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Molecular weight fractionation of poly(methyl methacrylate) using Gas Anti-Solvent techniques

Emma M. Coen[a,*], John F. Quinn[a,b], Fariba Dehghani[c], Neil R. Foster[c], Thomas P. Davis[a,b]

[a]*Cooperative Research Centre for Polymers, School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia*

[b]*Centre for Advanced Macromolecular Design, , School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia*

[c]*School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia*

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Abstract

The solubility of poly(methyl methacrylate) in acetone, expanded by carbon dioxide, was studied at 20 °C for a variety of molecular weights and architectures. The suitability of the Gas Anti-Solvent method for fractionation of poly(methyl methacrylate) was investigated with positive results. The threshold pressure for precipitation of various monodisperse molecular weights was investigated, and the effectiveness of this technique to fractionate a polymer with a broad molecular weight distribution was evaluated. The pressure required to precipitate polymers was found to be low, generally below 60 bar.

Keywords: Supercritical fluids; Fractionation; Polymer processing

1. Introduction

Polymers have been fractionated by a variety of dense gas technologies. Several studies have investigated polymer dissolved directly into a supercritical fluid, and then precipitated by variation of pressure and temperature [1–5]. Polymers investigated in studies concerned with fractionation using supercritical fluids include polystyrene [4], polyethylene [3] and polydimethylsiloxane [4,6]. Fractionation of different architectures of molecules have been investigated, as in Ref. [2], where star poly(ethylene oxide) was fractionated from linear poly(ethylene oxide) of lower molecular weight using 1-chloro-1,1-difluoroethane. Supercritical fluids that have been employed for fractionation include ethane [1], ethylene, carbon dioxide [4–6], chlorodifluoroethane [2], propane and propylene [1,3].

Additionally, organic solvents have been used to tune the behavior of the supercritical fluids, as in the previous work by Bungert et al. in which the fractionation of low molecular weight polystyrene using a mixture of cyclohexane and supercritical carbon dioxide was investigated [7].

The Gas Anti-Solvent (GAS) technique is well known as a method for fractionating various materials [8–10]. The first reported work using the GAS process for purification was a solubility study of β-carotene in toluene or *n*-butanol expanded with carbon dioxide [11]. The GAS process has been used for the separation of isomers in a fundamental study in which a mixture of *ortho*- and *para*-hydroxybenzoic acid was separated by dissolution in methanol and expanding with carbon dioxide [12]. Low molecular weight materials, such as citric acid and oxalic acid, have been successfully separated by the GAS technique [9]. Similarly, separating low molecular weight materials, the fractionation in a single step of the protein systems lysozyme-ribonuclease, alkaline-phosphatase and trypsin-catalase, dissolved in DMSO and precipitated with CO_2, have been studied using the GAS process [13].

The GAS technique has several significant advantages when compared to traditional ‘solvent tuning’ methods. The pressure of the system can be controlled, and the diffusion of the anti-solvent throughout the system is rapid [8].

The work described herein differs substantially from

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[*] Corresponding author. Tel.: +612-9385-4324; fax: +612-9385-5966. *E-mail address:* e.coen@unsw.edu.au (E.M. Coen).

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previous studies in that anti-solvent techniques are utilized. The fractionation can be achieved at significantly lower pressures and temperatures when compared to other supercritical techniques. The GAS technique typically requires pressures in the order of 40–70 bar.

Since molecular weight affects the solubility of a given polymer [14], the objective of this study was to determine if solvent properties can be tuned to preferentially precipitate a high molecular weight fraction leaving the low molecular weight fraction in solution. In this study, the molecular weight of the star polymers differ by an order of magnitude from the linear precusor material ($\sim 1.2\times10^6$ g mol^{-1} for star shaped polymers, $\sim 6\times10^4$ g mol^{-1} for the linear component), which is present in significant amounts when polymerization is terminated. A simple method for fractionation of this material on the scale of grams is extremely desirable, as the reaction is of low yield. To obtain appreciable amounts of star polymer, grams of impure polymer must be processed.

