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Thermal stability and EL efficiency of polymer thin film prepared from TPD-acrylate

M. Tamada[a,*], H. Koshikawa[a], T. Suwa[a], T. Yoshioka[b], H. Usui[b], H. Sato[b]

[a]*Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Watanuki 1233, Takasaki, Gunma 370-12, Japan*

[b]*Department of Material Systems Engineering, Tokyo University of Agriculture and Technology, Nakacho 2-24-16, Koganei, Tokyo 184, Japan*

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Abstract

A new acrylate bearing *N*,*N*′-diphenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) was synthesized to apply for hole transport layer of an electroluminescent (EL) device. The thin film of this monomer was fabricated with physical vapor deposition. The obtained thin film was preliminarily irradiated with UV light and then heated up to 400 K in vacuum. The resulting polymer film, 60 nm thick, which had a polymer conversion of 96% had a smooth surface. This even surface could be maintained up to the heating of 420 K. These processes of deposition and polymerization were monitored with in situ reflection infrared spectroscopy. The EL device made of polymer thin film had three times higher efficiency than that from the monomer thin film.

Keywords: Thin film; Thermal stability; UV polymerization

1. Introduction

Organic thin films are very useful when applied to opto-electronic devices like an electroluminescent device [1]. Such a thin film requires homogeneity and stability. These properties lead to excellent durability in the device performance. This is because a voltage supplied to the thin film in the direction of the film thickness induces a very high electric field. A homogeneous thin film is fabricated with physical vapor deposition by using unsymmetrically structural chemicals such as *N*,*N*′-diphenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) [2]. In this TPD, methyl groups were introduced into a symmetrical triphenyamine dimer to induce unsymmetry. Keeping in mind thermal stability, several units of molecular structure were combined. Large molecular materials were synthesized to raise the glass transition temperature and they improve the thermal stability of the thin films [3–5].

Polymerization is a key technique to satisfy both the homogeneity and the thermal stability of the thin film [6,7]. However, the preparation of thin films from polymers has been carried out with wet processes such as spin coating and dipping [8]. These methods have an inevitable problem in which the obtained film was contaminated with solvent-originated impurity. We have been developing the dry fabrication technique of polymer thin films, namely, vapor deposition polymerization [9] and thin film polymerization [10] to overcome such contamination. In the previous study, we performed the thin film polymerization of the acrylate having triphenyamine (TPA-Ac) [10]. We showed a possibility that the thin film polymerization could realize all dry processing in the fabrication of EL. In the present paper, we are aiming at thermal stability of the polymer hole transport layer. A novel monomer, acrylate having TPD (TPD-Ac) was synthesized and its thin film of the monomer was fabricated on the ITO substrate with physical vapor deposition. The obtained thin film was polymerized by UV and heating. The thermal stability of the resulting film was investigated.

2. Analytical methods

2.1. Monomer

Fig. 1 shows the chemical structure of the acrylate monomer having TPD moiety, *N*-(4-acryloyloxymethyl-phenyl)-*N*′-phenyl-*N*,*N*′-bis(4-methylphenyl)-[1,1′-biphenyl]-, 4′-diamine (TPD-Ac). This monomer was synthesized by the following four steps:

* Corresponding author. Tel.: +81-27-346-9414; fax: +81-27-346-9687.
E-mail address: tamada@taka.jaeri.go.jp (M. Tamada).

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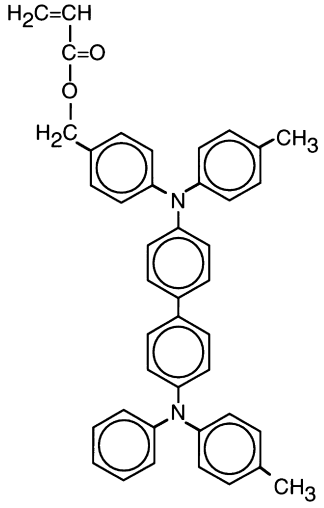

Fig. 1. Chemical structure of TPD-Ac.

