

Sample Pretreatment for Aggregate-Free PVC Molecular Weight Measurement by Size-Exclusion Chromatography

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ABSTRACT: The procedure of aggregate-free poly(vinyl chloride) (PVC) solutions for size-exclusion chromatography (SEC) at room temperature using tetrahydrofuran (THF) as the mobile phase is proposed. PVC was dissolved in 1,2,4-trichlorobenzene (TCB) at 130 or 140°C for 6 h, precipitated in methanol, filtrated, and dried. The pretreated PVC was again dissolved in THF and SEC measurements were performed at room temperature. High molecular weight (MW) PVC required a higher pretreatment temperature of 140°C. The existence of aggregates sometimes could not be observed by a refractive index detector, but a light-scattering detector attached to the SEC columns could detect them clearly. The slope of the relationship between the MW and retention volume at the high MW region was steep compared with that at the other part of the peak and it was also a good indicator of the existence of aggregates. The pretreatment of PVC resulted in the decrease in MW averages, which was attributed to the disappearance of aggregates and not to the degradation of PVC. The pretreatment at 150°C resulted in the degradation of PVC. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1801–1809, 1998

Key words: poly(vinyl chloride); aggregates; aggregate-free pretreatment; size-exclusion chromatography; light scattering

INTRODUCTION

Size-exclusion chromatography (SEC) is a rapid analytical technique for measuring the molecular weight distribution (MWD) as well as molecular weight (MW) averages of a polymer. The separation by SEC is based on the molecular size of the polymer in solution and thus the polymer must be dispersed on a molecular level in the solution. This situation is often encountered for most polymers except polar or ionic polymers which require the addition of an electrolyte to the polymer solution to make the complete dispersion.^{1,2} However,

the presence of macromolecular aggregates of poly(vinyl chloride) (PVC) is found in the solution when the polymer is dissolved at room temperature in tetrahydrofuran (THF), although THF is a good solvent for PVC and it complicates the MW measurements.³

Various procedures have been reported to break up the aggregates of PVC in the solution. Rudin and Benschop-Hendrychova found that the ultrasonic treatment of the PVC solution in THF for 15 min destroyed the aggregates and the addition of a small amount of nonionic surfactant to the THF solution prevented the simultaneous degradation of PVC molecules.³ Heating a PVC solution in THF at 120°C for 3 h was also found to dissociate the aggregates.^{4,5} Abdel-Alim and Hamielec reported that heating the solution at 90°C for 10

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min was generally adequate.⁶ Their PVC samples were prepared at polymerization temperatures between 30 and 70°C. It has been known that the amount of aggregates in PVC increases as the polymerization temperature decreases,⁷ and heating the PVC solution at even 120°C for 2 h is not believed to be effective for low-temperature polymerized PVC.⁸ Heating a PVC solution in THF above its boiling point is not simple to perform and a specially equipped autoclave apparatus is required. THF is a peroxide-forming ether and is somewhat hazardous. Besides these problems, the procedures reported above³⁻⁶ may not be effective, because they proved the breaking up of the aggregates from the SEC chromatograms obtained by using a refractive index detector (RI). The RI chromatogram is sometimes not adequate to observe the disintegration of the aggregates as discussed in the present work (see discussion on Figs. 2 and 3).

Recently, Pang and Rudin reported the preparation of aggregate-free PVC solutions in 1,2,4-trichlorobenzene (TCB) by heating at 120°C for 12 h, followed by the SEC measurement at 110°C using TCB as the mobile phase.⁹ However, the use of a high-temperature SEC apparatus is not simple and specific equipment is required because the SEC measurement at high temperatures and the prolonged heating of PVC solutions over 100°C may accelerate the degradation of the PVC. It was, therefore, an objective of this study to establish a simple alternate procedure for the preparation of aggregate-free PVC solutions to perform the SEC measurement at room temperature without using a high-temperature SEC apparatus.

