Aromatic Imide구조를 갖는 Polysulfonates의 연구 (제1보). N,N-Bis(hydroxyalkyl)diimides에 의한 Poly(imide-sulfonate)s의 합성 및 특성고찰

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

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요약 : N,N'-Bis(hydroxyalkyl)pyromellitic diimides 및 N,N'-bis(hydroxyalkyl)-3,3', -4,4' -benzophenonetetracarboxylic diimides를 disulfonyl chlorides와 pyridine에서 반응하여 aromatic imide구조를 갖는 polysulfonates를 합성하였다. 이들 poly(imide-sulfonate)s의 구조는 model Compounds와 IR스펙트럼을 비교하여 확인하였으며 1780—1770cm^{-1} 및 1730 —1700cm^{-1}에서 이미드의 특성밴드와 1220—1180cm^{-1}에서 술포네이트의 특성밴드가 나타났다. 얻어진 폴리머는 inherent viscosity가 0.31—0.38 dl/g의 값을 가졌으며 대부분의 유기 용매에 잘 녹지 않았다. 또한 이들 폴리머의 열안정성에 대해서도 조사하였다.

Abstract : A series of polysulfonates containing aromatic imides was synthesized by the reaction of N,N'-bis(hydroxyalkyl)pyromellitic diimides or N,N'-bis(hydroxyalkyl) -3,3',4,4' -benzophenonetetracarboxylic diimides with disulfonyl chlorides in pyridine. The structures of these poly(imide-sulfonate)s were identified by comparison of IR spectra with those of model compounds. Characteristic absorption bands of imide were observed at 1780—1770cm^{-1}, and 1730—1700cm^{-1} and that of sulfonate at 1220—1190cm^{-1}. The inherent viscosities were in the range of 0.31—0.38 dl/g. These polymers were fairly insoluble in common organic solvents. Thermal stability of the polymers was also investigated.

Introduction

Since Thomson[1] reported the synthesis of polysulfonates derived from diphenols, various polysulfonates[2,3] based on diphenols or bisphenol A derivatives have been prepared. And workers[4,5] have studied the synthesis of copolymers using two different functional groups in aminoalcohols or aminophenols. However, few have reported the synthesis of polysulfonates containing aromatic imides.

The present work was undertaken to synthesize poly(imide-sulfonate)s by the reaction of N,N'-bis(hydroxyalkyl)pyromellitic diimides or N,N'-bis(hydroxyalkyl) —3,3', 4,4' -benzophenonetetracatoxylic diimides with disulfonyl chlorides [eq.(1)] and to investigate some of their properties.

Experimental

Materials

Pyromellitic dianhydride(PMDA) was purified by recrystallization from methyl ethyl ketone; mp 286°C. 3,3¹, 4,4¹ -Benzophenanetetracarboxylic dianhydride (BPDA) was purified by sublimation at 260—270°C/1mmHg; mp 206—207°C. 2—Aminoethanol and 3—aminopropanol were purified by distillation under atmospheric pressure; bp 170—171°C and 187°C, respectively.

m-Benzenedisulfonyl chloride (MBSC) was purified by recrystallization from n-hexane; mp 62—63°C. 4,4' -Biphenyldisulfonyl chloride (BPSC) was purified by recrystallization from ligroin; mp 205—207°C.
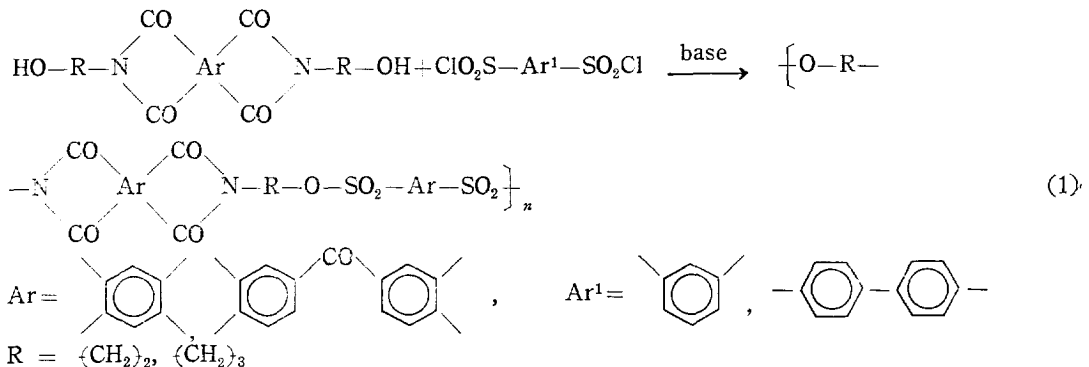
All the solvents used were purified in usual manner.[6]

