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### Monitoring of Originated Polymer in Pure Monomer with Gradient Polymer Elution Chromatography (GPEC)®

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## MONITORING OF ORIGINATED POLYMER IN PURE MONOMER WITH GRADIENT POLYMER ELUTION CHROMATOGRAPHY (GPEC)<sup>®\*</sup>

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### 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

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\* 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].

## EXPERIMENTAL

### **HPLC Equipment**

Gradient elution was performed with a 4 solvent gradient pump (Waters Model 600E). A Waters intelligent sample processor (WISP, Model 712B) was used to inject 5  $\mu$ l pure styrene. A Waters photodiode array detector (Model 996) was used to monitor the formed polystyrene scanning from 200 to 345 nm. The chromatogram was reproduced by the Waters Millennium 2010 photodiode array software and recorded by a NEC Powermate 486/33i computer. The Waters group is located in the U.S.A.

The water was purified with a Milli-Q system from the Millipore Corporation. Tetrahydrofuran (THF) without stabilizer was obtained from Rathburn U.K.

### **HPLC Conditions**

The injection volume of the monomer samples was 5  $\mu$ l without dilution. A linear gradient was used starting with 100% water (as nonsolvent) to 100% THF (as good solvent) in 30 min. The eluent flow was 1 ml/min. The temperature was 30°C.

The column was a Waters Nova-Pak CN, 3.6 x 150 mm, column packed with spherical 4 $\mu$ , 60Å particles. The polystyrene sample was the DOW 1683 broad standard (U.S.A.). The polystyrene narrow standards were obtained from Polymer Laboratories (U.K.). The styrene monomer (polymer free) was obtained from Nevcin Polymer, the Netherlands. With this monomer all dilutions were made. The stored styrene (containing polymer) was obtained from the University of Technology, Eindhoven, the Netherlands.

### **Cloudpoint Observations**

The micro cloudpoint titrations were performed in a 4 ml Waters WISP vial, sealed with a self sealing septum. The temperature was at roomtemperature (24°C). The

nonsolvent, methanol was added with a 100  $\mu$ l syringe, Hamilton (U.S.A.) The cloud-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 of the molecular mass and a little dependent of 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 spectrophotometric method complicated.

With the gradient method the concentration (peak height 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 distilled styrene at  $-4^{\circ}\text{C}$ . 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  $M_w = 250,000$ ) 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

TABLE 1

Cloudpoints of polystyrene in styrene\*

Sample	Conc. Mg/ml (PPM)	Sample volume $\mu$ l styrene (Containing polymer)	Added NS $\mu$ l methanol at cloudpoint*	Nonsolvent % methanol
Polystyrene Dow 1683 (Mw 250,000)	12,000	400	130	24,5
	1,200	400	150	27,3
	120	400	200	33,3
	12	400	Not visually detectable	-
Polystyrene (Mw 11,600)	10,000	400	265	39,8
	1,000	400	370	48,1
	100	400	520	56,5
	10	400	Not visually detectable	-
Styrene TUE	unknown	400	150	27,3

\* Visual observation of the cloudpoint at a temperature at 24,0°C.

