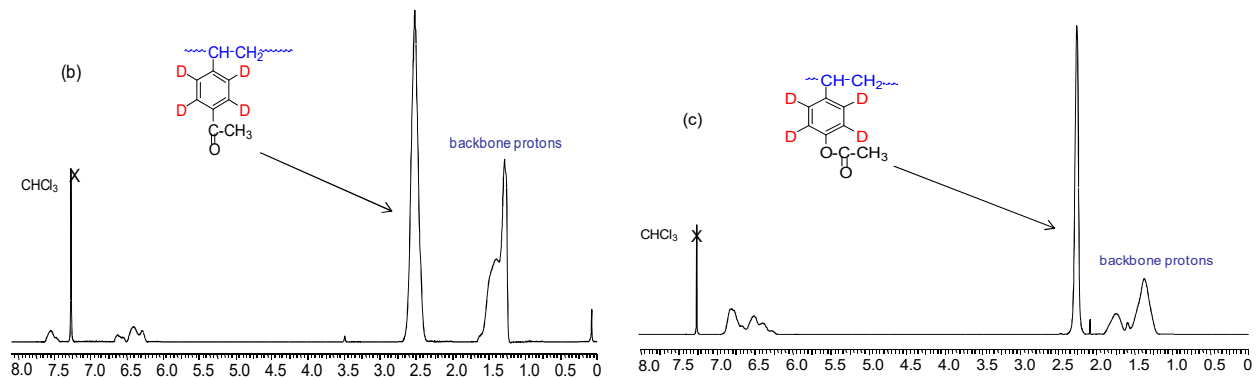


Fig. 4 FT-IR spectra of (a) ACPS- d_4 and (b) PAS- d_4 and (c) PS- d_4 . The spectra have been shifted vertically for clarity.

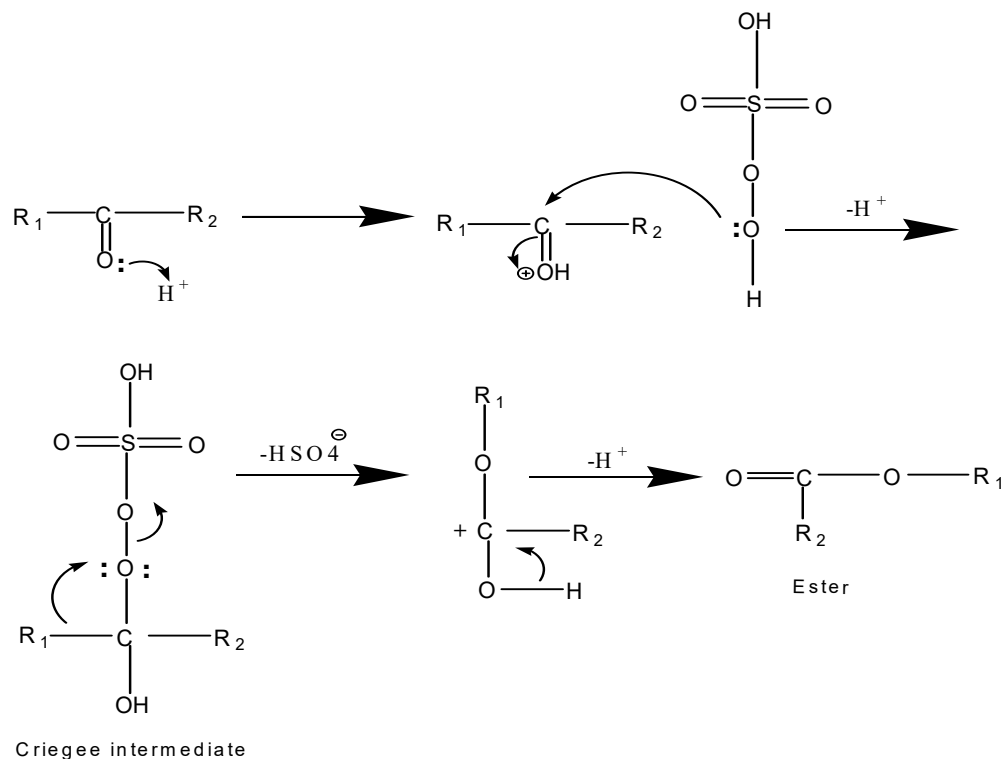


Fig. 5 The mechanism scheme of Baeyer-Villiger reaction.²⁰

Table 1. Oxidation of Acetylated PS-*d*₄ to PAS-*d*₄ under various conditions

System	Results
Potassium persulfate	No reaction at all.
Sodium perborate in acetic acid	Partial acetylation.
Peracetic acid	Works well.

4. Conclusion

In conclusion, ACPS-*d*₄ and APS-*d*₄ can be obtained by a simple chemical transformation of PS-*d*₅ under thermal conditions. The PS-*d*₅ was acetylated using cyclohexane as solvent instead of carbon disulfide and acetyl chloride as the acetylating agent. The acetyl group was converted to an acetoxy group to obtain APS-*d*₄ by Baeyer-Villiger oxidation. the oxidation was completed after 142 h. This method offers cost-effective and alternative route to preparing deuterated polymers that otherwise have to be prepared from the deuterated monomers.

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