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Preparation of Amine-Containing Poly(amide-sulfone)s Using Vinylsulfone Reactive Monomers and Their Properties

Young-Min Jeon, Tai-Ho Lim, Soo-Han Kim, Jong-Gyu Kim, and Myoung-Seon Gong*

Department of Chemistry and Institute of Basic Science, Dankook University, Chungnam 330-714, Korea

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Abstract: A series of new, vinyl sulfone-containing monomers was prepared by *p*-aminophenyl vinyl sulfone (**1**) with various acid chlorides such as adipoly chloride, terephthaloyl chloride and isophthaloyl chloride. Finally, tertiary amine-containing poly(amide-sulfone)s were prepared by the Michael-type addition polymerization using *N,N*-dimethylethylenediamine (DMEDA), *p*-phenylenediamine and piperazin. To evaluate the relevant properties for permselective membranes and enzyme substrate, various physical properties such as molecular weight, solubility, quaternization behavior and thermal properties were examined.

Keywords: poly(amide-sulfone)s, vinyl sulfone, Michael addition, tertiary amine.

Introduction

General synthetic procedures for polysulfones, which have been extensively used as biocompatible, immobilized enzymes substrate, solvent-resistant and membrane materials, are prepared by polycondensation[1-3] or polyaddition[4-8] of sulfone monomers. Other pathways for polysulfones include copolymerizations employing sulfur dioxide,[9-11] and oxidation of polysulfides.[12]

It has also been disclosed that tertiary amine-containing polysulfone can be used to prepare composite membranes for separation of CO_2,[13] blood purification,[14] cationic/anionic mosaic membranes for desalination,[15] and pervaporation membranes for purification of ethyl *tert*-butyl ether.[16] Many studies focus on the development of highly permselective membranes for CO_2 separation. In principle, a high CO_2 permselectivity can be achieved by selectively increasing the solubility and/or diffusivity of CO_2 in the membrane. As such, introducing amino groups onto the polymer chains is expected to enhance the CO_2 permselectivity because of the selective weak acid-base interactions between amino groups and CO_2 molecules that could facilitate the permeation of CO_2.

High molecular weight tertiary amine-containing poly (amide-sulfone)s were easily prepared by reacting divinyl sulfone-containing monomers with various diamine derivatives via Mychael-type addition polymerization.[17,18] In this system, three kinds of functional groups such as amide, sulfone and amine group, which contribute to the mechanical properties, permeability, and the active site, respectively, were introduced in the polymer backbone. In this experiment, various physical properties such as molecular weight, solubility, quaternization behavior and thermal properties were examined for the evaluation of new poly(amide-sulfone)s.

*Corresponding Author. E-mail: msgong@dankook.ac.kr

Experimental

Materials. *p*-Aminophenyl vinyl sulfone (**1**) was prepared by reaction of 2-[(4-aminophenyl)sulfonyl]ethyl hydrogen sulfate with NaOH. Adipoyl chloride, terephthaloyl chloride, isophthaloyl chloride, *N,N'*-dimethylethylenediamine (DMEDA), piperazine, triethylamine and *p*-phenylenediamine (Aldrich Chem. Co.) were used as received. THF was dried over sodium and calcium hydride in the presence of benzophenone and was distilled. *N*-Methylpyrrolidinone (NMP) and acetonitrile were dried from molecular sieves and distilled over phosphorus pentoxide. Dimethylsulfoxide (DMSO) and chloroform were used without further purification.

Instruments. Molecular weights were measured with Waters HPLC using three columns (3, 4, and 5Å) by using THF as eluent at 30 °C. Inherent viscosity was determined by Cannon-Ubbelode viscometer in 1.0 g/dL in DMF at 20 °C. FTIR spectra were obtained with a Biorad Excaliber FTS-3000MX spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. DSC measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10 °C/min. TGA measurements were carried out on a Shi-

madzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen.

Preparation of *N,N'*-Bis[4-(vinylsulfonyl)phenyl]adipamide (2). 1 (5.00 g, 27 mmol) and triethylamine (3.03 g, 30 mmol) were dissolved in THF (20 mL) for 20 min under nitrogen atmosphere. Adipoyl chloride (2.37 g, 13 mmol) in THF (10 mL) was added dropwise slowly through dropping funnel. The reaction mixture was continuously stirred at 40 °C for 24 h. The solvent was evaporated and the crude residue was washed with distilled water. The solid product was crystallized in DMSO/chloroform (v/v= 2/1) and dried *in vacuo* at 60 °C. *N,N'*-Bis[4-(vinylsulfonyl)phenyl]terephthalamide (**3**) and *N,N'*-bis[4-(vinylsulfonyl) phenyl]isophthalamide (**4**) were also prepared by the similar method described above.