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

N, N'-Bis(hydroxyalkyl)pyromellitic diimides and N,N'-bis(hydroxyalkyl)—3,3', 4,4'-benzophenonetetracarboxylic diimides were prepared according to the modified process of Mosher's[7] method which described the preparation of aromatic imides. The general reaction procedure is as follows.

A solution of 0.1 mole of PMDA(or BPDA) and 0.2 mole of corresponding aminoalcohol in 200ml of N,N-dimethylformanide (DMF) was refluxed for 4 hr and then cooled to room temperature. The reaction product was crystallized by pouring the reaction mixture into 500ml of water,followed by filtration. The crude product was purified by recrystallization from DMF-benzene mixed solvent, washed several times with water and then dried in *vacuo* at 60°C for 24 hr. The results are summerized in below.

N,N'-Bis (2-hydroxyethyl)pyromellitic Diimide (I). 70%, white platelets, mp; 276°C, IR (KBr); 3500-3200(νOH) 3030(νCH of aromatic) 2940(νCH of aliphatic) 1780 and 1720 (imide I bands due to νC=O of imide) 1390 (imide II

$$\text{HO—R—N} \overset{\text{CO} \quad \text{CO}}{\underset{\text{CO} \quad \text{CO}}{\diagup\diagdown \text{Ar} \diagup\diagdown}} \text{N—R—OH} + \text{ClO}_2\text{S—Ar}^1\text{—SO}_2\text{Cl} \xrightarrow{\text{base}} \left(\text{O—R—} \right.$$

$$\left. \text{—N} \overset{\text{CO} \quad \text{CO}}{\underset{\text{CO} \quad \text{CO}}{\diagup\diagdown \text{Ar} \diagup\diagdown}} \text{N—R—O—SO}_2\text{—Ar—SO}_2 \right)_n \qquad (1)$$

$$\text{Ar} = \bigcirc \quad , \quad \bigcirc\text{CO}\bigcirc \quad , \quad \text{Ar}^1 = \bigcirc \quad , \quad -\bigcirc-\bigcirc-$$

$$\text{R} = (\text{CH}_2)_2, (\text{CH}_2)_3$$

band due to axial stretching of imide ring) 1130 (imide Ⅲ band due to transverse stretching of imide ring) 1050(νC-0), ^{1}H NMR (DMSO-d$_6$); δ3.70 (s, 8H, CH$_2$CH$_2$) 4.93 (s, 2H, OH)8.20 (s, 2H, imide-Ph), Anal. Calcd for C$_{14}$H$_{12}$N$_2$O$_6$; C(55.27) H(3.98) N(9.21). Found C(55.41) H(4.07) N(9.03), lit[3]; 75% mp; 271°C.

N,N'-Bis(3-hydroxypropyl)pyromellitic Diimide (Ⅱ). 73%, white platelets, mp; 240°C, IR (KBr); 3400-3200(νOH) 3040 2920 1770 and 1700 (imide Ⅰ) 1395 (imide Ⅱ) 1130 (imide Ⅲ) 1035 (νC-0), ^{1}H NMR (DMSO-d$_6$); δ1.70 (quint, 4H, C-CH$_2$-C) 3.50 (m, 8H, CH$_2$-C-CH$_2$) 4.27 (t, 2H, OH) 8.10 (s, 2H, imide-Ph), Anal. Calcd for C$_{16}$H$_{16}$N$_2$O$_6$; C(57.83) H(4.85) N(8.43). Found C(57.67) H(4.68) N(8.56).

