

## Aminated Poly(arylene ether sulfone)

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### Synthesis and Characteristics of Aminated Poly(arylene ether sulfone) as Thermostable Anion Exchanger

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: poly(arylene ether sulfone) (PAES)  
. 1° - Aminated poly(arylene ether sulfone) (1° - APAES) PAES  
, 3° - APAES 1° - APAES  
PAES APAES FT - IR H<sup>1</sup> - NMR , DSC TG  
. PAES 가 T<sub>g</sub> 가 ,  
1° - APAES 3° - APAES 1.19 1.45 meq/g .

ABSTRACT : In this study, poly(arylene ether sulfone) (PAES) having thermal stability and excellent mechanical properties was synthesized to be useful for the matrix of anion exchange resin. 1° - Aminated poly(arylene ether sulfone) (1° - APAES) was prepared by reduction reaction after lithiation of PAES. Then 3° - APAES was prepared by alkylation of the amine group of 1° - APAES. The structures of PAES and APAESs were confirmed with FT - IR and <sup>1</sup>H - NMR spectroscopy. Also, thermal properties of the resins were characterized by DSC and TG analysis. The introduction of amine groups in PAES resulted in the increase of glass transition temperature and decrease of initial thermal degradation temperature. The ion exchange capacities of 1° - APAES and 3° - APAES were 1.19 and 1.45 meq/g, respectively.

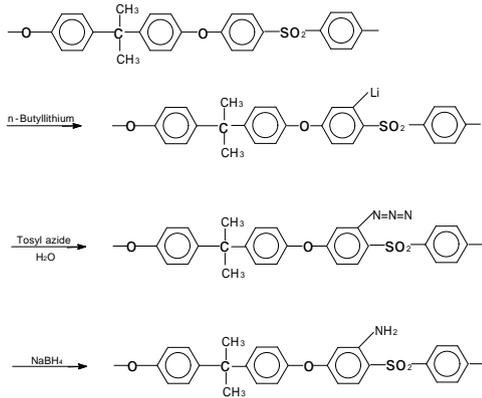
Keywords : anion exchanger, thermostable ion exchanger, poly(arylene ether sulfone), amination.

가  
Green, Bio, ECO  
가 가 가

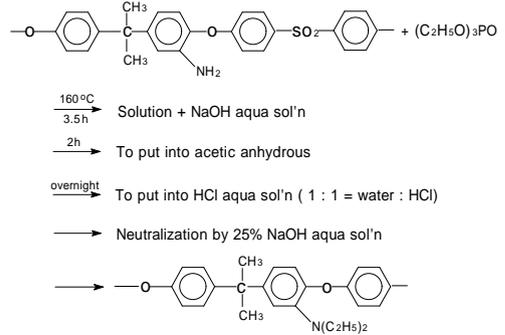
가 1,2 가  
 가 가  
 가 3 가  
 (pure water)  
 4-6 가 7  
 poly(ether sulfone) (PES), poly(arylene ether sulfone) (PAES)  
 가 8-10  
 가 PAES  
 PAES 1° -  
 PAES (1° - APAES) 1° -  
 APAES 3° - 가 PAES  
 (3° - APAES)  
 fourier transform infrared  
 (FT - IR) proton nuclear magnetic resonance  
 (1H - NMR), thermogravimetric (TG)  
 differential scanning calorimetry (DSC)

PAES 4,4' -  
 dichlorodiphenylsulfone (4,4' - DCDS) Aldrich  
 , bisphenol - A Junsei  
 dimethylacetamide  
 (DMAc), toluene potassium carbonate (K<sub>2</sub>CO<sub>3</sub>)  
 . p -  
 Toluene sulfonyl chloride n - butyllithium, sodium  
 borohydride Aldrich  
 sodium azide Junsei  
 tetrahydrofurane (THF)  
 triethyl phosphate acetic anhydrous  
 isopropyl alcohol  
 (IPA), magnesium sulfate anhydrous, chloroform,  
 petroleum ether, charcoal, nitrobenzene, hydrochloric  
 acid (HCl), ethanol, methanol, sodium hydroxide  
 (NaOH)  
 Poly(arylene ether sulfone) (PAES) 10 PAES  
 4 가  
 DMAc 500 mL toluene 250 mL  
 K<sub>2</sub>CO<sub>3</sub> 40 g (0.289 mol)  
 4,4' -  
 DCDS 45 g (0.157 mol) 155  
 , bisphenol - A 36 g (0.157 mol)  
 가 6  
 methanol methanol  
 70 24  
 PAES  
 p-Toulene sulfonyl chloride 11 Chloroform 250  
 mL p - toluene sulfonyl chloride 100 g  
 1250 mL petroleum ether 가  
 charcoal 가  
 Tosyl azide . IPA 600 mL p - toluene  
 sulfonyl chloride 100 g (0.52 mol)  
 sodium azide 40.56 g (0.624  
 mol) 117 mL 가 1

Aminated Poly(arylene ether sulfone)



Scheme 1. Reaction scheme of the synthesis of 1° - APAES.



