Preparative Scale Isocratic Chromatographic Purification of a Polyethylene Mono-Alcohol Accompanied by High Resolution Evaluation of Molecular Weight Distribution

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ABSTRACT: A simple preparative-scale adsorption chromatographic method for separating a commercially available polyethylene mono-alcohol from its non-functional polyethylene impurities has been established using silica as the stationary phase and toluene at 75°C as the isocratic eluant. Characterization of the chromatographic fractions by ^{1}H-NMR spectroscopy also provided unexpected comprehensive information on the molecular structure and molar mass distribution of the polyethylene mono-alcohol.
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Key words: chromatography; polyethylene (PE); mass distribution; MALDI; block copolymers

INTRODUCTION

The chromatographic separation of polymeric materials is well known in the literature; however, to the best of our knowledge, no preparative-scale examples exist which utilize the interaction of the polymer with the stationary phase (SP) as the sole means of resolution.[1] Most techniques rely on a combination of precipitation, sorption, and/or size exclusion mechanisms, controlled by solvent polarity gradients and/or temperature gradients to achieve separation.[2,3] In the late 1960s, Meunker and Hudson showed that a variety of carboxy- and hydroxyl-functionalized mono-functional and telechelic hydrogenated polybutadienes and polyiosbutylenes could be fractionated on silica gel according to their molar fraction of functionality using stepwise elution with solvent mixtures of progressively greater elution power.[4] More recently, several new methods of separating and characterizing polymers have appeared, apart from size exclusion chromatography (SEC) which is widely used. Temperature rising elution fractionation[5] (TREF) and crystallization analysis fractionation (CRYSTAF) are both good examples of techniques which have been used successfully on polyolefins.[6]

In the present work, we have found a polymer/SP/solvent system that not only provides a facile means of purifying PE700-OH but in effect fractionates the end-functional polymer itself according to polarity and therefore molecular weight, as a result of the terminal group–SP interaction being much greater than the polymer chain–SP interaction. Since the interaction is strong and the polymer has a relatively low molecular weight, we believe that any size exclusion effects are insignificant in this separation. Using end-group analysis by ^{1}H-NMR spectroscopy, the fractionation also serendipitously allowed us to evaluate the molar mass distribution of the polymer. The results were compared to the M_n derived from the ^{1}H-NMR spectrum and the matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectral distribution of the same polymer with its end group converted to a phosphonium bromide salt functionality.

EXPERIMENTAL SECTION

Materials

The polyethylene mono-alcohol (PE700-OH) (average M_n ca. 700 g mol^{-1}), phosphorous tribromide, triphenylphosphine, Riedel-de Haen toluene and all-*trans*-retinoic acid (ATRA) were purchased from Sigma-Aldrich Co. Ltd., Gillingham, U.K. and silica gel for chromatography was obtained from VWR International Ltd, Lutterworth, U.K.

Methods

^{1}H-NMR spectra were recorded at 80°C using d_8-toluene as the solvent in 5 mm NMR tubes on either a

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DRX-500 (500 MHz) or an AV-400 (400 MHz) Bruker instrument using the residual solvent resonance as an internal reference and chemical shifts are given in ppm. MALDI-ToF mass spectra were recorded on a Shimadzu Biotech Axima CFR instrument in reflectron mode, calibrated using protein standards.

Purification of PE700-OH

PE700-OH (3.050 g) was dissolved in 15.0 mL of toluene at 80°C. The chromatography column was prepared by mixing silica gel (110 g) with toluene, charging the slurry to a water-jacketed column (270 mm long × 35 mm internal diameter) and pre-heating to 75°C using a water circulator (Grant W6). The hot PE700-OH solution was charged to the top of the silica gel and the column was eluted with further hot toluene (~ 75°C). When the initial eluate (~ 100 mL) started to show signs of polymer precipitate on cooling, small fractions were collected (30 × 15 mL) until precipitation was no longer visible on cooling. The fractions were individually concentrated under reduced pressure at room temperature and finally dried *in vacuo* at 70°C to constant mass. Each fraction was weighed and analyzed by ^{1}H-NMR spectroscopy.

