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UV polymerization of triphenylaminemethylacrylate thin film on ITO substrate

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Abstract

A thin film of triphenylaminemethylacrylate was fabricated by physical vapor deposition onto an indium–tin oxide substrate over a temperature range from 230 to 290 K. This thin film was subsequently polymerized by UV irradiation in vacuum with the aim of fabricating electroluminescent devices. Polymerization of the thin film in vacuum was investigated by in-situ FT–IR reflection absorption spectroscopy. UV irradiation achieved a polymer conversion of around 100%. Though the polymerization time increased at the lower temperature of the substrate, the surface flatness of the thin film was improved. The polymerization mechanism was elucidated as a simple radical polymerization on the basis of the order of monomer consumption rate. The number-average molecular weight increased with decreasing UV intensity.

Keywords: UV polymerization; Thin film; Acrylate

1. Introduction

Polymer thin films have generally been prepared by means of spin coating [1,2] and dipping [3] after the polymer was dissolved in an organic solvent. In such a wet process, there is an inevitable problem that the polymer film obtained includes a residual impurity from the solvent. With this in mind, a technique of vapor deposition polymerization has been developed as a solvent-free process. An oriented polyamide thin film has been fabricated by evaporating two bifunctional monomers of diamine and dichloride onto a substrate [4]. As an alternative technique to this polycondensation system, a thin film of vinyl polymer can be formed by evaporating a vinyl monomer in the presence of an active source such as a red-hot filament [5] or an ultraviolet lamp [6]. The use of vinyl monomer leads to the executive function of the polymer since it is feasible that any functional group can be introduced into the vinyl monomer as a side group.

To simplify this solvent-free process for making thin films, we aim to deposit a thin film of the vinyl monomer and then to irradiate the deposited thin film with UV light to polymerize it. This is a first example of polymerization of a deposited thin film of vinyl monomer in which the film thickness is less than 100 nm while the monomer coating, some tens of μm thick, has been polymerized by UV and electron beam irradiation in a curing process [7]. For the purpose of application in an electroluminescent device, a novel acrylate containing triphenylamine (TPA) was synthesized since acrylates have been polymerized by UV irradiation [8] and the derivatives of TPA have been widely used as hole transport materials [9].

Fourier transform infrared reflection absorption spectroscopy (FTIR–RAS) was used for in-situ observation of the polymerization of a thin film on indium–tin oxide coated (ITO) substrate. Though this type of spectroscopy achieves both high sensitivity and an analysis of molecular orientation [10], the complex spectrum is observed without using a highly reflective substrate such as silver [11]. However, the wavenumber region lower than 2000 cm^{-1} in FTIR–RAS on an ITO substrate was found to be equivalent to that of a highly reflective substrate [12].

In the present paper, the polymer thin film was prepared by depositing the acrylate containing TPA on the ITO substrate, and subsequently by UV irradiation, to investigate the polymerization of the thin film in detail. The deposition and

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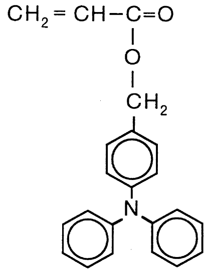

Fig. 1. Chemical structure of TPA–Ac.

polymerization were carried out while varying the substrate temperature and the UV intensity to elucidate the polymerization mechanism. The resulting thin film was evaluated by molecular weight, surface roughness and electroluminescence.

2. Experimental

2.1. Monomer

Fig. 1 shows the chemical structure of triphenylamine-methylacrylate (TPA–Ac). This monomer was synthesized as follows. Triphenylamine (TPA, Tokyo Kasei) was formylated by the Vilsmeier reaction. The formylated TPA (TPA–CHO) was then reduced to TPA–CH_2OH by sodium borohydride. Finally, the TPA–CH_2OH was reacted with acryloylchloride in dry tetrahydrofuran (THF). The crude TPA–Ac was purified by chromatography. The NMR of TPA–Ac in $CDCl_3$ was measured at 323 K with a JEOL α-500 spectrometer operating at 500 MHz. The peaks were obtained at the value of δ from TMS: 5.14 [s, 2H, $-CH_2-$, 5.81, 6.42 [$J = 10.4$ Hz, 17.4 Hz, d, 2H, $CH_2{=}CH-$], 6.15 [$J = 17.4$ Hz, m, 1H, $CH_2{=}CH-$], and 6.99–7.24 [m, 14H, aromatic protons]. The melting point of the synthesized TPA–Ac was 341 K.

