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Synthesis, Characterization, and Extraction of Segmented Siloxane-Alphatic-Aromatic Copolymers: A Comprehensive Study

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ABSTRACT

A study was conducted to synthesize segmented copolymers consisting of Siloxane-Alphatic-Aromatic copolymer segments using a three-step polymerization reaction. The chemical composition of the copolymers was analyzed using Gradient Elution Chromatography GEC and Nuclear Magnetic Resonance NMR spectroscopy after Soxhlet extraction. The study also developed a solid phase extraction method to extract the Siloxane SI, Aliphatic ALE, and Aromatic ARE homopolymers from the copolymers simultaneously. Some samples of the copolymers exhibited complete solubility in chloroform due to their low content of Aliphatic-Aromatic copolymer ARE. The findings provide insights into the synthesis, characterization, and extraction of segmented copolymers.

تركيب و توصيف و استخلاص البوليمرات المتشابكة سيلوكسان-أليفاتية-عطرية: دراسة شاملة

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الكلمات المفتاحية:
استخلاص بوليمر
بوليمرات متشابكة
تفاعل بلمرة
بوليستر
كروماتوجرافيا تدرجية

الملخص

تم إجراء دراسة لتخليق البوليمرات المجزئة المكونة من شرائح كوبوليمر سيلوكسان-أليفاتيك-عطري Si-ALE-ARE باستخدام تفاعل بلمرة ثلاثي الخطوات. تم تحليل التركيب الكيميائي للبوليمرات باستخدام تقنيات كروماتوغرافيا الانتقال التدريجير GEC والرنين المغناطيسي النووي NMR بعد استخلاص العينات بواسطة جهاز سوكسليت. كما وضحت الدراسة طريقة الاستخلاص الصلبة لاستخلاص البوليمرات المتجانسة للسيلوكسان والأليفاتيك والعطري من البوليمرات المجزئة بشكل متزامن. أظهرت بعض عينات البوليمرات قابلية كاملة للذوبان في الكلوروفورم بسبب انخفاض محتواها من البوليمر الأليفاتيك-عطريARE. توفر النتائج نظرة عميقة حول تخليق البوليمرات المجزئة, وتوصيفها, واستخلاصها.

1. Introduction

Aliphatic-Aromatic copolymer ARE is a thermoplastic polyester that exhibits excellent mechanical properties, such as high stiffness and strength, as well as good chemical resistance and dimensional stability. It is highly resistant to hydrolysis and has low water absorption. ARE can withstand high temperatures of up to 150°C, making it suitable for applications in the automotive, electrical, and electronic industries. Its excellent properties make it an ideal material for manufacturing parts such as gears, bearings, and electrical components.

While Siloxane-Alphatic copolymer SI-ALE copolymers are known for their stiffness and toughness at high temperatures, ARE exhibits exceptional mechanical properties, chemical resistance, and dimensional stability. Despite their advantages, both polymers are prone to hydrolysis and can be affected by prolonged exposure to water. Therefore, their use requires careful consideration of the intended application and conditions of use. [1, 2]

Furthermore, incorporating a polyorganosiloxane segment such as Siloxane polymer SI into a wide variety of homopolymers to form block or segmented copolymers is possible due to the many organic-reactive end groups that can be placed onto the siloxane segment, including carboxyl, hydroxyl, amino, and epoxy, among others. However, the lack of compatibility between the polar segments, such as AER or ALE, and the non-polar SI segment can hinder the incorporation of SI into the polyester backbone. Moreover, the incompatibility of SI with the ALE or AER segment can cause the block copolymers to lose their mechanical properties when the SI content increases to a certain level. [3,4] To overcome these disadvantages, thermoplastic elastomers based on ABA-type triblock prepolymers, such as PEO-SI-PEO, PPO-SI-PPO, and polyether-polysiloxane-polyether copolymers with alkyl and polyether substituents, have been developed. [5, 6]

These polymers serve as the soft segments to improve the

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compatibility between the polar comonomers, such as DMT and BD, and the non-polar SI segments. The hydrophilic ether, PEO, and PBO can lead to relative miscibility of the SI with the aromatic polyester and due to the hydroxyl termination, covalent incorporation into the polyester backbone. [7, 8]

The incorporation of SI into homopolymers to form copolymers provides a unique opportunity to combine the properties of different polymers, such as the excellent heat resistance and cold resistance of SI with the stiffness and toughness of ALE or ARE. However, the compatibility between the polar and nonpolar segments needs to be carefully considered to prevent the loss of mechanical properties. The development of thermoplastic elastomers based on ABA-type triblock prepolymers has shown promise in improving the compatibility between the segments, leading to relatively miscible copolymers with improved mechanical properties. The synthesis of SI-ALE-ARE multiblock copolymers using transesterification in the melt state has also been demonstrated, with the developed extraction method providing a means to separate the complicated mixture of copolymers and homopolymers for further analysis. Overall, these findings provide insights into the synthesis and characterization of SI-ALE-ARE copolymers for potential applications in various industries. [9, 10].

