

폴리(이미드-아라미드-설펜)의 합성과 그들의 열적성질

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(2011년 12월 1일 접수, 2012년 3월 5일 수정, 2012년 3월 7일 채택)

Preparation of Poly(imide-aramid-sulfone)s and their Thermal Properties

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(Received December 1, 2011; Revised March 5, 2012; Accepted March 7, 2012)

초록: 이미드/아라미드/설펜기가 교대로 도입된 poly(imide-aramid-sulfone)s을 divinyl sulfone(DVS)과 N^1, N^4 -bis(4-(vinylsulfonyl)phenyl)terephthalamide (**2**)를 pyromellitic diimide와 반응하여 높은 수율로 제조하였다. 또한 고분자를 닦은 3가지 모델 화합물인 N -[2-(p -aminophenylsulfonyl)ethyl]phthalimide (**3**), 2,2'-(2,2'-sulfonylbis(ethane-2,1-diyl))diisindoline-1,3-dione (**4**), 및 N, N -bis(4-(2-(1,3-dioxoisindolin-2-yl)ethylsulfonyl)phenyl)terephthalamide (**5**)을 p -aminophenyl vinyl sulfone, DVS, **2**와 phthalimide와 반응하여 얻었다. 축합 중합은 phthalimide 기와 DVS의 마이클 첨가 반응에 의하여 균일 용액으로 진행되며 tetrabutylammonium hydroxide (TBAH)가 촉매로 작용하여 poly(imide-aramid-sulfone)s **6-12**의 분자량이 큰 중합체를 얻을 수 있었다. DVS/**2**의 구성비는 1/0, 3/1, 2/1, 1/1, 1/2, 1/3, 및 0/1이다. 얻어진 고분자들은 극성 용매인 N, N -dimethylformamide, dimethylsulfoxide, N -methylpyrrolidinone 및 tetrahydrofuran에 잘 용해하였다. 그 밖에 분자량, 점도 그리고 열적 성질을 평가하였다.

Abstract: A series of poly(imide-aramid-sulfone)s with alternately introduced imide/aramid groups were prepared by reacting divinyl sulfone (DVS) and N^1, N^4 -bis(4-(vinylsulfonyl)phenyl)terephthalamide (**2**) with pyromellitic diimide. Three model compounds, N -[2-(p -aminophenylsulfonyl)ethyl]phthalimide (**3**), 2,2'-(2,2'-sulfonylbis(ethane-2,1-diyl))diisindoline-1,3-dione (**4**), and N, N -bis(4-(2-(1,3-dioxoisindolin-2-yl)ethylsulfonyl)phenyl)terephthalamide (**5**), resembling polymers were prepared with good yields by reacting p -aminophenyl vinyl sulfone, DVS, and **2** with phthalimide. Condensation polymerization was carried out by Michael-type addition reaction of the difunctional phthalimide group with the DVS group in the presence of tetrabutylammonium hydroxide (TBAH), resulting in poly(imide-aramid-sulfone)s **6-12** with moderate molecular weights and good yields. They were highly soluble in polar solvents such as N, N -dimethylformamide, dimethylsulfoxide, N -methylpyrrolidinone and tetrahydrofuran. The ratios of DVS/**2** were 1/0, 3/1, 2/1, 1/1, 1/2, 1/3, and 0/1. Molecular weight and physical properties such as solubility, viscosity, and thermal properties of the polymers were examined.

Keywords: tetrabutylammonium hydroxide, vinyl sulfone, Michael addition, poly(imide-aramid-sulfone)s.

Introduction

Aromatic polyimides are well accepted as high-performance polymers due to their high thermal and chemical stabilities, excellent mechanical properties, and high glass transition temperatures.^{1,2} They are widely used in various fields, including the aerospace and electronic industries. However, these polymers are difficult to process due to their high glass transition

temperatures, high melting temperatures, and limited solubility in organic solvents.^{3,4} Considerable efforts have been made to improve the solubility and/or melting processability of polyimides while maintaining their positive properties.⁵⁻⁷ Therefore, significant synthetic efforts in the area of high-performance polymers have focused on improving processability and solubility through the design and synthesis of new monomers. A variety of structural modifications to the polyimide backbone, such as insertion of a flexible linkage on the main chain,⁸ utilization of noncoplanar or asymmetric monomers,⁹ and incorporation of pendent groups in the polymer

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backbone,^{10,11} can be employed to modify polymer properties, either by lowering the inter-chain interactions or by reducing the stiffness of the polymer chain. Depending on the types and degrees of structural modifications, the melting temperatures can be lowered and solubility improved, resulting in processable materials.

