WHITEPAPER

10 reasons why academics should be using multi-detector SEC for polymer characterisation

Discover the benefits of multi-detector SEC for characterising the molecular weight and structure of synthetic polymers

MOLECULAR SIZE

MOLECULAR STRUCTURE

MOLECULAR WEIGHT

Introduction

Polymers are fundamental in our everyday life. Thanks to their numerous properties they can be used in plastics, fibres, adhesives or rubber, but polymers are also in our bodies in the form of proteins. The large number of polymers produced nowadays by both the industrial and the academic world includes polymers with different chemical natures and structure. Polymer scientists are constantly developing new types of synthetic polymers and modifying natural polymers to create materials with a wide variety of properties. The continuous research to produce better performing polymers has driven the academic world to synthesise novel polymers by means of several polymerisation techniques. The polymer synthesis process is continuously developing in order to produce model polymers with the desired characteristics. A ‘perfect’ polymer or, at least, a well-characterised polymer, is what scientists need in order to gain a better understanding of the relationship between structure and properties. Being able to correlate the polymers molecular characteristics with their physical properties leads to a better formulation and application of the polymers produced. Thus, it is evident that the full characterisation of the materials synthesised is fundamental for polymer scientists. The use of multi-detector Size Exclusion Chromatography (SEC), allows researchers to measure the absolute molecular weight, dispersity and structure of their materials. Having accurate and precise information about the polymers produced quickly is fundamental for the synthesis and modification of novel materials, which can be tailored to have desired physical properties.

SEC, also known as Gel Permeation Chromatography (GPC), is a liquid chromatography technique commonly used for the characterisation of polymers. The analysis of the materials is based on a separation mechanism that involves the distribution of the molecules between the pores of the column and the eluent. The distribution of the molecules within the pores and the eluent is a diffusion mechanism and the molecules do not interact with the column. This leads to the separation of the polymers in terms of their molecular size, as the name Size Exclusion Chromatography suggests, and not in terms of their molecular weight. The technique is carried out under good solvent conditions and can utilise a variety of good solvents for different types of polymers making this a universal technique that most polymer scientists find useful to have.

This white paper lists ten reasons why an academic scientist should use a multi-detector SEC system.

Figure 1 - Advanced multi-detector SEC system: OMNISEC

1) Full and immediate characterisation of polymers synthesised from a variety of monomers

Multi-detector SEC is an essential technique for the complete characterisation of polymeric materials synthesised in a research laboratory. It is a universal characterisation technique that allows you to analyse a huge variety of materials. It is rapid and reliable and it provides the researcher with absolute molecular weight and distribution information along with composition and structural information. The full characterisation obtained from the analysis of a polymer by SEC is possible thanks to the presence of the different detectors that can be found in the SEC system. The presence of two concentration detectors, such as Refractive Index (RI) and UV detectors, allows the analysis of copolymers to be carried out. The light scattering detectors such as Right-Angle and Low-Angle Light Scattering (RALS/LALS) or Multi-Angle Light Scattering (MALS) allow for the calculation of absolute molecular weight and molecular weight distribution. Furthermore, the presence of a viscometer detector provides structural information of the material. Thus, with a single analysis of a polymer a huge amount of information can be gathered thanks to the separation process and the several detectors of the SEC system. If you are synthesising polymers, you know how important it is to immediately characterise what you have obtained from your polymerisation in order to understand if you were successful with your synthesis. A polymer chemist usually aims to obtain a polymer with certain molecular weight and dispersity values and that information can easily be gathered by using SEC. Multi-detector SEC gives you the possibility to analyse a huge variety of polymers that differ in terms of their chemical composition and structures. It provides the information needed to carry out modifications to your synthetic procedure or to just move on with the development of your new material.

