

Aromatic Imide 구조를 갖는 Polysulfonates의 연구. (제 2 보). N,N'-Bis(hydroxyphenyl) diimides에 의한 Wholly Aromatic Poly(imide-sulfonate)s의 합성 및 특성 고찰

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Polysulfonates Containing Aromatic Imides. II. Synthesis and Properties of Wholly Aromatic Poly(imide-sulfonate)s derived from N,N'-Bis (hydroxyphenyl) diimides

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요약 : N,N'-bis(hydroxyphenyl)pyromellitic diimides 혹은 N,N'-bis(hydroxyphenyl)-3,3', -4,4'-benzophenonetetracarboxylic diimides를 aromatic disulfonyl chlorides와 반응하여 imide linkage를 갖는 wholly aromatic polysulfonates를 합성하였다. 얻어진 폴리머의 inherent viscosity는 0.25-0.35dl/g의 값을 가졌으며, DMF나 DMSO와 같은 극성용매에 녹았다. 이들 poly(imide-sulfonate)s는 TGA분석결과 335-365°C에서 10%중량감소가 일어났으며 비교적 우수한 열안정성을 나타내었다. 또한 500°C에서의 잔여 중량비율은 62-72%로서 폴리머내의 디이미드성분의 중량비율과 거의 일치하였다.

Abstract: Wholly aromatic polysulfonates containing imide linkages were synthesized from N,N'-bis(hydroxyphenyl) pyromellitic diimides or N,N'-bis(hydroxyphenyl)-3,3', 4,4'-benzophenonetetracarboxylic diimides and aromatic disulfonyl chlorides. The resulting polymers had inherent viscosities in the range of 0.25-0.35dl/g and were soluble in polar solvents such as DMF and DMSO. These poly(imide-sulfonate)s revealed relatively good thermal stability. TGA data showed 10% weight losses at 335-365°C and residual weights at 500°C were about 62-72% that were almost correspondent to weight percentages of diimide components in the polymer.

properties.

Introduction

Thermostable polymers such as polybenzimidazoles¹, polyamides², polyimides³, polysulfonamides⁴ and polysulfonates⁵ have been the subject of research for a number of years. Most of the reported polysulfonates^{6,7} were obtained by interfacial polycondensation of diphenols or bisphenol A derivatives with disulfonyl chlorides. However, few have reported polysulfonates containing imide linkages.

In a previous article⁸, we have reported the synthesis of poly(imide-sulfonate)s from N,N'-bis(hydroxyalkyl) diimides and investigated some properties.

It'll be worth while to examine wholly aromatic polysulfonates containing imide linkages that are expected to exhibit good thermal stability. Therefore, the present work was undertaken to synthesize wholly aromatic poly(imide-sulfonate)s by the reaction of N,N'-bis(hydroxyphenyl)pyromellitic diimides or N,N'-bis(hydroxyphenyl)-3,3', 4,4'-benzophenonetetracarboxylic diimides with aromatic disulfonyl chlorides[eq. (1)] and to study some of their