General synthetic procedures for polysulfones, which have been extensively used as biocompatible, immobilized enzyme substrates and solvent-resistant membrane materials, are prepared by polycondensation¹²⁻¹⁴ and polyaddition¹⁵⁻¹⁹ of sulfone monomers. Other pathways for polysulfones include copolymerization employing sulfur dioxide²⁰⁻²² and oxidation of polysulfides.²³ In the present study, we investigated the use of divinyl sulfone derivatives as a monomer for the synthesis of soluble polyimide. The use of divinyl sulfone derivatives as monomers for the synthesis of polyimides was newly suggested since they can be used to impart special functionality to polymers as well as improve processibility.²⁴⁻²⁷ This paper describes the use of vinyl sulfone-containing monomers, their Michael-type addition polymerization with diimide derivatives in the presence of quaternary ammonium hydroxide, and the characterization of new poly(imide-aramid-sulfone)s, which have a flexible alkyl group and a rigid aramide moiety in their backbone. In this experiment, we prepared new poly(imide-aramid-sulfone)s and analyzed their various physical properties such as molecular weight, solubility, thermal properties, and viscosity for the evaluation of new poly(imide-aramid-sulfone)s.

Experimental

Materials. Phthalimide and pyromellitic diimide (Aldrich Chem.) were recrystallized from ethyl acetate. Divinyl sulfone (DVS, Aldrich Chem. Co., 95%) was purified by column chromatography (Silica Gel) using methylene chloride/hexane (3/1). Tetrabutylammonium hydroxide (TBAH, Aldrich Chem.) was used without further purification. *p*-Aminophenyl vinyl sulfone (**1**) was prepared by reaction of 2-[4-aminophenyl)sulfonyl]ethyl hydrogen sulfate with NaOH. *N*-Methylpyrrolidinone (NMP) was dried from molecular sieves and tetrahydrofuran (THF) was distilled over sodium and calcium hydride. *N*¹,*N*⁴-bis(4-(vinylsulfonyl)phenyl)terephthalamide (**2**) was prepared by a previously reported method.^{28,29}

Instruments. Molecular weights were measured by Waters HPLC using three columns (3, 4, and 5 Å) using THF as an eluent at 30 °C. Inherent viscosity was determined by a Cannon-Ubbelode viscometer in 10 g/dL of DMF at 20 °C. FTIR

spectra were obtained with a Biorad Excaliber FTS-3000MX spectrophotometer, and ¹H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. DSC measurements were performed on a Shimadzu DSC 60 under nitrogen at a heating rate of 10 °C/min. TGA measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen. The elemental analyses were performed using a CE Instrument EA1110.

Representative Preparation of Model Compound 2,2'-(2,2'-sulfonylbis(ethane-2,1-diyl))diisoindoline-1,3-dione (4**).** To a solution of phthalimide (1.18 g, 8 mmol) and DVS (0.47 g, 4 mmol) dissolved in NMP (20 mL), aqueous TBAH was added dropwise at 50 °C within 30 min. After stirring for 12 h, the reaction mixture was precipitated into methanol, and the precipitate compound was isolated by filtration. The solid product was washed with ethanol and dried in vacuo at 60 °C. Other model compounds, *N*-[2-(*p*-aminophenylsulfonyl)ethyl]phthalimide (**4**), *N*¹,*N*⁴-bis(4-(2-(1,3-dioxoisindolin-2-yl)ethylsulfonyl)phenyl)terephthalamide (**5**), were also prepared by the method described above.

3: Yield 90%. Mp. 210 °C. FTIR (KBr, cm⁻¹) 3360 (N-H), 3071 (Ar C-H), 2975 (C-H), 1765, 1697 (C=O), 1588 (Ar C=C), 1401, 1303 (O=S=O), 1130 (C-N), 713. ¹H NMR (DMSO-*d*₆, ppm) 7.8 (s, 4 H, Imide Ar-*H*), 7.4 (d, 2 H, -SO₂-Ar-*H*), 6.5 (d, 2 H, -NH₂-Ar-*H*), 6.2 (s, 2 H, -NH₂), 3.8 (t, 2 H, -CH₂-), 3.5 (t, 2 H, -CH₂-). Anal. Calcd for C₁₆H₁₄N₂O₄S (330.07): C, 58.17; H, 4.27; N, 8.48; S, 9.71. Found: C, 58.09; H, 4.25; N, 8.52; S, 9.69.

