

Comprehensive exploration of Synthesis and Characterizations of Ester-Siloxane Multiblock Copolymers

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Abstract

This research paper presents a comprehensive study on the synthesis and characterization of Ester-Siloxane multi block copolymers. Two different synthesis methods, namely the one-prepolymer method and the two-prepolymer method, were employed to prepare the copolymers. The distribution of the Ester segment within the copolymers was analyzed using refractive index and ultraviolet detectors coupled with size exclusion chromatography (SEC). SEC-FTIR spectroscopy was utilized to investigate the distribution and composition of the Siloxane segment. Gel permeation chromatography (GEC) was employed to assess copolymer purity based on Siloxane content. Atomic force microscopy (AFM) was utilized to visualize the morphology of Siloxane domains in the copolymers. The results revealed the presence of well-defined Siloxane-rich domains in the form of spheres. Moreover, the occurrence of spherulitic crystal structures was observed in random copolymers with low Siloxane content and small Siloxane segment length. This research provides valuable insights into the manufacturing process, characterization, and structural aspects of multi-block ester-siloxane polymers, and contributes to the understanding of polymer design, the relationship between composition and molecular structure, and the material properties.

Key words: Copolymer, -Siloxane multiblock, One-prepolymer, Two-prepolymer, Polycondensate.

استكشاف مفصل لتصنيع وتوصيف كوبوليمرات متعددة الكتل من إستر-

سيلوكسان

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الملخص:

يقدم هذا البحث ورقة بحثية حول تصنيع وتوصيف البوليمرات المتعددة الكتل المكونة من إستر-سيلوكسان. حيث تم استخدام طريقتين مختلفتين لإعداد هذه البوليمرات المتعددة الكتل، وهما طريقة البوليمر الأولي و طريقة البوليمرين الأوليين. تم تحليل توزيع قطاع الإستر داخل البوليمرات باستخدام مقياس الانكسار و الكاشف فوق البنفسجي المرتبطين بالكروماتوغرافيا بالحجم المستبعد (SEC). بينما تم دراسة توزيع قطاع السيلوكسان، بالكروماتوغرافيا المرتبطة بالتحليل الطيفي بالأشعة تحت الحمراء (SEC-FTIR) واستخدمت كروماتوغرافيا الاختراق الجلدي (GEC) لتقييم نقاء البوليمر بناءً على محتوى السيلوكسان. وباستخدام المجهر القوى الذري (AFM)، تم تصور هيكلية مجالات السيلوكسان في البوليمرات. أظهرت النتائج وجود مجالات غنية بالسيلوكسان ذات هياكل محددة جدًا وعلى شكل كرات. كما لوحظ وجود هياكل بلورية كروية في البوليمرات العشوائية ذات محتوى سيلوكسان منخفض و طول قطاع سيلوكسان صغير. يوفر هذا البحث رؤى قيمة حول عملية التصنيع والتوصيف و الهيكلية لبوليمرات إستر-سيلوكسان المتعددة الكتل، كما و يسهم في فهم تصميم البوليمرات و العلاقة بين التركيب و البنية الجزيئية و خواص المواد.

الكلمات الرئيسية: البوليمرات المشتركة ، البوليمر المسبق الأحادية و الثنائية، متعدد الكتل استرسيلوكسان ، متعدد التكتيف.

1. Introduction

Multiblock copolymers have gained significant attention in recent years due to their unique properties and potential applications in various fields such as materials science, polymer engineering, and biomedical applications. Among the different types of multiblock copolymers, Ester-Siloxane copolymers have emerged as a promising class of materials due to their desirable combination of organic and inorganic characteristics. The incorporation of ester and Siloxane segments within a copolymer structure offers the opportunity to combine the mechanical properties, processability, and biocompatibility of ester-based polymers with the thermal stability, chemical resistance, and low surface energy of Siloxane-based polymers [1-3].