2) Polymers and polymerisation development

In research, a wide range of polymer applications are being investigated and the polymers involved in such applications are continuously studied and improved in order to obtain the optimum performance of the end products. If you are aiming to develop a new polymer or improve the performance of the polymer for a certain application, the molecular characteristics of that polymer are of a great importance. We now know that characteristics such as the molecular weight and molecular weight distribution alongside the chemical composition and the structure of the polymer can have a deep impact on the polymer properties. New polymers come from challenging development processes and from the introduction of accurate small changes in the synthesis procedures. Among the large variety of changes applicable to polymer synthesis, we can find, for example, the use of a different types of monomer during polymerisation, the addition of chain functionalities, the change of conditions for the synthetic reactions or the modification of the structure of the polymers. The success, or otherwise, of polymerisations or polymer reactions can be verified with the analysis of the resulting materials by multi-detector SEC, which gives you the absolute molecular weight, dispersity and structural information you need. Multi-detector SEC then becomes a support and development tool for both new products and polymerisation techniques used for the synthesis of novel polymers.

3) Synthesis of well-defined polymers

In academia, the synthesis and development of well-defined polymers in terms of molecular weight, dispersity and structure is becoming more and more important thanks to the extensive study on the relationship between structure and properties. Understanding the behaviour of a ‘perfect’ well-defined polymer in relation to certain properties can lead to the formulation of behavioural models. These models can then be applied to the not so perfect polymers commonly obtained in big bulk reactions in the industrial word and contribute to a better understanding of the behaviour of such industrial polymers.

There are several polymerisation techniques that you can use for the synthesis of well-defined polymers. These techniques are in continuous development and among them we can name controlled free radical polymerisations (ATRP, RAFT, NMP) and living anionic or cationic polymerisations. For example, if you are using living anionic polymerization[1] for the synthesis of your materials, you know that this technique can provide well-defined polymers in terms of molecular weight, molecular weight distribution, microstructure and chain-end functionality. However, for living anionic polymerisation the choice of the monomer, solvent, initiator and reaction conditions is crucial. You will also be aware of the negative impact of impurities, such as air, on the polymerisation which results in side-products, i.e. polymers with unwanted characteristics. In addition, living anionic polymerisation allows you to obtain a desired molecular weight and dispersity which can be confirmed by multi-detector SEC. In fact, this technique offers the possibility to discover if your material is exactly what you were aiming for or if it contains polymer chains as a result of side reactions occurring during polymerisation.

The concept of well-defined polymers can also be extended to branched polymers. For instance, in the synthesis of a star polymer; in order to define it as a well-defined polymer, you need to know not only the molecular weight of your star polymer but also the molecular weight characteristics for the arms and the number of the arms that you have actually synthesised. Multi-detector SEC allows you to calculate the absolute molecular weight data of your linear precursors, if used, and of your final branched polymer. It also gives you the possibility to calculate the number of arms in a star polymer, or more generally the degree of branching, by using a viscometer detector in the system.

4) Structural information

The polymer architecture is an important polymer characteristic that plays a big part in determining the polymer properties. It is possible to get structural information directly from the analysis of your materials by multi-detector SEC. The use of a viscometer detector in the SEC system allows you to look at Mark-Houwink plots (Log intrinsic viscosity vs Log molecular weight) and assess whether there are structural differences within the sample or between samples. In the Mark-Houwink plots you can also observe differences in terms of molecular density as a function of molecular weight, where the molecular density is related to the structure of the polymer. In addition, it is also possible to get information regarding the size of your materials as a function of molecular weight. The size of the particle in solution is expressed as Rh, hydrodynamic radius, or Rg, radius of gyration and both parameters can be calculated thanks to the multiple detectors present in the SEC system.

The structural differences within a sample can be due, for example, to the presence of branching or conformational changes. A branched polymer is a material where the main chains are connected to other chains through the presence of branch points. Branched polymers are characterised by different physical properties in comparison to linear polymers of equivalent molecular weight. Thus, in research it is important to understand if the synthesis resulted in a linear polymer, a branched polymer or a mixture of branched and linear polymers. In addition, if a branched polymer has been synthesised, the calculation of the degree of branching is important because the degree of branching can influence the physical properties of the material.

