Synthesis and Air Separation of Soluble Terpolymers from Aniline, Toluidine, and Xylidine

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ABSTRACT: A series of terpolymers were synthesized by oxidative polymerization of aniline, *o*-toluidine, and 2,3-xylidine with three monomer ratios using ammonium persulfate as an oxidant in two acidic media. The yield and intrinsic viscosity of the terpolymers were studied by changing the polymerization temperature and medium. The resulting terpolymers were characterized by ^{1}H–NMR, wide-angle X-ray diffraction, differential scanning calorimetry, thermogravimetry, and constant pressure-variable volume methods. The results showed that the terpolymers are amorphous and exhibit enhanced solubility, high thermostability, and high char yield, greater than 35 wt % at 900°C in nitrogen. A blend membrane of the terpolymer with ethyl cellulose shows good air-separation ability. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 790–798, 2001

Key words: aniline oxidative copolymerization; *o*-toluidine copolymer; 2,3-xylidine–containing terpolymer; structure; thermostability; decomposition kinetics; air-separation membrane

INTRODUCTION

Nitrogen-containing conductive polymers have attracted attention recently because they have been reported to exhibit high gas and liquid separation ability. Polyaniline is the most attractive polymer because of its chemical, thermal and air stability, ease of synthesis, and the highest oxygen/nitrogen separation factor (up to 30).[1] A unique character of polyaniline is its ability to be reversibly and controllably doped and undoped by common acids and bases. The doping process could be employed to greatly enhance the gas and liquid permselectivity through the polyaniline membrane. However, polyaniline is partially soluble only in a few organic solvents with high boiling point such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide, and dimethylsulfoxide (DMSO). Poor solubility causes not only difficulty in investigating the structure of polyaniline but also poor solution and thermal processabilities. The aim of the present study was to synthesize a soluble terpolymer in common solvents, including chloroform, tetrahydrofuran, ethylene chloride, and benzene, through introduc-

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ing a methyl group on the rigid polyaniline main chain, to describe the variations in yield, intrinsic viscosity, crystallinity, and thermostability with comonomer ratio, and to explain the structural and property modification inducing by terpolymerizing. To date no report about the above-mentioned terpolymers has been found.

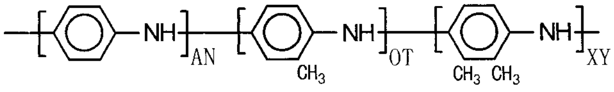
EXPERIMENTAL

Reagents

Aniline, *o*-toluidine, 2,3-xylidine, ammonium persulfate, and all solvents were commercially obtained and used without further purification. Ethyl cellulose (Shantou Xinning Chemical Works, Guangdong Province, China) has a viscosity of 0.04–0.08 Pa/s measured in ethanol/toluene and a degree of substitution about 2.4.

Polymerization

Terpolymers were prepared by oxidative polymerization of three monomers by using a previously described method.[2] A typical procedure for the preparation of the terpolymer from aniline/*o*-toluidine/2,3-xylidine (50/30/20) is as follows: To 250 mL of a 1*M* HCl solution was added 30 g (0.5 mol) $LiCl{\bullet}H_2O$, 9.2 mL (0.10 mol) aniline, 6.4 mL (0.06 mol) *o*-toluidine, and 4.9 mL (0.04 mol) 2,3-xylidine in a 500-mL two-neck glass flask. Ammonium persulfate $[(NH_4)_2S_2O_8]$ [22.8 g (0.1 mol)] was dissolved separately in 100 mL 1*M* HCl to prepare an oxidant solution. Both solutions were cooled in an ice/NaCl (2/1, w/w) bath to −15°C. The monomer solution was then treated with the oxidant solution added dropwise at −15–−8°C in about 2 h (the total molar ratio: monomer/oxidant = 1/2). Immediately, after the first 20 drops the reaction solution turns blue-violet. The reaction mixture was stirred for 48 h at −15–−10°C. The terpolymer hydrochloride salt precipitates gradually and slowly during the polymerization process. The terpolymer salt formed was isolated from the reaction mixture by filtration and washed with an excess of distilled water to remove the oxidant and oligomers. The hydrochloride salt was subsequently neutralized in 0.1 *M* ammonium hydroxide for 24 h to obtain the base form of terpolymer. The terpolymer base was washed with excess water. A bluish-black solid fine powder was left to dry in ambient air for 1 week. It should be noted that no inhibitor was used during the polymerization period because we attempted to obtain the terpolymer with as high a molecular weight as possible. The terpolymer of 4 g was obtained with a yield of about 20%. This terpolymer exhibits the following nominal structure:



Measurements

The intrinsic viscosity for the terpolymers in NMP was measured with a Ubbelodhe viscosimeter at 25°C.