During the last decades, mixtures of different copolymerization of polycondensates such as polyamides, polyesters, and polycarbonates with polysiloxane have attracted big interest from both the scientific and industrial point of view[4-6]. The inherent ability of polycondensates to undergo exchange reactions facilitates compatibilization when polycondensates are used as components in polymer copolymerization and blending [7]. Incorporation of polydimethylsiloxane into polyesters has been shown to yield several attractive properties while retaining many of the excellent properties of the corresponding homopolymers [8].

Two different experimental procedures were used to synthesize multi block segmented polybutylene cyclohexanate-polydimethylsiloxane copolymers. First one (a one-prepolymer method) based on the method developed by Kiefer et.al [9], and the second method (a two- prepolymers method), based on the method developed by O'Malley et.al [10]. Depending on the copolymerization procedure a random or a perfectly alternating multiblock copolymer were obtained. The obtained copolymers were fractionated using chromatography techniques. Size exclusion

chromatography (SEC), was used to determine the copolymer molecular mass and gradient elution chromatography (GEC), was used to determine the chemical composition.

Block copolymers frequently exhibit phase separation in which blocks of like type associate into domains whose dimensions are on the order of 10 nm. The morphology of monodispersedi- and tri-block copolymers consists of highly ordered spheres, cylinders, or lamellae, and criteria for phase separation and predictions of domain size and shape have been developed in terms of molecular and thermodynamic. Random and alternating block copolymers (ABAB-ABA) in which both the A and B blocks are polydisperse exhibit a morphology that is generally less ordered, and rigorous calculations for predicting the morphology have not been attempted [11]. Although crystallization and higher-order structure formation in block copolymers have been extensively studied, for multiblock copolymers have not been studied properly [12].

To fully exploit the potential of Ester-Siloxane copolymers, it is crucial to understand their synthesis, molecular structure, and morphology. This research paper aims to provide a comprehensive investigation of the synthesis and characterization of Ester-Siloxanemultiblock copolymers, focusing on two different synthesis methods: the one-prepolymer method and the two-prepolymer method. In this article, also the formation of microstructure observed with atomic force microscopy technique will be presented for the multiblock copolymers, in which polyester is crystallized in the condition when polysiloxane is in the rubbery state.

2. Experimental Work

2.1. Multiblock copolymer synthesis

Perfectly alternating multiblock copolymers (Figure 1-a) were synthesized using two prepolymers method based on the method that developed by O'Malley et.al to synthesis Siloxane-aliphatic polyester copolymer[10]. Additionally the polymerization was carried out by reacting two difunctional prepolymers Siloxane and Ester, having ester and hydroxyl end group respectively. Random multiblock copolymers (Figure 1-b) were synthesized using one prepolymer method [9], by reacting a difunctional end-capped

Siloxane oligomer with a mixture of 1,4-butandiol and 1,4-dimethylcyclohexanedicarboxylate.

The first approach of the copolymerization involved first preparing a functionalized polyester oligomer, then reacting it with an ester-functional siloxane oligomer to produce alternating segmented copolymers. The raw materials were charged to a flask, heated to 110°C, catalyst was added, and the reaction continued at 160°C for 3h under nitrogen. Then temperature is raising to 220°C under reduced pressure for 5-6h. The second approach used for the synthesis of the Ester-Siloxane copolymer involved charging diacid and butandiol monomers in a 1:1.5 molar ratio into a reactor with a distillation arm to collect methanol and excess butandiol. The conditions of the reaction were exactly similar to the first method.

The Ester-Siloxane copolymers were soluble in chloroform, and three copolymers of each type were synthesized to investigate the effect of siloxane concentration and molecular mass. The initial concentrations of the siloxane segments before starting the copolymerization were 10, 10, and 25 weight percentages. These concentrations are referred to as the "theoretical" siloxane concentrations in this paper. The synthesized products were purified from the homopolymers using soluble and non-soluble solvents.