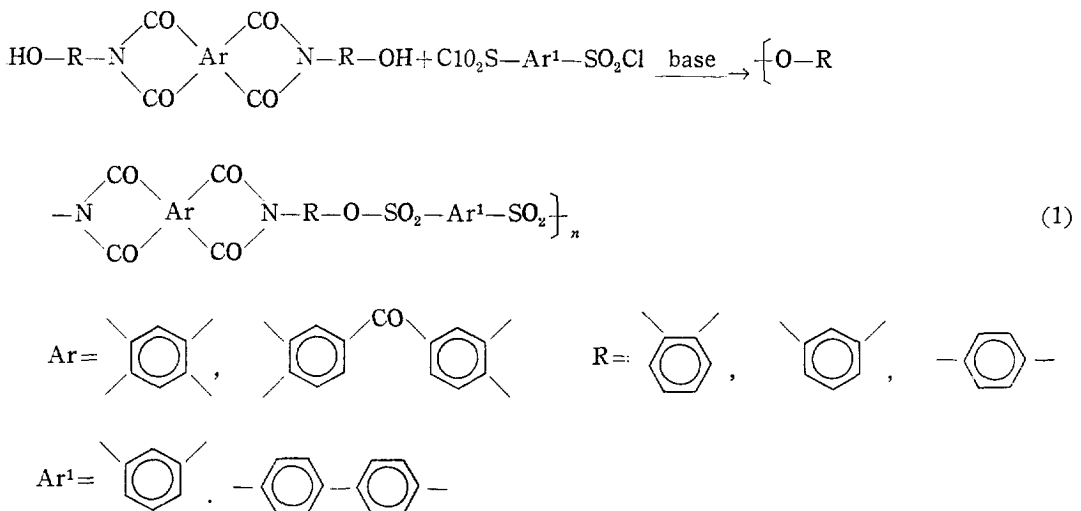
Experimental

Materials

Pyromellitic dianhydride(PMDA) was purified by recrystallization from methyl ethyl ketone; mp 286°C. 3,3', 4,4'-Benzophenonetetracarboxylic dianhydride(BPDA) was purified by sublimation at 260-270°C/1 mmHg; mp 206-207°C. o-Aminophenol and p-aminophenol were recrystallized from ethanol; mp 176°C and 190°C, respectively. m-Aminophenol was recrystallized from toluene; mp 122-123°C. m-Benzenedisulfonyl chloride(MBSC) was purified by recrystallization from n-hexane; mp 62-63°C. 4,4'-Biphenyldisulfonyl chloride(BPSC) was recrystallized from ligroin; mp 205-207°C. All the solvents used were purified in the usual manner⁹.

Preparation of N, N'-Bis (hydroxyphenyl) diimides

N,N'-Bis (hydroxyphenyl)pyromellitic diimides and N,N'-bis(hydroxyphenyl)-3,3', 4,4'-benzophenonetetracarboxylic diimides were prepared from PMDA (or BPDA) and corresponding aminophenol according to the same pro-



cedure that of N,N'-bis(hydroxyalkyl)diimides described in previous article⁸. The results are as follows.

N,N'-Bis(2-hydroxyphenyl)pyromellitic Diimide (I). 75%, light yellow platelets, mp; 400°C (dec.) IR (KBr); 3500-3200 (ν_{OH}) 3040 (ν_{CH} ; aromatic) 1770 and 1700 (imide I bands due to $\nu_{C=O}$ of imide) 1380 (imide II band due to axial stretching of imide ring) 1100 (imide III band due to transverse stretching of imide ring) ¹H NMR(DMSO- d_6); δ 6.90-7.50(m, 8H, N-Ph-O) 8.40 (s, 2H, imide-Ph) 10.1 (s, 2H, OH), Anal. Calcd for C₂₂H₁₂N₂O₆; C(66.00) H(3.02) N(7.00). Found C(65.82) H(2.91) N(6.84), lit¹⁰: 72.5%, mp 402-403 (dec.).

N,N'-Bis(3-hydroxyphenyl)pyromellitic Diimide (II). 56%, pale yellow platelets, mp; 425°C (dec.) IR(KBr); 3500-3200(ν_{OH})3040 1770 and 1700(imide I) 1370 (imide II)1100(imide III), ¹H NMR(DMSO- d_6); δ 6.80-7.40(m, 8H,N-Ph-O) 8.20 (s, 2H, imide-Ph) 9.73(s, 2H, OH), Anal. Calcd for C₂₂H₁₂N₂O₆; C(66.00) H(3.20) N(7.00). Found C(66.16) H(3.19) N(6.86), lit¹¹: 41%, 425-427°C(dec.).

N,N'-Bis(4-hydroxyphenyl)pyromellitic Diimide (III). 50%, pale yellow platelets, mp; 495-497(dec.), IR (KBr); 3500-3200(ν_{OH}) 3060 1700(imide I) 1400 (imide II) 1120(imide III), ¹H NMR(DMSO- d_6); δ 5.70-7.23(quant, 8H, N-Ph-O) 8.17(s, 2H, imide-Ph) 9.70(s, 2H,OH), Anal. Calcd for C₂₂H₁₂N₂O₆; C(66.00) H(3.02) N(7.00). Found C(66.18) H(3.16) N(7.16).