Calculation of the composition from the ^{1}H-NMR spectra of a sample

The calculation of sample composition was based on the ratio of the integrations (R) in the ^{1}H-NMR spectrum of a sample of the resonance due to the -CH_2-OH hydrogens present only in the PE700-OH at $\delta = 3.38$ and that of the -CH$_2$-CH_3 hydrogens which are present in both components (PE700-OH and PE impurity) at $\delta = 0.9$ as shown in eq. (1).

$$R = \frac{I_{3.38}}{I_{0.9}} \quad (1)$$

The mole fraction of PE impurity (χ_{PE}) in the PE700-OH was then found from R using eq. (2).

$$\chi_{PE} = \frac{2 - 3R}{3R + 2} \quad (2)$$

Based on the assumption that the non-functional PE and the PE700-OH were the only two components present, the χ_{PE} data for each chromatographic fraction was then used to calculate the purity of each sample and indeed was used on the ^{1}H-NMR spectrum of a sample of the polyethylene alcohol as received from the supplier.

Derivatization of PE700-OH and preparation of MALDI-ToF MS samples

Preparation of polyethylene bromide (PE700-Br)

PE700-OH (1.489 g; 2.00 mmol) and toluene (10 mL) were charged into a two-necked round-bottomed flask equipped with a magnetic stir bar and a reflux condenser under a nitrogen atmosphere. The mixture was stirred at 80°C for 30 min. PBr_3 (188 μL, 2.00 mmol) was then added dropwise via a syringe and the mixture was stirred at 80°C for 5 h under a nitrogen atmosphere. The hot reaction mixture was added slowly to cold, stirred MeOH (100 mL) and the off-white precipitate formed was filtered off and dried *in vacuo* to constant mass (1.238 g). The off-white solid was characterized by ^{1}H-NMR spectroscopy and the conversion of alcohol to bromide was found to be ~ 50%. The crude product was used without further purification. ^{1}H-NMR (d_8-toluene, AV400, 80°C, 400 MHz): δ 3.32 (t, 2H [-CH_2-Br]), 3.04 (t, 2H residual [-CH_2-OH]) 1.28–1.70 (m, 304H backbone [-CH_2-]), 0.93, (t, 10.6H [-CH_3]).

Preparation of polyethylene phosphonium bromide (PE700-PPh$_3$Br)

Crude PE700-Br (0.529 g 0.69 mmol), toluene (10 mL), and PPh_3 (1.39 g, 5.30 mmol) were charged to a two-necked round-bottomed flask under a nitrogen atmosphere and stirred for 4 days at 110°C. The reaction mixture was allowed to cool to around 80°C and was added slowly to stirred petroleum ether 40–60° (0°C). The yellow precipitate formed was washed into a cellulose extraction thimble and washed in a Soxhlet apparatus for 4 h with petroleum ether 0–60° to remove excess PPh_3. The washed precipitate was dried *in vacuo* to provide a white solid (0.303 g), the conversion by ^{1}H-NMR spectroscopy was 63% relative to the starting material and no attempt was made to further purify the product. ^{1}H-NMR (d_8-toluene, AV400, 80°C, 400 MHz): δ 7.98 (b, 6H [Ar-*H*]), 7.35 (b, 9H [Ar-*H*]), 4.33 (b, 2H [-CH_2-PPh$_3$]), 1.70–1.10 (b, 321H backbone [-CH_2-]) 0.90 (t, 9.5H [-CH_3]).

MALDI-ToF MS sample preparation

PE700-PPh$_3$Br (1 mg) was ground together with ATRA (10 mg) in a mortar and pestle. A small amount of this paste was pressed onto the stainless steel MALDI target plate, removing any loose particles with a stream of compressed nitrogen.