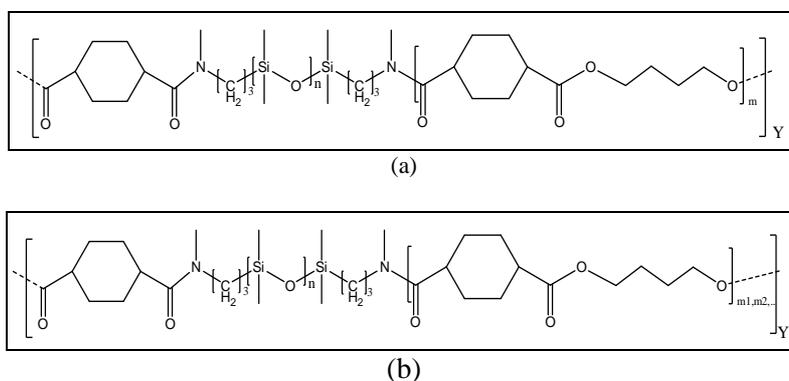


Figure 1. Chemical structure of (a) perfectly alternating Ester-Siloxane copolymers and (b) random Ester-Siloxane copolymers

2.2. Characterization techniques

The chemical compositions of the purified copolymers were determined from the 300 MHz ^1H nuclear magnetic resonance (^1H -NMR) spectra, 300 MHz (a Varian Unity Inova).

The average molecular masses were determined using a SEC. The results are summarized in Table 1. The UV detector was connected to the chromatography system in order to monitor the Ester segment distribution along the molecular mass distribution.

The Siloxane content along the molecular mass distribution was obtained using FTIR off line coupling to the SEC using an LC-transform device and a Germanium disk. Tetrahydrofuran (THF) was used as a solvent with a flow rate set at 1 mL/min. Mixed-E column was used in SEC, which packed with Pl gel silica particles with 3 μm diameter and the column was working at 30 $^\circ\text{C}$ and the samples were prepared in THF at concentration of 5 mg/mL.

GEC was successfully used to monitor the chemical composition of the Ester-Siloxane copolymers by fractionation based on the chemical composition. This was done using a mixture of THF and hexane with a flow rate of 1 mL/min and the concentration was varied with time as it is illustrated in Figure 2.

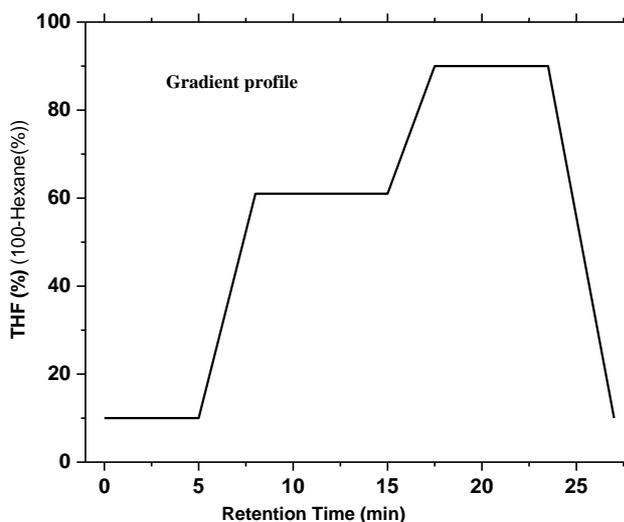


Figure 2: Gradient elution chromatography solvents profile.

AFM images were obtained using a Veeco multimode AFM (model no. MMAFMLN) in non-contact mode. A low resonance frequency silicon cantilever (60 kHz, $K = 50$ N/m) was used. Samples were attached to the sample holder with double-side adhesive tape. Experiments were conducted under ambient conditions with a scan rate of 0.5 to 0.7 Hz. Simultaneous capture of topography and phase images was performed in tapping mode. The focus of this report is on the phase images, which reflect the sample's elastic and viscoelastic properties [13].