2.2. Apparatus and film fabrication

Fig. 2 shows the inner layout of a vacuum chamber for physical vapor deposition and for the subsequent UV-induced polymerization. As a substrate, indium–tin oxide (ITO) coated glass, 38 mm long, 26 mm wide and 1 mm thick, was fixed below the temperature regulated plate. In a vacuum of 2×10^{-4} Pa, a crucible containing TPA–Ac was heated up to 360 K. The thickness of the depositing film was estimated with a thickness monitor (STM-100, Sycon Instruments). After film deposition, the TPA–Ac film was irradiated by low pressure mercury lamps without breaking the vacuum. The UV intensity was varied by using a combination of 20 and 40 W lamps (VUV-20/A-V and VUV-40/A-V, ORC). The resulting three conditions of UV irradiation were measured with a UV illuminometer (Model UV-MO2, ORC); these were 0.29, 0.22 and 0.08 mW cm^{-2} at the substrate position. Polymerization of the deposited TPA–Ac film was monitored in situ by FTIR–RAS. For this measurement, a *p*-polarized IR beam was introduced onto the surface of the ITO substrate at an incident angle of 80° thorough a ZnSe window. The reflective spectrum was measured with an external HgCdTe detector (GL-12045 wide band MCT, Mattson) every 20 s with a resolution of 4 cm^{-1}.

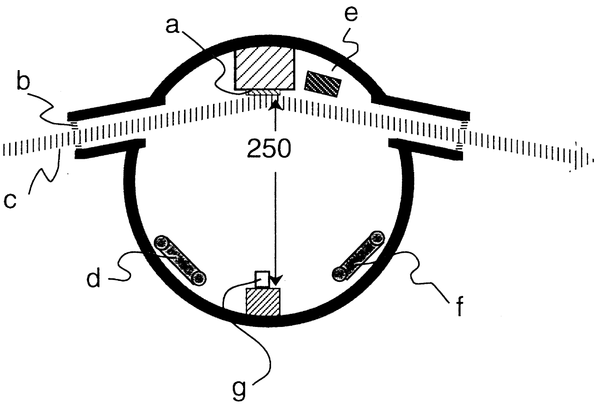

Fig. 2. Inner layout of a vacuum chamber for physical vapor deposition and subsequent UV-induced polymerization: (a) ITO substrate; (b) ZnSe window; (c) IR beam; (d) 20 W low pressure mercury lamp; (e) quartz-oscillator thickness monitor; (f) 40 W low pressure mercury lamp; (g) crucible.

2.3. Analysis

Molecular weights of the poly-TPA–Ac film obtained were estimated by gel permeation chromatography (GPC) using a styrene–divinylbenzene gel column. The elution of poly-TPA–Ac was detected at 301 nm with the UV detector, using THF as elution solvent.

Polymerization of the thin film was evaluated by the degree of polymer conversion, which was estimated by in-situ FTIR–RAS from reduction of the vinyl CH_2 scissoring peak and was finally calculated from the peak area ratio of the polymer to the monomer in the GPC chart. The surface morphology of the film deposited on the ITO substrate was observed with a differential interference microscope (Nikon Optiphoto). The thickness of the film obtained was measured with a spectroellipsometer (MASS-102H-SP, Five Lab). Electroluminescence was evaluated with a luminance meter (BM-8, TOPCON) after tris(8-quinolinolato)-aluminium (Alq_3, Tokyo Kasei) 50 nm thick, and an aluminium electrode 150 nm thick, were deposited on the poly-TPA–Ac film by means of physical vapor deposition.

