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## Special Offers:

WinGPC Unity  
Upgrade with  
Report  
Designer

WinGPC Unity  
Upgrade with a  
Unity Notebook  
computer

WinGPC Upgrade  
from version 6  
  
from version 4

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## New Software Generation Unveiled

### WinGPC Unity Macromolecular Chromatography Data System



PSS pioneers a fresh approach to meet the challenges of structure elucidation and de-formulation of macromolecules with the launching of WinGPC

Unity Macromolecular Chromatography Data System (MCDS). You only need to know one software product, WinGPC Unity, to perform advanced characterization and structure determination. WinGPC Unity provides a simple and unique user interface. Raw data, sample information, parameters and results are stored in a validated and secure database. Obtain absolute and relative molar masses, distributions, chemical composition, co-

monomer distributions, block copolymer molar masses; determine branching and macromolecular architecture; quantify additives, residual monomers; Determine end-group functionalities and perform heparin QA tests according to EP, U.S.P. and DAB. Use 3-D surface plots and contour maps to view chromatography data acquired in two dimensions. The PSS WinGPC Unity MCDS is available now.

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## Characterization of Polymer Systems Using 2-Dimensional Chromatography

M. Nazeem Jahed and Rick Nielson

### Introduction

As polymer systems become more complicated with a variety of blends, grafts, co- and ter-polymers, linear, branched and hyper-branched architectures, it has become necessary to address the need for more selective techniques to determine accurately the chemical composition distribution along with the molecular weight distribution. In this issue we will describe the **2-Dimensional Chromatography** approach. The discussion will cover the separation mechanisms typically used for the two dimensions, the equipment/instrumentation setup and one example polymer characterization. Data collection and manipulation is straightforward with the **PSS WinGPC Unity MCDS**, and the

2-Dimensional chromatography module.

### 2-Dimensional Chromatography

The advantage of on-line 2-Dimensional chromatography is the ability to provide information about the chemical composition and molar mass of the polymeric sample within a single analysis. Typically, **Liquid Adsorption Chromatography (LAC) and Size Exclusion Chromatography SEC** are combined to separate complex polymers selectively with respect to their chemical composition or functionality followed by separation according to hydrodynamic volume (or molar mass). In LAC, separation occurs because of adsorptive interactions between the macromolecules and surfaces of the stationary phase particles,

whereas in a SEC separation relies on the migration of the macromolecules through the pores of the stationary phase. In SEC larger molecules are excluded from entering the pores of the stationary phase, and elute earlier than the smaller molecules, which permeate through the pores of the stationary phase. A schematic of the separation mechanism is shown in **Figure 1**.

A plot of log molecular weight vs. elution volume in **Figure 2** shows that for LAC, the elution volume increases with molecular weight, while for SEC the elution volume decreases with increasing molecular weight. However, between LAC and SEC there is a region known as

[Continues on page 3](#)

# High Sensitivity Viscometer Covers Broad Molecular Weight Range



**ETA 1001  
Asymmetric  
Four Capillary  
Viscometer**

A conventional gel permeation chromatography (GPC) system normally includes a refractive index (RI) or ultra-violet (UV) detector, called a concentration detector because the signal intensity of known molar masses [detector response] has to be established using reference standards. There are opportunities that the calibration standards and samples differ chemically or structurally, where the RI/UV test yields only apparent molecular masses; [relative to the calibration standards used]. This would be adequate in cases like quality control, however, not in situations when a real value is necessary. In such cases, it is important to add a detector that is sensitive to molar mass of the

