Effect of Acid Acceptor on Synthesis of New Copolyamide with Piperazine Moiety

SHIGEJI KONAGAYA, OSAMU WATANABE, ATSUSHI KAJI

Toyobo Research Center, 1-1 Katata 2-Chome, Ohtsu, Shiga 520-0292, Japan

ABSTRACT: Effect of acid acceptor (AA) on the low temperature solution polymerization of the copolyamide 4I-PIP(20) from isophthaloyl chloride, 4,4′-diaminodiphenylsulfone, and piperazine (their diamine component ratio is 80–20) was studied. The type and amount of AA had a large effect on not only the polymerization condition and polymerization degree of 4I-PIP(20), but also on its microstructure. Pyridine was the most favorable AA, since it gave a homogeneity to the polymerization solution of 4I-PIP(20), and that it was most suitable for the synthesis of 4I-PIP(20) with high polymerization degree. The H-NMR measurement made it clear that 4I-PIP(20) prepared with pyridine was random copolyamide. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 921–928, 2000

INTRODUCTION

In reverse osmosis (RO) systems, chlorine is usually added to feed water for control of microorganisms and prevention of membrane fouling by microbiological growth. An ideal membrane for RO desalination is required to have higher chlorine resistance.[1] In particular, polyamide membranes deteriorate rapidly when exposed to low chlorine concentrations in water solution.[2,3] Different amide polymers were attempted toward improvement of membrane resistance to chlorine, among which polypiperazine amides were the most promising. Polypiperazine amides surely have high water permeability and a good resistance to chlorine. However, since polypiperazine amides have a poor solubility to aprotic solvents such as N-methyl-2-pyrolidone (NMP) and N,N-dimethylacetamide (DMAC), and poor mechanical and thermal stabilities in water, they are not suitable for the raw material of a commercial hollow fiber RO membrane. Thus several kinds of piperazine copolyamides have been prepared for the purpose of improving the above defects.[4–8] Recently the authors also have developed a promising membrane material, 4I-PIP(20) copolyamide, from isophthaloyl dichloride (IPC), piperazine (PIP) and 4,4′-diaminodiphenylsulfone (4DDS), which shows a good RO performance and a good resistance to chlorine.[9] Commercialization of hollow fiber membrane from 4I-PIP(20) requires the know-how of the synthesis of 4I-PIP(20) with high polymerization degree and clarification of the microstructure of 4I-PIP(20).

S. Konya and M. Yokoyama[10] studied the effect of AA on the low temperature solution. polycondensation of acyl dichlorides and diamines, using tertiary amines (pKa 5.26–10.74), and showed that a maximum of the polymerization degree appeared when an AA of almost the same pKa value as a diamine was used. And they showed that solvents also affected the polymerization degree.

S. Hong II and B. C. Kim[11] studied the factors affecting the polycondensation of wholly aromatic polyamides, poly(p-phenyleneterephthalamide),
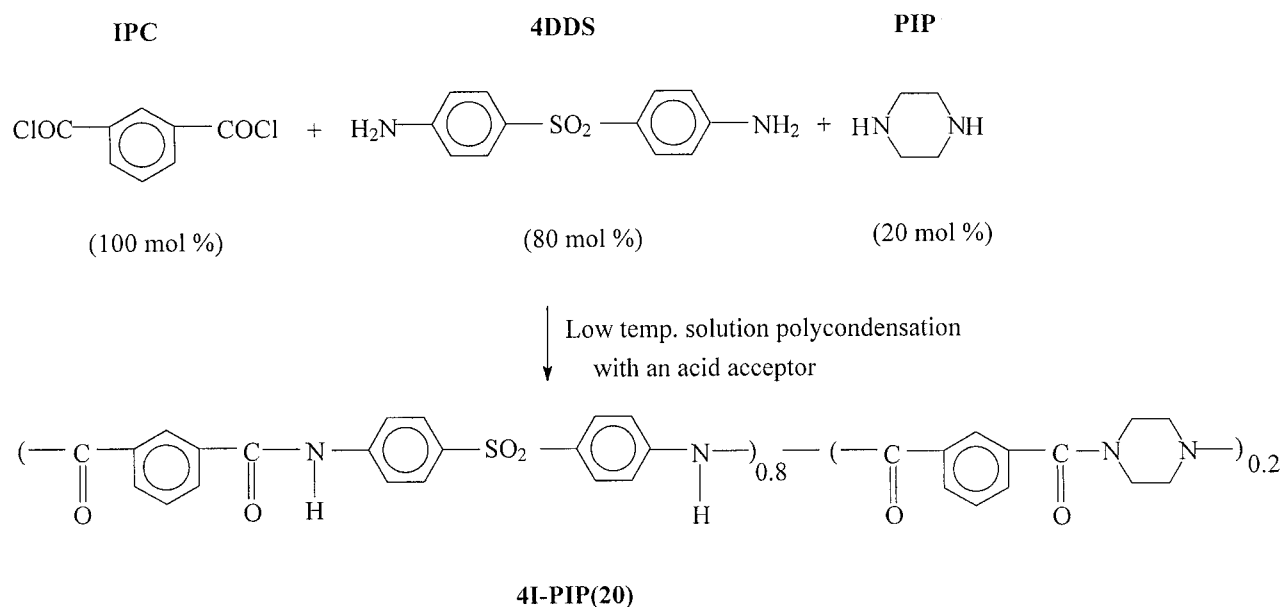
Figure 1   Low temperature solution polycondensation of 4I-PIP(20) copolyamide.