2.1.1. N,N′-Diphenyl-N,N′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD)

TPD was synthesized by a modified Ullmann condensation. A 500 ml three-neck flask fitted with a mechanical stirrer and a condenser was charged with 20 g (59.5 mmol) of *N,N′*-diphenyl-[1,1′-biphenyl]-4,4′-diamine, 311 g (1430 mmol) of 4-iodotoluene, 36.5 g (246 mmol) of anhydrous potassium carbonate, 30.4 g (160 mmol) of copper (I) iodide, and 5.55 g (21 mmol) of 18-crown-6. This reaction mixture was heated at 473 K for 24 h. After cooling and the addition of 200 ml of toluene, the reaction mixture was filtered. After the evaporation of solvent and unreacted iodotoluene, the obtained crude product was purified by using column chromatography (silica gel, toluene:hexane = 50:50), yield 20 g (65%).

2.1.2. N-(4-formylphenyl)-N′-phenyl-N,N′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD-CHO)

TPD was formylated by the Vilsmeier reaction. Under nitrogen atmosphere, 10 ml of dry *N,N*-dimethylformamide (DMF) was put into a 100 ml three-neck flask equipped with a nitrogen inlet, a dropping funnel, a magnetic stirrer, and a condenser. Then, phosphorous oxychloride (5.94 g, 38.7 mmol) was dropped at 273 K. After 2.5 h of stirring at 273 K, 20 g (38.7 mmol) of TPD and 50 ml of dry DMF was added and stirred for 6 h at 373 K. After cooling, the reaction mixture was poured over 200 g of water–ice mixture containing 15 g of sodium acetate. The precipitated solid was washed with water twice and dried. The unreacted TPD and the diformylated product were removed by column chromatography (silica gel, toluene:hexane = 67:33 to 100:0). The TPD-CHO was obtained as a yellow powder, yield 9.18 g (43%).

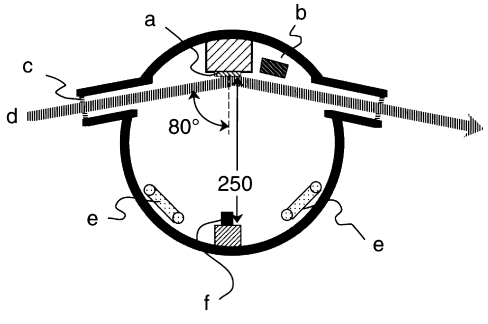

Fig. 2. Inner layout of an apparatus for physical vapor deposition and polymerization of the monomer thin film and its in situ IR spectroscopy system: (a) ITO substrate; (b) quartz-oscillator thickness monitor; (c) ZnSe windows; (d) polarized IR beam; (e) low-pressure mercury lamps; and (f) evaporation source.

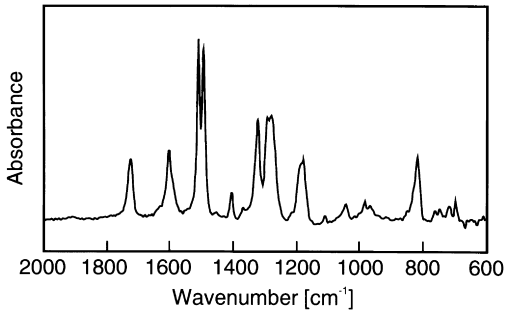

Fig. 3. IR reflection spectrum of TPD-Ac thin film on ITO substrate.

2.1.3. N-(4-hydroxymethylphenyl)-N′-phenyl-N,N′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD-CH_2OH)

Under nitrogen atmosphere, 11.7 g (21.5 mmol) of TPD-CHO and 160 ml of the mixture of benzene and ethanol (1:1) were added into a 200 ml three-neck flask equipped with a nitrogen inlet and a magnetic stirrer. After dissolution of TPD-CHO, 1.02 g (26.9 mmol) of sodium borohydride was added to the reaction mixture. After stirring for 2 h at ambient temperature, the solvent was removed by evaporation and the residual solid was washed with water to remove inorganic salts. A benzene solution of the crude product was