4: Yield 87%. Mp. 260 °C. FTIR (KBr, cm⁻¹) 3075 (Ar C-H), 2970 (C-H), 1709, 1663 (C=O), 1580 (Ar C=C), 1305 (O=S=O), 1139 (C-N). ¹H NMR (DMSO-*d*₆, ppm) 7.8 (s, 8H, Imide Ar-*H*), 3.8 (t, 4 H, 2 -CH₂-), 3.5 (t, 4 H, 2 -CH₂-). Anal. Calcd for C₂₀H₁₆N₂O₆S (412.07): C, 58.25; H, 3.91; N, 6.79; S, 7.77. Found: C, 58.21; H, 3.94; N, 6.72; S, 7.69.

5: Yield 87%. Mp. 385 °C. FTIR (KBr, cm⁻¹) 3374 (-CO-NH-), 3075 (Ar C-H), 2970 (C-H), 1773 (amide C=O), 1710, 1670 (imide C=O), 1588 (Ar C=C), 1503, 1394, 1301 (O=S=O), 717. ¹H NMR (DMSO-*d*₆, ppm) 10.8 (s, 2H, 2 -CO-NH-), 8.0 (s, 4 H, Ar-*H*), 7.8 (s, 8 H, 2 Imide Ar-*H*), 7.5 (d, 4 H, 2 -SO₂-Ar-*H*), 6.5 (d, 4 H, 2 -NH₂-Ar-*H*), 3.7 (t, 4 H, 2 -CH₂-), 3.6 (t, 4 H, 2 -CH₂-). Anal. Calcd for C₄₀H₃₀N₄O₁₀S (790.14): C, 60.75; H, 3.82; N, 7.08; S, 8.11. Found: C, 60.78; H, 3.86; N, 7.03; S, 8.13.

Representative Copolymerization of Vinylsulfone-containing Monomers with Pyromellitic Diimide. In a round-bottomed flask (100 mL) equipped with a condenser

and a nitrogen inlet system, pyromellitic diimide (1.30 g, 6 mmol), DVS (0.35 g, 3 mmol), **2** (1.49 g, 3 mmol), and LiCl (0.10 g) were dissolved in NMP (10 mL). The solution was maintained at 50 °C for 1 h with vigorous stirring. The aqueous TBAH was added dropwise to a mixture of DVS, pyromellitic diimide, and **2**. After the reaction mixture was maintained at 80 °C for 24 h and precipitated into methanol and washed with distilled water. The solid product was dissolved in NMP and reprecipitated into methanol. The resulting polymer **9** was filtered and dried in vacuo at 60 °C. Polymers composed of DVS/2= 1/0 (**6**), 3/1 (**7**), 2/1 (**8**), 1/2 (**10**), 1/3 (**11**), and 0/1 (**12**) were also prepared by the method described above.

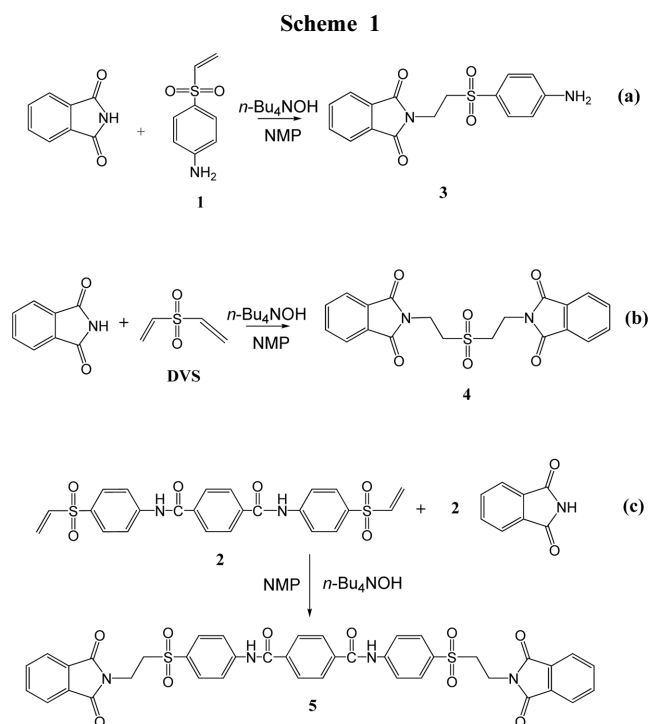
6: Yield 86%. FTIR (KBr, cm^{-1}) 3080 (Ar C-H), 2970 (C-H), 1774, 1715 (C=O), 1580 (AromC=C), 1392, 1362, 1302 (O=S=O), 1120 (C-N), 729 ($-\text{CH}_2-$). ^1H NMR (DMSO- d_6 , ppm) 8.3 (s, 2H, Diimide Ar CH), 3.8 (t, 4 H, 2 $-\text{CH}_2-$), 3.5 (t, 4 H, 2 $-\text{CH}_2-$). Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_6\text{S}$ (334.30): C, 50.30; H, 3.02; N, 8.38; S, 9.59. Found: C, 50.48; H, 3.06; N, 8.36; S, 9.61.

