

# Change in GPC Elution Volume of Polymers by Adsorption onto Porous Glass as Column Packing

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## Synopsis

The elution volume of polystyrene or of poly(ethylene glycol) of various molecular weights was measured in both tetrahydrofuran and benzene at 40 or 60°C by means of gel permeation chromatography utilizing columns packed with crosslinked polystyrene gel or porous glass. When the polystyrene gel was used as the column packing, a relationship between  $\log [\eta]M$  and the peak elution volume for polystyrene agreed with that for poly(ethylene glycol). Using columns packed with glass, however, the elution volume of polystyrene was smaller than that of poly(ethylene glycol) at the same  $\log [\eta]M$ . The results are considered to be attributable to the adsorption of poly(ethylene glycol) onto the glass. The effect of the adsorption on the elution volume was evaluated by assuming a universal calibration for columns containing porous glass; the deviation of the elution volume from the universal calibration curve increased with increase in molecular weight. At lower temperatures, even polystyrene was adsorbed onto the glass. Therefore, to reduce the adsorption of polymers on glass, it is necessary to increase the temperature or use surface treatment when porous glass is used as a GPC column packing.

## INTRODUCTION

Since Moore<sup>1</sup> developed crosslinked polystyrene gel, gel permeation chromatography (GPC) has been used as an effective method for characterizing the polydispersity of polymers. At present, crosslinked polystyrene gel of various pore sizes is on the market. In recent years, moreover, the application of aqueous gels or of other supports to GPC column packing has made possible the determination of the polydispersity of water-soluble polymers in aqueous systems.<sup>2-5</sup> Some authors have investigated the universal calibration of GPC varying polymer type, temperature, and solvent.<sup>6-9</sup> For example, Benoit et al.<sup>8</sup> reported that the relationship between  $\log [\eta]M$  and peak elution volume was the same for various homopolymers and copolymers. According to Cantow et al.,<sup>9</sup> on the other hand, a relationship between end-to-end distance and peak elution volume for some polymers gave a single curve, regardless of polymer type or temperature. However, polystyrene and other organic gels have the disadvantage that the degree of swelling of the gels varies with change in experimental condition such as temperature or solvent and that the gels are liable to degrade at high temperatures. Recently, silica or the porous glass called Controlled-Pore Glass or Bio-Glass has begun to be used as GPC column packing.<sup>3-5</sup> Silica and glass can be used at high temperatures. In addition, it is not necessary for such inorganic supports to take into account swelling by temperature or by solvent. When silica or porous glass having surface polarity is used as packing, the elution volume of samples is presumed to be affected by their adsorption onto the support. Cooper et al.,<sup>10</sup> treating the surface of porous glass and applying it to a GPC column

packing, obtained an elution curve different from the curve by applying untreated porous glass using polyisobutene as sample.

This report deals with a change in the GPC elution volume of polymers by applying porous glass to the column packing. The samples used were monodisperse polystyrene standards and monodisperse poly(ethylene glycols). For comparison with these homopolymers, styrene-ethylene oxide block copolymers were also used as samples.

## EXPERIMENTAL

The polymers used were the monodisperse polystyrene standards produced by Pressure Chemical Company, the monodisperse poly(ethylene glycols) by Nishio Industry Co., Ltd., and the styrene-ethylene oxide block copolymers prepared in tetrahydrofuran at  $-78^{\circ}\text{C}$  by anionic polymerization using cumyl potassium as an initiator.<sup>11</sup> The molecular weight  $M$  of the polystyrene standards was supplied by Pressure Chemical Company. The molecular weight of the poly(ethylene glycols) and the block copolymers was determined by means of vapor pressure osmometry from benzene solutions at  $37^{\circ}\text{C}$  using a Mechrolab model 302 A vapor pressure osmometer. The composition of the copolymers was determined by measuring high-resolution NMR spectra of solutions in carbon tetrachloride at room temperature using a Varian A-60 NMR spectrometer. Solution viscosity was measured in both tetrahydrofuran and benzene at 40 or  $60^{\circ}\text{C}$  using Ubbelohde dilution viscometers. The intrinsic viscosities  $[\eta]$  were obtained from a Huggins plot.