N,N-Bis(2-hydroxyethyl)-3,3',4,4'-benzophenonetracarboxylic Diimide (Ⅲ). 77%, reddish yellow platelets, mp; 209°C, IR(KBr); 3500-3400 (νOH) 3050 2980 1780 and 1700(imide Ⅰ) 1650 (νC=O of ketone) 1390(imide Ⅱ) 1090 (imide Ⅲ) 1050 (νC-O), ^{1}H NMR (DMSO-d$_6$); 3.57 (s, 8H, CH$_2$ CH$_2$) 5.70 (s, 2H, OH) 8.00 (s, 6H, imide-Ph), Anal. Calcd for C$_{21}$H$_{16}$N$_2$O$_7$; C(61.77) H(3.95) N(6.89). Found C(61.81) H(3.77) N(7.04).

N,N'-Bis(3-hydroxypropyl) -3,3', 4,4'-benzophenonetetracarboxylic Diimide (Ⅳ). 75%, white platelets, mp; 169°C, IR(KBr); 3400-3200 (νOH) 3060 2920 1780 and 1700 (imide Ⅰ) 1650 (νC=O) 1380(imide Ⅱ) 1120 (imide Ⅲ) 1050 (νC-O), ^{1}H NMR (DMSO-d$_6$); 1.72(quint, 4H, C-CH$_2$-C) 3.52(m, 8H, CH$_2$-C-CH$_2$) 8.07 (s, 6H, imide-Ph), Anal. Calcd for C$_{19}$H$_{20}$N$_2$O$_7$; C (63.28) H(4.62) N(6.44). Found C(63.14) H(4.77) N(6.61).

Polymerization

A typical procedure for the synthesis of poly (imide-sulfonate)s is as follows. In a flask equipped with stirrer, 0.608g (2.0mmole) of diimide I was dissolved in 50ml of pyridine at 80°C. While stirring, 0.550g (2.0mmole) of MBSC was added and the mixture was stirred at the same temperature for 24hr. During the polycondensation reaction, polymer was precipitated out. The polymer was filtered and washed several times with chloroform. The crude polmer was extracted with pyridine for 12hr to remove unreacted diimide Ⅰ, followed by filtration. The resulting polymer was washed again and finally dried in *vacuo* at 60°C for 24hr. The yield of white powdery polymer was 0.918g (98%). The inherent viscoity determined

$$ (2) $$
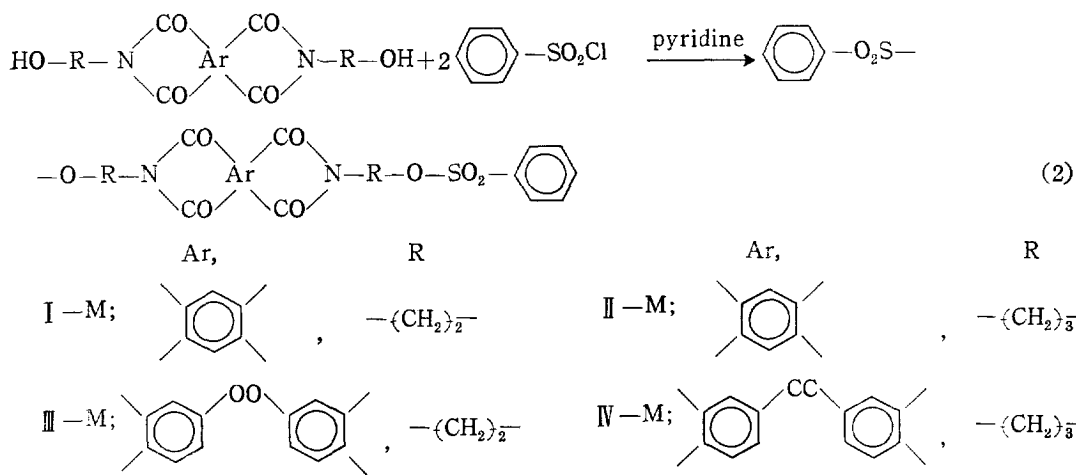
-at a concentration of 0.5g/dl in m-creol at 30°C
-was 0.33dl/g.

Results and Discussion

Model Reactions

To study the general scope of the polycon-
-densation reaction of N,N'-bis(hydroxyalkyl)
diimides and to identify the structures of poly
(imide-sulfonate)s, model compounds were syn-
thesized by condensation reaction of diimides
with benzenesulfonyl chloride (eq. (2)).