and concluded that pyridine was more effective than triethylamine as an acid aceptor.

D. Liu et al.[12,13] studied the effects of AA in solution polycondensation on sequence structure, random degree (B), and number of average sequence (Ln) of aromatic-aliphatic copolyamides, and concluded that the pKa of AA usually has to be similar to the pKa of diamines used as monomers in order to obtain the aromatic-aliphatic copolyamide with higher B and less Ln. AA in the low temperature solution polycondensation control the polymerization degree and the microstructure of copolyamide.

Since the pKa of PIP is much different from that of 4DDS, the selection of an AA for the copolymerization of 4I-PIP(20) possibly have a large effect on not only the solution polycondensation conditions and polymerization degree, but also sequence structure, random degree (*B*) and number of average sequence (*Ln*), of 4I-PIP(20). Judging from the control of the polymerization degree of 4I-PIP(20), systems in which the copolyamide remains in solution will be considered first.[14] So it is very important to know the most favorable AA for the low temperature solution polycondennsation in aprotic solvent such as NMP and DMAC.

This study is related to the effect of AA on the synthesis of the copolyamide (4I-PIP(20) with the use of IPC, PIP, and 4DDS and its microstructure.

EXPERIMENTAL

Materials

PIP, triethylamine (TEA), *N*-methyl-morpholine (NMM), *N,N*-diethyl-aniline (NDA), and pyridine (PY) were purchased from Nacalai Tesque company. PIP, NMM, and NDA were used as purchased. TEA and PY were purified by distillation before use. 4DDS and IPC were used as described before.[15] NMP and DMAC were dried over molecular sieves more than one day before use.