9: Yield 89%. FTIR (KBr, cm^{-1}) 3335 (br, Ar-NH-), 3075, 3055 (Ar C-H), 2975, 2935 (C-H), 1772 (C=O), 1719, 1672 (C=O), 1585 (C=C), 1525, 1502 (Ar-NH-), 1392, 1304 (O=S=O), 1250, 1142, 1080 (C-O and C-N), 720. ^1H NMR (DMSO- d_6 , ppm) 10.7 (br, 1H, 1/2 $-\text{CO}-\text{NH}-$), 8.3 (s, 2H, Diimide Ar CH), 8.1 (s, 2 H, 1/2 Ar-H), 7.5 (d, 2 H, 1/2x2 $-\text{SO}_2-\text{Ar}-\text{H}$), 6.5 (d, 2 H, 1/2x2 $-\text{NH}_2-\text{Ar}-\text{H}$), 3.8 (t, 4 H, 2 $-\text{CH}_2-$), 3.5 (t, 4 H, 2 $-\text{CH}_2-$).

12: Yield 89%. FTIR (KBr, cm^{-1}) 3340 (br, Ar-NH-), 3080, 3056 (Ar C-H), 2970, 2935 (C-H), 1772 (C=O), 1717, 1674 (C=O), 1589 (C=C), 1523, 1501, 1393, 1301 (O=S=O), 1251, 1139, 1080 (C-O and C-N), 721. Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_4\text{O}_{10}\text{S}$ (712.09): C, 57.30; H, 3.39; N, 7.86; S, 9.00. Found: C, 57.33; H, 3.36; N, 7.83; S, 9.02.

Results and Discussion

Preparation of Model Compounds. A model compound study was performed before polymer synthesis to obtain information regarding the feasibility of the reaction for polymer formation and to obtain model compounds for comparison with the polymers in Scheme 1, which shows the synthetic scheme for preparing the various phthalimide-armed sulfone model compounds. The model reaction was based on the procedure of the Michael addition reaction and involved the incorporation of pyromellitic diimide to DVS in the presence of TBAH. Simple model compound **3** was prepared from **1** and phthalimide



in the presence of TBAH with 93% yield (Scheme 1(a)). The reaction of DVS with phthalimide in NMP also produced the desired product phthalimide-armed model compound **4** with 91% yield (Scheme 1(b)). Other model compound **5** containing amide unit using **2** was prepared as shown in Scheme 1(c).

The imide-aramid-sulfone model compounds were confirmed by ^1H NMR, IR spectral assignment, and elemental analysis. In the IR spectra, the model compounds **3**, **4**, and **5** showed characteristic absorption bands around 1710–1670 and 1300 cm^{-1} , corresponding to the imide and sulfone linkages, respectively. In the NMR spectra of **3**, **4**, and **5**, characteristic alkyl protons appeared at 3.5–3.8 ppm as two triplets. In Figure 1(a), a singlet sharp peak at 6.1 ppm was due to the amino protons of model compound **3**. The symmetrical model compound **4** showed simple resonance signals such as phthalimide and methylene protons as shown in Figure 1(b). The multiplet resonance signals at 8.0–7.6 ppm were due to the aromatic protons of compound **5**, which has low solubility in common organic solvents but is highly soluble in polar aprotic solvents. The incorporation of a simple vinyl sulfone group into the imide and amide moieties enhanced its solubility.