The solubility of the polymers was evaluated using the following method: A powder sample (5 mg) was added into 0.5 mL of solvent and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, the solubility of the polymers was characterized semiquantitatively. A higher concentration up to 3% was also tested and the solubility seems the same as the solubility at 1%.

^1H–NMR spectrum was obtained in deuterated chloroform using a Bruker MSL-300 spectrometer operated at 300.13 MHz. The summation number to obtain the ^1H–NMR spectrum was 444.

Wide-angle X-ray diffractograms were recorded using Rigaku RAX-10 diffractometry with monochromatized CuK_α (λ = 0.1541 nm) radiation operated at 30 kV and 20 mA in a reflection mode. The scanning rate is 8°/min. The precision for the measurement of Bragg angle (2θ) is 0.01°.

Differential scanning calorimetry (DSC) measurement was performed using a DSC unit of a TA Instrument 2000 with the sample size of 5 mg at a heating rate of 20°C/min.

Thermogravimetry was carried out at a heating rate of 10°C/min in nitrogen (40 mL/min) with the sample size of 1.1 mg using a TGH Perkin–Elmer 7 series Thermal Analysis System and in static air with a sample weight of 0.9 mg using NETZSCH TG 209 Geratebau GmbH thermal analyzer.

The blend thin film of AN/OT/XY (50/30/20) terpolymer with ethyl cellulose was made by pouring the casting solutions in chloroform with a concentration of 1.6 wt % onto a glass plate and evaporating the casting solvent at 25°C for about 20 h. The thin film had a thickness of about 15 μm. The composite membrane was fabricated from the thin film and the porous polysulfone

Table I Copolymerization of Aniline (AN), *o*-Toluidine (OT), and 2,3-Xylidine (XY) with Monomer : Ammonium Persulfate of 2 : 1 for 48 h

AN/OT/XY (mol %)	Polymerization			Intrinsic Viscosity (dL/g)	Color of Solid Terpolymer Base
	Medium	Temperature (°C)	Yield (%)		
50/30/20	1*M* HCL	−15[a]	20	0.79	Darkviolet
34/33/33	1*M* HCl	−15[a]	22	0.20	Darkviolet
20/50/30	1*M* HCl	−15[a]	21	0.61	Darkviolet
50/30/20	1*M* HCl	21	16	0.79	Darkviolet
34/33/33	1*M* HCl	21	15	0.32	Darkviolet
20/50/30	1*M* HCl	21	17	0.62	Darkviolet
50/30/20	1*M* H_2SO_4	19	21	0.66	Darkgreen
34/33/33	1*M* H_2SO_4	19	20	0.75	Darkgreen
20/50/30	1*M* H_2SO_4	19	21	0.20	Darkgreen

[a] LiCl•H_2O was added into the polymerization solution to prevent freezing of polymer mixture.

support, which has a 10–45 nm pore size, 100–200 μm thickness, and a nonwoven fabric supporter. Actual air-separation measurement was performed using a constant pressure-variable volume method. Feed gas was compressed air with an oxygen content of 20.9 vol % directly from an air compressor. The permeate flux of oxygen-enriched air (OEA) through the composite membranes was calculated by measuring the change in the volume of the OEA at a constant pressure gradient across the composite membranes. The measurement of the oxygen concentration Y_{O_2} in the permeated OEA was performed on a QF1901 type gas analyzer. The effective membrane area was 50 cm^2. The actual air-separation property of the composite membrane was evaluated with the devices operating at a steady-state condition of temperature and pressure. Actual air-separation properties across AN/OT/XY (50/30/20) terpolymer (20 wt %) with ethyl cellulose (80 wt %) blend thin-film composite membrane were observed at 22–50°C and 300–650 kPa transmembrane pressure difference. The reproducibility was within 2%.

RESULTS AND DISCUSSION

Synthesis of Terpolymers from Aniline, *o*-Toluidine, and 2,3-Xylidine

The copolymerization of aniline, *o*-toluidine, and 2,3-xylidine with ammonium persulfate as an oxidant in 350 mL 1*M* HCl or 1*M* H_2SO_4 aqueous solution afforded blackish-violet precipitates as products. Aniline, *o*-toluidine, and 2,3-xylidine with three monomer ratios copolymerized in 1*M* HCl at −15°C for 48 h. It was found that the terpolymer yield was almost not affected by the monomer ratio as listed in Table I. The yield remained at 20–22%. However, the intrinsic viscosity of the terpolymers was significantly influenced by the monomer ratio.