The GPC elution volumes of the polymers were measured in tetrahydrofuran at 40 and  $60^{\circ}\text{C}$  using a Waters Associates GPC model 200 equipped with a differential refractometer as concentration detector. Similar GPC measurements were carried out in benzene at  $60^{\circ}\text{C}$ . The GPC apparatus was equipped with five stainless steel columns 122 cm long, containing the crosslinked polystyrene gel with pore sizes of 50-80, 150-350, 700-3000,  $10^3$ , and  $8.5 \times 10^3$  Å produced by Waters Associates, or eight columns 61 cm long containing Controlled-Pore Glass with pore sizes of 75, 75, 170, 170, 350, 700, 700, and 1,400 Å by Electro-Nucleonics, Inc. Siphon volume was 5 ml, and injection loop was 2 ml. Flow rate was controlled to 1.0 ml/min using a Milton Roy minipump. Polymer concentration was adjusted to 0.1-0.2 wt %. In this concentration range, the effect of polymer concentration in the elution volume was hardly discernible.

## RESULTS AND DISCUSSION

Characterization of the polymers used are detailed in Table I. The samples designated PSt are the monodisperse polystyrene standards. The samples labeled PEG are the monodisperse poly(ethylene glycols). Samples Block-1 and Block-2 are the AB block copolymers of polystyrene and poly(ethylene oxide) prepared by anionic polymerization in our laboratory.<sup>11</sup> The molecular weights of the copolymers are uncertain because of determination by means of vapor pressure osmometry. The composition of the block copolymers is denoted by the weight percentage of the polystyrene block.

Figure 1 shows the relationship between  $\log M$  and peak elution volume  $V_e$  for polymers eluted in tetrahydrofuran at  $40^{\circ}\text{C}$ , utilizing columns packed with

TABLE I  
Characterization of Polymers

Polymers	MW	$[\eta]_{\text{THF}}^{40^\circ\text{C}}$	$[\eta]_{\text{THF}}^{60^\circ\text{C}}$	$[\eta]_{\text{benzene}}^{40^\circ\text{C}}$	$[\eta]_{\text{benzene}}^{60^\circ\text{C}}$	Composition <sup>c</sup>
PSt-1	20,400 <sup>a</sup>	0.147	0.129	0.147	0.135	
PSt-2	10,500 <sup>a</sup>	0.098	0.083	0.091	0.091	
PSt-3	4,000 <sup>a</sup>	0.056	0.040	0.054	0.047	
PSt-4	2,030 <sup>a</sup>	0.043	0.034	0.035	0.034	
PEG6000	11,300 <sup>b</sup>	0.167	0.153	0.187	0.175	
PEG4000	3,800 <sup>b</sup>	0.091	0.078	0.094	0.075	
PEG2000	2,030 <sup>b</sup>	0.064	0.057	0.062	0.059	
PEG1000	1,110 <sup>b</sup>	0.044	0.036	0.033	0.035	
Block-1	40,000 <sup>b</sup>	0.298	0.267	0.327	0.307	13.3
Block-2	39,500 <sup>b</sup>	0.314	0.286	0.342	0.319	5.5

<sup>a</sup> Molecular weight proposed by Pressure Chemical Company.

<sup>b</sup> Molecular weight determined by V. P. O. from benzene solutions at 37°C.

<sup>c</sup> Composition denoted by the weight percentage of polystyrene blocks.