2. Methodology and Experimental Work

The methodology used in this research involved the synthesis of segmented copolymers consisting of SI, ALE, and ARE segments using a polyesterification method in a three-step polymerization reaction. The chemical composition of the copolymers was analyzed using gradient elution chromatography (GEC) and nuclear magnetic resonance (NMR) spectroscopy after Soxhlet extraction. To extract the SI, ALE, and ARE homopolymers from the copolymers simultaneously, a solid phase extraction method was developed. This method involved a Soxhlet extraction in the first step followed by two steps of solution precipitation using different solvents. The extracted fractions and insoluble fractions were further characterized using GEC, intrinsic viscosity measurements, and NMR spectroscopy. The results provided insights into the synthesis and characterization of the segmented copolymers and the development of efficient extraction methods for their analysis**.**

2.1 Copolymer Synthesis and Extraction Process

A series of segmented SI-ALE-ARE copolymers was prepared using a polyesterification method, in a three-step polymerization reaction. In the first step, the amino end groups were converted to ester groups by reacting SI oligomers with excess DMCH. In the second step, BD and DMCH were added, and the reaction was allowed to proceed with slow nitrogen flow at 160 °C for three hours. In the third step, DMT was added in the required percentage, based on the amount of DMCH. The reaction was allowed to proceed further with a slow nitrogen flow at 180 °C for another two to three hours. At the end of the copolymerization, an aliquot of titanium catalyst was added before taking the reaction to a reduced pressure to reach high conversions. The final temperature reached was 240°C under high vacuum. The copolymerization reaction is illustrated in figure 1.

In order to investigate the effect of the ARE content on the copolymer's properties, four segmented copolymers of polydimethylsiloxane-copolyester were synthesized utilizing SI oligomers with similar molar masses (1000 g/mol). The SI content in the polymerization feed was kept constant at 10 wt %. The reaction was carried out in a reactor to which a distillation arm was connected. Methanol that evolved during the reaction and the excess butanediol at the end of the reaction were removed via the distillation arm.

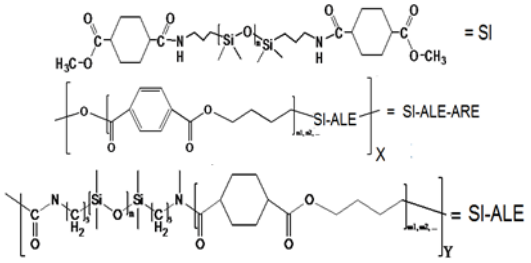

Figure 1: Chemical structures of the obtained mixture.

Due to the fact that ARE is not soluble in chloroform, Soxhlet extraction of the soluble copolymer was carried out. The yield of the copolymerization was determined gravimetrically and then by adding 80 wt % of chloroform solvent, a white mixture was obtained. More details on the extraction process are shown in Figure 1.

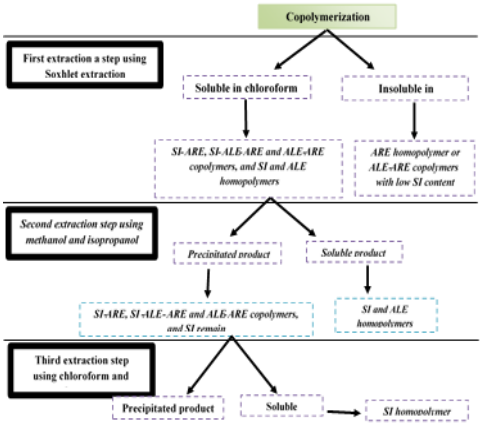

Figure 2: Schematic illustration of the extraction steps for purification of the SI-ALE-ARE copolymers.

The extraction continued for 24 h. The insoluble fractions were dried under vacuum for 24 h at 40 °C, and then the masses of the fractions were determined. The soluble fractions were further extracted in order to remove the SI and the ALE homopolymers (see Figure 2), further the soluble fractions were investigated by GEC after each extraction step.

