Summary: The major problem in applying gradient polymer elution chromatography is the lack of applications. In this chapter a number of different applications are presented of separations between polymers and between polymers and small molecules. Also a systematic approach based on a solvent screening covering the whole range of polarity is suggested. Except for polycarbonate and SBS rubber the separation of other tetrahydrofuran soluble polymers, than applied in previous chapters, is based on solubility. For these polymers also the separation can be predicted from cloud-point observations.

Chromatographic Conditions for Polymer Separations

Introduction

The aim of the HPLC experiments is to achieve separation between tetrahydrofuran soluble polymers in a mixture. A reasonable impression of the chance of success of such a separation can be obtained from a polymer screening test.

This test is performed using two gradient runs. The first run using water and the second run using 2,2,4-trimethyl pentane as starting eluent (non-solvent). Both gradient systems have tetrahydrofuran as solvent.

These two gradient runs cover the whole range of solvent polarity. The graphical presentation of these results will be discussed.

HPLC Apparatus

The experiments in this study have been carried out with different HPLC components (Waters Chromatography (U.S.A.)). The applied gradient pumps are all based on the M600 quaternary solvent delivery series (M600E, M625, M616). The series M712 and M996 auto injectors were applied. In some experiments a temperature control module (TCM) was used to keep the column at 40°C. In many experiments photo diode array detection was used applying the model M996 with Millennium 2010 software. For non-UV absorbing polymers the detection was carried out by using an evaporative light scattering detector (ELSD) (ACS, U.K.).

(GPEC®) is a registered trademark of Waters Chromatography B.V.
Chromatographic Conditions

The gradient run with 2,2,4-trimethyl pentane started at 100% 2,2,4-trimethyl pentane and moved linearly to 100% tetrahydrofuran in 30 min.

The water gradient started at 50% water - 50% tetrahydrofuran and moved linearly to 100% tetrahydrofuran in 30 min.

In most experiments the flow rate was 1 ml/min. The column for the screening test was a Nova-Pak, Cyano Propyl (CN) 75x3.9 mm packed with spherical 4 μm particles (Waters Chromatography U.S.A.).

In most samples the polymer concentration was 10 mg/ml (THF). The injection volumes were between 2-10 μl.

Introduction

To obtain a good quantitation and identification of a polymer mixture (blend) a separation can be of great help. No systematic study to separate tetrahydrofuran soluble polymers has been carried out so far. The aim in this chapter is to separate mixtures of tetrahydrofuran soluble polymers according to a solubility mechanism. The polymers applied in this chapter are mostly commercial samples. No strong adsorption was found based on the solid phase extraction test.

Results

Polymer Screening

No study has been published to set-up a systematic separation of tetrahydrofuran soluble polymer blends. The advantage of tetrahydrofuran is that this solvent is miscible with 2,2,4-trimethylpentane and with water. With two gradient runs, 2,2,4-trimethylpentane - tetrahydrofuran and water - tetrahydrofuran, nearly the whole range of solvent polarity is covered. The results that can be obtained from these two runs are; a first impression of the quality of the separation and the characterisation of the polymers in terms of solubility parameters.

The System Water - Tetrahydrofuran

The first screening is based on the system water - tetrahydrofuran. Titrimetric cloud-point values and the chromatographic cloud-point values are given in Table 1. The differences are relatively small, except for poly(carbonate). It is known that tetrahydrofuran is not a strong solvent for poly(carbonate). The differences are of the same order as for the polymer standards. This is a very good result because many commercial polymers showed broad to very broad peaks in chromatography. The peak broadening is ascribed to the molecular mass and the chemical composition distribution of the polymers.

Poly(phenoxy) resin in Figure 1 shows the broadest peak with another broad peak for poly(urethane) (Figure 2). The difference between styrene-butadiene copolymer and poly(carbonate) is only 6% but the separation is close to baseline separation. In the case of narrow peaks, as in Figure 4, even a difference of 4% between styrene-butadiene copolymer and poly(butadiene) provides an acceptable separation.
Table 1: Titrimetric Cloud-Points and Chromatographic Cloud-Points for Tetrahydrofuran Soluble Polymers with Water as Non-Solvent