It is known that low-density polyethylene (LDPE)¹⁰ or isotactic polypropylene (PP)¹¹ has aggregates when it is dissolved in TCB or *o*-dichlorobenzene (ODCB) at high temperatures, which was observed when a light-scattering detector (LS) was used for the SEC measurement. The aggregates in LDPE were eliminated by heating it in TCB at 160°C for 1 h and cooling it to 145°C for the SEC measurement.¹⁰ The PP sample was dissolved in decalin at 140°C for 2 h, then diluted with hot cyclohexane (70°C), and the SEC measurement was performed at 70°C using cyclohexane as the mobile phase.¹² The alternative procedure was to dilute the PP solution in decalin with hot cyclohexane (75°C) to 10 times volume and the SEC measurement was performed at 60°C using cyclohexane/decalin (9/1) as the mobile phase.¹¹ These experiments to make aggregate-free polymer solutions required the dissolution of

polymers over their melting or softening points. PVC is sensitive to heat and degradable at high temperature, and it is not wise to leave the PVC solution for many hours under high temperature.

Here, the procedure to prepare aggregate-free PVC solutions for the SEC measurement at room temperature using THF as the mobile phase is reported. PVC was first dissolved in TCB at high temperatures, precipitated in methanol, and dissolved in THF, followed by the SEC measurement using THF as the mobile phase at room temperature.

EXPERIMENTAL

Samples and Solvents

Three commercial PVC samples obtained from Mitsubishi Chemical Co., (Yokkaichi, Japan) with different degrees of polymerization (P) ($P = 2350$, 1300, and 800) [henceforth, referred to as PVC ($P = 2350$), PVC ($P = 1300$), and PVC ($P = 800$), respectively] were used as test samples. The values of P were determined by specific viscosity according to the test method.¹³ TCB was used for the sample pretreatment and THF was used as the mobile phase. THF was filtered through a 0.2 μm filter, and TCB, through a 0.65 μm filter.

SEC Measurements

SEC measurements were performed with a Jasco TRIROTAR-V liquid chromatograph (Jasco, Tokyo 192, Japan) equipped with a light-scattering (LS) detector Model miniDawn (Wyatt Technology Co., Ltd., Santa Barbara, CA) and an RI detector Model RID-300 (Jasco, system A). Two SEC columns of Shodex KF-806L (Showa Denko, Tokyo 105, Japan), which were linear columns packed with polystyrene gels exclusively used for polymer separation, were used at $25 \pm 2^\circ\text{C}$. Signal acquisition and processing were done with a software of Wyatt ASTRA®. In some experiments, a Waters 150CV liquid chromatograph equipped with an RI detector was used (system B). Two SEC columns of Ultrastyrigel linear MR 5E were used at $30 \pm 1^\circ\text{C}$ and signal acquisition and processing were done with a Waters 820J data processor and the software Excel® for system B.

The mobile phase was THF and the flow rate was 1.0 mL/min. The injection volume of the sample solutions was 0.1 mL. The light source of an

LS detector was a 20 mW semiconductor laser and the wavelength was 690 nm. The specific refractive index increment (dn/dc) in THF, 0.113 mL/g, was calculated knowing the values of 0.119 at 436 nm, 0.116 at 546 nm, and 0.115 at 589 nm (ref. 14) and plotting these values against λ^{-2} (ref. 15). The column calibration for system B was done using polystyrene standards with narrow MWDs.

Treated (as mentioned in next paragraph) and untreated PVC samples were dissolved in THF at the concentration of 0.1% and the PVC solutions were filtered through a 0.2 μm filter after leaving it for 2 h.

Sample Pretreatment

A portion of 0.05 g of PVC was added to 50 mL of TCB in an Erlenmeyer flask of a 100 mL volume and a Dimroth reflux condenser was attached to the top of the flask which was placed in an oil bath. Dissolution of the PVC samples in TCB was achieved by stirring the samples with a magnetic stirrer at specified temperatures and hours: 120°C for 12 h, 130°C for 6 h or 12 h, 140°C for 6 h or 12 h, or 150°C for 6 h. To prevent oxidative degradation of PVC, 0.1 wt % of 2,6-di-*tert*-butyl-4-methylphenol was added to the TCB.

