Preparation of Ultrathin Films of Aromatic Polyamides and Aromatic Poly(amide–imides) by Vapor Deposition Polymerization

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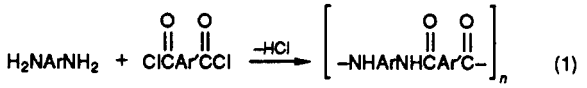
ABSTRACT: Ultrathin films of aromatic polyamides and aromatic poly(amide–imides) were prepared by vapor deposition polymerization. Terephthaloyl chloride and some aromatic diamines were evaporated under reduced pressure, giving polyamide films directly on a substrate. The evaporation of 4-(chloroformyl)-phthalic anhydride together with aromatic diamines afforded films of poly(amide–amic acids), which in turn were converted to poly(amide–imides) by heat treatment. The thermal stability, chemical inertness, and dielectric properties of these polymer films were comparable with those of polymer films obtained by a conventional solution method.

Introduction

Wholly aromatic polyamides (aramids) are members of high-temperature resistant polymers, and some of them are used as flame-resistant fibers, high-strength and high-modulus fibers, and high-performance plastics.[1] The most popular method for synthesis of aramids is the one starting from diamine–diacid chloride monomer pairs by low-temperature solution polycondensation (eq 1).[2]



(1)

In 1980, Ikeda and his co-workers[3] demonstrated that poly(*p*-phenyleneterephthalamide) (Du Pont's "Kevlar" molecule) could be successfully prepared by vapor-phase polymerization of *p*-phenylenediamine and terephthaloyl chloride. In 1985, we reported for the first time the preparation of ultrathin films of aromatic polyamide and polyimide by vapor deposition polymerization.[4-6] The thickness of the films was in the range of 50–1000 nm. Later, similar work on ultrathin films of aromatic polyimides was reported by both Salem et al.[7] and Lamb et al.[8]

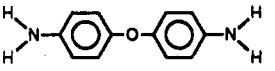
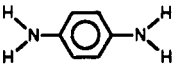
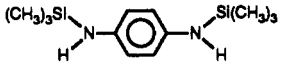
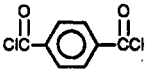
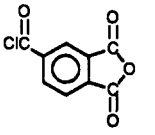
The present article deals with further studies on the preparation and characterization of ultrathin films of aramids and aromatic poly(amide–imides) by vapor deposition polymerization.

Experimental Section

Materials. Table I shows the monomer structures: bis(4-aminophenyl) ether (ODA), *p*-phenylenediamine (PPDA), and *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (SiPPDA) used as diamine monomers and terephthaloyl chloride (TPC) and 4-(chloroformyl)phthalic anhydride (CPA) used as carboxylic acid components. ODA, PPDA, and TPC were obtained commercially and purified by sublimation before use. CPA and SiPPDA were prepared according to the literature[9,10] and purified by distillation.

Polymer Film Preparation. Polyamide Film from ODA and TPC. ODA and TPC were evaporated by heating at 165–175 and 40 °C, respectively, under a pressure of (0.8–2) × 10^{-4} Torr. The evaporation rate of each monomer was individually controlled with a quartz oscillator-type rate monitor. The polyamide film was formed on an aluminum substrate kept at 20 °C, at a deposition rate of 0.3–13.6 nm·s^{-1}, which was measured by a quartz oscillator-type thickness monitor. The infrared (IR) spectrum of the film showed absorptions at 3400 (N–H) and 1650 cm^{-1} (C=O), which are characteristic of the amide group.

