

Liquid Chromatography of Polymer Mixtures Applying Combination of Exclusion and Full Adsorption Mechanisms.

I. Analysis of Polystyrene in its Mixture with Polymethylmethacrylate Single Column/Single Eluent Approach

MIROSLAV JANČO,^{1,*} TATYANA PRUDSKOVA,² and DUŠAN BEREK¹

¹Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovakia;

²Research Institute of Plastics, Perovsky proezd 35, 111 112 Moscow, Russia

SYNOPSIS

Components of polymer mixtures with different chemical composition can be separated by liquid chromatography by applying appropriate conditions (column packing, eluent, temperature, and pressure) in which just one type of macromolecule is eluted in the size exclusion mode while the other component is fully retained within on column packing. The feasibility of this idea has been demonstrated using the mixtures of polystyrene (PS) plus polymethylmethacrylate (PMMA) with silica gel as the column packing and toluene as an eluent. The PMMA was retained by the silica gel at ambient temperature and moderate pressures of several MPa while the PS was eluted by a typical SEC mechanism. Furthermore, the molar mass distribution of the PS could be determined in one step with the same precision as if injected alone. Surprisingly large amounts of PMMA were trapped within the column prior to its SEC characteristics being influenced. After a series of analyses the column has to be regenerated with a brief flushing with a desorbing liquid, tetrahydrofuran in the system studied. The re-equilibration of the column with the initial eluent, toluene, was fast and a new series of analyses could be started soon after the characterization step had seen finished. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Size exclusion chromatography (SEC), also called gel permeation chromatography, is the most commonly used method for molecular characterization of polymers. However, the straightforward application of conventional SEC procedures to polymer mixtures is possible only if the mean hydrodynamic volumes of particular constituents of multicomponent polymer systems are fairly different so that the species of given chemical composition can be fully resolved by the column used. In this case one observes two, or several, peaks on the chromatogram, one for each polymeric constituent, and their mean

molar mass (M) and molar mass distribution (MMD) data can be separately calculated in the usual way.

To extract the M and MMD values of constituents of polymer mixtures from chromatograms containing partially overlapped peaks, one must use the methods of mathematical deconvolution and estimate the shapes of MMD functions. An alternative method is to apply detectors with different sensitivities for particular constituents, including highly specific detectors that can see only one constituent of the polymer mixture. The latter approach can also be used if the peaks of particular constituents are completely unresolved. However, the SEC retention volumes of coeluting polymers are mutually influenced due to intermolecular interactions of macromolecules both in the injected solution and in the chromatographic zones traveling along the col-

* To whom correspondence should be addressed.

umn. The mutual influence grows with the extent of zone overlapping as well as with the increasing incompatibility of polymer mixture constituents.¹ Consequently, the M and MMD data calculated from a SEC chromatogram containing partially resolved or fully overlapped peaks are of rather limited precision.

To avoid the above problems, the constituents of the analyzed polymer mixture can be selectively modified, e.g., by degradation or crosslinking to change the size of their macromolecules or to make them insoluble. Another approach comprises the batch pre-separation steps, e.g., by selective dissolution or precipitation. These procedures, however, are often difficult to carry out quantitatively and are highly demanding as to the sample, time, and especially manpower consumption.

The most elegant and straightforward procedures for pre-separation of polymer mixtures prior to proper SEC analysis undoubtedly involve liquid chromatography. The chromatographic procedures are fast, non-laborious, and need relatively small amounts of sample. Often, they can be carried out in an on-line arrangement so that the pre-separation is directly followed by the SEC analysis of at least one constituent of the polymer mixture.

Any chromatographic mechanism can be applied to pre-separation of polymer mixtures, however, procedures based on adsorption, partition, and precipitation/dissolution are the most likely to be applied to synthetic polymers.

Several interesting ideas have been published in this area, e.g., Balke's "orthogonal chromatographic" procedures²; "gel permeation chromatography under critical conditions" (Belenkii and Gankina,³ Tennikov et al.,⁴ Gorbunov and Skvortsov,⁵ and Pasch⁶); or the Hunkeler et al.^{7,8} proposal to use nonsolvents as a mobile phase for analysis of polymers while the samples are injected as solutions in good solvents, limiting conditions. However, the above procedures have currently not developed to the stage needed for their application to the routine analysis of polymer mixtures.