3. Results and discussion

3.1. UV polymerization

TPA–Ac was deposited on the ITO substrate at 250 K and the thin film thus obtained was observed by in-situ IR–RAS. Fig. 3 shows the IR spectrum in the region from

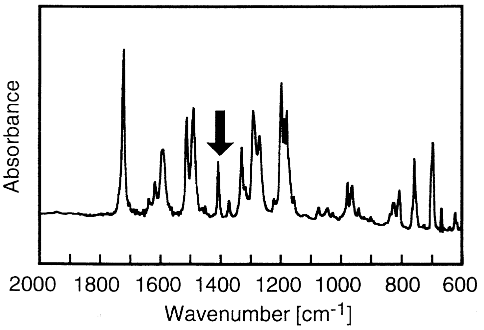

Fig. 3. IR spectrum of TPA–Ac on ITO substrate at 250 K. Peak with arrow is vinyl CH_2 scissoring absorption.

2000 to 600 cm^{-1}. The isolated peak at 1406 cm^{-1} was assigned to vinyl CH_2 scissoring vibration (VS). This peak intensity corresponds to the film thickness of the TPA–Ac, since it is proportional to film thickness in FTIR–RAS [13]. If UV irradiation can induce the polymerization of TPA–Ac thin film deposited on ITO, the peak intensity of the VS absorption will decrease with conversion from the monomer to the polymer. Fig. 4 shows the difference in the reduction of the peak intensity of VS absorption between UV irradiation at 0.29 mW cm^{-2} and its temporal break. The UV irradiation on the thin film induced a remarkable decrease in the peak intensity of VS absorption. When the UV lamps were turned off, this rapid reduction turned into a gradual decrease. Then, turning on the UV lamps reduced the intensity sharply once again. Finally, the peak intensity was close to zero. This behavior indicates that UV irradiation can induce polymerization in the thin film state. The polymer conversion can reach around 100% with continuous UV irradiation at 250 K. Post-polymerization slowly proceeds at 250 K, also. Thus it was found that turning the UV lamps on and off could control the polymer conversion.

Deposition of TPA–Ac on the ITO substrate and subsequent UV irradiation at 0.29 mW cm^{-2} were further carried out at substrate temperatures of 230, 250, 270 and 290 K. Fig. 5 shows the polymer conversion curves estimated by the reduction of VS absorption. The UV-induced polymerization can proceed even at a substrate temperature of 230 K. The rise of the substrate temperature with UV irradiation accelerated the polymerization. In all cases the polymer conversion reached around 100%, although polymerization gradually retarded with increase of polymer conversion. Table 1 lists the substrate temperature, the irradiation time to achieve a polymer conversion of 95% and higher as evaluated by IR, and the polymer conversion as estimated by the reduction of VS absorption in in-situ FTIR–RAS and by the area ratio of polymer to monomer on the GPC chart. The polymerization time of 154 min at a substrate temperature of 230 K was shortened by roughly one-tenth by raising the substrate temperature to 290 K. The final polymer conversions estimated by in-situ FTIR–RAS were confirmed by those estimated by GPC.

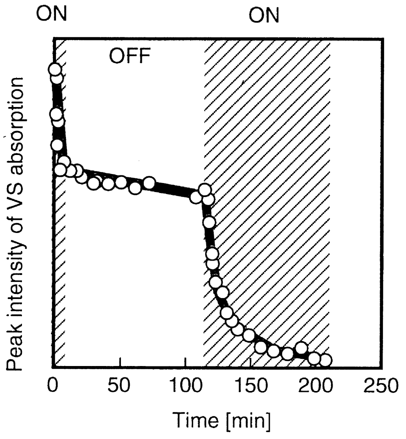

Fig. 4. Change of vinyl CH_2 scissoring absorption with and without UV irradiation at a substrate temperature of 250 K.

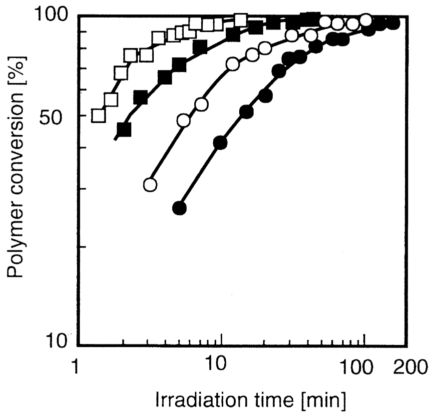

Fig. 5. Effect of substrate temperature for deposition and subsequent UV irradiation on polymer conversion: (●) 230 K; (○) 250 K; (■) 270 K; (□) 290 K.