An example of branched polymer synthesis carried out with the support of a multi-detector SEC system is given Hutchings *et al*. on hyperbranched polymers.[2] In this work the synthesis of a series of polystyrene long-chain hyperbranched polymers, called HyperMacs, was carried out using the living anionic polymerisation technique and Williamson coupling reaction. The entire synthetic procedure was followed by using multi-detector SEC. The coupling reaction that produced the hyperbranched polymer was sampled over time and these samples together with the final product were all characterised by multi-detector SEC. The chromatograms obtained from the sampling showed the conversion of the macromonomer into dimer, trimer, tetramer and higher molecular weight polymers. Thanks to the use of the multi-detector SEC, the molecular weight, molecular weight distribution and structural information were obtained. The degree of branching, or branching factor g', was calculated for each hyperbranched polymer synthesised in order to verify the presence of the branched architecture after the synthesis. The branching factor g' is calculated by using the intrinsic viscosity values obtained from the viscometer detector.

Another example can be observed in Figure 2, where the Mark-Houwink plot of three different polymers is shown. The three polymers; a linear, 4-arm and 8-arm star polymer, show different values of intrinsic viscosity across the entire molecular weight distribution. The lower intrinsic viscosity values demonstrated by the two stars in comparison to the linear polymer is due to the higher density of these branched polymers. It is well known that branched polymers, such as stars, are characterised by a more compact structure in comparison to linear polymers of same molecular weight. Thus, the differences between the three samples can be clearly visualised and measured thanks to multi-detector SEC and the Mark-Houwink plot.

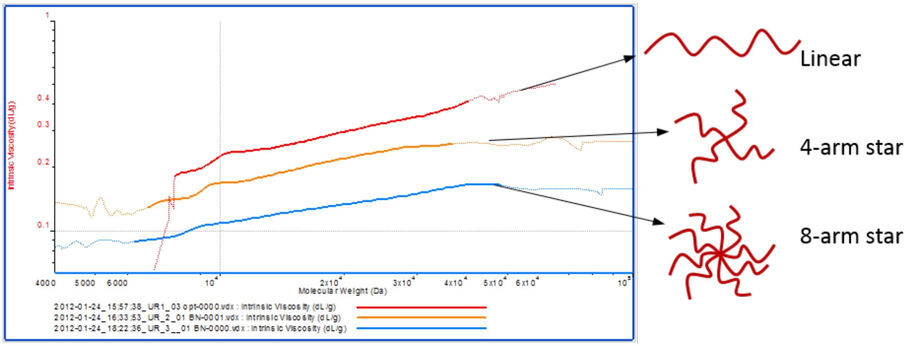

Figure 2 - Overlay of a Mark-Houwink plots of linear PEG (red line) and 4- and 8- arm PEG star polymers (orange and blue line respectively)

5) Control over reactions involving polymer modification

The manufacturing of a polymer does not just involve polymerising the monomer, but also other types of reaction that are carried out on the polymers after primary polymerisation in order to obtain the specified characteristics. These types of reactions are modification reactions that can introduce or modify functional groups present on the polymer chains, i.e. functionalisation reactions,[3] or introduce branching in the polymer, creating new branched materials. If you are interested in functionalisation reactions, you can use multi-detector SEC in order to check the chromatograms of your well-defined polymer, which must remain monomodal, indicating that your polymer is stable during the functionalisation reaction, and to check the molecular weight values that may vary in accordance to the type of functionalisation. During the synthesis of branched polymers, the reactions you may come across are, for example, coupling reactions, that change the chromatogram of your linear precursor and result in structural and molecular weight changes. There are several types of coupling reactions that can be carried out on linear polymers and that can lead to branched polymers. Most of the time the final product of these reactions is a mixture of linear unreacted polymer and the desired branched polymers.   Multi-detector SEC has been used to monitor the progress of coupling reactions leading to polymers such as stars[4] or hyperbranched polymers.[5] In the synthesis of asymmetric three-arm stars by Hutchings *et al.*[4] the coupling reactions used to join together a 'short' arm (10 kg·mol^{-1}) and two 'long' arms (90 kg·mol^{-1}) to create asymmetric three-arm stars, were monitored by multi-detector SEC and provided chromatograms as shown in Figure 3.