3. Results and Discussion

The chemical compositions of the Ester-Siloxane copolymers were determined using $^1\text{H-NMR}$. Figure 3 shows four examples of $^1\text{H-NMR}$ spectra of Ester-Siloxane copolymers (Al-1, Al-2, Ra-1 and Ra-3). The spectra clearly show the presence of the methyl groups attached to the silicon atoms δ 0.07 ppm. The chemical shifts at δ 1.4–2.4 ppm are assigned to the protons on the cyclohexane and methene units in the main chain. The chemical shift at δ 4.1 ppm is due to the protons in the methylene group attached to the carbonyl group along the backbone of the copolymer, indicating the presence of the polyester segment. The small chemical shift at δ 4.25 ppm corresponds to the proton in a butanol unit located at the chain end. The chemical shift at δ 3.24 ppm corresponds to the protons in the methene group attached to amide group. The proton of the amide group appears at the chemical shift δ 7.6 ppm, which provides confirmation of the formation of the copolymers.

Several $^1\text{H-NMR}$ spectra of the Ester-Siloxane did not show chemical shifts at δ 3.24 and at δ 4.25 ppm because the concentration of amide and the chain ends was too low for detection. Similar chemical shifts were obtained for random Ester-Siloxane copolymers, as is illustrated for examples Ra-1 and Ra-3. $^1\text{H-NMR}$ spectra of Ester-Siloxane copolymers, prepared using the one-prepolymer method, were also used to determine the chemical composition of these copolymers by integrating the peaks at δ 0.07 and at δ 4.1 ppm and using the method that published by Vuckovic et al. [8]. The $^1\text{H-NMR}$ results are included in Table 1.

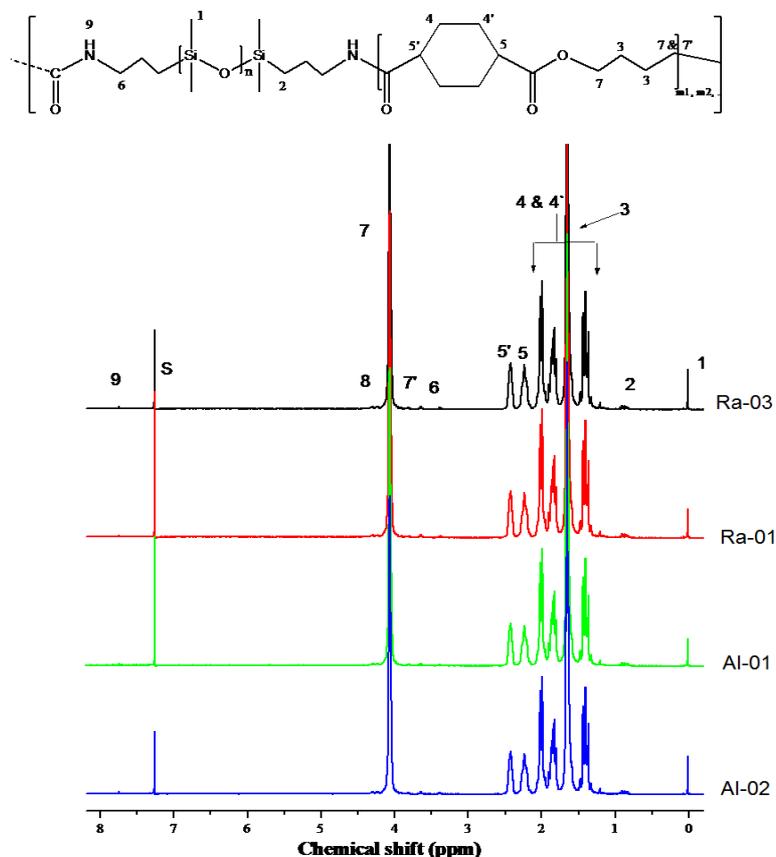


Figure 3: Typical $^1\text{H-NMR}$ spectra of Ester-Siloxane copolymers (Al-01, Al-02, Ra-01 and Ra-03).

Table 1 presents the chemical compositions and molecular masses of the synthesized Ester-Siloxane copolymers. Although the experimental value of the siloxane content calculated from the $^1\text{H-NMR}$ spectra was lower than the theoretical values, this difference can be attributed to the initial concentration of siloxane in the copolymerization feed. The theoretical values were determined directly from the initial feed composition before starting the copolymerization reaction, while the experimental values were obtained through analysis of the final copolymer composition using $^1\text{H-NMR}$ spectroscopy. This slight discrepancy between the

theoretical and experimental siloxane contents is not uncommon and can be influenced by factors such as differences in reactivity ratios or potential side reactions during the copolymerization process.

