(51) Venkatachalam, C. M. *Biopolymers* **1968**, *6*, 1425.
(52) Chou, P. Y.; Fasman, G. D. *Biophys. J.* **1979**, *26*, 367.
(53) Toniolo, C. *CRC Crit. Rev. Biochem.* **1980**, *9*, 1.
(54) Raj, P. A.; Balaram, P. *Biopolymers* **1985**, *24*, 1131.
(55) Toniolo, C.; Bonora, G. M.; Stavropoulos, G.; Cordopatis, P.; Theodoropoulos, D. *Biopolymers* **1986**, *25*, 281.
(56) Benedetti, E.; Di Blasio, B.; Pedone, C.; Lorenzi, G. P.; Tomasic, L.; Gramlich, V. *Nature (London)* **1979**, *282*, 630.
(57) Lorenzi, G. P.; Jäckle, H.; Tomasic, L.; Pedone, C. *Biopolymers* **1983**, *22*, 157.
(58) Bonora, G. M.; Toniolo, C.; Mascagni, P.; Gibbons, W. A. *Proc. 14th Int. Symp. Chem. Nat. Prod., Poznan, Poland* **1984**, C58.
(59) Donzel, B.; Rivier, J.; Goodman, M. *Biochemistry* **1977**, *16*, 2611.
(60) Naider, F.; Becker, J. M. *CRC Crit. Rev. Biochem.* **1986**, *21*, 225.

Vapor Deposition Polymerization: A Study on Film Formation in Reaction of Pyromellitic Anhydride and Bis(4-aminophenyl) Ether

Masayuki Iijima* and Yoshikazu Takahashi

Institute for Super Materials, ULVAC Japan, Ltd., 5-9-7 Tohkohdai, Tsukuba, Ibaraki 300-26, Japan. Received July 21, 1988; Revised Manuscript Received January 4, 1989

ABSTRACT: A course of the vapor deposition polymerization between pyromellitic dianhydride (PMDA) and bis(4-aminophenyl) ether (ODA) was determined. The surface of deposited film of two monomers was rough due to the high crystallinity, whereas the film prepared by coevaporation of PMDA and ODA had a smooth surface. A collision of the functions of an acid anhydride and an amine occurred by the migration of the monomers and the oligomers on the substrate. The formation of a charge transfer (CT) complex was newly observed in the first step of the polycondensation by using absorption spectra and ESR spectra. The CT complex disappeared as the polymerization proceeded.

Introduction

Demands of polyimides especially in electronics have been growing because of their excellent heat resistance, chemical stability, and dielectric property. Preparation of thin films by a wholly dry system is one of the most important technologies in this field.

Iijima et al.[1,2] and Salen et al.[3] independently reported the new method for the preparation of polyimide films via vapor deposition polymerization.[1-3] In this method, a stoichiometric amount of both monomers, a tetracarboxylic dianhydride and a diamine, was evaporated simultaneously to form a poly(amic acid) thin film, and subsequent heating of the film afforded a polyimide thin film. Thus, this technology readily offers polyimide thin films 0.1–10 μm thick.

Since the polycondensation, in the solution polymerization, always proceeds via a collision of functional groups, a carboxylic anhydride and an amine, we generally choose a solution medium to accelerate the efficient collision of these groups. In the vapor deposition polymerization, although the collision should be limited, because of the restriction of a free movement of the functional groups, we actually observed the fairly fast polycondensation in this method. In this paper, we describe our observations of the course of polycondensation between pyromellitic dianhydride and bis(4-aminophenyl) ether to clarify the nature of this new class of polymerization.

Experimental Section

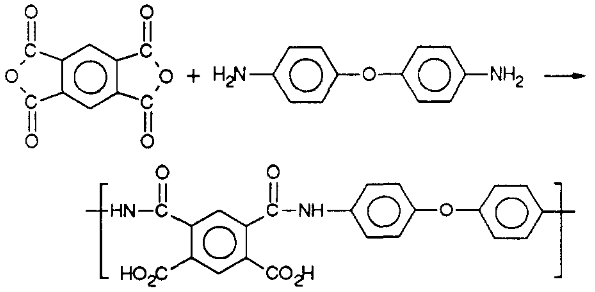
Deposition of Pyromellitic Dianhydride and Bis(4-aminophenyl) Ether. Both pyromellitic dianhydride (PMDA) and bis(4-aminophenyl) ether (ODA) were purified by sublimation under reduced pressure before use. These monomers were deposited on a substrate by heating at 180 ± 2.5 and 160 ± 2.5 °C, respectively, under a pressure of 2×10^{-6} Torr. Since the deposition rate of each monomer under these conditions was 5 Å/s, the rate of coevaporation of these two monomers to prepare the polymeric film was 10 Å/s.