After heating a PVC–TCB mixture at specified temperatures and hours, the PVC solution was left at room temperature for 30 min and then a threefold volume of methanol was added to the solution and PVC was precipitated. The PVC product was filtrated on a 0.65 μm filter, washed with ethyl ether, and dried at room temperature for 1 h and then at 50°C for 1 h.

RESULTS AND DISCUSSION

SEC Measurements of Untreated PVC Samples

RI and LS chromatograms for the three untreated PVC samples are shown in Figures 1, 2, and 3, respectively. Figure 1 shows those for untreated PVC ($P = 800$) and also shows clearly bimodal distributions both in the RI and LS chromatograms. The first peaks in both chromatograms that appeared at retention volumes V_R between 14.0 and 15.3 mL are attributed to supermolecular aggregates, and the intensity of the first peak in the LS chromatogram was very much larger than that of the RI chromatogram compared with the main peaks at V_R between 15.6 and 19 mL.

This intensity difference of both chromatograms, LS and RI, between an aggregate peak and a main peak was shown clearly in the relationship between log MW and V_R . The relationship over $V_R = 15.6$ mL was almost linear, but the slope was extremely large, from 15.6 mL down to 15.0 mL. The relationship between $V_R = 14.0$ and 15.0 mL was almost flat and showed the same MW of 1.5×10^6 irrespective of the V_R . The range between $V_R = 14.0$ and 15.0 mL corresponded to that for aggregates and that between $V_R = 15.0$ and 15.6 mL corresponded to that for the mixture of aggregates and completely dispersed macromolecules. It is interesting to notice that the relationship between log MW and V_R resembles the relationship between MW and the intrinsic viscosity where the slope of the log–log plot of the intrinsic viscosity versus MW exhibited the abnormal “drop” in the slope at the high MW region,⁹ although the phenomenon was opposite.

Figures 2 and 3 are RI and LS chromatograms and the relationship between log MW and V_R for untreated PVC ($P = 1300$) and untreated PVC ($P = 2350$), respectively. The aggregate peaks on the RI chromatograms were not observed but those on the LS chromatograms appeared as a shoulder at the high MW region. Similarly to the relationship between log MW and V_R in Figure 1, the slopes of the relationship became steep below V_R at 15.2 mL for PVC ($P = 1300$) and at 14.8 mL for PVC ($P = 2350$), which explains the existence of aggregates in this region. Therefore, the presence of the secondary peaks at the high MW region of the RI and/or LS chromatograms and the steep slope of the relationship between log MW and V_R at this region indicate the existence or nonexistence of the aggregates.

Preparation of Aggregate-free PVC Solutions in THF

The validity of the sample pretreatment for aggregate-free PVC solutions in THF is shown in Figures 4 and 5. PVC ($P = 2350$) was dissolved in TCB at 130°C for 6 h (Fig. 4) or at 140°C for 6 h (Fig. 5), precipitated in methanol, dried, and redissolved in THF, followed by SEC measurement. A small shoulder on the LS chromatogram was still observed in Figure 4, but the shoulder almost disappeared in Figure 5. The deflection point, where the slope changes, of the relations between MW and V_R moved to the higher MW region than in Figure 3 as $V_R = 14.7$ mL in Figure 4 and $V_R = 14.6$ mL in Figure 5. The slope at the

