GEL PERMEATION CHROMATOGRAPHY INVESTIGATIONS INTO POLYMER MORPHOLOGY

I WILLOUGHBY, G SAUNDERS, A WILLIAMS

Polymer Laboratories Ltd, Now a part of Varian, Inc., Essex Road, Church Stretton, Shropshire SY6 6AX, UK, Tel (+44) 01694 723581 Fax (+44) 01694 722117 Email GPC@polymerlabs.com

Introduction

Gel permeation chromatography (GPC) is a technique for polymer molecular weight determination. In a GPC experiment, polymer molecules are separated and detected in a packed column on the basis of size in solution. The simplest form of GPC then converts size into molecular weight using a calibration generated from a series of polymer standards of known molecular weight. The advantage of GPC is that physical separation occurs and so distributed information is obtained. In conventional GPC no information is gained regarding the morphology of the polymer. The increase in the information content of the experiment, detectors must be chosen which respond to specific properties. Coupled to a GPC system these detectors enhance the power of GPC. Such devices include viscometers, light scattering detectors and ultra-violet detectors. Presented here is an overview of these detectors and their application to the analysis of polymer morphology. Examples of information obtained will be highlighted using a range of polymer systems to show the applicability of the techniques to commercial and R&D materials.

Complex Polymer Materials

The ever increasing drive of the polymer chemistry community to derive more and more complex designer materials to fuel the technological advances of the 21st century has resulted in the desire to elucidate and structurally define materials more closely. It is widely understood that polymers may be synthesised in a variety of complex morphological structures, as highlighted schematically in Figure 1. These complex architectures are responsible for the enhanced properties of the materials. As a result of this structure-function based relationship, the characterisation of the complex morphologies is becoming increasingly important. The combination of GPC with different multiple detection options offers the lab-based researcher the opportunity to fully characterise the structure of the synthetic materials.

PL-GPC 50 Plus

Since the inception of size exclusion chromatography (SEC, also known as gel permeation chromatography or GPC), the technique has matured into a popular and versatile method for determining the molecular weight distribution of polymers. SEC is a key parameter that affects many of the physical properties of these materials. SEC has now become one of the mainstays of the polymer analysis laboratory, and is often the first method selected for the analysis of a new material.

To meet the increasing popularity of SEC, Polymer Laboratories, now a part of Varian, Inc., introduced the PL-GPC 50, a versatile integrated SEC instrument capable of operating from ambient temperature to 50°C. Fully software controlled and capable of operation with integrated light scattering and viscometry detectors, the PL-GPC 50 represented a major advance in affordable and user-friendly instrumentation.

Based on the success of the PL-GPC 50 Plus, Figure 2, Polymer Laboratories has now introduced the PL-GPC 50. This instrument retains the excellent features of the original design but includes several advances to further enhance performance capability. One such feature is the differential refractive index detector, which has been improved to increase sensitivity and stability. Also, a major change has been made to the control system, introducing a fully scheduling capability allowing all aspects of the instrument control to be automated, greatly increasing the power of the utility.

Case Study (1) - Hyperbranched Polymers

A range of polyester based ABnAB polymers were synthesised by the condensation of the A and B end groups 1. The branching in the system was introduced through the use of the chain transfer agent. This reaction pathway is shown schematically below in Figure 8. The branching agents were varied in length through the size of the ABnAB branching agent. The molecular weight distributions obtained for each of the samples (Figure 7) are effectively random, showing no trend between the molecular weight of the material and the branching agent used. However, the Mark-Houwink plots (also Figure 7) obtained from the viscosity data highlights a clear group trend, related to the degree of cross-linker used and the length of the branching structures. The data collected showed a clear growth in both molecular weight and intrinsic viscosities with respect to reaction time, however the measured intrinsic viscosity was found to be much lower than the value predicted from a Mark-Houkwk plot derived from a linear PMAA.

Summary

Gel permeation chromatography (GPC) is a well-established and long standing technique for the determination of polymer molecular weight distributions. The information content of a GPC experiment can be extended significantly by adding different detector options, for example, light scattering, viscometry, ultra violet and FTIR detection. These different analytical detection methods can be used to analyse polymer materials which have a wide variety of branched morphologies, structural differences, which can vastly effect the properties of the materials.

Multi detector GPC with light scattering detectors and viscometers can be used to probe the branching structures of a wide variety of polymers including long-chain branched, hyperbranched and star polymers.

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