Synthesis of 4I-PIP(20) Copolyamide

Poly(isophthaloyl 4,4′-diaminodiphenylsulfone piperazine), 4I-PIP(20), of which the diamine component ratio is 80–20, was prepared by low temperature solution polymerization method[14,15] (Fig. 1). The diamine components and an AA were dissolved in NMP or DMAC under nitrogen atmosphere. The solution was cooled below 5°C in an ice bath and then an equimolar amount of IPC was added, the solution temperature being kept below 60°C. The solution was stirred for one hour in the ice bath and for another hour at a room temperature. The polymer solution was poured into methanol. The polymer precipitate was crushed and washed several times with water by a home mixer. The purified polymer was dried for a period of one day under vacuum at 150°C.
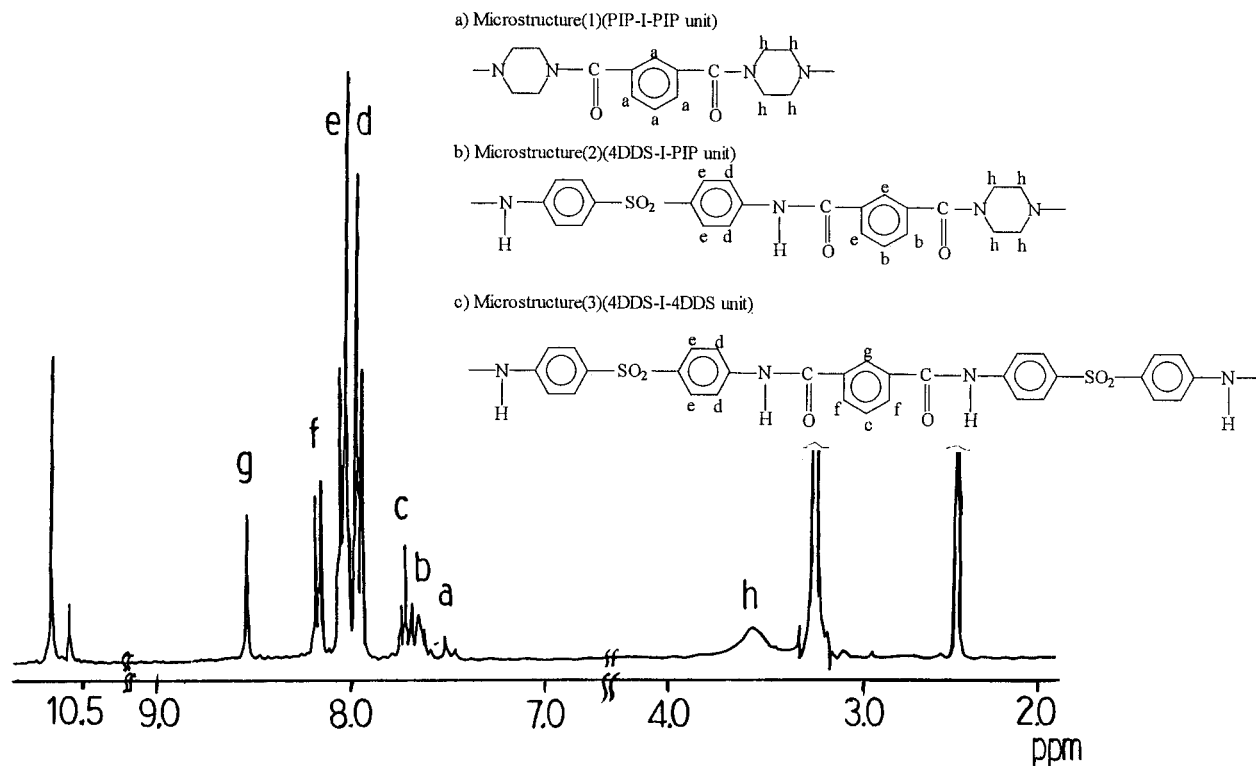
Figure 2 H-NMR spectrum of 4I-PIP(20). Measurement conditions: 300 MHz in d6-DMSO at 50°C.

Characterization

Reduced Viscosity (η sp/C)

Reduced viscosities of copolyamides were measured at a concentration of 0.5 g/dL in NMP at 30°C.

NMR Spectrum

The ^{1}H-NMR spectrum was measured to confirm the piperazine content and the microstructure of the copolyamide 4I-PIP(20) on Varian XL-300 spectrometer (300 MHz—NMR spectrum) using dimethyl sulfoxide-d6 (d6-DMSO) as a solvent.[16-20]

GPC (Gel Permeation Chromatogram)

GPC was measured by the use of high speed liquid chromatography with an RI detector (Waters Associates) under the following conditions:

Column: Shodex GPC [AD 802/S × 2 + 803/S + 80M/S (4 columns)]
Eluent: *N,N*-dimethylfomamide + 0.01 N-LiBr
Flow rate: 0.9 mL/min

Temperature: 55°C
Pressure: 700 psi

Molecular weight (MW) was calibrated with commercial standard polystyrene polymers.

RESULTS AND DISCUSSION

Synthesis and Characterization of 4I-PIP(20) Copolyamide

Synthesis of 4I-PIP(20), a copolyamide with piperazine ring, was studied, whose components are PIP, 4DDS, and IPC (molar ratio of PIP to 4DDS = 20/80). The 4I-PIP(20) polymer obtained with the use of PY as a AA is a solid light brown powder. The copolyamide composition was determined by NMR spectrum, shown in Figure 2. The NMR spectrum showed that the copolyamide composition measured was almost the same as the monomer composition.