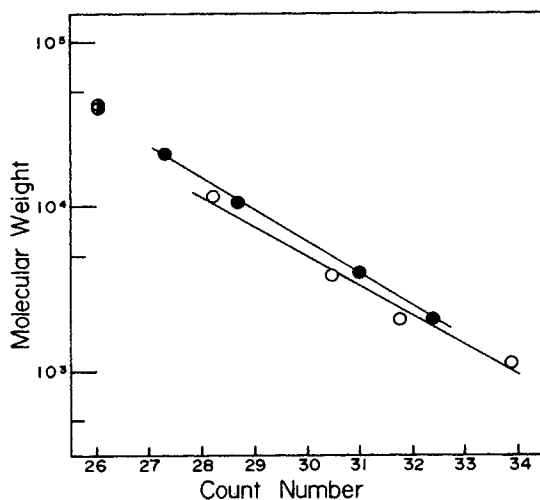


Fig. 1. Relationships between molecular weight and elution volume in tetrahydrofuran at 40°C utilizing columns packed with polystyrene gel: (●) polystyrene; (○) poly(ethylene glycol); (◐) styrene-ethylene oxide block copolymer.

the crosslinked polystyrene gel. The elution volume is expressed by count number. As shown in Figure 1, the relationship gives a straight line for individual polystyrene and poly(ethylene glycol). In general, this relationship is characteristic of the polymer type and varies with change in experimental conditions such as temperature or solvent, because the elution volume of polymers depends on their hydrodynamic volume in solution when crosslinked polystyrene gel is used as the column packing.<sup>12</sup> Figure 2 shows the result drawn over again for Figure 1 by a plot of  $\log [\eta]M$  vs.  $V_e$ . The relationship between hydrodynamic volume and  $V_e$  has been investigated theoretically or experimentally by some authors<sup>6-9</sup> and considered to be a universal calibration for linear flexible-coil

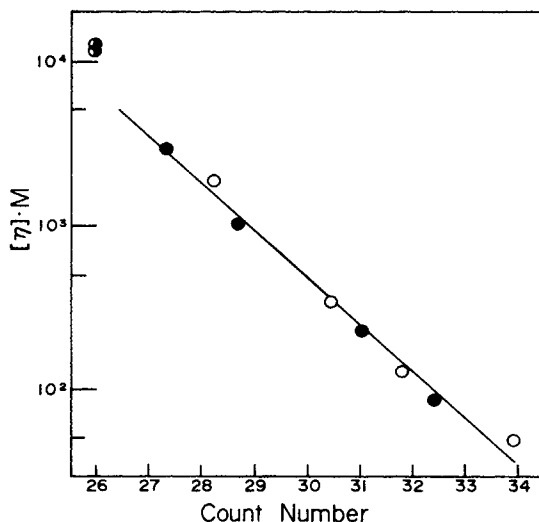


Fig. 2. Plots of  $\log [\eta]M$  vs.  $V_e$  in tetrahydrofuran at 40°C utilizing columns packed with polystyrene gel: (●) polystyrene; (○) poly(ethylene glycol); (◐) styrene-ethylene oxide block copolymer.

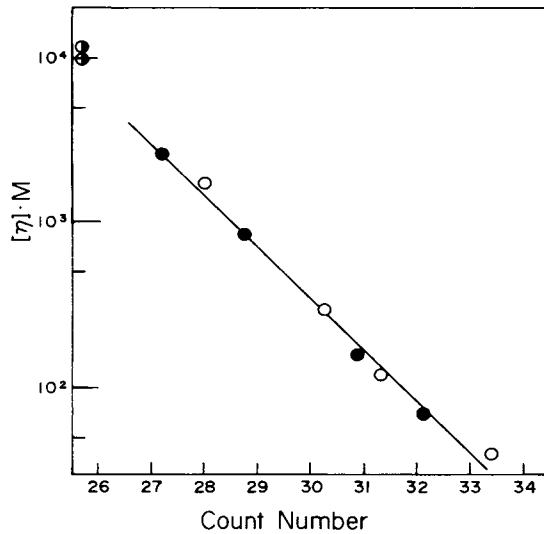


Fig. 3. Plots of  $\log [\eta]M$  vs.  $V_e$  in tetrahydrofuran at 60°C utilizing columns packed with polystyrene gel: (●) polystyrene; (○) poly(ethylene glycol); (⊙) styrene-ethylene oxide block copolymer.

polymers. As shown in Figure 2, the relationship is the same for the samples used. In Figure 3, the relationship obtained at 60°C is also the same for the samples. Using columns packed with the crosslinked polystyrene gel, consequently, the polymer molecules are considered to be separated only by the hydrodynamic volume in solution.

