

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

Copolymer Compositional Drift across Molecular Weight Measured by LC-FTIR

William W. Carson^a; James L. Dwyer^b; Boris Boumajny^a

^a Spectra Analysis, Inc., Marlborough, Massachusetts, USA ^b Consultant, Ventec, Concord, Massachusetts, USA

To cite this Article Carson, William W. , Dwyer, James L. and Boumajny, Boris(2008) 'Copolymer Compositional Drift across Molecular Weight Measured by LC-FTIR', *International Journal of Polymer Analysis and Characterization*, 13: 6, 463 – 470

To link to this Article: DOI: 10.1080/10236660802503017

URL: <http://dx.doi.org/10.1080/10236660802503017>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Copolymer Compositional Drift across Molecular Weight Measured by LC-FTIR

William W. Carson,¹ James L. Dwyer,² and Boris Boumajny¹

¹Spectra Analysis, Inc., Marlborough, Massachusetts, USA

²Consultant, Ventec, Concord, Massachusetts, USA

Abstract: Copolymer end-use properties depend critically on both molecular weight distribution and comonomer composition distribution. Tolerance of variations of compositional drift can be very small in certain applications. While it is relatively easy to measure bulk composition, it requires special methods to map compositional drift. This article describes instrumentation that interfaces infrared spectrometry to liquid chromatography and the data processing techniques employed to characterize the compositional variation of copolymers. An example provides a demonstration of this technique. The technique provides value both to the polymer engineer producing a product and to end users of polymer products.

Keywords: Chromatography; Compositional drift; Composition vs. molecular weight; Copolymer; FT-IR; GPC-IR; Infrared spectroscopy; LC-IR; Styrene-butadiene

INTRODUCTION

“The primary motivation for determining the molecular structure of a polymer chain is to relate the structures to the performance properties of the polymer in end use. If the polymer chains are completely characterized and the structural basis of its properties are known, the polymerization reaction can be optimized and controlled to produce the optimum properties from the particular chemical system.”^[1]

Submitted 11 September 2008; accepted 25 September 2008.

Correspondence: James L. Dwyer, Ventec, 245 Main St., Concord, MA 01742, USA. E-mail: dwyerpadre@msn.com

This article describes the characterization of compositional drift in copolymers by combined liquid chromatography/Fourier transform-infrared (LC-FTIR) analysis. A copolymer is defined as a polymer with more than one segment species.^[2]

Polymer products are formulated to meet an array of physical, thermal, and chemical property requirements. Homopolymers provide limited ability of adjustment for such simultaneous requirements. Polymer blends often provide flexibility, but can exaggerate the poor properties of components. Copolymerization is widely used to modify the properties of man-made plastics to specific needs, for example to reduce crystallinity, modify glass transition temperature, or to improve solubility. Copolymers can provide a continuum of adjustment to balance the properties of different monomers.

“It was realized by Staudinger, as early as 1930, that when two monomers copolymerize, the tendency of each monomer to enter the chain can differ markedly.”^[3]

Monomer molecules can either react with another monomer molecule to form a dimer, or they can react with previously formed polymer chains. The reaction rates of the monomer species typically are not identical, and they will give rise to varying compositions of the forming polymer chains. The varying comonomer composition of the population of polymer chains is described as compositional drift.

In copolymers, important properties like heat distortion temperature, decomposition temperature, and toughness depend not only upon the molecular weight distribution, but also upon the chemical composition distribution. Some products are very intolerant of a composition drift of 3–5%. Copolymers used for optical applications are one such example. Composition drift in styrene acrylonitrile (SAN) copolymers is undesirable, because polymer chains of differing composition are incompatible and cause phase separation, plus refractive index change with composition. The result is a hazy, rather than optically clear product.^[4] Conversely, for gradient index lenses (GRIN) a “controlled trajectory of copolymer composition is required.”^[5] Compositional drift is inherent in most copolymers, and copolymer product properties can be controlled/optimized by controlling composition drift characteristics. The synthesis process must incorporate controls to either reduce composition drift or tailor it to a profile that yields desired product final properties. Origins of compositional heterogeneity are typically:

1. Inherent copolymer composition drift due to any differences in the reaction kinetics of the comonomers.
2. The synthesis methods employed, such as monomer addition protocols, block copolymerization, graft polymers, etc.