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cloud-Point % Water</th>
<th>Chromatography % Water</th>
<th>( \Delta ) Poly(styrene) Retention Index (PI)</th>
<th>Peak Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Poly(butadiene)</td>
<td>6</td>
<td>5</td>
<td>-1</td>
<td>1.08</td>
</tr>
<tr>
<td>2 Styrene-Butadiene Copolymer</td>
<td>7</td>
<td>9</td>
<td>+2</td>
<td>1.03</td>
</tr>
<tr>
<td>3 Poly(dimethyl siloxane)</td>
<td>7</td>
<td>4</td>
<td>-3</td>
<td>1.09</td>
</tr>
<tr>
<td>4 Poly(sulfone)</td>
<td>8</td>
<td>8</td>
<td>0</td>
<td>1.05</td>
</tr>
<tr>
<td>5 Poly(carbonate)</td>
<td>9</td>
<td>3</td>
<td>+6</td>
<td>1.10</td>
</tr>
<tr>
<td>6 Poly(styrene)</td>
<td>12</td>
<td>12</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>7 Poly(vinyl chloride)</td>
<td>13</td>
<td>7-13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8 Poly(urethane)</td>
<td>15</td>
<td>16</td>
<td>+1</td>
<td>0.95</td>
</tr>
<tr>
<td>9 Styrene-Acrylonitrile</td>
<td>17</td>
<td>17</td>
<td>0</td>
<td>0.94</td>
</tr>
<tr>
<td>10 Poly(phenoxyl) Resin</td>
<td>22</td>
<td>24</td>
<td>+2</td>
<td>0.84</td>
</tr>
<tr>
<td>11 Styrene-Maleic Anhydride Copolymer</td>
<td>24</td>
<td>30</td>
<td>+8</td>
<td>0.80</td>
</tr>
<tr>
<td>12 Poly(methyl methacrylate)</td>
<td>29</td>
<td>29</td>
<td>0</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Figure .1: Chromatogram of poly(phenoxyl) resin; Chromatographical conditions: concentration 0.5% w/v, injection volume 10\( \mu \)l, flow 1 ml/min, gradient from 100% water to 100% tetrahydrofuran in 60 min. (linear), detection UV, \( \lambda =261 \) nm and column Nova-Pak cyanopropyl (CN), 3.9x75 mm, 60Å and 4 \( \mu \)m spherical particles, operating at ambient temperature.
Figure 2: Separation of a poly(urethane) and poly(carbonate) mixture; Chromatographical conditions: concentration TPU 0.5% w/v, PC 0.1% w/v, injection volume 10μl, flow 1 ml/min, gradient from 100% water to 100% tetrahydrofuran in 60 min. (linear), detection UV, λ=261 nm and column Nova-Pak cyano-propyl (CN), 3.9x75 mm, 60Å and 4 μm spherical particles, operating at ambient temperature.

Figure 3: Mixture of poly(carbonate) and styrene-butadiene copolymer; Chromatographical conditions: concentration SBS 0.5% w/v, PC 0.1% w/v, injection volume 10μl, flow 1 ml/min, gradient from 100% water to 100% tetrahydrofuran in 60 min. (linear), detection UV, λ=261 nm and column Nova-Pak cyano-propyl (CN), 3.9x75 mm, 60Å and 4 μm spherical particles, operating at ambient temperature.
The System 2,2,4-Trimethylpentane - Tetrahydrofuran

The second part of the polymer screening is based on the gradient 2,2,4-trimethylpentane - tetrahydrofuran (Table 2). Apart from two exceptions for the system 2,2,4-trimethylpentane - tetrahydrofuran, the correlation between the titrimitically obtained cloud-point values and the chromatographical obtained cloud-point values are also good.

The first exception is the same exception as that for the water - tetrahydrofuran system i.e. poly(carbonate). In the poor solvent tetrahydrofuran the poly(carbonate) tends to adsorb on the cyano-propyl sorbent.

The second exception is styrene-butadiene copolymer. As shown in Table 6.4 poly(butadiene) has a strong affinity to polar sorbents when dissolved in 2,2,4-trimethylpentane. In addition poly(styrene) tends to adsorb when dissolved in non-polar solvents. Therefore, it will be very likely that styrene-butadiene copolymer will adsorb on the cyano-propyl sorbent. It takes 19% tetrahydrofuran to remove the copolymer from the sorbent.