Similar GPC measurements were carried out by the use of columns packed with the porous glass called Controlled-Pore Glass. The relationship between  $\log [\eta]M$  and  $V_e$  for the samples in tetrahydrofuran at 40°C is shown in Figure 4. In contrast to the results obtained by the use of columns packed with cross-

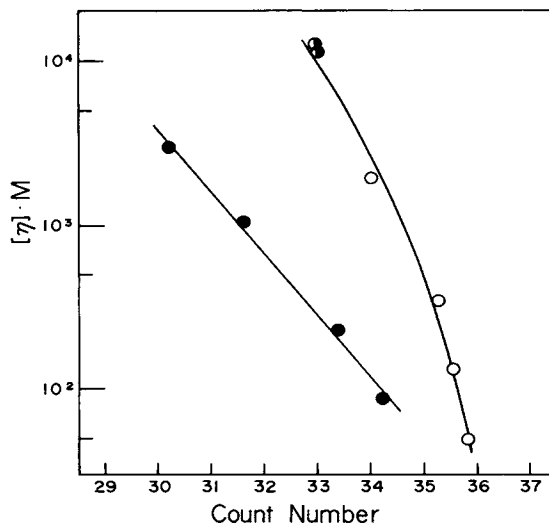


Fig. 4. Plots of  $\log [\eta]M$  vs.  $V_e$  in tetrahydrofuran at 40°C utilizing columns packed with porous glass: (●) polystyrene; (○) poly(ethylene glycol); (⊙) styrene-ethylene oxide block copolymer.

linked polystyrene gel, the relationship for polystyrene is distinct from that for poly(ethylene glycol) and the elution volume of poly(ethylene glycol) is larger than that of polystyrene at the same  $\log [\eta]M$ . The elution volume of the block copolymers is similar to that of the corresponding poly(ethylene glycol). The behavior of the block copolymers in the columns is considered to be governed by that of the poly(ethylene oxide) block because the styrene content is too small. The results can be attributed to the adsorption of poly(ethylene glycol) or of the poly(ethylene oxide) block onto the glass in the columns.

The elution volume of the polymers was also measured in both tetrahydrofuran and benzene at 60°C using the same columns. Figure 5 shows a plot of  $\log [\eta]M$  vs.  $V_e$  for the polymers in each solvent at 60°C. In benzene, poly(ethylene glycol) and the block copolymers were not eluted. These polymers are considered to be completely adsorbed on the glass. Consequently, the effect of the adsorption of polymers onto the glass on elution volume is considered to be changed by polymer type, temperature, and solvent. This concept is supported by results from both polystyrene and poly(ethylene glycol) in tetrahydrofuran at 40 and 60°C. Comparing the result obtained at 40°C with that at 60°C, even the elution volume of polystyrene in tetrahydrofuran at 40°C is evidently affected by the adsorption. The relationships between  $\log [\eta]M$  and  $V_e$  for polystyrene in both tetrahydrofuran and benzene at 60°C are shown respectively by two different lines in Figure 5, but they appear to be almost the same with an error of about 0.2 count. If the polystyrene molecules are separated only by the hydrodynamic volume in solution at 60°C by the use of columns packed with porous glass, the relationship can be assumed as a universal calibration. By this assumption, the information on the effect of the adsorption of poly(ethylene glycol) onto the glass will be found.

