

Liquid Exclusion Chromatography. A Technique for Monitoring the Growth of Polymer Particles in Emulsion Polymerization

S. SINGH and A. E. HAMIELEC, *Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada*

Synopsis

An experimental investigation of the growth of polymer particles in the emulsion polymerization of styrene and of vinyl acetate is reported. The growth of polymer particles in the size range of 200–6500 Å was monitored by liquid exclusion chromatography (LEC). This relatively new analytical technique permits very rapid analysis for particles as small as 200 Å and should prove extremely useful as an online monitor of polymer particle size for the control of latex reactors.

INTRODUCTION

In the past decade, gel permeation chromatography (GPC) or liquid exclusion chromatography (LEC) has been used extensively for the separation of polymer molecules according to their size in solution. Recently, these techniques have been adapted for the analogous separation of colloidal dispersions according to size. There are two complementary approaches to the use of column chromatography to separate particle suspensions according to size. The more powerful technique, LEC, utilizes porous packing and relies mainly on steric exclusion from the pores of the packing for size separation. The other, called hydrodynamic chromatography (HDC), utilizes nonporous packing and relies on velocity profiles in interstitial regions for size separation.

In 1971, Krebs and Wunderlich¹ prepared silica gel having very large pores (500–50,000 Å) which allowed column chromatography and, in particular, LEC of large poly(methyl methacrylate) and polystyrene latex particles. More recently, Gaylor et al.² and Coll et al.³ developed the technique further by careful selection of emulsifier and electrolyte to optimize resolution. Small⁴ recently reported on the development of HDC following the theory of Guttman and Di-Marzio.⁵ Cassassa⁶ has pointed out that it is not possible to make a phenomenological distinction between the separating mechanisms of LEC and HDC and that likely both mechanisms are operable with or without porous packing. HDC has been further developed by McHugh⁷ and Stoitsits et al.⁸

The basic separating mechanisms of LEC and HDC are compared diagrammatically in Figure 1. A bed packed with porous or nonporous packing presents the particles suspended in the carrier solvent with a tortuous path through a large number of capillary-like tunnels. Larger particles are excluded from regions near the capillary wall where axial velocities are small and hence experience on the average a higher velocity and smaller retention time. Porous packing presents an additional force for size separation by steric exclusion from the pores.

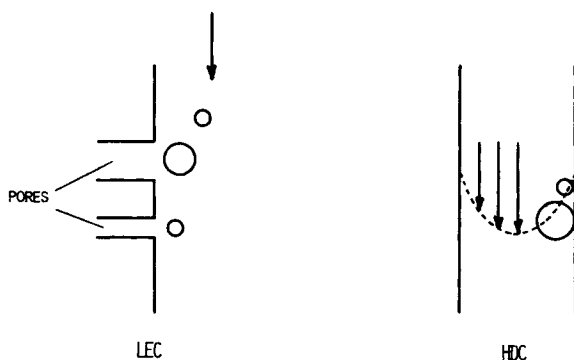


Fig. 1. Diagrammatic representation of the mechanisms of particle separation by liquid exclusion chromatography (LEC) and hydrodynamic chromatography (HDC).

The upper limit for size separation would likely be a result of plugging of interstitial capillaries.

LEC has certain advantages over competing analytical methods of measurement of particle size in the submicron range. For example, the Joyce-Loebl disk centrifuge is difficult to use with particles smaller than 1000 Å. Analysis time is too long considering the stability of the instrument. In addition, the density of the latex particle must be known with considerable accuracy if an accurate particle size is to be obtained.