2. Experimental

2.1. Materials

Acetone (HPLC grade) was used as supplied by Sigma Aldrich. Carbon dioxide (industrial grade/purity 99.5%), was used as supplied by BOC gases. Linear poly(methyl methacrylate) standards of varying molecular weight characterized by GPC were used. The 5.9×10^4 and 1×10^4 g mol^{-1} standards were prepared by catalytic chain transfer polymerization (CCTP) (polydispersity 1.8), and the 9×10^4 and 3×10^5 g mol^{-1} standards were supplied by Sigma Aldrich.

Fig. 1 shows a schematic of the reactions utilized in preparing the macromonomer and the star polymer.

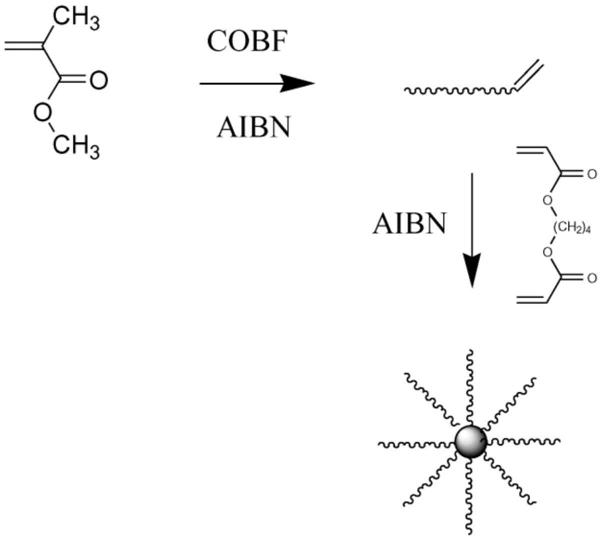

Fig. 1. Reaction mechanism for the formation of star poly(methyl methacrylate), via poly(methyl methacrylate) macromonomers.

Poly(methyl methacrylate) macromonomer was synthesized using CCTP. Methyl methacrylate (Aldrich, 99.9%) was purified by percolating over a column of activated basic alumina. Cobaloxime boron fluoride (COBF) was synthesized using the method of Bakac et al. [15]. A solution of methyl methacrylate (50 ml) in dry toluene (150 ml) was deoxygenated by bubbling nitrogen through it for 1 h. Using a syringe, 160 ml of this solution was then transferred to a two-neck flask under nitrogen, containing azobisisobutyronitrile (0.1044 g). A separate solution (10 ml) of 0.24 mg ml^{-1} COBF in methyl methacrylate was prepared, and then diluted to give a solution with concentration 0.024 mg ml^{-1}. Following deoxygenation, 6 ml of this solution were added to the reaction vessel. The solution was then allowed to polymerize at 60 °C for 24 h, with agitation. The resulting macromonomer was then collected via precipitation in *n*-hexane. The molecular weight was determined via size exclusion chromatography (SEC) and the yield via gravimetry ($M_w = 59{,}000$; yield = 78%).

Poly(methyl methacrylate) stars were prepared using a slight variation in the method of Antonelli et al. [16]. Following isolation, macromonomer (10.0 g) was redissolved in toluene (30 g). After dissolution, 1,4-butanediol diacrylate (2.0 g) and AIBN (0.1254 g) were added to the toluene solution. The mixture was then allowed to copolymerize at 80 °C for 72 h, giving a multi-armed star polymer with a highly branched core. The final polymer was isolated by evaporation of the solvent and residual monomer, initially in a fume cupboard, and then in a vacuum oven at 30 °C for 3 days. The molecular weight distribution was then measured using SEC. The molecular weight of the star polymer was 1.2×10^6 g mol^{-1}.