N,N'-Bis(2-hydroxyphenyl) -3, 3', -4, 4'- benzophenonetetracarboxylic Diimide (IV). 74%, light greenish yellow platelets, mp; 348°C, IR (KBr); 3500-3400(ν_{OH}) 3060 1780 and 1700

(imide I) 1650($\nu_{C=O}$ of ketone) 1380(imide II) 1100(imide III), ¹H NMR(DMSO- d_6); δ 6.73-7.37 (m, 8H, N-Ph-O) 8.13(s, 6H,imide-Ph) 9.77 (s, 2H, OH), Anal. Calcd for C₂₉H₁₆N₂O₇; C(69.03) H(3.20) N(5.58). Found C(68.90) H(3.34) N(5.77).

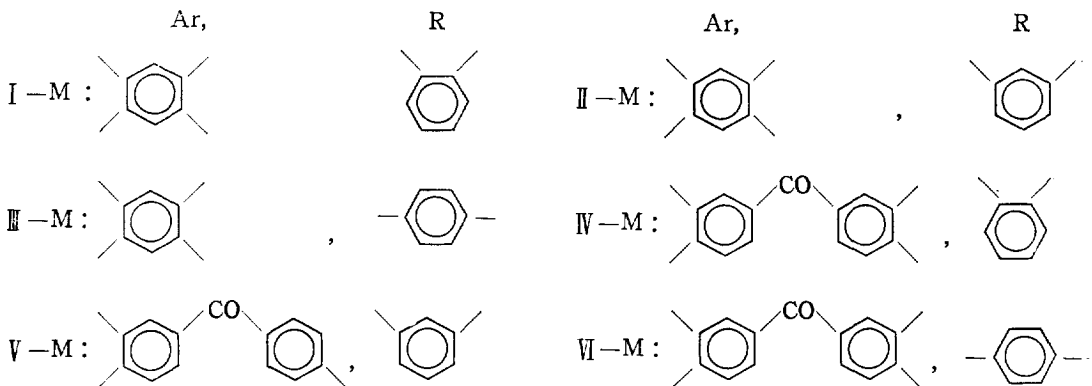
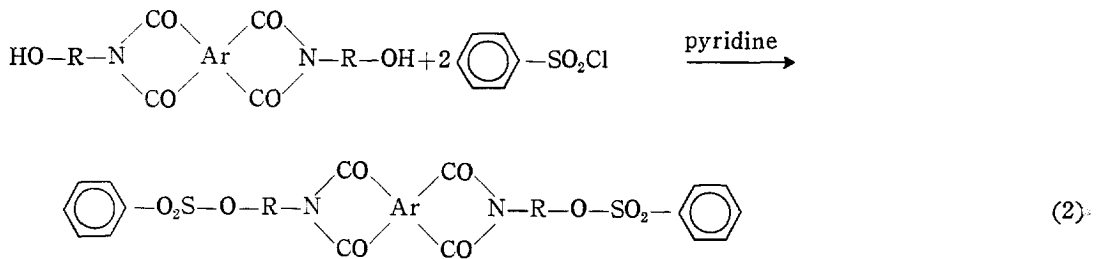
N,N'-Bis(3-hydroxyphenyl) -3, 3', 4, 4'-benzophenonetetracarboxylic Diimide (V). 56%, light yellow plate lets%, mp; 361°C, IR (KBr); 3500-3200(ν_{OH}) 3050 1770 and 1700 (imide I) 1670($\nu_{C=O}$) 1390(imide II) 1100 (imide III), ¹H NMR(DMSO- d_6); δ 6.73-7.63 (m, 8H, N-Ph-O) 8.22(s, 6H, imide-Ph) 9.70 (s, 2H, OH), Anal. Calcd for C₂₉H₁₆N₂O₇; C(69.03) H(3.20) N(5.58). Found C(69.21) H(3.01) N(5.46).

N,N'-Bis(4-hydroxyphenyl) -3, 3', 4, 4' -benzophenonetetracarboxylic Diimide(VI). 44.%, pale yellow platelets, mp; 432°C(dec.), IR(KBr); 3500-3200(ν_{OH}) 3060 1780 and 1700 (imide I) 1660($\nu_{C=O}$) 1390(imide) 1120(imide III), ¹H NMR(DMSO- d_6); δ 6.83-7.53(m, 8H, N-Ph-O) 8.33(s, 6H, imide-Ph) 9.90(s, 2H, OH), Anal. Calcd for C₂₉H₁₆N₂O₇; C(69.03) H(3.20) N(5.58). Found C(68.94) H(3.37) N(5.65).

