

Trends in Polymer Separations: Better and More Information on Polymer Distributions

Peter Schoenmakers

Polymer-analysis group, Faculty of Science, University
of Amsterdam, Nieuwe Achtergracht 166,
1018 WV Amsterdam, The Netherlands
(pschoen@science.uva.nl)

Polymer separations are performed routinely and reliably in many laboratories and for many purposes. Size-exclusion chromatography (SEC) is by far the most common separation technique for polymers, but interactive liquid chromatography (i-LC) is increasingly important. SEC is the workhorse of polymer separations. It yields a separation according to the size of polymer molecules in solution, which after appropriate calibration can be transformed into a molecular-weight distribution (MWD). A number of methods are available for such a calibration. Conventionally, narrowly distributed standards of known molecular weight are used. This is an excellent way to calibrate, provided that the standards and the analyte polymer are chemically identical. In case ideal standards are not available, molecular-weight sensitive detectors (light scattering, viscometry, or a combination of both) can be used very elegantly. For molecules that are too small, mass spectrometry (MS) may be used in many cases for off-line calibration and in some cases (hydrophilic polymers) in an on-line ("hyphenated") combination with SEC. SEC offers satisfactory solutions, except for copolymers with varying composition (composition drift), in which case all common calibration methods – with the possible exception of MS – are flawed.

Yet even in the most difficult cases there are imminent solutions. i-LC can be used to separate polymers according to chemical composition or functional (end) groups and thus provides a different ("orthogonal") way to characterize polymers. In comprehensive two-dimensional liquid chromatography the entire sample is first separated according to one mechanism, after which every fraction is separated in a second dimension based on a different principle. For polymers that dissolve in organic solvents, the combination of i-LC and SEC (LC×SEC) appears to be most useful [1]. The technique may be slow, but it is not difficult to implement or apply. LC×SEC provides excellent impressions of mutually dependent size and composition (or functionality) distributions of complex polymers. It also offers a way out of the maze of accurately determining MWDs for copolymers. Although calibrating the second-dimension SEC system for each point along the first-dimension LC separation may be cumbersome and laborious, the approach is rigorously correct.

Having described the field of polymer separations in the two paragraphs above may create the impression that we little left to be desired. For this reason, polymer separations is often seen as a mature field. This impression is deceptive. We have a lot left to do.

SEC is a low-resolution technique. The separation based on molecular size is convoluted with chromatographic band broadening, both due to the separation process (column) and from the instrument (extra-column). It is hard to take the three effects apart [2]. If we subject the SEC effluent to a light-scattering or viscometry detector, the sample we measure is still polydisperse rather than monodisperse. The characteristic molecular-weight averages (number-average molecular weight, M_n , and weight-average molecular weight, M_w) may be

reasonably repeatable (within one laboratory), but are poorly reproducible (between laboratories) [3]. If we search for a compromise between speed and resolution, SEC is behind other forms of LC. If we aim for miniaturized separation methods (e.g. to reduce the amounts of solvents used) SEC lags far behind. Higher resolution than in SEC may be achieved by i-LC, with either solvent programming (gradient elution) or temperature programming (temperature-gradient interaction chromatography, TGIC) [4]. The latter technique, which has been pioneered by Taihyun Chang in Korea, is especially promising for high-resolution polymer separations. By cooling the effluent between the column and the detector, TGIC allows use of all SEC detectors.

Polymer separations cannot be served by SEC alone. Other separation principles are needed for characterizing other distributions. Some of these are relatively well developed, such as gradient-elution LC for separating copolymers according to chemical composition and – to a somewhat lesser extent – isocratic ("critical") liquid chromatography for the separation of functional polymers according to the type and number of functional groups or end groups. Some other separation mechanisms are still at the early stages of development, such as molecular-topology fractionation (MTF) for separation according to the degree of branching [5].

Comprehensive two-dimensional liquid chromatography of polymers has been developing rapidly in recent years. Apart from the conventional LC×SEC applications (chemical-composition distribution and molecular-weight distribution, CCD×MWD, of copolymers; functionality-type distribution and MWD, FTD×MWD, of functional polymers), we have been exploring MTF×SEC for characterizing branched polymers and comprehensive two-dimensional critical chromatography for characterizing block copolymers.

The field of polymer separations is still growing. Thus, by definition, it is not mature. There is much room for growth, because the state of the art leaves quite a lot to be desired. Polymer separations will be growing for a while.

References

- 1 A. van der Horst and P.J. Schoenmakers, *J. Chromatogr. A* **1000** (2003) 693.
- 2 S.-T. Popovici, W.Th. Kok and P.J. Schoenmakers *J. Chromatogr. A* 1060 (2004) 237.
- 3 D. Berek, *Polymery/Polymers* **49**(5) (2004) 313.
- 4 T. Chang, *J. Polym. Sci., Part B: Polym. Phys.* **43** (13) (2005) 1591.
- 5 D.M. Meunier, P.B. Smith and S.A. Baker, *Macromolecules* **38** (12) (2005) 5313.