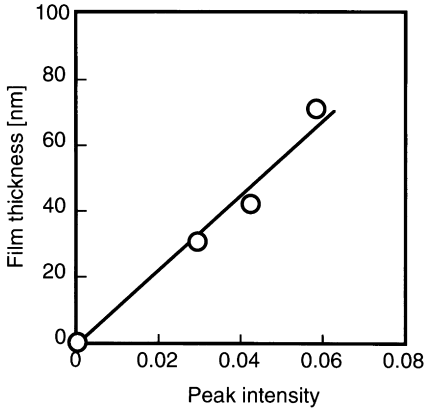

Fig. 4. Relationship between film thickness and the peak intensity at 1510 cm^{-1}.

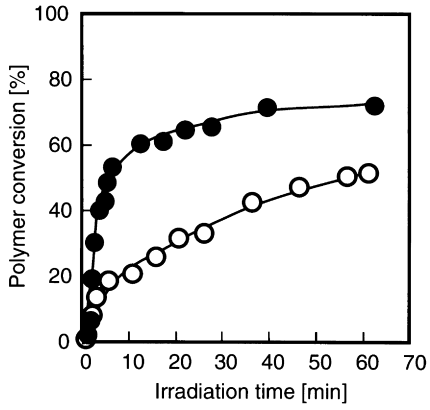

Fig. 5. Polymer conversion curves in UV polymerization: (○) at 300; and (●) at 340 K.

poured into hexane, and a light yellow powder was obtained, yield 9.97 g (85%).

2.1.4. N-(4-acryloyloxymethylphenyl)-N′-phenyl-N,N′-bis(4-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD-Ac)

Under nitrogen atmosphere, 8.82 g (16.2 mmol) of TPD-CH_2OH, 2.04 g (20.2 mmol) of triethylamine and 40 ml of dry tetrahydrofuran (THF) was added into a 100 ml three-neck flask fitted with a nitrogen inlet, a magnetic stirrer and a dropping funnel, and the solution was subsequently cooled to 273 K. The mixture of 1.83 g (20.2 mmol) of distilled acryloyl chloride and 15 ml of THF was dropped. After 2 h of stirring, the reaction vessel was allowed to warm up to room temperature, and stirring was continued for an additional 10 h to complete the reaction. The precipitated salt was removed by filtration. After evaporation of THF, the residual solid was washed with distilled water and purified by column chromatography (silica gel; benzene:hexane = 67:33 to 100:0), yield 4.94 g (51.1%). The glass transition temperature, T_g, was 368 K.

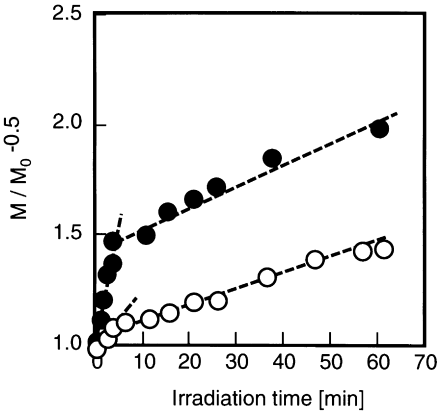

Fig. 6. Plot of reciprocal square root of monomer concentration normalized by initial concentration of monomer against irradiation time: (○) at 300; and (●) at 340 K.

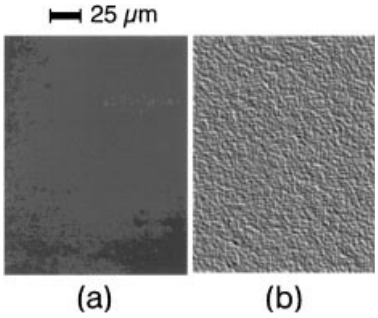

Fig. 7. Surface morphologies after deposition and consequent UV-polymerization of TPD-Ac thin film: (a) at the substrate temperature of 300; and (b) at 340 K.