Polymerization

A typical procedure for the synthesis of wholly aromatic poly(imide-sulfonate)s is as follows. In a flask equipped with a stirrer, 0.800g(2.0 mmole) of diimide II was dissolved in 50ml of pyridine at 80°C. While stirring, 0.550g(2.0 mmole) of MBSC was added and the mixture was stirred at the same temperature for 24hr. The polymer was precipitated by pouring the polymerized mixture into 500ml of cold isopropyl alcohol and the resulting polymer was filtered. The filtered product wa

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then washed several times with isopropyl alcohol and chloroform. The crude product was precipitated twice from pyridine solution by addition of isopropyl alcohol, washed again and finally dried in vacuo at 60°C for 24hr. The yield of dark brown powdery polymer was 0.734g(61%). The inherent viscosity determined at a concentration of 0.5g/dl in m-cresol at 30°C was 0.34dl/g.

Results and Discussion

Model Reactions

Model compounds were prepared by condensation reaction of diimides with benzenesulfonyl chloride [eq. (2)] to confirm the reactivity of the hydroxy group of the imide to sulfonyl chlorides.

Table I. Model Compounds

Model Compound	Color	Yield (%)	mp (°C)	Calcd			Found		
				C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
I-M	LB	59	264	60.00	2.96	4.12	60.17	3.18	4.32
II-M	LB	62	273	60.00	2.96	4.12	60.14	2.78	3.96
III-M	— ^a	—	—	60.00	2.96	4.12	—	—	—
IV-M	LB	65	300	62.75	3.08	3.57	62.61	3.21	3.73
V-M	LB	71	231	62.75	3.08	3.57	62.59	2.94	3.41
VI-M	—	—	—	62.75	3.08	3.57	—	—	—

^a Could not be obtained

Abbreviations LB: light brown

These model compounds were also expected to identify the sulfonate linkage of the polymers. The model reaction was carried out with 2.0mmole of corresponding diimide and 4.0m mole of benzenesulfonyl chloride in 50ml of pyridine at 80°C for 24hr. The product was precipitated by pouring the reaction mixture into 500ml of cold isopropyl alcohol, followed by filtration. The filtered product was washed several times with isopropyl alcohol and chloroform. The crude product was precipitated again from pyridine solution by addition of isopropyl alcohol to remove unreacted diimide and washed again. The model compound was

Table II. IR and ¹H NMR Spectra of Model Compounds

Model Compound	IR(KBr) absorption bands (cm ⁻¹) and ¹ H NMR (DMSO-d ₆) peaks (δ: ppm)
I—M	IR; 3100-3040(ν _{C-H} : aromatic)1780 and 1730 (imide I bands) 1380 (imide II) 1180 (ν _{S=O}) 1110 (imide III) ¹ H NMR; 7.20-7.80(br, 18H, N-Ph-O and SO ₂ -Ph)8.23 (S, 2H, imide-Ph)
II—M	IR; 3080-3060 1780 and 1720 1370 1190(ν _{S=O}) 1100 ¹ H NMR; 7.00-8.07(m, 18H, N-Ph-O and SO ₂ -Ph) 8.32(S, 2H, imide-Ph)
IV—M	IR; 3100-3040 1780 and 1730 1670 (ν _{C=O} of ketone) 1200(ν _{S=O})1100 ¹ H NMR; 7.10-7.70 (m, 18H, N-Ph-O and SO ₂ -Ph)7.83-8.33(m, 6H, imide-Ph)
V—M	IR; 3100-3060 1780 and 1725 1670 1370 1220(ν _{S=O}) 1100 ¹ H NMR; 6.87-7.98(m, 18H, N-Ph-O and SO ₂ -Ph) 8.00-8.17(br, 6H, imide-Ph)

Abbreviations; s: singlet, m: multiplet, br: broad.

then dried in *vacuo* at 60°C for 24hr. The results of model reactions are summarized in Table I.