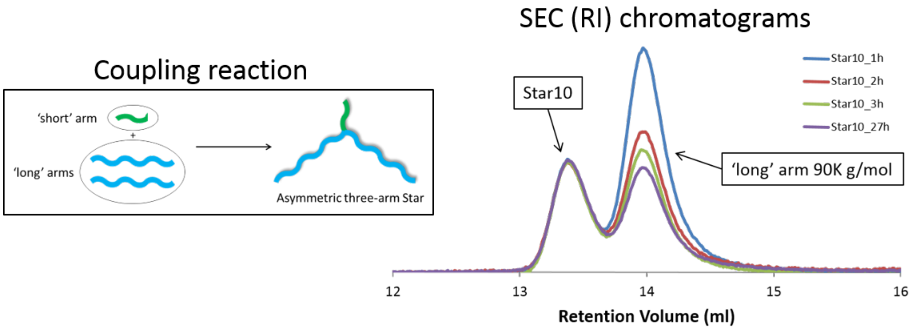

Figure 3 - SEC (RI detector) chromatograms of an asymmetric three-arm star (Star10) synthesised by Williamson coupling reaction. Samples are taken after 1, 2, 3 and 27 hours

Figure 3 shows the reaction schematic and the Refractive Index (RI) chromatograms that are obtained by analysing the polymer samples by multi-detector SEC. Thanks to the sampling and the SEC analysis of each sample taken from the reaction mixture during the reaction time, it is easy to see if the reaction is actually working. The overlaid chromatograms in Figure 3 show that the reaction is working because the concentration of the 'long' arm (used in excess in the reaction) decreases over time, as it can be stated by the observation of the peak at ca. 14 ml of retention volume. Furthermore, a new peak that was not present in the starting materials chromatograms appeared at lower retention volumes (ca. 13.5 ml). In addition, SEC makes possible the identification of the end of the reaction, which is when no further decrease of the 'long' arm concentration in the RI chromatogram is observed.

Figure 4 shows what you can get by monitoring a coupling reaction of a linear polymer for the synthesis of an hyperbranched polymer, called HyperBlock[5], with multi-detector SEC. By sampling the reaction at different times and running the sample through a multi-detector SEC system, you can obtain a series of chromatograms as shown in Figure 4. The main peak at high retention volume represents the linear precursor (macromonomer P(S-I-S)65_31) of the hyperbranched polymer (HB65_31), and the peaks that increase in each injection are the dimer the trimer and so on toward higher molecular weight materials. Both the light scattering (RALS) and the Refractive Index (RI) detector are very useful for monitoring the evolution of the reaction. The success of the reaction can be confirmed with SEC by observing the development of high molecular weight species. When no further increase in molecular weight is observed, the reaction can be considered finished.

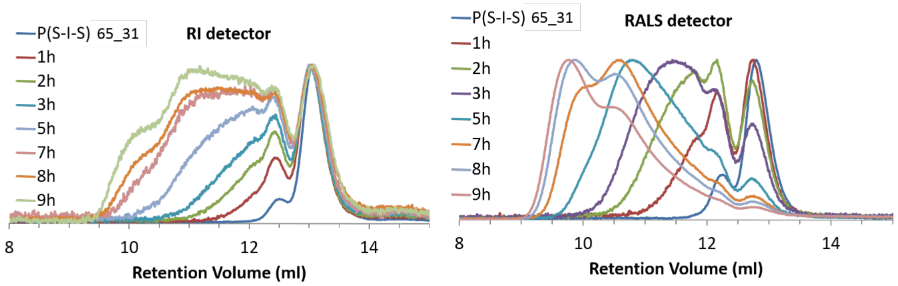

Figure 4 - SEC chromatograms of samples taken at different times during the synthesis of the hyperbranched polymer HyperBlock HB65_31 resulting from the coupling reaction of macromonomer P(S-I-S)65_31