Table I
Structure and Symbol of Monomers

ODA	bis(4-aminophenyl) ether	
PPDA	*p*-phenylenediamine	
SiPPDA	*N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine	
TPC	terephthaloyl chloride	
CPA	4-(chloroformyl)phthalic anhydride	

Polyamide Film from PPDA and TPC. PPDA and TPC were evaporated by heating at 80 and 40 °C, respectively, under a pressure of 2 × 10^{-3} Torr. The polyamide film was formed on an aluminum substrate at 80 °C at a deposition rate of 0.3 nm·s^{-1}. The IR spectrum exhibited characteristic amide absorptions at 3400 (N–H) and 1650 cm^{-1} (C=O). The inherent viscosity of the polymer was 0.73 dL·g^{-1} in concentrated sulfuric acid, measured at a concentration of 0.5 g·dL^{-1} at 30 °C.

Polyamide Film from SiPPDA and TPC. SiPPDA and TPC were evaporated by heating at 60 and 80 °C, respectively, under a pressure of 2 × 10^{-3} Torr. The polyamide film was formed on an aluminum substrate kept at 80 °C at a deposition rate of 0.03 nm·s^{-1}. The IR spectrum showed absorptions at 3400 (N–H) and 1650 cm^{-1} (C=O), which are characteristic of the amide group. The inherent viscosity of the polymer was 0.14 dL·g^{-1} in concentrated sulfuric acid.

Poly(amide–imide) Film from ODA and CPA. ODA and CPA were evaporated by heating at 165 and 70 °C, respectively, under a pressure of 5 × 10^{-5} Torr. The deposited film was formed on an aluminum substrate at 20 °C at a deposition rate of 0.4 nm·s^{-1}. In order to obtain the poly(amide–imide) film, the deposited film was heated at 300 °C for 1 h under vacuum. The

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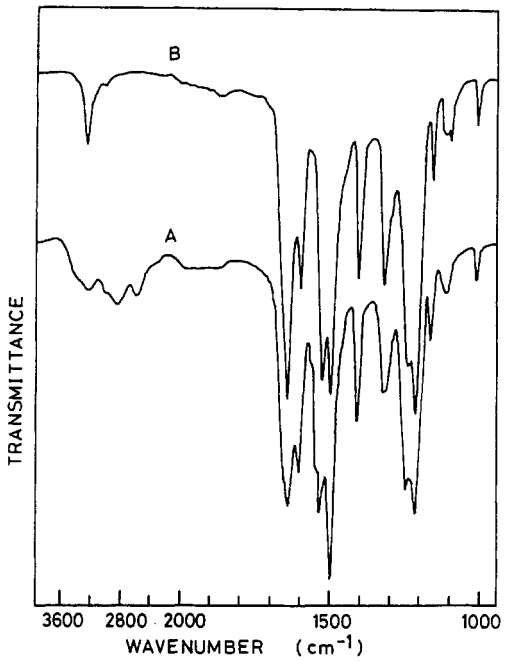


Figure 1. IR spectra of the deposited film from ODA and TPC (A) immediately after deposition and (B) after heating at 200 °C for 1 h.

IR spectrum of the heated film exhibited absorptions at 1780, 1720, 1380, and 725 cm^{-1} due to an imide linkage and absorptions at 3400 (N–H) and 1650 cm^{-1} (C=O) corresponding to an amide group.

Measurements. As in our previous work,[5] the same apparatus was used for the vapor deposition process. The IR spectra were recorded on a Nicolet 5DXB Fourier transform infrared spectrophotometer by the attenuated total reflectance (ATR) method using a sample film on an aluminum foil. The dielectric constant at 10 kHz was measured at 20 °C by a Yokogawa–Hewlett–Packard 4275A-LCR bridge. Thermogravimetry (TG) was performed with a Shinkuriko HP-TG 3000 thermal analyzer.

Results and Discussion

Preparation of Polyamide Films. Before preparation of polyamide and poly(amide–imide) ultrathin films by vapor deposition polymerization, the deposition behavior of each monomer was examined on an aluminum substrate by means of IR spectroscopy. It was revealed that ODA was deposited on the substrate, while other monomers such as PPDA, SiPPDA, TPC, and CPA were not deposited individually due to their higher vapor pressure. When the component monomers were evaporated simultaneously, they tended to deposit smoothly on the substrate. These observations indicated that simultaneous evaporation of the component monomers was essential for the preparation of the polyamide and poly(amide–imide) films.

