

Polyethersulfone/Polyetherethersulfone Copolymers with the Same Chemical Composition and Different Melt-Viscosity

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ABSTRACT: Random, block, and alternative polyethersulfone/polyetherethersulfone copolymers (phenyl: ether: sulfone = 7 : 4 : 3) with similar molecular weights and polydispersity were synthesized using different synthetic strategies. DSC and DMA analyses indicated that all copolymers are amorphous and possess extremely close glass transition temperature. The random copolymer displayed higher modulus and complex viscosity. It is interesting to find that the alternative copolymer exhibited a melt viscosity of 281 Pa s, which is much lower than that of the block copolymer (646 Pa s) and the random copolymer (1641 Pa s) at 4 s⁻¹. Moreover, the alternative copolymer showed obviously higher elongation at break of 101.9%. These behaviors were highly related to their different sequence distribution. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40149.

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INTRODUCTION

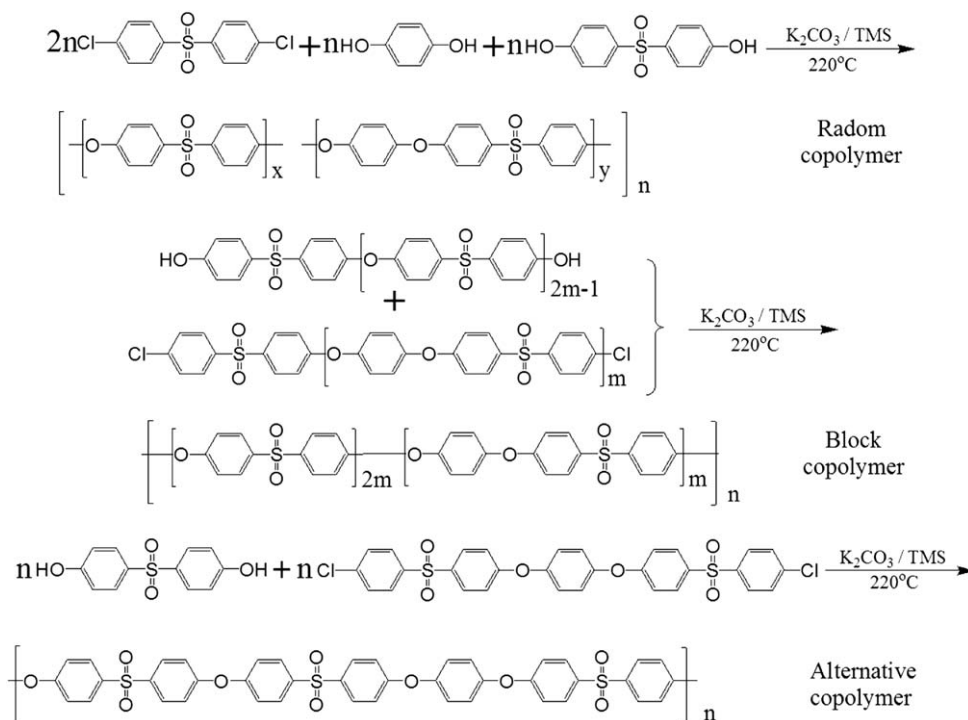
Polyethersulfone (PES) has attracted more and more attention as a fascinating engineering material because of its great potential for a variety of applications, which is attributed to its excellent mechanical properties and superior environmental resistance, as well as outstanding thermal and thermo-oxidative stability. Although these merits make PES attractive as a high performance engineering thermoplastic, its correspondingly high glass transition temperature always resulted in a very high processing temperature. Meanwhile, other high performance engineering thermoplastics are also facing the similar troubles. Different kinds of PES polymers have been prepared successfully¹⁻⁹; however, there is no good method to improve their melt processability without adverse influence on mechanical properties and thermal stability.

A systematic study has been carried out in our group on the thermal behaviors of aromatic thermoplastic polymers containing ether, ketone, and sulfone linkages.¹⁰⁻¹⁴ These polymers have been reported in literature, and a wide spectrum of characteristics may be obtained by opportunely balancing the ratio between the ether and other linkages.^{15,16} For instance, though showing a similar thermal property with typical PES, PES/PEES (polyethersulfone/polyetherethersulfone) copolymers have a higher flexibility of molecular chains due to the presence of a larger number of ether linkages in the PEES units.¹⁷ Most

researches have been concentrated on the basic thermal and mechanical properties of PES/PEES copolymers, but only rare, brief report have been focused on the effect of sequence distribution on their final properties.