As expected from the cloud-point values obtained by titration the elution order at water - tetrahydrofuran is opposite to the sequence in 2,2,4-trimethylpentane - tetrahydrofuran (Figure 5). For example the polar styrene-acrylonitrile copolymer is repelled by the non-solvent in the 2,2,4-trimethylpentane - tetrahydrofuran system (last peak) and attracted by the non-solvent water in the system water - tetrahydrofuran (first peak in Figure 4). For example poly(acrylonitrile) (Appendix 13) has a very high polar solubility parameter and is thus very attractive to water.

The main problem in gradient polymer elution chromatography is explaining peak broadening. The classic examples of this are poly(styrene) and poly(carbonate). They exhibit narrow peaks in said non-solvent - solvent systems. The polymers poly(sulfone), poly(urethane) and poly(phenox) resin do give very broad peaks in both systems. The molar mass distribution of the three polymers is broad, 2.5-3 (Mw/Mn by GPC), but not extreme. It is likely that chemical or structural differences will result in this peak broadening.

The copolymers styrene-butadiene and styrene-acrylonitrile give narrow peaks in the water - tetrahydrofuran system and broad peaks in the 2,2,4-trimethylpentane - tetrahydrofuran system. A very little adsorption of the polar part in the copolymer may cause this peak broadening. Deactivation of the sorbent with a polar solvent (modifier) will improve the peak symmetry [1].
Figure 4: Chromatogram with reversed elution of (1) poly(methyl methacrylate), (2) styrene-acrylonitrile copolymer, (3) poly(styrene), (4) styrene-butadiene copolymer and (5) poly(butadiene); Chromatographical conditions: concentration 10 mg/ml, injection volume 10 μl, flow 1 ml/min, gradient from 100% water to 100% tetrahydrofuran in 15 min. (linear), detection UV, λ=350 nm (opalescent) and column Nova-Pak cyano-propyl (CN), 3.9x75 mm, 60 Å and 4 μm spherical particles, operating at 40°C temperature.

Figure 5: Chromatogram with normal elution order of (1) styrene-butadiene copolymer, (2) poly(styrene) and (3) styrene-acrylonitrile copolymer; Chromatographical conditions: concentration 10 mg/ml, injection volume 10 μl, flow 1 ml/min, gradient from 100% 2,2,4-trimethylpentane to 100% tetrahydrofuran in 15 min. (linear), detection UV, λ=261 nm and column Nova-Pak cyano-propyl (CN), 3.9x75 mm, 60 Å and 4 μm spherical particles, operating at ambient temperature.
Table 2: Titrimetric Cloud-Points and Chromatographic Cloud-Points for Tetrahydrofuran Soluble Polymers with 2,2,4-Trimethylpentane as Non-Solvent

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cloud-Point % TMP</th>
<th>Chromatography % TMP</th>
<th>Δ %</th>
<th>Poly(styrene) Retention Index (PI)</th>
<th>Peak Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Poly(sulfone)</td>
<td>11</td>
<td>16</td>
<td>+5</td>
<td>2.05</td>
<td>Broad tailing</td>
</tr>
<tr>
<td>2 Styrene-Maleic Anhydride Copolymer</td>
<td>20</td>
<td>24</td>
<td>+4</td>
<td>1.85</td>
<td>Narrow</td>
</tr>
<tr>
<td>3 Poly(phenoxy) Resin</td>
<td>24</td>
<td>27</td>
<td>+3</td>
<td>1.78</td>
<td>Broad tailing</td>
</tr>
<tr>
<td>4 Poly(urethane)</td>
<td>23</td>
<td>24</td>
<td>+1</td>
<td>1.88</td>
<td>Broad tailing</td>
</tr>
<tr>
<td>5 Poly(carbonate)</td>
<td>27</td>
<td>8</td>
<td>-19</td>
<td>2.24</td>
<td>Narrow</td>
</tr>
<tr>
<td>6 Styrene-Acrylonitrile Copolymer</td>
<td>28</td>
<td>24</td>
<td>-4</td>
<td>1.85</td>
<td>Broad</td>
</tr>
<tr>
<td>7 Poly(methyl methacrylate)</td>
<td>30</td>
<td>31</td>
<td>+1</td>
<td>1.68</td>
<td>Broad</td>
</tr>
<tr>
<td>8 Poly(vinyl chloride)</td>
<td>46</td>
<td>34.51</td>
<td>-</td>
<td>-</td>
<td>Several peaks</td>
</tr>
<tr>
<td>9 Poly(styrene)</td>
<td>59</td>
<td>59</td>
<td>0</td>
<td>1</td>
<td>Narrow</td>
</tr>
<tr>
<td>10 Styrene-Butadiene Copolymer</td>
<td>100</td>
<td>81</td>
<td>-19</td>
<td>0.46</td>
<td>Broad</td>
</tr>
<tr>
<td>11 Poly(dimethyl siloxane)</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12 Poly(butadiene)</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Peak broadening is reversed for the copolymer styrene-maleic anhydride. A broad peak (weak adsorption) in the water - tetrahydrofuran system and a narrow peak in the 2,2,4-trimethylpentane - tetrahydrofuran system.