The films on the substrate (thickness around 0.5 μm) were formed by the simultaneous evaporation of ODA and TPC at 20 °C at a deposition rate of 0.3 $nm \cdot s^{-1}$. The IR spectrum of the as-deposited film (Figure 1A) exhibited characteristic amide absorptions at 3400 (N–H) and 1650 cm^{-1} (C=O), which was almost identical with that of the cured polyamide film (Figure 1B). The IR study revealed that the evaporated TPC immediately reacted with ODA deposited on the substrate, giving polyamide. In addition, in the IR spectrum of the as-deposited film, there are fairly strong bands in the 2800–2600-cm^{-1} region. This suggested that the as-deposited film contained significant amounts of polyamide oligomer of low molecular weight. When the as-deposited film was cured at 200 °C for 1 h under vacuum, these absorptions disappeared and the decrease of film thickness was hardly observed. This clearly suggests that further polycondensation proceeds smoothly by heating the as-deposited film.

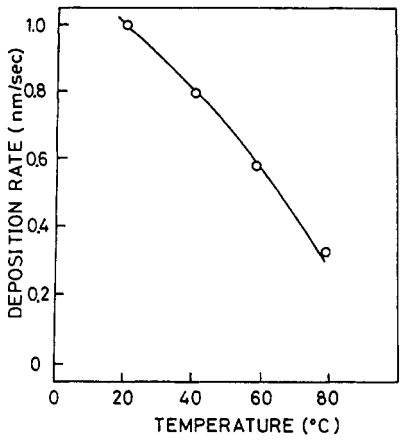


Figure 2. Effect of substrate temperature on the deposition rate of the polymer from PPDA and TPC.

Table II
Preparation of Poly(*p*-phenyleneterephthalamide)

diamine component	substrate temp, °C	deposition rate, $nm \cdot s^{-1}$	η_{inh},[a] $dL \cdot g^{-1}$
PPDA[b]	30	1.0	0.07
PPDA	80	0.3	0.73
SiPPDA[c]	30	0.1	0.06
SiPPDA	80	0.03	0.14

[a] Measured at a concentration of 0.5 $g \cdot dL^{-1}$ in concentrated sulfuric acid at 30 °C. [b] Deposition was carried out with heating TPC at 40 °C and PPDA at 80 °C under a pressure of 2×10^{-3} Torr. [c] Deposition was carried out with heating TPC at 80 °C and SiPPDA at 60 °C under a pressure of 2×10^{-3} Torr.

The deposition rate of polymers is generally influenced by both evaporation rate of component monomers and substrate temperature. When the deposited film was prepared at 20 °C at a faster evaporation rate of the monomers, which corresponds to a faster deposition rate, and then was subjected to heat treatment at 200 °C for 1 h under vacuum, both the absorption intensity of the IR spectrum and the thickness of the cured film decreased markedly probably due to removal of polyamide oligomer of much lower molecular weight (less than 500). Thus, it is supposed that a faster deposition at a lower substrate temperature resulted in the formation of low molecular weight polyamide oligomers.

Figure 2 shows the effect of substrate temperature on the deposition rate of the polyamide from PPDA and TPC. It was observed that the deposition rate fell gradually as the substrate temperature was increased. The effect of substrate temperature on the inherent viscosity of the polyamide from PPDA and TPC is shown in Table II. It appears that the polyamide having a higher inherent viscosity could be obtained at a higher substrate temperature. It seems when the substrate temperature is higher, the as-deposited oligomer of lower molecular weight should be removed readily from the substrate. Thus, when the deposition rate was slower, the polymer with a higher molecular weight remained on the substrate.

