

## Novel Gradient Elution Chromatography Atomic Force Microscopic Hyphenated Offline Coupling Technique for Copolymers Morphology Investigation

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### Abstract

In this work two different types of synthesized Polydimethylsiloxane-polybutylenecyclohexalate (PDMS-PBCH) composition using gradient elution chromatography (GEC). Furthermore, multiblock copolymers were fractionated based on the copolymer chemical a new novel hyphenated offline coupling technique was developed, to provide morphology information as a function of Polydimethylsiloxane (PDMS) segment distribution in the copolymer. In this hyphenated technique the outcome of the GEC was collected on a disc using LC-transform and then scanned using atomic force microscopy (AFM) to investigation the morphology for each fraction of the same chemical compositions' copolymer. The results show that various surface morphology was obtained with some evidence of phase separation forming PDMS spherical domain and other types of morphology for both types of copolymers. This indicates the advantages of using the newly proposed HPLC-LC-transform-AFM offline hyphenated techniques for investigating the complex morphology of multiblock PDMS-PBCH copolymers.

**Keywords:** Polysiloxane-Polyester Copolymers, Liquid Chromatography, GEC-LC-transform-AFM

## Introduction

Compared with polyester and polysiloxane homopolymers polysiloxane-polyester copolymer system should have some unusual features, such as a very strong segregation between the two segments and pronounced surface activity of the polysiloxane segment, both of which result from the non-polar nature of siloxane [1-3]. The resistance of siloxane containing polymers to oxygen reactive ion etching also suggests potential uses for these types of copolymers in microlithography [4-6]. Surprisingly, no systematic investigation of the morphology of these materials has been undertaken, in contrast to the large body of work on other copolymers of polysiloxane systems this due to complexity of the copolymer that came from the chemical composition heterogeneity as well as the variation in molecular mass. In general, the obtained images will show disordered structures which are difficult to assign to the classical morphologies of spheres, cylinders, or lamellae. Thus, Liquid chromatography fractionations of the copolymers to reduce the chemical heterogeneity and then preparation of fractions with defined chemical compositions distribution for subsequent morphology study was suggested in this paper to be used. The chromatographic systems were selected here due to its high speed and high resolving power [7]. In order to obtain a more detailed picture for such heterogeneous copolymers it is necessary to separate the copolymer sample into a series of narrower chemical distribution fractions [8-10].

There are three main forms of liquid chromatography have been used to fractionate polymers. These are gel permeation chromatography (GPC), liquid chromatography at critical condition (LC-CC) and gradient elution chromatography (GEC) [11,12].

In order to obtain 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). The connection point utilized in LC-FTIR fractionating method was equipped with a nitrogen gas nebulizer that permitted the vaporization of solvents utilized in the HPLC. The solutes leaving a tight drag segment were kept onto a pivoting intelligent circle, permitting dissipation of the portable stage dissolvable, trailed by FTIR examination in the samples compartment of the IR spectrometer. Further a critical improvement in the utilization of LC-FTIR examination was introduced when Goede utilized LC-FTIR and Atomic powers microscopy (AFM) disconnected strategy to concentrate on the thermal properties of individual stages in polymer combinations after fractionation to different portions [13].

In this work GEC techniques was used to fractionate based on the chemical compositions of the copolymers. Moreover, the fractionated deposited copolymers indirectly on the germanium disc were redissolved and divided into two fractionations based on the chemical composition and thin films were made from that for surface morphology investigation using atomic force microscopy (AFM) technique. This a new novel hyphenation offline coupling techniques was developed to provide morphology information as a function of PDMS distribution and it might be extended to be used for other copolymer systems.