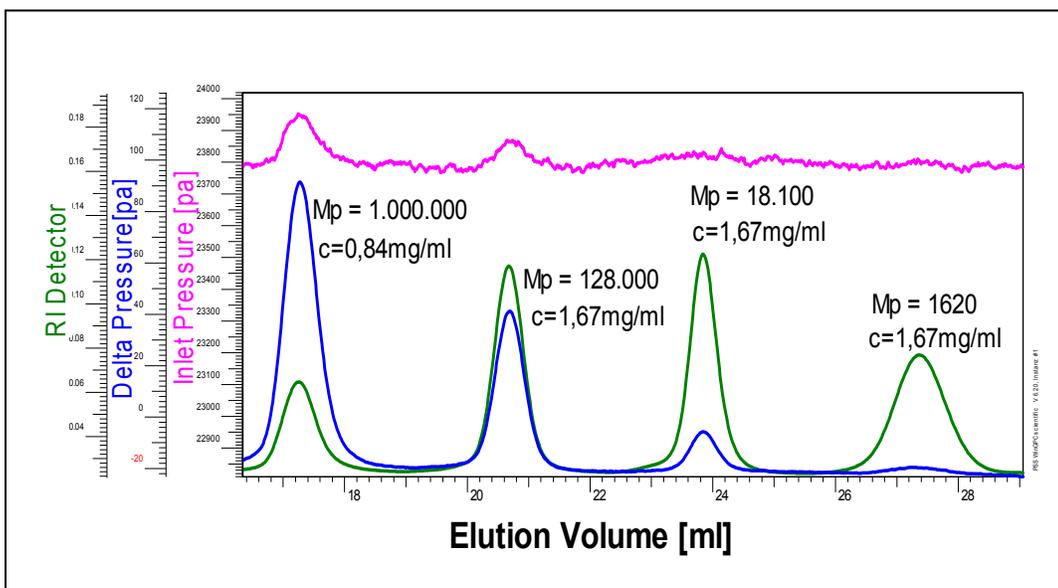
sample, i.e., viscometers -which integrate easily into an existing GPC system.

### Four Capillary Viscometers

Commercial capillary viscometers rely on measuring changes of pressure to elucidate the viscosity. The design still used today in most commercial viscometers is the old symmetric 4-capillary bridge, which splits flow 50:50 to sample and reference side. It is mandatory that the bridge is balanced, and the capillary i.d.'s are perfectly matched. If the capillaries do not match perfectly, the intrinsic viscosity and molecular weight measurements will be in error. However, with the **ETA 1001** innovative asymmetric 4 capillary

bridge design offered by PSS, the flow split is 80:20 (sample: reference), so much greater mass gets detected, (i.e. greater sensitivity). The result is much better signal-to-noise, even at very low molecular weights, and superior response over the older bridge design throughout the entire MW range, even as low as a few hundred Daltons. This becomes clear in Figure 1, which displays the GPC separation of four polystyrene standards (PS ReadyCal red) detected through refractive Index (RI) signal [Agilent HP 1100] and viscosity signals: inlet and delta pressure from the viscometer **ETA 1001**, captured with the power of WinGPC Unity software and viscosity module.

Note the quality of the delta pressure in comparison to inlet pressure signal. The lower molecular weights are still detectable by the four-capillary viscometer, even at concentration and injection volume typical of conventional GPC. The standard with lowest molar mass is detectable. (Mp = 1620 D, c = 1.6729 mg/ml). It is safe to say that the four capillary asymmetric design used in the ETA 1001 shows unsurpassed sensitivity, easily detecting compounds down to a few hundred molecular weight. The polystyrene data presented in Figure 1 also point out the difference between a concentration detector and a detector sensitive to molar mass. Since the RI detector's signal power depends only on sample concentration, the peak heights and areas of all standards are proportional to the concentration. Conversely, the viscometer's peaks of high molecular weight standards are more intense than peaks produced by low molecular weight species, because the signal intensity responds to concentration and viscosity.