3.2. Mechanism

The mechanism of thin film polymerization was investigated at various substrate temperatures. At the experimental temperature of the substrate, the rates of polymer conversion were calculated from the increment of polymer conversion divided by the corresponding interval of irradiation time. Fig. 6 shows the logarithmic plot of conversion rate expressed by the change of polymer conversion per minute against log M/M_0 (M is the peak intensity of VS absorption

Table 1
Comparison of polymer conversion estimated by means of FT–IR with that by GPC at various substrate temperatures with UV irradiation of 0.29 mW cm^{-2}

Substrate temperature (K)	Time (min)	Polymer conversion (%)	
		FT–IR	GPC
230	154	96	94
250	102	95	95
270	42	99	95
290	13	96	94

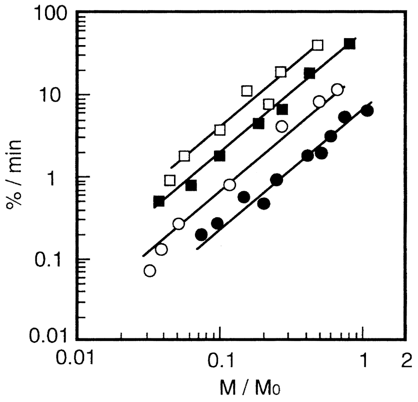

Fig. 6. Logarithmic plot of polymer conversion rate against log M/M_0 at different substrate temperatures: (●) 230 K; (○) 250 K; (■) 270 K; (□) 290 K.

and M_0 is its intensity at the start of UV irradiation). In all cases there were linear relationships between the logarithmic conversion rate and the logarithm of M/M_0. The obtained slopes of the curve fitting lines were 1.5, which corresponds to the order of the monomer consumption rate in thin film polymerization. Therefore, the equation

$$d[M/M_0]/dt = A[M/M_0]^{1.5} \quad (A: \text{ constant})$$

should hold. If M/M_0 is the monomer concentration in a radical polymerization, this equation can be derived from the following polymerization schemes by applying a stationary state [14]:

$$\text{Initiation}: \ M \rightarrow M\cdot \ (I: \text{ rate of radical production})$$

$$\text{Propagation}: \ M + P_n\cdot \rightarrow P_{n+1}\cdot \ (k_p: \text{ rate constant of propagation})$$

$$\text{Termination}: \ P_m\cdot + P_n\cdot \rightarrow P_{m+n} \ (k_{t1}: \text{ rate constant of termination})$$

where M is monomer, $M\cdot$ monomer radical, $P\cdot$ polymer radical and P polymer. In this simple mechanism, a monomer is activated by UV irradiation and then a polymer chain is propagated by reacting with the monomer. Finally, the polymerization is terminated by two polymers. On the assumption of the stationary state, A is equal to $k{\cdot}I^{0.5}$ ($k = k_p k_{t1}^{-0.5}$). As a result, the polymer conversion rate is expressed by using the monomer consumption rate as follows:

$$d[M/M_0]/dt = k{\cdot}I^{0.5}[M/M_0]^{1.5} \quad (1)$$

where k is the rate constant for monomer consumption, I is constant at a certain intensity of UV light. Therefore, integrating equation (1) leads to the following linear relation between the -0.5 th power of M/M_0 and the irradiation time:

$$[M/M_0]^{-0.5} = k{\cdot}I^{0.5}{\cdot}t + \text{constant}.$$

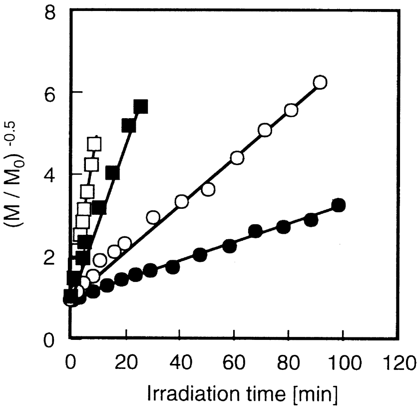

Fig. 7. Relationship between $(M/M_0)^{-0.5}$ and irradiation time at different substrate temperatures: (●) 230 K; (○) 250 K; (■) 270 K; (□) 290 K.