With increasing the polymerization temperature from −15 to 21°C, the yield decreased slightly and was also not affected by the variation of monomer ratio. The yield will increase from 15–17% to 20–21% with a variation in reaction medium from HCl to H_2SO_4. It can be seen that the terpolymer yield is slightly dependent on the reaction medium and temperature but, to some extent, almost not dependent on comonomer ratio. On the contrary, the intrinsic viscosity of the terpolymers exhibits an apparent dependency on the comonomer ratio and reaction medium but almost no dependency on the reaction temperature. The minimum intrinsic viscosity was obtained at 0.20–0.32 dL/g for AN/OT/XY (34/33/33) with 1*M* HCl as reaction medium, which probably results from the most flexible molecular chain, in turn resulting from the most random sequence distribution of the three-monomer unit along the main chain of the terpolymer. The most random sequence distribution induces distortions in the chains, reducing the conjugation and increasing the chain flexibility. As a consequence, an enhanced solubility of the terpolymers will occur in most common organic solvents.

Table II Solubility and Solution Color of Aniline (AN), *o*-Toluidine (OT), and 2,3-Xylidine (XY) Terpolymer Bases Prepared at −15°C in Organic Solvents

AN/OT/XY (mol)	NMP	DMSO	$CHCl_3$	THF	Ethylene Chloride	Benzene	Acetone	CCl_4	Acetic Acid	Ethanol
100/0/0	MS (DB)	PS (DB)	SS	SS	SS	IS	IS	IS	IS	IS
50/30/20	S (BV)	S	S (V)	S (BV)	S (BV)	S (BV)	MS (RV)	PS (RV)	PS (DG)	PS (BV)
34/33/33	S (BV)	S	S (V)	S (BV)	S (BV)	S (BV)	MS (RV)	PS (RV)	PS (DG)	PS (BV)
20/50/30	S (BV)	S	S (V)	S (BV)	S (BV)	S (BV)	MS (RV)	PS (RV)	PS (DG)	PS (BV)
0/100/0	S (BV)	S	MS (V)	PS (BV)	PS(BV)	PS (BV)	PS (BV)	SS	PS (B)	SS

IS = insoluble; MS = mainly soluble; PS = partially soluble; S = soluble; SS = slightly soluble. The letters in parentheses indicate the color of terpolymer solution in the solvents: BV = bluish violet; DB = dark blue; DG = dark green; RV = reddish violet; V = violet.

Solubility of Terpolymers from Aniline, *o*-Toluidine, and 2,3-Xylidine

It can be seen from Table II that AN/OT/XY terpolymers were completely soluble in NMP, DMSO, chloroform, tetrahydrofuran, ethylene chloride, and benzene when the terpolymer concentration is about 1–3 g/100 mL solvent. They can be partially soluble in acetone, tetrachloromethane, glacial acetic acid, and absolute ethanol. Apparently, a very good solubility of the terpolymers has been observed and results from the presence of a large number of methyl substituents on the aniline ring and random-sequence structure of the comonomer unit, which increases the distance between the macromolecular chains and then significantly reduces the interaction between the chains of terpolymers. The intrinsic viscosity of the terpolymers is comparable to that of polyaniline and poly(*o*-toluidine), but the solubilities of the terpolymers and polyaniline or poly(*o*-toluidine) were much different for each other, as listed in Table II. These results suggest that the solubility is primarily determined by molecular structure rather than intrinsic viscosity of the polymers.[3]

In addition, better solubility was an evidence that the polymerization products were indeed copolymer containing the three monomers rather than a simple mixture of the corresponding homopolymers,[4–6] because both polyaniline and poly(*o*-toluidine) exhibit much poorer solubility and 2,3-xylidine does not homopolymerize at this polymerization condition.[5,6]

^{1}H–NMR Spectrum of Aniline/*o*-Toluidine/2,3-Xylidine (34/33/33) Terpolymer

^{1}H–NMR spectra of terpolymers are characterized by three main signals, which exactly correspond to the three types of protons on the terpolymer chains. The ^{1}H–NMR spectrum of AN/OT/XY (34/33/33) terpolymer exhibits a strong sharp peak centered at 2.18 ppm due to methyl groups, a medium broad peak centered at 6.78 ppm due to protons on the phenylene unit, and a weak broad peak centered at 5.37 ppm due to –NH– and $–NH_2$ groups, as shown in Figure 1. This spectrum does not provide much information on the calculation