**Figure 1**

### RI and Viscometry Detector Signals of Polystyrene Mixture (PSS PS ReadyCal red)



Inlet and delta pressure signals: ETA 1001 viscometer  
RI signal: Agilent HP 1100; Injection volume = 100 µl  
Columns: three PSS SDV linear M, WinGPC Unity Data System

## Is WinGPC Unity Software Right for you?

Last month PSS Polymer Standards Service officially launched WinGPC Unity Macromolecular Chromatography Data System (MCDS), a concrete realization of software that meets the basic requirements of modern laboratories for acquiring and processing chromatographic data. WinGPC Unity is a pre-eminent chromatographic data system that meets the challenges of structure elucidation and de-formulation of macromolecules for fast-paced modern laboratories. The WinGPC Unity MCDS works on a local PC or in a client/server setup (for larger institutions). WinGPC Unity communicates with a variety of laboratory devices and data systems from different manufacturers; it allows the combined acquisition and processing of the data. WinGPC Unity brings powerful automation, manipulation and documentation capabilities through a simple and unique user interface. Raw data, sample information, parameters and results are stored in a validated and secure database. Information retrieval and sharing is a breeze.

Four live case scenarios from everyday identify decision-making scenarios faced by scientists and companies. In each case, note how the unique benefits of Unity satisfy specific needs and requirements.

### Case 1:

A manufacturer of pharmaceutical products needs fully validated GPC software in different working areas, using the existing infrastructure. The software must be compatible with methods at other working places. GPC measurements have to be carried out and controlled from various departments. The analytical staff from different labs and offices, corporate-wide, must have on-

line access to the data initially processed at the measurement site. The comprehensive analysis of the measurement is done in specialist departments; this should be possible even without having the equipment to execute GPC measurements on their own.

### Reasons to choose WinGPC Unity

- It is compliant with all national and international GPC standards (e.g. ISO, EN, ASTM, DIN, JS), making it easier and faster to put your products on the market
- Offers comprehensive software validation easy to verify in audits
- Has a central relational database with straightforward data management and search routines
- Integrates all GPC data in the existing worldwide LIMS system
- Offers high level data security and central access control using existing authentication mechanisms (e.g. a domain server)
- Guarantees accessibility and support world wide
- Handles all current and future tasks, minimizing training and support costs
- Allows a comprehensive and fast data exchange between labs in different countries
- Offers in client/server mode business-wide control over your analytical jobs, no matter where you presently are ("data follows people" technology)
- Permits data acquisition via LAN, allowing a flexible, friendly use of the existing infrastructure
- Facilitates the creation and publication of results and reports in the intranet, or via e-mail

*Case 1 Solution:*  
After a comprehensive test phase, the company chooses the PSS Client/Server GPC solution for distributed working

### Case 2:

A research lab needs a GPC system to build up a new working direction. The conceptual formulation demands further processing of the primary GPC data with self-programmed software. An older HPLC instrument and a computer with MS Win 95 need be integrated in the new setup.

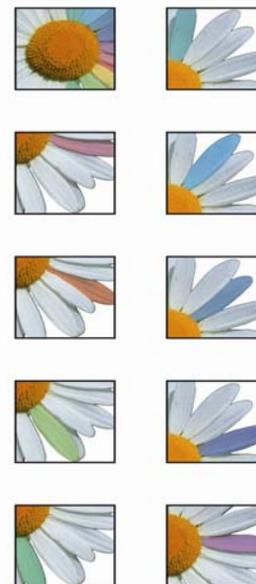
### Reasons to choose WinGPC Unity

- It allows the integration of the HPLC instrument and further use of the old personal computer
- The data export function facilitates further processing of GPC data
- Easy to learn user interface, minimizes learning curve time requirement
- Straightforward integration of results into research reports

*Case 2 Solution:*  
One Simple WinGPC setup for a single station system

### Case 3:

A central analytical laboratory that operates a (heterogeneous) chromatography infrastructure has to upgrade the equipment in order to meet customer requirements. The upgrade



## Is WinGPC Unity Software Right for you? (From page 5)



includes the purchase of new special detectors and the development of new analytical and data processing methods. Special requirement emphasis is placed on flexibility for all staff members to use the complete equipment.