2 .2 Characterization Techniques

2.2.1 Gradient Elution Chromatography (GEC)

This technique is widely used in the separation of multiphase polymers according to their chemical composition. It allows for separation of copolymer molecules from their respective homopolymers. This is achieved by varying the mobile phase solvent composition. [11, 12]

Here the GEC the copolymers fractionate based on the chemical composition using a mixture of chloroform and hexane with a flow rate of 1 mL/min. The technique was performed using a dual pump HPLC comprising of Waters 2690 separation module (Alliance), Agilent 1100 series variable wavelength detector, and PL-ELS 1000 detector. Data was recorded and processed using PSS WinGPC unity (Build 2019) software. The separation was achieved using a bare silica column (Nucleosil C18-5 µm (250 mm x 4.6 mm)), working at 30 °C. Samples were prepared at a concentration of 5 mg/mL, and the flow rate was 1 mL/min.

2.2.2 Intrinsic viscosity measurements

The intrinsic viscosities of the products of the copolymerization, as well as the soluble (chloroform) and insoluble fractions were determined using Ubbelohde viscometer in solvents ratio of 70 to 30 of trichloroethylene and phenol mixture. The measurement of efflux times is carried out at 25 °C, by visual observation of the passage of the liquid meniscus past two lines marked on the viscometer, at which times a stopwatch is started and stopped. An Ubbelohde viscometer, with a regular size of 10 ml, was calibrated at 25°C according to the general procedure given in ISO3104, ISO3105, BS188, IP Method 71, and ASTM Method D445. [13]

3.2.3 Nuclear Magnetic Resonance (NMR) spectroscopy

1H-NMR was performed as routine analysis for the determination of the molecular structures as well as ARE macromonomer incorporation efficiencies. Identification was achieved using a Varian VXR, 300 MHz spectrometer. When precise integration data was needed, the Varian Unity Inova, 400 MHz or 600 MHz spectrometer was used. Samples were prepared in NMR borosilicate tubes. 20-30 mg of sample was added to the sample tube and topped up with standard d-solvent to the 5 mm height mark. [14]

3. Results and Discussion

3. 1 Copolymer Extraction Process

Although it is reported in literature that SI-ARE multiblock copolymers with up to 60 wt % of ARE content are completely soluble in chloroform. [15, 16]

When polycaprolactone was used as a linkage between the SI and ARE segments similar to the ALE in our copolymer systems, the entire series

of our SI-ALE-ARE copolymers was only partially soluble in chloroform.

Various gradient profiles were tried; however, Figure 3 shows the best and final gradient profile that was used in this work in which the GEC analyses were done using hexane and chloroform as solvents.

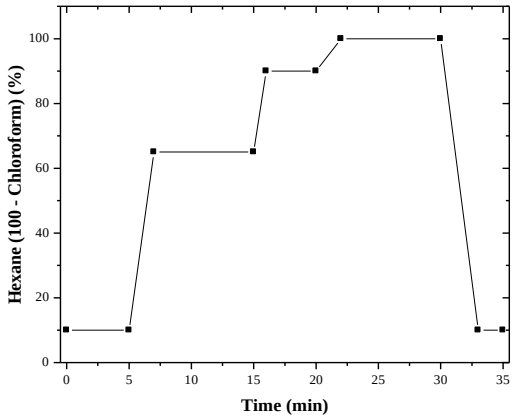

Figure 3: Gradient elution profile used in HPLC to fractionate SI-ALE-ARE copolymers (stationary phase: Nucleosil C18 - 5 µm, mobile phase: chloroform/hexane; ELSD detector, flow rate 1 mL/min).

Gradient elution profile used in HPLC was started at 10:90 of (chloroform/hexane, (v/v)), held constant for 5 min, then changed linearly within 2 min to 65:35 (chloroform/hexane, (v/v)), and held constant for 8 min and then changed linearly within 1 min to 90:10(chloroform/hexane, (v/v)), and held constant for 4 min and then changed linearly within 2 min to 100:0 (chloroform/hexane, (v/v)) and held constant for 8 min and then changed linearly within 3 min to 10:90 (chloroform/hexane, (v/v)) and held constant for 3 min.

Figure 4 shows a typical example of the results obtained from GEC for the soluble fraction of the S-3 sample. The SI-ALE-ARE fraction is at about 13.5 min retention time. The other side products (such as SI, ALE homopolymers, SI-ALE, and SI-ARE copolymers) can also be seen at different retention times as shown in (Figure 4 a, b, c). Even after three extraction steps, the SI homopolymer and SI-ARE copolymer remained in the SI-ALE-ARE copolymers. What was really surprising is the small peak that showed at 25 min elution time, which was attributed to the formation of a co-polyester of ALE-ARE as another side product.