6) Monitoring the purity of polymers during purification steps

In polymer chemistry it is common to have a sample with a mixture of different polymer chains, not only in terms of their molecular weight but also their structure. This can be seen, for example, when synthesising branched polymers and, if your aim is to obtain a model branched polymer for further studies, a purification step is necessary. For example, in the work reported by Hutchings *et al.*[4] on the synthesis and characterisation of a series of asymmetric three-arm stars, the stars were purified and the purification processes was followed by using multi-detector SEC. In this work, the synthesis of the branched polymers was carried out by using Williamson coupling reaction and the 'macromonomer approach'. The employment of this procedure involves the use of a large excess of one of the arms in order to push the reaction toward the formation of the end product, the star polymers. The presence of unreacted arm in the final product was expected and thus after the coupling reactions the purification of the star polymers was required. The purification of the star polymer was carried out by fractionation and the polymer purity was controlled by SEC. As shown by the RI chromatograms in Figure 5a, within one fractionation procedure it is possible to see how the asymmetric three-arm star (Star10) mixture fractions collected each time contain different amount of unreacted arm (at high retention volume). From the first fraction collected (A1) to the last (A5) the amount of 'long' arm increases relatively to the star as expected in a fractionation procedure. After repeating the procedure of purification by fractionation several times it is possible to obtain three-arm star polymers free of impurities (Star20_end of fractionation) as clearly seen in the overlaid RI SEC chromatograms in Figure 5b.

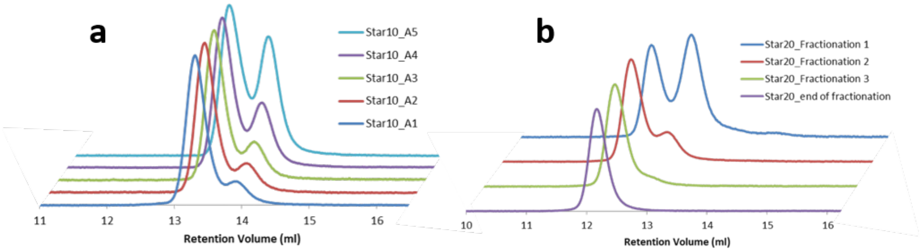

Figure 5 - a) SEC chromatograms (RI detector) of the Star10 polymer mixtures collected during a single cycle of purification by fractionation. b) SEC chromatograms (RI detector) of the Star20 polymer mixtures from the starting crude material to the final 'pure' star after being processed through three fractionation cycles

7) Establishing if polymers are changing during use

Several applications where polymers are employed, can lead to the modification of the polymer with implications for product performance. It is often crucial to understand what is happening to a polymer if its performance changes during use. By multi-detector SEC it is possible to monitor changes in molecular weight, molecular weight distribution and structure, as a result of material changes occurring during processing. An example of this can be found in ink-jet printing technology where polymer solutions are commonly printed on to a variety of substrates for graphic applications or digital fabrication. Work carried out by Wheeler *et al.*[6] on this topic has shown that linear polymers can degrade during a printing process and the design of the ink-jet systems needs to take into account the degradation process of the polymers. Polymers are added in small amount to ink formulation in order to obtain a mechanically robust film. However, the polymer concentration and the molecular weight of the polymers added to the ink can affect the printing processes in terms of drop ejection and breakup. Wheeler *et al.* investigated the degradation of three linear poly(methyl methacrylate) (PMMA) samples used in the ink with different printing processes. The study was made possible thanks to multi-detector SEC that allowed them to monitor the changes in the molecular weight and molecular weight distribution of the PMMA resulting from different printing processes.