2.2. GAS Apparatus

A schematic of the GAS apparatus used in this study is shown in Fig. 2. The main component of the GAS apparatus was a high pressure view cell (Jerguson sight gauge AS-32 model). The clear borosilicate glass plate allowed for observation of the expansion of the organic phase, and the

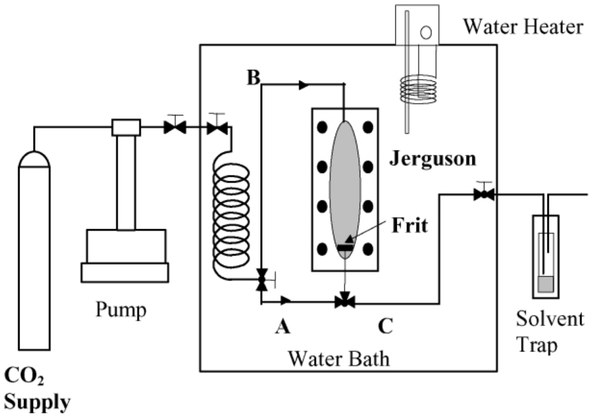

Fig. 2. Schematic diagram of GAS apparatus.

precipitation of the polymer. A frit at the bottom of the view cell was placed to ensure uniform dispersion of the carbon dioxide and to collect precipitated material. Liquid carbon dioxide was supplied from a cylinder and pressurized with a syringe pump (ISCO model 100DX), which was also used to control the pressure of the system. Sno-trik valves and Swagelok needle valves were used to isolate the system from the pump and to control the flow rate, respectively. Carbon dioxide was passed through the pre-heating coil, prior to the high pressure view cell, to approach the operating temperature. Carbon dioxide was fed into the view cell via lines A during the expansion and precipitation stage, or B, during the washing stage. A three way valve was used to control flow of carbon dioxide from the heating coil to line A or line B. The system pressure was monitored by a pressure transducer (Druck DRC 911) coupled to a Druck pressure indicator. The temperature of the water bath was controlled by a Thermoline Unistat heater/circulator. The experimental rig can be heated to 40 °C and pressurized to 200 bar.

2.3. GAS Procedures

A solution of 10% (w/w) poly(methyl methacrylate) in acetone (10 g) was prepared and transferred to the vessel. The vessel was then partially closed. The system was purged with carbon dioxide to a pressure of approximately 3 bar through line A to remove air, and the vessel was then sealed. The system was then left for 1 h to achieve thermal equilibrium. Carbon dioxide was then introduced to the vessel via line A, at 4 bar min^{-1}. Addition of carbon dioxide was monitored using the pressure indicator. The rate of addition of carbon dioxide was controlled by the needle valve on line A. At each temperature, the onset of precipitation for a given molecular weight of poly(methyl methacrylate) was monitored visually (by observing the onset of precipitation) and the pressure in the system noted. The pressure at which precipitation occurs has been referred to as the 'threshold pressure' [12]. The fractionation of polymer was performed using a similar method.

After precipitation of the polymer was complete, the organic solvent was purged from the vessel via line C. The purging process was achieved by feeding carbon dioxide from line B to line C at the threshold pressure. The addition of constant pressure carbon dioxide, at the threshold pressure will minimize the changes in expansion volume, minimizing additional precipitation or re-dissolution of the precipitated polymer. At least 100 ml of pressurized carbon dioxide was used in washing the organic solvent from the precipitated polymer. The organic solvent sample was then transferred to a collection vial, and the organic solvent allowed to evaporate off. Precipitated polymeric material was collected on the top of the frit in the vessel, washed with carbon dioxide for at least 20 min to remove residual solvent, and the system was then depressurized.

2.4. Measurements of molecular weight distributions

Molecular weight distributions were measured by SEC using a Shimadzu modular system, comprising an auto injector, two Polymer Laboratories PLgel 10 μm mixed-B columns and a differential refractive index detector. The eluent was tetrahydrofuran (THF) at 30 °C with a flow rate of 1 ml min^{-1}. The system was calibrated using narrow poly(methyl methacrylate) standards ranging from 200 to 10^7 g mol^{-1}, (supplied by Sigma Aldrich).

3. Results and discussion

3.1. Threshold pressures

Prior to attempting fractionation of polymer with a bimodal molecular weight distribution, the pressure required to precipitate a system of known, narrow molecular weight was determined. These threshold pressures provided a guideline for the pressures at which fractionation may occur.