Table1: The chemical compositions and molecular masses of the obtained Ester-Siloxane copolymers.

Sample no.	Siloxane Mn (g mol ⁻¹)	Siloxane (wt %)	Ester-Siloxane Mn (g mol ⁻¹)
Ra-01	1000	9.74	16665
Ra-02	2000	9.20	17171
Ra-03	2000	22.70	20239
Al-01	1000	12.42	18640
Al-02	2000	13.10	18235
Al-03	2000	27.21	17420

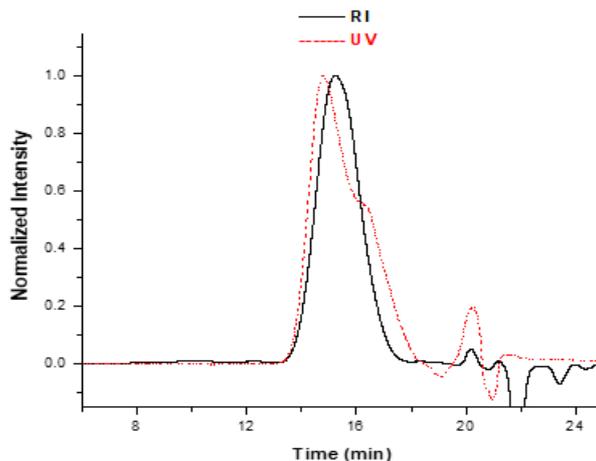
The resulted data in Table 1 also shows that the percentage of unreacted siloxane increases as the overall siloxane content and segment length in the copolymers is increased. Notably, all the Ester-Siloxane copolymers prepared using the two-prepolymer synthetic approach exhibited relatively high siloxane incorporation compared to those made via the one-prepolymer method. This can be attributed to the structural differences between the two approaches. In the one-prepolymer method, the siloxane and ester monomers are combined directly. This leads to a lower concentration of the ester-containing reactive groups relative to the siloxane groups, which can restrict the incorporation of the longer ester segments into the final copolymer chain. In contrast, the two-prepolymer approach first produces a functionalized polyester oligomer, which is then reacted with the ester-functional siloxane oligomer. This helps maximize the incorporation of the siloxane segments, resulting in copolymers with higher overall siloxane content, even after accounting for any unreacted prepolymer fractions. The net result is that the Ester-Siloxane copolymers made via the two-prepolymer route generally exhibit a higher siloxane content in the final copolymer chains compared to the one-prepolymer method.

Figure 4(a) provides a representative illustration of the size exclusion chromatography (SEC) results, employing both refractive index (RI) and UV detectors, for aEster-Siloxane copolymer with a Siloxane content of 10%. The average molecular mass of the copolymer was determined from these measurements. The UV signal, measured at 310 nm, served as an indicator of the concentration of Ester (ester group, C=O) segments in the copolymer samples, while the molar mass distribution within the copolymers was determined from the RI response.

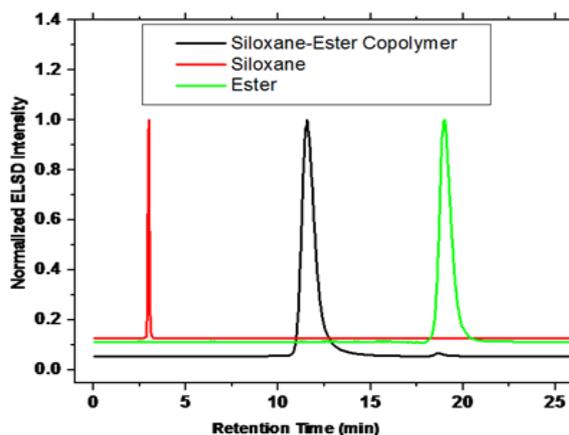
In the depicted example, the UV peaks are observed to be shifted towards the right of the RI peak. This observed phenomenon suggests that the lower molar mass copolymer molecules contain a higher proportion of Ester segments compared to the higher molar mass copolymer molecules. In other words, the lower molecular weight fractions of the copolymer possess a relatively greater concentration of Ester segments, while the higher molecular weight fractions have a relatively lower concentration of Ester segments. This observation implies that the incorporation of Siloxane into the copolymer structure has an impact on the distribution of Ester segments across different molecular weight fractions. The specific reasons behind this shift in UV peaks and its correlation with the molar mass distribution would require further investigation and analysis. However, this finding provides valuable insights into the composition and distribution of Ester segments within the copolymer matrix.

