

STUDY ON POLYSULFONE-POLYESTER BLOCK COPOLYMERS

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Abstract

Synthesis and characterization of a series of Polysulfone (PSF)-Polyester (PEs) block copolymers were studied.

The degree of randomness (B) of these block copolymers was calculated from the intensities of their proton signals in ^1H NMR spectra and lies in the region of $0 < B < 1$. It was shown that the degree of randomness (B) and the average sequence length (L) in block copolymers were relatively dependent on the reaction conditions, various feed ratios and structure of diols.

The phenomenon was observed, when the PSF-PEs block copolymers dissolved in different solvents they had different viscosities and molecular conformations.

The PSF-PEs block copolymers had better solvent resistance than homo-polysulfone.

INTRODUCTION

A great number of block copolymers have been prepared and characterized^[1].

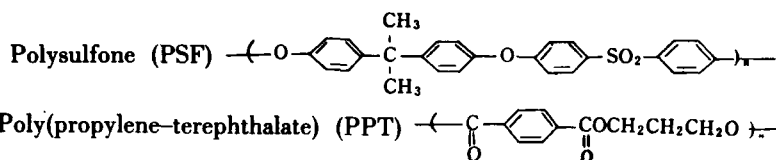
The polyarylethersulfone, commonly known as "Polysulfone" attributes its current states to its outstanding oxidative, thermal, hydrolytic and dimensional stability and very good mechanical properties^[2]. The combination of these properties and its high T_g enables these polymers to be utilized over a broad range of temperature under required service conditions. However, poor solvent resistance and environmental stress cracking of polysulfone are noted and have been attributed to its amorphous rigid thermoplastic nature^[3]. We believe that the incorporation of a second crystalline component would greatly improve the material performance.

Since polyesters such as poly(ethylene-terephthalate), poly(butylene-terephthalate) etc. have been reported to be crystalline polymers^[4], we have synthesized a series of block copolymers of PSF-PEs e.g., PSF-PPT, PSF-PBT, PSF-PDET etc.

The PSF-PEs block copolymers were characterized by solubility, viscosity, IR and ^1H NMR spectra. The copolymers have better solvent resistance than PSF homopolymer.

EXPERIMENTAL

The polysulfone, polyesters and polysulfone-polyesters used in the experiments were as follows:



was dissolved, 0.63g(3.1mmol) terephthaloyl chloride was added. The reaction temperature raised rapidly to 217°C which maintained for 1.5h.

When the evolution of gaseous HCl ceased, the stoichiometric amount of dried diols was added (e.g., 0.11g(1.2mmol) 1,4-butanediol) and reaction temperature was kept at 217°C for 1h. Then 3ml triethylamine was added and the solution became viscous. After two hours at this temperature, by cooling the reaction solution to room temperature, the product was coagulated in methanol solution. The filtered product was washed twice with methanol and then washed four times with distilled water and then dried. The block copolymer PSF-PBT with a reduced viscosity 0.32 in CHCl_3 at 30°C was obtained.

Polymer characterization^[7]

The reduced viscosities of block copolymers were measured in CHCl_3 and *o*-chlorophenol respectively, at 30°C.

The ^1H NMR data were obtained on a Varian FT-800A spectrometer.

RESULTS AND DISCUSSION

Polysulfone-polyester block copolymers containing segments of PSF and PEs(e.g., PPT,PBT,PHT,PDET,PTET) were synthesized by interaction of dihydroxy-alcohols (e.g., propanediol, butanediol, hexandiol, diethylene-glycol, triethylene-glycol) with terephthaloyl chloride in the presence of terephthaloyl end-capped polysulfone oligomer, see Table 1.

Table 1 Preparation of PSF-PEs block copolymers

Copolymer	Mole fraction of reactants			Reduced viscosity	
	PSF	Acid chloride	Diol	for PSF	for PSF-PEs
PSF-PPT	0.5	6.6	6.0	0.20	0.49
PSF-PBT	0.5	6.6	6.0	0.20	0.33
PSF-PHT	0.5	6.6	6.0	0.20	0.34
PSF-PDET	0.5	6.6	6.0	0.20	0.33
PSF-PTET	0.5	6.6	6.0	0.20	0.36

Characterization of PSF-PEs block copolymers

As seen in Table 1, the first indication of the presence of block copolycondensate is an increase of the reduced viscosity of the solution from 0.20 to 0.49 for PSF-PPT after a two-stage reaction. However, the crude product of reaction often contains a mixture of polymeric species, so it is preferable to eliminate homopolysulfone before studying their physical properties.