The precise mechanism of vapor deposition polymerization is not fully understood yet; however, a general picture of the reaction taking place on a substrate is shown below. There is a statistical equilibrium between adsorption and desorption of the two monomer molecules on the substrate. The rates of deposition and removal of the monomers are governed by vapor pressure of each molecule

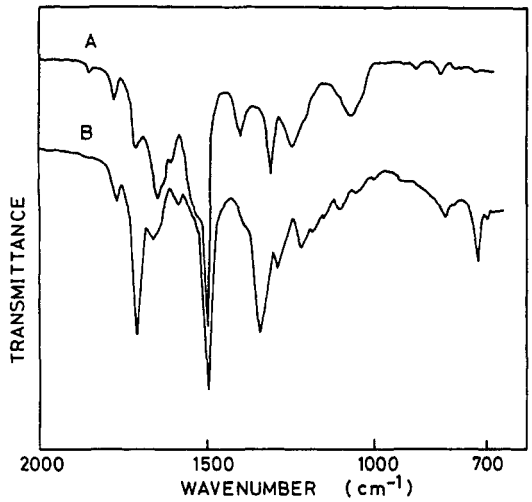


Figure 3. IR spectra of the deposited film from ODA and CPA (A) immediately after deposition and (B) after heating at 250 °C for 1 h.

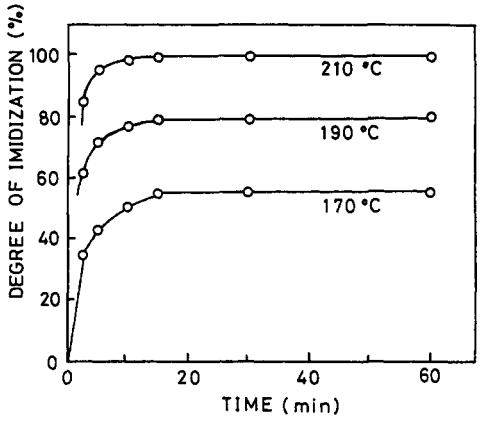
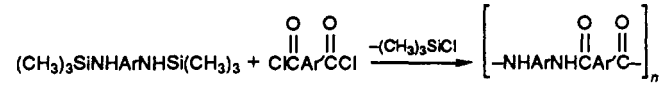


Figure 4. Temperature dependence of the degree of imidization of the deposited film obtained from ODA and CPA at various temperatures.

and substrate temperature. On the substrate, the linking reaction can take place by migration of the adsorbed molecules, leading to the formation of the oligomer. Further combination of the monomers with the oligomer produces polymer molecules with higher molecular weight.

During vapor deposition polymerization, polymer molecules on the substrate have some molecular weight distribution. Monomers and oligomers with low molecular weights can escape from the substrate during deposition. This desorption is rapid when the substrate temperature is high. It presumably accounts for the results in Table II showing that the deposition rate is slow, giving a final polymer with a high molecular weight, when the substrate temperature is high.

We recently demonstrated a novel synthetic method for obtaining aromatic polyamides from *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines and aromatic diacid chlorides by low-temperature solution polymerization by elimination of trimethylsilyl chloride.[10] The N-silylated diamine method was applied to the preparation of polyamide film through vapor deposition polymerization (eq 2).



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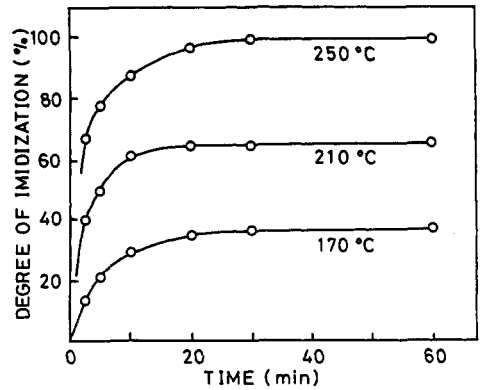
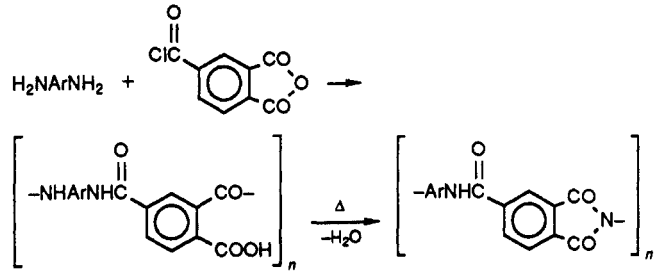


