

## Applying Size Exclusion Chromatography SEC-LC Transforms Microscopic Hyphenating Techniques in Copolymer Micro-Morphology Characterization

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### الملخص :

تعتبر تقنية كروماتوجرافي الاستبعاد الجزيئي (SEC) هي التقنية الأكثر شيوعاً واستخداماً لتحديد توزيع الوزن الجزيئي للمواد البوليميرية، وقد شهدت تطور كبير في السنوات الأخيرة فاستخدمت لتحديد الوزن الجزيئي المطلق وتشكل سلسلة البوليمر وحجمها والتفرع بالإضافة إلى خصائص محلول البوليمر. ولفهم وتحديد النتائج لهذه التقنية تم دراسة نوعان من البوليمرات المشتركة والتي تحتوي على سلاسل متعددة من البوليمرات وهي (PDMS-PBCH). في هذه الورقة تم توضيح توزيع الكتل الجزيئية للبوليمرات المشتركة لمقطع PDMS عن طريق استخدام جهاز SEC-FTIR والذي يستخدم فيه قرص من герمانيون كناقل (LC-transform ) لتجمیع العینة بعد خروجها من SEC ليتم عرضه بواسطته على جهاز FTIR . أيضاً في هذه الورقة تم تحسين تقنية الاقتران (hyphenated technique) وذلك لتسهيل دراسة أساسيات تشكيل الكتل الجزيئية للبوليمر المشترك وأيضاً تشكل PDMS. إضافة إلى ذلك تم التحقق من مورفولوجيا البوليمر المشترك لكل جزء من الكتل الجزيئية المتماثلة باستخدام تقنية SEC-AFM. من خلال نتائج FTIR تم الحصول على متوسط التركيب الكيميائي للبوليمر المشترك وكانت النتائج المتحصل عليها مرئية وواعدة لاستخدام هذه التقنيات في دراسة البوليمرات المشتركة الأخرى.

## Abstract

Two types of polydimethylsiloxane-polybutylenecyclohexylate (PDMS-PBCH) multiblock copolymers were fractionated based on the copolymer molecular mass using size exclusion chromatography (SEC). The PDMS segment distribution along the copolymers molecular mass distribution was investigated by SEC-FTIR off line coupling using LC-transform. Furthermore a novel hyphenated offline coupling techniques was developed, to provide morphology information as a function of copolymer molecular mass and the PDMS content. This hyphenated technique was between SEC and AFM in order to investigate the copolymer morphology of each similar molecular mass fraction; and by taking the advantages of the FTIR results the average chemical composition of the copolymer was also obtained and the results in general were promising for such new hyphenated technique.

**Keywords:** PDMS copolymers, size exclusion chromatography, SEC- LC-transform-AFM.

## 1. Introduction:

Fractionations of copolymers either as a means of determining the distribution of specific property (molecular mass, chemical heterogeneity and so on) for the characterization of this copolymer or the preparation of fractions with defined distribution (mainly molecular mass or chemical compositions) for subsequent physical or chemical testing, is a valuable and widely used technique [1]. One of useful ways of performing fractionations on copolymer systems is by using chromatographic systems, due to its speed and high resolving power it can be considered the most effective technique [2].

Chromatography process may be defined as those in which the solute is transferred between two phases, one of which is stationary and the other moving, often traversing a long tube called a column [3].

Three main forms of liquid chromatography have been used to fractionate polymers and in some cases to determine average molecular masses. These are size exclusion chromatography (SEC or gel permeation chromatography (GPC)), liquid chromatography



at critical condition (LC-CC) and gradient elution chromatography (GEC) [4].

In order to characterize heterogeneous copolymers it is necessary to separate such copolymer samples not into unique molecules each weight a particular molecular mass, but into a series of narrower molecular mass distribution fractions. This is required in order to obtain a more detailed picture of the copolymer structure and these separated fractions may be required for further analysis such as the chemical composition or the microstructure investigate by a wide range of techniques such as Fourier-transform infrared spectroscopy (FTIR) [5].