The migration behavior of the monomers on a substrate was observed by scanning electron microscopy (SEM) reported by Takagi et al.[4] A silicon wafer and a glass plate were used as a substrate and a mask, respectively, and placed as illustrated in Figure 1, where the vapor of the monomers comes from the normal direction of the substrate.

Measurement. Infrared (IR) spectra were measured on a Nicolet FT-IR 5DXB spectrometer by the ATR method, where the sample films were deposited on an aluminum foil. Ultraviolet–visible (UV–vis) spectra were recorded on a Hitachi UV-VIS 323 spectrometer. SEM photographs were taken on an Akashi DS-130C. Electron spin resonance (ESR) spectra were measured by JES-ME3X. The sample films were deposited on a poly(ethylene terephthalate) (PET) film, and they were packed with rolling in a glass tube to measure ESR spectra. The *g* value was calibrated by using 2,2-diphenyl-1-picrylhydrazyl as the standard (g = 2.0036).

Results and Discussions

Poly(amic acid) is produced by the vapor deposition polymerization of PMDA and ODA as shown in eq 1.


(1)

We have tried to determine the migration of each monomer, PMDA and ODA, using the partially masked substrate as shown in Figure 1.[4] Rough surfaces with tiny islands, probably indicating their high crystallinity, were observed in the uncovered area of the film. The growing patterns of the island were also observed for the range of a few micrometers from the edge in the masked area in both cases. These facts indicate that a fair amount of monomer molecules apparently migrated from the uncovered area to the masked area. When PMDA and ODA

0024-9297/89/2222-2944$01.50/0 © 1989 American Chemical Society

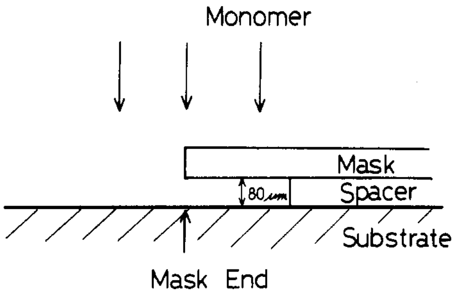


Figure 1. Apparatus for observation of the migration of evaporated substances.

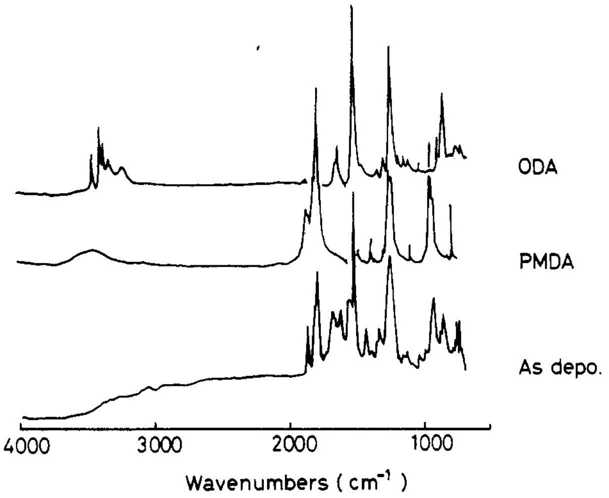


Figure 2. IR spectra of PMDA, ODA, and coevaporated film as deposited.

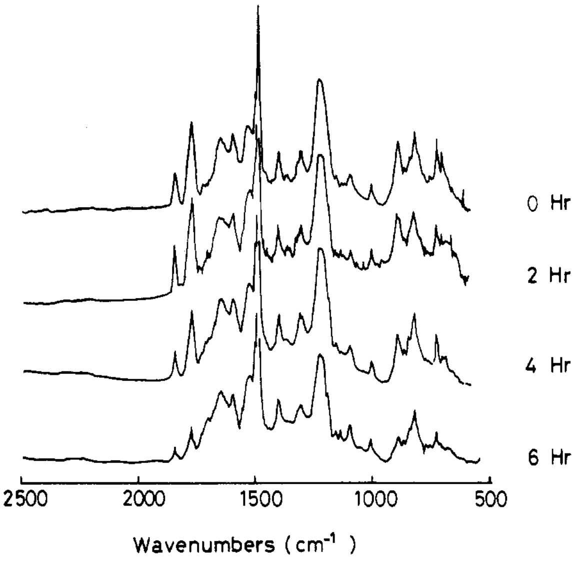


Figure 3. Change of IR spectra of coevaporated film with time measured in air at 25 °C.

were coevaporated with the same deposition rate, the surface of the film of resulted copolymer was smooth in contrast to the case of monomers, and the film grew in masked area similar to the case of monomers.