Another example where multi-detector GPC has been used is to monitor the degradation of polystyrene (PS) during processing. In this work the PS sample was processed 5 times through a capillary rheometer in order to simulate the moulding and re-moulding process. The chromatograms measured after each re-processing step are shown in Figure 6.

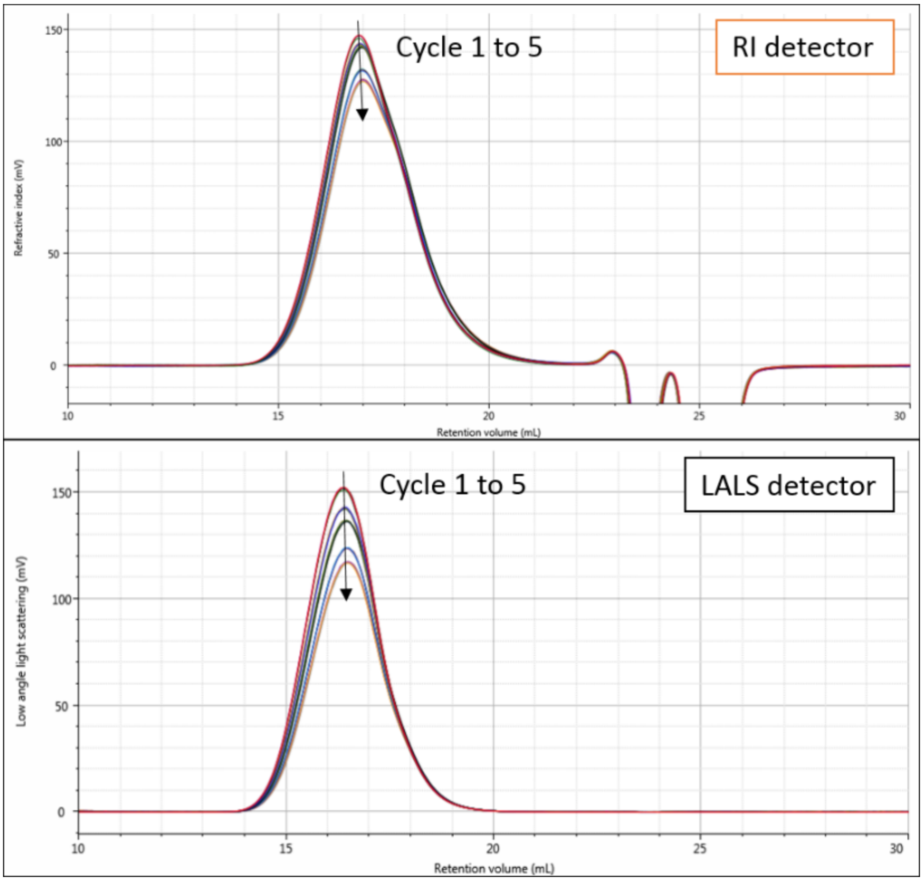

Figure 6 - Overlaid RI and Light Scattering (LALS) chromatograms of five PS samples injected four times and analysed by multi-detector SEC, OMNISEC system

In Figure 6 the chromatograms reported show 20 injections that correspond to each of the five samples measured four times. The perfect overlay of each of this injections of the same sample demonstrates the great repeatability of the multi-detector SEC system. The refractive index (RI) and Light Scattering (LALS) chromatograms of the sample clearly show differences after each processing cycle whereby a decrease in the intensity of the chromatograms can be observed. Looking at the molecular weight distribution it is possible to see that each cycle of processing affects the polymer in a way that decreases the molecular weight and so changes the properties of the material.