We report here an investigation of the high-speed analysis of the size of growing polymer particles. This was the first step in an attempt to develop an on-line monitor for emulsion polymerization. With the use of packing with large pores, excellent resolution was obtained in the size range of 200–10,000 Å. Coll et al.³ used smaller pores and observed an upper resolution limit of about 3000 Å. We also investigated the effect of carrier fluid flow rate on peak separation in the range of 0.8–7.6 ml/min. The effect of flow rate on the particle diameter–retention volume calibration curve was minimal, and thus analysis time was re-

TABLE I

| Column no. | Packing type | Mean pore diameter, Å | Packing size, mesh |
|------------|--|----------------------------|----------------------------------|
| 1 | Fractosil 25,000 (E. Merck, Darmstadt) | 30,000 | 120–230 |
| 2 | Fractosil 10,000 | 14,000 | 120–230 |
| 3 | Fractosil 5,000 | 4,900 | 120–230 |
| 4 | CPG-10-1250 (Corning Glass Works, Corning, N.Y.) | 1,100 | 120–200 |
| 5 | BioGlass 2500 } in equal BioGlass 1500 } proportions BioGlass 1000 } | 2500 1500 1000 | 100–200 100–200 100–200 |
| 6 | (Corning Biological Products, Medfield, Mass.) Glass } in equal Glass } proportions Glass } | 400–800 200–400 <100 | 75–125 μ 75–125 μ 75–125 μ |
| | (Waters Associates, Inc.) | | |

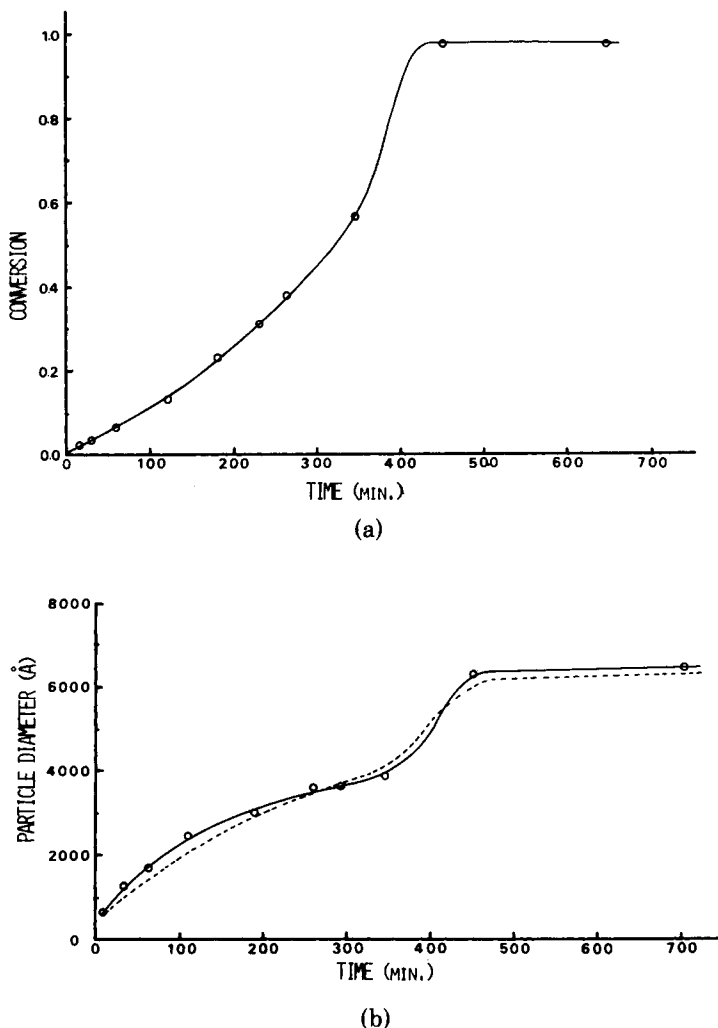


Fig. 2. (a) Conversion-time history for the surfactant-free emulsion polymerization of styrene at 70.5°C. (b) Particle diameter-time history for the surfactant-free emulsion polymerization of styrene at 70.5°C: (O) measured by LEC; (- -) measured by electron microscopy.⁹

duced from several hours to about 15–20 min. We believe that analysis time could be reduced further with the use of yet higher flow rates and smaller-diameter packing materials. Unfortunately, the flow rate of the carrier fluid was limited by the capacity of the pump employed in this investigation.