The narrow standard poly(methyl methacrylate) gives peak broadening for both solvent systems. For both solvent systems poly(methyl methacrylate) is attracted to the sorbent.

A special case is poly(vinyl chloride). The chromatogram of poly(vinyl chloride) consist of many peaks and the shape of the peaks is not reproducible. Structure differences are a possible cause of the observed phenomena. Leijenaar [2] and Staal [3] reported the presence of poly-conjugate double bonds in poly(vinyl chloride).

Additional information is needed to explain peak broadening. Selecting and applying the strongest solvent and deactivation of the sorbent are the chromatographic answers to peak broadening. Information of the molecular mass distribution (GPC) and the shape of the turbidity titration curve may also explain peak broadening. The best approach is fractionation of the sample and identification of the structure of the fractions by infrared (IR) or nuclear magnetic resonance spectroscopy (NMR) [4].
Discussion

The correlation between cloud-points obtained by chromatography and obtained by titration is good, even for these commercial samples with a broad molecular mass distribution. This supports the general theory that the chromatography is dominated by a solubility mechanism. The practical application is that by applying cloud-points obtained by titration the chromatographic separation can be predicted.

Also the exceptions can be explained. The weak adsorption was not observed in previous solid phase extraction experiments. On the other hand the weak adsorption supports the general theory that adsorption can be expected applying poor solvents.

The main problem in gradient polymer elution chromatography is explaining peak broadening. The classic examples of this are poly(styrene) and poly(carbonate). They exhibit narrow peaks in said non-solvent solvent systems. The polymers poly(sulfone), poly(urethane) and poly(phen oxy) resin do give very broad peaks in both systems. The molar mass distribution of the three polymers is broad. 2.5-3 ($M_w/M_n$ by GPC), but not extreme. It is likely that chemical or structural differences will result in this peak broadening.

The copolymers styrene-butadiene and styrene-acrylonitrile give narrow peaks in the system water - tetrahydrofuran and broad peaks in the system 2,2,4-trimethylpentane - tetrahydrofuran. A very little adsorption of the polar part in the copolymer may cause this peak broadening. Deactivation of the sorbent with a polar solvent (modifier) may improve the peak symmetry [1].

References

### Suppliers of Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Mass</th>
<th>Dispersity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Poly(butadiene) (PB)</td>
<td>$10^7$-$10^9$</td>
<td>1.02-1.08</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>2 Styrene-Butadiene Copolymer (SB) [40% S]</td>
<td>$1.2 \times 10^5$</td>
<td>1.4</td>
<td>FINA (414)</td>
</tr>
<tr>
<td>3 Poly(dimethyl siloxane) (PDMS)</td>
<td>$1.03 \times 10^5$</td>
<td>2.36</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>4 Poly(sulfone) (PSF)</td>
<td>$6.7 \times 10^4$</td>
<td>3.28</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>5 Poly(carbonate) (PC)</td>
<td>$4 \times 10^4$</td>
<td>2.59</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>6 Poly(styrene) (PS)</td>
<td>$1.62 \times 10^2$-$3.15 \times 10^6$</td>
<td>1.1-1.16</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>7 Poly(vinyl chloride) (PVC)</td>
<td>$1.22 \times 10^4$</td>
<td>2.13</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>8 Poly(urethane) (TPU)</td>
<td>$8.5 \times 10^4$</td>
<td>2.6</td>
<td>Morton Chemical Morthane 371</td>
</tr>
<tr>
<td>9 Styrene-Acrylonitril Copolymer (SAN) [67% S]</td>
<td>$1.75 \times 10^5$</td>
<td>2.4</td>
<td>DOW Tyrl 602</td>
</tr>
<tr>
<td>10 Poly(phenoxyl) resin (PPR)</td>
<td>$3.1 \times 10^4$</td>
<td>3.7</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>11 Styrene-Maleic Anhydride Copolymer (SMA) [50% S]</td>
<td>-</td>
<td>-</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>12 Poly(methyl methacrylate) (PMMA)</td>
<td>$7.35 \times 10^2$-$1.3 \times 10^6$</td>
<td>1.22-1.04</td>
<td>Polymer Laboratories</td>
</tr>
<tr>
<td>13 Poly(vinyl acetate) (PVA)</td>
<td>$1.25 \times 10^5$</td>
<td>2.37</td>
<td>Scientific Polymer Products</td>
</tr>
<tr>
<td>14 Styrene-Acrylate-Acrylic Acid Copolymer (SAA)</td>
<td>$1.02 \times 10^4$</td>
<td>2.0</td>
<td>S.C. Johnson Polymer</td>
</tr>
</tbody>
</table>
Development and Application of a Gel Permeation Chromatography System for the Characterization of Rigid Rod Polymers