The model reaction was carried out with
2.0mmole of corresponding diimide and 4.0
mmole of benzenesulfonyl chloride in 50ml
of pyridine at 80°C for 24hr. The product was
precipitated by pouring the reaction mixture
into 500ml of of cold tetrahydrofuran (THF),
followed by filtration. The filtered product was
washed several times with THF and chloro-
form. The crude product was precipitated ag-
ain from pyridine solution by addition of THF
to remove unreacted diimide and washed ag-
ain. The model compound was then dried in
vacuo at 60°C for 24hr. The results of model
reactions are summerized in Table I.

Diimide III and IV underwent homogeneous
reactions, whereas model compound I —M and
II —M were precipitated out during the cond-
ensation reaction of corresponding diimide. All
model compouds were slightly soluble in dim-
ethylsulfoxide (DMSO), m-cresol, methanol and
acetic acid.

It is noted that sulfonate compounds are re-
adily hydrolyzed[9] and these model compounds
are also susceptible to hydrolytic cleavage by
a small amount of water.

Model compounds showed similar band patt-
ern in imide and sulfonate regions in IR spe-
ctrum. The most characteristic absorption ba-
nds of imide were found at $1780-1770cm^{-1}$,
and $1730-1700cm^{-1}$ (imide I bands) and that
of sulfonate at $1220-1180cm^{-1}$ (symmetric stre-
tching of S=O). No hydroxy group absorption
band or peak was observed in IR and ^{1}H NMR
spectra. The IR and ^{1}H NMR spectral data are
listed in Table II.

In order to determine an adequate solvent
and acid acceptor for the synthesis of poly(im-
ide-sulfonate)s, polymerization of diimide I with
MBSC was carried out in various solvents and
acid acceptors. The viscosity was measured in
distilled m-cresol to prevent hydrolytic cleav-
age of polymers.

The effects of polymerization solvent and
acid acceptor are summerized in Table III. As
shown in Table III, pyridine which acted as
a solvent and acid acceptor was superior to
others with respect to yield and viscosity.

Polycondensation of diimide I in pyridine pro-
ceeded along with polymer precipitation, which
yieldedl imited molecular weight poly(imide-
sulfonate) (ηinh=0.33) despite of the high yield.

When the reaction was carried out in DMF

Table I. Model Compounds

Model Compound	Color	Yield (%)	mp (°C)	Calcd			Found		
				C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
I —M	W	98	261	53.43	3.45	4.79	53.60	3.62	4.96
II —M	W	99	208	54.90	3.95	4.57	54.76	3.83	4.39
III —M	DB	99	180	57.55	3.51	4.07	57.36	3.67	3.91
IV —M	DB	99	143	58.65	3.94	3.91	58.83	3.79	4.06

Abbreviations; W; white, DB; dark brown

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

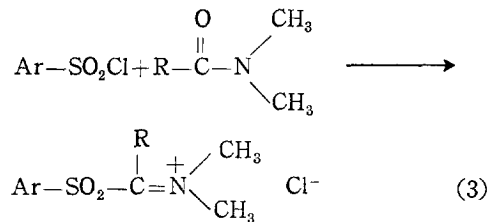| Modle Compound	IR(KBr) absorption bands (cm⁻¹) and ¹H NMR (DMSO-d₆) peaks (δ:ppm)
I —M	IR; 3080(νC-H: aromatic)2940 (νC-H: aliphatic) 1770 and 1720 (imide I bands) 1400(imide Ⅱ) 1200 (νS=0) 1125(imide Ⅲ) 1035(νC-0) ¹H NMR; 4.18 (br, 4H, OCH₂) 4.83 (br,4H, NCH₂) 7.17-7.70(m,10H, SO₂-Ph) 8.17 (s, 2H, imide-Ph)
Ⅱ —M	IR; 3040 2960 1770 and 1720 1400 1180 (νS=0) 1120 1030 ¹H NMR; 3.77(br, 4H,·C-CH₂-C) 4.20-4.93 (br, 8H, CH₂-C-CH₂) 7.13-7.80 (m, 10H, SO₂-Ph) 8.17 (s, 2H, imide-Ph)
Ⅲ —M	IR; 3050 2940 1780 and 1710 1670(νC =0 of ketone) 1395 1190(νS=0) 1120 ¹H NMR; 4.50-5.30 (br, 8H, CH₂CH₂) 7.13-7.70(m, 10H, SO₂-Ph)7.93- 8.33(br, 6H, imide-Ph)
Ⅳ —M	IR; 3060 2940 1770 and 1710 1670 1330 1200 (νS=0) 1120 ¹H NMR; 4.17(br, 4H, C-CH₂-C)4.67 -5.33 (br, 8H, CH₂-C-CH₂) 7.10- 7.70 (m,10H, SO₂-Ph) 7.83-8.17 (br, 6H, imide-Ph)