The second indication of the presence of block copolymer is its IR spectra. The vibration spectrum of a block copolymer generally corresponds to the superposition of the homopolymers; thus the technique of IR absorption spectroscopy can give interesting results only in special cases, ie., when two different kinds of units have sufficiently distinctive bands, such as PSF-PEs block copolymers.

An aromatic hydroxyl absorption at 3450cm^{-1} has been found in IR spectra of the polysulfone oligomer; a carbonyl absorption at 1730cm^{-1} , 1040cm^{-1} in IR spectra of the PSF-PEs block copolymers and no absorption in the region of the hydroxyl group. However, IR spectra can merely indicate the existence of a copolymer, but not the presence of blocks.

Hence, the third indication of the presence of block copolymers is the ^1H NMR spectra. It is successfully used for the characterization of PSF-PEs block copolymers. The ^1H NMR spectra of the polysulfone and polysulfone polyesters block copolymers are shown in Figures 1—3 and the assignments of the proton signals are listed in Table 2.

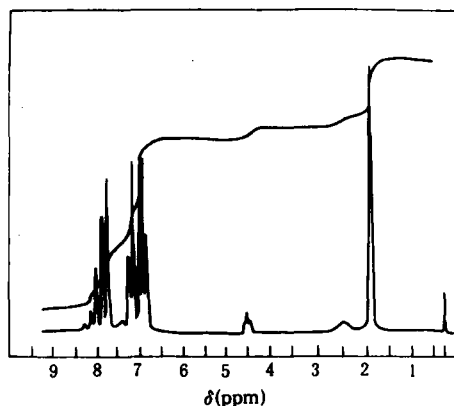


Fig. 1 ^1H NMR spectra of PSF-PPT

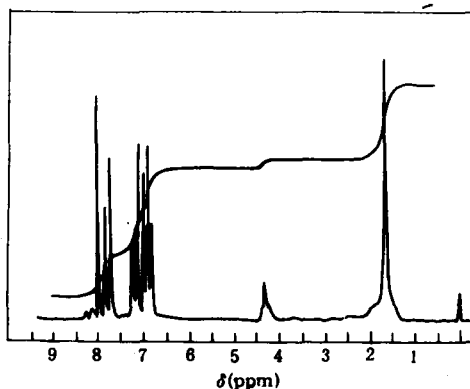


Fig. 2 ^1H NMR spectra of PSF-PHT

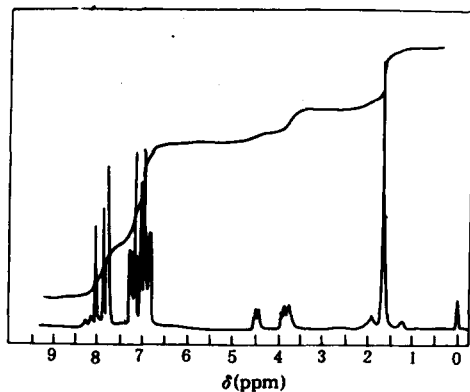


Fig. 3 ^1H NMR spectra of PSF-PTET

Table 2 Assignments of proton signals and their chemical shifts in the ^1H NMR spectra of polysulfone and its copolymers (ppm)

Type Proton
Labelled

$$\begin{array}{c}
 \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(\text{CH}_3)_2 \text{---} , \text{---PSF---O---C(=O)---C}_6\text{H}_4\text{---C(=O)---O---PSF---} , \text{---CH}_2\text{CH}_2\text{CH}_2\text{---} , \\
 \text{---O---CH}_2\text{CH}_2\text{---OCH}_2\text{CH}_2\text{---O---} ; \text{---PSF---O---C(=O)---C}_6\text{H}_4\text{---C(=O)---O---R---} , \\
 \text{---CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{---} , \text{---CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{---} ; \\
 \text{---} \text{C}_6\text{H}_4 \text{---SO}_2\text{---} , \text{---R---O---C(=O)---C}_6\text{H}_4\text{---C(=O)---O---R---} , \\
 \text{---O---CH}_2\text{CH}_2\text{---OCH}_2\text{CH}_2\text{---OCH}_2\text{CH}_2\text{---O---} ,
 \end{array}$$