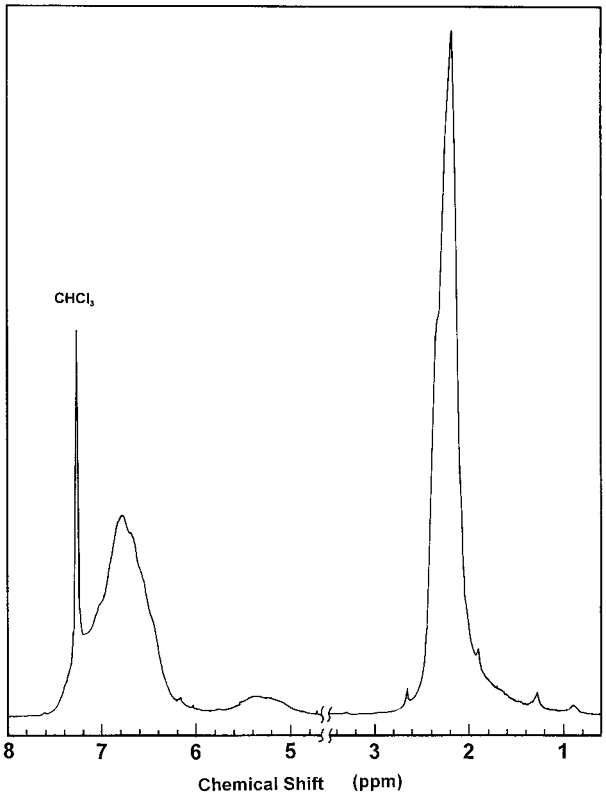


Figure 1 ^{1}H–NMR spectrum of the terpolymer base with aniline/*o*-toluidine/2,3-xylidine molar ratio of 34/33/33 in deuterated chloroform at 300.13 MHz.

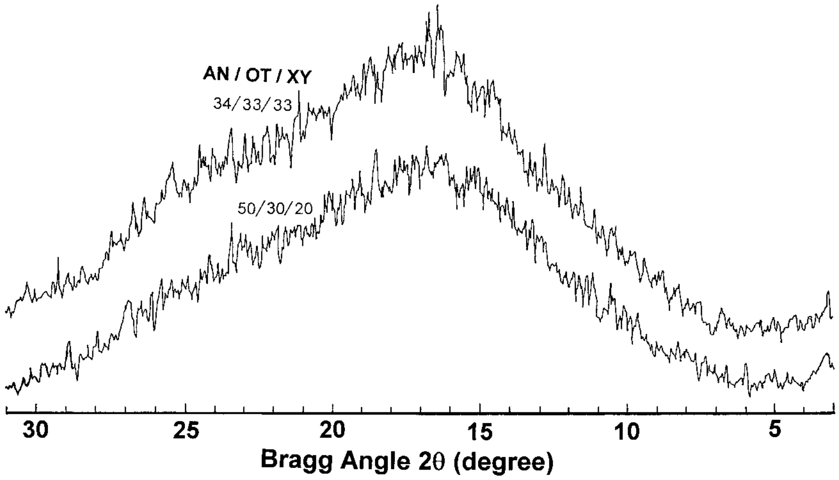


Figure 2 Wide-angle X-ray diffraction diagrams of the as-polymerized terpolymer powders with aniline/*o*-toluidine/2,3-xylidine molar ratios of 34/33/33 (upper) and 50/30/20 (lower).

of sequence distribution of the comonomer units. Only a broad peak of phenyl protons and a single peak from methyl groups plus much better solubility compared with that of homopolymers (Table II) suggest that three comonomer units randomly distribute in the terpolymer chain. It can be seen that there is a medium shoulder peak (2.31 ppm) on the left of the strongest peak of methyl protons. On the basis of the NMR results of AN/XY and AN/OT bipolymers reported previously[5,6] and a comparison of the area of major peak (2.18 ppm) with that of the left shoulder peak (2.31 ppm), it is found that the major peak is attributed to the methyl groups on the benzenoid unit and the medium shoulder peak attributed to the methyl groups on the quinoid unit. Furthermore, it can be roughly calculated that the ratio of benzenoid to quinoid units on the terpolymer is 2 : 1. The calculation of the actual AN/OT/XY molar ratio in AN/OT/XY (34/33/33, feed ratio) terpolymer appears possible on the basis of its NMR spectrum because aromatic proton and methyl proton contents can be calculated according to the peak areas at 6.78 and 2.18 ppm, respectively. Through this method, the AN/OT/XY molar ratio calculated from Figure 1 might be 14/40/46. It is higher XY unit content that gives the terpolymer better solubility in several normal solvents (Table II). The top of the broad peak from phenyl protons was observed at 6.78 ppm due to protons of *p*-disubstituted benzene. This might suggest a linear structure of the terpolymer synthesized by oxidative copolymerization.