Polymerization. Polymerizations of DVS and **2** with pyromellitic diimide were carried out by addition polymer-

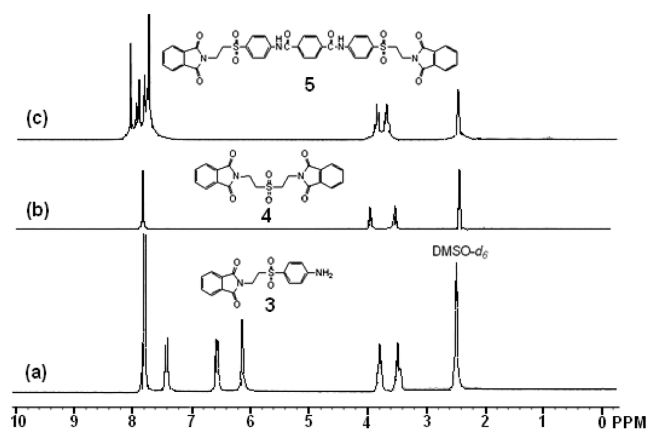
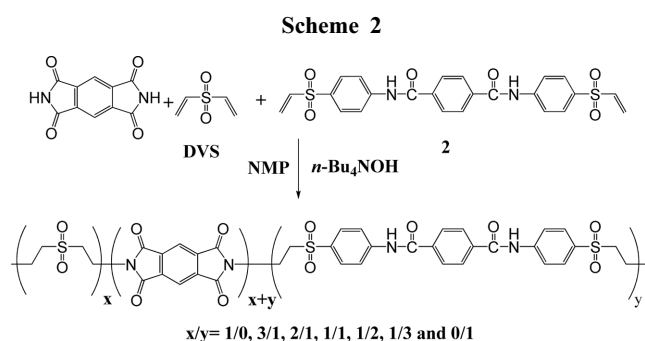


Figure 1. ^1H NMR spectra of model compounds: (a) **3**; (b) **4**; (c) **5**.



ization via Michael-type addition reaction as shown in Scheme 2.^{30,31} It was possible to prepare simple poly(imide-aramid-sulfone)s **6** and **12** by reacting DVS and **2** with pyromellitic diimide, respectively. Solubility was high in polar aprotic solvents assuming the solubility of model compound **5** in polar aprotic solvent. Thus, the copolymerizations of DVS and **2** with various mole ratios of DVS and **2** in pyromellitic diimide

were carried out in NMP solution with the aid of LiCl. The ratios of DVS and **2** were DVS/2 = 1/0, 3/1, 2/1, 1/1, 1/2, 1/3, and 0/1.

Michael-type addition polymerization gave polymers of moderate molecular weights judging from the viscosity data. The NMP-soluble portions of polymers obtained from addition polymerization possessed inherent viscosity of 0.52–0.82 dL/g. The DVS-containing polymers **6–9** showed moderate molecular weights. Tough films of polymers could be cast from solution. When the films were cast on a glass plate, tough films of polymers adhered very strongly to the glass surface.

The results of the polymerizations are summarized in Table 1 along with the data on viscosity and molecular weight. The obtained polymers were identified as poly(imide-aramid-sulfone)s. The FTIR spectra of the polyimides are shown in Figure 2. The absorption peaks around 1715 and 1670 cm^{-1} were from asymmetric and symmetric stretching of the imide carbonyl group, respectively. The peak at 1140–1080 cm^{-1} was due to the imide C–N vibration. The absorption peak of the sulfone group was observed around 1300 cm^{-1} . The absorption peak at 720 cm^{-1} was from the C–H out-of-plane vibration in the aromatic groups. In addition, the peaks around 1590 (aromatic C=C) cm^{-1} were gradually stronger in Figure 2 (a)–(e), which was due to an increased amount of monomer **2**. At the same time, the peak around 3400 cm^{-1} also increased with the decreasing molar ratio of DVS.