Structure of
copolymers

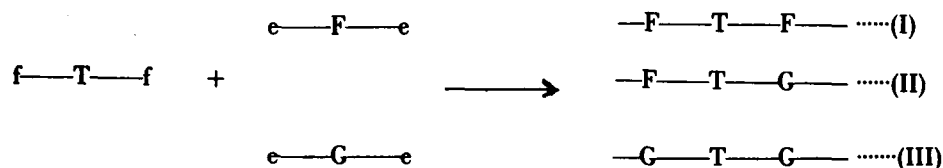
	a	b	c	d	e	f	g	h	i	j	k	k	l
	H	H	H	H	H	H	H	H	H	H	H	H	H
PSF	1.69	7.25	6.92	6.99	7.85								
PSF-PPT	1.69	7.25	6.92	6.99	7.85	8.28	8.17	8.06		4.52	1.94		
PSF-PBT	1.68	7.25	6.92	6.99	7.84	8.28	8.17	8.08		4.38	1.95		
PSF-PHT	1.69	7.25	6.93	7.00	7.85	8.28	8.13	0.08		4.34	1.96		1.70
PSF-PDET	1.69	7.25	6.93	7.00	7.85	8.30	8.15	8.02		4.50		3.88	
PSF-PTET	1.69	7.25	6.93	7.00	7.85	8.28	8.17	8.08		4.47		3.70—3.90	

The chemical shifts of protons of polysulfone residue in these PSF-PEs block copolymers have the same values, correspondingly the phenylene protons of the terephthalic acid residue in PSF-PEs are also found to have the same chemical shifts, lying in the region of 8.30 to 8.02ppm, independent of the structure of the surrounding diols, except for PSF-PDET.

In the ^1H NMR spectra of the resulting copolymers there are three signals in the region of 8.30 to 8.02ppm. This fact may be attributed to the electronegativities of these diols and PSF, when the terephthalic acid is located between the diols, the chemical shifts of phenylene protons are displaced to the region of the stronger field and equal to 8.02ppm for PSF-PDET; when the terephthalic acid is located between the dihydroxyl-terminated PSF, the chemical shifts of phenylene protons are displaced to the region of the weaker field and equal to 8.30ppm; when the terephthalic acid is located between the dihydroxyl-terminated PSF and diols, the chemical shifts of phenylene proton are displaced to 8.19ppm; because the electronegativities of these diols are larger than that of dihydroxyl-terminated PSF.

Determination of the composition and sequential structure of copolymer^[8]

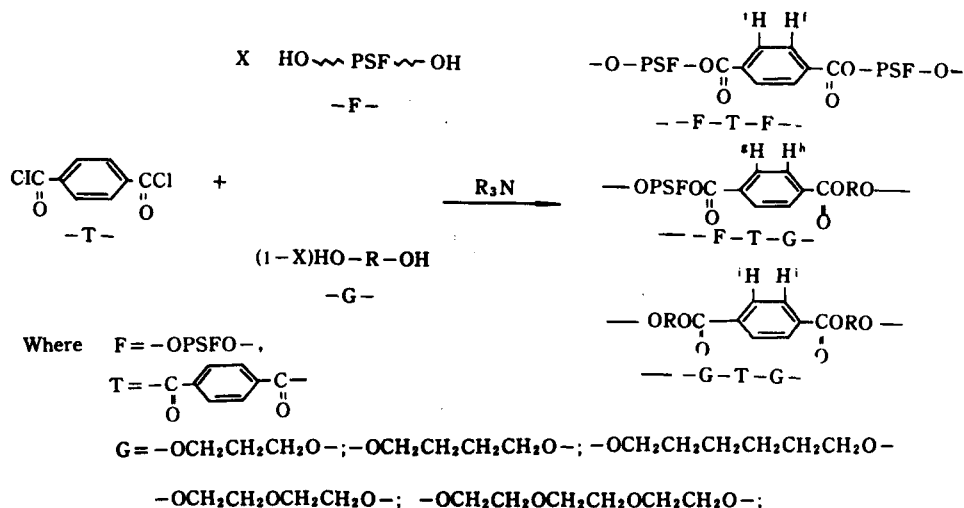
On copolycondensation of an intermonomer with two comonomers three types of triads can be formed: two homogeneous (I and III) and one heterogeneous (II)



the quantitative ratio of triads I—III characterizes the structure of the copolymer. For instance, the absence of the heterogeneous triad F—T—G indicates the formation of a homopolymer mixture, and the absence of homogeneous triad indicates the formation of a regularly alternating copolymer.