In the synthesis of copolymers a significant effort is made to control compositional drift, as the composition characteristics have a strong effect on the physical/chemical properties of the resultant product. Dual detector (UV plus refractive index) methods have been employed to map comonomer distribution in copolymers, but this approach is limited to those copolymers in which one species contains a chromophore, while the other does not.

This article describes a technique for measuring compositional drift in copolymers. The technique is based on the coupled instrumentation of gel permeation chromatography (GPC) and Fourier transform-infrared spectroscopy (FT-IR). The polymer analysis described here was performed using the DiscovIR-LCTM instrument coupled to the eluant outlet of a GPC column.

As shown in Figure 1, the DiscovIR instrument nebulizes the column eluant and deposits the sample analytes, free of mobile-phase solvent, onto a rotating infrared-transparent disk. This deposit track passes through the sample beam of a built-in infrared interferometer, which continuously collects IR spectra of the track. The result is a time-ordered set of spectra of the deposited GPC eluant. From this data set one can extract the time vs. absorbance of specific spectral peaks in the form of infrared chromatograms. These chromatograms can be used to

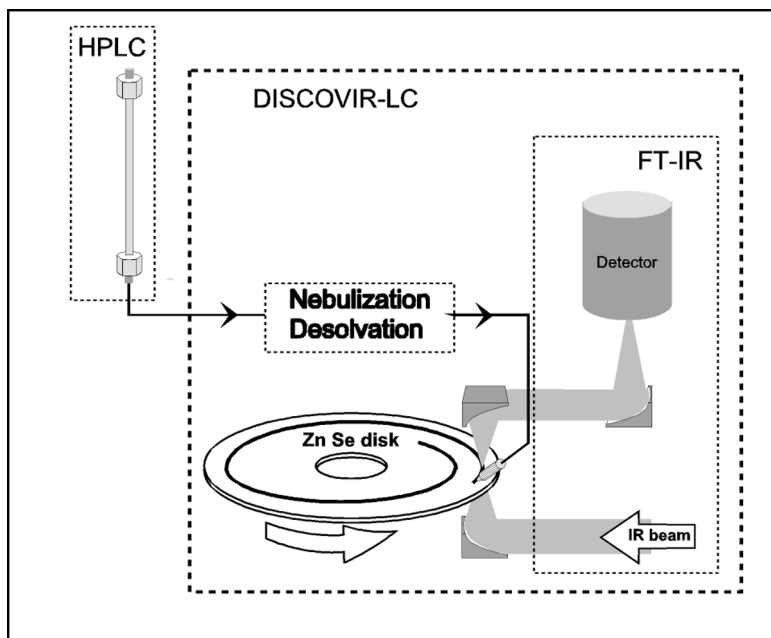


Figure 1. Principal components in the hyphenated LC-IR system.

characterize the changing composition of comonomers along the elution profile. The instrument incorporates a computer equipped with infrared data collection/processing software, which provides the user the ability to transform spectra and infrared chromatograms with a variety of mathematical functions.

EXPERIMENTAL SECTION

The sample material was the styrene-butadiene-styrene (SBS) copolymer StereonTM 721AC, graciously provided by the Firestone Company. This is a solution-polymerized block copolymer of butadiene and styrene. Such materials are blended with polystyrene to form polymer alloy products with improved impact resistance and toughness.

Details of the LC-FTIR operation are as follows:

- Column: Jordi 50 X 1 cm mixed bed linear divinyl benzene (DVB)
- Mobile phase: tetrahydrofuran (THF)
- Sample: 5 μ L of 12 mg/mL Firestone 721AC styrene/butadiene copolymer, THF solvent
- Mobile phase flow rate: 1 mL/min

Column eluant was fed to the DiscovIR. The solvent-free eluant was deposited as a solid phase track, which was immediately scanned to generate a time-ordered set of infrared spectra. Functional group chromatograms were generated by scanning the time-ordered data set along the time axis to generate infrared band chromatograms for styrene and butadiene.