To the best of our knowledge, the high performance engineering thermoplastics are developing toward higher thermal and mechanical performance.¹⁸⁻²¹ Hence, the contradiction between thermal stability and high melt viscosity at high processing temperature has become the bottleneck of the development of high performance thermoplastics.²²⁻²⁴ Actually, one of the most efficient approaches to decrease the melt viscosities of polymers is to decrease their molecular weights, which is widely used by many commercial polymer products such as polyaryletherketones and thermoplastic polyimide.²⁵⁻³⁰ For example, two brands of commercial polyetherketone plastics launched by Victrex plc, including VICTREX HT P45 and P22, have different melt-viscosity, which are caused by their different molecular weights.

In this article, a new strategy is presented to decrease the melt viscosity and enhance the mechanical properties via changing sequence distribution. The results of the present study may greatly contribute to the development of some high-performance polymers with low-viscosity and improved processability. This effort will provide a new insight into the molecular design of engineering thermoplastics.



Scheme 1. Synthetic routes of the block, random, and alternative PES/PEES copolymers.

EXPERIMENT

Materials

Hydroquinone (HQ, Liaoning Pharmaceutical & Commercial Co.) and 4,4'-dihydroxydiphenylsulfone (DHDPS, Taizhou Jinhai Pharmaceutical & Chemistry Co., Ltd.) were obtained from commercial sources and used as received. 4,4-Dichlorodiphenylsulfone (DCDPS, Changzhou Yangguang Chemical Co., Ltd.) was recrystallized twice from toluene. Tetramethylene sulfone (TMS, Dalian Jinzhou Chemical) was distilled under vacuum and stored under nitrogen until use. Potassium carbonate (K_2CO_3) was dried at $120^\circ C$ for 24 h before used for polymerization.

Synthesis of PES/PEES Random Copolymers

The typical syntheses procedures were as follows: to a suspension of DCDPS (114.86 g, 0.4 mol) and K_2CO_3 (57.96 g, 0.42 mol) in TMS (686 mL) in a 1000-ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet with a thermometer, and a Dean–Stark trap with a condenser, were added HQ (22.02 g, 0.2 mol), DHDPS (50.05 g, 0.2 mol). Then toluene (150 mL) was added slowly to the solution. After refluxing for 2 h, toluene was removed. Under stirring and the protection of nitrogen, the mixture was heated at $180^\circ C$ for 30 min and $200^\circ C$ for 1 h, then at $220^\circ C$ for 3 h. After that, the reaction mixture was cooled to room temperature and poured into a large excess of cold water. The precipitated copolymers were washed several times with water and alcohol, and successively dried under vacuum at $80^\circ C$ overnight.

Synthesis of PES/PEES Alternating Copolymers

PES/PEES alternating copolymers were synthesized by the two-step reaction methods. Firstly, as shown in Scheme 1, the trim-

mer oligomer has been prepared by HQ and excessive DCDPS. Typical procedures are as follows: to a 3000 mL three-necked flask with the same equipment as above, were added HQ (55.0 g, 0.5 mol), DCDPS (717.5 g, 2.5 mol), anhydrous K_2CO_3 (138.0 g, 1 mol), DMAc (1800 mL), and toluene (200 mL). The system was allowed to reflux for 6 h. After the removal of toluene, the reaction mixture was heated to $155^\circ C$. Four hours later, the mixture was cooled and filtered to remove salts. The filtrate was poured into water. After removing excess DCDPS by alcohol, pure trimmer oligomer (54 g) was recrystallized from DMF. Secondly, the synthetic procedure was same with that of random copolymers, according to the feed ratios as follows: DCDPS (12.5135 g, 0.05 mol), previous synthetic trimmer oligomer (30.5755 g, 0.05 mol), and anhydrous K_2CO_3 (7.245 g, 0.0525 mol).

Synthesis of PES/PEES Block Copolymers

Block copolymers were prepared by the two-step reaction methods as described previously.¹⁷ Two kinds of oligomers had shown the same degree of polymerization (n) value to synthesize block copolymer sample with the same mole composition (50 : 50).