Scheme 2. Reaction scheme of the synthesis of 3° - APAES.

3 L 1  
tosyl azide가 oil  
3  
magnesium sulfate anhydrous  
Azidated PAES  
가 500 mL 4 THF 200 mL  
PAES 10 g (0.0225 mol)  
cold bath  
(dry ice/alcohol) 가 -78  
n -  
butyl lithium 4.338 mL (0.0444 mol)  
가 30 THF  
15 mL tosyl azide 13.275 g (0.0675 mol)  
- 35 가  
15 - 78 cold bath  
- 50 15  
ethanol/ (2:3)  
가 azidated  
poly(arylene ether sulfone)  
ethanol/ (4:1)  
30  
1°-APAES 가  
250 mL 4 THF 60 mL  
ethanol 6 mL azidated PAES 3 g  
(0.0057 mol) - 60

sodium borohydride powder  
1.0773 g (0.0285 mol) 가 가  
24 1 L  
methanol 60 2  
3 40  
Scheme 1  
3°-APAES 가  
4 1° - APAES 3 g (0.0069 mol)  
triethylphosphate 100 mL 160  
3 30 180 mL  
NaOH 45 g 50  
가 2  
acetic anhydrous  
/ (1:1) 3  
25% NaOH 가  
100 Scheme 2  
FT-IR Spectrophotometer.  
Nicolet MAGNA - IR  
560 FT - IR 32  
9 cm<sup>-1</sup> KBr  
NMR Spectrophotometer.  
Bruker AC - 300  
300 MHz

deuterated methyl sulfoxide  
 tetramethylsilane  
 GPC(Gel Permeation Chromatography)  
 PAES, 1° - APAES 3° - APAES  
 UV 가 Waters Model 600  
 GPC N - methyl - 2 -  
 pyrrolidone (NMP) 1.0 mL/min  
 , 0.3 wt% 200 μL

DuPont TA Model 2100 DSC  
 10 /min 25 250

DuPont Model 2100 TG  
 10 /min 25

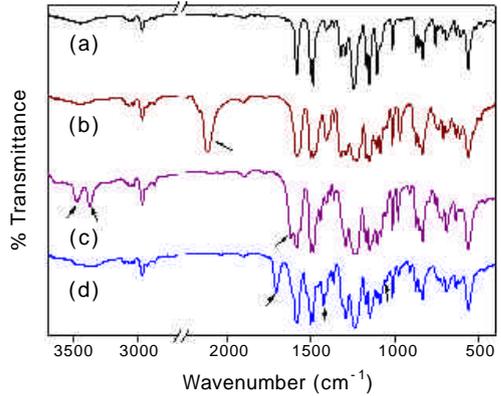
800  
 C, H, S, N  
 Fisons He

180 150 mL/min  
 O

Heraeus  
 1° - APAES 3° - APAES  
 1 N HCl 1 N NaOH  
 가 3 -OH  
 1 N NaOH

80  
 1° - APAES 3° - APAES 0.5 g 1 N KCl  
 0.0998 N HCl 50 mL  
 48  
 10 mL Metrom Titrino 716  
 0.1 N NaOH

FT-IR  
 PAES  
 1° - APAES  
 3° - APAES  
 FT - IR Figure 1  
 . Figure 1(b) 2118 cm<sup>-1</sup>



**Figure 1.** FT - IR spectra of (a) PAES, (b) PAES modified with azide, (c) 1° - APAES, and (d) 3° - APAES.

- N=N=N  
 가 PAES  
 가  
 Figure 1(c) (b)  
 가 3374 cm<sup>-1</sup>  
 N - H 가, 3474  
 cm<sup>-1</sup> N - H  
 가 1619 cm<sup>-1</sup> N - H  
 가  
 가  
 Figure 1(d) NH₂ 가  
 1425 cm<sup>-1</sup> Ar - N - CH₂ - C - H  
 가 , 1650 cm<sup>-1</sup>  
 3 C - N 가  
 가 1 가  
 1H-NMR . Figure 2 PAES

1° - APAES 3° - APAES 1H -  
 NMR . Figure 2(b) PAES  
 . Figure 2(b)  
 가  
 가  
 , H<sub>d</sub>  
 H<sub>d</sub>(U) 7.85