Butadiene styrene copolymer presents strong spectral bands for both comonomers. A number of the bands are well resolved from bands of the other comonomer. Figure 2 is a spectrum of a bulk sample of the styrene/butadiene copolymer. The band at 966 cm^{-1} is the trans-butadiene

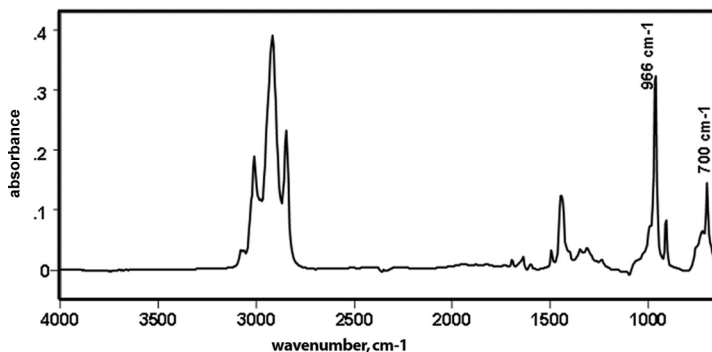


Figure 2. Bulk spectrum of Firestone 721 styrene trans-butadiene.

absorbance. There is very little absorbance by polystyrene in this region. The styrene comonomer has strong absorbance at 700 cm^{-1} , with very little contribution of the butadiene. Styrene bands at 1493 cm^{-1} and 1605 cm^{-1} are also usable.

DATA ANALYSIS METHODOLOGY

The Lambert-Beer law is normally expressed with respect to solution molar concentrations. Here it is applied to the spatial density of comonomer functional groups present on a macromolecule:

$$A_{\nu i} = \varepsilon_{\nu i} b C_{\nu i} \quad (1)$$

where $A_{\nu i}$ is absorbance of component i at wave number ν , $\varepsilon_{\nu i}$ is extinction coefficient of functional group I , b is film thickness, and C_i is the fraction of component i in the FTI sample beam.

At any point along the deposited chromatogram, the spectral peak intensity of a comonomer is the product of both the comonomer concentration and deposit film thickness, as per Equation (1). If spectral bands from each component are ratioed, however, the thickness term drops out of the fraction, and the intensity ratio is due solely to the relative amounts of the comonomers and their extinction coefficients. This is expressed in Equation (2), where absorbance ratios of two species are proportional to their mass amounts. Subscripts in the following equations are stated for the styrene/butadiene copolymer described in the Experimental Section.

$$\frac{A_{\text{styrene},t}}{A_{\text{diene},t}} = k \frac{b C_{\text{styrene},t}}{b C_{\text{diene},t}} = k \frac{C_{\text{styrene},t}}{C_{\text{diene},t}} \quad (2)$$

$$k = \frac{\varepsilon_{\nu,\text{styrene}}}{\varepsilon_{\nu,\text{diene}}}, \text{ ratio of relative absorptivities}$$

Note that the film thickness in Equation (1) is present in the numerator and denominator, and so drops out of Equation (2). If one selects wave numbers of two different sample comonomers and generates a ratio of those chromatograms, the resulting ratio chromatogram directly reflects the relative species concentrations and not the mass amounts at all points of the chromatogram.

If the bulk styrene content of the sample is known, the value of k can be determined as per Equation (3); in the sample analyzed, the bulk styrene content was 10%. To solve for (k), the absorbance values of the styrene chromatogram and the diene chromatogram are integrated over the GPC elution profile.

$$\frac{\sum_{t1}^{t2} A_{\text{styrene},t}}{\sum_{t1}^{t2} A_{\text{diene},t}} = k \cdot \frac{(\text{bulk_fraction_styrene})}{(\text{bulk_fraction_diene})} \quad (3)$$

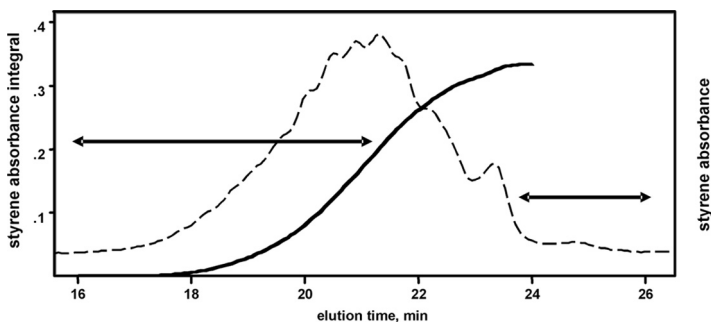


Figure 3. Chromatogram of the styrene 700 cm^{-1} band and chromatogram integral.

The styrene chromatogram (700 cm^{-1}) and its sigmoid-shaped integral are shown in Figure 3. The integral scalar value is obtained from the maximum value of the integral curve, and a similar integral is obtained for the integral of the diene absorbance chromatogram. The value of k was then determined as per Equation (3).