DISCUSSION

The commercially available PE mono-alcohol was quoted by the supplier as being mono-terminated with –OH groups, having an "average M_n ca. 700 g mol^{-1}" (T_m = 108°C) and a polydispersity index (PDI) of 1.09. The material as supplied is therefore of "narrow molecular weight distribution." The supplier gives the impurity content as 15–20% of "unreacted hydrocarbons" and this was taken to

mean that a non-functional polyethylene of similar molecular weight was present. This could indeed be seen in the ^{1}H-NMR spectrum of the impure sample, with the integration of the resonances corresponding to the terminal methyl hydrogens ($\delta = 0.90$ ppm, triplet) being greater than the theoretical value derived from the integration of the resonance for the methylene hydrogens ($\delta = 3.37$ ppm, triplet) adjacent to the hydroxyl group. Although it is possible to prepare terminally functional polyethylene by anionic polymerization,[7–9] we believe that the present material is probably prepared using a procedure first described by Gibson and coworkers, a degenerative transfer polymerization of ethylene using a bis(imino)pyridine iron catalyst and triethylzinc as a co-catalyst.[10,11] Matyjaszewski and coworkers have also reported using this procedure to prepare PE macromonomers and subsequently block and graft copolymers via controlled radical polymerization.[12] This type of catalyst provides zinc-terminated PE chains which are insoluble in the reaction solvent (*o*-xylene) at a M_n of over ~ 700 g mol^{-1} when the polymerization essentially stops. This is the same as the M_n quoted by the supplier and similar to that found by us using ^{1}H-NMR spectroscopy and subsequent calculations (~ 760 g mol^{-1}). The terminal zinc species is then oxidized with air to provide Zn-O- endgroups which are subsequently hydrolyzed *in situ* with HCl to the alcohol. The oxidation/hydrolysis steps do not seem to be 100% efficient and results in some chains being methyl terminated, in effect yielding a non-functional PE impurity with a similar M_n to the mono-alcohol. From this we assume that the degree of polymerization of the PE-OH and the PE contaminant are equivalent (i.e., have the same distribution) and we also assume that that there is no branching, unsaturation, or isomerism of either component, thus the purity can be estimated from the ^{1}H-NMR spectrum [eqs. (1) and (2)]. The molecular weight was subsequently estimated from the ratio of -(-CH_2-)- to -CH_2-OH protons, once the contribution from the alkyl hydrogens present in the PE impurity had been subtracted. The PE700-OH was found to be 71% pure with a nominal average M_n of 760 g mol^{-1}. For the particular application, we had in mind for this material, it was important to minimize the percentage of the PE impurity, ideally to 0%.

The PE700-OH was therefore purified by isocratic column chromatography using silica gel in a water-jacketed column at 75°C, and hot toluene as the eluant. The fractions were evaporated to dryness, weighed, and the residues were characterized by ^{1}H-NMR spectroscopy. The early ones were found to contain the PE impurity and only very low levels of PE-OH, whereas the later fractions seemingly contained high-purity PE-OH. The proportions of the two components (PE-OH and PE impurity) present in the fractions were calculated from their ^{1}H-NMR spectra in the same way as previously discussed, using the same assumptions. The recovered total mass of each fraction was then divided into the masses of each component present using mole ratios derived from the ^{1}H-NMR spectra of each recovered fraction. The derived masses of both components were then plotted for all fractions (Fig. 1).

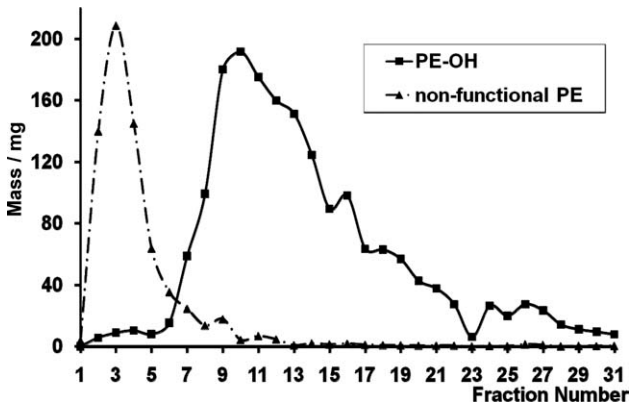


Figure 1 Analysis of the column fractions by mass recovery and ^{1}H NMR spectroscopy.