In several studies high-resolution ^1H NMR method was successfully used to determine the quantitative ratio of triads I and III in polycondensation copolymers.

We have investigated the spectra of some PSF-PEs synthesized by interaction of terephthaloyl chloride, various diols and dihydroxyl-terminated polysulfone in order to choose a system of initial compounds convenient for ^1H NMR studies.



On the other hand, in the ^1H NMR spectra copolymer such as PSF-PPT, PSF-PBT, PSF-PHT, PSF-PDET, PSF-PTET three peaks are observed in the region of 8.02—8.30ppm, as shown in Fig. 4

For instance, PSF-PBT copolymer has three kinds of terephthalic acid residue (—T—), one of which is adjacent to dihydroxyl-terminated polysulfone (—F—) at both sides F—T—F; one to diols (—G—) at both sides G—T—G, and the third one to dihydroxyl-terminated polysulfone (—F—) and diol (—G—), F—T—G(or G—T—F). The proton signals appear at 8.06, 8.17, 8.28 ppm, respectively. The intensities of these peaks represents the amount of the "heterolinkage" and "homolinkages".

When three kinds of signals due to homolinkages and heterolinkages are observed in the ^1H NMR spectra of a copolymer, one can determine the average sequence length (L) and the degree of randomness (B) of the copolymer by known procedure^[9] as shown in the following:

PSF-PBT is taken as an example:

Molar fractions of dihydroxyl-terminated polysulfone (P_F), and butanediol (P_G) are obtained from the intensities of the three kinds of signals in the ^1H NMR spectrum;

that is, $P_F = P_{FTF} + P_{FTG/2}$ (1)

$P_G = P_{GTG} + P_{FTG/2}$ (2)

where P_{FTF} , P_{FTG} , and P_{GTG} represent the ratio of the integrated intensities of FTF, FTG and GTG signals, respectively to the total intensity of the terephthalic acid residues.

If one could inspect the units along the PSF-PEs copolymer chain from one end to the other,

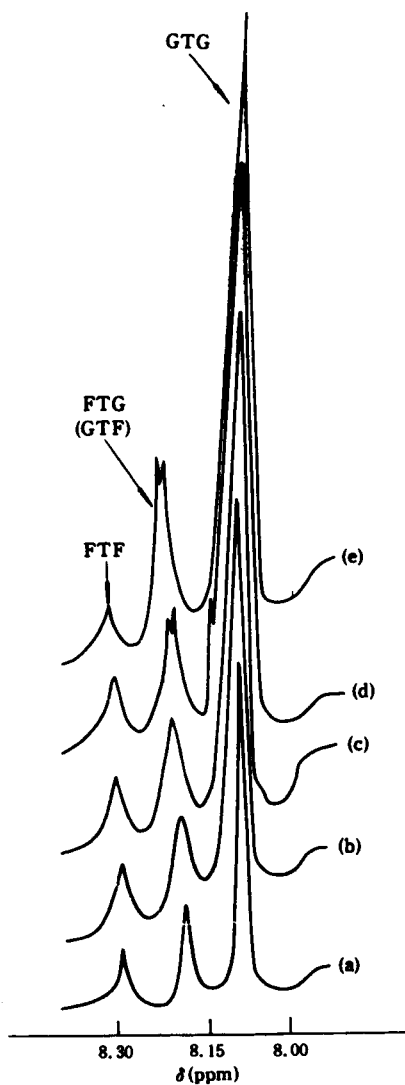


Fig. 4 ^1H NMR spectra of PSF-PEs ((a) PSF-PPT; (b) PSF-PBT; (c) PSF-PHT; (d) PSF-PDET; (e) PSF-PTET.)

the probability of finding an F unit next to a G unit would be

$$P_{GF} = P_{FTG}/2P_G \quad (3)$$

similarly, a G unit exists next to an F unit with a probability of

$$P_{FG} = P_{FTG}/2P_F \quad (4)$$

The degree of randomness is defined by

$$B = P_{FG} + P_{GF} \quad (5)$$

when $B = 1$, the F and G units have a random distribution, and the probability of finding a copolymer unit obeys Bernoulli statistics. When $B < 1$, these units tend to cluster in blocks of F units and blocks of G units, and when $B = 0$ is a homopolymer mixture, whereas when $B > 1$, the

sequence length becomes shorter, and when $B = 2$ in an alternative copolymer.