The microstructure of the polymer can be analyzed according to the following procedure:[16-20]

The structure of 4I-PIP(20) can be expressed by the following equation:

[—(—I—P—)n—(—I—S—)m—]x

  I = IPC unit, P = PIP unit, S = 4DDS unit   (1)
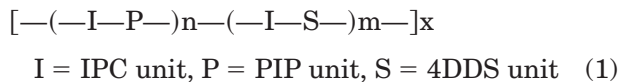
The number-average sequence lengths of the —(—I—P—)—unit [$m = \mathrm{Ln(IP)}$] and the —(—I—S—)—unit [$n = \mathrm{Ln(IS)}$] are given by

$$\mathrm{Ln(IP)} = [(P_{S\text{-}I\text{-}P})/2 + P_{P\text{-}I\text{-}P}]/[(P_{S\text{-}I\text{-}P})/2] \quad (2)$$

$$\mathrm{Ln(IS)} = [(P_{S\text{-}I\text{-}P})/2 + P_{S\text{-}I\text{-}S}]/[(P_{S\text{-}I\text{-}P})/2] \quad (3)$$

where $P_{P\text{-}I\text{-}P}$, $P_{S\text{-}I\text{-}S}$, and $P_{S\text{-}I\text{-}P}$ represent the proportion of the P—I—P, S—I—S, and S—I—P units. These three kinds of IPC residues, P—I—P, S—I—S, and S—I—P were identified at 7.4–8.6 ppm as a benzene signal in d6-DMSO shown in Figure 2.

  The degree of sequence distribution of 4I-PIP(20) may be defined by the above terms:

$$B = [1/\mathrm{Ln(IP)}] + [1/\mathrm{Ln(IS)}] \quad (4)$$

If $B < 1$, these units tend to cluster in blocks of each unit, and $B = 0$ in homopolymer mixture, whereas if $B > 1$, the sequence length becomes shorter, and $B = 2$ in an alternating copolymer.

  The microstructure of 4I-PIP(20) was analyzed from the H-NMR spectrum with the above equations.

  Peaks were grouped into five groups, S(a), S(b), S(d), S(e), and S(f), which were assigned to the positions of benzene rings as shown in Figure 2. Then $P_{P\text{-}I\text{-}P}$, $P_{S\text{-}I\text{-}S}$, and $P_{S\text{-}I\text{-}P}$ were calculated as follows:

$$S(P—I—P) = S(a)/2 = 12.2/4 = 3.05$$

$$S(S—I—S) = S(f)/2 = 70/2 = 35$$

$$S(S—I—P) = [S(e) - S(d) + S(b)]/4$$
$$= (28 + 27.3)/4 = 13.8$$

where S(P—I—P), S(S—I—S), and S(S—I—P) represent the proportion of the P—I—P, S—I—S, and S—I—P units.

$P_{P\text{-}I\text{-}P} = S(P—I—P)/[S(S—I—S) + S(P—I—P)$

  $+ S(S—I—P)] = 3.05/(35 + 3.05 + 13.8) = 0.266$
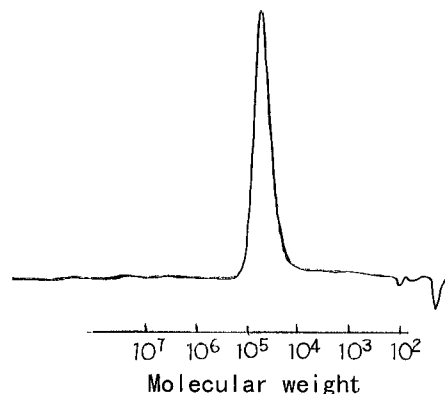
Figure 3 Gel permeation chromatogram of 4I-PIP(20) prepared with PY as an acid acceptor.

$P_{S\text{-}I\text{-}S} = S(S—I—S)/[S(S—I—S) + S(P—I—P)$

  $+ S(S—I—P)] = 35/(35 + 3.05 + 13.8) = 0.675$

$P_{S\text{-}I\text{-}P} = S(S—I—P)/[S(S—I—S) + S(P—I—P)$

  $+ S(S—I—P)] = 13.8/(35 + 3.05 + 13.8) = 0.059$

The number-average sequence lengths, $Ln(IP)$ and $Ln(IS)$, are given below.

$$Ln(IP) = [(P_{S\text{-}I\text{-}P})/2 + P_{P\text{-}I\text{-}P}]/[(P_{S\text{-}I\text{-}P})/2] = 1.44$$

$$Ln(IS) = [(P_{S\text{-}I\text{-}P})/2 + P_{S\text{-}I\text{-}S}]/[(P_{S\text{-}I\text{-}P})/2] = 6.07$$