Additionally, the resonance peak from –NH– and $-NH_2$ protons is very weak, indicating that the terpolymer has a high molecular weight. If the molecular weight of the terpolymer is low enough, there must be so many $-NH_2$ protons and then a strong peak from $-NH_2$ protons would appear in the NMR spectrum.

Wide-Angle X-ray Diffractogram of the Terpolymers

Wide-angle X-ray diffractograms of AN/OT/XY terpolymer–base powders are shown in Figure 2. Both terpolymers, with AN/OT/XY ratios of 50/30/20 and 34/33/33, exhibit a broad peak at $2\theta = 16.7°$ and a very broad shoulder peak at $2\theta = 20–28°$. This broad peak is characteristic of the diffraction by an amorphous polymer. It was reported that the strongest broad peak of polyaniline base is located at $2\theta = 19–20°$.[7,8] These results indicate that the introduction of methyl groups on the aniline unit increases intermolecular chain spacing and amorphous structure compared with that on polyaniline. An amorphous structure is required for the preparation of the gas-separation membranes having high permeating performance.

DSC Thermograms of the Terpolymers

AN/OT/XY terpolymers are amorphous polymers and do not show any sharp transition peak, as shown in Figure 3. Note that there is a very broad exothermic peak at temperatures above 180°C. This exotherm could be attributed to a series of chemical reactions, involving bond scissioning (such

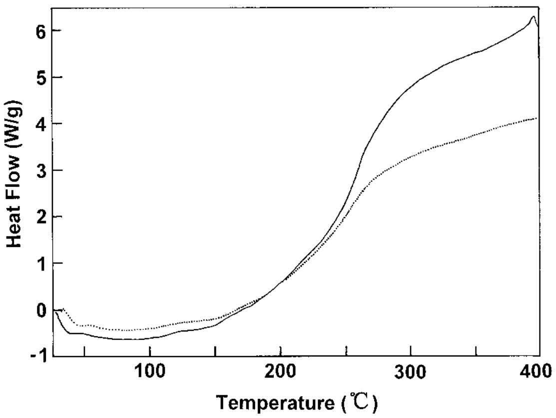


Figure 3 DSC thermograms of the terpolymer powders with aniline/*o*-toluidine/2,3-xylidine molar ratios of 34/33/33 (· · ·) and 50/30/20 (—) at a heating rate of 20°C/min.

as the exclusion of methyl groups), followed immediately by new bond formation and crosslinking.[4] This reaction process has been confirmed by the weight loss results discussed later. A similar exotherm was observed in the DSC pattern of aniline and *o*-ethylaniline copolymers[4] and AN/OT and AN/XY bipolymers.[5,6]

Thermogravimetric Thermograms of the Terpolymers

Figures 4 and 5 shows the thermogravimetry (TG), derivative thermogravimetry (DTG), and the second-derivative thermogravimetry (2DTG) curves of AN/OT/XY terpolymer powders in static air and flowing nitrogen. It should be noted that there is a 2% weight loss in the temperature range 180–350°C in the TG curve of AN/OT/XY (50/30/20) terpolymer in air. Very similarly, two terpolymers with AN/OT/XY ratios of 50/30/20 and 34/33/33 also exhibit a very small weight loss (3–5%) in the temperature range from 180 to 350°C in nitrogen. This temperature range exactly corresponds to the range of exothermic peak of the DSC curves.

Additionally, more weight loss for the terpolymer with AN/OT/XY ratio of 50/30/20 than of 34/33/33 is coincident with the larger exotherm from AN/OT/XY (50/30/20) terpolymer (Fig. 3). Apparently, this small and slow weight loss is the result of the chemical reaction of terpolymers, such as exclusions of methyl groups and hydrogen and subsequent crosslinking between terpolymer chains. Another reason for the small initial weight loss may be evaporation of small amounts of low molar mass compounds. For example, the evaporation of water and dopant (HCl) could cause this behavior, although the evaporating temperature should be lower and evaporating rate should be faster, which means this might not be the primary reason for the behavior.