8) Structure and physical properties relationship

The understanding of the relationship between structure and properties of a polymer is important when we want to use a polymer in a particular application. Polymers can behave differently depending on their structure and molecular weight characteristics. For example, it is known that the physical properties of branched polymers are different from the properties of linear polymers of same chemical composition and same molecular weight. Star polymers are characterised by a globular shape and a compact structure, which are not observed in a linear polymer with the same molecular weight. Branched polymers such as stars, graft copolymers, miktoarm stars, H-shaped polymers, dendrimers and hyperbranched polymers have interesting properties because of their structures. Among these different types of polymers, star polymers, for example, have been used as model branched polymers to understand the relationship between molecular architecture and physical properties. The properties of a polymer can be deeply affected by the presence of branched points. An example of this can be found in the ink-jet printing process carried out using polymers characterised by the presence of branching.[7] Wheeler *et al.* has shown that the performance of polymers utilised in the ink-jetting process could be improved by incorporating branching. The evaluation, by multi-detector SEC, of linear and hyperbranched polymers was carried out before and after jetting. While the linear polymers showed degradation, the hyperbranched polymers with high degree of branching were largely unaffected by the process. Thus, thanks to the presence of a branching architecture the degradation of the polymers, common for linear polymers, was suppressed during printing. The degree of branching (g’) of the hyperbranched polymers was also calculated thanks to the viscosity data obtained by using the multi-detector SEC.

9) Rheology and the importance of a full characterised polymer

The rheological properties of the materials have a huge influence in polymer processing and the dependence of rheology upon polymer architecture has been a subject of study for many years and has involved several types of polymers. The rheological behaviour of a material is strictly connected to its molecular structure. In particular, the relationship between chain branching and rheology of polymers has been largely investigated over the years due to the common presence of branching in industrial materials. In the academic world the synthesis of model branched polymers, such as stars and H-shaped polymers, has helped greatly in the understanding of the rheology of branched polymers. In order to understand the relationship between rheology and polymers characteristics it is important not only to synthesise model polymers but also to have well-defined polymers in terms of molecular weight, dispersity and structure. It is well-known that parameters such as molecular weight, dispersity and chain branching have a huge influence over polymer properties such as rheology. In order to have a well characterised polymer you need an accurate analytical technique. This technique, for a polymer chemist, has to be the multi-detector SEC. Thanks to the combination of synthetic strategies and material characterisation provided by multi-detector SEC, the rheology study can be carried out in order to develop or prove a theory to predict the rheology of branched polymers and then apply this theory for the design of industrial polymers with the desired properties. An example of the influence of branching on the rheological properties can be found in the study of long-chain hyperbranched polystyrene polymers called HyperMacs.[8] For these materials it was found that the highly branched structure frustrated the formation of entanglements even when the overall molecular weight of individual polymer molecules was well above the entanglement molecular weight threshold for linear polystyrene. Chain entanglement was only observed when the molecular weights of the linear macromonomers, the linear precursors of the hyperbranched polymers, were above the entanglement molecular weight of polystyrene. This study makes clear the necessity to have molecular weight values of both the hyperbranched polymers and the linear polymer precursors to understand the effect of the branching on the rheology.

10) Morphology and full characterised Block Copolymers

Morphology is one of the physical properties of a material that polymer scientists may be interested in when synthesising block copolymers. Block copolymers are a type of copolymer where two or more chemically different polymer blocks are linked together by covalent bonds. Due to the chemically incompatible nature of the blocks, block copolymers have the ability to form nano-scale morphologies through microphase separation of the blocks. The self-organisation of block copolymers in different morphologies is influenced by several parameters and among them the molecular weight of the polymer chains and the composition play an important role. The morphology that a block copolymer assumes can have a deep impact on other physical properties of the material itself. Among these are tensile mechanical properties, which are strongly dependent on the materials morphology. Thermoplastic elastomers are an example of the use of block copolymers based on their mechanical properties.