The degree of sequence distribution of 4I-PIP(20) is defined by the following B value:

$$B = [1/Ln(IS)] + [1/Ln(IP)] = 0.86$$

Since $B = 0.86$ ($B < 1$), these units tend to cluster a little in blocks of each unit, but the microstructure of 4I-PIP(20) prepared with PY as an AA proved to be a random copolymer. GPC indicated a single peak as shown in Figure 3, which revealed that 4I-PIP(20) was not the mixture of the homopolymers [poly(isophthaloyl piperazine), 4I-PIP(100)] and poly(isophthaloyl 4,4′-diaminodiphenylsulfone) [4I-PIP(0)], but a copolyamide. Calibrated MW of the 4I-PIP(20) was as follows:

$$M_n = 31,000,\ M_w = 47,000,\ M_w/M_n = 1.51$$

  Next, the effects of AA on the polycondensation conditions of 4I-PIP(20) and its microstructure were studied for the purpose of the synthesis of 4I-PIP(20) with a high polymerization degree.

Table I Effect of the Type of AA and Solvent on the Polycondensation of 4I-PIP(20)[a]

Type of AA	pKa in Water	Solvent	Appearance of Reaction System		η sp/C (dL/g)
None	—	NMP		Clear	0.37
		DMAC	Yellow	Clear	0.52
TEA	10.7	NMP	Orange	ppt	0.98
		DMAC	Orange	ppt	0.64
NMM	7.41	NMP	Red	ppt	1.37
		DMAC	Orange	ppt	0.73
NDA	6.56	NMP	Blue	Clear	0.90
		DMAC	Yellow	Clear	0.73
PY	5.26	NMP	Yellow	Clear	0.78
		DMAC	Yellow	Clear	0.76

[a] Polycondensation conditions: IPC//4DDS/PIP///AA = 10//8/2///20(mol//mol/mol///mol). 4I-PIP(20)/Solvent = 24 wt/vol %.

Effects of AA and Solvents on Solution Polymerization of 4I-PIP(20)

Since there is a large difference in the basicity between piperazine and 4,4′-diaminodiphenylsulfone, the type of AA possibly has a large influence on the low temperature solution polymerization, in particular, polymerization degree.[10] The copolymerization was carried out, changing the type of AA such as TEA, NMM, NDA, and PY. The copolymerization results are shown in the Table I.

Reduced viscosities of the 4I-PIP(20) depended upon pKa values (basicity) of AA. Reduced viscosity increased with the increase of pKa, reached a maximum, and then decreased with increasing pKa. The 4I-PIP(20) with the highest reduced viscosity was prepared by the use of NMM as an AA, of which pKa is similar to that of 4DDS. AA with higher pKa such as TEA is not effective for the synthesis of with higher polymerization degree.

However, such AA gave a heterogeneous solution and exhibited a poor reproducibility of the 4I-PIP(20) copolyamides with high polymerization degree. In addition, it is difficult to remove the impurities such as acceptors/hydrogen chloride salts from the copolyamide because of the heterogeneity.

On the other hand, aromatic amine acceptors such as NDA and PY gave a homogeneous solution of 4I-PIP(20) with a little lower polymerization degree. The 4I-PIP(20) obtained with PY were more easily purified, compared with the 4I-PIP(20) prepared by the use of the above aliphatic AA. On the other hand, it was troublesome to purify the 4I-PIP(20) obtained with NDA because of a poor solubility of NDA to water.

Effects of the Concentration of Reactants on the Polymerization Degree of 4I-PIP(20)

Effects of the concentration of reactants on the polymerization degree were studied at the constant molar ratio of AA to the theoretical amount of hydrogen chloride in NMP and DMAC solvent systems. The results are shown in Figures 4 and 5.

In the case of the use of TEA as an AA, the cloudiness of the polymerization solution increased and the polymerization degree of 4I-PIP(20) decreased with the increase of the reactant concentration in both solvents. In the case of an aromatic amine acceptor such as NDA and PY, the polymerization degree of 4I-PIP(20) increased with the increase of the reactant concentration, while the solution was kept transparent in both solvents. As mentioned above, 4I-PIP(20) prepared with PY was more easily purified than that with NDA, because of good solubility of PY to water.
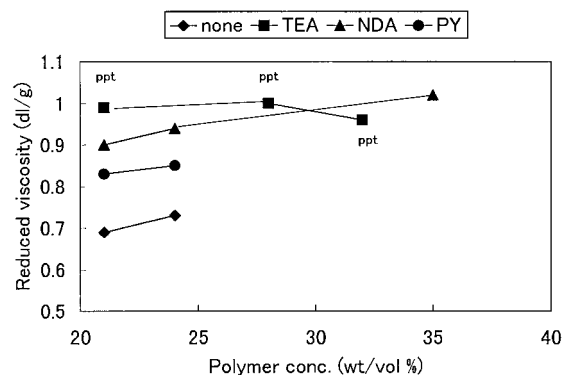