Rose M. Nelson
Malcolm W. Warren

The Dow Chemical Company

Purpose of Work

Provide an understanding of chemistry of polymerization of PBO (polybenzoxazole).

Understand effect of processing parameters.
Understand effects of aging on polymer strength.
Compare PBO to competitive products.

\[ \text{Chemical Structure} \]
Materials of Construction

**Pump:**
Waters dual piston pump (Model 510) equipped with a Swip Precision sapphire pump head retrofit kit.
Pump heads connected to Hastelloy C-276 connector with Hastelloy C tubing.
Pulse dampener/pressure transducer obtained from Scientific Systems, Inc.; cover plate machined out of Hastelloy C.

**Injector:**
Hastelloy C manual injection valve with 2 microliter internal loop, obtained from Valco Instruments, Inc.
Valve controlled by Valco Digital Valve Interface (air actuator).

**Column:**
Hastelloy C column end-fittings (Valco).
Column frits of UHMW polyethylene with chlorotrifluoroethylene rings (Upchurch).
Column body of polished Hastelloy C tubing.
All components sent to Polymer Laboratories to be packed with 10 micron particle size, 4000 Angstrom SAX packing material.

**Detector:**
Spectra Physics UV2000 (variable wavelength UV/Visible) with Hastelloy C flow cell.

**GPC Conditions**
Column: 4.6 X 150 mm Polymer Labs 4000 Angstrom SAX, 10 micron particle size
Injection: 2 microliters of 5 mg polymer in 20 mL of mobile phase
Mobile phase: Methane sulfonic acid (MSA) / 5% Methane sulfonic anhydride (MSAA) / 0.1 M methane sulfonic acid, sodium salt
Flow rate: 0.1 mL/min
Detector: 425 nm for PB0, 325 nm for Kevlar® and Technora® aramid fibers
Calibration: PBO Standards, plot IV vs. retention time
Data system: Polymer Laboratories PL Caliber® GPC/SEC software

**Safety Considerations**
Instrument should be placed in a hood with an acid scrubber.
Analyst should wear goggles, a rubber apron and rubber gloves.
The area should be blocked off while the analyst is handling the MSA.
The area should be inspected after use to insure that any acid spills are cleaned up.
Mobile phase continuously sparged with helium, and vented into a gas scrubber containing a solution of sodium carbonate or sodium bicarbonate.
Consult MSDS for MSA and MSAA prior to use.
Height-Normalized Chromatograms of PBO Standards

Calibration Curve for PBO Standards
Chromatograms for PBO Dopes and Small Molecule (Orange II Dye)

Precision of GPC Method

Data from eight injections of a single solution.
Concentration Effect for PBO

Applications: Molecular Weight as a Function of Reaction Time
Applications: Effect of Shear on MWD of PBO

Increasing time of shear -->

Applications: Effect of UV Exposure

100 hours sun test
Control

100 hrs sun test
Applications: Analysis of Rigid Rod Polymers

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Technora® is a registered trademark of Teijin Ltd. Japan.
PL Caliber® is a registered trademark of Polymer Laboratories Ltd.