The data in Figure 1 show that most of the nonpolar, non-functional PE impurity was eluted first, in fractions 1–6. From fraction 7 onwards the more polar PE-OH becomes the main component. This presumably takes place because the PE interacts less strongly with the polar silica SP than the PE-OH does. By using the data derived from the ^{1}H-NMR spectra of each fraction along with the mass collected, it was possible to calculate the purity of the PE-OH. This was found to be 72.6% and is in good agreement with the figure derived from the ^{1}H-NMR spectrum of the impure as supplied PE700-OH before column chromatography (71%) within experimental error. The agreement of these two figures suggests that the assumptions that the non-functional PE is the only significant impurity present and that this has the same $\overline{DP_n}$ as the PE-OH are valid, and that the treatment of the data is correct. Further manipulation of the ^{1}H-NMR spectral data of the later fractions also allowed the molecular weight of the PE-OH in each fraction to be determined. The molar masses of the PE-OH in fractions 1–6 were not plotted as these fractions were made overwhelmingly of the non-functional PE impurity (Fig. 2).

The molar mass of each PE-OH fraction was determined by comparing the peak area of the ^{1}H-NMR resonance due to the -CH_2-OH hydrogens to those due to the -CH_2- hydrogens of the PE chain, once any influence of any residual PE impurity had been subtracted. Rather serendipitously, the molecular weight was found to decrease with each fraction

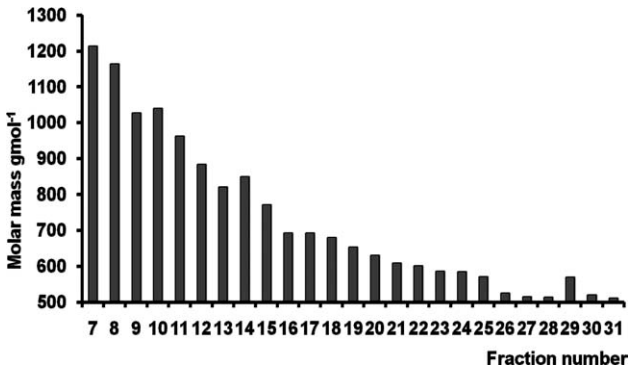


Figure 2 The variation of molar mass with column fraction, determined by ^{1}H-NMR spectroscopy for fractions 7–31.

collected, the fractions presumably eluting differentially as a result of increasing overall polarity of each PE-OH fraction as the chain length decreases. In addition, the molar mass distribution of the PE-OH was established by plotting the mass fraction against the molar mass of fractions 7–31 (Fig. 3). Note: The horizontal axis in Figure 3 is molar mass not fraction number as in Figure 2, since when two fractions were of equal or near equal molar mass (e.g., 16 and 17) the masses of these fractions were combined for plotting the data in Figure 3.