Table III shows the stable and kinetic parameters of the thermal degradation of the terpolymers. For the same terpolymer of AN/OT/XY (50/30/20), higher thermostability was observed in air than in nitrogen, because the terpolymer exhibits higher decomposition temperatures (T_d, determined through TG curve), higher temperature (T_{dm}, determined through DTG curve) at the maximum weight-loss rate, and lower maximum decomposition rate [$(d\alpha/dt)_m$]. The char yield of the terpolymer at 900°C is zero. This results from the thermo-oxidative decomposition, which occurred following the thermal decomposition. In nitrogen, as shown in Table III, AN/OT/XY (34/33/33) terpolymer exhibits higher thermostability, slower decomposition rate, and greater char yield than those of AN/OT/XY (50/30/20) terpolymer. However, AN/OT/XY (34/33/33) terpolymer is significantly less stable than polyaniline[9] because a large number of methyl groups on the terpolymer chains are easily excluded from the chains at an elevated temperature.

The kinetic parameters of the thermal degradation for the terpolymers are calculated[10–13]

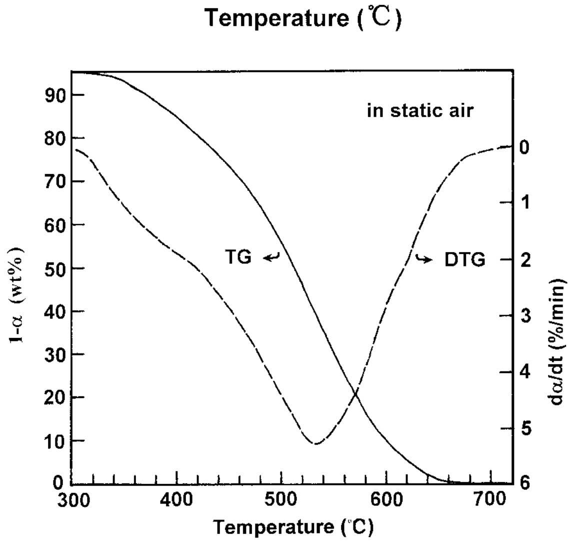


Figure 4 Thermogravimetry (TG, —) and derivative thermogravimetry (DTG, - - -) of the terpolymer powder with aniline/*o*-toluidine/2,3-xylidine molar ratio of 50/30/20 at a heating rate of 10°C/min in static air.

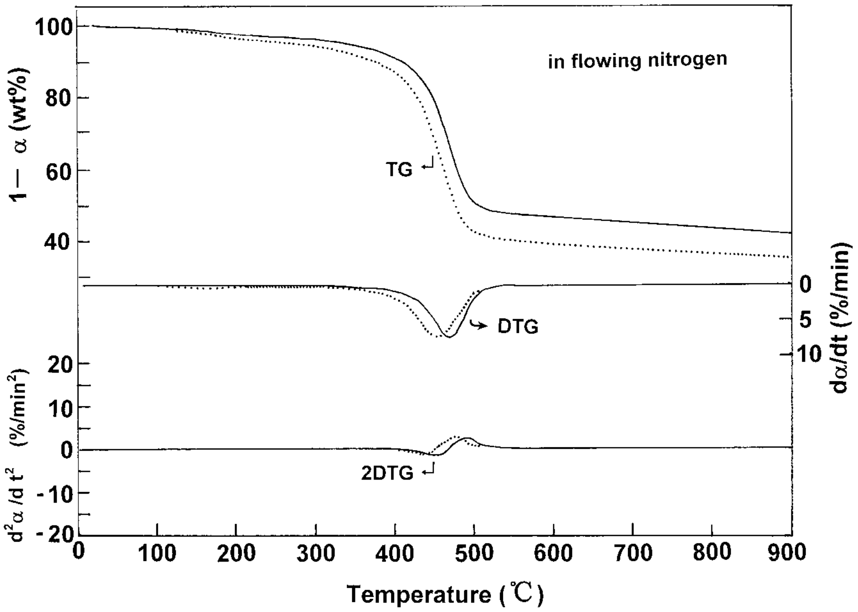


Figure 5 Thermogravimetry (TG), derivative thermogravimetry (DTG), and the second-derivative thermogravimetry (2DTG) of the terpolymer powders with aniline/*o*-toluidine/2,3-xylidine molar ratios of 34/33/33 (—) and 50/30/20 (· · ·) at a heating rate of 10°C/min in flowing nitrogen.

through Figure 6 by the Friedman method by eq. (1):

$$\ln(d\alpha/dt) = \ln Z + n \ln(1 - \alpha) - E/RT \qquad (1)$$

and the Kissinger method by eq. (2):

$$n = |(d^2\alpha/dt^2)_{L\max}|/|(d^2\alpha/dt^2)_{R\max}| \qquad (2)$$

It can be seen that the activation energy E, decomposition reaction order n, and frequency factor $\ln Z$ values are all larger in nitrogen than those in air.