Diimide III and VI produced no model compounds probably due to the poor solubility, i.e. about 800ml of pyridine was required to dissolve 2.0mmole(0.800g and 1.008g, respectively) of each diimide. All other diimides underwent homogeneous reactions. Relatively poor yields of model compounds were probably due to low nucleophilicity of these diimides. Model compounds were soluble in hot DMF, dimethylsulfoxide(DMSO) and m-cresol. As mentioned in previous article ^{8,12}, these model compounds were also susceptible to hydrolytic cleavage by a small amount of water. IR spectra of model compounds showed similar band pattern in imide and sulfonate regions. The most characteristic absorption bands of imide were found at 1780-1770cm⁻¹, and 1730-1700cm⁻¹ (imide I bands) and that of sulfonate at 1220-1180cm⁻¹(symmetric S=O stretching). No hydroxy group absorption band or peak was observed in IR and ¹H NMR spectra. The IR and ¹H NMR spectral data are listed in Table II.

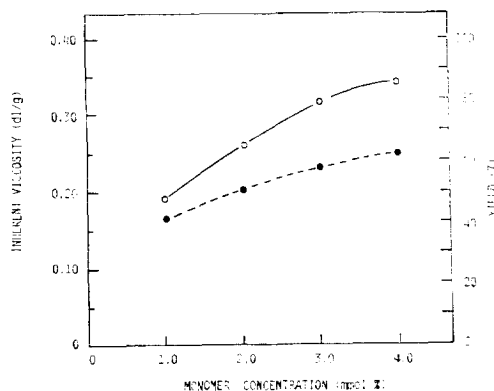


Fig. 1. Effect of monomer concentration on inherent viscosity and yield; inherent viscosity: (○—○), yield:d:(●—●) Polycondensation was carried out with diimide II and MBSC in pyridine at 80°C for 24hr.

Aromatic Imide 구조를 갖는 Polysulfonates의 연구. (제2보). N,N'-Bis(hydroxyphenyl) diimides에 의한 Wholly Aromatic Poly(imide-sulfonate)s의 합성 및 특성 고찰

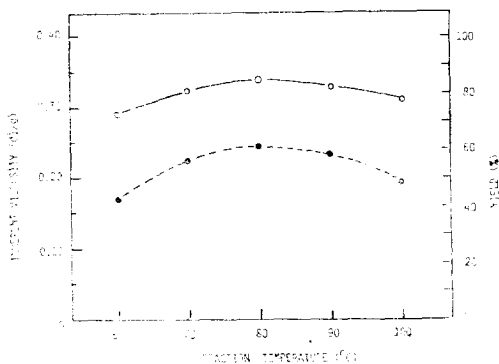


Fig. 2. Variations of inherent viscosity and yield with reaction temperature; inherent viscosity: (○—○), yield: (●—●). Polycondensation was carried out with 2.0 mmole of diimide II and MBSC in 50ml of pyridine for 24hr.

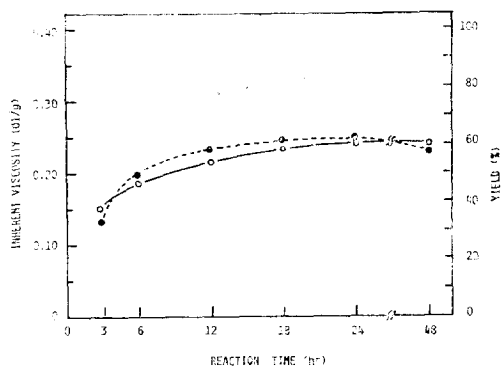


Fig. 3 Extent of polymerization and yield versus reaction time; Extent of polymerization: (○—○), yield: (●—●). Polymerization was carried out with 2.0 mmole of diimide II and MBSC in 50 ml of pyridine at 80°C.

In order to determine an adequate solvent and acid acceptor for the synthesis of wholly aromatic poly(imide-sulfonate)s, polycondensation of diimide II with MBSC was carried out under various conditions: in an aprotic polar solvent such as DMSO, DMF, N,N-dimethylacetamide(DMAC) or pyridine and in the presence

of acid acceptor such as pyridine or triethylamine at 80°C. As was discussed in previous article³, the test results revealed that pyridine which acted as a solvent and acid acceptor was superior to others. Also, polymerization in amide type solvents produced on polymer.

Figure 1 illustrates the effect of concentration of the reactant on inherent viscosity and yield. Maximum solubility of diimide II in pyridine at 80°C was about 5.0 mmole percent. Therefore, the test was carried out in the range of 1.0-4.0 mmole percent. The preferred concentration for this type of polycondensation reaction was around 4.0mmole percent.