Subsequently, the M_n, M_w, and PDI were calculated from the mass fraction and molecular weight data yielding M_n = 816 g mol^{-1}, the M_w = 859 g mol^{-1}, and the PDI = 1.05. The PDI is in good agreement with the value of 1.09 quoted by the supplier, whilst the M_n is higher than the nominal value quoted by the supplier. The supplier indicates that its data derive from a calibrated SEC analysis and we assume that this refers to the impure PE700-OH with its PE impurity. This may in part account for the difference with our data. Our value of 816 g mol^{-1} for M_n calculated from the purified fractions of PE-OH is also higher than our earlier value of 760 g mol^{-1} deduced from appropriate manipulation of our own ^{1}H-NMR data from the impure sample of PE700-OH containing the PE impurity. This evaluation did, however, take account of the presence of the impurity and assumed only that it had the same $\overline{DP_n}$ as the PE700-OH. The value of 816 g mol^{-1} versus 760 g mol^{-1} might be explained at least in part if the shortest, most polar fractions of the PE-OH failed to be eluted from the chromatographic column under the isocratic conditions employed. Irrespective of this, the molecular weight fractionation achieved simultaneously with the simple adsorption chromatographic procedure originally planned as purification process, and intended only to remove the non-functional PE impurity, is quite remarkable. Bearing in mind that the PDI of the sample originally supplied was quoted as 1.09, i.e., the sample falls within the category of having a "narrow molecular weight distribution" the additional high resolution of the molecular weight achieved in the chromatographic separation is even more impressive.

Another analytical technique capable of achieving high resolution of the molecular weights of organic oligomeric materials is MALDI-ToF mass spectrometry (MS) and we thought it would be valuable to generate some comparative data from such analysis. Unfortunately, however, consultation with the literature indicated that polyolefins are notoriously difficult to analyze by MALDI-ToF MS due to the ease with which they fragment under laser ablation, and hence require the sample to be dilute in the matrix (1 sample/10 matrix) and the use of a low laser power.[13] ATRA has, however, been shown to be a valuable matrix in the case of polyolefins.[14] Preliminary in-house experiments with this matrix confirmed that neither the PE700-OH nor its non-functional PE impurity could be observed using MALDI-ToF MS. These molecules apparently fail to ionize at laser energies low enough to prevent excessive fragmentation. It was decided, therefore, to derivatize the PE700-OH with an ionic functionality and this was achieved via conversion of the terminal alcohol group to an alkyl bromide followed by reaction with triphenylphosphine to yield a terminal phosphonium bromide functionality, a procedure which has been used successfully by Lin-Gibson et al. to analyze hydroxy-functional PE by MALDI-ToF MS.[14] Though these reactions proceeded reasonably well using the as-supplied PE700-OH the conversions were not 100% (Scheme 1), and the final phophonated product was contaminated with starting material and bromo-intermediate.

From a MALDI-ToF MS perspective, this was not a particular problem because only the phosphonated species was expected to undergo analysis in the MS.

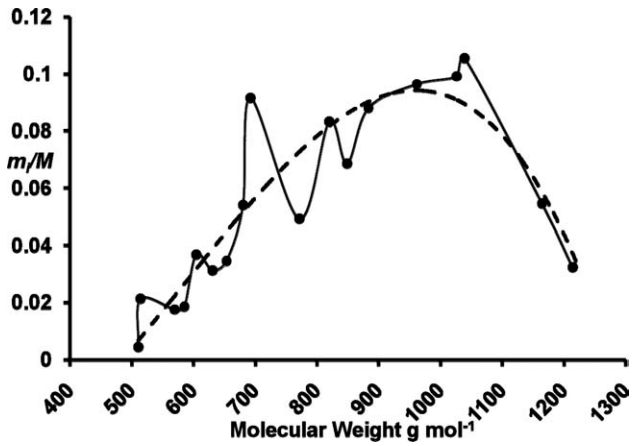
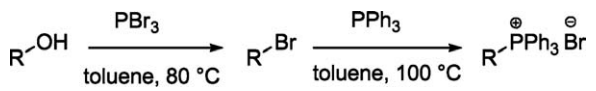


Figure 3 The molecular weight distribution for the PE-OH polymer derived from the ^{1}H-NMR spectra of the chromatographic column fractions.