To demonstrate the use of LEC in an off-line mode in following the growth of polymer particles in emulsion polymerization, the experimental study of surfactant-free styrene emulsion polymerization after Goodall et al.⁹ was repeated. They followed the growth of particles in the size range of 700–6500 Å by electron microscopy and found the particles to be monodispersed. Figure 2(b) (dotted line) shows the growth of polymer particles measured by Goodall et al.⁹ using electron microscopy. To evaluate LEC with soft latex particles, we also investigated surfactant-free vinyl acetate emulsion polymerization.

EXPERIMENTAL

The following monodispersed particles were used as standards for the determination of the diameter-retention volume calibration curve: Polystyrene (PS) diam. 1.011 μ , PS 0.760 μ , and PS 0.481 μ from Union Carbide Corp., South Charleston, West Virginia; PS 0.312 μ and PS 0.234 μ from Dow Chemical Co., Midland, Michigan; PS 0.1760 μ from E. F. Fullam Inc.; PS 0.100 μ from Sohio, Cleveland, Ohio; PS 0.091 μ from E. F. Fullam Inc.; and silica 0.023 μ from (du Pont Ludox) Sohio, Cleveland, Ohio.

The calibration curve based on polystyrene standards was found to be universal by Coll et al.³ This observation was confirmed in the present investigation using latex particles having a variety of compositions.

The carrier solvent, which was water, contained 1 g/l. Aerosol OT (BDH Chemicals Co.) and 1 g/l. potassium nitrate. The carrier solvent employed here was identical to that recommended by Coll et al.³ No further optimization with regard to emulsifier and electrolyte type and amount was attempted.

A set of six columns (4 ft \times $\frac{3}{8}$ in.) with a total length of 24 ft were packed with porous silica and porous glass. Details of the packing material employed in each of the six columns are shown in Table I.

The flow rate of the carrier fluid was maintained at 7.6 ml/min. Solute charges were always less than 1 mg and were increased with larger particles. No attempt was made to inject a precise amount of solute (number of polymer particles). The detector was a Pharmacia UV spectrophotometer operated at 254 nm with a cell of 10-mm path length. The carrier fluid volume was monitored with a 5-ml siphon.

The surfactant-free emulsion polymerization of styrene was carried out at 70.5°C in a 5-liter round-bottom flask equipped with a condenser, stirrer, thermometer, and nitrogen purge. Freshly distilled styrene (181 g) and distilled water (1990 g) were allowed to equilibrate in the reaction flask for 30 min under stirring and nitrogen purge. Potassium persulfate (1.995 g) was dissolved in 10 ml distilled water at 70°C and then added to the reaction flask. This immediately initiated the polymerization. Samples of the latex were withdrawn at specified times, diluted at room temperature, and injected into the LEC to determine polymer particle diameter. It is unlikely that latex dilution at room temperature would result in complete extraction of unreacted styrene monomer from the polymer particles. The glass transition point of a solution of 10 wt % styrene in polystyrene is estimated to be about 25°C based on measurements

TABLE II
Measured Variances of LEC Chromatograms for the Surfactant-Free Emulsion Polymerization of Styrene at 70.5°C^a

| Reaction time, min | Particle diameter, Å | Variance, ml ² |
|--------------------|----------------------|---------------------------|
| 9.85 | 645 | 18.0 |
| 120 | 2480 | 17.1 |
| 705 | 6430 | 14.0 |

^a PS standard with diameter 0.312 μ had a variance of 14.2 and that with diameter 0.100 μ had a variance of 18.0.

