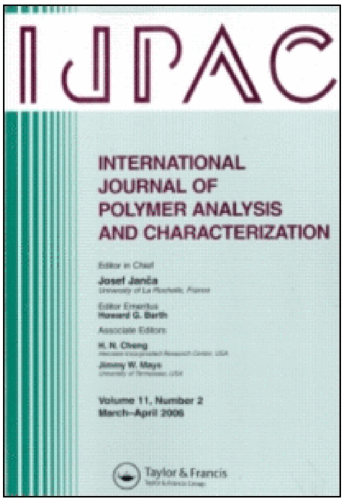

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Separation and Simultaneous Molecular Weight Determination of PVDF in PVDF/PMMA Blends Based on Adsorption/Size Exclusion

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With dimethylsulfoxide (DMSO) as the eluent, a PMMA (poly(methyl methacrylate)) standard injected in a polystyrene/divinyl benzene column at 35°C does not elute out. On the other hand, under the same chromatographic conditions, a PVDF standard (poly(vinylidene fluoride)) will elute out. We use this property to separate PVDF from PMMA in a blend of the two polymers. The blend is dissolved in DMSO, filtered, and directly injected. The chromatogram features the peak that corresponds to the PVDF and the solvent peaks, but the PMMA is absent. The molecular weight distribution of the PVDF can be calculated using a broad molecular weight PVDF standard.

Keywords:

INTRODUCTION

There are three modes of separation in the chromatography of polymers[1]. In the size exclusion mode, the hydrodynamic volume of the polymeric chain is the factor controlling the elution time. In the adsorption mode, it is the adsorptive interaction between the polymeric chain and the stationary phase that dominates. In the critical mode the effects of size exclusion and adsorption compensate each other exactly.

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The transition from one mode to the other can be done by changing the composition or by changing the temperature of the eluent and keeping the composition unchanged.

Blending two or more polymers allows one to obtain a material with new properties that can have significant advantages over the single polymers. It is often a cheaper alternative to designing new materials. Characterizing the molecular weight distribution of a blend is difficult since the two components of the blend will often partially coelute. Consider the case of a polymer blend (say, A and B, A being the component of interest). If one can find the chromatographic conditions where polymer B is fully adsorbed, and if under these conditions A is in the exclusion mode, one could separate the two polymers and obtain the molecular weight distribution of polymer A with a single chromatographic analysis. The advantages of this method are obvious when compared to an extraction method. This method could be quick to implement because the separation/fractionation would be done in one injection.

In this article we describe a method to characterize blends of polyvinylidene fluoride/polymethyl methacrylate (PVDF/PMMA). The goal is to obtain the chromatogram of the PVDF component and its concentration in the blend.

INSTRUMENTATION

A Waters 600 pump with a 717 plus autosampler and a 410 differential refractometer were used. The measurements at 95°C were made with a Waters GPC 2000. A MiniDawn MultiAngle Light Scattering detector (MALS) from Wyatt Technologies was used. The column set consisted of two Plgel Mixed B and one guard-column (Polymer Laboratories, Ltd.). The eluent was ACS certified dimethylsulfoxide (DMSO) from Fisher Scientific. The PMMA narrow molecular weight standards were purchased from Polymer Laboratories, Ltd.

RESULTS

PMMA

We observed that when a PMMA standard is injected into a chromatographic system consisting of a set of two PL mixed B columns at 35°C, with DMSO as eluent, no peak was recorded in the chromatogram obtained with a differential refractometer. On the other hand, when a PVDF sample was injected under the same conditions, a peak was visible.

One reason that could explain this observation is the refractive index increment of the PMMA in DMSO. If it were close to zero, one would expect to see no signal even if the polymer does elute. The published value for the refractive index increment of PVDF in DMSO is –0.06 mL/g at 632 nm[2]. Using literature data[3], we calculated the refractive index increment of PMMA in DMSO and found 0.02 mL/g. This value is low but is not zero. It was confirmed by our measurements (not detailed here). Another explanation must be found for the absence of a peak when PMMA is injected.