In this paper we shall discuss various possibilities for chromatographic discrimination of the constituents of polymer mixtures through a combination of SEC and full adsorption mechanisms. We shall also verify the idea that active, preferably non-swelling, solid SEC column packing such as silica gel, porous glass, alumina, or porous carbon can be used in combination with eluent of low or medium polarity. Under these conditions, the more polar constituent of the polymer mixture is retained within the column and cannot interfere with a less polar

polymer that is eluted according to a size-exclusion mechanism. In other words, the more polar polymer is trapped within the column while the less polar polymer is analyzed by the conventional SEC procedure. After analysis or a series of analyses have been accomplished, the adsorbed polymer is eliminated from the column by a brief flushing with a more polar, desorbing liquid, that is an "SEC eluent."

In the following series of papers we shall concentrate on binary model mixtures comprising polymers, narrow fractions of which are readily available. Many of our conclusions, however, can be both generalized to other polymers and extrapolated to multicomponent polymer systems.

At least two questions immediately arise in connection with the above idea: (i) how much of a polar polymer can be trapped within a conventional SEC column, and (ii) does the adsorbed polymer influence the SEC retention characteristics of the eluting polymer.

These two questions can be combined into one: Is this simple idea experimentally feasible? In the following sections we shall show that it is possible to combine exclusion and full adsorption mechanism in a single column/single eluent system.

EXPERIMENTAL

A size exclusion chromatography system was used, comprised of the Waters Model 501 pump, the Model PK 1 injector valve with a 12 μ L loop (Institute of Chemical Processes Fundamentals, Czechoslovak Academy of Sciences, Prague, Czech Republic), and a RIDK 102 differential refractive index detector (Laboratory Instruments Co., Prague, Czech Republic). A Model DDL-21 evaporative light-scattering detector (Cunow, Cergy Pointoise, France) was also employed. Pressure was measured with a custom-made pressure gauge (0–25 MPa) (Institute of Chemical Processes Fundamentals, Czechoslovak Academy of Sciences, Prague, Czech Republic). The refractive index difference or scattered light signals were recorded on a Type TZ two-pen chart recorder (Laboratory Instruments Co., Prague, Czech Republic). The data were also collected on-line using a Waters PC-Based Data Acquisition System.

Chromatographic measurements were made on bare silica gel sorbent SGX-500 (Tessek Co., Prague, Czech Republic). Approximately 3.5 g of material was packed in a 250 mm stainless steel column with an ID of 6 mm.

Narrow polystyrene (PS) standards with mass-average molar masses of 666, 2.6 K, 10.1 K, 17.5 K, 37 K, 97.2 K, 233 K, 498 K, 1.2 M, 2 M, and 6.77 M g/mol (polydispersity 1.06–1.20) were obtained from Pressure Chemicals Co., USA.

10 μL of PS solutions in toluene were injected in the course of calibration curve determinations. The injected concentration was 1.0 mg/mL with the RIDK-102 detector and 0.5 mg/mL with the DDL-21 detector system. A broad sample of PS with 15 K g/mol was also used, prepared at the Polymer Institute by radical polymerization.

To study the adsorption effects, 200 μL portions of polymethylmethacrylate (PMMA) solutions in toluene with concentration of 10 mg/mL were repeatedly injected into the column. A broad PMMA, prepared by radical polymerization at the Polymer Institute and having a molar mass of 8 K g/mol, was used for this purpose.

Analytical-grade toluene, obtained from Lachema (Brno, Czech Republic), was used as mobile phase at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Our preliminary experiments showed that narrow and broad fractions of polymethyl methacrylate were