In 1986 research into LC-FTIR interfaces was revolutionized by the invention of Gagel and Biemann [6]. The interface used by them was equipped with a nitrogen gas nebulizer that allowed the vaporization of solvents used in the SEC. The solutes exiting a narrow-bore column were deposited onto a rotating reflective disc, allowing evaporation of the mobile phase solvent, followed by FTIR analysis in the sample compartment of the IR spectrometer. Further a significant development in the use of LC-FTIR analysis was presented when Goede used LC-FTIR and Atomic forces microscopy (AFM) offline technique to study the thermal properties of individual phases in polymer mixtures after fractionation to various fractions.[7] . In his a new hyphenated technique combines the separation power of liquid chromatography and the ability of infrared spectroscopy to identify almost any organic compound, with the AFM ability to be used for thermal analysis of individual phases in polymer mixtures.

In this paper, SEC that allowed fractionations based on the hydrodynamic volume (molecular mass) of the copolymers will be coupled to FTIR using a LC-transform device to provide clear chemical compositions characterization of several PDMS copolymers for specific molecular mass distribution. Moreover, the fractionated deposited copolymers indirectly on the germanium disc were redissolved and divided either into three fractionations based on the molecular mass and thin films were made from that for micro-morphology investigation using atomic force microscopy (AFM) technique. Although this novel hyphenation offline coupling

techniques were developed to provide morphology information as a function of copolymer molecular mass and the PDMS content, it could be extended to be used for other copolymer systems.

## 2. Experimental

### 2.1 Copolymers synthesis

Polydimethylsiloxane-polybutylenecyclohexalate (PDMS-PBCH) multiblock copolymers:

Random multiblock copolymers (Scheme 1-a) were synthesized using one prepolymer method [8] by reacting a difunctional end-capped PDMS oligomer with a mixture of 1, 4-butandiol and 1, 4-dimethylcyclohexanedicarboxylate.

Perfectly alternating multiblock copolymers (Scheme 1-b) were synthesized using two prepolymers method based on the method that developed by O'Malley et.al to synthesis PDMS-aliphatic polyester copolymer [9]. And the polymerization was carried out by reacting two difunctional prepolymers PDMS and PBCH, having ester and hydroxyl end group respectively. The synthesized products were purified from the homopolymers using soluble and non-soluble solvents.

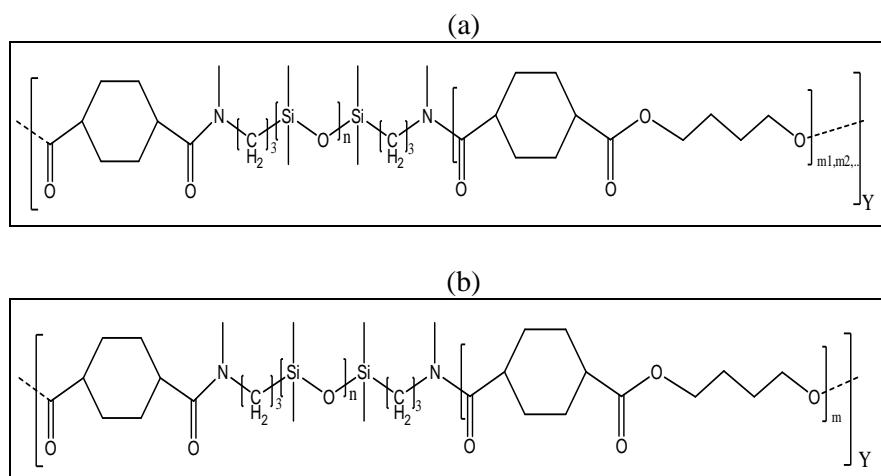


Figure 1: Chemical structure of (a) random PDMS-PBCH copolymers and (b) perfectly alternating PDMS-PBCH copolymers

The chemical compositions of the investigated copolymers were determined from the  $^1\text{H-NMR}$  spectra, 300 MHz (a Varian Unity Inova), and the average molecular masses were determined using a RI detector attached to chromatography system. The obtained results are summarized in Table 1.