The number-average sequence length of an F unit (L_{nF}) and a G unit (L_{nG}) are given by

$$L_{nF} = 1/P_{FG} \quad (6)$$

$$L_{nG} = 1/P_{GF} \quad (7)$$

The fraction of the GTG, GTF(FTG) and FTF linkages, which are shown in Table 3, were obtained from the ^1H NMR spectra of the PSF-PEs block copolymers have different copolycondensation ratio (see Fig. 4, Fig. 5 and Table 4) represent sequence distribution in PSF-PBT with various copolycondensation ratios.

Table 3 Influence of reactivity of diol on the structure of the polysulfone-polyester block copolymers

Structure of block copolymers	Triad content (mole fractions)		
	GTG	GTF(FTG)	FTF
PSF-PPT	0.69	0.23	0.08
PSF-PBT	0.70	0.22	0.09
PSF-PHT	0.81	0.11	0.08
PSF-PDET	0.68	0.23	0.09
PSF-PTET	0.73	0.17	0.11

Table 4 Sequence distribution in PSF-PBT with various copolycondensation ratios

Number of copolymer		Triad content(mole fractions)		
		GTG	GTF(FTG)	FTF
1	Intensity of peak	9.6	1.5	0.7
	Relative ratio	0.81	0.13	0.06
2	Intensity of peak	4.1	1.3	0.5
	Relative ratio	0.70	0.22	0.09
3	Intensity of peak	3.0	1.4	0.9
	Relative ratio	0.57	0.26	0.17
4	Intensity of peak	2.0	1.3	1.2
	Relative ratio	0.44	0.29	0.27

From Figure 5 and Table 4 it is shown that the increase in the feed ratios of butanediols in copolycondensation leads to an increase in the GTG of triad content, and decrease in the FTF of triad content. The parameter P_F , P_G , P_{GF} , L_{nF} , L_{nG} and B shown in Table 5. were calculated from eqs. (1)–(7). From the values of B , which are < 1 , from 0.53 for PSF-PTET to 0.74 for PSF-PPT, it is obvious that these polymers are block copolymers.

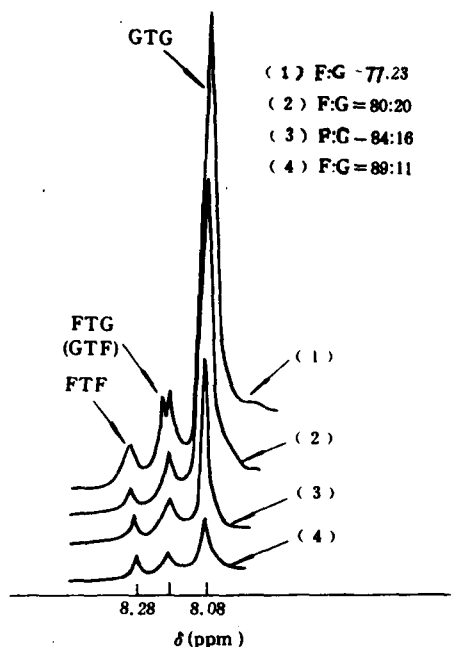


Fig. 5 ^1H NMR spectra of the PSF-PBT block copolymers obtained at various ratios of HO-PSF-OH(F) and HO-(CH₂CH₂CH₂CH₂)-OH(G)

Table 5 Sequence distribution in various PSF-PEs

Structure of block copolymer	Relative content units, mole fraction		Probability of finding of unit		Degree of randomness of copolymer B	Block length	
	P_F	P_G	P_{GF}	P_{FG}		L_{nF}	L_{nG}
PSF-PPT	0.19	0.81	0.14	0.60	0.74	1.67	6.99
PSF-PBT	0.20	0.80	0.14	0.56	0.70	1.80	7.30
PSF-PHT	0.13	0.87	0.07	0.42	0.49	2.39	15.5
PSF-PDET	0.21	0.79	0.14	0.55	0.69	1.83	7.04
PSF-PTET	0.19	0.81	0.10	0.43	0.53	2.33	9.80