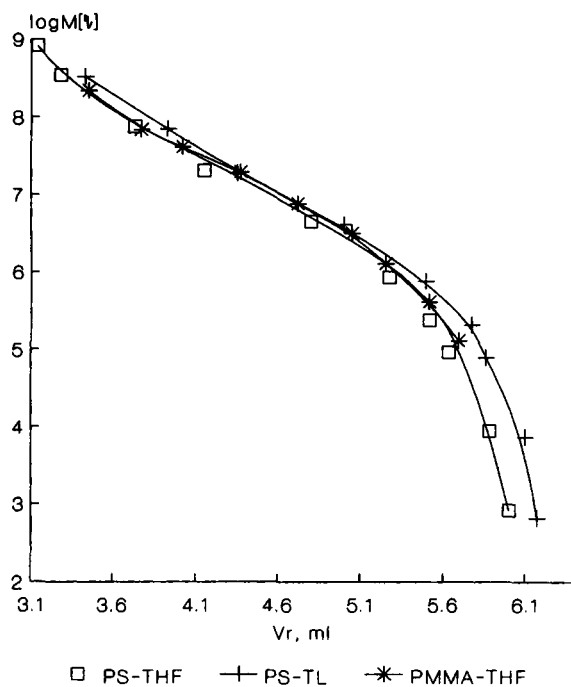


Figure 1 Universal calibration curves for PS in THF and toluene and for PMMA in THF. Column SGX-500.

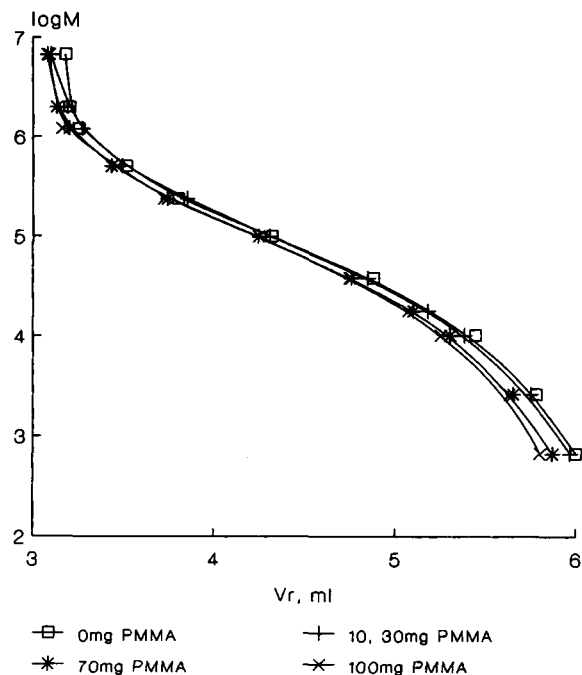


Figure 2 Influence of adsorption of PMMA on the calibration curves for PS. Column SGX-500 and toluene as eluent.

fully retained within a column packed with silica gels with 50 nm-pore diameter when toluene was used as eluent at ambient temperature. On the other hand, it is known that polystyrene is eluted in the SEC mode in many solvents over SiO_2 -based column packings and that it follows a universal calibration,⁹ e.g., coincides in benzene and trichloromethane.¹⁰ We have confirmed the same behavior of PS in tetrahydrofuran and toluene (Fig. 1). Moreover, PMMA and PS give the same universal calibration curve in tetrahydrofuran (Fig. 1). One can conclude that toluene can be used as “adsorbing eluent” for PMMA while it is an SEC eluent for PS. On the other hand, tetrahydrofuran is the SEC eluent for both polymer species and it can be used as desorbing liquid for PMMA.

The adsorbing ability and capacity of silica gel with $D = 50$ nm in toluene for PMMA was checked with a polymer of molar mass 8 K g/mol. 200 μL of PMM solution containing 10 mg/mL of polymer was repeatedly injected into the column and the baseline was steadily controlled. After a given number of injections the calibration curves for PS were measured. The results are summarized in Figure 2. We found no measurable deviation of the PS calibration curve up to at least 3 mg of PMMA adsorbed per one gram of silica gel column packing. In other words, at least 600 analyses of 1:1 mixtures of PMMA plus PS can