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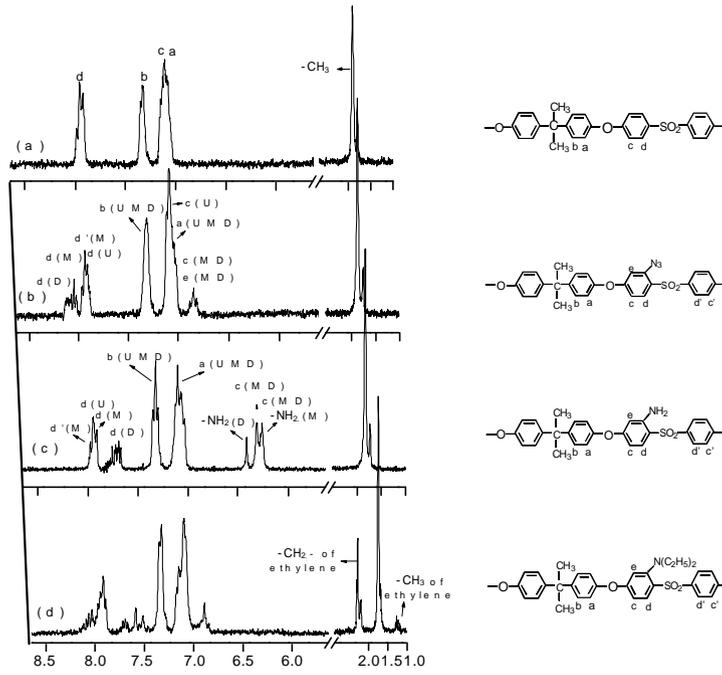


Figure 2. <sup>1</sup>H-NMR spectra of (a) PAES, (b) PAES modified with azide, (c) 1°-APAES, and (d) 3°-APAES.

Table 1. Molecular Weight of PAES, 1°-APAES and 3°-APAES

samples	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w / \bar{M}_n$
PAES	39631	64528	1.628
1°-APAES	40935	66455	1.623
3°-APAES	44013	71841	1.632

가  
 , H<sub>d</sub>(M)  
 8.04 , 가  
 , H<sub>d</sub>(M)  
 7.95 , 6.95 7.1  
 H<sub>c</sub>(U)  
 H<sub>a</sub>(U,M,D)  
 6.76 6.86  
 H<sub>c</sub>(M,D) H<sub>e</sub>(M,D)  
 12  
 Figure 2(c) 1°-APAES <sup>1</sup>H-NMR  
 , H<sub>d</sub>(U)  
 7.89 ,  
 H<sub>d</sub>(D) 7.69  
 가  
 H<sub>d</sub>(M) 7.85 ,  
 가  
 H<sub>d</sub>(M) 7.95

7.23 7.35  
 H<sub>b</sub>(U,M,D)  
 6.98 7.1  
 H<sub>a</sub>(U,M,D)  
 6.27  
 H<sub>e</sub>(M,D)  
 6.19  
 H<sub>c</sub>(M,D) 1  
 6.32 1  
 13  
 Figure

Figure 2(d) 3° - APAES <sup>1</sup>H - NMR  
 Figure 2(c) 1  
 6.19 1  
 6.32  
 -CH<sub>2</sub>-  
 2.07  
 -CH<sub>3</sub> 1.25 3  
 가  
 PAES, 1° - APAES 3° - 가  
 APAES GPC  
 Table 1 Table 1  
 PAES 1° - APAES 3° - APAES 가  
 가  
 DSC Figure 3 PAES, 1° -  
 APAES 3° - APAES DSC  
 PAES 133 T<sub>g</sub>, 1° -  
 APES 147 T<sub>g</sub>가, 3° -  
 APAES 135 T<sub>g</sub> 가  
 T<sub>g</sub>  
 PAES  
 T<sub>g</sub>가 가  
 가

T<sub>g</sub>가  
 1° - APAES 3° - APAES T<sub>g</sub>가  
 1  
 3  
 3° - APAES  
 1  
 PAES T<sub>g</sub>  
 TG Figure 4 PAES  
 1° - APAES 3 -  
 APAES TG  
 10%  
 PAES 510, 1° -  
 APAES 3° - APAES 440  
 DSC  
 T<sub>g</sub>  
 가  
 C - N 305 KJ/mol, C - H  
 411 KJ/mol PAES

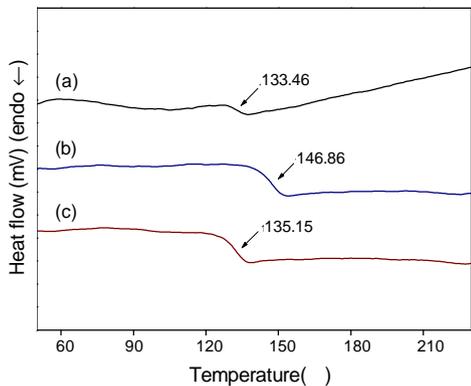


Figure 3. DSC thermograms of (a) PAES, (b) 1° - APAES, and (c) 3° - APAES.