In the ^1H NMR spectrum of polymers **6–9**, alkylene protons derived from the vinyl group exhibited broad peaks between 3.5–3.8 ppm. The vinyl sulfone protons around 6.1–6.9 ppm disappeared completely as the polymerization proceeded. ^1H NMR spectra of **10**, **11**, and **12** were not obtainable due to the low levels of solubility of **10** and **11** in DMSO. Elemental

Table 1. Results of Condensation Polymerization of Divinyl Sulfone and Pyromellitic Diimide with Terabutylammonium Hydroxide

Polymers	Properties	PI ^a	DVS ^b	2 ^c	η_{inh}^d	M_w^e	Yield (%)
6		1	1	0	0.58	8600	85
7		4	3	1	0.68	9162	89
8		3	2	1	0.67	10764	87
9		2	1	1	0.82	16900	86
10		3	1	2	0.77	-	92
11		4	1	3	0.88	-	93
12		1	0	1	-	-	99

^aPyromellitic diimide. ^bDivinyl sulfone. ^c*N,N*-Bis(4-(vinylsulfonyl)phenyl)terephthalamide. ^dInherent viscosities were measured in NMP/LiCl in 1 g/dL at 25 °C. ^eWeight average molecular weight obtained from the THF soluble portion.

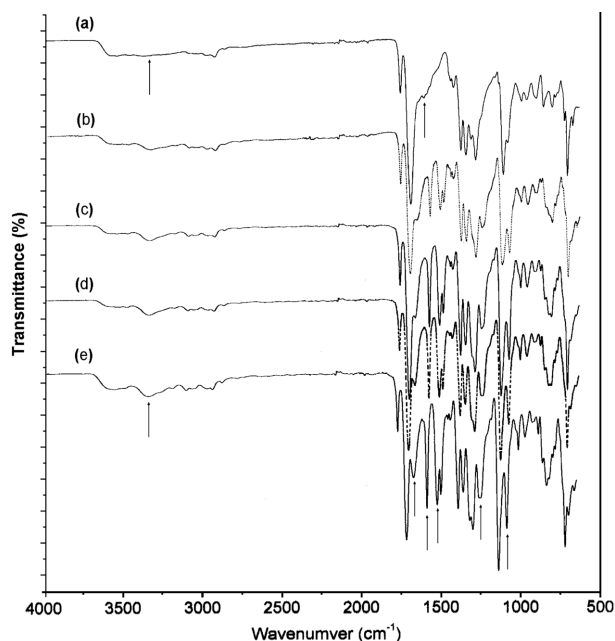


Figure 2. Superimposed FTIR spectra of (a) **6**; (b) **7**; (c) **9**; (d) **10**; (e) **12**.

analysis also supported the formation of polymers **6-12** and matched well with the calculated data.

Solubility. The solubility of the poly(imide-aramid-sulfone)s was investigated using various common organic solvents as listed in Table 2. With an increasing ratio of **2** to DVS, the solubility gradually decreased. Most polymers were soluble in polar aprotic solvents such as NMP, DMF, sulfolane, and DMSO but insoluble in toluene, chloroform, and ethanol. However, polymers **6-9** exhibited solubility in THF upon slight heating. In a comparison of the chemical structures of polymers **6** and **12**, we noticed that **10**, **11**, and **12** had high contents of amide linkages, which possibly caused the lack of

Table 3. Thermal Analysis Data of Various Poly(imide-sulfone)s Prepared from Various Content of DVS and **2**

Polymers	Properties	T_{ID}^a	T_{exo} or T_{endo}^b	$T_{10\%}^c$	Char residue(%)	
					(°C)	450 °C
6		315	258	365	37	28
7		318	300	338	53	39
8		320	332	325	55	42
9		325	329	360	56	43
10		326	335	362	56	45
11		326	385	369	57	49
12		350	-	400	56	45

^aInitial decomposition temperature. ^bTransition temperature obtained from exotherm or endotherm. ^cTemperature showing a 10% of weight loss.

solubility in solvent.

This indicates a strong inter- or intramolecular dipole interactions in the polymer chain caused by the polar sulfone and imide groups. Polymers **8-11** were more soluble in NMP/LiCl salt solution than in NMP only since the lithium salt destroyed the strong hydrogen bonds between the amide unit-containing polymer chains.

Thermal Properties. Differential scanning calorimetry was used to characterize the thermal behaviors of the poly(imide-aramid-sulfone)s prepared in this experiment. The DSC and TGA data are summarized in Table 3.