**Table1: The chemical compositions and the molecular masses of the investigated copolymers.**

Sample No.	PDMS Mn (gmol-1)	PDMS (wt%)	PDMS-PBCH Mn (g mol-1)
R-1	1200	9.40	18164
R-2	1200	22.70	21243
AL-1	1200	11.02	18265
AL-2	1200	26.22	20435

## 2.2 Characterization techniques:

### 2.2.1 Chromatography fractionation

SEC-LC-transform-FTIR analysis was performed to evaluate the PDMS content throughout the copolymer samples. Separation according to molecular mass in the size exclusion chromatography (SEC) column was the first step of SEC-LC-transform-FTIR. SEC analyses were carried out with a dual pump SEC system comprising of the following unites: Waters 2690 Separation module (Alliance), Agilent 1100 series variable wavelength detector. SEC was coupled off line to FTIR using LC-transform supported with a Germanium disk. THF was used as a solvent with flow rate set at 1 mL/min. Mixed-E column was used in SEC, which packed with PI gel silica particles with 3  $\mu\text{m}$  diameter and the column was working at 30 °C and the samples were prepared in THF at concentration of 15 mg/mL.

The second step of SEC-LC-transform-FTIR that follow the separation according to molecular mass in the SEC column, is automatically fractions deposited on germanium disc as dry, which was then inserted in a FTIR spectrometer for chemical composition analysis. The run time for accumulation of IR data was in each case determined by the time at which the last chromatographic peak eluted in the LC system. The disc was rotated at 10°/min inside the

optics module, which agrees with the speed at which deposition was performed. This creates a map of the PDMS content as a function in the molecular mass distribution of the copolymer. The infrared spectra were obtained with a Perkin Elmer 1650 Fourier-transform infrared spectrophotometer.

### 2.2.2 Fractions morphology investigation using AFM analysis

AFM images were obtained on a multimode AFM model no. MMAFMLN, with a Nanoscope IIIa controller from Veeco, operating in non-contact mode, and using a low resonance frequency silicon cantilever with a resonance frequency of about 60 kHz and a spring constant of  $K = 50$  N/m. The substrate containing the polymer samples was attached to the sample holder with double-side adhesive tape. All experiments were carried out under ambient conditions. The scan rate was set in the range of 0.5 to 0.7 Hz. Topography and phase images were captured simultaneously for the tapping mode. The focus in this report will be placed on the phase images, which is a function of elastic and viscoelastic properties of the sample [10].

All AFM images were enhanced in the Veeco imaging software program and subjected to a plane fitting and flattening procedure, which eliminates the image bow resulting from non-linear scanner movement. Additionally, digital filtering was carried out to remove noise and clarify the structures present in the image. Since the filtering is a very sensitive process that can generate unreal features or remove existing features, the filtering was kept to a minimum. Only noise and image artifacts were eliminated using lowpass filtering. The typical sequence of the applied image treatment was: auto-flattening, planefit, and lowpass filtering.

The last step involves the coupling of SEC with AFM in a novel way to create a hyphenated technique, LC-FTIR-AFM. During this step and in order to collect fractions for AFM analysis from the chromatography fractionation technique LC-transform supported with a Germanium disk was used, three small pieces of mica (5x5 mm<sup>2</sup>) were attached to the Germanium disk and the eluted samples were collected on these pieces. Each eluted copolymer sample from SEC system was collected on three mica pieces to form three

fractions. Mica is used as a substrate, since it is inexpensive and easy to cut into pieces for the isolation of individual solute spots. Due to the rough surface of the obtained films all these fractions were redissolved and smooth thin films were made from that for micro-morphology investigation using AFM technique.