## Experimental

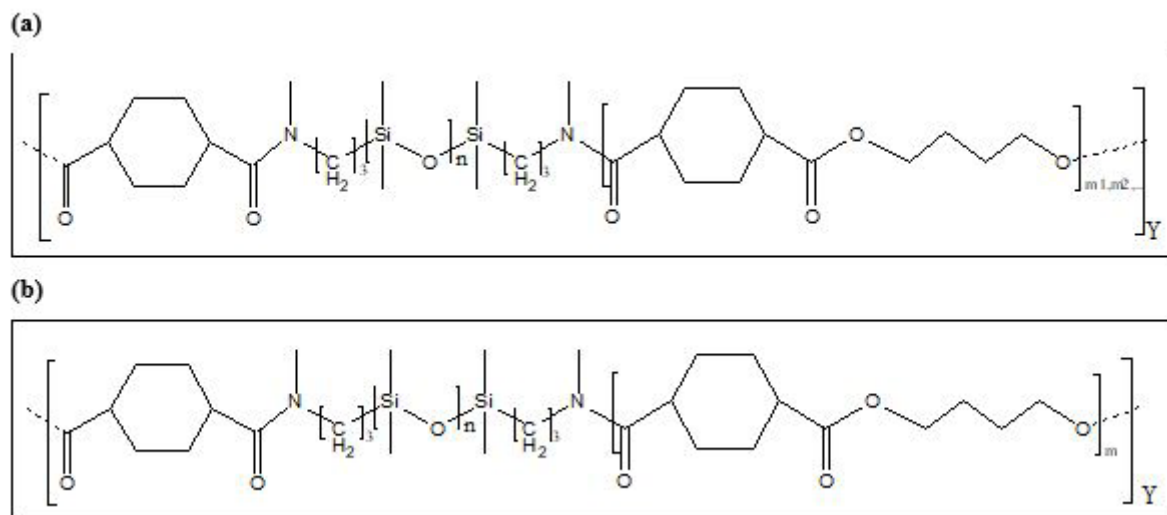
### Polysiloxane-Polyester Copolymers Samples:

The chemical compositions of the investigated polysiloxane-polyester copolymers are summarized in Table 1.

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

Sample no.	Siloxane Mn(g mol <sup>-1</sup> )	Siloxane (wt%)	Copolymer Mn (g mol <sup>-1</sup> )
R-1	1500	9.20	17170
R-2	1500	22.70	20240
AL-1	1500	12.0	18240
AL-2	1500	26.2	19420

Polydimethylsiloxane-polybutylenecyclohexalate (PDMS-PBCH) multiblock copolymers: The two types are 1) Random multiblock copolymers (Scheme 1-a) and 2) Perfectly alternating multiblock copolymers (Scheme 1-b).



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

## Characterization Techniques:

### Fractionations by Gradient Elution Chromatography (GEC)

GEC was used successfully in monitoring the chemical composition of PDMS-PBCH copolymers by fractionation based on the chemical composition using mixture of THF and hexane with flow rate of 1 mL/min and with concentration varied with time as it is illustrated in Figure 2. The separation was performed using a dual pump HPLC comprising of the following units: Waters 2690 Separation module (Alliance), Agilent 1100 series variable wavelength detector, PL-ELS 1000 detector and data was recorded and processed using PSS WinGPC unity (Build 2019) software. The separation was done through a bare silica column (Nucleosil 100) working at 30 °C and the samples were prepared in THF at concentration of 5 mg/mL.

### Fractions morphology investigation by AFM

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 [14].

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 low-pass filtering.