2: Yield 83%. FTIR (KBr, cm^{-1}) 3362 (N-H), 3060 (aromatic C-H), 2944, 2873 (aliphatic C-H), 1697 (*C=O*), 1588 (-*CH*=*CH*$_2$), 1517, 1395, 1312 (-*SO*$_2$-), 1254, 1138, 1086 (*C-O*, and *C-N*), 970. ^{1}H NMR (DMSO-d_6, ppm) 10.36 (s, 2 H, 2 -N*H*-), 7.80~6.88 (s, 8 H, 2 -NH*Ar*SO$_2$-), 6.21~7.00 (m, 6 H, 2 -C*H*=C*H*$_2$), 2.39 (t, 4 H, 2 -COC*H*$_2$-), 1.62 (m, 4 H, -C*H*$_2$C*H*$_2$-). Anal. Calcd for $C_{22}H_{24}N_2O_6S_2$ (476.57); C, 55.45; H, 5.08; N, 5.88; S, 13.46. Found: C, 55.48; H, 5.05; N, 5.83; S, 13.62.

3: Yield 85%. FTIR (KBr, cm^{-1}) 3362 (N-H), 3105 (aromatic C-H), 1678 (*C=O*), 1588 (-*CH*=*CH*$_2$), 1530, 1401, 1312 (-*SO*$_2$-), 1260, 1144, 1099 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.36 (s, 2 H, 2 -NH-), 7.88~6.88 (s, 12 H, -CO*Ph(p)*CO- and 2 -NH*Ar*SO$_2$-), 6.21~7.02 (m, 6 H, 2 -C*H*=C*H*$_2$). Anal. Calcd for $C_{24}H_{20}N_2O_6S_2$ (496.56); C, 58.05; H, 4.06; N, 5.64; S, 12.91. Found: C, 58.12; H, 4.05; N, 5.63; S, 12.89.

4: Yield 81%. FTIR (KBr, cm^{-1}) 3375, 3105, 3060 (aromatic C-H), 1678 (*C=O*), 1594 (-*CH*=*CH*$_2$), 1523, 1395, 1312 (-*SO*$_2$-), 1247, 1144, 1093 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.36 (s, 2 H, 2 -NH-), 7.90~6.88 (s, 12 H, -CO*Ph(m)*CO- and 2 -NH*Ar*SO$_2$-), 6.20~7.01 (m, 6 H, 2 -C*H*=C*H*$_2$). Anal. Calcd for $C_{24}H_{20}N_2O_6S_2$ (496.56); C, 58.05; H, 4.06; N, 5.64; S, 12.91. Found: C, 58.08; H, 4.08; N, 5.59; S, 12.93.

Representative Polymerization of Vinyl Sulfone-Containing Monomers with Various Diamines. In a round bottomed flask (20 mL) equipped with a condenser and a nitrogen inlet system, placed **3** (1.0 g, 2.09 mmol), DMEDA (0.185 g, 2.09 mmol) dissolved in NMP (10 mL). The solution was maintained at 120 °C for 48 h with vigorous stirring. The reaction mixture was precipitated in distilled water and washed with methanol. The solid product was dissolved in NMP and reprecipitated in methanol. The resulting polymer (**5**) was filtered and dried *in vacuo* at 60 °C. Polymer **6**, **7**, **8**, and **9** were also prepared by the similar method described above.

5: Yield 98%. FTIR (KBr, cm^{-1}) 3331 (*N-H*), 3182, 3120, 2944 (aromatic C-H), 2867, 2803 (aliphatic C-H), 1678 (*C=O*), 1588 (aromatic *C=C*), 1523, 1460, 1395, 1318 (-*SO*$_2$-), 1260, 1138, 1093 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.32 (s, 2 H, 2 -*NH*-), 7.90~6.88 (s, 8 H, 2 -NH*Ar*SO$_2$-), 3.55~2.32 (m, 18 H, 2 -SO$_2$-C*H*$_2$C*H*$_2$N(C*H*$_3$)C*H*$_2$-), 2.62 (m, 4 H, 2 -COC*H*$_2$-), 1.82 (m, 4 H, -C*H*$_2$C*H*$_2$-). Anal. Calcd for $C_{28}H_{36}N_4O_6S_2$ (564.72); C, 55.30; H, 6.43; N, 9.92; S, 11.36. Found: C, 55.25; H, 6.45; N, 9.93; S, 11.39.