The threshold pressure as a function of molecular weight at 20 and 50 °C is shown in Fig. 3. At both temperatures, threshold pressure decreases as the molecular weight increases. Furthermore, threshold pressures are greater at the higher temperature due to increased solubility of the polymer and decreased solubility of carbon dioxide in the organic solvent. The threshold pressure varied significantly over the molecular weights considered, which indicated that fractionation was feasible. A large change in threshhold pressure can be seen in Fig. 3, at an approximate molecular weight of 8×10^4 g mol^{-1}. At 20 °C, this corresponds to a threshold pressure of 30 bar, and at 50 °C, this corresponds to a pressure at 40 °C. The expansion of acetone is well characterized [17], and has a period of slow expansion, which eventually accelerates, resulting in rapid expansion of the organic solvent as pressure is increased. The discontinuity

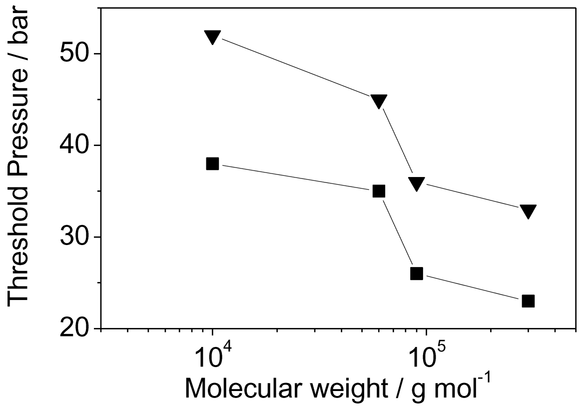

Fig. 3. Threshold pressure as a function of molecular weight, for linear monodisperse poly(methyl methacrylate) standards, at 20 °C (▼) and 50 °C (■).

in slope of threshold pressure corresponds to the onset of rapid expansion.

3.2. Separation of linear polymers

Once the threshold pressures for the standards were known, fractionation of two linear poly(methyl methyacrylate) standards was attempted. Two poly(methyl methylacrylate) standards were mixed in a 1:1 ratio (by weight), and a 10% (w/w) solution in acetone prepared. The molecular weights of the two linear standards were 6×10^4 and $9.2 \times 10^4\ \mathrm{g\ mol^{-1}}$. Both standards had polydispersity of 1.8. Precipitation was visually observed to commence at 26 bar. The heavy fraction was collected on the frit, and the light fraction purged from the view cell at 26 bar.

The molecular weight distributions of the two standards prior to fractionation, and the molecular weight distributions of the heavy and light fractions after fractionation, are shown in Figs. 4 and 5, respectively. It can be seen that despite the similarity in molecular weight, it was possible to separate the heavy and light fractions. A change in molecular weight occured for both fractions. The lower molecular weight fraction decreased from 6×10^4 to $5.1 \times 10^4\ \mathrm{g\ mol^{-1}}$ and the higher molecular weight fraction increased from 9.2×10^4 to $1.1 \times 10^5\ \mathrm{g\ mol^{-1}}$. A significant decrease in polydispersity is noted for both the high molecular weight material from 1.8 to 1.5 and for the lower molecular weight material from 1.8 to 1.4. The decrease in polydispersity and molecular weight suggests that relatively high molecular weight material in the $6 \times 10^4\ \mathrm{g\ mol^{-1}}$ standard was redistributed to the heavier fraction and that relatively low molecular material from the $9.2 \times 10^4\ \mathrm{g\ mol^{-1}}$ standard was redistributed to the light fraction.

3.3. Separation of star polymers from linear polymers

The formation of star polymers from macromonomer does not result in a perfectly complete reaction of macromonomer. The GAS technique was utilized to separate the macromonomer precursor, and the star polymer product. Precipitation was visually observed to commence at 23 bar, however, slight cloudiness of the solution was visible from 10 bar. The heavy fraction was collected on the frit, and the light fraction purged from the system at 24 bar.