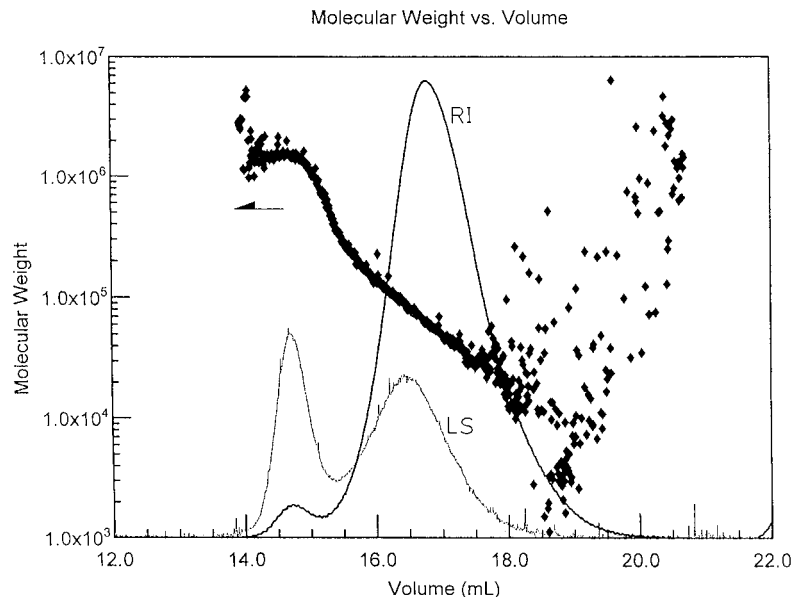


Figure 1 RI and LS chromatograms for untreated PVC ($P = 800$) and relations between MW and retention volume.

high MW region was small compared with that in Figure 3 and it was almost the same as that at the main region. This approach is a good indication of the disappearance of the aggregates.

It can be said that the pretreatment of PVC in TCB at 140°C for 6 h was enough to make an aggregate-free PVC solution in THF. The pretreatment of PVC in TCB at 130°C for 6 h still

retains a small amount of aggregates in a PVC solution in THF. The superimposed LS chromatograms of Figures 4 and 5 explain these results as shown in Figure 6. The PVC sample pretreated at 130°C showed the presence of aggregates at V_R between 13.3 and 14.0 mL, which were not detected in the PVC sample pretreated at 140°C.

The preparation of aggregate-free PVC solu-

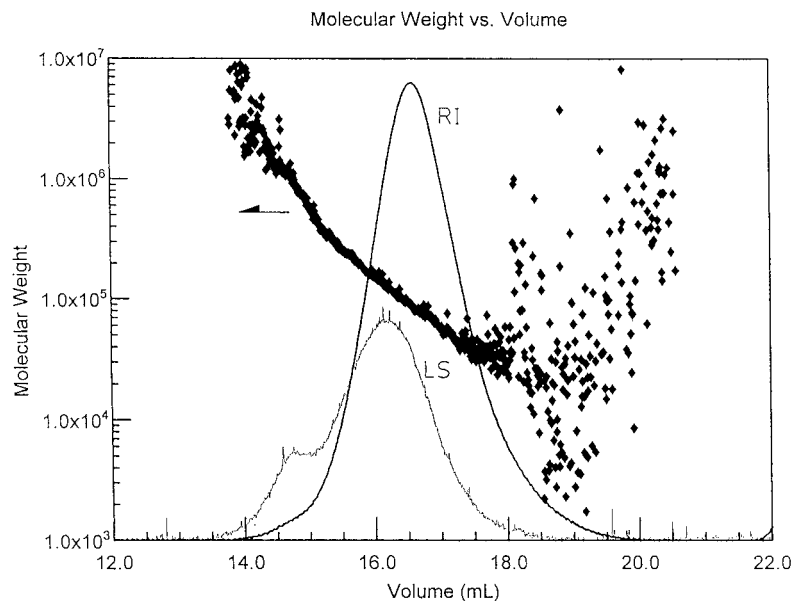


Figure 2 RI and LS chromatograms for untreated PVC ($P = 1300$) and relations between MW and retention volume.