Figure 3 shows the DSC and TGA thermograms of polymer **6** and its resembling model compound **4**. Model compound **4** showed an apparent endothermic peak at 250 °C as shown in Figure 3(a), followed by an abrupt decomposition around 350 °C. Especially, polymer **6** obtained from DVS and pyromellitic diimide without an amide unit showed a partial melt-

Table 2. Solubility of Various Poly(imide-aramid-sulfone)s Obtained from Various Content of DVS and **2**

Polymers	Solvents							
	DMF ^a	DMSO ^b	NMP ^c	Chloroform	EA ^d	AN ^e	THF ^f	Methanol
6	○	○	○	△	△	○	○	X
7	○	○	○	X	X	○	○	X
8	○	○	○	X	X	△	△	X
9	○	○	○	X	X	△	△	X
10	△	○	○	X	X	X	X	X
11	△	△	△	X	X	X	X	X
12	△	X	X	X	X	X	X	X

○: Good soluble. △: Medium. X: Insoluble. ^a*N,N*-Dimethylformamide. ^bDimethyl sulfoxide. ^c*N*-Methylpyrrolidinone. ^dEthyl acetate. ^eAcetonitrile. ^fTetrahydrofuran.

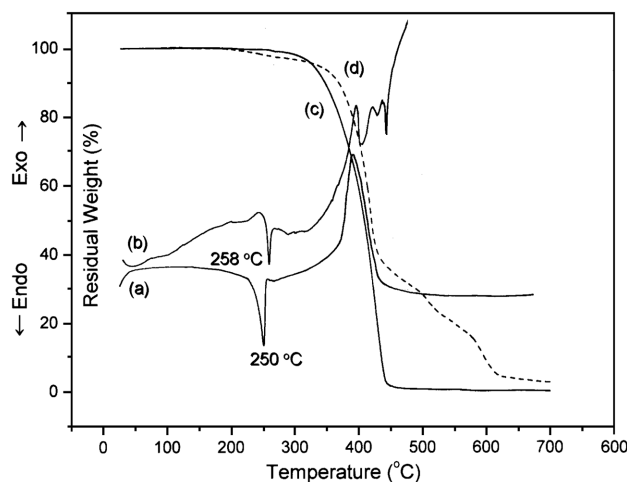


Figure 3. DSC thermograms of (a) model compound **4**; (b) polymer **6**; TGA traces of (c) model compound **4**; (d) polymer **6**.

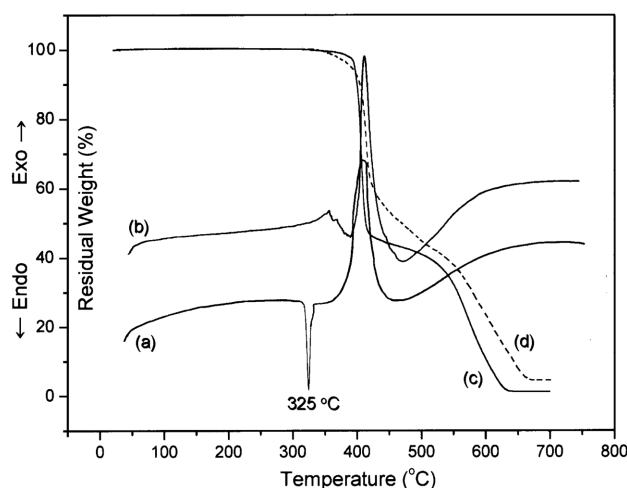


Figure 4. DSC thermograms of (a) model compound **5**; (b) polymer **12**; TGA traces of (c) model compound **5**; (d) polymer **12**.

ing temperature of 258 °C (Figure 3(b)), which was coincident with the melting temperature determined in a capillary tube, and a multi-stage decomposition profile, whereas model compound **4** showed only a one-stage decomposition as shown in Figure 3(c) and (d). This finding indicates that polymer **6** possessed a high portion of ethylene units in its main chain.

In its DSC curve, a melting temperature of 325 °C for model compound **5** was observed, whereas polymer **12** showed little weight loss at a temperature of 350 °C (Figure 4(a) and (b)). Polymer **12** derived from **2** showed a multi-stage decomposition behavior and began to lose weight at 350 °C in nitrogen as shown in Figure 4(c). Model compound **5** showed a two-stage decomposition in the TGA thermogram, which was due