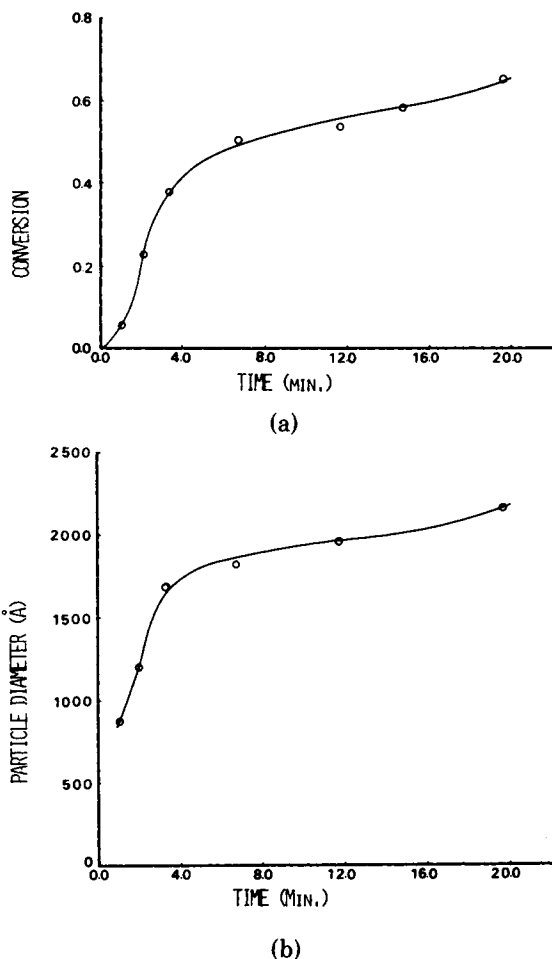


Fig. 3. (a) Conversion-time history for the surfactant-free emulsion polymerization of vinyl acetate at 85°C. (b) Particle diameter-time history for the surfactant-free emulsion polymerization of vinyl acetate at 85°C measured by LEC.

of limiting conversions.¹⁰ One might, therefore, expect that the polymer particles would contain a few per cent styrene monomer during analysis by LEC. The effect on particle diameter would be small. These polymerizations of styrene were almost identical to those done by Goodall et al.⁹

Surfactant-free emulsion polymerization of vinyl acetate was done at 85°C using the equipment and procedure given above. Freshly distilled vinyl acetate (25 ml), dimethylethanolamine (0.1 ml), and distilled water (695 g) were charged to the reaction flask and allowed to equilibrate for 30 min at 85°C under stirring and nitrogen purge. Ammonium persulfate (1.042 g) was dissolved in 5 ml distilled water at 85°C and added to the reaction flask to initiate polymerization. Samples of latex were withdrawn, diluted, and injected into the LEC to measure polymer particle growth.

In the polymerizations of styrene and vinyl acetate, monomer conversion was measured by gravimetry in the usual manner.

