Analytical Polymer Science

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Polymers are inherently complex multi-component systems exhibiting several distributed properties. Obviously, the foremost distribution would be the molar mass. Other distributions such as chemical composition, functionality and molecular architecture etc add more to the complexity of already complex systems. These properties superimpose over each other, therefore, analysis with regard to one property does not reveal any information with respect to other properties as a function of the measured property. Spectroscopic techniques such as NMR, FTIR etc divulge only average values but not the distributions. Hence, hyphenated and multidimensional approaches for analysis of these complex systems are imperative to attain a fairly representative picture in order to develop real structure-property correlations.

To realize the multi-dimensionality, first dimension has to be a non-destructive separation method. The fractions from first dimensions can then be analyzed by any other technique. The most widely used separation technique in analysis of polymers is HPLC (column based separation technique)[1-6] along with rather moderately employed field flow fractionation, FFF (an open channel separation technique)[7], especially to overcome the limitations of HPLC-based approaches for polymer analysis. The size exclusion chromatography (SEC) is the work horse of polymer laboratories that separates with regard to size of the polymer species in the dilute solution that is then correlated to their molar mass by external calibration or absolute molar mass with the help of molar mass sensitive detectors such as light scattering and/or viscometry. Various modes of interac-

tion chromatography such as Liquid Chromatography at Critical Conditions (LCCC), Liquid Chromatography under Limiting Conditions (LCLC), Temperature and Solvent Gradient Interaction Chromatographic Modes (TGIC and SGIC) are also used for analysis of polymers with respect to different properties such as chemical composition, functionality, and molar mass etc. Asymmetrical Field-Flow Fractionation (AF4) and Thermal Field-Flow Fractionation (ThFFF) are commonly employed modes of FFF for polymer analysis[7].

In FFF, all problems related to the stationary phase such as undesired adsorption, shear degradation of large macromolecules, co-elution of linear and branched macromolecules etc, can be avoided. Off-line and on-line hyphenations of these different modes of liquid chromatography, and with spectroscopic techniques disclose very important information about polymer heterogeneity that is not possible by employing these techniques independently. The coupling of these separation methods to the information rich detectors can also reveal important information.

Briefly, the interaction parameter describes the separation mechanism in liquid chromatography of polymers[8]. In Size Exclusion Chromatography (SEC), its value is negative where retention decreases with increase in molar mass. In Liquid Adsorption Chromatography (LAC), value of interaction parameter is positive. The mid-point between these two extremes is Critical Adsorption Point (CAP) and value of interaction parameter at this point is zero. Polymers elute in order of decreasing molar

mass in SEC and in order of increasing molar mass in LAC. The molar mass independent elution is observed at CAP. This special mode of liquid chromatography of polymers is called Liquid Chromatography at Critical Conditions (LCCC).

LCCC allows separation of polymers with regard to distributions other than molar mass such as other block, functionality, architecture etc. Liquid chromatography under limiting conditions is also based on exclusion-adsorption equilibrium and can be adjusted by using different mobile phase and sample solvent.

The basic requirement of any polymer lab is a size exclusion chromatograph that is first test to determine the propagation of size which is then correlated to the molar mass through an appropriate calibration curve (generally polystyrene). The values obtained shall be accurate only for linear polystyrene. By conventional SEC, the molar masses are either under or overestimated. Multiple detection systems are often used to overcome this problem. These multiple detectors also include molar mass sensitive detectors such light scattering or viscosity. The improved detection systems could not fully overcome the limitations but reduce these discrepancies to great extent.

Temperature and solvent gradient HPLC allows for separation of polymer with regard to chemical composition. This mode of LC is mostly used for high resolution separation of oligomers as well as for high polymers. Another important and widely used liquid chromatographic method is liquid chromatography at critical conditions. It makes one of the segments chromatographically invisible and separation with regard to other distributions could be realized.

Since, polymers are very complex, therefore, a single, stand-alone technique is usually not enough to obtain true picture of the composition of the sample. Introduction of multiple detectors improve the situation but still could not fully overcome the limitations. Hyphenations of different modes of LC with each other and with other spectroscopic techniques is the obvious choice for more detailed insight into the product. For two-dimensional LC, samples are separated by one mode of LC with regard to one distribution and fractions are subjected to analysis in the second dimension by any other mode of LC of polymers. The hyphenations can be realized on-line or off-line. Both on-line and off-line approaches have their own pros and cons. Similarly, LC separation can also be hyphenated to spectroscopic techniques (such as NMR, mass spectrometry, FTIR etc.). These hyphenations of different modes of LC with each other and with spectroscopic technique reveal very important information about molecular heterogeneity that was not possible otherwise.

The column-based fractionation technique suffers from degradation of the samples, unavoidable adsorption, limited exclusion limits etc due to presence of porous stationary phase.

These problems can be overcome by Field-Flow Fractionation (FFF). The narrow ribbon-like channel of FFF is constructed by clamping a Mylar or polyimide spacer with a specific cut-out between two flat surfaces. The carrier liquid is pumped from the injector through the channel to the detectors. The sample is injected in front of the channel inlet. In the FFF channel a laminar parabolic flow profile develops due to its high aspect ratio and leads to the development of zones of varying flow velocities in increasing order from the walls to the center of the channel. The applied field determines the type of FFF technique. Flow field-flow fractionation and thermal field-flow fractionation are the important techniques of FFF used in polymer analysis. Asymmetrical Flow Field-Flow Fractionation (AF4) has almost completely replaced symmetrical mode of FFF. If the external field is temperature gradient, the FFF technique is termed as thermal-FFF. It is also a useful technique for molar mass and chemical composition analysis of polymers. The detailed account of recent applications of the different modes of HPLC of polymer, FFF and their hyphenations with each other and with spectroscopic techniques is given in some recent and important review articles and monographs[1-7,8]. Different modes of HPLC are used commonly for polymer analysis with regard to molar mass, chemical composition, topology, functionality etc. The utilization of FFF is limited to special cases, such as branched polymers, polymers with gel content, polymers susceptible to degradation under sheer stress, polymeric nano-composites etc.

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