6: Yield 97%. FTIR (KBr, cm^{-1}) 3323 (N-H), 3098, 3047, 2938 (aromatic C-H), 2855, 2809 (aliphatic C-H), 1659 (*C=O*), 1594 (aromatic *C=C*), 1530, 1401, 1324 (-*SO*$_2$-), 1260, 1144, 1086, 1041 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.78 (s, 2 H, 2 -*NH*-), 7.90~6.88 (s, 12 H, -CO*Ph(p)* CO- and 2 -NH*Ar*SO$_2$-), 3.52~2.34 (m, 18 H, 2 -SO$_2$-C*H*$_2$C*H*$_2$N(C*H*$_3$)C*H*$_2$-). Anal. Calcd for $C_{28}H_{32}N_4O_6S_2$ (584.71); C, 57.52; H, 5.52; N, 9.58; S, 10.97. Found: C, 57.54; H, 5.47; N, 9.54; S, 10.79.

7: Yield 95%. FTIR (KBr, cm^{-1}) 3330 (N-H), 3105, 2932 (aromatic C-H), 2848, 2803 (aliphatic C-H), 1678 (*C=O*), 1588 (aromatic *C=C*), 1523, 1401, 1318 (-*SO*$_2$-), 1247, 1138, 1080, 1041 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.82 (s, 2 H, 2 -*NH*-), 7.90~6.88 (s, 12 H, -CO*Ph(m)*CO- and 2 -NH*Ar*SO$_2$-), 3.58~2.32 (m, 18 H, 2 -SO$_2$-C*H*$_2$C*H*$_2$N(C*H*$_3$) C*H*$_2$-). Anal. Calcd for $C_{28}H_{32}N_4O_6S_2$ (584.71); C, 57.52; H, 5.52; N, 9.58; S, 10.97. Found: C, 57.48; H, 5.49; N, 9.56; S, 10.84.

8: Yield 98%. FTIR (KBr, cm^{-1}) 3339 (N-H), 3105, 3054, 2932 (aromatic C-H), 2861 (aliphatic C-H), 1671 (*C=O*), 1588 (aromatic *C=C*), 1523, 1401, 1324 (-*SO*$_2$-), 1254, 1138, 1086, 1010 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 10.8 (s, 2 H, 2 -*NH*-), 6.4, 7.90~6.80 (s, 16 H, -CO*Ph (p)*CO-, 2 -NH*Ar*SO$_2$- and -NH-*Ph*-NH-), 3.56-2.32 (m, 8 H, 2 -SO$_2$-C*H*$_2$C*H*$_2$-). Anal. Calcd for $C_{28}H_{32}N_4O_6S_2$ (604.70); C, 59.59; H, 4.67; N, 9.27; S, 10.61. Found: C, 59.62; H, 4.65; N, 9.33; S, 10.59.

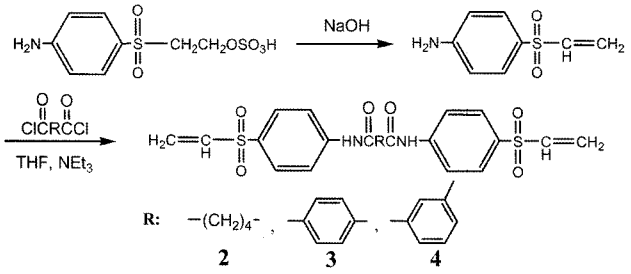
9: Yield 98%. FTIR (KBr, cm^{-1}) 3105, 3054, 2938 (aromatic C-H), 2816 (aliphatic C-H), 1652 (*C=O*), 1594 (aromatic *C=C*), 1530, 1408, 1318 (-*SO*$_2$-), 1254, 1144, 1080, 1009 (*C-O*, and *C-N*). ^{1}H NMR (DMSO-d_6, ppm) 7.89~6.82 (s, 12 H, -CO*Ph(p)*CO- and 2 -NH*Ar*SO$_2$-), 3.52, 2.34 (m, 8 H, 2 -SO$_2$-C*H*$_2$C*H*$_2$-), 2.62 (m, 8 H, piperazine). Anal. Calcd for $C_{28}H_{30}N_4O_6S_2$ (582.69); C, 57.71; H, 5.19; N, 9.62; S, 11.01. Found: C, 57.74; H, 5.12; N, 9.57; S, 11.03.