Fig. 7 shows the plots of $[M/M_0]^{-0.5}$ against irradiation time at the various polymerization temperatures. Since linear relationships were obtained, it was confirmed that the thin film polymerization of TPA–Ac on ITO substrate at polymerization temperatures from 230 K to 290 K could be elucidated as a simple radical polymerization mechanism.

The slopes of these linear relations in Fig. 7 corresponds to the product of k and $I^{0.5}$. In these experiments, $I^{0.5}$ was constant since the UV intensity was adjusted to 0.29 mW cm^{-2}. Fig. 8 shows the plot of the product of k and $I^{0.5}$ against the inverse temperature of polymerization. The activation energy of polymer conversion was obtained as 95 kJ mol^{-1} from the slope of the curve fitting line.

At the three different UV intensities, the conversion rate was observed by in-situ FTIR–RAS. The rates of polymer conversion were calculated in the same way. Fig. 9 shows the logarithmic plot of the polymer conversion rate against log M/M_0. The polymer conversion rate was proportional to the 1.5 th power of M/M_0 when the UV intensity was 0.29 mW cm^{-2}. However, the reaction order of M/M_0 increased with decrease of the UV intensity and is close to secondary at a UV intensity of 0.08 mW cm^{-2}. This result indicates that the termination of thin film polymerization is

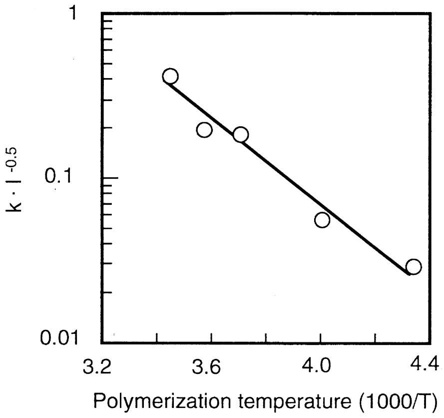

Fig. 8. Relationship between rate constant of polymer conversion and inverse temperature of polymerization.

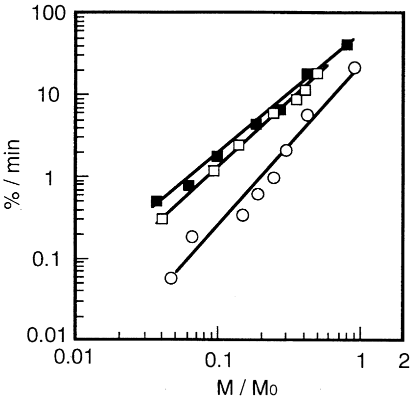

Fig. 9. Effect of UV intensity on reaction order in thin film polymerization: (■) 0.29 mW cm^{-2}; (□) 0.22 mW cm^{-2}; (○) 0.08 mW cm^{-2}.

changed to a one-molecular termination as follows [15]:

Termination : $P_m\cdot \rightarrow P_m(\cdot)$

(k_{t2} : rate constant of termination)

where $P_m(\cdot)$ is a less reactive radical. The deactivation of the polymer radical is caused by a decrease in the concentration of polymer radicals. In the thin film, such a decrease is considered to affect the termination mechanism since the radicals should diffuse in a direction parallel to the film surface to react with each other effectively.

Assuming the stationary state, the monomer consumption rate is expressed as follows:

$$d[M/M_0]/dt = k\cdot I[M/M_0]^2 \quad (k = k_p/k_{t2})$$

Thus the polymer conversion rate is proportional to the product of I and the second power of $[M/M_0]$ at a UV intensity of 0.08 mW cm^{-2}.

3.3. Evaluation of the thin film

The poly-TPA–Ac thin film obtained on the ITO substrate was evaluated for molecular weight, surface morphology, film thickness and electroluminescence.

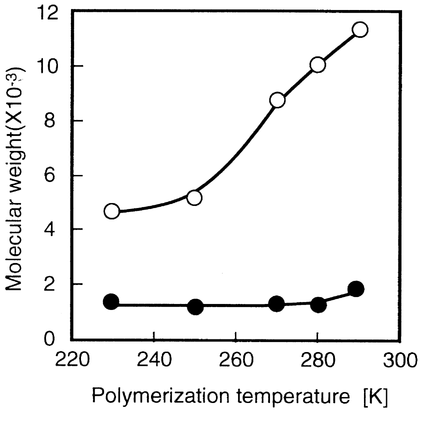

Fig. 10. Effect of polymerization temperature on molecular weight at a UV intensity of 0.29 mW cm^{-2}: (○) M_w; (●) M_n.