### 3. Results and Discussion

The size exclusion chromatography (SEC) system was used to fractionate the PDMS-PBCH copolymers based on hydrodynamic volume (molecular mass) using SEC mechanism, then the eluted fractions were analyzed using LC-FTIR . Data obtained by LC-FTIR analysis is presented as a so-called Gram-Schmidt chromatogram, which is a graphical representation of how the IR response changes over the duration of the experiment. In other words, the Gram-Schmidt representation illustrates the total IR absorbance as a function of time, where the time axis can be correlated with the retention time in the SEC chromatogram. The ratio of C=O/Si—O FTIR bands in the IR spectra was used to identify the PDMS content along the elution time of the SEC curve. Figure 2 shows the Graham Schmidt plot overlaid with the ratio of C=O/Si—O FTIR bands for a PDMS-PBCH random multiblock copolymer with 10% PDMS content. The FTIR ratio shows that high molecular weight copolymer has the lower content PDMS than the small molecular weight copolymer. Further the surfaces of the collected fractions from SEC for 10% PDMS content random PDMS-PBCH copolymers were imaged via tapping mode AFM at ambient temperature and the resulting phase DDD images are also shown in Figure 2.

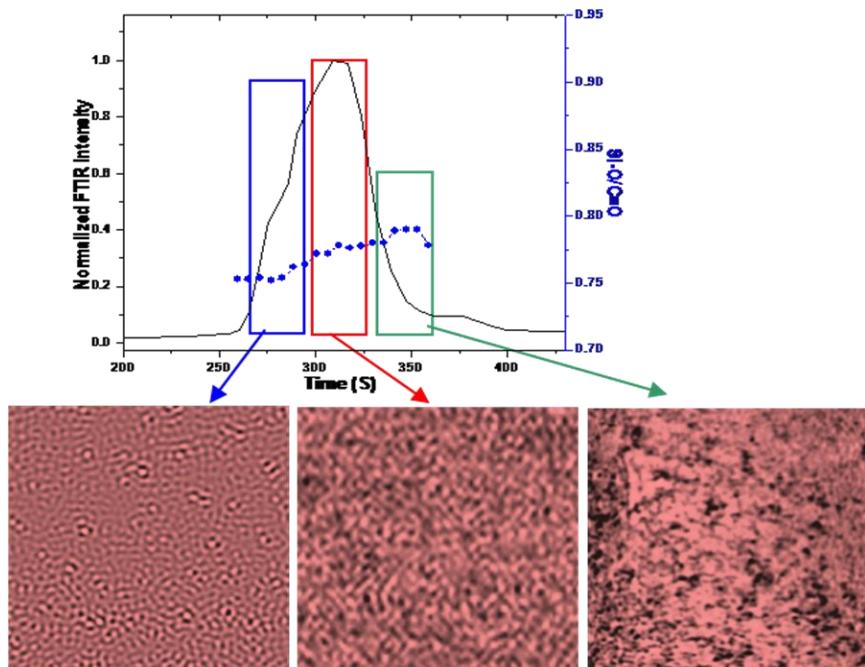


Figure 2: A Graham Schmidt plot overlaid with the ratio of C=O/Si-O FTIR bands and AFM images (1000 nm<sup>2</sup>) taken for each a signed fraction of a PDMS-PBCH random multiblock copolymer with 10% PDMS content.

The thermodynamic incompatibility of the PDMS soft segment and the PBCH hard segments results in two-phase microstructure. Spheres of PDMS domains is the type of surface morphology that obtained for all the fractions for 10% PDMS content copolymer, what is interesting here is the patent or the order that can be seen for the first fraction, which has high molecular mass and shows low PDMS content from the FTIR results. This order or pattern indicates that this fraction mainly consists of PDMS-PBCH di-block or tri-block copolymers.