### Reasons to choose WinGPC Unity

- Compatible with existing equipment
- Integrates new instruments independent of the manufacturer
- Supports not only evaluation of conventional GPC data, but also a lot of special methods/tasks and is modular
- Meets the requirements of all national and international standards
- Is fully validated and easily satisfies the needs of internal and external auditors
- Uses the same user interface and data structure for all possible tasks
- Has a safe and consistent database structure, guaranteeing maximum data security
- Allows a flexible distribution and assignment of the existing resources
- Data evaluation licenses are free of charge
- Creates task and customer specific result reports
- Supports the results distribution by e-mail, fax and internet

*Case 3 Solution:  
PSS WinGPC with  
network support  
(Multi system / multi  
station setup) for data  
acquisition and  
processing  
Department-wide*

### Case 4:

A production lab needs a complete GPC system for quality control to meet the demanding requirements of the customers.

### Reasons to choose WinGPC Unity

- Data acquisition and processing can be fully automated
- Of the high availability and stability of PSS WinGPC
- WinGPC generates customer specific result reports
- WinGPC can automate the acceptance criteria of products with specific, targeted reports
- The measurement results can easily be merged into the existing LIMS

*Case 4 Solution:  
WinGPC Unity for 3  
Robust and easy to use  
Compact GPC systems  
for quality control*

From the decision-making presentation above it is possible to generalize some of the features that are important to users in the marketplace: **Stability and reliability** for data acquisition (stand-alone computers and computer networks, that are readily convertible. **Flexibility** to support various computer and operating systems as well as adaptability of the data system to the laboratory conditions (mainly devices and or export procedures are beneficial).

**Easy to implement and integrate** into the lab, (not resource-intensive). The seamless modular

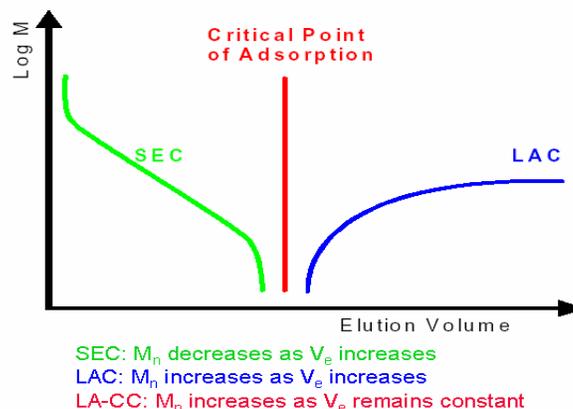
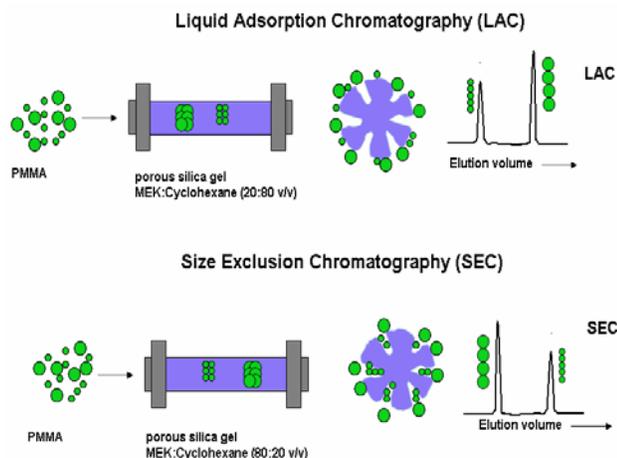
structure facilitates training. The user interface provides the functions that are relevant to the task at hand, and therefore the user does not spend time learning difficult functions.

All users have their own specific needs and demands, **easy to validate**, whether or not they work in regulated laboratories. Independent from the size of the data system used, experience shows that the validation of a software package is often one of the biggest problems for the end user. The comprehensive validation of WinGPC offers not only solutions for standard systems and methods but also for highly sophisticated systems with special detectors. You can easily check the validation of your data acquisition systems on-site to document the usefulness for your measurements.