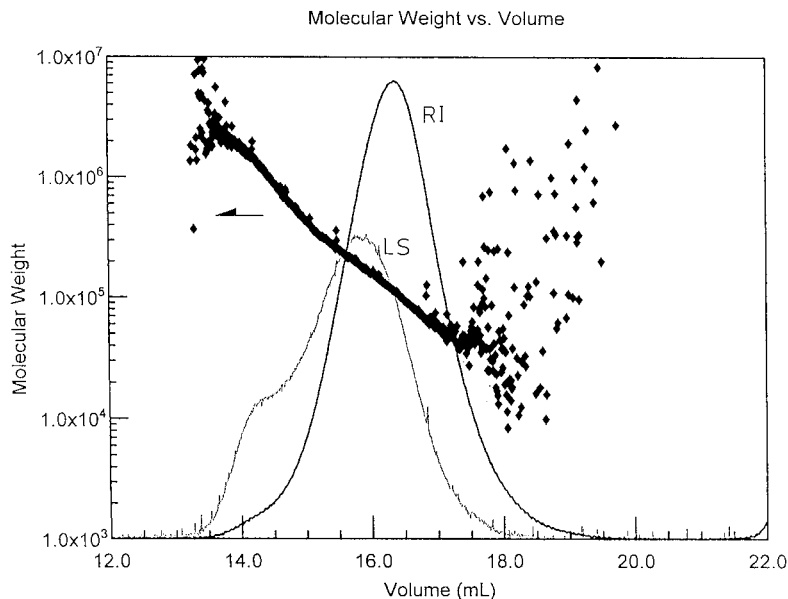


Figure 3 RI and LS chromatograms for untreated PVC ($P = 2350$) and relations between MW and retention volume.

tions without degradation of the PVC during the pretreatment was of primary importance in our study. A comparison was made of the effects of the pretreatment of the PVC at different temperatures and is shown in Table I and Figure 7. Absolute MW averages in Table I were obtained with system A, and PS equivalent MW averages, with system B. The pretreatment seems to result in

the degradation because of the decrease in MW averages, if MW averages are compared with absolute MW averages: The pretreatment at 130°C for 6 h resulted in the decrease in 13% for M_n , 21% for M_w , and 42% for M_z compared with the untreated PVC. However, the PS equivalent MW averages between the treated and the untreated PVC were almost identical and it means that the

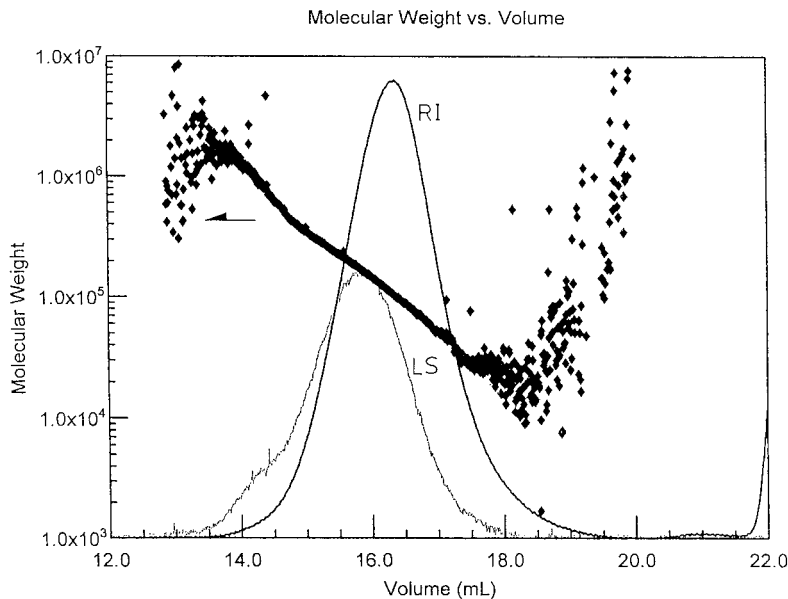


Figure 4 RI and LS chromatograms of PVC ($P = 2350$) treated in TCB at 130°C for 6 h and measured at room temperature in THF.

