MONITORING OF ORIGINATED POLYMER IN PURE MONOMER WITH GRADIENT POLYMER ELUTION CHROMATOGRAPHY (GPEC)*

W. J. STAAL¹, P. COOLS²,
A. M. VAN HERK², AND A. L. GERMAN²

¹Waters Chromatography Group
Penningweg 33
P.O. Box 166
4870 AD Etten-Leur, The Netherlands

²Eindhoven University of Technology
Laboratory of Polymer Chemistry and Technology
P.O. Box 513
5600 MB Eindhoven, The Netherlands

ABSTRACT

The analysis of the amount of polymer in pure monomer with cloudpoint measurements gives, only a qualitative answer. Now by use of a liquid chromatograph and gradient elution the amount of polymer can be measured fully automated. Also an impression of the molar mass can be achieved.

INTRODUCTION

One of the important parameters in polymerization is the purity of the monomers. The factors that have a negative influence on the polymerization process are, contaminants and polymer formed during storage. One of the most

* GPEC is a registered trademark of the Waters chromatography group
common tests to check the presence of polymer in the monomer is the cloudpoint test. This test is described in the ASTM method 2010, polymer content of styrene monomer [1].

By adding a nonsolvent to the monomer the polymer will precipitate. This can be visually observed as a cloudpoint. This test gives a qualitative answer. In this case polystyrene and its monomer are taken as example. As a nonsolvent, methanol is used the most for this application. The problem with methanol is that the oligomers of polystyrene are soluble up to $n = 5$. Therefore these oligomers are not detectable with the methanol cloudpoint test. Another reason that this test is just a qualitative one is because of the amount of methanol, required for the precipitation, is dependent of the molecular mass of polystyrene [2].

Chromatography can also be applied for this application. With Gel Permeation Chromatography (GPC) a separation can be achieved on molecular mass. The problem with this technique is the limited separation. For separating traces of polymer from the monomer, the monomer must be injected without dilution. This leads to an overload of the column and as result a bad separation. With Gradient Polymer Elution Chromatography (GPEC) traces of polymer and oligomers [3] can be separated from the pure monomer.

The styrene monomer is injected pure in a stream of a nonsolvent (water). In this nonsolvent, monomer, oligomers and polymer are retained on the top of the column or a guard column [4] as suspension.

By adding a solvent (THF) to the nonsolvent (water) in a gradient the monomer, oligomers and polymer will redissolve and elute from the column [5]. The separation is so good that even oligomers are also separated from the monomer. Very small amounts of polymer can be detected with this method. Also the molecular mass can be calculated referring to well defined polymer standards [4], [6].

By adding a nonsolvent to the monomer the polymer will precipitate. This can be visually observed as a cloudpoint. This test gives a qualitative answer. In this case polystyrene and its monomer are taken as example. As a nonsolvent, methanol is used the most for this application. The problem with methanol is that the oligomers of polystyrene are soluble up to $n = 5$. Therefore these oligomers are not detectable with the methanol cloudpoint test. Another reason that this test is just a qualitative one is because of the amount of methanol, required for the precipitation, is dependent of the molecular mass of polystyrene [2].

Chromatography can also be applied for this application. With Gel Permeation Chromatography (GPC) a separation can be achieved on molecular mass. The problem with this technique is the limited separation. For separating traces of polymer from the monomer, the monomer must be injected without dilution. This leads to an overload of the column and as result a bad separation. With Gradient Polymer Elution Chromatography (GPEC) traces of polymer and oligomers [3] can be separated from the pure monomer.

The styrene monomer is injected pure in a stream of a nonsolvent (water). In this nonsolvent, monomer, oligomers and polymer are retained on the top of the column or a guard column [4] as suspension.

By adding a solvent (THF) to the nonsolvent (water) in a gradient the monomer, oligomers and polymer will redissolve and elute from the column [5]. The separation is so good that even oligomers are also separated from the monomer. Very small amounts of polymer can be detected with this method. Also the molecular mass can be calculated referring to well defined polymer standards [4], [6].
nonsolvent, methanol was added with a 100 µl syringe, Hamilton (U.S.A.). The cloudpoints were observed visually, using a black background. The mixing was performed by intensive shaking during titration. The methanol was obtained from Rathburn (U.K.).