However, the ^{1}H-NMR spectrum of the phosphonated species was difficult to interpret quantitatively because of contamination with precursor materials. In addition, it was not possible to deduce whether or not the PE700-OH had been derivatized statistically and that the molecular weight distribution of the final product reflected accurately that of the PE700-OH precursor. Nevertheless, the phosphonated sample did undergo successful MALDI-ToF MS analysis from an ATRA matrix and the molecular weight distribution obtained is shown in Figure 4. Adjusting the data to account for the presence of -$PPh_3^+Br^-$ in place of -OH, the molecular weight data for the PE700-OH precursor calculated from this mass spectrum are M_n = 641 g mol^{-1}, M_w = 676 g mol^{-1}, and PDI = 1.04. Each of these data is lower than the corresponding data from our chromatographic analysis, with the lower PDI in particular probably reflecting the loss of some of the distribution during the derivatization steps. The lower values for M_n and M_w suggest that the loss is at the higher molecular weight end of the distribution, and it does not seem unreasonable that the chemical modification becomes less efficient as the chain length of the PE-OH increases. Bearing this in mind, and the potential loss of material at the low molecular weight end of the distribution in our chromatographic analysis, the relative values of the respective M_n, M_w, and PDI parameters obtained from the two procedures are at least consistent with each other.

SUMMARY AND PERSPECTIVES

The non-functional PE impurity in a commercially sourced polyethylene mono-alcohol (PE700-OH) has been removed in a simple preparative scale chromatographic method using silica as the SP and toluene at 75°C as the isocratic solvent. Serendipitously, the purification process also provides a high resolution fractionation of the PE700-OH according to molecular weight. ^{1}H-NMR spectroscopic analysis of the chromatographic fractions coupled with mass balance also allows comprehensive information to be deduced with regard to the molecular structure and molecular weight distribution of the polyethylene mono-alcohol. Conversion of the terminal alcohol function of the PE700-OH into a triphenylphosphonium bromide salt also allowed MALDI-ToF MS of the PE700-OH using an ATRA matrix. Molecular weight distributions of the PE700-OH deduced from



Scheme 1 Derivatization of the PE700-OH to provide the phosphonium bromide salt.

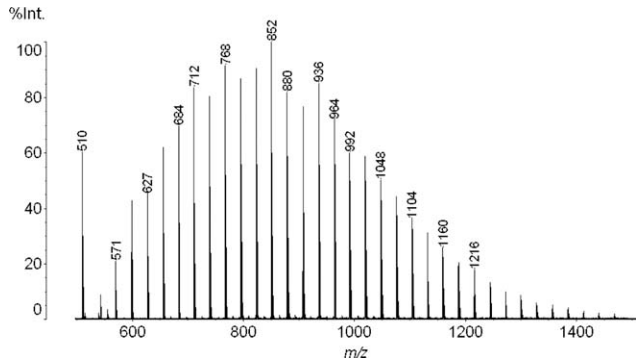


Figure 4 The MALDI-ToF molecular weight distributions for the PE-$PPh_3^+Br^-$ polymer. The peaks at m/z = 510 and 600 are due to a matrix adduct.

^{1}H-NMR spectroscopic analysis of the impure starting material, from our chromatographic resolution, and from MALDI-ToF MS analysis, are reported and discussed.

The facile chromatographic method developed has provided us with "pure" samples of PE-OH which we are in the process of exploiting in particular copolymer synthesis and related applications, upon which we will report in due course. However, the simultaneous serendipitous evaluation of the molecular weight distribution at high resolution may well have generic value to other groups involved in the characterization, for example, of telechelic precursors, block and graft copolymer components, and other polymeric materials falling in the oligomeric category. The primary requirement would seem to be either a rather hydrophobic backbone with a terminal or terminal groups which allow substantial interaction with silica in a non-polar eluant, or potentially a rather polar or hydrophilic backbone with a hydrophobic terminal or terminal groups to allow interaction with an appropriate SP under reverse phase conditions. Somewhat related ion-pairing procedures are used by chromatographers for identification purposes in the analytical scale analysis of small molecules, but as in the present work it seems that the concept can be adapted for the preparative fractionation and evaluation of the molecular weight distribution of organic oligomeric materials.

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