It is shown that the degree of randomness of the PSF-PEs block copolymers lies in the region of $0 < B < 1$

From Table 5, it is shown that the degree of randomness (B) and the average sequence length (L) in these block copolymers are relatively dependent on the reaction condition, various feed ratios and structure of diols. As shown below:

B : PSF-PPT > PSF-PBT > PSF-PDET > PSF-PTET > PSF-PHT

L_{nF} : PSF-PHT > PSF-PTET > PSF-PDET > PSF-PBT > PSF-PPT

L_{nG} : PSF-PHT > PSF-PTET > PSF-PDET, PSF-PBT > PSF-PPT

An increase in the length of chain of diols of copolycondensation leads to decrease in the degree

of randomness (B) and an increase in the average length of block (L_{nF} or L_{nG}).

Properties of solution of the block copolymers

When the PSF-PEs block copolymers were dissolved in *o*-chlorophenol and chloroform respectively, different viscosities and molecular conformations were observed (see Table 6).

Table 6 Reduced viscosity of the PSF-PEs block copolymers (in chloroform and in *o*-chlorophenol, respectively, at 30°C)

Type of PSF-PEs block copolymers	Reduced Viscosity (R.V)	
	in CHCl_3	in <i>o</i> -chlorophenol
PSF-PPT	0.38	0.56
PSF-PBT	0.30	0.43
PSF-PHT	0.40	0.49
PSF-PDET	0.42	0.49
PSF-PTET	0.39	0.48

The results show that dilute solutions of the PSF-PEs block copolymers are clear in *o*-chlorophenol, which is a good solvent for both blocks, whereas the solutions of the mixtures of the corresponding homopolymers at comparable concentration are two-phase systems.

It is shown that higher concentration of block copolymers in CHCl_3 tends to give solutions which are thixotropic and, particularly, for the higher molecular weight species, iridescent. This indicates an orientation of the solute similar to that noted in solutions of Polysulfone-Nylon 6 copolymers.^[8c]

An abrupt increase in the viscosity of solution of PSF-PBT block copolymers in chloroform is noted as the concentration is higher. (see Fig. 6)

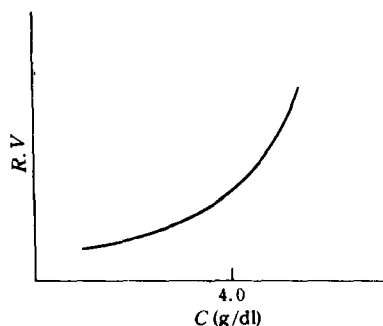


Fig. 6 Effect of concentration of solution of PSF-PBT block copolymer in CHCl_3 on reduced viscosity at 30°C

Solvent resistance of block copolymers

The PSF-PEs block copolymers, including PSF-PPT, PSF-PBT, PSF-PHT, have better solvent resistance than homopolysulfone. PSF-PBT is taken as an example. results are shown in Figure 7.

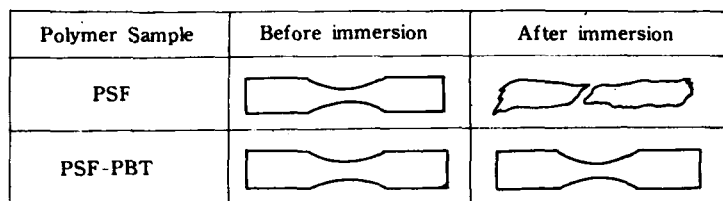


Fig. 7 Shape of films of PSF and PSF-PBT before and after 15 min. immersion in acetone

The results show that the film of polysulfone-polybutyleneterephthalate(PSF-PBT) block copolymer after immersion in acetone for 15min. remains unchanged, but the homopolysulfone (PSF) film becomes cracked.

It is evident that incorporation of crystalline polyester blocks would greatly improve the chemical and stress-cracking resistance of amorphous polysulfone. Consequently, the PSF-PEs block copolymers (e.g., PSF-PPT; PSF-PBT; PSF-PHT) have better solvent resistance than PSF homopolymer.

Keywords:

Polysulfone-polyester block copolymer; Degree of randomness, sequential structure of copolymer.

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