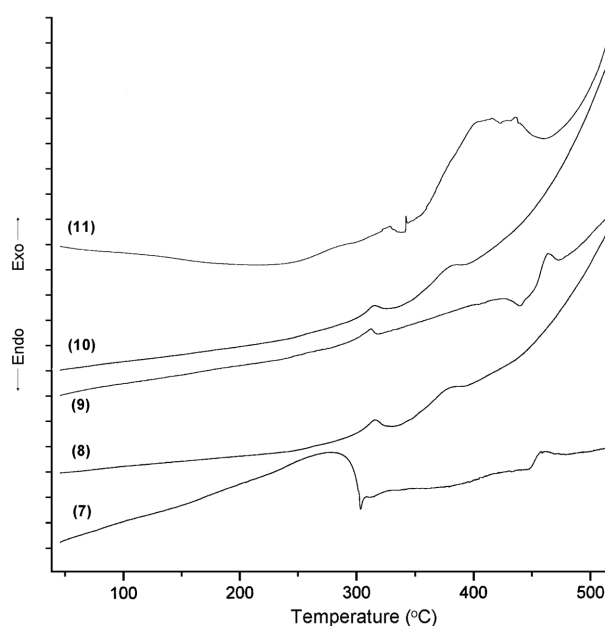


Figure 5. DSC thermograms of poly(amide-sulfone)s: (a) **7**; (b) **8**; (c) **9**; (d) **10**; (e) **11**.

to the existence of both alkylene units and a rigid amide moiety.

In a series of polymers, DSC endotherm indicating melting temperature was observed in polymer **7** at 300 °C, but it was not strong as shown in Figure 5. In the second heating, no glass transition and melting temperatures were observed, even though enough time was given to cool in air. These results imply that polymers **8-11** formed an amorphous solid directly after the first heating, and thus a high portion of amorphous domains existed in the polymer texture. The absence of sharp reflection between 10° and 90° is an evidence of the non-crystalline state in the X-ray diffraction. More experiments are needed to understand the cause of the thermal transition observed for the polymer. Higher transition temperatures were expected for the polymers incorporating amide units, but polymers **8-12** did not show glass transition temperatures.

Thermal stability data are listed in Table 3 and TGA traces in Figure 6. At about 400 °C, detectable weight loss of the polymer was observed. The initial decomposition temperature (T_d , 300–350 °C) exhibited a similar trend regardless of the chemical structure of polymers **6-9**. Polymers **6-9** sustained 10% weight loss at 365, 338, 325, and 360 °C at a heating rate of 10 min⁻¹, and their residual weights ranged from 37 to 56% at 450 °C in nitrogen as shown in Figure 6. On the other hand, polymers **10-12** showed higher than 10% weight loss compared to those of alkyl polysulfone-based polymers **6-9**. Polymers **10-12** gave residual weights varying from 45 to 49% at

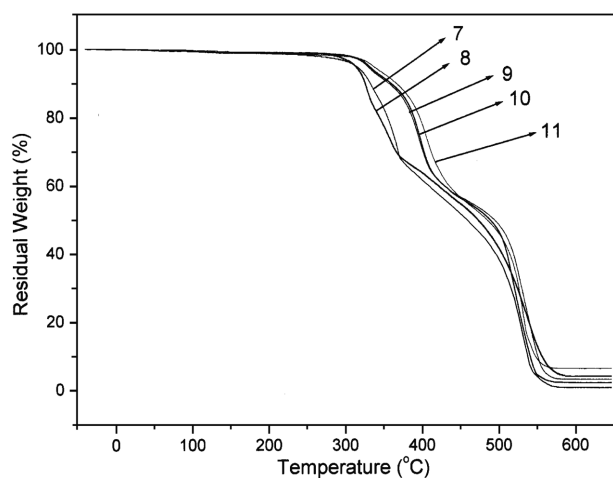


Figure 6. TGA thermograms of poly(amide-sulfone)s: (a) **7**; (b) **8**; (c) **9**; (d) **10**; (e) **11**.

500 °C in nitrogen as shown in Table 3 and Figure 6. The thermal stabilities of **10-12** were superior to those of polymers **6-9**, which was due to the rigid aromatic amide moieties.

Conclusions

A series of novel poly(imide-aramid-sulfone)s were synthesized from DVS and *N,N'*-bis(4-(vinylsulfonyl)phenyl)terephthalamide (**2**) monomers and pyromellitic diimide by introducing a pyromellitic diimide group into the backbone chain via Michael-type addition polymerization. This reaction is a facile and simple method for the preparation of polyimide and gave various poly(imide-aramid-sulfone)s with moderate molecular weights and good yields. The poly(imide-aramid-sulfone)s showed high solubility in common organic solvents such as NMP, DMF, DMAc, and THF as well as good thermal stability with 28~49% of residual weight at 500 °C.

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