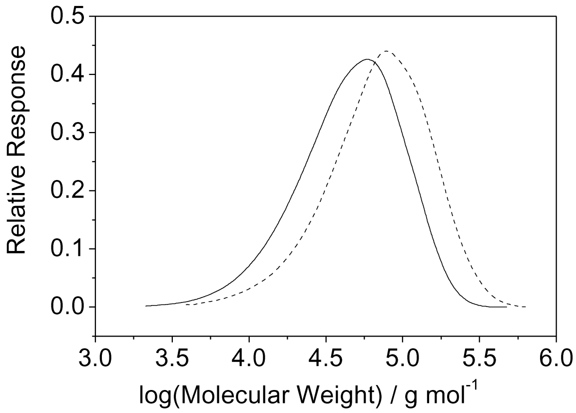

Fig. 4. Molecular weight distribution for linear polymer standards prior to separation, where (—) is the $6 \times 10^4\ \mathrm{g\ mol^{-1}}$ standard and (- - -) is the $1.1 \times 10^5\ \mathrm{g\ mol^{-1}}$ standard.

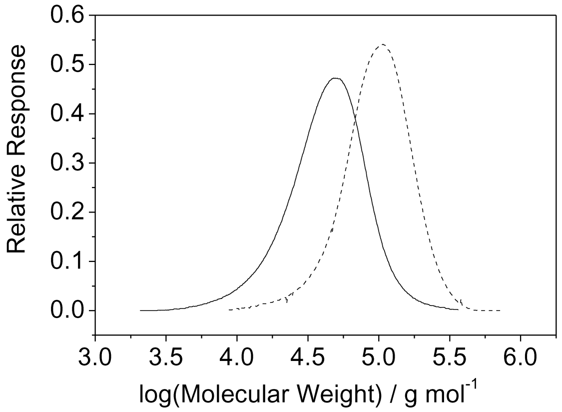

Fig. 5. Molecular weight distribution of linear polymer separated by GAS at 20 °C and 26 bar, from a 10 wt% solution of poly(methyl methacrylate) in acetone. (—) is the light fraction with a molecular weight of $5.1 \times 10^4\ \mathrm{g\ mol^{-1}}$ and (- - -) is the heavy fraction with a molecular weight of $9.2 \times 10^4\ \mathrm{g\ mol^{-1}}$.

The molecular weight distributions shown in Fig. 6 indicate the separation of star polymer and macromonomer was relatively successful. A small amount of low molecular weight material is still present in the heavy fraction, and some high molecular weight material can be observed in the light fraction. However, the improvement in purity of the star polymer is significant.

4. Conclusions

The GAS technique can be used to fractionate poly(methyl methacrylate) on the basis of molecular weight for both linear/linear polymers and linear/star polymers. The

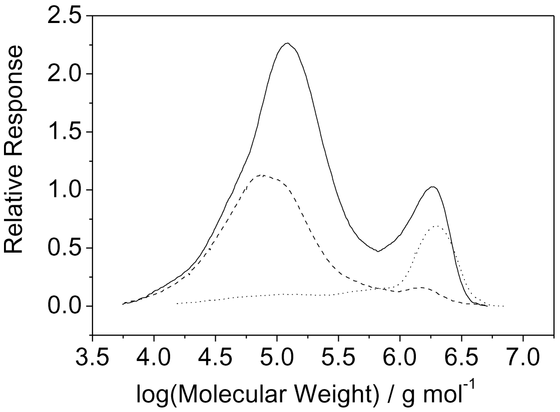

Fig. 6. Molecular weight distribution for a mixture of linear and star polymers separated by GAS at 20 °C and 23 bar. The original polydisperse polymer is indicated by (—), (- - -) is the light fraction and (···) is the heavy fraction.

fractionation of polymers using the GAS technique is significant, as prior work has focused on fractionation of low molecular weight material. One processing step can separate molecular weights that differ by only a factor of 2. The GAS technique achieves fractionation for poly(methyl methylacrylate), and may be applicable to other solvent and polymer systems. The fractionation of polymers using the GAS technique suggests the potential for 'one-pot' synthesis in a pressure vessel, then fractionation of polymeric materials, where the polymer is manufactured in a solution polymerization, with fractions precipitated by the addition of carbon dioxide.

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