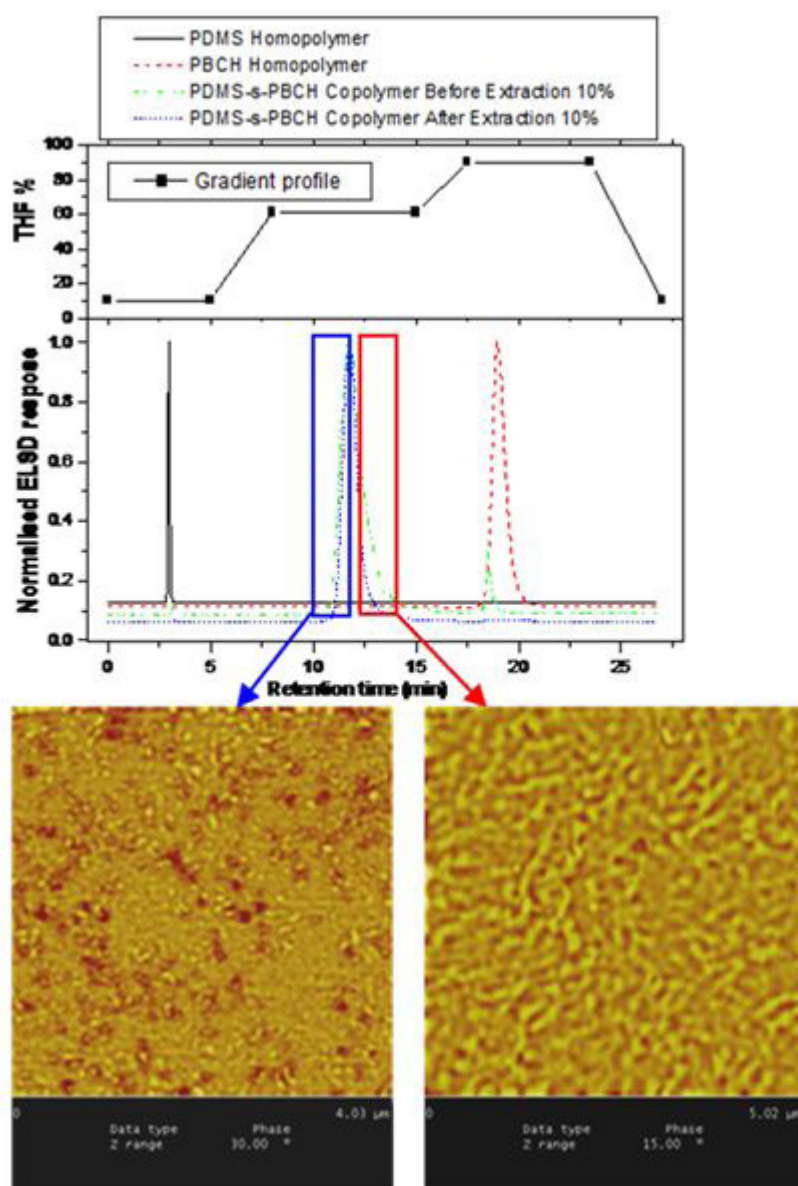
In order to collect fractions for AFM analysis from the chromatography fractionation technique LC-transform supported with a Germanium disk was used, small pieces of mica (5x5 mm<sup>2</sup>) were attached to the Germanium disk and the eluted samples were collected on these pieces. Each eluted copolymer sample from GEC system was collected on two mica pieces to form two fractions of the copolymer fractionated based on the chemical compositions. Due to the rough surface of the obtained

films all these fractions were re-dissolved and smooth thin films were made from that for surface morphology investigation using AFM technique.

## Results and Discussion

The surfaces of the collected fractions from GEC for 10% PDMS content random PDMS-PBCH copolymers were imaged via tapping mode AFM at ambient temperature and the resulting phase images are shown in Figure 1. The thermodynamic incompatibility of the PDMS soft segment and the PBCH