Using the column temperature as a parameter, we undertook the characterization of the critical diagram of PMMA in DMSO. We injected one by one five PMMA narrow standards with molecular weights

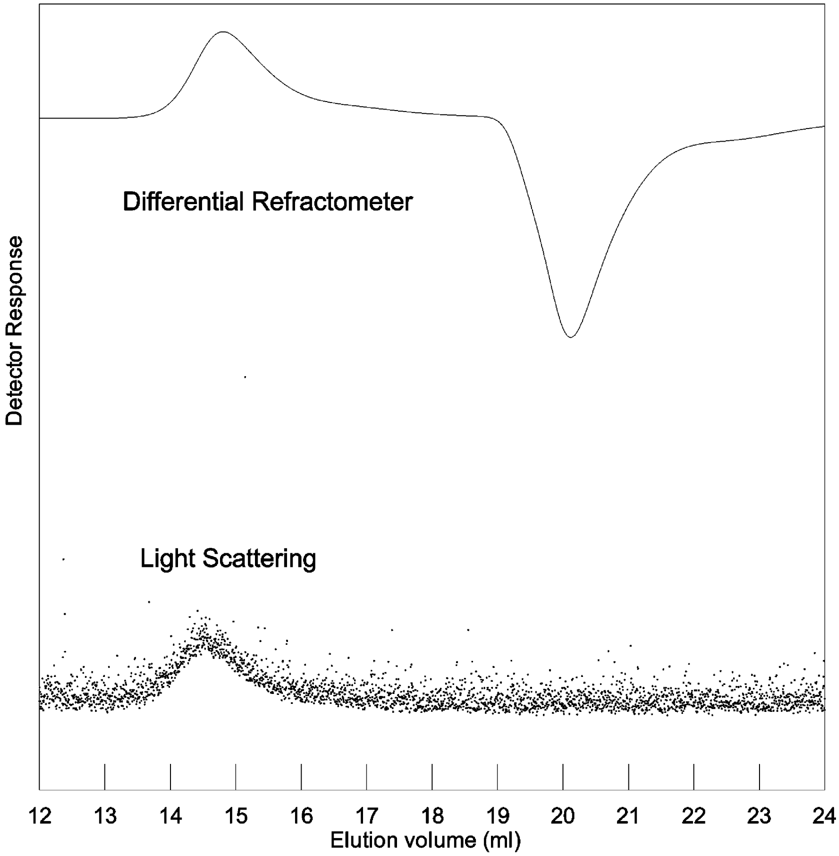

FIGURE 1 Raw detector voltages (refractometer and light scattering) for the PMMA standard with Mp = 212 000 g/mol at 50°C. The solvent peak visible in the refractometer trace does not show up in the light scattering chromatogram.

ranging from 5700 to 210 000 g/mol at different temperatures. Because near the critical temperature the PMMA standards elute together with the solvent peaks, the refractometer was ineffective. Instead, we used a MALS detector because it is insensitive to the presence of small molecules. Other detectors such as a viscometer or evaporative light scattering could be used. The low refractive index increment of PMMA in DMSO resulted in a bad signal-to-noise ratio. We had to prepare relatively concentrated solutions and inject large volumes of solution. Also, since we are interested in the elution time only, we monitored one angle at 132.3°. This is the highest available angle and it is characterized by a better signal-to-noise ratio than the lower angles. Figure 1 shows a typical set of refractive index (RI) and light scattering (LS) traces recorded by the MALS detector at 50°C for one of the standards. As can be seen, the solvent peak present in the refractometer chromatogram is not visible in