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

Table Ⅲ. Effect of Solvent and Acid Acceptor in the Polycondensation of Diimide I with MBSCᵃ

Solvent	Acid acceptor	Yield (%)	ηinhᵇ (dl/g)
Pyridine	Pyridine	98	0.33
Pyridine	Triethylamine	46	0.23
DMSO	Pyrridine	47	0.25
DMSO	Triethylamine	37	0.18
DMF	Pyridine	—ᶜ	—
DMAC	Pyridine	—	—

ᵃ Polycondensation was carried out with 2.0m mole of each monomer and 4.0 mmole of acid acceptor in 50ml of solvent at 80°C for 24hr.
ᵇ Determined at a concentration of 0.5g/dl in m-cresol at 30°C.
ᶜ Could not be isolated.

or N,N-dimethylacetamide(DMAC), no polymer was obtained due to the formation of ammonium salts [10,11] of aromatic sulfonyl chloride with N,N-dialkylamides according to eq. (3).

$$Ar-SO_2Cl + R-\overset{O}{\overset{\|}{C}}-N\overset{CH_3}{\underset{CH_3}{\diagup}} \longrightarrow$$

$$Ar-SO_2-\overset{R}{\overset{|}{C}}=\overset{+}{N}\overset{CH_3}{\underset{CH_3}{\diagup}} \quad Cl^- \qquad (3)$$

The use of triethylamine was attempted in place of pyridine, but it appeared less effective as an acid acceptor. It is known that aromatic sulfonyl chlorides react readily with tertiary amine to form sulfonamides and alkyl chlorides[11,12] according to eq.(4). This interfering reaction would lead to chain termination in this type of polycondensation reaction.

$$Ar-SO_2Cl + R_3N \longrightarrow Ar-SO_2N\overset{R}{\underset{R}{\diagup}} + RCl \quad (4)$$
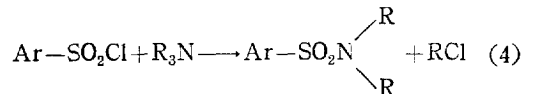
Figure 1 illustrates the effect of concentration of the reactant on the inherent viscosity and yield. The preferred concentration for this solution polycondensation was about 4.0 mmole percent.
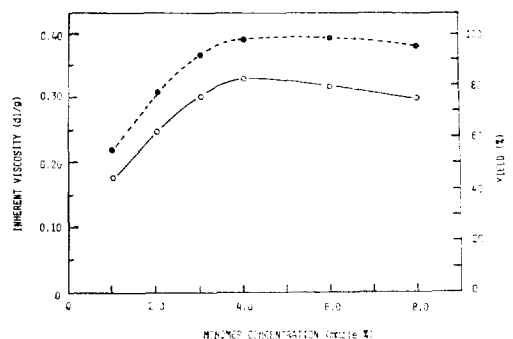

Fig. 1. Effect of monomer concentration on inherent viscosity and yield; inherent viscosity: (0-0), yield: (●······●). Polycondesnation was carried out with diimide I and MBSC in pyridine at 80°C for 24hr.

Aromatic Imide구조를 갖는 Polysulfonates의 연구 (제1보). N,N-Bis(hydroxyalkyl) diimides에 의한 Poly(imide-sulfonate)s의 합성 및 특성고찰
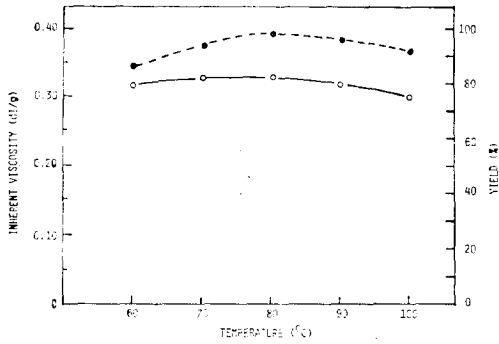

Fig. 2. Variations of inherent viscosity and yield with reaction temperature; inherent viscosity: (0-0), yield:(●···●). Polymerization was carried out with 2.0 mmole of diimide I and MBSC in 50ml of pyridine for 24hr.