2.2. Apparatus

Fig. 2 shows the inner layout of an apparatus for physical vapor deposition and polymerization of the monomer [11]. Indium–tin oxide (ITO) coated glass (Geomatec Co. Ltd.) was used as a substrate. The substrate was fixed beneath the temperature-controlled plate after being washed with a detergent and then treated with ozone plasma [12]. The distance between the substrate and the evaporation source was 250 mm. A quartz-oscillator thickness monitor was set near the substrate position. A polarized infrared (IR) beam was introduced onto the substrate through a ZnSe window at an incident angle of 80°. The reflected IR was analyzed with an HgTeSe external detector (Mattson FT-IR) every 20 s to monitor the deposition and polymerization of the monomer on the substrate in vacuum. Two low-pressure mercury lamps of 20 and 40 W (VUV-20/A-V and VUV-40/A-V, ORC manufacturing Co. Ltd.) were used to induce the polymerization of the deposited thin film.

2.3. Thin film fabrication and UV & thermal polymerization

The crucible containing TPD-Ac was heated up to 513 K

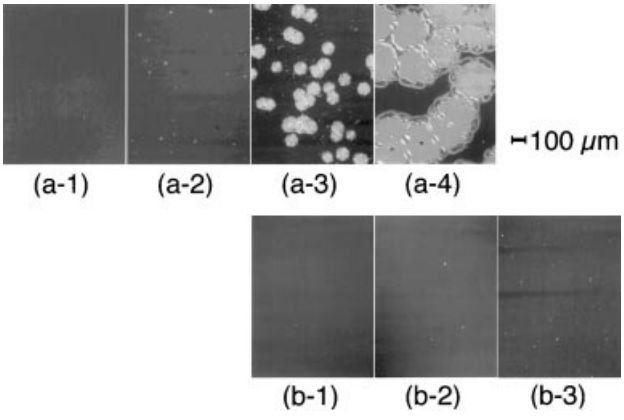

Fig. 8. Thermal stability of monomer thin film and polymer thin film fabricated by UV irradiation at 300 K: (a-1) monomer thin film heated at 350 K; (a-2) at 360 K; (a-3) at 370 K; (a-4) 380 K; (b-1) polymer thin film heated at 370 K; (b-2) at 380 K; and (b-3) 390 K.

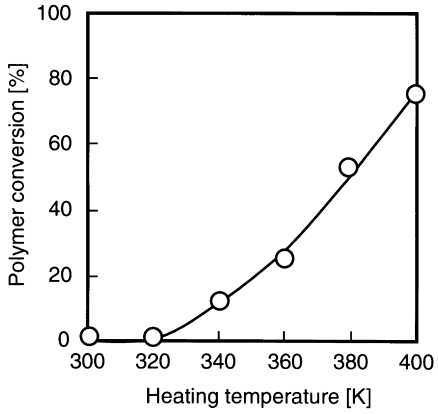

Fig. 9. Polymer conversion in thermal polymerization. Substrate temperature was raised stepwise with 10 min intervals.

as an evaporation source. When the thin film reached 60 nm, the deposition was stopped. Then, the UV light of 253.7 nm was irradiated with 0.29 mW/cm^2 (UV illuminometer, Model UV-MO2, ORC manufacturing Co. Ltd.) to polymerize the monomer thin film. For the thermal polymerization, the substrate temperature was raised stepwise.

2.4. Molecular weight thermal resistance and surface observation

The thickness of the depositing thin film was estimated by the linear relationship between the IR peak intensity and the thickness of the thin film obtained. The thickness of the thin film obtained was measured with optical interference (Nanoscope Model 911-9150, Anelva Co. Ltd.) after deposition of Ag on it. The weight average molecular weight, M_w, was estimated with gel permeation chromatography (GPC) by using a gel column (TSK gel/super HM-M, TOSO Co. Ltd.) after the thin film was dissolved into tetrahydrofuran. Polymer conversion was calculated at IR peak intensity of vinyl scissors' vibration (1406 cm^{-1}) from the following equation and was confirmed with the corresponding chromatogram:

$$\text{Polymer conversion [\%]} = \left(1 - \frac{\text{peak intensity at a certain time}}{\text{initial peak intensity}}\right) \times 100.$$

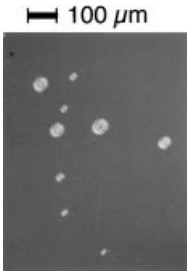

Fig. 10. Surface observation of thermally polymerized thin film heated up to 400 K.