To generate a chromatogram that directly expresses the styrene comonomer as a fraction % of material, we used the following algebraic transformation.^[6]

$$\frac{A_{\text{styrene},t}}{A_{\text{diene},t}} = k \frac{C_{\text{styrene},t}}{C_{\text{diene},t}} = k \frac{C_{\text{styrene},t}}{(1 - C_{\text{styrene},t})} \quad (4)$$

To simplify notation, let:

$$|q_t| = \frac{1}{k} \cdot \left| \frac{A_{\text{styrene},t}}{A_{\text{diene},t}} \right| \quad (5)$$

Algebraic substitution yields

$$|C_{\text{styrene},\% ,t}| = \left| \frac{q_t}{(1 + q_t)} \right| \cdot 100 \quad (6)$$

RESULTS

A sample of the Stereon 721 AC was injected onto the GPC column, and a spectral data set was obtained. The following data operations were then performed:

1. Absorbance chromatograms were generated from the data set of the spectral bands at 700 cm^{-1} (styrene) and 967 cm^{-1} (diene).

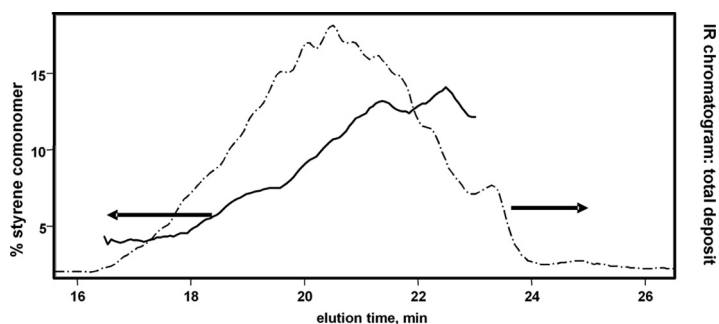


Figure 4. Total elution chromatogram (dotted line) and % styrene content (solid line).

2. These chromatograms were integrated over the elution profile, and their scalar integral values were used to obtain the value of k , as per Equation (3).
3. A peak ratio chromatogram [A_{700}/A_{967}] was created from the chromatograms obtained in step 1.
4. The ratio chromatogram was transformed as per Equations (4)–(6) to obtain a chromatogram of the styrene composition across the elution profile.

Figure 4 displays the total infrared chromatogram of the sample as a dotted line. The computed styrene content is displayed as the solid line, which varies significantly across the elution profile. Although the bulk concentration of the styrene in the sample is 10%, it varies from <5% of the highest molecular weight eluant, and is 10–15% in the low molecular weight tail of the distribution.

Note that the styrene content chromatogram is truncated at both ends of the distribution. The styrene content chromatogram is generated from a ratio of two absorbances and tends to vary considerably when the denominator of this ratio approaches zero.

CONCLUSIONS

Heretofore, composition drift of copolymers has been determined by laborious and time-consuming polymer fractionation and multi-sample analysis. Dual detector systems to resolve comonomer species have proved successful, but have the limitation of samples containing a chromophore for one comonomer and not for the other. The technique described here integrates chromatography and spectrometry into one

instrument configuration, operating in real time. The data analysis software included enables data transformation. A methodology is employed that generates a time-ordered data set of infrared spectra of the fractions eluting from the GPC column. Chromatograms of spectral bands specific for the comonomers are extracted, and a ratio of these chromatograms is then generated. This ratio chromatogram is transformed into a chromatogram of percent concentration of a comonomer, independent of changing mass of polymer across the elution profile. The combination of the physical instrumentation used and the data processing algorithms developed constitute a practical, general tool for measurement of polymer composition drift.

REFERENCES

- [1] Koenig, J. L. (1999). *Spectroscopy of Polymers*, 2nd ed. New York: Elsevier, p. 1.
- [2] D'Alelio, G. F. (1952). *Fundamental Principles of Polymerization*. New York: John Wiley, p. 9.
- [3] Cowie, J. M. G. (1991). *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed. New York: Chapman and Hall, p. 105.
- [4] Schiers, J., and D. Priddy. (2003). *Modern Styrenic Polymer: Polystyrenes and Styrenic Copolymers*. New York: John Wiley. p. 58.
- [5] Asua, J. M., ed. (2007). *Polymer Reaction Engineering*. Oxford: Blackwell.
- [6] Liu, M. X., and J. L. Dwyer. (1996). Quantitative analysis of copolymers by GPC/FT-IR. *Appl. Spectrosc.* **50**, 349–356.