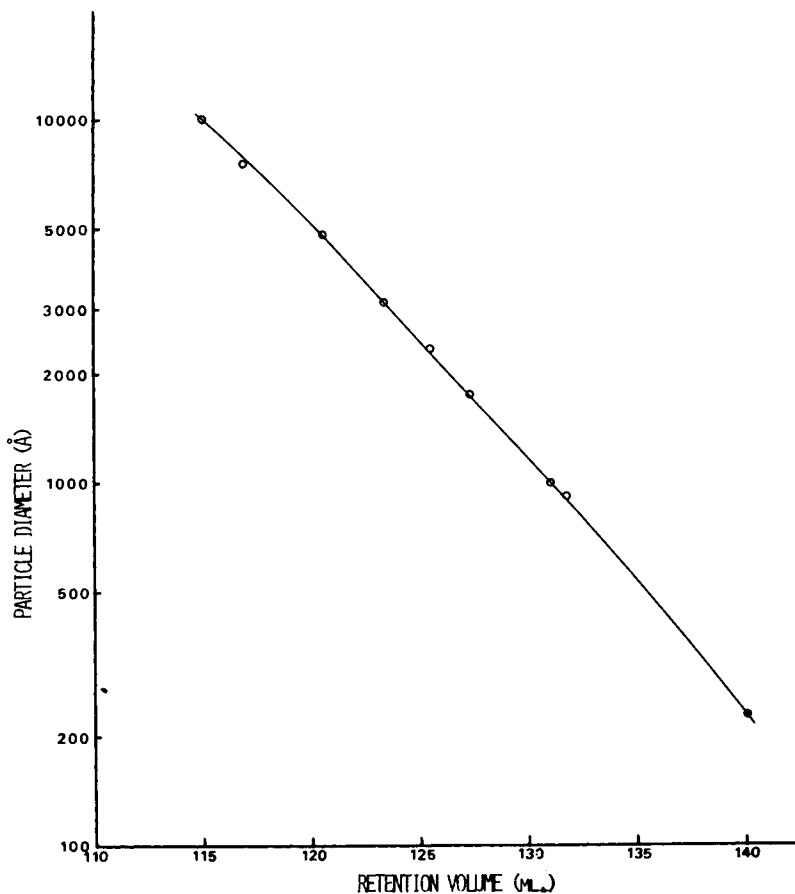


Fig. 4. Particle diameter-retention volume calibration curve for LEC obtained using polystyrene latex standards and silica: (○) PS standards; (●) silica standard.

RESULTS AND DISCUSSION

The particle diameter-retention volume calibration curve obtained is shown in Figure 4. The point on the curve at 230 Å is for silica, and the remaining points are for monodispersed polystyrene latices. Over the range of 200–10,000 Å, the calibration curve indicates satisfactory peak separation. The extent of axial

TABLE III
Measured Variances of LEC Chromatograms for the Surfactant-Free Emulsion Polymerization of Vinyl Acetate at 85°C

| Reaction time, min | Particle diameter, Å | Variance, ml ² |
|--------------------|----------------------|---------------------------|
| 1 | 870 | 26.7 |
| 2 | 1195 | 23.6 |
| 3.3 | 1710 | 26.2 |
| 6.7 | 1800 | 28.3 |
| 11.7 | 1950 | 26.6 |
| 19.7 | 2020 | 27.1 |

dispersion has not been of concern in this investigation of monodispersed latices and has, therefore, not been investigated here.

The growth of polystyrene particles measured by LEC and EM is shown and compared in Figure 2(b). It is seen that excellent agreement is obtained between LEC and electron microscopy even though the polymerizations were done in different laboratories. The conversion-time history shown in Figure 2(a) was measured in our laboratory and shows the typical acceleration in polymerization rate at higher conversions. As expected, the growth of the particle diameter also accelerates for the same reason. It should be emphasized that the LEC analysis time for each of the points shown in Figure 2(b) was about 15–20 min. It was also of interest to measure the variances of the LEC chromatograms for the samples in Figure 2(b) and to compare these with those for the PS standards available commercially. This is done in Table II. It is seen that the variance decreases with increasing time and particle size. This is to be expected because of the nature of emulsion polymerization where a finite time for particle nucleation is required. It can also be observed that the variances of the PS standards are of the same order as those found for our surfactant-free polymerization. This indicates that our polymer particles are essentially monodispersed or at least as much so as the PS standards. It should be mentioned that the above interpretation assumes that the variance due to axial dispersion is independent of particle size. This may indeed not be the case. However, a comparison of the variances for PS standards with those obtained for our styrene polymerizations is certainly valid. Goodall et al.⁹ showed that these polystyrene particles were monodispersed using electron microscopy.

The conversion-time and particle diameter-time histories for our emulsion polymerizations of vinyl acetate are shown in Figures 3(a) and (b). The results here are again as expected. The fact that PVAc latex particles are soft at room temperature did not cause any difficulties with LEC analysis. The measurement of the variances of the LEC chromatograms of PVAc particles indicated that these particles were almost monodispersed. These are tabulated in Table III.

To show that LEC could be used with soft as well as hard latex particles, we analyzed a number of polymer types including butylacrylate and butylacrylate/styrene/acrylonitrile and found no problems with column plugging as might have been expected.

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