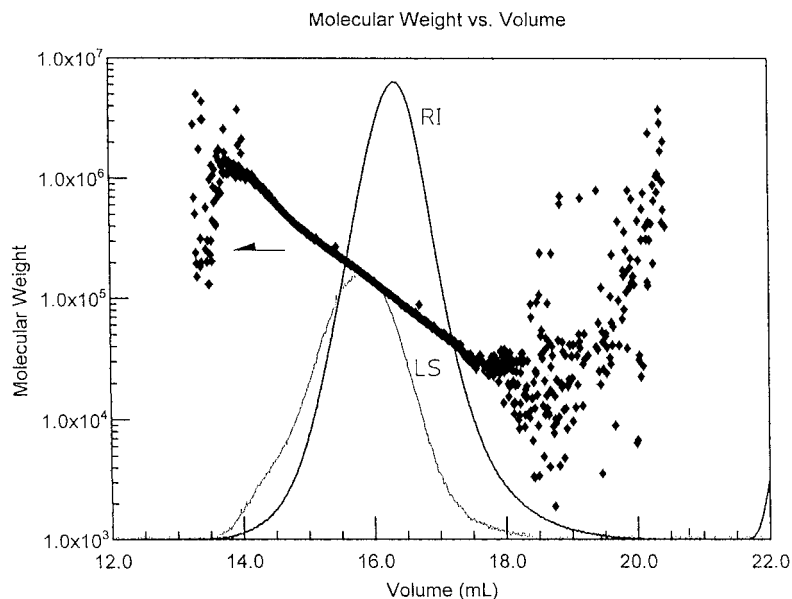


Figure 5 RI and LS chromatograms of PVC ($P = 2350$) treated in TCB at 140°C for 6 h and measured at room temperature in THF.

decrease in absolute MW averages by pretreatment was attributed to the disappearance of aggregates and not to the degradation of the PVC. Figure 7 shows the MW distributions of pretreated and untreated PVC ($P = 2350$) and supports the above conclusion. Both distributions are almost the same and show no degradation by the pretreatment and the portion of the aggregates

over $MW 1 \times 10^6$ decreased and that of the low MW region increased. The presence of aggregates results in the increase in the LS intensity compared to the same MW of nonaggregate PVC; thus, MW at this region becomes higher compared with the nonaggregate PVC molecules, and, therefore, the decrease in MW averages by the pretreatment was obvious.

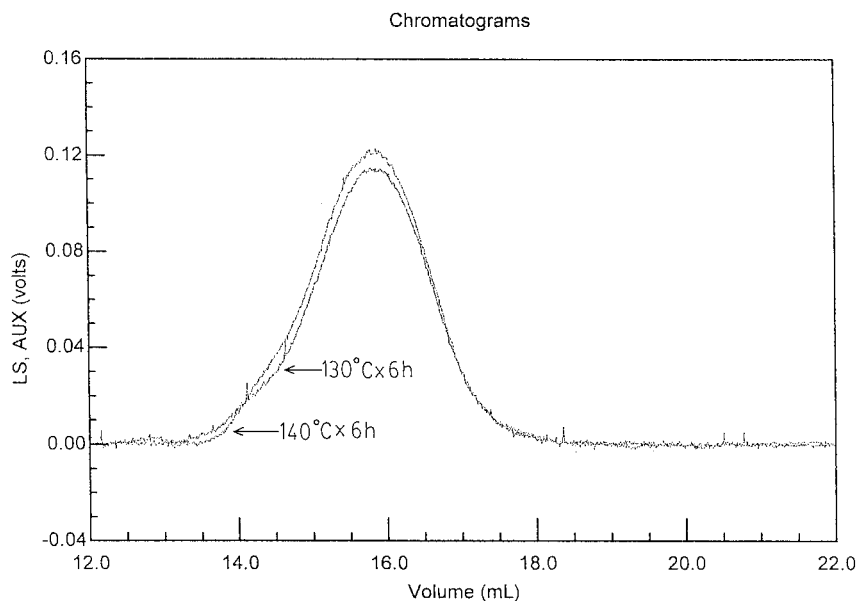


Figure 6 LS chromatogram overlay of PVC ($P = 2350$) treated in TCB at 130°C for 6 h and at 140°C for 6 h.

