NON-SIZE EXCLUSION CHROMATOGRAPIC CHARACTERIZATION OF COMPLEX POLYMERS: CHALLENGES AND SOLUTIONS

Yefim Brun

DuPont Central Research & Development, Experimental Station, Wilmington, DE, USA
yefim.brun@dupont.com

ABSTRACT

Non-size exclusion chromatography, often called interaction polymer chromatography (IPC), is a series of liquid chromatography techniques employing non-size exclusion separations for polymer characterization. The need for such techniques is dictated by the complexity of the polymer systems. Thus, SEC, where steric analyte-stationary phase interaction provides separation by molecular size, is useful mostly for polymer molecular mass distribution determination, and usually yields little information regarding various chemical heterogeneities in the polymer system different from the size of the macromolecules, e.g., chemical composition distribution, chain blockiness, functional groups, etc. The IPC techniques provide separations by aforementioned structural molecular properties and in such a way are complimentary to SEC.

The specific selectivity of the chromatographic process, i.e. its retention mechanism, can be controlled by an appropriate combination of polymer – stationary phase interaction forces. Thus, for molar mass independent elution, the attractive polymer/substrate enthalpic interaction is exactly balanced by entropic confinement penalty. Such conditions are usually called critical point of adsorption (CPA). In isocratic chromatographic mode, i.e. at constant eluent composition and temperature, elution at CPA leads to separation by number or interaction strength of moieties (e.g. end-groups). If the CPA conditions for various fractions of a complex polymer, e.g. copolymer or polymer blend, are achieved in a solvent gradient mode, then separation by chemical composition or microstructure of the polymer chains can be observed. Temperature gradient in the vicinity of the CPA can produce a very selective separation of stereoisomers, etc.

The goal of this presentation is to demonstrate how the mechanism of retention in various IPC techniques can be modulated to yield a required selectivity of the chromatographic process for a comprehensive characterization of complex polymers and polymer formulations. We will show how the molecular-statistical theory of polymers in confined (porous) media (chromatographic columns) can be used to describe such selectivity in terms of molecular parameters of the polymer chains, as well as for optimization of the chromatographic process, i.e. selection of chemistry of stationary and mobile phases, solvent and temperature gradient profiles, pore and column geometry. Several examples will be discussed, i.e. separation of statistical and block-copolymers obtained by Reversible Addition Fragmentation Polymerization (RAFT) with cyanomethyl-substituted trithiocarbonate functional group, characterization of melt-derived copolyesters with fluorinated side chains, as well as branched polyacetals and polyamides.