As shown in Figure 2, adequate reaction temperature was about 80°C. The lower temperature should reduce the polymerization rate. Although polymer solubility and reaction rate

Table III. Poly(imide-sulfonate)s^a

Polymer	Diimide	Disulfonyl chloride	Color	Yield (%)	η_{inh}^b (dl/g)
I-a	I	MBSC	brown	45	0.29
I-b	I	BPSC	brown	56	0.25
II-a	II	MBSC	dark brown	61	0.34
II-b	II	BPSC	dark brown	64	0.31
III-a	III	MBSC	— ^c	—	—
III-b	III	BPSC	—	—	—
IV-a	IV	MBSC	brown	62	0.30
IV-b	IV	BPSC	brown	67	0.27
V-a	V	MBSC	white	71	0.35
V-b	V	BPSC	light brown	74	0.32
VI-a	VI	MBSC	—	—	—
VI-b	VI	BPSC	—	—	—

^a Polymerization was carried out with 2.0 mmole of each monomer in 50ml of pyridine at 80°C for 24hr.

^b Measured at a concentration of 0.5g/dl in m-cresol at 30°C.

^c Could not be obtained.

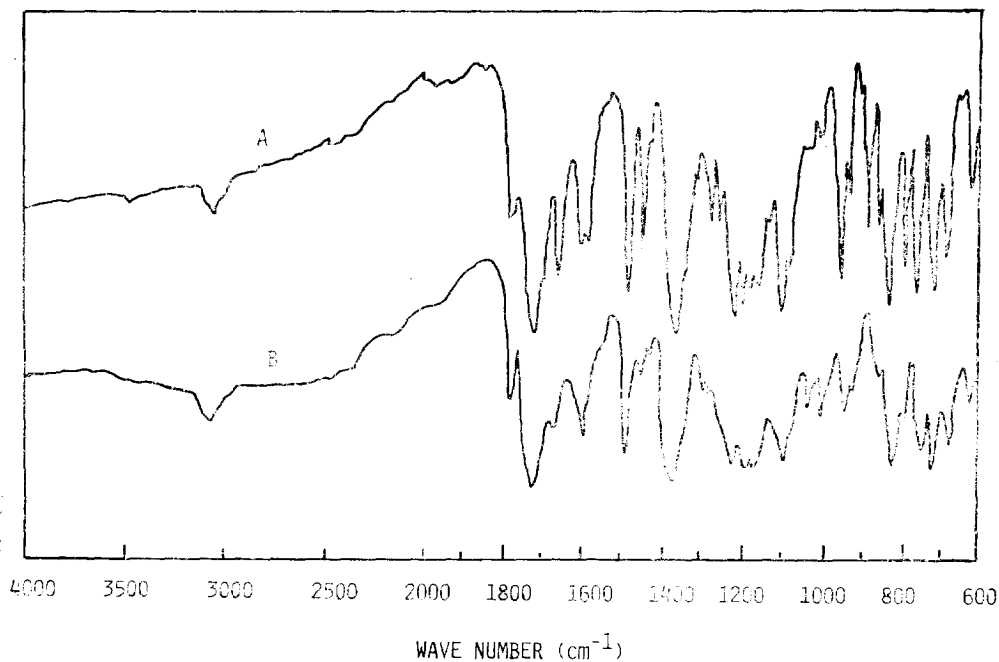


Fig. 4. Infrared spectra of the model compound and polymer; (A) model compound V—M (KBr), (B) poly(imide-sulfonate) V—b (KBr).

are expected to increase with the temperature, there is probably a great increase in the rate of side reactions which limit main reaction¹². When the reaction time was longer than 24hr, no remarkable increase in the degree of poly-

Table IV. Solubility^a of Poly(imide-sulfonate)s

Polymer	Solvent						
	DMF	DMSO	S.A	AcOH	THF	CH ₂ Cl ₂	MeOH
I—a	++	++	++	—	—	—	—
I—b	+-	+	++	—	—	—	—
II—a	+	++	++	—	—	—	—
II—b	+	+	+	—	—	—	—
IV—a	++	++	+	—	—	—	—
IV—b	+	++	+	—	—	—	—
V—a	+	++	+	—	—	—	—
V—b	+	++	+	—	—	—	—

^a ++ : soluble, + : soluble by heating, + : partially soluble, — : insoluble.