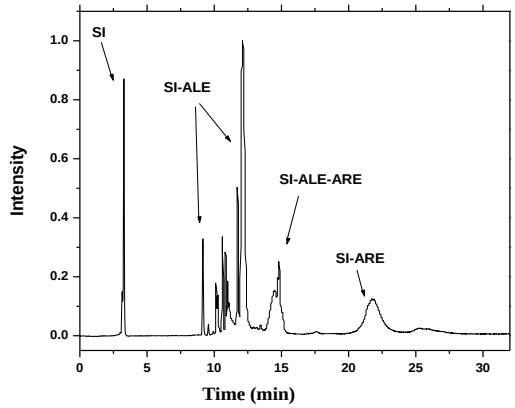

Figure 4a: Typical example of GEC results of the soluble fraction obtained from the first step of extraction.

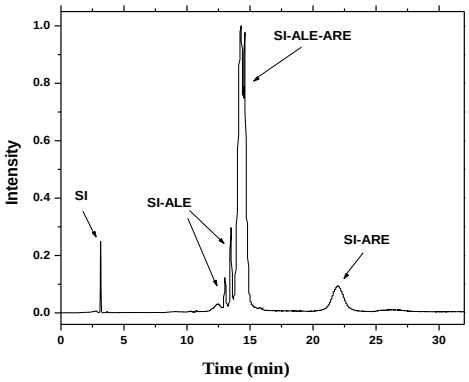

Figure 4b: Typical example of GEC results of the soluble fraction obtained from second step of extraction.

a.

Figure 4c: Typical example of GEC results of the soluble fraction obtained from the third step of extraction.

The Ubbelohde viscometer was used for measurement of dilute solution viscosity of SI in order to determine the intrinsic viscosity [η] of the SI-ALE-ARE copolymers. The kinematic viscosity η (mm2/s) of a liquid may be calculated from a mean measured flow time t (s) using the formula:

$h = Ct$ *(1)*

Where C is a constant = 0.004855 (mm2/s)/s.The obtained results are tabulated in Table 1

The Mark and Houwink constants of the SI-copolyester copolymers are not reported in literature, and thus the molar masses for these new copolymers were not obtained. However, from the viscosity values, one can predict which copolymer might have the higher molar mass (S-3), and which the lowest one (S-2).

Table 1: The intrinsic viscosity [η] of SI-ALE-ARE copolymers (series S)

Sample	Copolymerization product [η]	Soluble fraction [η]	Insoluble fraction [η]
S-1	0.27	0.26	0.29
S-2	0.22	0.22	0.24
S-3	0.25	0.23	0.28

3. 2 Structure and composition of the SI-ALE-ARE copolymers

The structure and composition of the SI-ALE-ARE copolymers were determined by 1H-NMR spectroscopy. A typical 1H-NMR spectrum of an SI-ALE-ARE copolymer (sample S-3) is shown in Figure 4. All the chemical shifts in the spectrum were assigned to the chemical structure of the copolymer according to the Cambridge Soft Chem. Office 2006 using the NMR-prediction software program.

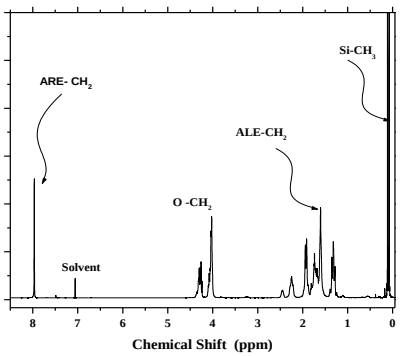

Figure 5: Typical ^{1}H-NMR spectrum of SI-ALE-ARE copolymers

The ALE and ARE molar fractions, with respect to 1 mol of SI segment, which has a degree of polymerization of 13 units, were calculated from 1H-NMR spectra using the integration of the chemical shifts at δ = 4.3 ppm (I(OCH2)ARE), δ = 4.1 ppm (I(OCH2)ALE) and δ = 0.07 ppm (I(CH3)SI), and then applying the following equations:

$$X_{ALE}=\{I(OCH_2)_{ALE}/4\}/\{[I(OCH_2)_{ALE}+I(OCH_2)_{ARE}]/4+I(CH_3)_{IS}/(6*13)\} \quad (2)$$

$$X_{ARE} = \{I(OCH_2)_{ARE}/4\}/\{[I(OCH_2)_{ALE} + I(OCH_2)_{ARE}]/4 + I(CH_3)_{SI}/(6*13)\} \quad (3)$$

$$X_{SI} = 1 - X_{ARE} - X_{ALE} \quad (4)$$

Where X_{ALE} is the molar fraction of the ALE segment, X_{ARE} is the molar fraction of the ARE segment, and X_{SI} is the molar fraction of the SI segment. The molar fractions here were obtained based on one mole of SI oligomer with a molar mass of 1000 g/mol. The corresponding mass percentages are given by:

$$ALE\ wt\ \% = [X_{ALE} M_{rALE} / (X_{ALE} M_{rALE} + X_{ARE} M_{rARE} + X_{SI} M_{rSI})] * 100 \quad (5)$$

$$ARE\ wt\ \% = [X_{ARE} M_{rARE} / (X_{ALE} M_{rALE} + X_{ALE} M_{rALE} + X_{SI} M_{rSI})] * 100 \quad (6)$$

$$SI\ wt\ \% = 100 - ARE\% - ALE\% \quad (7)$$

Where ALE wt % is the mass percent of the ALE segments and Mr ALE is the molar mass of the base unit of the ALE segment (186 g/mol).

ARE wt % is the mass percent of the ARE, and Mr ARE is the molar mass of the base unit of the ARE segment (192 g/mol). The SI wt % is the mass percent of the soft SI segment, and Mr SI is the molar mass of the SI segment (1000 g/mol). Table 2 shows a summary of the results obtained.

Table 2: Chemical compositions of SI-ALE-ARE copolymer series

Sample	Polymerization feed			Actual copolymers composition determined from ^{1}H-NMR spectra		
	SI wt %	ALE wt %	ARE wt %	SI wt %	ALE wt %	ARE wt %
S-1	10	10	80	8.9	78.8	12.3
S-2	10	20	70	9.2	68.6	22.2
S-3	10	30	60	9.1	56.4	34.5

The values of the mass ratios of the ALE, ARE, and SI segments determined from the 1H-NMR spectra agree with the values of feed compositions of the reaction mixture in the copolymerization reactions. The incorporation of the ARE segment into the copolymer chains was proven by Soxhlet extraction using chloroform. It is well known that they ARE homopolymer is insoluble, while the SI-ALE copolymers are soluble in chloroform. The results obtained after the Soxhlet extraction showed that all the samples comprised both a soluble and an insoluble fraction. The chemical compositions of the soluble and insoluble fractions were investigated by 1H-NMR spectroscopy. The spectra of both fractions contained signals of Si–CH3 protons from the SI segments and signals of aromatic rings from the ARE segments, in addition to the ALE signal at δ 4.1 ppm. The chemical compositions of all fractions were determined using the equations Eq 2 – Eq 7. The results are tabulated in Table 3. The extracted and insoluble fractions differ in their compositions and contain considerably different amounts of SI, ALE, and ARE segments. However, it can be concluded that both the extracted and insoluble fractions have a segmented (multiblock) structure.

Table 3: ^{1}H-NMR analysis of chloroform soluble and insoluble fractions of the SI-ALE-ARE copolymer series

Sample	Soluble fraction in chloroform			Insoluble fraction in chloroform		
	SI wt %	ALE wt %	ARE wt %	SI wt %	ALE wt %	ARE wt %
S-1	12.3	84.3	3.4	7.2	41.2	51.6
S-2	12.5	74.5	13.0	5.8	32.2	52.2
S-3	13.6	74.0	12.4	4.5	34.1	61.4

The insoluble fractions of the copolymer contained 51.6 – 61.4 wt % ARE segments while the soluble fractions contained only 3.0 – 12.4 wt %. The soluble fractions of the SI-ALE-ARE copolymer with 12.4 wt % content ARE will be in near future further investigated in electro-spinning to form nano-fibers.

4. Conclusion

In conclusion, this study successfully synthesized a series of segmented copolymers consisting of SI, ALE, and ARE segments using a polyesterification method in a three-step polymerization reaction. The chemical composition of the copolymers was analyzed using GEC and NMR spectroscopy after Soxhlet extraction, and a solid phase extraction method was developed to extract the SI, ALE, and ARE homopolymers from the copolymers simultaneously. Some samples of the SI-ALE-ARE copolymers were found to be completely soluble in Chloroform, which was attributed to the low content of ARE in these samples. These results provide valuable insights into the synthesis and characterization of segmented copolymers and the development of efficient extraction methods for their analysis, which could have potential applications in various fields including electro-spinning to form Nano-fibers.

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