The **compliance with all national and international regulations** for data acquisition and processing (ISO, ASTM, DIN, Pharmacopoeias etc.) is also of great importance. With an integrated chromatography software solution, these requirements are much easier to meet than with several different packages. No longer will an analytical chemist have to spend most of the time learning multiple software products, or validating and integrating multiple processes and data formats into the data flow. Using WinGPC will result in **lower overhead costs** and a better use of your human resources.

USA and Canada, customers e-mail [pssusa@polymer.de](mailto:pssusa@polymer.de) for more information, a detailed brochure or to order. Everywhere else email: [info@polymer.de](mailto:info@polymer.de).

## 2D Liquid Chromatography *(continued from page 1)*



**Figure 1. Separation by Liquid Adsorption (LAC) and Size-Exclusion Chromatography (GPC/SEC)**

**Figure 2. Molecular weight dependence for different chromatographic techniques**

the Critical Point of Adsorption at which macromolecules having the same chemical composition all elute at the same elution volume irrespective of their molecular weight (elution volume is independent of molecular weight).

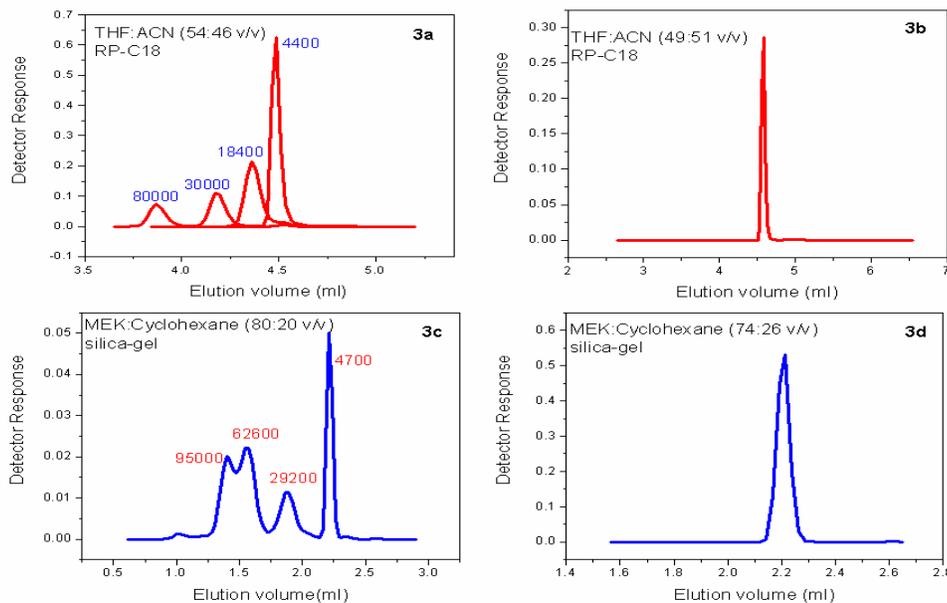
different molar masses results in the elution of all polystyrene standards at the same elution volume (3b). The critical conditions (3d) for poly(methyl methacrylate) on a silica-gel column were obtained by using a mobile phase composition of

methyl ethyl ketone-cyclohexane (74:26 v/v)<sup>1</sup>. LA-CC has been used to separate homopolymers from their copolymers and is of importance when de-formulating competitive materials of unknown sample composition.

### Liquid Adsorption Chromatography at Critical Conditions (LA-CC)

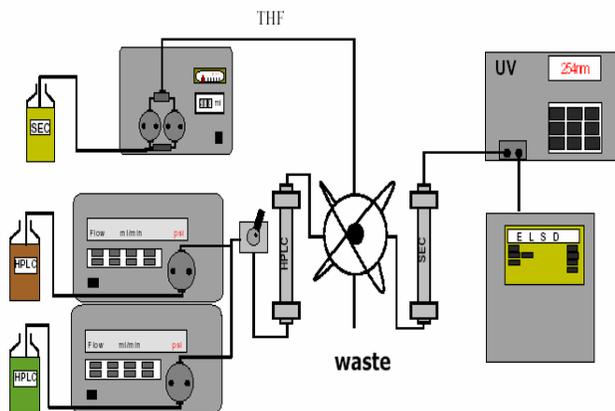
In 2-Dimensional chromatography, Liquid Adsorption chromatography at Critical Conditions (LA-CC) is often used as the 1st-dimension (the HPLC system is operated under these critical conditions for a specific polymer), while the 2nd -dimension is SEC/GPC.