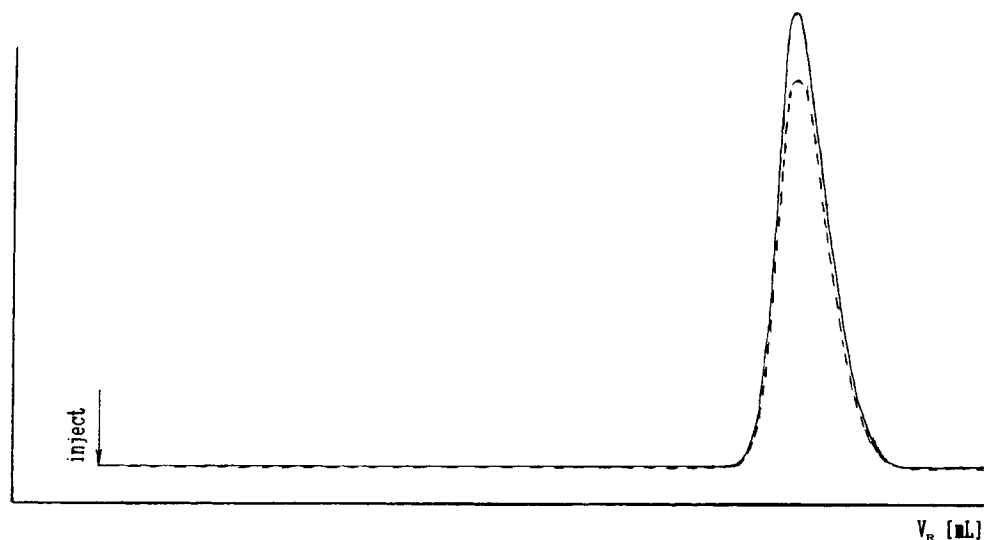


Figure 3 Typical chromatograms of a broad PS injected alone (—) and in the mixture with broad PMMA (---) into a silica gel column using toluene as eluent.

be made with a typical 250×6 mm SEC column packed with about 3.5 g of silica gel—before which it is necessary to remove trapped PMMA by flushing the column with a desorbing liquid. Certainly, the limiting amount of adsorbed polymer that still does not influence the calibration curve of non-adsorbed polymer must be checked for each chromatographic system (column packing/nonpolar solvent/more polar polymer). Still, this result indicates that the sorbent capacity will not limit the experimental feasibility of the procedure tested.

The calibration curve for PS shifted significantly toward lower retention volumes when the column packing trapped more than 10 mg of PMMA (Fig. 2). The shift to lower V_R can easily be explained, since the effective pore size of silica gel is decreased by the adsorbed macromolecules. It is probable that some repulsive interactions between the loops of adsorbed PMMA and passing PS macromolecules also increase this effect, since PMMA and PS in toluene are incompatible.¹¹

After the silica gel column packing had been saturated with PMMA, i.e., at 28.5 mg of adsorbed PMMA per one gram of silica gel (about 100 mg of PMMA per column used), polymethyl methacrylate started to elute, producing poorly shaped peaks.

At the point of saturation, the PS calibration curve was further shifted towards lower retention volumes in the region of lower molecular mass of PS. Surprisingly, however, the V_{RS} of higher polystyrenes practically coincided with the retention volumes measured with bare silica gel not containing adsorbed PMMA. The shifts were even lower for highest polystyrene (Fig. 2). The discussion of this

unexpected behavior will require further experimental data.

The adsorbed PMMA was flushed from the column with 25 ml of THF. The desorbing liquid was evaporated and the dry PMMA weighed. The recovery of PMMA was found to be almost 100%. Subsequently, the column was re-equilibrated with 20 ml of toluene, i.e., approximately three volumes of liquid within the column, in order to obtain a stable baseline as determined with a RI detector. The freshly injected PMMA was again fully retained within the column and the PS calibration curve perfectly coincided with the initial one, i.e., with the calibration curve measured prior to any PMMA adsorption. This shows that the column reequilibration is so fast and complete that precise and repeatable SEC results can be obtained even after long-term multiple use.

The direct influence of the PMMA presence on the M and MMD data of PS measured by SEC was

Table I Molar Mass Characteristics for the Same Polystyrene Obtained with Using Different Columns Packing and Toluene as Eluent

Polymer	M_w	M_n	M_w/M_n
PS 1			
Column PL-gel	14800	9100	1.6
PS 1			
Column Si-500	15200	8900	1.7
PS 1 + PMMA			
Column Si-500	15000	8700	1.7

tested with a broad PS sample. This was injected both alone and together with PMMA (1:1 by weight); the result is shown in Figure 3. The data calculated from presented chromatograms are collected in Table I, where the control values obtained with SEC using polystyrene gel are also given. The agreement of particular values is very good.

CONCLUSION

Using an active gel and a non-polar eluent, it is possible to separate constituents of a polymer mixture differing in their polarity. The more-polar adsorbing polymer is fully retained within the column, while the non-adsorbed polymer can be directly analyzed in the SEC mode. The retained macromolecules can be quantitatively desorbed in the next step and analyzed separately. The eluent and column switching procedures would allow for the analysis of the retained polymer in a next step.

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