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Fabrication of Dye Dissolved Polymer Film Using Thermal Treatment under Ultra High Vacuum

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A poly(methyl methacrylate) (PMMA) film capable of dissolving an organic dye was prepared at an elevated temperature under ultra high vacuum (UHV). Residual solvents in PMMA film which may reduce the threshold power of irradiated light to breakdown were analyzed by means of quadrupole mass spectroscopy. It has been established that treatment of the polymer under UHV is essential for optical use.

Optical responses of organic compounds to high peak power light irradiation including ultra short pulses are of current interest. Advancement for more than two decades in nonlinear organic compounds such as urea, 2-methyl-4-nitroaniline (MNA)[1)] and so on[2)] provided us with fertile knowledge on the dependence of nonlinear susceptibility on molecular structure, the fast response to ultrashort light pulses, and the high light-power durability against dielectric breakdowns. Such development has also been stimulated by a measurement that analyzes pulse compression in the intracavity of a femtosecond pulsed laser with insertion of third-order nonlinear organic films.[3)] In many cases of the experiment, we need to fabricate an optically transparent and high quality thin film dissolving functional dye molecules to obtain meaningful data on optical properties. A well-known method for making a dye-dissolving polymer film on an appropriate substrate is thin film formation based on slow evaporation of solvents from a dilute solution of polymers dissolving organic dyes ($\sim 10^{-5}$ mol) under ambient conditions. Optical qualities of the film obtained by the slow evaporation from solutions are quite insufficient for use under strong light irradiation, because it includes large amounts of residual solvents and micro pores which are formed in the evaporation process of solvents. The previously reported procedure of thin film formation under vacuum ($\sim 10^{-1}$ Pa) could drastically reduce both oxidation and formation of pores by residual air in the sample.[4)] We have here, a newly developed treatment of polymers under ultra high vacuum (UHV; $\sim 10^{-5}$ Pa) which is evaluated by quadrupole mass spectroscopy. In this paper, this new process for fabricating optical quality organic materials under UHV is discussed.

A quadrupole mass spectrometer (QMS, AQA-200; ANELVA) and a nude ionization gauge (NIG, UHV-24; Varian) with a multi-gauge controller (Varian) were attached to a UHV chamber evacuated by a turbo molecular pump (TMP, V60; Varian) where the ultimate pressure was 2×10^{-6} Pa (Fig.1). Sensitivity of QMS using a Faraday cage collector with a micro channel plate was 7.5×10^{-3} A/Pa for nitrogen gas (minimum partial pressure for detection; 6.6×10^{-12} Pa). A commercial PMMA (Aldrich, Average MW; 1.2×10^{4}) was purified by reprecipitation with acetone/water mixture after filtration of insoluble impurities. The purified powder of PMMA was set in the UHV chamber which was evacuated at room temperature (RT; 27 ℃) for more than two days to the ultimate pressure of the system. Temperature of the sample was controlled from RT to 80 ℃ at a heating rate of 0.3 degree/minute. While increasing the temperature from RT to 80 ℃, mass spectrum was measured at about 52 ℃. The mass spectrum measured at 80 ℃ was analyzed under thermal equilibrium conditions. After 12 hours curing at 80 ℃, the temperature of the sample was changed from 80 ℃ to 110 ℃ at a rate of 0.06 degree/minute. The mass spectrum at 110 ℃ was again analyzed under thermal equilibrium. After 7 h curing at 110 ℃, the temperature of the sample was again changed from 110 ℃ to 150 ℃ at a rate of 0.7 degree/minute. The mass spectrum at 150 ℃ was subsequently analyzed under thermal equilibrium conditions. After cooling down to room temperature and chamber baking, artifacts due to contamination of the ion source of mass spectrometer were checked. High resolution solid-state ^{13}C-NMR spectroscopy was performed on the sample by a JEOL GSH-200 spectrometer at the resonance frequency of 50.23 MHz, with details of the experiment previously reported.[5)] Damage by light irradiation was evaluated on the dye-dissolving film by lifetime measurement to breakdown using a dye laser in combination with a Q-switched Nd:YAG laser (DCR-2: Quanta-Ray).

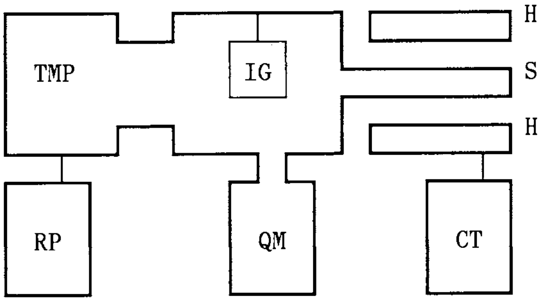

Fig.1. Schematic drawings of UHV chamber; S: sample cell, QM: quadrupole mass spectrometer, TMP: turbomolecular pump, RP: oil rotary pump, H: heater, IG: nude ionization gauge, CT: temperature controller.