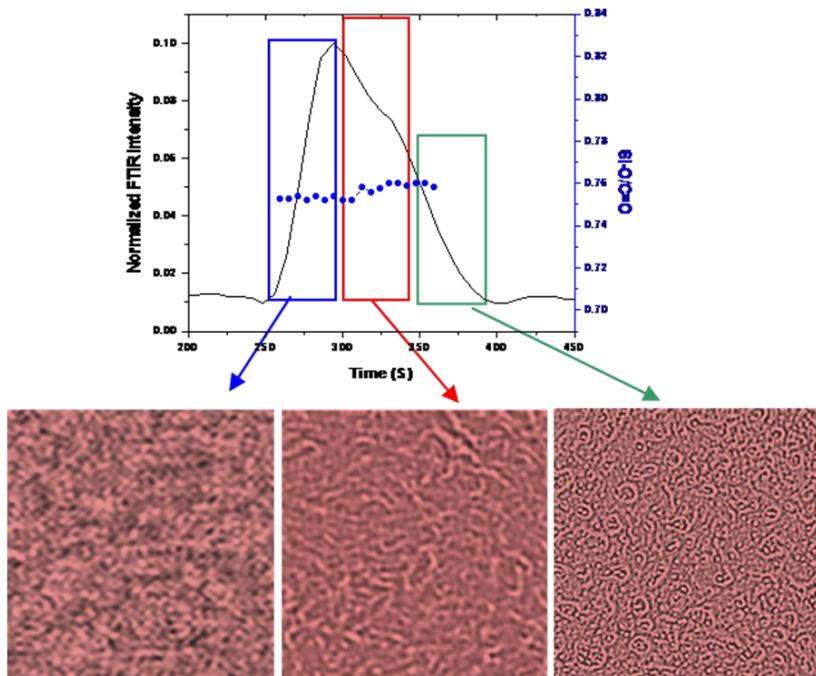


Figure 3: A Graham Schmidt plot overlaid with the ratio of C=O/Si-O FTIR bands and AFM images (1000 nm<sup>2</sup>) taken for each a signed fraction of a PDMS-PBCH perfectly alternating multiblock copolymer with 10% PDMS content.

Figure 3 shows spheres of PDMS domains in surface phase images that correspond to both high and medium molecular mass fractions (first fraction and second fraction in Figure 3 respectively). These fractions were obtained when 10% PDMS content perfectly alternating PDMS-PBCH copolymers fractionated based on the molecular mass. However, bright domains were also observed in the low molecular mass fraction (third fraction), which could be either remains of polyester homopolymer or crystalline domains of the polyester segment in the copolymers. Similar type of bright domains was attributed as crystalline domains of polybutylene terephthalate when polybutylene terephthalate polyethylene oxide polydimethylsiloxane multiblock copolymers were investigated using AFM tapping mode by M. Dahrouch and coworkers [11].

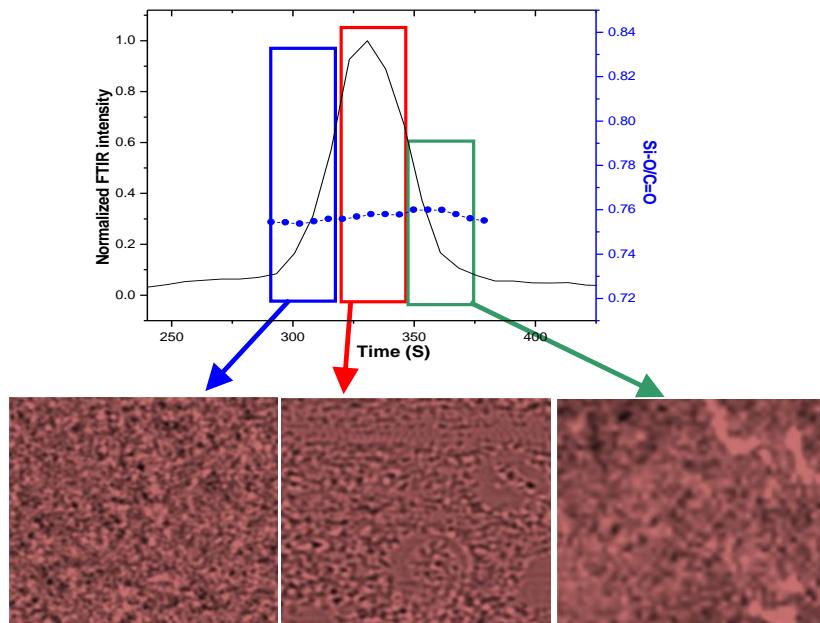


Figure 4: A Graham Schmidt plot overlaid with the ratio of C=O/Si-O FTIR bands and AFM images ( 1000 nm<sup>2</sup> ) taken for each a signed fraction of a PDMS-PBCH random multiblock copolymer with 25 % PDMS content.