When synthesising linear block copolymers, it is important to think about the fact that the changes in molecular weight and composition result in different morphologies. However, further studies[09],[10] have shown that the molecular structure of block copolymers also influences the morphology that these materials can assume. Thus, molecular weight, composition and structure are all important parameters that need to be taken into account when producing block copolymers. The characterisation by multi-detector SEC of the polymers allows the determination of these characteristics and contributes to the prediction of the type of morphology assumed by the material under study.

In a recent work Hutchings *et al*.[5] investigated the effect of a branched architecture on the morphology of block copolymers. A series of linear triblock copolymers (macromonomers) of polystyrene and polyisoprene were synthesised and characterised by multi-detector SEC. The different molecular weights and compositions, in terms of polystyrene weight fraction, that characterised the series of the linear precursors polymers, resulted in several different morphologies of the polymers. The linear triblock copolymers were then converted to hyperbranched polymers, called HyperBlocks, by using coupling reactions. The presence of branch points in the HyperBlock resulted in a dramatic change of the triblock copolymer morphology. For example, in Figure 7 the data obtained by multi-detector SEC and morphology analysis (Transmission Electron Microscopy, TEM) are shown for the HyperBlock, HB65_31, and its linear precursor, macromonomer P(S-I-S)65_31. Both the macromonomer and HyperBlock have the same PS content (31%) but different molecular weight and structure. The linear copolymer, the macromonomer, shows a cylindrical morphology while the HyperBlock's morphology lacks of the long-range order which was characteristic of its linear precursor. The composition of the two samples was the same and so the morphology should have been the same according to the theoretical predictions. Consequently, the change of the morphology was attributed to the transformation of the architecture of the polymer. Therefore, with this example of academic research we can see that being able to fully characterised by multi-detector SEC the polymers synthesised gives a great contribution to the understanding of the materials properties and, by consequence, of the most suitable application for such materials.

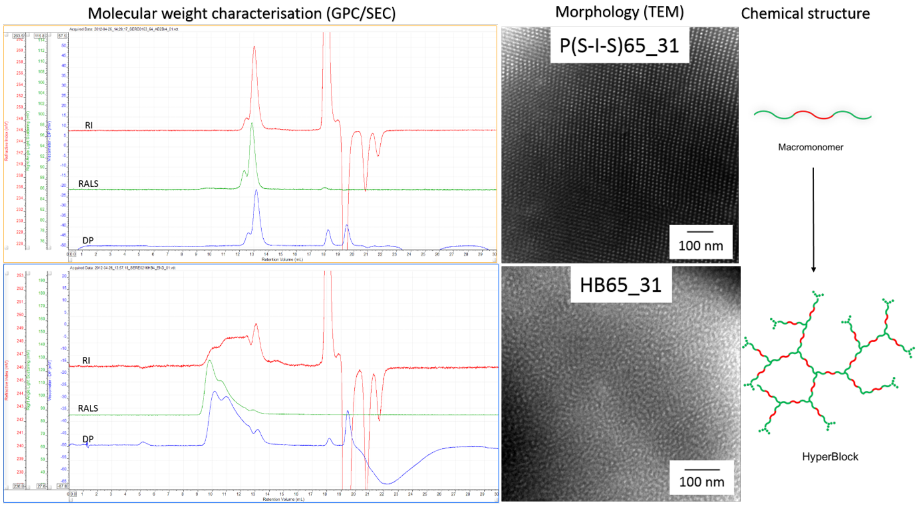

Figure 7 - Multi-detector SEC chromatograms and TEM micrographs of a linear triblock copolymer precursor (macromonomer P(S-I-S)65_31) and the resulting hyperbranched polymer (HyperBlock HB65_31)

Summary

In conclusion, the ten points above clearly show the importance of having a multi-detection SEC in your lab. The full characterisation of the materials synthesised is fundamental for polymer scientists in order to develop polymers and polymerisation techniques. The characterisation of your materials in terms of molecular weight, molecular weight distribution and structure will give you the possibility to gain a further insight in your research and provide you with improved quality for your results and publications.

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