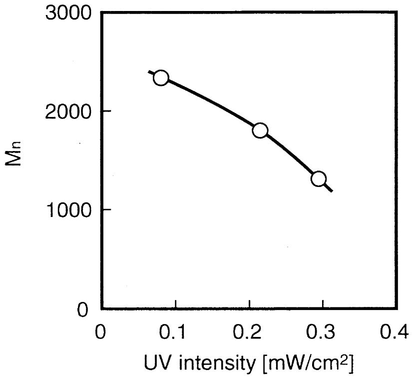

Fig. 11. Effect of UV intensity on M_n at a polymerization temperature of 270 K.

Fig. 10 shows the effect of polymerization temperature on the weight- and number-average molecular weights (M_w and M_n) at a UV intensity of 0.29 mW cm^{-2}. At a polymerization temperature of 230 K, M_w and M_n were roughly 4.7×10^3 and 1.5×10^3, respectively. M_n was independent of substrate temperature less than 290 K and showed a slight increase at 290 K. In contrast, M_w increased with increasing polymerization temperature and reached 1.1×10^4 at 290 K. Accordingly, the rise of the substrate temperature increased the molecular weight. The resulting degree of dispersity is thought to increase with the rise of the polymerization temperature. At a polymerization temperature of 270 K, the UV intensity was changed from 0.29 to 0.08 mW cm^{-2}. Fig. 11 shows the effect of UV intensity on M_n. The reduction of UV intensity caused the increment of M_n. This increase is considered to be caused by the shift of the polymerization mechanism from a two-molecular termination to a one-molecular one.

Fig. 12 shows the surface morphology of the film fabricated by deposition of TPA–Ac on the ITO substrate and subsequent UV irradiation of 0.29 mW cm^{-2} at various temperatures of the substrate. At 230 K the film surface had no observable roughness. Roughness appeared as convex aggregations like small islands at 250 K. The distance between the islands increased with rising deposition temperature. This roughness was already observed when the thin film deposited at 290 K was taken out of the vacuum chamber before UV irradiation. Thus the roughness of the thin film surface is not formed by shrinkage after polymerization but by nonuniform sticking in the deposition process. This nonuniformity was considered from the point of

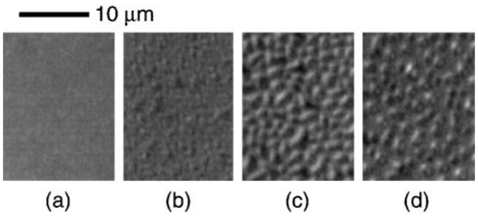

Fig. 12. Surface morphology of poly-TPA–Ac film prepared on ITO substrate at various temperatures: (a) 230 K; (b) 250 K; (c) 270 K; (d) 290 K.

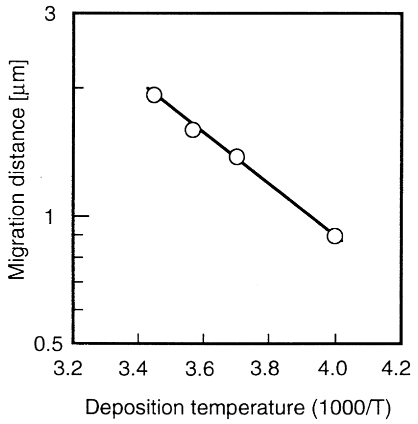

Fig. 13. Relationship between migration distance and inverse temperature of deposition.

view of TPA–Ac molecular migration on the substrate surface. It is assumed that TPA–Ac molecules migrate a certain distance and form a seed for islands after sticking. The islands are then formed by the continuous aggregation of migrating TPA–Ac molecules. In this case, the inverse of island density, $1/n$, corresponds to the exclusive area for one domain. Therefore the surface migration distance is given by $1/n^{1/2}$ [16]. Fig. 13 shows the plot of surface migration distance against inverse temperature of the deposition. The activation energy for the surface migration of a TPA–Ac molecule was calculated, from the linear relation obtained, as 11.5 kJ mol^{-1}. The reason why an even surface is produced at a deposition temperature of 230 K is as follows. The migration distance at the deposition temperature of 230 K is estimated as 0.57 μm. The density of islands is calculated at 3 islands/μm^2. At this density of islands on the substrate, the formed islands adhere to one another and the resulting thin film has an even surface.