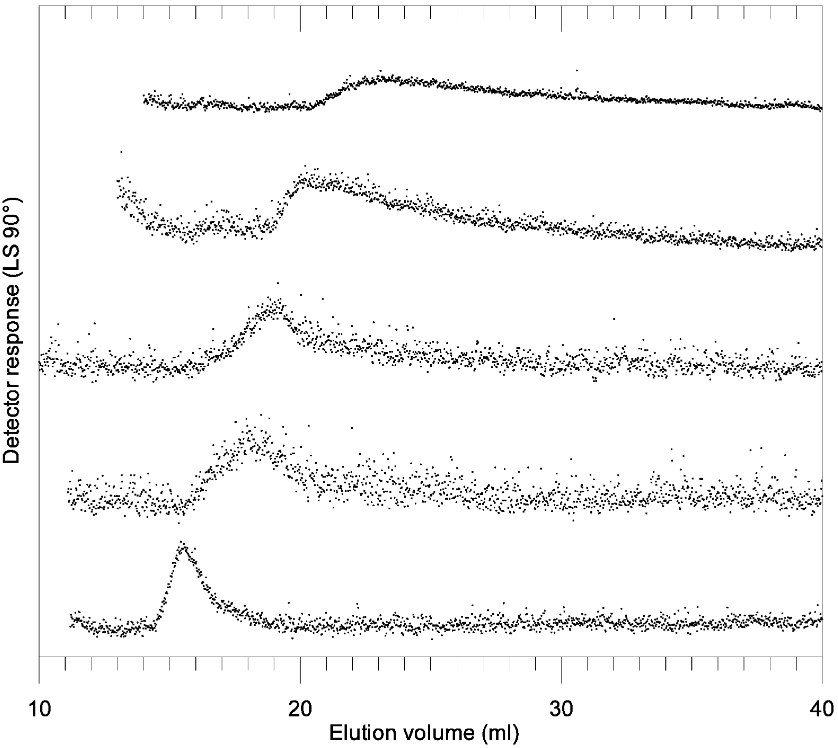

FIGURE 2 Light scattering chromatograms for the PMMA narrow standard with Mp = 100 000 g/mol measured at different column temperatures. From bottom to top: 50°C, 42°C, 41°C, 39°C, and 37°C.

the MALS chromatogram. The chromatograms obtained with the MALS detector for one of the PMMA standards are shown in Figure 2.

The resulting critical diagram is shown in Figure 3.

The fractionation of PMMA in this column is driven by entropic interactions at high temperature and by enthalpic interactions at low temperature. Because we can control the column temperature only by steps of 1°C, we were not able to precisely determine the critical temperature. According to this diagram, the critical temperature is around 41°C. This explains why, when we inject a PMMA sample into these columns at 35°C, the PMMA does not elute out.

PVDF

We do not have PVDF narrow molecular weight standards enabling us to undertake a study similar to that as for PMMA. We can plot the chromatograms obtained for a PVDF broad standard at different temperatures (Figure 4). As can be seen, there is a slight shift of the PVDF peak towards higher retention times with decreasing temperature. Steric

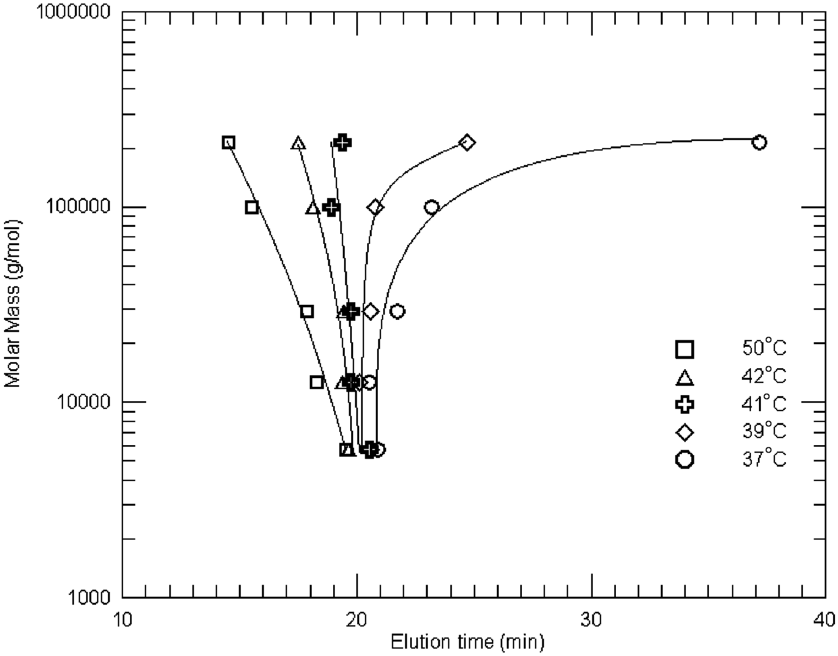

FIGURE 3 Critical diagram molar mass vs. elution time of PMMA in a Plgel Mixed B column set with DMSO as the mobile phase.