Figure 4(b) also shows a typical example of the GEC results for Al-01 before and after copolymer purification, and Siloxane and Ester homopolymers, using a mixture of hexane and THF solvents with a gradient profile as shown in the upside of the Figure 1. GEC analyses of Siloxane and Ester homopolymers were run separately. It was found that, the Siloxane sample eluted between 2.5 and 3 min. On the other hand, a Ester sample eluted at 18–21 min retention time. The GEC chromatograms were recorded for the copolymer after the Siloxane and Ester homopolymers were extracted from the copolymer. The GEC chromatogram of the purified copolymer shows one large fraction at about 12–15 min for

the copolymer. The complete absence of the homopolymer fractions proves the successful removal of the Siloxane homopolymers.



(a)



(b)

Figure 4: (a) SEC results, using RI and UV detectors, for a perfectly alternating Ester-Siloxane copolymer with 10% Siloxane content and (b) GEC results for Siloxane, Ester and Ester-Siloxane copolymers.

The random nature of the chemical composition of the copolymers that are produced by the one prepolymer method can be detected from the SEC results in Figure 5. A small shoulder is observed in the RI response that was not detected using the UV detector. This shoulder indicates that the high molecular mass copolymer chains consists of very small Ester segment lengths ($m = 1$) (as the ester group is not detected by UV detector). This type of randomness was not observed from SEC and GEC results in Figure 4 for a perfectly alternating copolymer. This is due to the large segment lengths of both Siloxane and Ester that were incorporated into the copolymer chain using the two prepolymers copolymerization method.

The SEC results presented in Figure 5 provide insights into the random nature of the chemical composition of copolymers produced using the one prepolymer method. In the RI response, a small shoulder is observed, which is not detected by the UV detector. This shoulder signifies that the copolymer chains with high molecular mass consist of very small Ester segment lengths ($m = 1$), as the ester group is not detected by the UV detector. This type of randomness, indicated by the presence of small Ester segment lengths, is distinct from the SEC and GEC results shown in Figure 4 for a perfectly alternating copolymer. In the perfectly alternating copolymer, the incorporation of Siloxane and Ester into the copolymer chain using the two prepolymers copolymerization method results in large segment lengths for both components.

The discrepancy in the observed randomness between the one prepolymer method and the two prepolymers copolymerization method can be attributed to the different approaches employed in their synthesis. In the one prepolymer method, the random distribution of Ester segments within the copolymer chains arises due to the simultaneous presence of Siloxane and Ester in the reaction mixture, leading to random incorporation during polymerization. This results in copolymer chains with varying Ester segment lengths, as evidenced by the shoulder in the RI response. On the other hand, the two prepolymers copolymerization method ensures a more controlled and alternating arrangement of Siloxane and Ester segments in the copolymer chains, leading to a lack of

observed randomness in the SEC and GEC results, as shown in Figure 4. This highlights the importance of the synthesis method in controlling the distribution and arrangement of segments within copolymer chains.