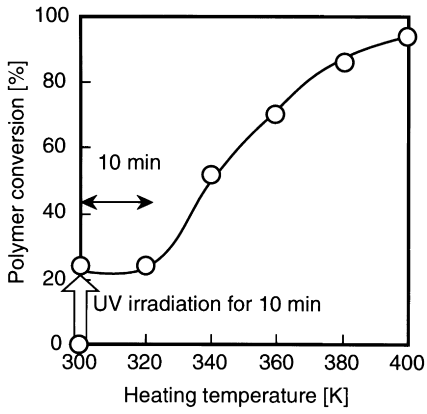

Fig. 11. Polymer conversion of the thin film in preliminary UV irradiation and consequent heating.

The surface of the obtained thin film was observed with differential interference microscope (Nikon Optiphoto, Nikon Co. Ltd.). To check the thermal stability, the obtained film was put in a fan oven for 10 min.

2.5. EL device

Tris(8-hydroxyquinolinato) aluminum (Alq_3, Tokyo Kasei Co. Ltd.), 60 nm thick, was deposited on the poly-TPD-Ac film. The alloy of Mg/Ag (10:1) was further deposited on Alq_3. Electroluminescence was measured with a luminance meter (Luminance meter BM-8, TOPCON Co. Ltd.) by supplying the voltage between ITO and Mg/Ag electrodes.

3. Results and discussion

3.1. Thin film fabrication and UV polymerization

In the wavenumber region less than 2000 cm^{-1} the ITO surface satisfies the condition for IR-reflection spectroscopy [13]. Fig. 3 shows the IR reflection spectrum of TPD-Ac deposited on the ITO substrate. The two large peaks at 1510 and 1495 cm^{-1} were assigned to the stretching vibration of

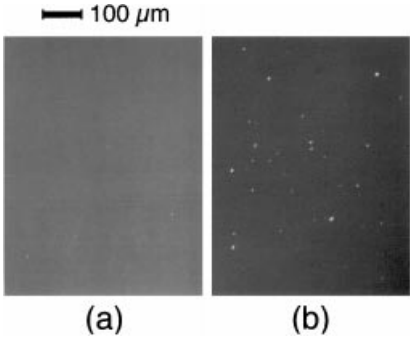

Fig. 12. Thermal stability of polymer film with combination of preliminary UV polymerization and consequent thermal polymerization: (a) at 420 K; and (b) 430 K.

Table 1
Polymer conversion, the molecular weight, thermal stability of the thin film obtained

Fabrication conditions	Polymer conversion (%)	Molecular weight (M_w)	Thermal stability (K)
Monomer thin film	0	588	350
UV polymerization at 300 K	51	3400	370
UV polymerization plus thermal polymerization	96	49 000	420

the TPD-Ac phenyl ring [14]. The small peak at 1406 cm^{-1} was assigned to vinyl scissors' vibration [15].

TPD-Ac thin films were deposited by monitoring the IR intensity at 1510 cm^{-1} and the thickness of the obtained films were measured. Fig. 4 shows the plot of the film thickness against the peak intensity. There was a linear relation between the film thickness and the peak intensity at 1510 cm^{-1}. Hence, any thickness of the film can be obtained since the IR peak was monitored with in situ spectroscopy. In the present experiment, the film deposition was stopped when the peak intensity reached 0.052 and the film, 60 nm thick, was obtained.