Figure 5. Temperature dependence of the degree of imidization of the deposited film obtained from PPDA and CPA at various temperatures.

Simultaneous evaporation of SiPPDA and TPC yielded a clear deposited film of the polymer, which was shown to be a polyamide by IR analysis. The inherent viscosity of the polyamide obtained by the N-silylated diamine method was found to be lower than that of the polyamide from PPDA and TPC (Table II), probably because SiPPDA has a higher vapor pressure and hence a shorter contact time with TPC compared with PPDA. Nevertheless, the N-silylated diamine method is useful for forming a polyamide coating on a metal substrate, because the trimethylsilyl chloride byproduct has a lower corrosive effect on a metal than the hydrochloric acid formed during the polycondensation of PPDA and TPC.

Preparation of Poly(amide-imide) Films. We also investigated the preparation of aromatic poly(amide-imide) films from aromatic diamines and CPA (eq 3).



(3)

The IR spectrum of the as-deposited film obtained from ODA and CPA is shown in Figure 3A. The carbonyl absorption of the amide moiety in the polymer backbone was observed at 1650 cm^{-1}, which indicated that the prepared film consisted of poly(amide-amic acid). This film was heated at 250 °C for 1 h under nitrogen. The IR spectrum of the heated film is shown in Figure 3B. In addition to an absorption at 1650 cm^{-1} due to the amide carbonyl, it gave characteristic imide absorptions at 1780, 1720, 1380, and 725 cm^{-1}. The progress of imidization was monitored by the IR technique. The absorption at 1380 cm^{-1} was used to follow the appearance of the imide moiety.[11] A fully imidized sample was prepared by thermal imidization of the deposited film at 300 °C for 1 h under vacuum. The imide content was plotted against heating times at different temperatures (Figures 4 and 5). From these results, it was found that the complete imidization of the poly(amide-amic acids), obtained from both ODA and PPDA, could be achieved at 210 and 250 °C, respectively. The results proved that the poly(amide-amic acids) required a higher imidzation temperature than the poly(amic acids) studied in our previous work.[5]

Table III
Vapor Deposition Conditions[a]

monomers		evaporation temp, °C		deposition	
acid component	diamine component	acid	diamine	pressure, Torr	rate, nm·s^{-1}
TPC	ODA	40	165	8×10^{-4}	0.3
		40	175	8×10^{-5}	13.6
TPC	PPDA	40	80	2×10^{-3}	1.0
TPC	SiPPDA	80	60	2×10^{-3}	0.1
CPA	ODA	70	165	5×10^{-5}	0.4
CPA	PPDA	70	80	2×10^{-4}	0.6

[a] Vapor deposition polymerization was carried out on the substrate at 20 °C.

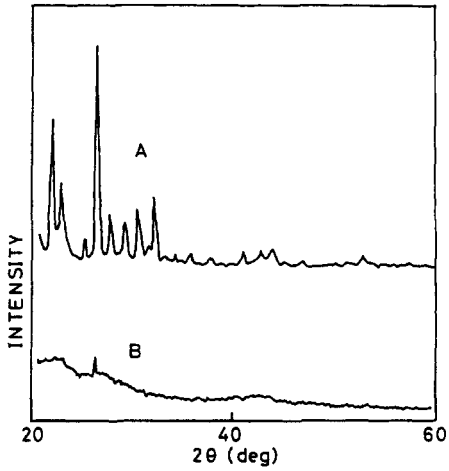


Figure 6. X-ray diffraction diagrams of (A) polyamide obtained from PPDA and TPC and (B) polyamide obtained from SiPPDA and TPC.