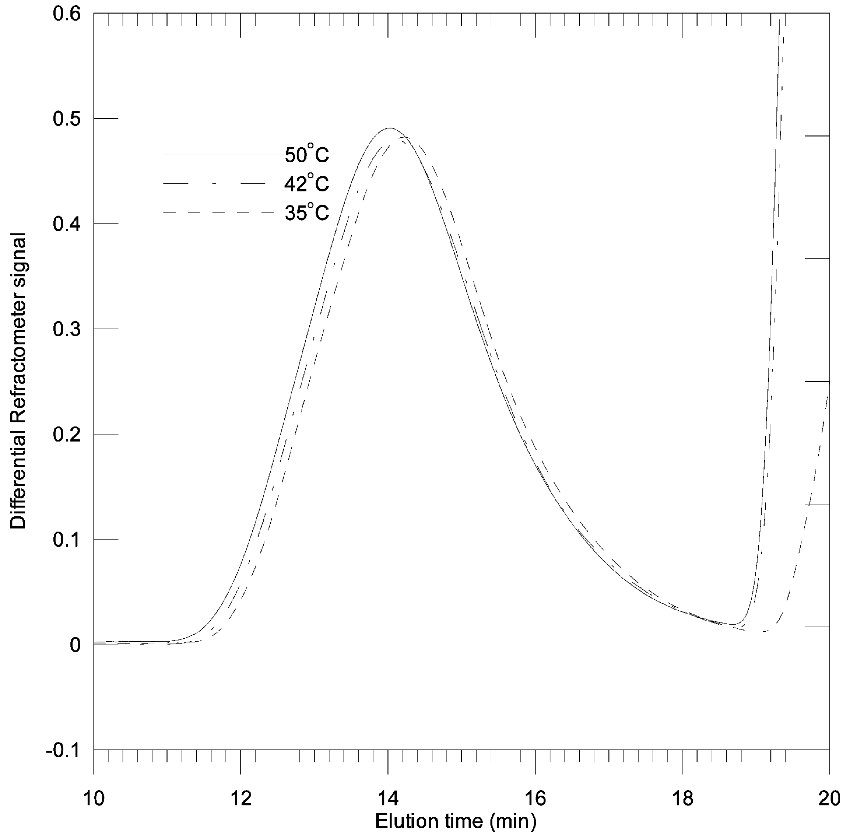

FIGURE 4 Chromatograms obtained for a PVDF broad standard at three different temperatures. PVDF elutes from the columns at any of these temperatures.

effects alone can explain this observation. The polymeric chain expands with increasing temperature and consequently has a larger hydrodynamic volume. This means that it will elute at earlier times.

APPLICATION TO THE CHARACTERIZATION OF PVDF/PMMA BLENDS

To illustrate the efficiency of the method, we consider a PVDF/PMMS 50/50 w/w blend. This blend was prepared from one PMMA and one PVDF broad standard. Each standard was dissolved