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

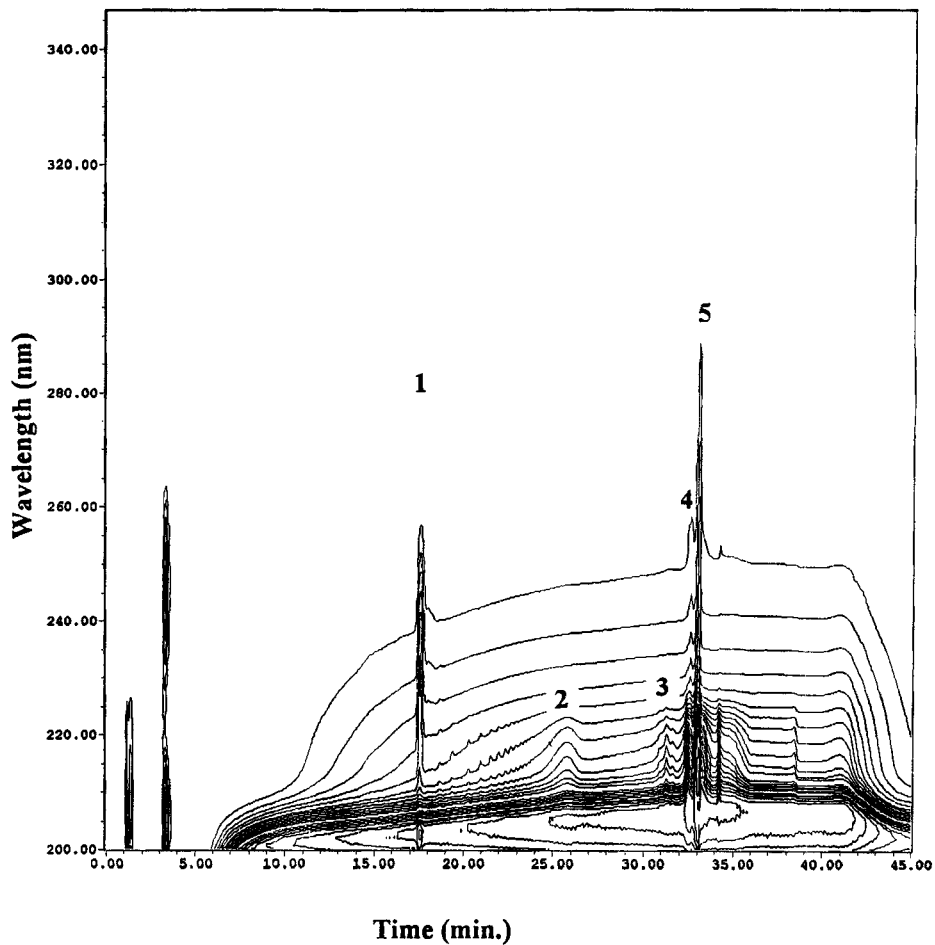


FIGURE 1. Retention time behaviour of styrene monomer and narrow polystyrene standards. Styrene monomer (1), oligomer Mw 2,020 (2), polymer Mw 50,000 (3), Mw 340,000 (4) and the summation of Mw 3,000,000 and Mw 8,000,000 (5). Concentration 2.7 mg/ml THF.