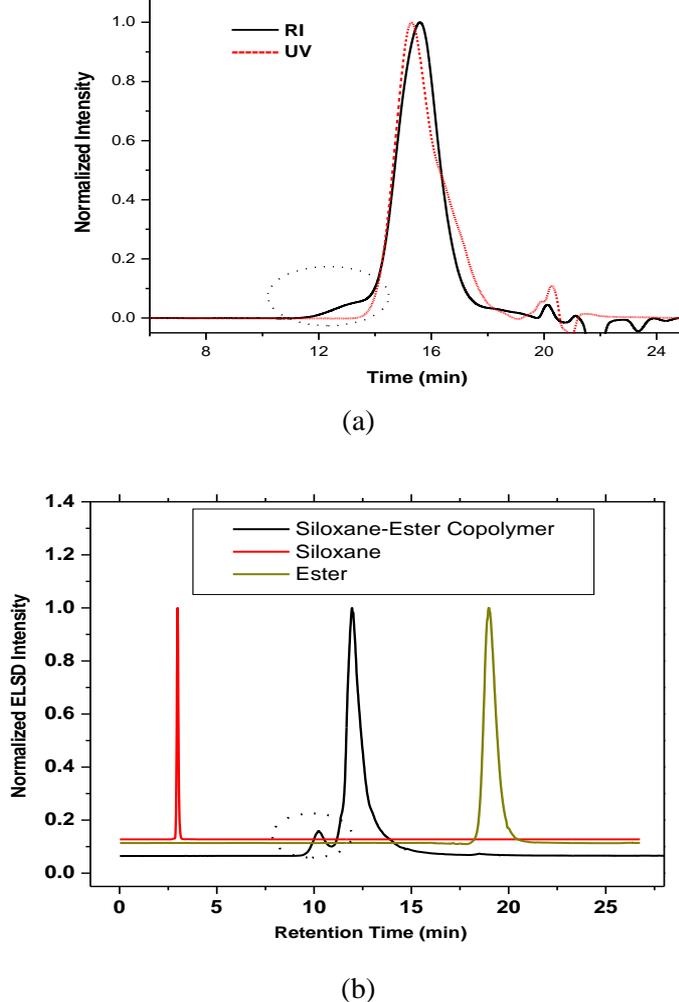
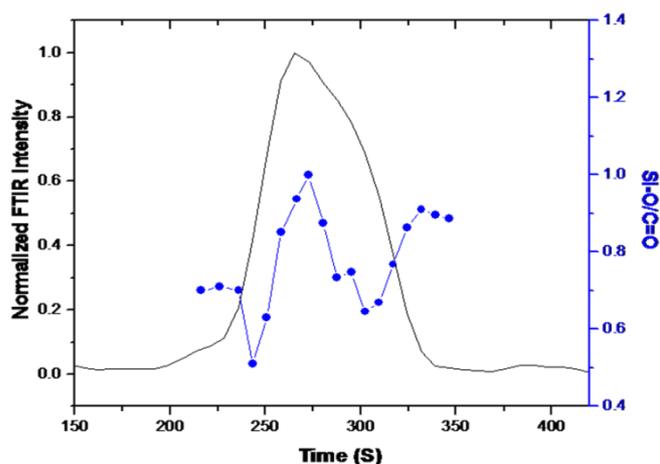
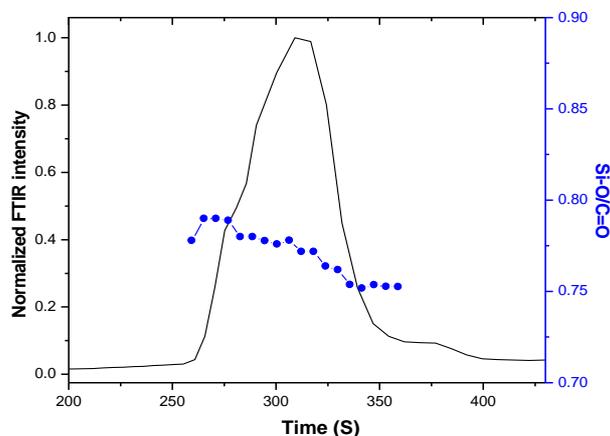


Figure 5: (a) SEC results with RI and UV detectors for random multiblock Ester-Siloxane copolymer with 10% Siloxane content and (b) GEC results for Siloxane, Ester and Ester-Siloxane copolymer

The SEC-FTIR results shown in Figure 6 show that the Siloxane content (and the Ester content) is randomly distributed along the molecular mass distribution of the alternating copolymer (not observed for a random copolymer) with a 25% Siloxane content.