Results and Discussion

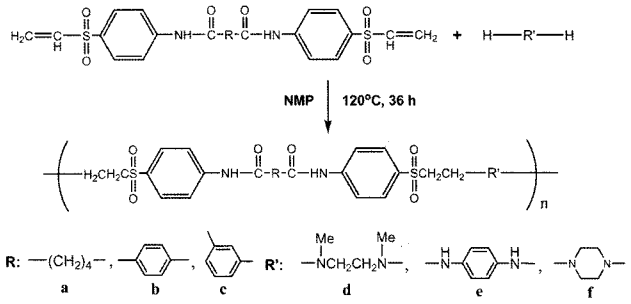
Preparation of Vinylsulfone-Containing Monomers. The reactions of adipoyl chloride, terephthaloyl chloride and isophthaloyl chloride with **1** were carried out in the presence of triethylamine as shown in Scheme I. The reaction was based on the condensation technique leading to good yields of **2**, **3**, and **4**.

The reactivity of **1**, which was deactivated by the electron-attracting sulfone group, toward acid chlorides was less than that of aniline.[19] In the IR spectra, the monomers **2**~**4** showed

Scheme I



Scheme II



the characteristic absorption bands at around 1680, 1590, and 1310 cm^{-1} corresponding to the amide, vinyl and sulfone linkages, respectively. In the NMR spectra of monomers **2**~**4**, the vinyl protons appear at 5.80~7.00 ppm as multiplets.

Polymerization. The polymerization of the corresponding divinyl sulfone with the diamine was carried out by addition polymerization via the Michael-type addition reaction, as shown in Scheme II.[17,18] Although it is possible to prepare polymers by reacting primary diamine derivatives with divinyl sulfones, the resulting secondary amine attacks the unreacted vinyl sulfone group. Thus, it is difficult to obtain linear polymers using primary diamine derivatives. The aromatic secondary amine shows poor reactivity toward the vinyl sulfone group. DMEDA, piperazine and *p*-phenylenediamine were chosen as the diamine derivatives.

The results of the polymerizations are summarized in Table I along with the viscosity and molecular weights of the polymers. The polymers obtained here were identified as tertiary amine-containing poly(amide-sulfone)s. In the IR spectra of polymers **5**~**8**, the characteristic absorption bands of N-H and C=O were exhibited at 3330 and 1660 cm^{-1}, respectively. In the ^1H NMR spectrum of polymers **5**~**7**, the alkyl protons exhibited broad peaks between 2.30~2.60 ppm. The peaks for the vinyl protons at around 5.80~7.00 ppm disappeared completely, whereas peaks for the methylene protons produced from the vinyl groups were present at 2.3 ~3.5 ppm. The elemental analysis also supported the formation of polymers **5**~**9**, and was well matched with the calculated data.

Solubility. The solubility of the poly(amide-sulfone)s was investigated using various common organic solvents, as listed in Table II. Polymers **5**~**8** exhibited good solubility in

Table I. Results of Polymerization of Various Vinyl Sulfone-Containing Monomers with Various Diamine Derivatives

Properties / Polymers	Monomers	Diamines	Viscosity (η_{inh})	MW	Yield (%)
5	**2**	DIEDA[a]	0.71	17,600	90
6	**3**	DIEDA	1.07	-	89
7	**4**	DIEDA	0.73	18,400	91
8	**3**	*p*-PDA[b]	1.13	-	90
9	**3**	Piperazine	0.85	-	90

[a]*N,N'*-Dimethylethtylenediamine. [b]*p*-Phenylenediamine.