Figure 4 Effect of polymer concentration and AA on solution polycondensation of 4I-PIP(20) in NMP.
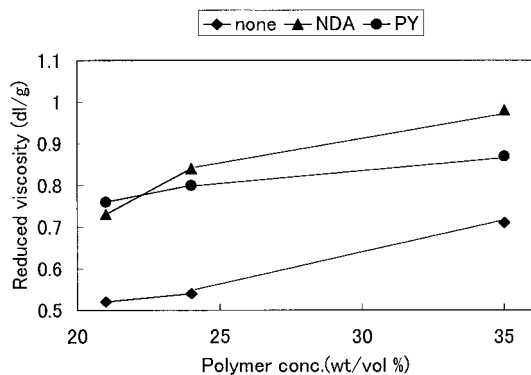
Figure 5 Effect of polymer concentration and AA on solution polycondensation of 4I-PIP(20) in DMAC.

Figure 7 Effect of AA on solution polycondensation of 4I-PIP(20) in DMAC.

Effects of the Amounts of AA on the Polymerization Degree of 4I-PIP(20)

Figures 6 and 7 showed the effects of the amounts of aromatic AA such as NDA and PY on the polymerization degree of 4I-PIP(20) at the fixed concentration of the reactants in NMP and DMAC solvents. In the use of NDA as an AA, polymerization solution was transparent up to the equimolar ratio of the AA to the theoretical amount of hydrogen chloride. The solution became heterogeneous over the equimolar ratio, while the polymerization degree fell. The heterogeneity of the polymerization solution possibly resulted in the concealment of the —COCl active sites by the polymer precipitates, which caused the decrease of the polymerization degree.

On the other hand, the copolymerization with the use of PY as an AA gave a clear solution containing 4I-PIP(20) with higher polymerization degree, despite a higher concentration of PY.
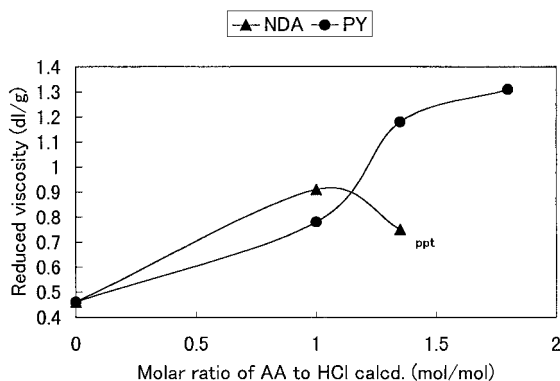
Relationship Between the Type of AA and the Homogeneity of the Polymerization Solution of 4I-PIP(20)

Figure 8 shows the influence of pKa values of AA on the homogeneity of the polymerization solution. Its homogeneity was dependent on the basicity of the acceptor used. The acceptors with higher basicity gave a heterogeneous polymerization solution at a lower concentration of AA, probably because the salts formed from AA and evolved hydrogen chloride acted as a precipitant of 4I-PIP(20) in the polycondensation solution. From the viewpoint of controlling polymerization degree of 4I-PIP(20) by its solution viscosity, a weak base type AA like pyridine is preferable to a strong base type one like TEA because the former gives the homogeneity of the polymerization solution, which is very important for adjusting the polymerization degree of 4I-PIP(20) by the measurement of the solution viscosity *in situ*.
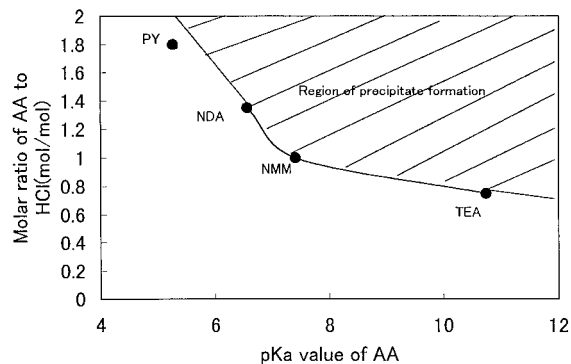

Figure 6 Effect of AA on solution polycondensation of 4I-PIP(20) in NMP.