Characterization

The glass transition temperatures (T_g) were determined by using a METTLER differential scanning calorimetry (DSC) 821e instrument at a heating rate of $20^\circ C/min$ under a nitrogen flow of 200 mL/min. The thermo-gravimetric analysis (TGA) was performed on a Perkin–Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of $10^\circ C/min$. Viscosity measurements of melts were performed on a Physica MCR300 dynamic rheometer at $320^\circ C$ in nitrogen. Gel

Table I. Inherent Viscosity, GPC Results, and Thermal Properties of Copolymers

Sample	η^a (dL/g)	M_n^b ($\times 10^4$)	M_w ($\times 10^4$)	PD ^c	T_g (°C)		$T_{d-5\%}$ (°C) ^d
					DMA	DSC	TGA
Random	0.41	3.79	5.27	1.39	221.4	215.3	599.3
Alternative	0.39	3.98	5.13	1.29	219.8	215.8	583.1
Block	0.39	3.02	5.36	1.33	221.7	215.6	581.7

^aInherent viscosity were measured at a concentration of 0.5 g/dL in DMAc at $25 \pm 0.1^\circ\text{C}$.

^bMolecular weight of the copolymers were calculated with the aid of polystyrene standards.

^cPolymer dispersity: M_w/M_n .

^d5% weight loss temperature in air.

permeation chromatography (GPC) using polystyrene as a standard was carried out using a Waters 410 instrument with Tetrahydrofuran as an eluent.

RESULTS AND DISCUSSION

Copolymer Synthesis

As shown in Scheme 1, random PES/PEES copolymer was synthesized by the nucleophilic polycondensation of DCDPS, DHDPS, and HQ. The alternative copolymer was prepared in two steps. Firstly, the trimmer oligomer was synthesized by the nucleophilic substitution reaction of HQ and large excess DCDPS. Then the polymerization reaction was carried out under the same condition with the random copolymer. The block copolymer was synthesized by a two-step reaction method. Both the two kinds of oligomers have shown the same repeat number of 8, which was controlled by monomer ration. The molecular weight of block copolymers is about 30,200 and the number of block repeat unit EES-block-ES is 1005. Therefore, the block repeat number in a polymer molecule is about 30 according to the molecular weight. Herein, the copolymer molecular weight was calculated in light of polystyrene standards, thus the number 30 is not the absolute accurate value. To avoid the possible influence of synthesis processes on the melt viscosity, all polymerization reactions were performed under same condition.

Regularly, the rheological properties of polymers are related to their molecular weights, glass transition temperatures, and aggregation morphologies. Furthermore, it was determined by the sequence distribution of soft-segment (i.e., PEES) and hard-segment (i.e., PES). In order to investigate the effect of sequence distribution on rheological property without other influences, both synthetic procedure and feed ration were accurately performed. All the obtained copolymers have the same chemical composition (phenyl : ether : sulfone = 7 : 4 : 3) base on polymerizable monomers (HQ, DHDPS and DCDPS) and feed ratios (1 : 1 : 2). Generally, the melt viscosity of the copolymers will increase dramatically with the increasing molecular weight. In order to decrease the influence of molecular weight on the rheological properties of the copolymers, the copolymers possessing similar molecular weight and molecular weight distribution were selected as research objects (Table I). However, it is difficult to control the molecular weight of copolymers. Thus, copolymers were prepared many times repeatedly under the same condition. After analysis by GPC, those which have a similar molecular weight were selected.

Thermal and Mechanical Properties of the Copolymers

Dynamical mechanical analysis, which provides information on glass transition and the damping property of the copolymer, is shown in Figure 1. It can be seen that all the samples exhibited one sharp loss peak corresponding to the glass transition temperature. Both block copolymer and random copolymer show similar T_g value (221.4 and 221.7°C), while the loss peak of alternative copolymer shifted toward lower temperature (T_g value 219.8°C). However, the glass transition temperature of all copolymers are extremely close, which is benefit of further decreasing impact of T_g on their melt viscosity. Random copolymer exhibits obviously higher modulus than that of the block and alternative copolymers at the temperatures less than its T_g . Figure 1 clearly indicates the beta relaxation of the three copolymers at about 80°C , and the relaxation strength of this relaxation is largest for the alternative copolymer, which would have resulted in the mechanical toughness of the alternative copolymer seen in Figure 2.³¹ There is no apparent effect of temperature on moduli of all copolymers at temperature above 230°C , which indicates that the moduli do not depend on sequence distribution under a certain temperature.