Table II. Solubility Properties of Polymers in Various Solvents

Solvent / Polymer	NMP	DMSO	EtOH	*m*-Cresol	THF	Chloroform	Toluene
5	++	++	--	++	+	+	–
6	++	++	--	++	–	–	–
7	++	++	--	++	+	–	–
8	+	+	--	+	–	–	–
9	–	–	--	–	–	–	–

--, insoluble; –, slightly soluble; +, soluble; ++, very soluble.

polar aprotic solvents such as NMP, DMF, and DMSO. Polymer **9** was less soluble in NMP than other polymers. In the comparison of the chemical structures of polymers **6** and **7**, we noticed that **6** had the para-position in the benzene ring, which can lead to the packing of the polymer chains. Polymers **8** and **9** showed less solubility than **6** and **7**. The reason for the lack of solubility of polymers **8** and **9** is that they are more crystalline than the other polymers and, consequently, the polymer chains in the terephthaloyl moiety are less mobile than those of polymers **5**, **6**, and **7** containing the alkyl moiety. Especially, all of the poly(amide-sulfone)s showed fairly good solubility in NMP-LiCl except for polymer **9**. The alkyl-containing poly(amide-sulfone)s displayed better solubility than the rigid aromatic polymers **8** and **9**. However, polymer **5** exhibited solubility in chloroform and THF and fairly good solubility in polar aprotic solvents at ambient temperature or on slight heating. The poly(amide-sulfone)s were dissolved or swelled in aqueous acidic solution, due to the protonation of the tertiary amine group. Especially polymer **5** was freely soluble in 1 M hydrochloric acid.

Michael-type addition polymerization gave polymers of moderate molecular weights judging from the viscosity and GPC data. The polymers obtained from the addition polymerization possessed inherent viscosities of 0.71~1.13 dL/g. The alkyl-containing polymer **5** showed a high molecular weight of 17,600. Tough films of polymers **5** and **7**, which were somewhat resilient, could be cast from their solutions. When the films were cast on a glass plate, the tough polymer films adhered very strongly to the glass surface.

Reaction with Halides. NMP, which can dissolve tertiary amine-containing poly(amide-sulfone)s as well as benzyl chloride or 1,4-dichloromethylbenzene, was selected as the solvent during the membrane preparation process. The quaternization reaction started to occur as soon as the polymer solution was mixed with the halide solution, and the reaction continued after the reaction solution was coated onto the glass substrate. The crosslinking resulted in the formation of a molecular network by forming quaternary ammonium salts through the reaction between the tertiary amine groups in the main chain of the polymer and the chloromethyl group in the halide molecule. The reaction with benzyl chloride was completed within 10 min at around 50 °C. On the other hand, the reaction with alkyl halides such as propyl bromide and 1,5-dibromopentane was accomplished in 5 h at around 50 °C. The polymers quaternized with the monohalide were soluble or swelled in distilled water and methanol.

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

In the series of polymers, polymer **5** derived from the long-chain aliphatic moiety exhibited a well-defined melting transition at around 139 °C, as shown in Figure 1(a). In the case

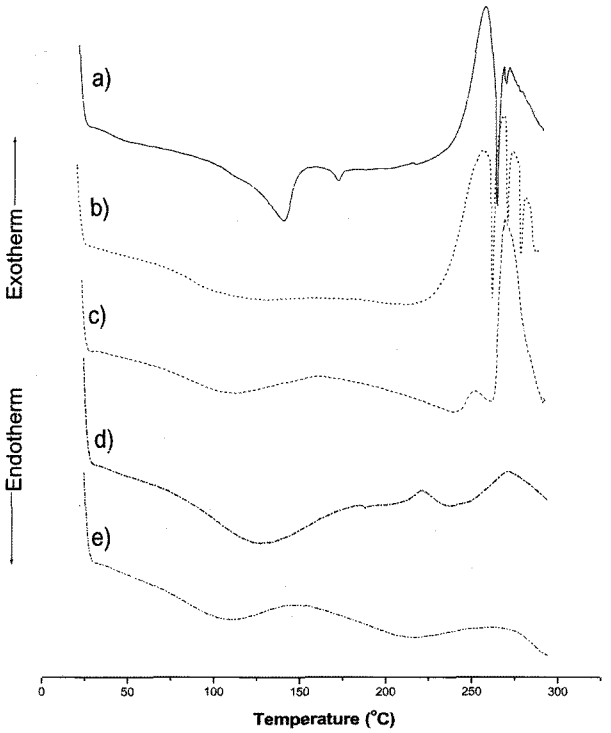


Figure 1. DSC thermograms of poly(amide-sulfone)s. (a) **5**, (b) **6**, (c) **7**, (d) **8**, and (e) **9**.