Influence of Operating Temperature on Air Separation

Actual air-separation properties across AN/OT/XY (50/30/20) terpolymer (20 wt %) with ethyl cellulose (80 wt %) blend thin-film composite membrane at 22–50°C and 640 kPa transmembrane pressure difference are shown in Figure 7. The oxygen permeation rate J_{O_2} will increase steadily but the oxygen concentration Y_{o_2} will decrease with increasing operating temperature. The J_{O_2} value at 50°C is 4.7-fold as high as the J_{O_2} at 22.8°C, but the Y_{o_2} at 50°C is 90% the size of the oxygen concentration at 22.8°C. These re-

Table III Thermally Stable and Kinetic Parameters of the Terpolymers from Aniline (AN), *o*-Toluidine (OT), and 2,3-Xylidine (XY) Calculated by Friedman Technique

					Char Yield				
AN/OT/XY (mol %)	Atmosphere	T_d (°C)	T_{dm} (°C)	$(d\alpha/dt)_m$ (%/min)	At 900°C (wt %)	E (kJ/mol)	n	$\ln Z$ (min^{-1})	r
50/30/20	Static air	424	524	5.2	0	37	0.6	3.1	0.9964
50/30/20	Flowing nitrogen	418	460	7.6	35	113	2.0 (1.4)[a]	16.9	0.9924
34/33/33	Flowing nitrogen	439	469	7.4	41	129	2.3 (1.2)[a]	19.3	0.9977

[a] The data in the blankets are obtained by Kissinger eq. (2).

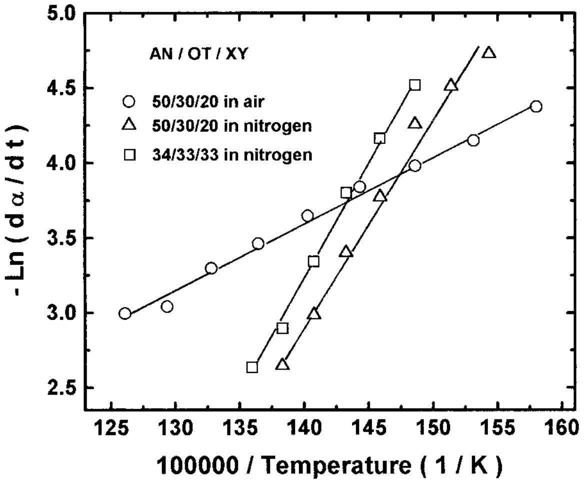


Figure 6 Friedman method (plot of $d\alpha/dt$ vs $1/T$) for the calculation of the activation energy of the thermal degradation of the terpolymer powders with aniline/*o*-toluidine/2,3-xylidine molar ratios of 50/30/20 (○) in static air, 50/30/20 (△) in flowing nitrogen, and 34/33/33 (□) in flowing nitrogen.

sults occur because higher temperature ordinarily generates less discriminating gaps or more free volume in the membranes. In addition, the air will become less condensable with increasing temperature. The slope of the OEA flux versus temperature curves increases with an increase in operating temperature, which is similar to that typically observed for other thin-film composite membranes.[14] It is known that the highest oxygen concentration achieved by pure ethyl cellulose membrane is about 37%.[15] Obviously, only the introduction of 20 wt % AN/OT/XY terpolymer can increase the oxygen concentration from 37 to 42.9%. This enhancement of oxygen concentration results totally from the high air-separation capability of AN/OT/XY terpolymer. The increase in the oxygen concentration from 37 to 42.9% is significant in industrial membrane-separation application.