Figure 4 shows the copolymer surface morphology that obtained when the PDMS content increases to 25%. In all the collected fractions from the SEC the spheres of the PDMS domains can still be seen in the polyester matrixes. On the other hand for alternating PDMS-PBCH copolymers with 25% PDMS content, when fractionated based on the molecular weight as it is illustrated in Figure 5 in addition to the spheres of the PDMS domains three phases of the PDMS domains and crystalline domains and the amorphous phase of the PBCH were observed: dark phase which is PDMS domains, bright phase which is crystalline domains of PBCH segment in the copolymer, and the third phase is amorphous PBCH segment

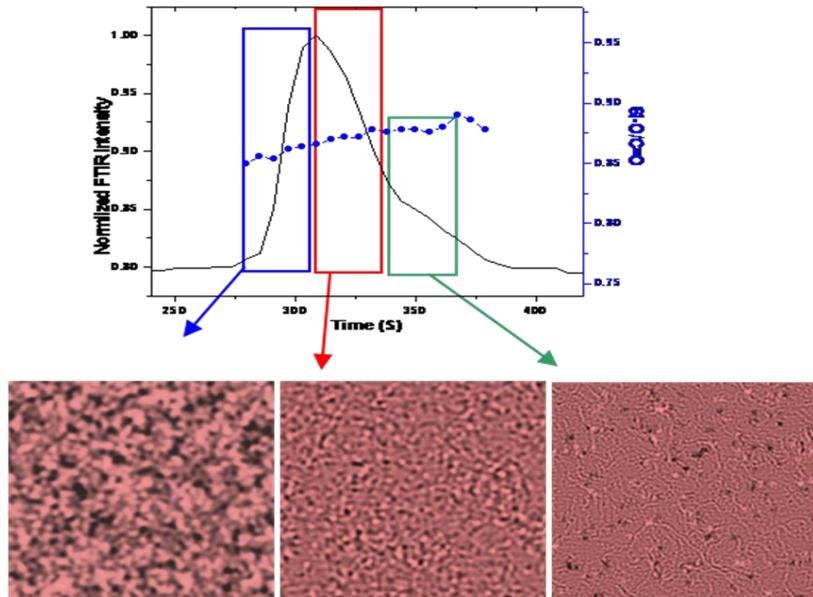


Figure 5: A Graham Schmidt plot overlaid with the ratio of C=O/Si-O FTIR bands and AFM images ( 1000 nm<sup>2</sup> ) taken for each a signed fraction of a PDMS-PBCH perfectly alternating multiblock copolymer with 25 % PDMS content.

Although it is well known that the most important factor driving to the phase separated morphologies in the PDMS- organic copolymers is the low solubility parameter of the PDMS when it compared with the other organic segment ( $\delta = 7.3\text{-}7.5 \text{ Cal } \frac{1}{2} \text{ cm}^{-3/2}$ ), [12], but the crystallization of the PBCH segment in the microdomain also can be considered another driving force for the phase separation in the PDMS-PBCH semicrystalline system, and obviously in this case due to the low glass transition temperature of the PDMS segment the crystallization can be confined within spherical nanoscale domains. The crystallization in nanoscale domains has been reported before in literature for diblock copolymers with strongly segregated systems with rubbery blocks[13].

The images that have been shown in figures ( 2-5 ) were obtained from the coupling of SEC with AFM in a novel way to create a hyphenated technique the obtained results are really providing

significant information about the copolymer morphology after fractionation based on the molecular mass.

### 5. Conclusions

Two different types of PDMS-polyester multiblock copolymers were fractionated using chromatography techniques: size exclusion chromatography (SEC). Then PDMS content along the molecular mass distribution was investigated using SEC-FTIR off line coupling technique. Moreover a new novel hyphenating offline coupling technique were developed, to provide micro-morphology information as a function of PDMS distribution or copolymer molecular mass and the PDMS content namely SEC-AFM. This novel technique provide a new way to study the morphology as a function of the copolymer molecular mass (SEC-AFM) and although some of the fractions morphology results did not show a very big significant change in the morphology, some other fractions did indeed showed a distinct morphology changes.

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