Table I MW Averages of the Treated and Untreated PVC ($P = 2350$) Sample

Condition	130°C 6 h	130°C 12 h	140°C 6 h	140°C 12 h	150°C 6 h	Untreated
Absolute MW average						
$M_n \times 10^{-5}$	0.905	0.838	0.809	0.789	0.856	1.038
$M_w \times 10^{-5}$	1.496	1.462	1.396	1.325	1.443	1.884
$M_z \times 10^{-5}$	3.375	2.960	2.647	2.522	3.018	5.859
PS equivalent MW average						
$M_n \times 10^{-5}$	1.309	1.247	1.221	1.185	1.122	1.284
$M_w \times 10^{-5}$	3.087	3.178	3.123	3.022	3.075	3.220
$M_z \times 10^{-5}$	6.240	5.428	5.894	5.554	6.000	6.216

Comparing the PS equivalent MW averages before and after heat treatment of the PVC samples may not be a good indicator of whether degradation has occurred. However, the comparison is the second best indicator of the degradation. Because MW averages calculated only from RI chromatograms using a PS calibration curve are not sensitive to the aggregates, the comparison of the PS equivalent MW averages of untreated and treated PVC from RI chromatograms is more practical, and if both values are nearly equal, then it can be estimated that there will be no degradation. Degradation is essentially estimated only by the coloration of the samples or the observation of the significant lowering the MW averages and the shift of the RI chromatograms to the lower MW region (higher V_R).

Absolute MW averages of the PVC decreased

with increasing the pretreatment temperature or time except in the case of 150°C where the PVC became colored and the RI chromatogram shifted to the low MW region. The increase in MW averages at 150°C may be attributed to the change in the chemical structure of PVC by the degradation that resulted in the increase in the scattering intensity.

The optimum conditions for the pretreatment of PVC ($P = 2350$) will be 140°C for 6 h. For linear MW samples such as PVC ($P = 1300$) and PVC ($P = 800$), the conditions at 130°C for 6 h may be enough to make the aggregates disappear. The results are shown in Figures 8 and 9. The MW averages of these two PVCs are listed in Table II. Similar results were obtained as in Table I. The peak attributed to aggregates for PVC ($P = 800$) (Fig. 1) disappeared completely (Fig. 9) and the

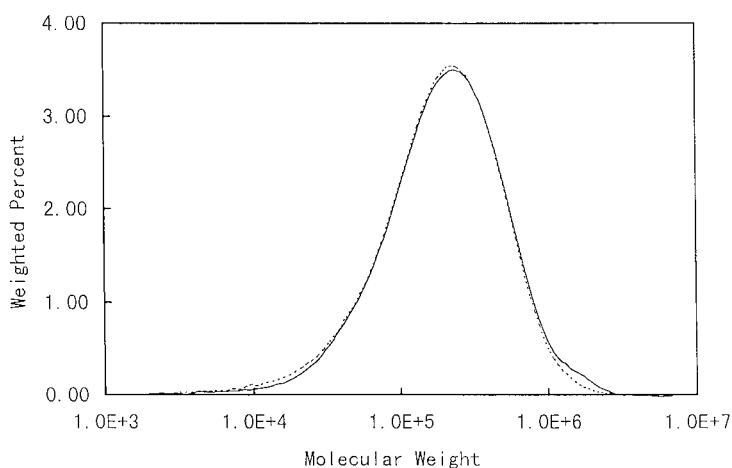


Figure 7 MWDs as PS equivalent MW of treated and untreated PVC ($P = 2350$): (—) untreated; (····) treated at 140°C for 6 h.