Figure 6 shows the effect of the adsorption on the elution volume by varying the molecular weight of poly(ethylene glycol) at both 40 and 60°C. In Figure 6,  $\Delta V_e$  is defined by a difference in elution volume between the universal cali-

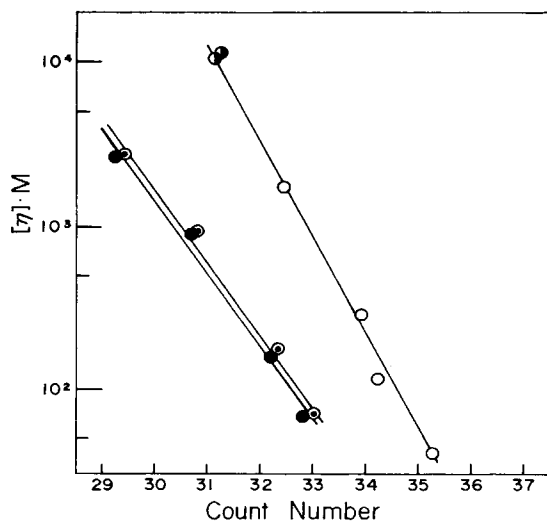


Fig. 5. Plots of  $\log [\eta]M$  vs.  $V_e$  in tetrahydrofuran or in benzene at 60°C utilizing columns packed with porous glass: (●) polystyrene; (○) poly(ethylene glycol); (◐) styrene-ethylene oxide block copolymer; (◑) polystyrene in benzene.

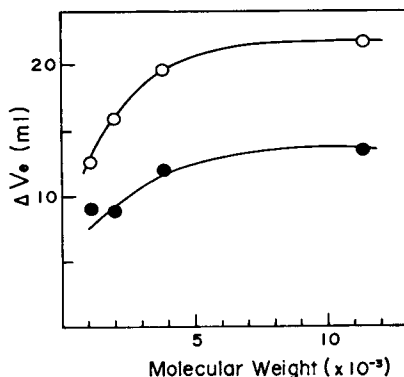


Fig. 6. Dependence of molecular weight of poly(ethylene glycol) on  $\Delta V_e$ : (O) 40°C; (●) 60°C.

bration assumed and the peak elution volume of poly(ethylene glycol) at the same  $\log [\eta]M$  using columns packed with porous glass. At both 40 and 60°C,  $\Delta V_e$  increases with increase in the molecular weight of poly(ethylene glycol). The effect of the molecular weight on  $\Delta V_e$  is remarkable, particularly below 5,000. On the other hand,  $\Delta V_e$  appears to scarcely increase with increase in molecular weight above 10,000. Results in Figure 6 evidently show that an increase in the elution volume of poly(ethylene glycol) is attributable to the adsorption onto the porous glass and suggest that poly(ethylene glycol) adsorbs onto glass not by endgroups but mainly by adsorption points on the polymer chain. At the same molecular weight of poly(ethylene glycol), the  $\Delta V_e$  at 60°C is smaller than that at 40°C. Therefore, the effect of the adsorption in elution volume is considered to be reduced by making polymers elute at higher temperature.

In conclusion, the relationship between  $\log [\eta]M$  and  $V_e$  is independent of polymer type when the columns are packed with crosslinked polystyrene gel. Utilizing columns packed with porous glass, the relationship for poly(ethylene glycol) differs from that for polystyrene and varies with change in experimental condition. When the polydispersity of a homopolymer is measured by GPC, the elution volume can be justified by using the corresponding calibration curve. However, the result from the columns packed with porous glass will be worse in accuracy than that from columns containing polystyrene gel because of the adsorption of sample onto the glass. In the case of a copolymer, the elution volume measured by the use of columns containing glass is hardly justified by any calibration curve because the effect of the adsorption onto the glass on the elution volume is considered to vary not only with molecular weight but also with composition. It is necessary to reduce the polarity of the surface of porous glass when columns packed with the glass are used to determine the polydispersity of polymers, especially that of copolymers.

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