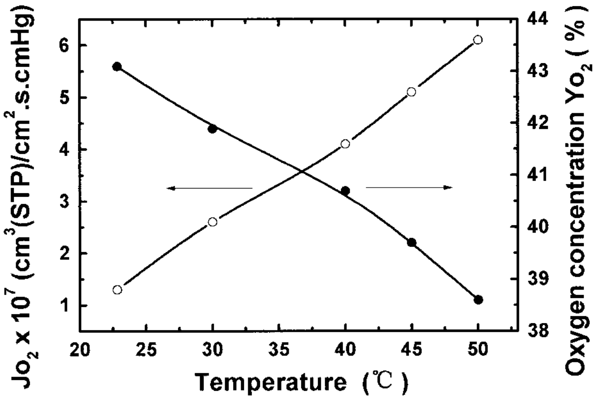


Figure 7 The dependency of air-separation performance on operating temperature for blend thin-film composite membrane of AN/OT/XY (50/30/20, HCl medium, −15°C) terpolymer (20 wt %) with ethyl cellulose (80 wt %) on polysulfone ultrafiltration porous membrane.

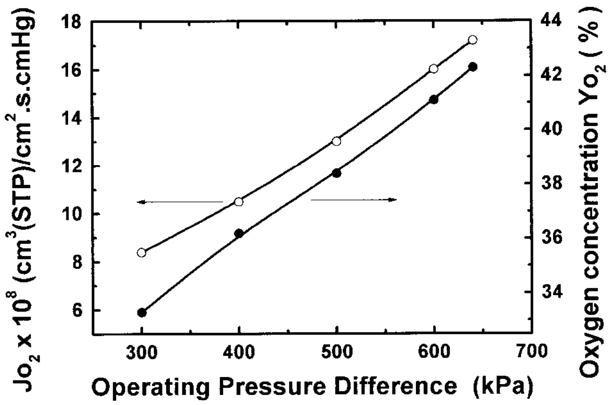


Figure 8 The dependency of air-separation performance on operating pressure for blend thin-film composite membrane of AN/OT/XY (50/30/20, HCl medium, −15°C) terpolymer (20 wt %) with ethyl cellulose (80 wt %) on polysulfone ultrafiltration porous membrane.

Influence of Transmembrane Pressure Difference on Air Separation

Figure 8 shows the influence of transmembrane pressure difference on actual air-separation properties through AN/OT/XY (50/30/20) terpolymer (20 wt %) with ethyl cellulose (80 wt %) blend thin-film composite membrane. Apparently, the oxygen permeation rate Jo_2 and oxygen concentration Yo_2 through the composite membrane increase simultaneously with increasing transmembrane pressure difference from 300 to 650 kPa at 25°C. The oxygen permeation rate Jo_2 and oxygen concentration Yo_2 at the pressure difference 650 kPa are 2.1- and 1.3-fold as high as those at the pressure difference 300 kPa, respectively. Similar results have been observed for other ultrathin-film composite membranes.[14–17] A concurrent increase in the oxygen permeation rate Jo_2 and oxygen concentration Yo_2 is believed to be attributed to a combination of an acceleration in the oxygen passing rate across the membrane with the compression between the thin film and porous support as the transmembrane pressure difference increases.

CONCLUSIONS

A series of soluble terpolymers from aniline, *o*-toluidine, and 2,3-xylidine were synthesized by oxidative polymerization in acidic media at −15 and 21°C. The terpolymers exhibit the highest intrinsic viscosity up to 0.79 dL/g but the polymerization yield is as low as 15–22%. The random molecular chain and amorphous supermolecular structures of the terpolymers have been confirmed by ^{1}H–NMR and wide-angle X-ray diffraction techniques, respectively. DSC and TG measurements indicate the occurrence of some exothermic reaction accompanied with a small weight loss during heating in a temperature range from 180 to 350°C. The terpolymers have a thermal degradation temperature of 418−439°C, a char yield of 35–41 wt % at 900°C, and higher degradation activation energy in nitrogen than in air. There is a good compatibility between AN/OT/XY terpolymer and ethyl cellulose in the blend membrane prepared by the solution-cast method. The blend thin-film composite membrane exhibits good air-separation performance. The highest oxygen permeation rate and oxygen concentration were found to be 6.1×10^{-7} cm^3 (STP)/cm^2 s^{-1} cmHg^{-1} and 43.1%, respectively, for the abovementioned composite membrane in a single step at the pressure difference range of 640 kPa. However, this oxygen concentration of 42.2% is much lower than about 60%, predicted theoretically on the basis of P_{O_2}/P_{N_2} values of pure polyaniline reported earlier.[18–20] Therefore, there is great potential in enhancing the oxygen concentration by increasing terpolymer content in the blend membrane.

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