(a)



(b)

Figure 6: SEC-FTIR results for Ester-Siloxane copolymers: (a) perfectly alternating and (b) random multiblock with 25% Siloxane content.

The uneven distribution could be due to the fact that when one Ester prepolymer segment is inserted into the copolymer chain the molecular mass of the copolymer increases suddenly by 1000 g/mol ($m = 10$), and thus the copolymer composition changes drastically, as observed from the changes in Si-O/C=O ratio in Figure 6. The AFM phase images in Figure 7 show a spherulitic crystal structure for the R-01 copolymer. This crystal structure was not observed for AL-01. This is attributed to either the high Siloxane content in the AL-01 copolymer or the fact that the one-prepolymer method may allow the Ester segment in the copolymer chain to grow very long ($m = 100$), with no interruption by Siloxane segments.

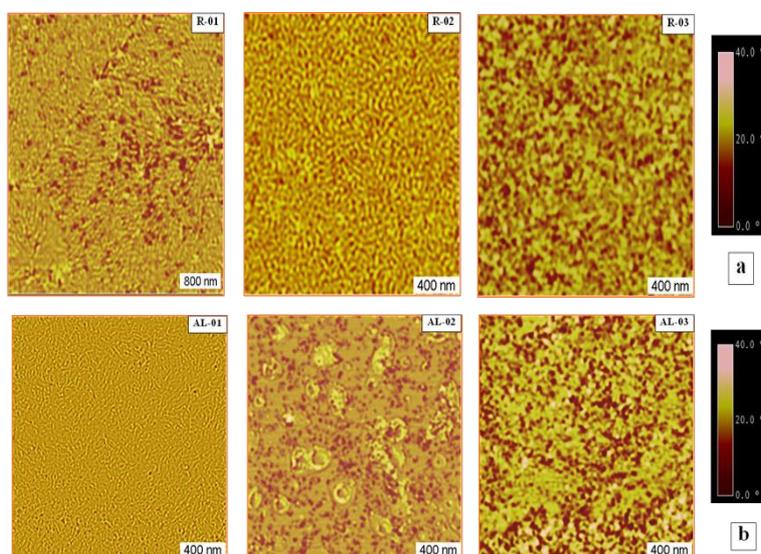


Figure 7: AFM phase images illustrating the surface morphology of Ester-Siloxane copolymers: (a) random multiblock and (b) perfectly alternating copolymers.

This length is sufficient to allow the Ester segment to fold in a lamella crystal order and then to form a spherulitic structure. This is not likely to occur for the AL-01 with a relatively small Ester segment length ($m=10$). In between the crystal structure of the R-01 spheres of Siloxane the domains are observed. The spheres of the Siloxane domains were also observed for the other copolymers. The

number and the size of the Siloxane domains increase with increasing Siloxane molecular mass and content. The bright areas that appear in the AL-02 copolymer could be crystalline Ester in the form of domains.

4. Conclusions

Two different type of Ester-Siloxane multiblock copolymers were successfully synthesized using a one-prepolymer method and two-prepolymer method. The Ester segment distribution along the molecular mass distribution was monitored using RI and UV detectors attached to a SEC system and the Siloxane segment distribution was also investigated using SEC-FTIR technique. GEC was used to investigate the copolymer purity by separation based on the Siloxane content. The findings highlight the importance of the synthesis method in controlling the distribution and arrangement of segments within copolymer chains. The one prepolymer method introduces randomness in the copolymer composition, while the two prepolymers copolymerization method allows for a more controlled and alternating copolymer structure. Spheres of Siloxane domains were observed from AFM phase images for all the copolymers in both series and a spherulitic crystal structure was only observed for random copolymers with low Siloxane content and small Siloxane segment length. Therefore, the research results provides valuable insights into the synthesis, characterization, and morphology of Ester-Siloxane multiblock copolymers, contributing to the understanding of copolymer design and the relationship between composition, molecular structure, and material properties.

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