The chromatograms in **Figure 3** illustrate the phenomenon of LA-CC. A series of polystyrene standards injected onto a reverse phase column, in THF-acetonitrile (54:46 v/v) mobile phase (3a) shows size-exclusion behavior. The elution volume increases with decreasing molar mass. However when changing the mobile phase composition to THF-acetonitrile (49:51 v/v)<sup>1</sup> the injection of the same mixture of polystyrene standards of

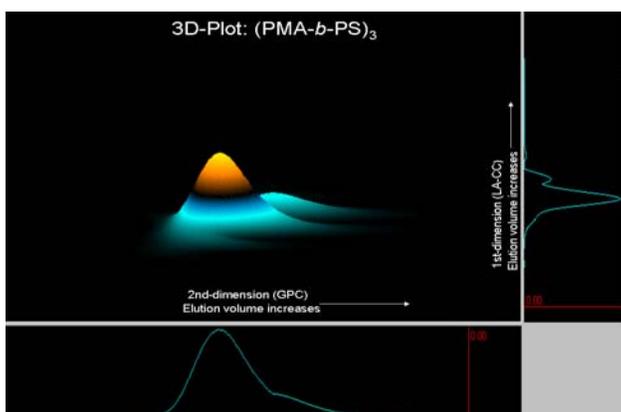


**Figure 3. Elution behavior of Polystyrene (3a, 3b) and Poly(methyl-methacrylate) (3c, 3d) at critical conditions**

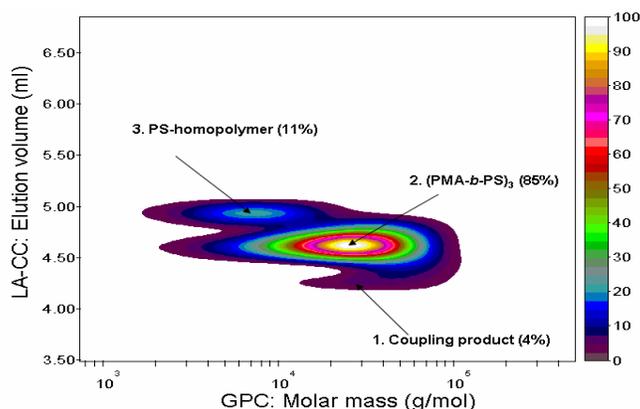
## 2D Liquid Chromatography *(continued from page 3)*



**Figure 4 Instrumentation**



**Figure 5a 3-Dimensional plot for the 3-arm Poly(methyl acrylate)/Polystyrene block copolymer (PMA-b-PS)<sub>3</sub>**



### Instrumentation of 2-D Chromatographic Analysis

As mentioned previously, the 1<sup>st</sup>-dimension of the 2D separation is typically LA-CC and the 2<sup>nd</sup>-dimension, SEC/GPC. The instrument arrangement for 2-Dimensional Analysis is shown in **Figure 4**. It consists of a solvent management system capable of pumping two (or more) solvents in isocratic or gradient mode, as well as a pump for the SEC/GPC solvent; A transfer valve is used to send the separated components from the 1<sup>st</sup>- to the 2<sup>nd</sup>- dimension. To include an autosampler will facilitate sample throughput and unattended automation. The use of a high-speed GPC column will decrease the analysis time for the 2<sup>nd</sup>-dimension separation. Achieve detection via a UV or preferably an evaporative light scattering detector (ELSD).

The PSS WinGPC Unity 2D software option allows one to calculate **automatically** the area/height and relative amounts, as well as the molecular weight averages from the 2-Dimensional Analysis. The user is free to set up an integration method for known polymer systems, or manually integrate specific peaks.