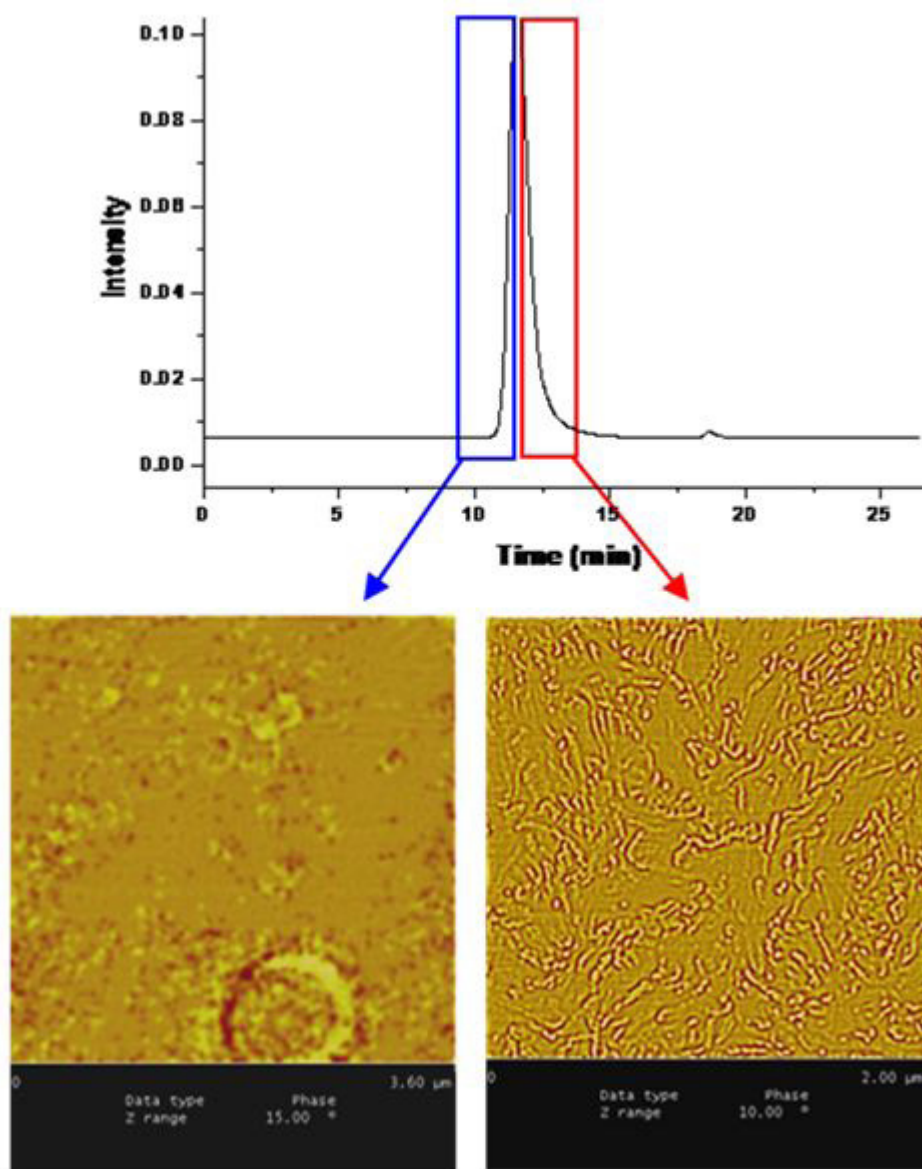
hard segments results in a two-phase microstructure. When the copolymer was fractionated based on the chemical composition using GEC (Figure 1), the obtained surface morphology shows PDMS domains in the rich PDMS fraction (first fraction in Figure 2). The sizes of these domains seem to be larger than that for the PDMS domains in the fractions obtained from SEC for this copolymer. In this image also some of the domains begin to connect with each other, which eventually will lead to change the type of morphology from spheres to bicontinuous phase as will be discussed later in 25% PDMS content copolymers.



**Figure 1:** GEC result for PDMS, PBCH homopolymers and PDMS-PBCH random multiblock copolymer with 10% PDMS content, when the above gradient profile was used and AFM images taken for each a signed fraction of the copolymer

PBCH copolymers. Figure 2 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 2 respectively). These fractions were obtained when 10% PDMS content perfectly alternating PDMS-PBCH copolymers fractionated based on the molecular mass.