As shown in Figure 2, preferred reaction temperature was around 80°C. The lower temperature should reduce the polymerization rate. Although reaction rate is expected to increase with temperature, there is probably a greater increase in the rate of side reactions which limit main reaction.[9]

When the reaction time was longer than 24hr, no appreciable increase in the degree of polymerization was observed as illustrated in Figure 3.
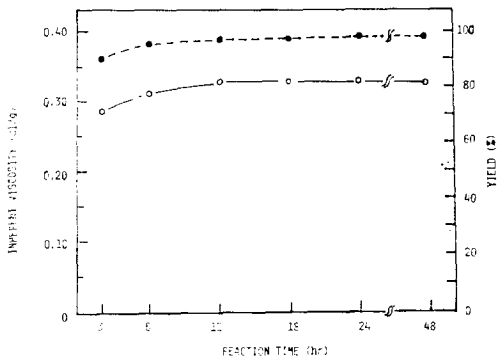
On the basis of these results, polyconden-

Fig. 3. Extent of polymerization and yield versus reaction time; extent of polymerization:(0-0), yield: (●···●). Polycondensation was carried out with 2.0 mmole of diimide I and MBSC in 50ml of pyridine at 80°C.

Table Ⅳ. Poly (imide-sulfonate)s[a]

Polymer	Diimide	Disulfonyl chloride	Color	Yield (%)	ηinh[b] (dl/g)
I —a	I	MBSC	white	98	0.33
I —b	I	BPSC	light yellow	98	0.31
Ⅱ—a	Ⅱ	MBSC	white	99	0.37
Ⅱ—b	Ⅱ	BPSC	white	99	0.33
Ⅲ—a	Ⅲ	MBSC	brown	99	0.37
Ⅲ—b	Ⅲ	BPSC	brown	99	0.33
Ⅳ—a	Ⅳ	MBSC	brown	99	0.38
Ⅳ—b	Ⅳ	BPSC	light brown	99	0.35

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

[b] Determined at a concentration of 0.5g/dl in m-cresol at 30°C.

sation 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 m mole percent (i.e. 2.0 mmole of each reactant was dissolved in 50ml of pyridine). As expected from the result of model reactions, all diimides underwent heterogeneous polycondensation reactions. The results are summerized in Table Ⅳ. The inherent viscosities were in the range of 0.31—0.38dl/g. The structures of polymer were identified by IR spectroscopy and spectra of poly(imide-sulfonate)s were quite similar to those of the model compounds. Strong bands appeared at 1780—1770cm⁻¹, and 1730—1700cm⁻¹ (imide I bands) and at 1220—1180 cm⁻¹ (symmetric stretching of s=o). No detectable hydroxy absorption band at 3500—3200cm⁻¹ was observed. Figure 4 shows the IR spectra of model compound I -M and poly(imide-sulfonate) I -b.