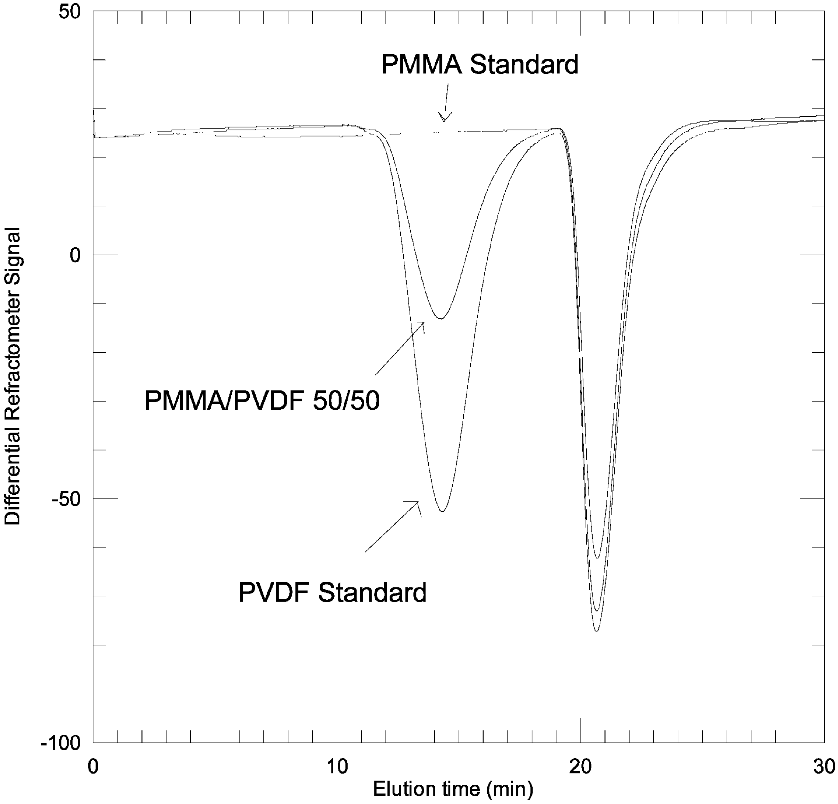

FIGURE 5 Chromatograms obtained in DMSO at 35°C for a PMMA standard, a PVDF standard, and a 50/50 w/w blend of each. Note that only the PMMA chromatogram features the solvent peak common to all chromatograms.

individually in DMSO and then equal volumes of the two solutions were mixed. The resulting solution was injected in the chromatographic system with the column at 35°C. The two individual solutions were also injected (Figure 5). The signal was monitored using a refractometer. The peak area of the chromatogram for the blend solution is only half that of the PVDF solution. There is no contribution from the PMMA. For the PMMA solution, the chromatogram does not show any peaks besides the solvent peaks. The same experiment can be done at 95°C. This time the PMMA standard displays a peak together with the PVDF (Figure 6).

A practical application of this method is the study of PVDF paints. PVDF paints are typically formulated with acrylic resins. These paints also contain a pigment and a solvent. In order to study a paint sample, it