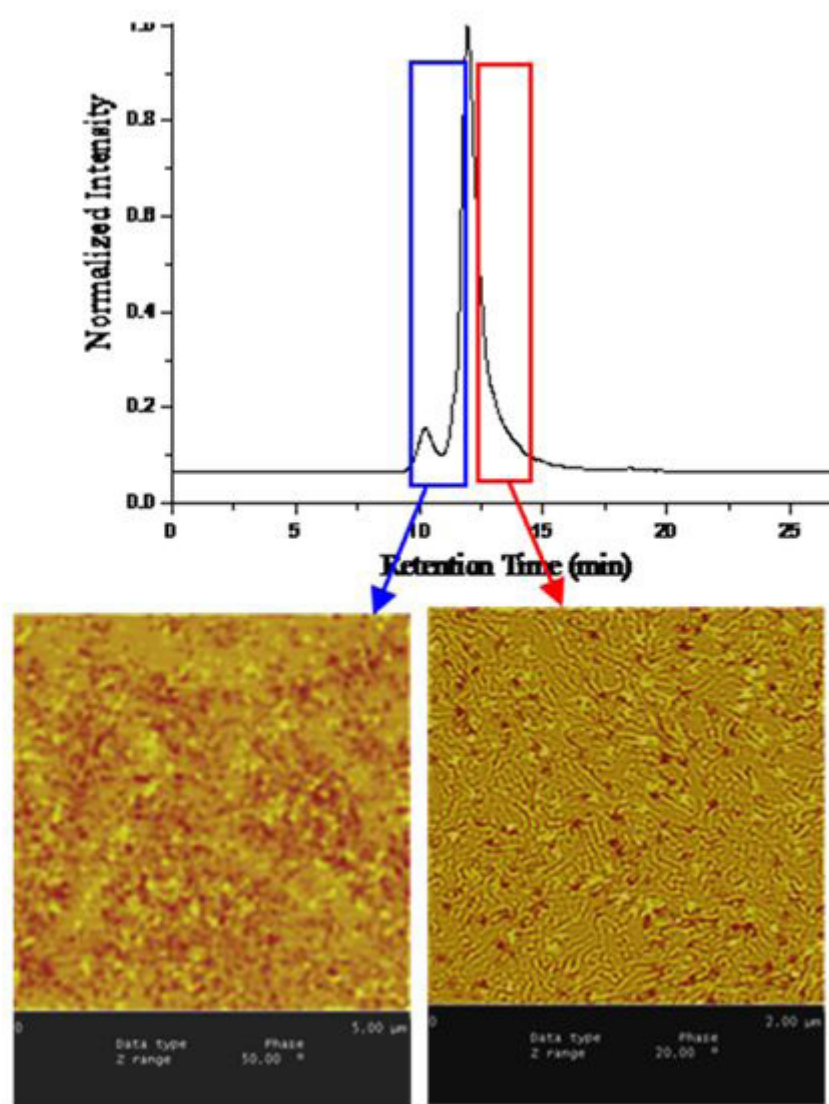
**Figure 2:** GEC results and AFM images taken for each a signed fraction of a PDMS-PBCH perfectly alternating multiblock copolymer with 10 % PDMS content

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 [15]. The nature of the bright domains that shown in Figure 2 was further investigated by using GEC analysis and as it is illustrated in Figure 3, the small peak at about 18 minutes retention time

in the GEC results is corresponding to the PBCH homopolymer that still present in the copolymer. Although the PBCH has been removed from the fractionated copolymers the bright domains are still appears in the phase image of the second fraction, which has the low PDMS content and this is proofing that these bright domains in fact are crystalline domains of PBCH segment in the copolymer chain. These domains have relatively irregular sizes and not uniformly distributed in the PDMS-PBCH amorphous matrix. 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 ( $= 7.3-7.5 \text{ Cal } \frac{1}{2} \text{ cm}^{-3/2}$ ), [16], 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 [17-21].