The thermal properties of the copolymers were also evaluated by DSC and TGA. The DSC curves indicate that these copolymers are amorphous, and the T_g values of the random, block, and alternative copolymers are 215.3°C , 215.8°C , and 215.6°C , respectively. These data are quite close to the results of dynamic mechanical analysis (DMA) test. Exactly, it can be considered that the sequence distribution hardly have any influence

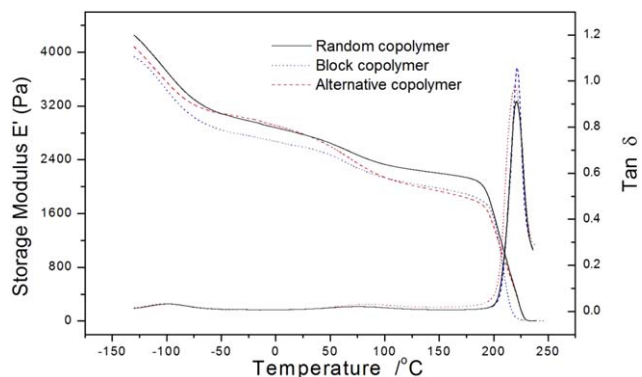


Figure 1. Storage moduli of various PES/PEES membranes as function of temperature from DMA experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

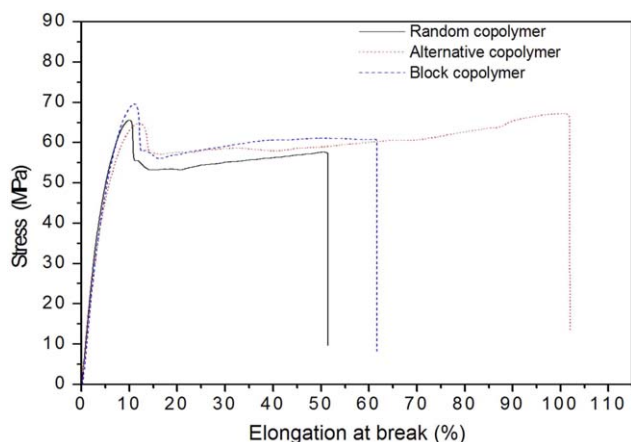


Figure 2. Typical nominal stress–strain curves for PES/PEES copolymers at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the glass transition temperatures of the copolymers. Meanwhile, the copolymers exhibit good thermal stability. As summarized in Table I, the temperatures at 5% weight loss are above 580°C, which means the copolymers have good thermal stability.

Figure 2 represents typical nominal stress–strain test curves of PES/PEES copolymer membranes. The average mechanical parameters for different copolymers obtained by stress–strain measurements are listed in Table II. Despite their similar molecular weights and same structure, the copolymers exhibit different tensile results. Firstly, all three copolymers have close tensile strength (σ), which is in the range of 64.5–69.5 MPa. Secondly, alternative copolymer shows minimal Young's modulus (E) and maximal elongation at break (ε). This result suggests that its molecular chain has the best flexibility, which may be associated with its regular sequence distributions of soft-segments and hard-segments. In other words, the molecular chains of PES/PEES copolymers can possess maximal flexibility when hard-segments uniformly disperse in the main chains.

Rheological Properties of the Copolymers

Generally, high molecular weight aromatic polymers suffer from poor processability, which limits their wide applications. Therefore, it is always attractive to prepare high-performance aromatic polymers with low melt viscosity, which is greatly helpful to improve processability. Complex viscosity (η) was measured with dynamic oscillatory tests conducted under isothermal heating conditions at 320°C (Figure 3). The complex viscosity performed as a function of shear rate. With further increasing of