Fig. 14 shows the effect of deposition temperature on the thickness of the poly-TPA–Ac thin film obtained and the peak intensity of VS absorption at the beginning of UV irradiation. The film thickness was not reduced by re-evaporation from the substrate during polymerization since the peak intensity of VS absorption was equivalent to the thickness of the obtained film. Accordingly, the difference in the film thickness is caused by the deposition process. At a deposition temperature exceding 250 K, the part of TPA–Ac which reaches the substrate re-evaporates without sticking.

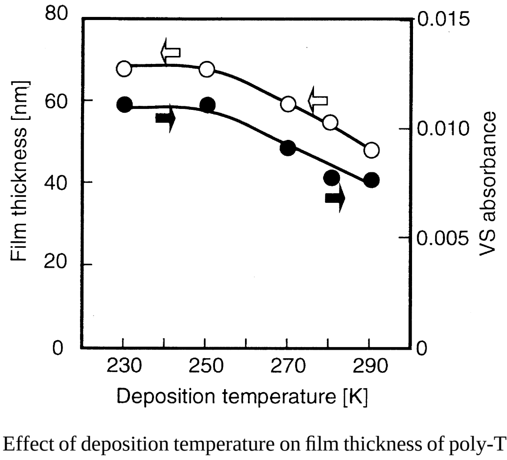

Fig. 14. Effect of deposition temperature on film thickness of poly-TPA–Ac and peak intensity of VS absorption at the beginning of UV irradiation.

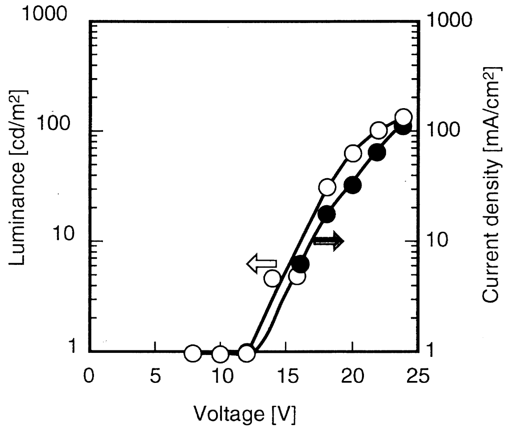

Fig. 15. Luminance and current density of EL device prepared by using poly-TPA–Ac film: (○) luminance; (●) current density.

The smooth surface film fabricated at the deposition temperature at 230 K was evaluated as an EL device after deposition of the Alq$_3$ layer and the Al electrode. Fig. 15 shows the effect of the supply voltage on the luminance and current density. An observable current flowed at a voltage higher than 12 V. Simultaneously the light-green emission from Alq$_3$ was observed, and increased with increasing voltage. This poly-TPA–Ac film was considered to be available as an EL device.

4. Conclusions

A new thin polymer film having TPA in the side chain has been fabricated by physical vapor deposition of synthesized TPA–Ac monomer and subsequent UV irradiation in a vacuum chamber. The polymerization of the thin film on an ITO substrate was observed in situ by means of FTIR–RAS. The polymer conversion reached around 100%, though the irradiation time of 154 min at a polymerization temperature of 230 K is roughly 10 times longer than that at 290 K. An even surface was accomplished at 230 K. The polymer conversion rate was elucidated by simple two-molecular termination mechanism at a UV intensity of 0.29 mW cm^{-2}. When the UV intensity decreased to 0.08 mW cm^{-2}, the reaction order of the consumption rate was changed from 1.5 to 2. In this case the termination was elucidated by one molecular mechanism. The M_n was independent of the polymerization temperature and increased with reduction of UV intensity. When an EL device was fabricated by depositing Alq$_3$ and Al on the polymer thin film obtained at 230 K, the emission of EL was achieved.

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