Typical vapor deposition conditions for the preparation of films of polyamides and poly(amide–amic acids) are shown in Table III. The deposited films could readily be prepared under higher pressure from more volatile monomers such as TPC and CPA, compared with the preparation of poly(amic acid) films from pyromellitic dianhydride.[5]

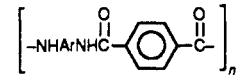
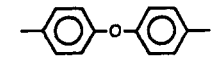
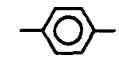
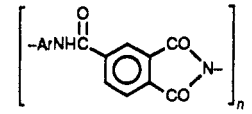
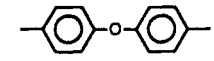
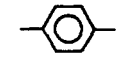
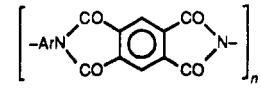
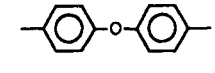
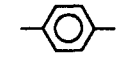
Characterization of Deposited Polymers. The crystallinity of the polyamide (Du Pont's "Kevlar" molecule, which is well-known as a highly crystalline polymer), obtained by two different routes was evaluated by X-ray diffraction studies. The vapor deposition polycondensation of PPDA with TPC afforded a white translucent film, indicating high crystallinity (Figure 6A). On the other hand, the N-silylated diamine method starting from SiPPDA and TPC gave an amorphous transparent film (Figure 6B). This can be explained by the bulkiness of trimethylsilyl group of SiPPDA interfering with the packing of growing polymer chains during polycondensation on the substrate.

The thermal stability of the polyamides and poly(amide–imides) was studied by means of TG. The TG curves of the polymers revealed that the weight loss began at 400 °C in air.

The chemical resistance of the polymer films was examined by immersing in various media. The films showed excellent stability to common organic solvents including ether, acetone, and methanol and to concentrated hydrochloric acid.

The dielectric constants of the polymer films are summarized in Table IV. Values for the polyamides were found to be 5–8, which are higher than those of the polyimide films. The poly(amide–imides) had moderate values of 4–5, which are in between the polyamides and polyimides. In addition, the polymers containing the *p*-phenylene moiety had somewhat higher values than the polymers having an oxydi-*p*-phenylene structure.

Table IV
Dielectric Constants of Various Polymer Films

polymer structure	–Ar–	dielectric constant
		6–7
		5–8
		4.6
		5.2
		3.5[7]
		4.0[7]

Conclusion

Ultrathin films of aromatic polyamides and aromatic poly(amide–imides) were successfully prepared on a substrate by a dry process involving vapor deposition polymerization. The rate of deposition and the molecular weights of the polyamides were highly dependent on the vapor pressure of the monomers and the temperature of the substrate. The N-silylated diamine method gave a transparent and amorphous polyamide film, which had the advantage of causing no corrosion of a metal substrate by the trimethylsilyl chloride byproduct, unlike the hydrochloric acid generated by other methods. The characteristic features of polyamide and poly(amide–imide) films such as thermal stability, chemical inertness, and dielectric properties were nearly comparable to those of polymer films obtained by a conventional solution method.

References and Notes

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Registry No. (ODA)(TPC) (copolymer), 26809-79-0; (ODA)(TPC) (SRU), 26854-93-3; (PPDA)(TPC) (copolymer), 26125-61-1; (PPDA)(TPC) (SRU), 24938-64-5; (ODA)(CPA) (copolymer), 26354-91-6; (PPDA)(CPA) (copolymer), 33659-35-7; (SiPPDA)(TPC) (copolymer), 106680-84-6; (SiPPDA)(TPC) (SRU), 24938-64-5.