### 2-D chromatography Illustration

The investigation of a 3-arm Poly(methyl acrylate)/Polystyrene block copolymer (PMA-b-PS)<sub>3</sub> is shown in figures 5a and 5b<sup>2</sup>. Separation in the 1<sup>st</sup>-dimension (LA-CC) was carried out at critical conditions for polystyrene with mobile phase THF:acetonitrile (49:51 v/v) and two reverse phase C18 columns as the stationary

phase<sup>2</sup>. The 2<sup>nd</sup>- dimension (SEC/GPC) was performed using THF and a PSS high-speed GPC column (SDV Linear M).

**Figure 5a** shows a 3D plot of the 3-arm block copolymer separated in both dimensions. The 1<sup>st</sup>-dimension (y-axis) represents separation according to chemical composition while the 2<sup>nd</sup>-dimension (x-axis) shows separation according to molecular weight

The 2-Dimensional contour plot shown in **Figure 5b** reveals the presence of three polymeric species in the sample, which are identified as: a coupling product (1), the 3-arm (PMA-b-PS)<sub>3</sub> block copolymer (2) and polystyrene homopolymer (3). The relative amounts of each of the three polymeric species present as well as the number and weight average molecular weights, polydispersity (D), and height of the peak contour (Z), are obtained from the 2D-software.

### References

1. Harald Pasch, Kibret Mequanint, Jörg Adrian, *e-Polymers* **2002**, no. 005.
2. Mei Li, Nazeem M. Jahed, Ke Min, and Krzysztof Matyjaszewski, *Macromolecules*, **2004**, *37*, 2434.

### Acknowledgments

Prof. Krzysztof Matyjaszewski (Carnegie Mellon University, Pittsburgh, USA) and Dr Harald Pasch (Deutsches Kunststoff-Institut, Darmstadt, Germany

**Figure 5b 2-Dimensional contour plot for the 3-arm Poly(methyl acrylate) /Polystyrene block copolymer (PMA-b-PS)<sub>3</sub>**

Number	Mn	Mw	D	Z
1	3.91905E+04	5.20667E+04	1.32855E+00	6.01037E+02
2	1.96820E+04	3.09179E+04	1.57087E+00	8.52078E+02
3	5.96989E+03	8.11936E+03	1.36005E+00	1.08033E+03

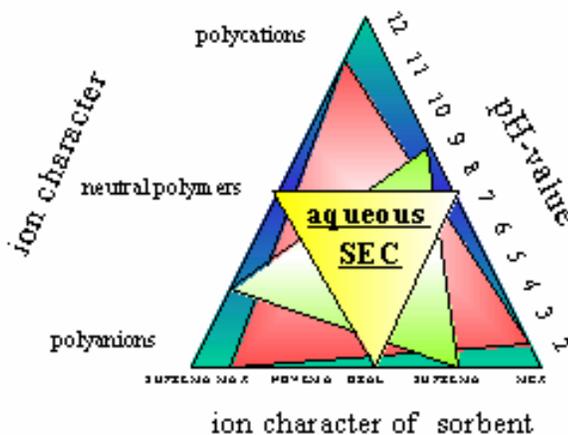
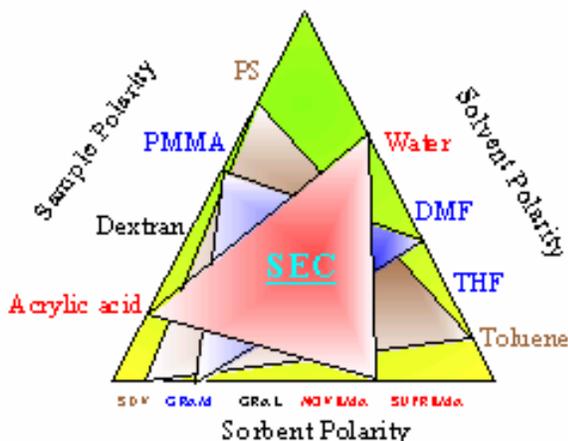
# Columns are the Key to Successful Polymer Separation

