Hydrodynamic Radius Characterization of a Vinyl-Type Polynorbornene by Size-Exclusion Chromatography with a Static and Dynamic Laser Light Scattering Detector

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Abstract

Both absolute molecular weight and molecular sizes (radius of gyration and hydrodynamic radius) of a vinyl-type polynorbornene eluting from size-exclusion chromatography columns were determined by combined with a static and dynamic laser light scattering detector. The hydrodynamic radius of polymer fraction eluting from size-exclusion chromatography columns was obtained from dynamic laser light scattering measurements at only a single angle of 90° by introducing a correction factor. According to the scaling relationship between molecular sizes and molecular weight and the ratio between radius of gyration and hydrodynamic radius, the vinyl-type polynorbornene took a random coil conformation in 1,2,4-trichlorobenzene at 150°C.

Keywords

Column liquid chromatography
Size-exclusion chromatography
Laser light scattering detection
Polynorbornene

Introduction

Both absolute molecular weight (M) and radius of gyration (Rg) of polymers can be obtained simultaneously when a two-angle laser light scattering (TALLS) detector is connected to a size-exclusion chromatography (SEC) or gel permeation chromatography, GPC) system [1, 2]. A new flow-mode dynamic laser light scattering (DLS) detector had been used for “on the fly” determination of hydrodynamic radius (Rf) of biomolecules eluting from the SEC columns, which allowed insights into the conformation and aggregation studies of biomolecules [3, 4]. More recently, it was used as a detector for high-throughput flow-injection and trap-flow analysis of biomolecules [5]. However, for synthetic polymers with larger size, collecting the DLS data at only a single angle of 90° is not sufficient to obtain an accurate Rf without correction.

The homopolymer vinyl-type polynorbornene is a special polymer with good mechanical strength, heat resistivity, good solubility in organic solvents and optical transparency, which can be prepared with metal complexes based on titanium, zirconium, cobalt, chromium, nickel and palladium [6, 7]. However, most studies on polynorbornene had focused on the catalyst activity and polymer yield, while few results on its molecular parameters and solution properties have been reported in the literatures. Mast et al. reported high molecular weight vinyl-type polynorbornene prepared with a nickel-based phosphoraneiminato complex in the presence of methylaluminoxane [8]. More recently, Li et al. found neutral nickel salicylaldiminato complexes activated with modified methylaluminoxane displayed extreme activity for the vinyl polymerization of norbornene [9].

In this study, the absolute molecular weight and molecular sizes (Rf and Rg) and their distributions of a vinyl-type polynorbornene prepared with a nickel-based catalyst were studied by SEC combined with a static and dynamic laser light scattering detector. A method of determining Rf of polymer by DLS at only a single angle of 90° combined with static laser light scattering (SLS) at two angles was presented.

Experimental

Size-exclusion Chromatography Coupled with Laser Light Scattering

The vinyl-type polynorbornene sample used in this study was prepared with a nickel-based catalyst and was coded as PNB-11 [9]. A PL-GPC 220 high temperature gel permeation chromatography...
(Polymer Laboratories Ltd.) coupled with an online PD2040/DLS laser light scattering detector (Precision Detectors Inc.) was used in this study. The columns used were three PLgel 10-μmMixed-B LS columns (300 x 7.5 mm). The eluent was 1,2,4-trichlorobenzene (TCB, Acros) stabilized with 5 x 10^-4 g mL^-1 2,6-di-tert-butyl-4-methylphenol (BHT, Acros) and was filtered with a 0.2-μm pore size membrane before use. The injection concentration and volume were 2-3 mg mL^-1 and 200 μL, respectively. All measurements were performed at 150 °C with a flow rate of 1.0 mL min^-1. The PD2040/DLS detector, which contained two angle (15° and 90°) SLS detectors and one angle (90°) DLS detector, was positioned before the differential refractive index (DRI) detector. A 30 mW, 680 nm semiconductor diode laser light source was used. Its flow cell, with a volume of 10 L, was located in the SEC oven. PrecisionAcquire32 software from Precision Detectors Inc. was used to acquire data from the PD2040/DLS detector and the DRI detector in 1 s intervals. The acquired data were processed with Discovery32 software (Precision Detectors Inc.) to obtain M and Rg of polymer at each retention volume (V_R). A typical accumulation time of 10 s with 5 μs sampling time for the flow-mode DLS detector was used in this study.

**Trap-flow Dynamic Laser Light Scattering**

The sample was injected and the eluent flow to the columns was stopped by switching the purge valve of the pump to the waste tube at a predetermined time to trap the fraction with a desired V_R in the light scattering flow cell, then intensity-intensity time correlation function was accumulated for a longer time, thus the flow-mode DLS detector served as a traditional batch-mode DLS detector. The intensity-intensity time correlation function was collected and deconvolved by PrecisionDeconvolve software (Precision Detectors Inc.) to obtain an apparent transitional diffusion coefficient D_app. The eluent flow was switched back to the columns to flush out the sample before trap-flow DLS of fraction at another V_R.