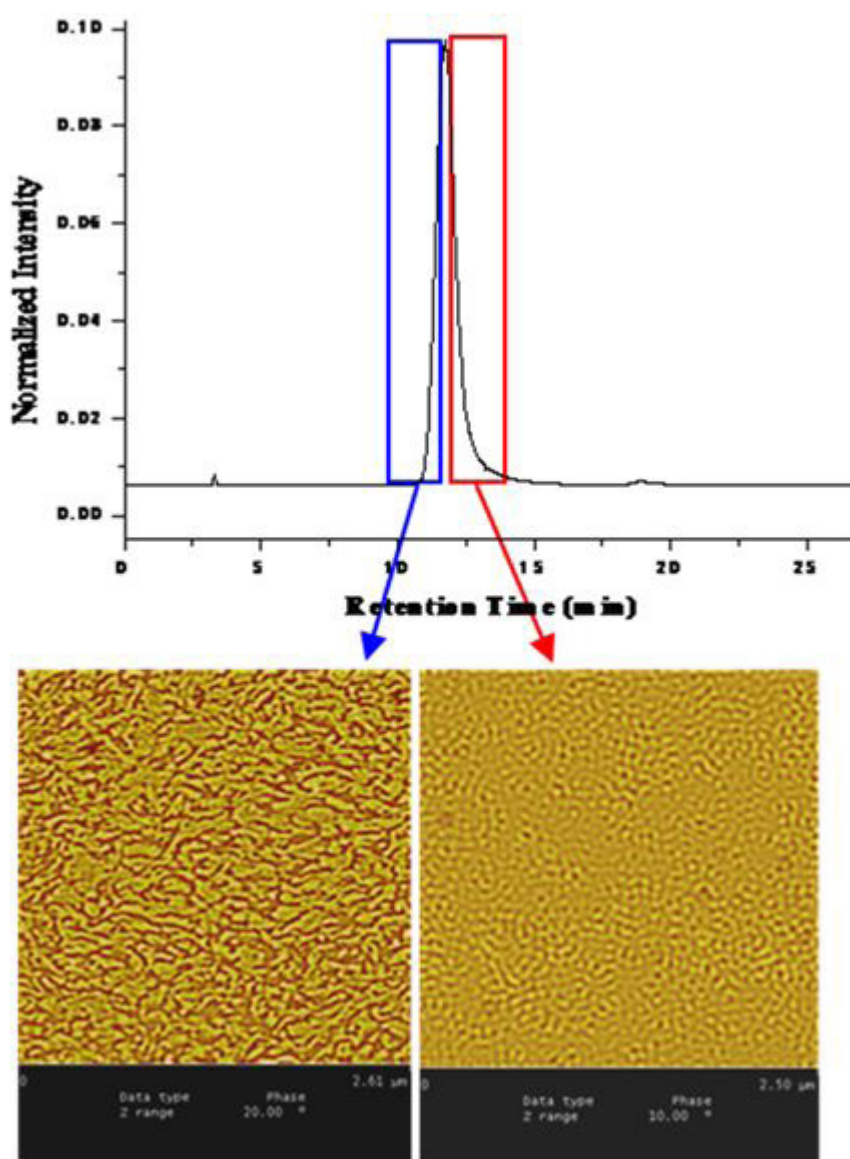
Figure 4 shows the copolymer surface morphology that obtained when the PDMS content increases to 25% for two copolymer fractions separated according to their chemical composition. Here a new type of morphology was obtained for the low PDMS content fraction, in which three phases were observed: dark phase which is PDMS domains, bright phase which is crystalline domains of PBCH segment in the copolymer, and the third phase is amorphous PBCH segment. Although the PDMS content is high in these fractions the bright domains are still seen. This illustrated the fact that in the copolymer chains themselves there is a phase separation as can be detected from the presence of three type of morphology in the same image.



**Figure 3:** GEC results and AFM images taken for each a signed fraction of a PDMS-PBCH random multiblock copolymer with 25 % PDMS content

Although the fascinating morphology of the three phases has been observed in several of the unfractionated copolymers, none is as clear as shown in the fractionated copolymers. This is a clear indication of the advantages of using the newly

proposed HPLC-LC-transform-AFM offline hyphenated techniques for investigating the complex morphology of multiblock PDMS copolymers.



**Figure 4:** GEC results and AFM images taken for each a signed fraction of a PDMS-PBCH perfectly alternating multiblock copolymer with 25 % PDMS content

On the other hand, in the case of alternating PDMS-PBCH copolymers with 25% PDMS content (Figure 4), two types of morphology were obtained; spheres of PDMS domains in a matrix of PBCH for the low PDMS content fraction and the rich PDMS content fraction shows bicontinuous phases type of morphology.

## Conclusions

Two different types of PDMS-polyester multiblock copolymers were fractionated using chromatography techniques: namely gradient elution chromatography (GEC) in order to separate the copolymer chains (molecules) based on their chemical composition. Then novel hyphenating offline coupling techniques was developed, to provide morphology information as a function of PDMS distribution namely GEC-AFM. These novel techniques provide new way to study the morphology as a func-

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tion of the chemical composition. The resulting images for the surface that obtained from all the fractions showed a fascinating morphology and did indeed show a distinct morphology change from each other. These fascinating types of morphologies show an obvious sign of the upsides of utilizing the recently proposed HPLC-LC-transform-AFM disconnected joined strategies for examining the complex morphology of multiblock copolymers.



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