To compare the thin film polymerization at different temperatures of polymerization, the thin films were fabricated at the substrate temperature of 300 and 340 K. Consequently, UV light was irradiated for 1 h by maintaining the temperature of each substrate. Fig. 5 shows the polymer conversion curves in this UV polymerization. The polymer conversions of the obtained thin films were 72 and 51% at the polymerization temperature of 300 and 340 K, respectively. The molecular weights, M_w, were 3400 and 7500 at the substrate temperature of 300 and 340 K, respectively. The polymer conversion exhibited a steep increment in the irradiation time less than 5 min. Then, the polymerization was gradually retarded. It is assumed that the monomer thin film polymerizes by the simple radical polymerization to elucidate the change in the conversion rate. The polymerization mechanism can conform to the following:

Initiation : $M \rightarrow M\cdot$ (I : rate of radical production),

Propagation : $M + P\cdot_n \rightarrow P\cdot_{n+1}$

(k_p : rate constant of propagation), and

Termination : $P\cdot_m + P\cdot_n \rightarrow P_{m+n}$

(k_t : rate constant of termination),

where M is the monomer, M· the monomer radical, P· the polymer radical and P the polymer. The steady state is applied to the radical concentration [16]. When the initial concentration of the monomer is termed M_0, the normalized monomer concentration, $[M/M_0]$, was expressed by

$$d[M/M_0]/dt = kI^{0.5}[M/M_0]^{1.5} \qquad (k = k_p k_t^{-0.5}),$$

$$[M/M_0]^{1.5} = kI^{0.5}t + \text{constant}.$$

Therefore, the reciprocal square root of normalized monomer concentration was plotted against irradiation time in Fig. 6. There was a bending point in each line around the irradiation time of 5 min. Before the bending point, the conversion rate at 340 K was markedly higher than that at 300 K. This difference is caused by k since I is constant under fixed UV irradiation. The value of k_p at 340 K is considered to have a larger value. After the bending point, the conversion rates increased similarly at 300 and 340 K. This change is assumed to be due to polymerization being restricted by the diffusion of the monomer in high polymer conversion.

Fig. 7 shows the surface morphologies after the deposition and the consequent UV-polymerization of TPD-Ac thin film at 300 and 340 K. The obtained film at 340 K had a rough surface while the polymer film fabricated at 300 K had a smooth surface. This roughness was already observed immediately after the deposition and was caused by migration of TPD-Ac on the substrate. Similar roughness was observed in the case of TPA-Ac [10]. The distance between the tops was fitted to the migration distance of the deposited molecules. If the substrate temperature is low enough to bind the tops closely, the smooth surface of the thin film will be deposited. Though the rate of polymer

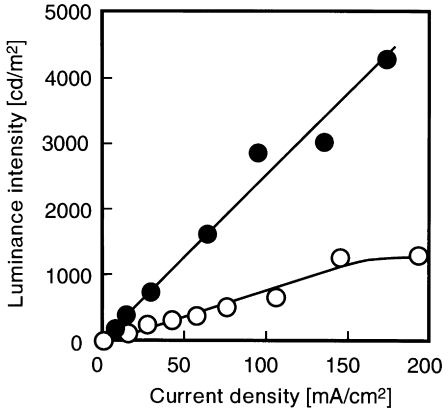

Fig. 13. Comparison of EL intensity from device made of the monomer thin film with that made of polymer thin film by combination of UV and thermal polymerization: (○) monomer device; and (●) polymer device.

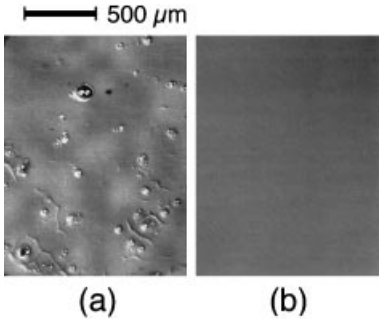

Fig. 14. Observation of monomer and polymer device after measurement of EL intensity: (a) monomer device; and (b) polymer device.

conversion and molecular weight were improved at 340 K, the roughness in the surface was worst for the EL devices.