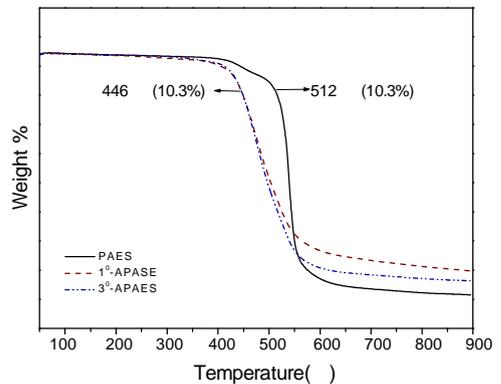
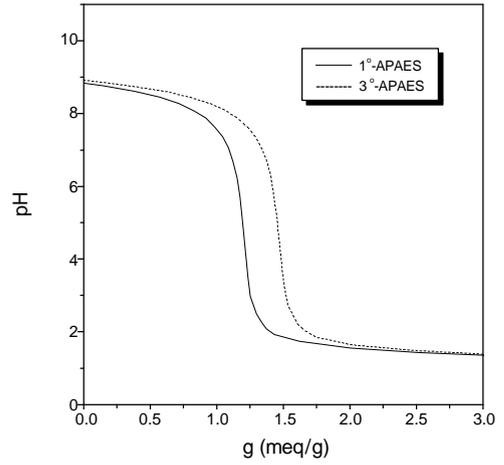


Figure 4. TGA curves of PAES, 1° - APAES, and 3° - APAES.

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**Table 2. Elementary Analysis of 1°-APAES and 3°-APAES**

	element (%)	an approximate number of elements per repeating unites	ion exchange capacity (meq/g)
1° - APAES	N	2.978	2.0
	C	66.828	
	H	4.722	
	S	7.103	
	O	13.815	
3° - APAES	N	2.491	1.8
	C	65.223	
	H	5.68	
	S	5.885	
	O	15.828	



**Figure 5.** Curves of pH versus ion exchange capacity of 1° - APAES and 3° - APAES.

358 KJ/mol

C - O PAES

C - N PAES

(EA). Table 2 APAES

1° - APAES 3° - APAES

0.96 가

1 : 1 가

1° - APAES 3° - APAES 2.0, 1.8 meq/g

3° - APAES 1° - APAES 가

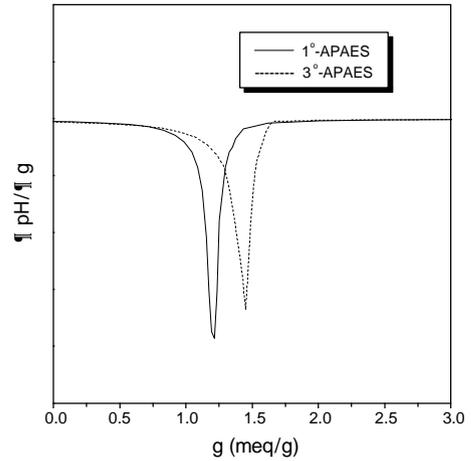
1 M

KCl 0.1 N HCl APAES

1° - APAES 3° - APAES

NaOH

g (meq/g) Figure 5



**Figure 6.** Curve fittings of a  $1/pH/1/g$  versus  $g$  by Lorenzian distribution for 1° - APAES and 3° - APAES.

$\partial pH / \partial g$  Lorenz Figure 6

$\partial pH / \partial g$  g

1° - APAES

3° - APAES 1.19 1.45 meq/g

3° - APAES

가 1° - APAES

1 3

가 PAES 1° - APAES 가  
 1° - APAES 3° - APAES  
 1° - APAES 3° - APAES  
 0.96 가  
 1° - APAES  
 가 3° - APAES 1.19 1.45 meq/g

14,15

PAES	APAES	DSC	FT - IR
NMR			TG
FT - IR		가	PAES
2118 cm <sup>-1</sup>	- N=N=N		1° -
	가		3374
APAES		가	
3474 cm <sup>-1</sup>	N - H		
	1619 cm <sup>-1</sup>	N - H	
	가		
	3° - APAES	NH <sub>2</sub>	
가	1425 cm <sup>-1</sup>	Ar - N - CH <sub>2</sub> -	
C - H		가, 1650 cm <sup>-1</sup>	
3	C - N		
가		가	
	1H - NMR		
		1° - APAES	
3° - APAES	가		
			PAES T <sub>g</sub>
133	1° - APES		147
3° - APAES	135	T <sub>g</sub>	
10%			

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