Gel Permeation Chromatography (GPC), Size Exclusion Chromatography (SEC), or Gel Filtration Chromatography (GFC) are names used interchangeably for a liquid chromatography technique to obtain the molecular weight distribution of a polymer. You must select the right eluent and the right column material to complete the separation successfully. Any interaction with the column must be prevented (contrary to normal HPLC methods that rely on those interactions). Only the entropy effects should influence the separation. The PSS Magic Triangle illustrates the interactions of sample, mobile

phase and stationary phase, to facilitate stationary phase selection between PSS stationary phases. Try to construct an equilateral triangle taking into consideration the polarity of sample and eluent or (in aqueous systems) the ion character and pH values. Once you selected the right column, the following steps will help you to be successful in GPC separation.

- 1- Determine the Plate Count, Asymmetry and Resolution of your column.
- 2- Completely fill the system with eluent. Make sure to use only the eluents that

- are compatible with the gel.
- 3- Use guard column to increase the column life.
- 4- Determine the molecular weight range of the separation with a calibration curve.
- 5- Perform a good sample preparation --Use a 0.45-micron filter to prevent solids from entering the column.
- 6- Use appropriate concentrations and injection volume balance to prevent column overload. The higher the molecular weight the lower the sample concentration.
- 7- Maintain a flow that agrees with the column diameter and viscosity of sample to prevent shearing and backpressure.



**Columns**  
GRAM

- MCX
- NOVEMA
- PFG
- POLEFIN
- SDV HR 3µm
- SDV 5µm
- SDV 10µm or 20µm
- SUPREMA

**Applicability Example**

- PMMA, Dextran, Cellulose nitrate
- Polyacrylic & Polymethacrylic Copolymers
- Sulfonated styrenes, Lignins, fruit juice
- Polycations, Proteins, bio-polymers
- Polyethylene-terephthalate, Nylon
- Polyolefins
- Oligomers, additives, small molecules
- Organic soluble polymers PS, PMMA
- Organic soluble polymers PS, PMMA
- Gelatin, PEO, PEG, Dextrans

**Eluent**

- DMF, DMAc, NMP, DMSO
- Aqueous
- Aqueous
- HFIP, Trifluoroethanol
- TCB, ODCB Decalin Xylene
- THF, Toluene, CHCl3
- THF, Toluene, CHCl3
- THF, Toluene, CHCl3
- Aqueous

**Mw Range**

- 100 to 1Million
- 100 to 5Million
- 100 to 5Million
- 100 to 10Million
- 1000 to 10 Million
- 100 to 1Million
- 100 to 10Million
- 100 to 50 Million
- 100 to 50 million

## PSS-USA Welcomes New Employees

By Michael Gray

I am pleased to announce that PSS-USA is expanding its workforce. Rick Nielson joined the organization as East Coast Regional Sales Manager and M. Nazeem Jahed joined as a 2-D Chromatography specialist.

Rick Nielson (top) formerly of Waters Corporation spent nearly 18 years in various capacities acquiring a wealth of knowledge of polymer characterization. Since 1986, Rick hosted the bi-annual International GPC Symposium

sponsored by Waters. With his expertise, he will support your polymer characterization needs to help you identify requirements and provide solutions on methodology development, software, equipment, consumables, customer training and support. You can reach Rick at [rielson@polymer.de](mailto:rielson@polymer.de).

Complimenting the PSS-USA team is M. Nazeem Jahed, who spent the past two years on post-doctoral work at Carnegie Mellon University,

with Prof. Krzysztof Matyjaszewski. He worked on the 2-D characterization of ATRP type polymers. Nazeem will support our clients with the WinGPC Unity software, the 2-D module and our light scattering and viscometer detectors for GPC analysis. You can reach Nazeem at [njahed@polymer.de](mailto:njahed@polymer.de).

Please join me in welcoming Rick and Nazeem; I look forward to working with them and I strongly believe they can assist you in your polymer characterization.



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