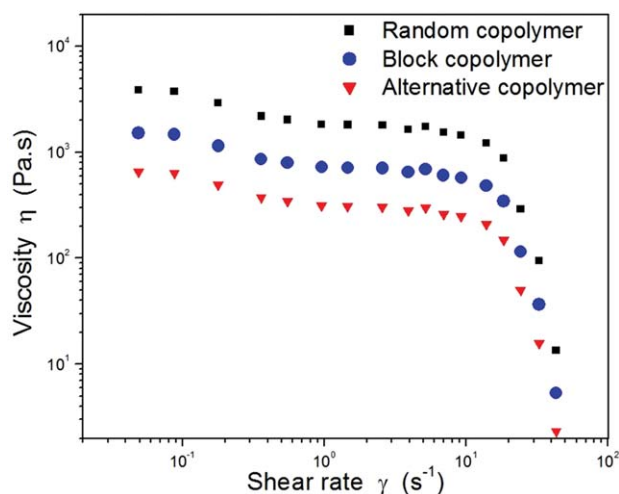
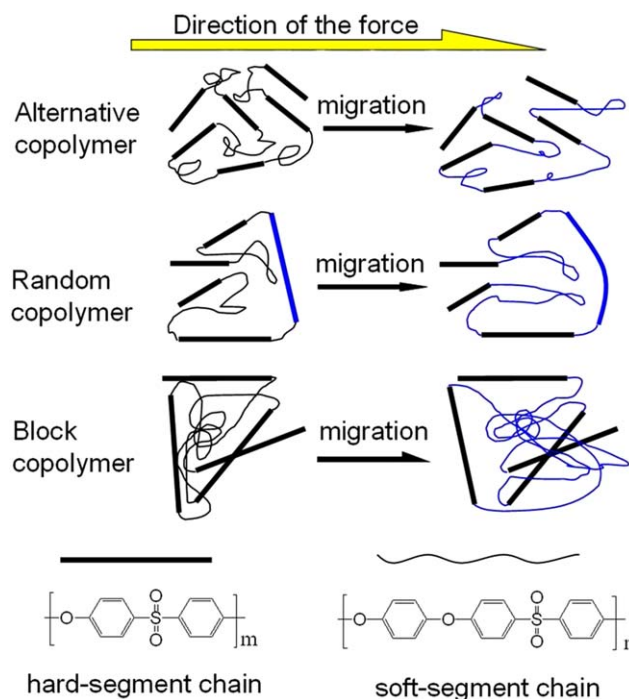


Figure 3. Dynamic frequency sweep tests of random, block, and alternative copolymer melts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the shear rate, the complex viscosity decreases, and the melt gives rise to a shear thinning behavior. In order to compare the complex viscosity (η) of different copolymers, the values obtained at 4 s⁻¹ was selected (Table II).

It is interesting to find that alternative copolymer exhibited the minimal melt viscosity of 281 Pa s, which was much lower than that of block copolymer (646 Pa s) and random copolymer (1641 Pa s) at 4 s⁻¹. As we all know, the polymer melt flow behavior is not the movement of a whole molecular chain, but the migration of a part of segments in molecular chain to



Scheme 2. Schematic representation of flow behavior evolution of the alternative, random and block PES/PEES copolymer melts. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Tensile Behaviors and Complex Viscosity of PES/PEES Copolymers

Copolymer	σ (MPa)	ε (%)	E (MPa)	η^a (Pa s)
Random	65.5	51.4	1362.4	1641
Alternative	64.5	101.9	1018.9	281
Block	69.5	61.7	1242.7	646

^aMelt viscosity were measured at a frequency of 4.0 s⁻¹ and 320°C.

surrounding hole along the direction of action of the force.³² Thus, the fluid flow behavior is performed by migration of the soft-segment portion firstly. In this study, the flow behavior evolution of the alternative, random, and block PES/PEES polymer melts is schematically illustrated in Scheme 2. The molecular chains of these copolymers are divided into soft-segments (-ether-phenyl-ether-phenyl-sulfone-phenyl-) and hard-segments (-ether-phenyl-sulfone-phenyl-). In the alternative copolymer, the soft-segments of alternative copolymer equidistantly dispersed in the main chains and their length is equal. This reasonable segment distribution of the alternative copolymer will lead to its lowest melt viscosity of copolymers despite the same chemical composition with other two polymers. It is also suggested that the connection types of soft-segment portion and hard-segment portion may be benefit to uniform distribution of surrounding hole in copolymers. Regularly, the soft-segment chain length can increase the capacity of the movement of the segments in molecular chain; on the other hand it also enhanced the entanglement of the molecular chains. Length and distribution of soft-segment chain of random copolymers are heterogeneous. Thus hard-segment chains may partially participate in the migration of molecular chain and lead to its highest melt-viscosity.

In term of the results and discussion above, molecular structure design and synthesis of high performance engineering thermoplastics should be considered in both the length and the distribution of the soft-segments in the molecular chains.

CONCLUSION

Random, block, and alternative copolymers of PES/PEES with the same chemical compositions (phenyl : ether : sulfone = 7 : 4 : 3) were successfully synthesized in order to investigate the effect of sequence distribution on their thermal, mechanical, and rheological property. The obtained copolymers possessed extremely close glass transition temperature, similar molecular weight and distribution. The results indicated that alternative copolymers exhibited an obviously higher elongation at break (101.9%) and least melt viscosity (281 Pa s), which was far below that of the block copolymers (646 Pa s) and the random copolymer (1641 Pa s). It is concluded that sequence distribution has great effect on complex viscosity.

ACKNOWLEDGMENTS

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