Properties of the Poly(imide-sulfonate)s

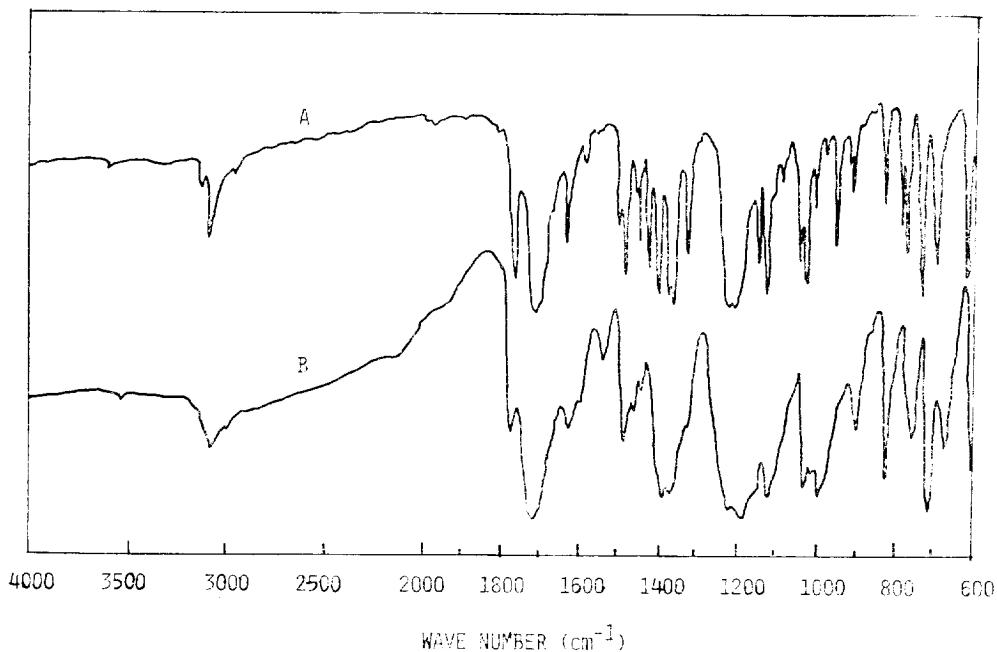Solubility of the poly(imide-sulfonate) was determined for powdery samples in excess sol-

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

Tabl Ⅴ. Solubility[a] of Poly(imide-sulfonate)s

Polymer	Solvent						
	DMF	DMSO	S.A	AcOH	THF	CH₂Cl₂	MeOH
I—a	—	—	++	+	—	—	—
I—b	—	—	+	+	—	—	—
Ⅱ—a	—	—	++	+	—	—	—
Ⅱ—b	—	—	++	+	—	—	—
Ⅲ—a	—	+—	+	+	—	—	—
Ⅲ—b	—	+—	++	+	—	—	—
Ⅳ—a	—	+—	+	+	—	—	—
Ⅳ—b	—	+—	+	+	—	—	—

[a] ∥ : soluble, + : soluble by heating, +— : partially soluble — : insoluble.
Abbreviations; S.A: concentrated sulfuric aicd, AcOH: glacial acetic acid, MeOH: methanol.

vent. The solubility data are listed in Table Ⅴ. As shown in Table Ⅴ, all these polymers were fairly insoluble in common organic solvents.

Table. Ⅵ Thermal Stability of Poly(imide-sulfonate)s[a]

Polymer	5% Weight loss at(°C)	10% Weight loss at (°C)	RW[b] (%)
I—a	217	263	22.4
I—b	248	332	32.3
Ⅱ—a	286	335	29.6
Ⅱ—b	294	330	33.5
Ⅲ—a	215	253	39.2
Ⅲ—b	203	262	45.7
Ⅳ—a	199	250	41.7
Ⅳ—b	193	312	47.7

[a] Observed in TGA in nitrogen (5°C/min).
[b] Residual weight.

Thermal stability of these poly(imide-sulfonate)s were evaluated by thermogravimetric analysis(TGA) in Table Ⅵ. These polymers exhibited 10% weight losses at 253—335°C and the residual weights at 500°C were 22—48%. An examination of the data reveals that BPSC gave more thermally stable poly(imide-sulfo-
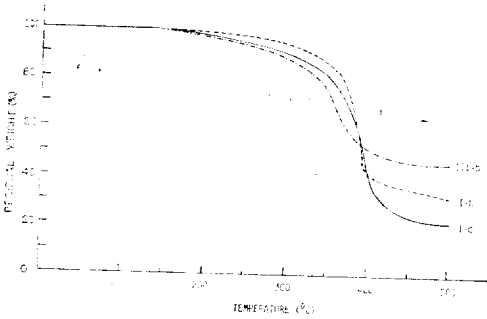
Fig. 5. TGA curves of poly (imide-sulfonate)s; polymer Ⅰ—a, Ⅰ—b and Ⅱ—b in nitrogen (5°C/min)

nate)s than MBSC. As for the diimide components, 3,3′, 4,4′-benzophenonetetracarboxylic diimides produced more thermally stable polymers than pyromellitic diimides.

It'll be worthwhile to examine wholly aromatic polysulfonates containing imide linkages that are expected to exhibit good thermal stability. So, we'll study the synthesis and characterization of wholly aromatic poly(imide-sulfonate)s in later.

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