Figure 2 shows the IR spectra of the deposited films of PMDA and ODA themselves and the coevaporated film. In the spectrum of the coevaporated film, the absorption around 3300–3500 cm^{-1} caused by an N–H stretching vibration was hardly seen compared with the case of ODA, and the absorption of the amide carbonyl bond of the poly(amic acid) structure newly appeared at 1650 cm^{-1}. On the other hand, the absorption of acid anhydride caused by PMDA was also observed. These facts indicated that a poly(amic acid) structure was partly formed by the reaction of PMDA and ODA, but the film still contained the unreacted monomers. Change of IR spectra of the coevaporated film at a certain lapse time at 25 °C is shown in Figure 3. The carbonyl absorptions of the acid anhydride at 1780 and 1850 cm^{-1} decreased, and the absorption of the amide bonding at 1650 cm^{-1} increased with time. The relationship of the absorbance with time is plotted in Figure 4. The half-life time ($t_{\mathrm{IR}1/2}$) estimated from this

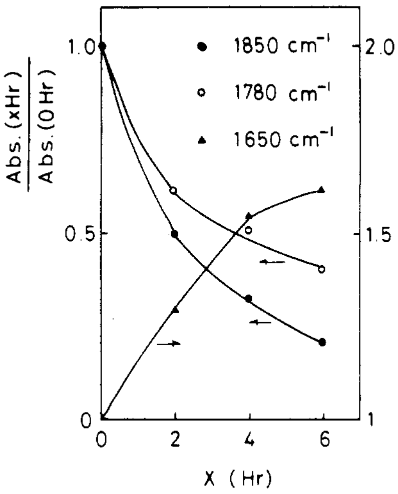


Figure 4. Relationship between time and relative absorbance in the IR spectra of coevaporated film.

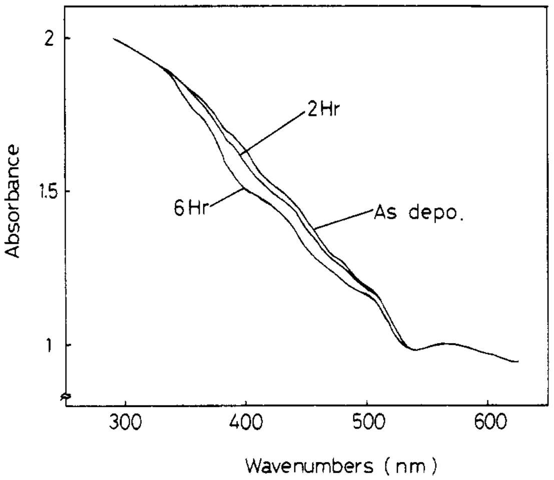


Figure 5. Absorption spectra of coevaporated film measured with an elapse of time.

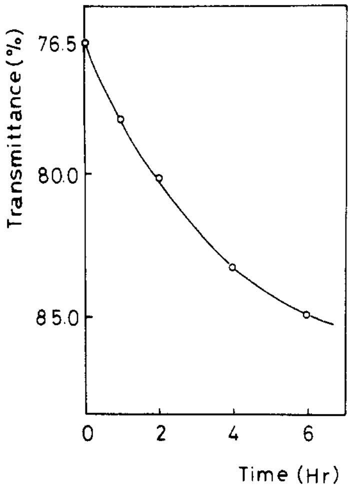


Figure 6. Relationship between time and relative absorbance at 480 nm of coevaporated film.

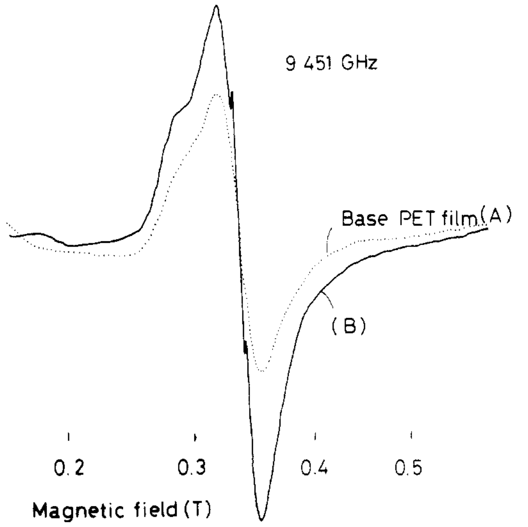


Figure 7. ESR spectra of (A) PET film and (B) coevaporated film on PET film.