RESULTS AND DISCUSSION

It is demonstrated in Table 1 that the cloudpoint is strongly dependent on the molecular mass and a little dependent on the amount of polymer. With spectrophotometers the intensity of the cloudiness can be measured as indication of the amount of polymer except for the oligomers [1]. The problem is that this suspensions are not stable. In some cases it takes 5-15 min. before the suspension is formed. With polymers at the level of molecular mass a million and more immediately flocculation takes place. This makes a quantitative spectrofotometric method complicated.

With the gradient method the concentration (peak hight or peak area of oligomers and polymer) can be calculated. Also an indication of the molecular mass can be achieved. In Figure 1 the contour plot of a test mixture of styrene and polystyrene standards is shown. This is a good demonstration of the separation power of a water-THF gradient between monomer, oligomers and polymer.

Figure 2 is a contour plot of one month stored destillated styrene at -4°C. Oligomer formation (A) and polymer formation (B) has already taken place. The level is about 1500 ppm (calculated from Figure 1).

In Figure 3 polystyrene (Dow 1683 Mw = 250,000) has been spiked to the styrene sample from Figure 2. The benefit of using a photodiode array detector is to monitor differences in the UV spectrum. Normally the UV spectrum from a molecular mass 1000 up to 20 million g/mol polystyrene is uniform. When the UV spectrum is different, other response factors have to be applied with GPEC. Two different response factors have to be applied. One for dissolved polystyrene and one for a turbid suspension of polystyrene in a nonsolvent water-THF combination. This colloidal suspension formation from molar mass 50,000 g/mol and larger was described by Engelhart and others [7].

In figure 3 the appearance of this colloidal suspension is clearly demonstrated by the spiked Dow 1683. This peak gives a response, far in the visual wavelength area. Comparing with dissolved polystyrene, the normal UV absorption spectrum of polystyrene is from the maximum at 261 nm to 300 nm.

CONCLUSIONS

Gradient Polymer Elution Chromatography is an easy technique to monitor the amount of polymer in pure monomer. Also an indication of the molar mass of the polymer can be achieved. No sample preparation is needed, pure monomer can be

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. Mg/ml (PPM)</th>
<th>Sample volume µl styrene (Containing polymer)</th>
<th>Added NS µl methanol at cloudpoint*</th>
<th>Non solvent % methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dow 1683 (Mw 250,000)</td>
<td>12,000</td>
<td>400</td>
<td>130</td>
<td>24,5</td>
</tr>
<tr>
<td></td>
<td>1,200</td>
<td>400</td>
<td>150</td>
<td>27,3</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>400</td>
<td>200</td>
<td>33,3</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>400</td>
<td>Not visually detectable</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mw 11,600)</td>
<td>10,000</td>
<td>400</td>
<td>265</td>
<td>39,8</td>
</tr>
<tr>
<td></td>
<td>1,000</td>
<td>400</td>
<td>370</td>
<td>48,1</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>400</td>
<td>520</td>
<td>56,5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>400</td>
<td>Not visually detectable</td>
<td></td>
</tr>
<tr>
<td>Styrene TUE</td>
<td>unknown</td>
<td>400</td>
<td>150</td>
<td>27,3</td>
</tr>
</tbody>
</table>

* Visual observation of the cloudpoint at a temperature at 24.0°C.
FIGURE 1. Retention time behaviour of styrene monomer and narrow polystyrene standards. Styrene monomer (1), oligomer Mw 2,020 (2), polymer Mw 50,000 (3), Mw 340,000 (4) and the summation of Mw 3,000,000 and Mw 8,000,000 (5). Concentration 2.7 mg/ml THF.

FIGURE 2. Stored styrene monomer and formed oligomer and polymer. Styrene monomer (A), oligomer content (B) and polymer content (C).
injected. With the use of an autosampler large numbers of samples can be handled. With the use of a photodiode array detector differences in response factors can be monitored. In the case of non absorbing polymers a mass detector can be used. This method can be very useful to monitor the start of a polymerization process, if no initial inhibition takes place.

FUTURE OUTLOOK

For detection at a level of 10 PPM and lower, more UV transparant solvents like dichloromethane and cyclohexane are advisable. In the case of non-UV absorbing polymers an Evaporative Light Scattering Detector (ELSD) can be applied.

ACKNOWLEDGMENT

Special acknowledgements are given to mr. J. Brassers and mr. C.Evers, arranging the equipment, and miss G. King of General Electric-ABS, from the plant in Amsterdam, for doing the HPLC analysis work.

REFERENCES

1. ASTM method D2121-68.