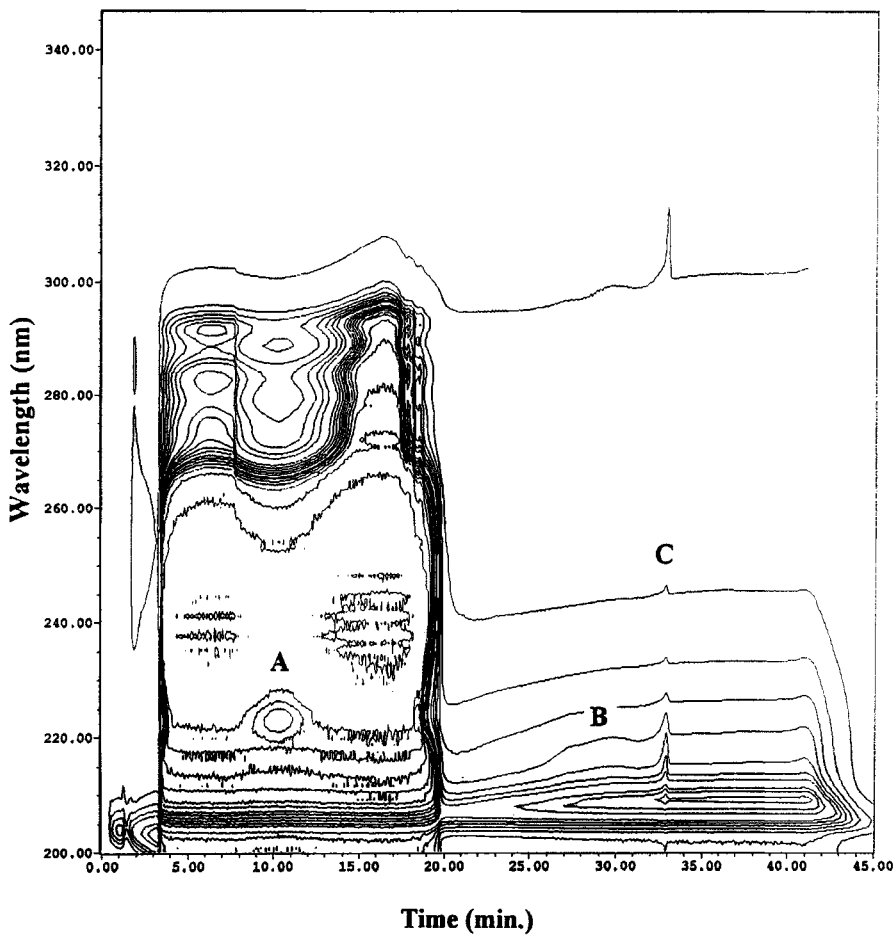


FIGURE 2. Stored styrene monomer and formed oligomer and polymer. Styrene monomer (A), oligomer content (B) and polymer content (C).



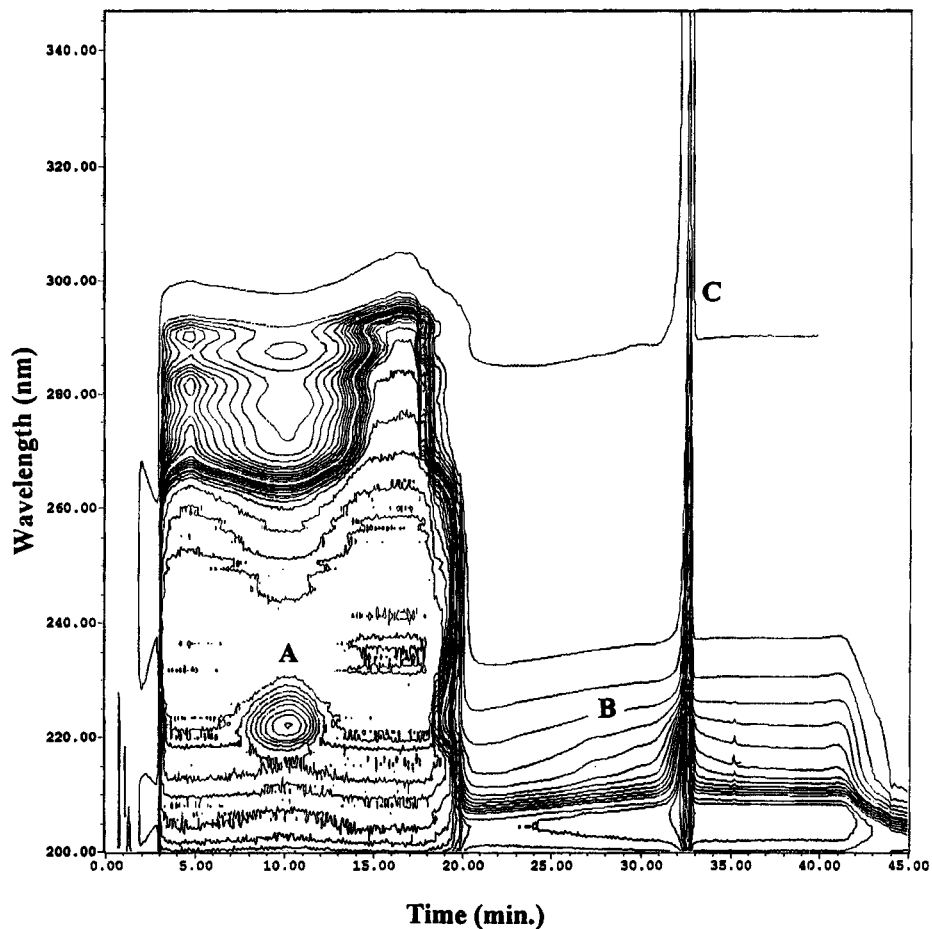


FIGURE 3. A mixture of stored styrene monomer and polystyrene (Dow 1683 Mw 250,000, 12,000 ppm). Styrene monomer (A), oligomer (B) and polymer (C / Dow 1683)

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 transparent solvents like dichloromethane and cyclohexane are advisable. In the case of non-UV absorbing polymers an Evaporative Light Scattering Detector (ELSD) can be applied.

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