Table III. Thermal Properties of Poly(amide-sulfone)s Obtained by Michael-Type Addition Polymerization

Properties / Polymers	T_{exo}[a]	T_{endo}[b]	T_d[c]	$T_{10\%}$[d]	Residual Weight (%)	
	(°C)				400 °C	500 °C
5	209	139	211	238	47.1	29.8
6	208	-	214	267	53.9	42.2
7	203,225	-	213	258	50.9	42.1
8	220,226	-	218	280	62.3	48.3
9	-	-	225	295	60.2	63.4

[a]T_{exo}: Temperature of exotherm. [b]T_{endo}: Temperature of endotherm. [c]T_d: Initial decomposition temperature. [d]$T_{10\%}$: Temperature determined at a weight loss of 10%.

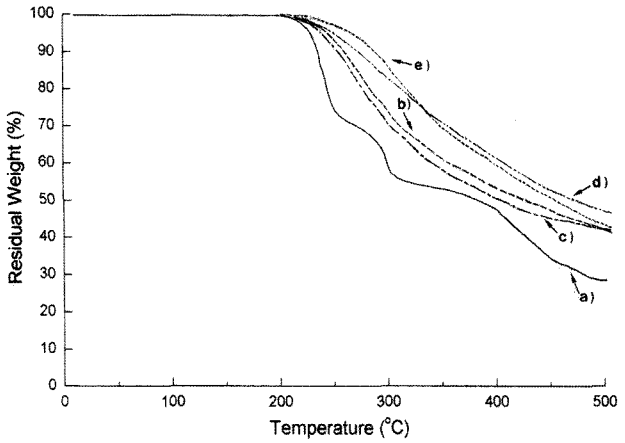


Figure 2. TGA traces of poly(amide-sulfone)s. (a) **5**, (b) **6**, (c) **7**, (d) **8**, and (e) **9**.

of the DSC traces of polymer **5**, the endothermic peak at around 139 °C was coincident with the corresponding temperature determined in a capillary tube. However, the melting temperatures could not be observed for polymers **6**~**9**. Higher transition temperatures were expected for the polymers incorporating aromatic units. Polymers **6**~**9** did not show either a glass transition temperature or melting temperature. Polymers **5**~**7** derived from DMEDA showed exothermic behavior, as shown in Figures 1(a)~(c), which is attributed to their thermal decomposition.

The thermal stability data are listed in Table III and the TGA traces in Figure 2. At about 200 °C, a detectable weight loss of the polymer was observed, as shown in Figures 2(a) ~(c). The initial decomposition temperature (T_d, 211~225 °C) exhibited a similar trend, regardless of the chemical structure of the polymers **5**~**9**. Polymers **5**, **6**, and **7** sustained a 10% weight loss at 238, 267, and 258 °C at a heating rate of 10 min^{-1}, and gave residual weights ranging from 30 to 42% at 500 °C in nitrogen, as shown in Figures 2(a), 2(b), and 2(c), respectively. On the other hand, the temperatures at which polymers **8** and **9** showed a 10% weight loss were higher than those of the DMEDA-based polymers. However, polymers **8** and **9** gave residual weights varying from 48 to 63% at 500 °C in nitrogen, as shown in Figures 2(d) and 2(e). The thermal stability of **8** and **9** was superior to that of polymers **5**, **6**, and **7**, due to their rigid aromatic moieties. Polymer **8** obtained from *p*-phenylenediamine showed higher viscosity than those obtained from the other diamines.

Conclusions

A series of new vinyl sulfone-containing amide monomers **2**, **3**, and **4** were prepared from *p*-aminophenyl vinyl sulfone with various acid chlorides such as adipoyl chloride, terephthaloyl chloride and isophthaloyl chloride. The Michael-type addition polymerization gave various poly(amide-sulfone)s with moderate molecular weights in good yields by reacting **2**~**4** with diamines such as DMEDA, piperazine and *p*-phenylenediamine. They showed good solubility in common organic solvents. They displayed good thermal stability showing 30~63% of residual weight at 500 °C. The design, development, and evaluation for the permselective membranes for CO_2 separation are in progress.

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