3.2. Thermal polymerization

The thermal stability is compared in the smooth surface films of the monomer and the polymer obtained at 300 K. Fig. 8 shows the surface observation after heating treatment for 10 min. After heating stepwise, the smoothness in the monomer thin film surface was maintained up to 350 K. At 360 K, small holes appeared in the thin film. The further rise of the temperature to 370 K which is slightly higher T_g enlarged the hole sizes. More than half the area of the substrate surface was uncovered with TPD-Ac at 380 K. In the case of the polymer thin film there was no damage up to 370 K. The small holes appeared at 380 K, which is 20° higher than the monomer thin film. When the heating temperature was raised to 390 K, the hole size did not become large but the hole numbers increased. The UV polymerization at 300 K improved the thermal stability of the thin film. We confirmed that polymerization was effective to improve the thermal stability of the thin film.

The polymerization temperature is an important factor to increase the polymer conversion and the molecular weight. In the UV irradiation, the higher polymer conversion and the molecular weight were given at 340 K than those at 300 K, though the surface became rough at 340 K. For the trial of the UV irradiation at the higher temperature, the effect of the rising substrate temperature on the deposited monomer thin film was investigated from the point of view of thermal polymerization. The TPD-Ac was deposited at the substrate temperature of 300 K and the substrate temperature was raised stepwise with 10 min intervals in vacuum. The polymer conversion was estimated with in situ IR spectroscopy. Fig. 9 shows a polymer conversion at each heating temperature for 10 min. The thermal polymerization was induced at 340 K and the rise of the substrate temperature increased the polymer conversion. At the heating temperature of 400 K, the polymer conversion reached 75% and M_w was 61 000. Thus, it was found that heating the substrate up to 400 K could thermally polymerize the thin film monomer.

Fig. 10 shows the surface observation of the thin film obtained by thermal polymerization when the substrate was heated up to 400 K stepwise. The resulting film had some holes. This damage in the film implies that the thermal stability of the film was not enough at the polymerization temperature under thermal polymerization.

Based on this finding, the UV irradiation and thermal polymerization were combined. Namely, UV light was preliminarily irradiated onto the deposited film and then the substrate temperatures were raised to thermally polymerize the film. Fig. 11 shows the polymer conversion of the thin film polymerization with preliminary UV irradiation and consequent heating. In the first step, UV irradiation for 10 min to the monomer thin film polymerized 20% of the monomer. Then, the polymer conversion reached to 96% in the second step of the substrate heating to 400 K. The M_w was 49 000 and the resulting polymer thin film had a smooth surface. This result indicates that the preliminary UV polymerization can suppress the damage shown in the simple thermal polymerization. The obtained film was heated for thermal stability, also. Fig. 12 shows the change of the surface morphology after heat treatment. The preliminary UV irradiation was effective on the thermal stability of the thin film. The small holes appeared at the heating temperature of 430 K. This polymer film is expected to be used at 420 K.

Table 1 summarizes the fabrication conditions, the polymer conversion, the molecular weight (M_w) and the thermal stability. For thermal stability, the temperature which can maintain the flat surface is listed in the table.

3.3. EL performance

The luminance intensity of the EL device made of monomer was compared with that from the polymer prepared by UV irradiation and heating. Fig. 13 shows EL intensities of the polymer and monomer devices. Maximum luminescence of 4300 cd/m^2 was performed in the polymer device. EL efficiency expressed by the luminance intensity divided by current density was improved by polymerization. The efficiency of polymer device was three times higher than the monomer device. Fig. 14 shows the device observed through the ITO substrate after measurement of the luminescence. The polymer device had little damages while there were lots of the damaged parts in the monomer device. These damages were problems in the durability of the EL device [17]. The thin film polymerization expects to overcome this problem.

4. Conclusions

We demonstrated the thin polymerization of acrylate bearing TPD moiety. The high polymer yield was achieved by combining the preliminary irradiation of UV light and the consequent heating. The obtained polymer thin film, 60 nm, can maintain the surface flatness up to 420 K. This excellent thermal stability was reflected in the EL

performance. The efficiency of the polymer device was three times higher than the monomer device. No damaged part in the polymer device was observed after EL measurement. The thin film polymerization of TPD-Ac will provide the thermal stability of the hole transport layer. Additionally, a superior EL device is expected to be produced by an all-dry process if thin film polymerization will be applied to the fabrication of the polymer hole transport layer.

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