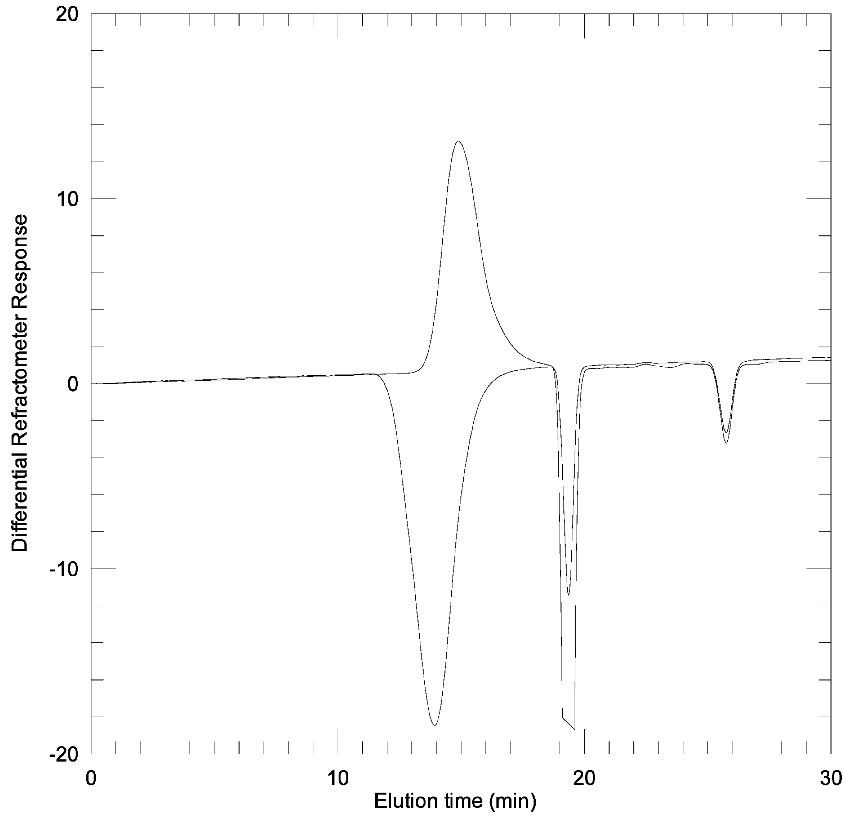

FIGURE 6 Chromatograms obtained in DMSO at 95°C for a PMMA standard (positive peak) and a PVDF standard (negative peak). Compare to Figure 5.

is first diluted in DMSO. Then the pigment is eliminated by filtration. The injection is made and the solvent elutes late in the chromatogram with the other solvent peaks. The resulting chromatogram shows a broad peak that is assigned to PVDF. To show that the chromatogram of the PVDF obtained by this method is identical to that of the original PVDF, we prepared a paint based on a known PVDF and injected it together with the raw PVDF. We compared the two chromatograms in Figure 7. As can be seen, the material recovered from the blend with this method can be identified based on its chromatogram. Finally, the molecular weight averages of the PVDF can be calculated using a broad standard calibration. The concentration in PVDF in the blend can be determined using the peak area and the known refractive index increment.

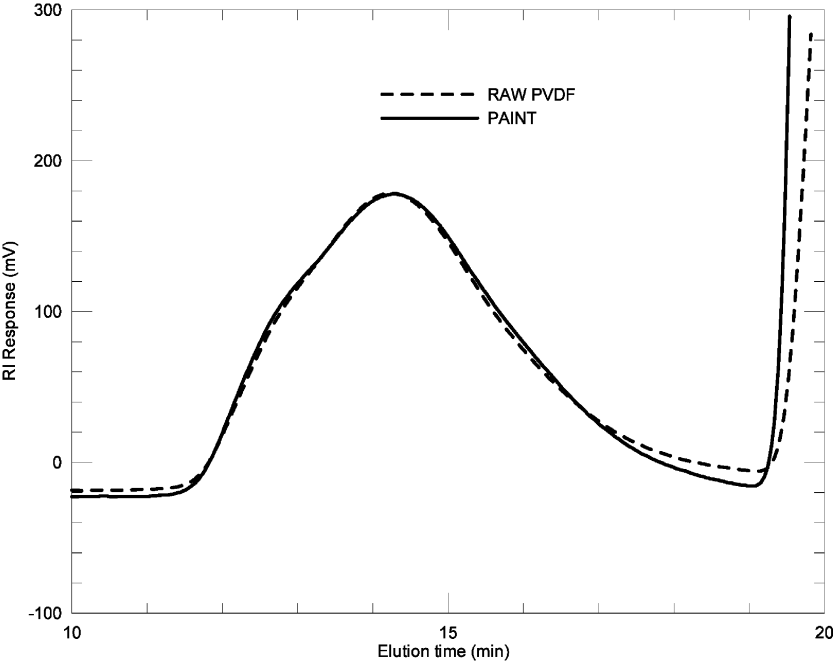

FIGURE 7 Chromatograms obtained at 35°C with DMSO as eluent. The dashed line is for a raw PVDF. The continuous line was obtained for a paint sample based on the same PVDF resin (includes PMMA, solvent, and pigment).

CONCLUSION

This method allows the extraction of PMMA from a PVDF/PMMA blend and obtaining the molecular weight distribution of the PVDF. This is done without a tedious extraction, but simply by making one injection in a conventional chromatographic system. We successfully applied this method to the characterization of PVDF paints.

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