For dilute solution, D_app measured at a finite scattering angle is related to sample concentration C and scattering angle θ by

\[ D_{app} = D(1 + k_2 C)(1 + R_g^2) \]  

where \( q = (4 

\text{nm} / \lambda_0) \sin(\theta/2) \) with \( \lambda_0 \) being the solvent refractive index and the wavelength of light in vacuum, respectively. D is the transitional diffusion coefficient at \( C \rightarrow 0 \) and \( \theta \rightarrow 0 \), \( k_2 \) is the diffusion second virial coefficient, \( f \) is a dimensionless number with a typical value between 0 and 0.2 [10–12].

In this study, the intensity-intensity time correlation function is accumulated for sample fraction eluting from the SEC columns, which is nearly monodisperse. The concentration of the eluted sample fraction is very low (with a typical magnitude of 0.1 mg mL^-1) and thus the dependence of D_app on C can be neglected. In this case

\[ D_{app} \approx D(1 + f R_g^2) \]  

The transitional diffusion coefficient D is related to hydrodynamic radius R_h according to the Stokes-Einstein equation

\[ D = \frac{k_BT}{6 \pi \eta_0 R_h} \]  

where \( k_B \), T and \( \eta_0 \) are the Boltzmann constant, absolute temperature and solvent viscosity, respectively. An apparent transitional diffusion coefficient D_app obtained at scattering angle \( \theta \) will give an apparent hydrodynamic radius R_app.

Then R_0 of the sample fraction can be calculated according to

\[ R_0 = \frac{k_BT}{6 \pi \eta_0 \gamma} \frac{C_0}{C} = \frac{k_BT}{6 \pi \eta_0 \gamma} \frac{D_{app}}{D} = R_{app}(1 + f R_g^2) \]  

That is to say, R_0 of sample fraction can be obtained from R_app, which was obtained from DLS at only a single angle of 90°, by introducing a correction factor k where \( k = (1 + f R_g^2) \). Obviously, k is different for molecule having different size. The bigger the molecular size, the larger the value of k. For example, k is 1.016 and 1.100 for molecule having 20 nm and 50 nm with f = 0.1, respectively. Neglecting the correction will not introduce much error for biomolecules less than 10 nm [3–5]. However, the correction is necessary to obtain an accurate R_0 for larger size polymer sample fraction.

**Results and Discussion**

Fig. 1 shows typical normal and trap-flow SEC-TALLS chromatograms of PNB-11 in TCB at 150 °C. From the normal chromatograms, it is observed that the SLS detector signal, which scales with the product of C and M, exhibits much greater intensity in the high M region, relative to the DRI detector response, which scales only with C. In addition, the scattering intensity of the 15° scattering angle is larger than that of the 90° scattering angle, indicating the angular discrepancy of the scattering intensity of macromolecules, which is used to calculate Rg and M of sample fraction at each V_R [1, 2]. However, the scattering intensity of this PNB-11 sample is not strong enough to obtain accurate on-line DLS data at accumulation time of only 10 s. For the trap-flow chromatograms, the sample was injected in the same concentration as the normal SEC-TALLS experiment, the eluent flow was switched to the waste tube at t1 to trap PNB-11 fraction with V_R = 16.55 mL in the light scattering flow cell, the SLS detector signal was recorded for a few minutes to t2, then intensity-intensity time correlation function was collected during t2 and t3. After DLS of the trapped fraction, the SLS detector signal was again recorded for a few minutes to t4 at which the eluent flow was switched back to the columns to flush out the sample. It can be seen that the SLS detector response hardly changed when eluent flow was switched to the waste tube, indicating that the PNBE-11 fraction with V_R = 16.55 mL was successfully trapped in the light scattering flow cell. It was observed that the trapped sample fraction could be retained in the light scattering flow cell for as long as 30 min.

DLS were performed on the trapped PNB-11 fractions with different V_R at accumulation time of 20-30 min. The normalized intensity-intensity time correlation function \( |g^{(1)}(t)|^2 \) for PNBE-11 fractions trapped at V_R = 15.0, 15.5, 16.0, 16.55 mL were shown in Fig. 2, which were deconvolved to obtain R_app. It was observed that the fraction trapped at a lower V_R had a larger delay time, since it had a larger size.

Logarithms of M, as well as Rg and R_0, as functions of V_R for PNB-11 in TCB at 150 °C were shown in Fig 3. R_0 was calculated from R_app and R_g.