Abbreviations; S.A: concentrated sulfuric acid, AcOH: glacial acetic acid, MeOH: methanol.

merization was observed as illustrated in Figure 3.

On the basis of these results, polycondensation of the other diimides was carried out with MBSC or BPSC in pyridine at 80°C for 24hr. The concentration of each reactant was 4.0 mmole percent (ie, 2mmole of each rea-

Table V. Thermal Stability^a of Poly(imide-sulfonate)s

Polymer	5% Weight loss (°C)	10% Weight loss (°C)	RW ^b at 500°C
I—a	269	352	64.7
I—b	291	353	62.7
II—a	287	350	64.9
II—b	289	335	62.4
IV—a	226	327	71.4
IV—b	280	342	66.6
V—a	296	365	70.7
V—b	284	356	68.8

^a observed in TGA in nitrogen (5°C/min)

^b Residual weight

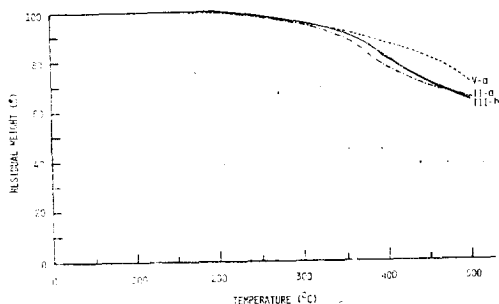


Fig. 5. TGA curves of poly(imide-sulfonate)s; polymer II-a, II-b and V-a in nitrogen (5°C/min).

ctant was dissolved in 50ml of pyridine). As expected from the result of model reactions, diimide III and VI gave no polymers. The results are summarized in Table III. The inherent viscosities were in the range of 0.25–0.35 dl/g. The structures of the polymer obtained were identified by IR spectroscopy and spectra of wholly aromatic poly(imide-sulfonate)s were quite similar to those of the model compounds. Strong absorption bands appeared at 1780–1770 cm^{-1} , and 1730–1700 cm^{-1} (imide I bands) and at 1220–1180 cm^{-1} (symmetric stretching of S=O). No detectable hydroxy absorption band was observed. Figure 4 shows the IR spectra of model compound V–M and poly(imide-sulfonate) V–b.

Properties of the Poly(imide-sulfonate)s

Solubility of the wholly aromatic poly(imide-sulfonate)s was determined for powdery samples in excess solvent. These polymers were soluble in polar solvents such as DMF, DMSO and *m*-cresol. The solubility data are listed in Table IV.

The thermal stability of these wholly aromatic poly(imide-sulfonate)s was evaluated by

thermogravimetric analysis(TGA) in nitrogen. Typical TGA curves are shown in Figure 5 and thermal stability data are summarized in Table V. 10% weight losses and residual weights at 500°C of these polymers were at 335–365°C and in the range of 62–72% of the original weight. As for the diimide components, 3,3', 4,4'-Benzophenonetetracarboxylic diimides produced more thermally stable polymers than pyromellitic diimides.

The residual weights of poly(imide-sulfonate)s obtained from MBSC were almost correspondent to the weight percentages of diimide components. For example, the residual weight of polymer II-a was 64.9% which is almost equal to the weight percentage of diimide component(66.1%). However, slight deviations between these two values were observed in polymers derived from BPSC. The residual weight of polymer III-b were 68.8% and weight percentage of diimide component is 64.2%. This difference is probably due to the contribution of BPSC on residual weight.

In thermogravimetric analysis, MBSC was completely exhausted above 426°C. However, residual weight of BPSC at 500°C was 16.9% and weight percentage of disulfonyl chloride component in polymer V-b is 35.8%. This contributes about 6% to residual weight of the polymer. Hence, estimated residual weight of polymer V-b at 500°C is about 70% which is almost identical to that of observed.

An examination of thermal stability data reveals that wholly aromatic poly(imide-sulfonate)s obtained in this research are more thermally stable than those obtained from N,N'-bis(hydroxyalkyl) diimides described in previous article⁸.

Thus, these wholly aromatic poly(imide-sulfonate)s show relatively good thermal stability.

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