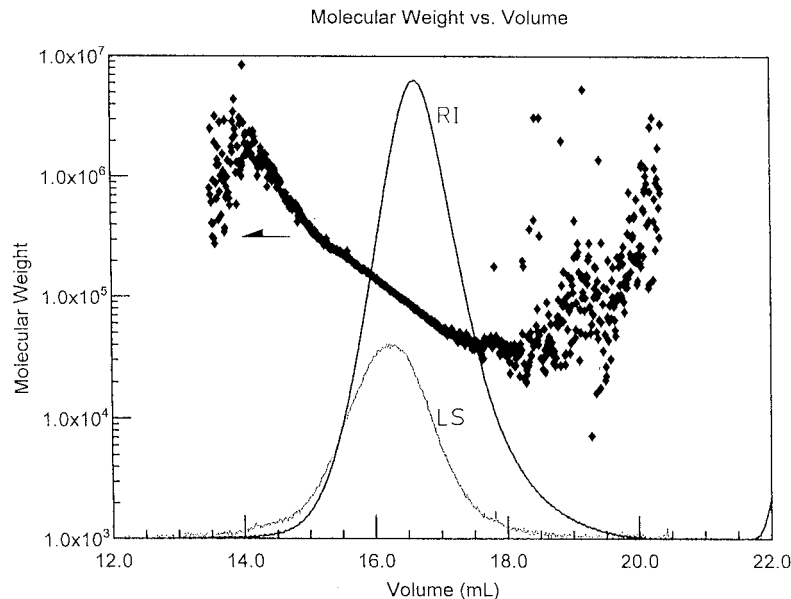


Figure 8 RI and LS chromatograms of PVC ($P = 1300$) treated at 130°C for 6 h and measured at room temperature in THF.

relation between MW and V_R is almost linear up to the high MW region. The pretreatment at 130°C for 12 h gave the same results as those at 130°C for 6 h.

Pang and Rudin⁹ proposed the dissolution of PVC in TCB at 120°C for 12 h, followed by the SEC measurement at 110°C using TCB as the mobile phase. The pretreatment temperature and time

at 120°C for 12 h was not enough for our procedure and the peak of aggregates was still observed. Our procedure needs the precipitation of the dissolved PVC in TCB into methanol and it would be natural to use higher temperature. The continuous stirring was required when the PVC was under the pretreatment; otherwise, the disappearance of aggregates was not perfect.

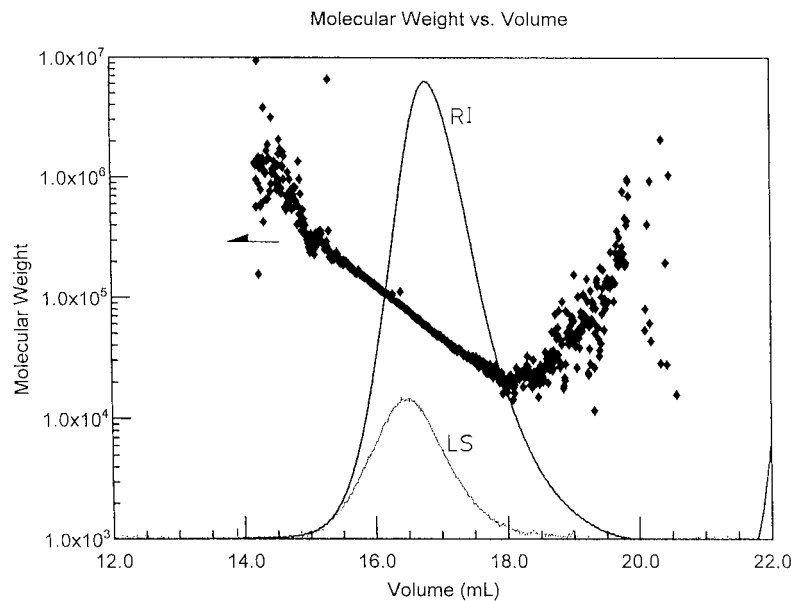


Figure 9 RI and LS chromatograms of PVC ($P = 800$) treated at 130°C for 6 h and measured at room temperature in THF.

Table II MW Averages of PVC ($P = 1300$ and $P = 800$) Samples Treated at 130°C for 6 h and Untreated

PVC	$P = 1300$		$P = 800$	
	Treated	Untreated	Treated	Untreated
$M_n \times 10^{-5}$	0.676 (0.888)	0.757 (0.978)	0.438 (0.623)	0.440 (0.656)
$M_w \times 10^{-5}$	0.988 (2.031)	1.216 (2.150)	0.637 (1.308)	1.005 (1.358)
$M_z \times 10^{-5}$	2.002 (4.043)	3.250 (4.013)	1.246 (2.223)	5.240 (2.322)

The values in the parentheses were obtained from using a PS calibration curve as the PS equivalent.

Similarly, the concentration of PVC for pretreatment was important and the doubling of the PVC content in TCB resulted in the existence of some amount of the aggregates. Losses of the portion of PVC materials, especially at low MW, by pretreatment were negligibly small.

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