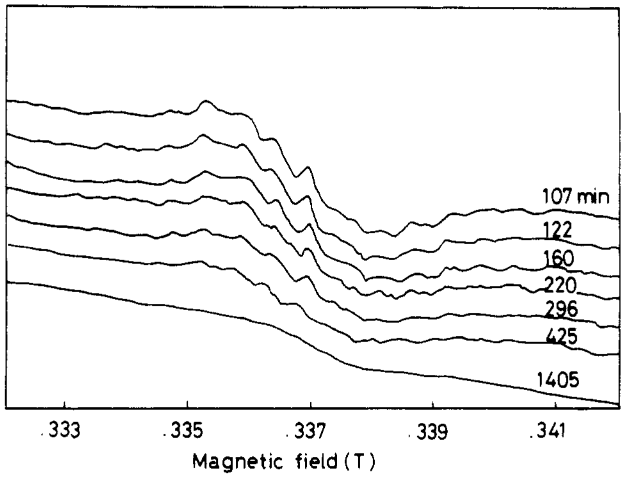


Figure 8. Magnified ESR spectra of coevaporated film measured with an elapse of time.

curve is approximately 210–230 min.

The absorption spectrum of the coevaporated film as deposite showed a absorption in the range 340–560 nm (Figure 5), which was characterized as the formation of a charge transfer (CT) complex.[5-9] The relationship between the time elapsed and absorbance at 480 nm shown Figure 6 was similar to the same relationship in the IR spectra ($t_{\mathrm{visl}/2}$ = 210 min). This may suggest that the complex disappears gradually due to polycondensation. This, so far as the present authors know, is the first example of the CT complex of these monomers, although PMDA and ODA have been known as electron acceptor and donor, respectively.

The mechanism of polycondensation, mentioned above, has also been supported by the ESR spectra of the coevaporated film deposited on PET film. Figure 7 shows the ESR spectra of the undeposited PET film used as a substrate and the coevaporated film on the PET film. The peaks observed in the wide range, 2600–4200 G, of the dotted spectra may be caused by impurities contained in the PET film. In the spectra of the coevaporated film, the organic radicals at 3370 G were ascertained by comparison with the spectra of the PET film. The magnified spectra around 3370 G changing with time are shown in Figure 8. The decrease of the minute structures with time coincided well with the changes in IR spectra and the CT band of absorption spectra. The half-life ($t_{\mathrm{ESR}1/2}$) estimated from Figure 9 is approximately 220 min.

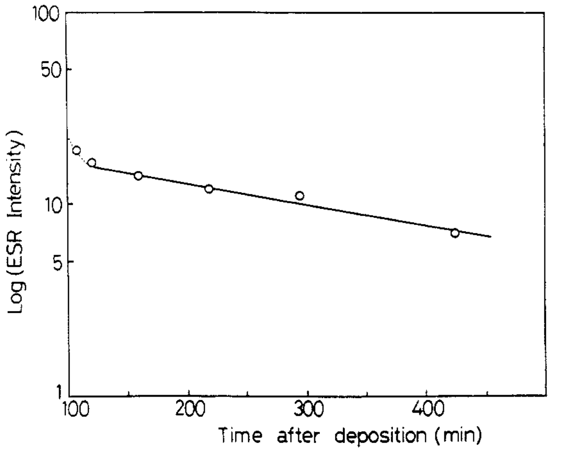


Figure 9. Decay of the hyperfine component in the ESR of codeposited film.

As described above the polycondensation reaction between PMDA and ODA proceeded on the surface of the substrate even at 25 °C. This fact should be explained by the migration of these monomers on the surface, and the formation of the CT complex at the first stage of the polymerization. Thus, it was concluded that the functional groups of the monomers had a fairly high frequency of collision in vapor deposition polymerization.

Acknowledgment. We thank Dr. H. Ueda, National Chemical Laboratory, for his helpful discussion about this work.

Registry No. PMDA, 89-32-7; ODA, 101-80-4; (PMDA)(ODA) (copolymer), 9043-05-4; (PMDA)(ODA) (SRU), 25038-81-7.

References and Notes

(1) Iijima, M.; Takahashi, Y.; Inagawa, K.; Itoh, A. *J. Vac. Soc. Jpn.* **1985**, *28*[5], 437.
(2) Takahashi, Y.; Iijima, I.; Inagawa, K.; Itoh, A. *J. Vac. Sci. Technol.* **1987**, *A5*, 2253.
(3) Salem, J. R.; Sequeda, F. O.; Duran, J.; Lee, W. Y. *J. Vac. Sci. Technol.* **1986**, *A4*, 369.
(4) Takagi, T.; Yamada, I.; Sasaki, A. *Thin Solid Films* **1976**, *39*, 207.
(5) Lagercrants, C.; Yhland, M. *Acta Chem. Scand.* **1962**, *16*, 1043, 1799, 1807.
(6) Ward, R. *J. Chem. Phys.* **1963**, *39*, 852.
(7) Achiba, Y.; Katsumata, S.; Kimura, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1272.
(8) Achiba, Y.; Kimura, K. *Chem. Phys. Lett.* **1973**, *19*, 45.
(9) Sharma, J. P.; Tiwari, R. D. *Microchem. J.* **1972**, *17*, 151.