Figure 8 Influence of the type and amount of AA on the homogeneity of the polycondensation solution of 4I-PIP(20).
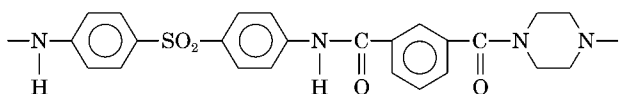
Table II   Effect of the Type and Amount of AA on the Microstructures of 4I-PIP(20)

| Type of AA	Molar Ratio of AA to HCl Calcd.	Molar Ratio of Microstructure (mol %)			Average Chain Length		Block Copolymerization Ratio
		$(1)^a$	$(2)^b$	$(3)^c$	$Ln(\text{IS})^d$	$Ln(\text{IP})^e$	$1/Ln(\text{IS}) + 1/Ln(\text{IP})$
None	0	9.7	18.6	71.7	8.70	2.04	0.61
TEA	1.0	11.4	19.4	69.3	8.14	2.17	0.58
NMM	1.0	12.4	15.7	71.8	10.12	2.58	0.49
NDA	1.0	10.8	18.1	71.1	8.88	2.20	0.57
PY	1.0	5.8	27.5	66.7	5.84	1.42	0.88
	1.1	5.2	27.9	66.9	5.80	1.37	0.90
	1.7	5.5	26.0	68.5	6.26	1.42	0.86
	1.75	5.2	29.0	65.8	5.54	1.36	0.92

^a Microstructure (1) P—I—P unit:
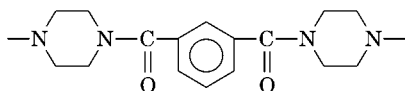
^b Microstructure (2) (S—I—P unit):

^c Microstructure (3) (S—I—S unit):
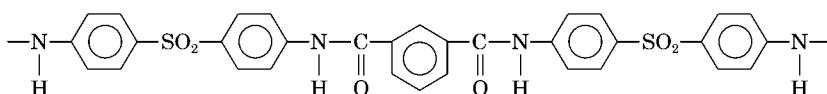
^d IS : iso-phthaloyl 4,4′-diaminodiphenylsulfoneamide unit.
^e IP : isophthaloyl piperazineamide unit.

Influence of the Type and the Amount of AA on the Microstructure of 4I-PIP(20)

Table II shows the sequence [molar fraction of three structural units, sequence length of each segment, and block caharacter of 4I-PIP(20)] obtained without AA and with the different AA such as TEA, NMM, NDA, and PY. Effect of the molar ratio of PY as an AA to hydrogen chloride calcd. on the microstructure of 4I-PIP(20) is also shown in Table II. There is some difference in the microstructure of the 4I-PIP(20) among the type of AA used. The microstructure of 4I-PIP(20) obtained with TEA and NDA was almost the same as that without AA. NMM produced a 4I-PIP(20) with the highest block copolymerization ratio, while PY gave the 4I-PIP(20) with randomness. Thus the type of AA had an influence on the microstructure of 4I-PIP(20).

There was no difference in the sequence among 4I-PIP(20) obtained with different amount of PY as shown in Table II. The amount of PY had no influence on the microstructure of 4I-PIP(20).

The type of AA had an influence on the microstructure of 4I-PIP(20), and the AA that gave the most random copolymerization of 4I-PIP(20) is PY, while NMM gave a random copolyamide.

CONCLUSIONS

The effect of AA on the low temperature solution polycondensation conditions and microstructure of the copolyamide, 4I-PIP(20), from piperazine, 4,4′-diaminodiphenylsulfone, and isophthaloyl dichloride (molar ratio of piperazine to 4,4′-diaminodiphenylsulfone = 20/80) was studied.

The types of AA had an influence on the homogeneity of the polymerization solution and polymerization degree of 4I-PIP(20). PY was suitable for the synthesis of 4I-PIP(20) with high polymer-

ization degree. In addition, H-NMR spectrum analysis made it clear that the microstructure of 4I-PIP(20) was influenced by the type of AA and 4I-PIP(20) produced with PY was a random copolyamide, while NMM gave 4I-PIP(20) with high block copolymerization ratio.

The type of AA had an influence on not only the polymerization condition and polymerization degree 4I-PIP(20) but also its microstructure. The most favorable AA for producing 4I-PIP(20) with high polymerization degree commercially is PY.

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