The results of mass spectrum analysis are summarized in Table 1. We performed no further correction for gas sensitivity (correction factors for acetone; 3.6, for water; 1.1, etc.). Although additional kinds of fragments other than those in Table 1 were observed, dominant fragments having pressures larger than 1×10^{-10} Pa (minimum partial pressure for detection; 6.6×10^{-12} Pa) were selected. After the temperature change from 27 ℃ to 80 ℃, the total pressure became about 27 times as large as that in the lower temperature, and the expected residual of acetone (fragments underlined; mass numbers of 15, 39, 43, 55 and 57[6)]) was observed. Fragments without assignment would result from the

Mass number /Assignment[6]	Temperature change[℃]			
	27 → (52) → 80		80 → 110	110 → 150
2 / H	(6.5)	24	0.49	2.5
14 / CH_2	(1.5)	2.5	1.0	0.83
15 / CH_3	(---)	>1350	---	---
16 / O	(4.0)	9.3	1.0	1.0
17 / OH	(1.8)	4.0	0.92	1.4
18 / H_2O	(1.4)	3.6	0.87	1.4
28 / CO	(1.1)	2.1	0.91	1.0
32 / O_2	(2.0)	3.7	1.0	0.89
39 / $H_3C\text{-}C{\equiv}C^+$	(>90)	>1700	0.45	5.7
40 / --	(4.0)	< 0.1	0.76	1.3
41 / --	(>110)	>3400	0.53	6.5
43 / CH_3CO	(---)	>2500	0.35	>27
44 / --	(3.2)	24	0.59	1.7
55 / $H_2C{=}C(CH_3)CH_2$	(>34)	>1900	0.32	10
57 / $(H_3C)_3C^+$	(>27)	>1300	0.33	> 8
59 / CH_3COCH_3 + H	(---)	>500	> 2	> 2
67 / $H_3C\text{-}C{\equiv}C\text{-}C{=}O$	(>13)	>350	0.31	> 6
69 / $CH_3(CH_2)C\text{-}C{=}O$	(>16)	>590	0.44	9.0
71 / --	(>10)	>470	> 1	> 2
73 / --	(---)	>300	---	---
77 / --	(---)	>90	> 1	> 1
79 / --	(---)	>140	> 1	> 2
81 / --	(---)	>160	---	> 2
83 / --	(---)	>360	> 1	> 3
85 / --	(---)	>250	> 1	> 2
87 / --	(---)	>80	---	---
91 / --	(> 4)	>80	> 1	> 1
97 / --	(> 3)	>170	---	> 1
98 / --	(---)	>190	---	---
99 / --	(> 3)	>80	> 1	> 1
111 / --	(---)	>58	> 1	> 1
Total pressure; Pa	($7.3x10^{-6}$) (→$1.6x10^{-5}$)	$7.3x10^{-6}$ →$2.0x10^{-4}$	$1.5x10^{-5}$ →$1.1x10^{-5}$	$7.5x10^{-6}$ →$1.1x10^{-5}$

Table 1. Partial pressure change of each fragment and total pressure change as a function of temperature of the sample, where ratios of the partial pressure after and before temperature change (P/P_0) are shown. The inequality sign means that partial pressure before temperature change is much lower than the minimum partial pressure for detection (nominal P_0 is taken for $6.6x10^{-12}$ Pa)

additives of plasticizer or polymerization-modifier included in the crude polymer. The fragment of number 41, volatile bellow 80 ℃, would be an unknown kind of additive. Even in the temperature change from 27 ℃ to 52 ℃, some fragments from acetone (mass number of 39, 55 and 57) were observed, which indicated that the polymer could also be degassed if it is left for

Assignment[7]/ Chemical shift[ppm]		Degassed PMMA	Undegassed PMMA
α-CH_3	[17]	<<1	<<1
Quart. C	[45]	17.5	18.3
OCH_3	[52]	10.8	10.1
CH_2	[57]	12.5	13.6
C=O	[178]	15.3	15.9

Table 2. Longitudinal relaxation time (T_1;sec) of degassed and undegassed PMMA

enough time at the lower temperatures. In the temperature change from 80 ℃ to 110 ℃, the total pressure was slightly lower, which indicated that almost all residuals were already drawn out at 80 ℃. Although the glass transition temperature (T_g) of PMMA is 92.4 ℃,$^{5)}$ the polymer was effectively degassed at $T<T_g$ under vacuum (1×10^{-4} Pa), because the matrix is softened even bellow the T_g of PMMA. The mass number of 41 and 43 were dominant fragments at 150 ℃, which were assigned as decomposites of PMMA or unpolymerized segments left in the crude polymer. The longitudinal relaxation time (T_1; sec)(Table 2) of quarternary carbon, CH_2, and C=O was reduced by degassing (at 110 ℃ for 2 days under UHV) and it is somewhat increased in the case of OCH_3. Residual solvents in a polymer matrix will probably soften the network of polymer. In general, when an additive was dissolved into the PMMA matrix, the T_g of PMMA was reduced due to a kind of plasticizer effect.$^{5)}$ The T_1 decrease by degassing, therefore, will be understood as a matrix hardening effect by removal of residual solvents. Lifetime against strong light irradiation of the degassed (at 110 ℃ for 2 days under UHV) and undegassed PMMA film dissolving PNP is shown in Table 3. The lifetime was apparently increased by degassing under UHV. Abrupt vaporization of the residual solvents in the sample due to energy dissipation followed by strong light irradiation is thought to form microscopic pores and, in effect, sometimes produces cracks and other macroscopic defects.

Sample	Lifetime/Peak power sec	 GW/cm^2	Lifetime/Peak power sec	 GW/cm^2
Degassed PNP/PMMA$^{a)}$	180	0.32	3.5	1.13
Undegassed PNP/PMMA$^{b)}$	180	0.17	1	1.13

Table 3. Lifetime by light (Q-SW Nd:YAG/dye laser, 10 Hz, 625 nm) irradiation of the degassed and undegassed PNP [(s)-(-)-N-(5-Nitro-2-pyridyl)prolinol] dissolved PMMA film. Absorption λ_{max} of PNP is 369 nm. a) 40 mol% PNP contents, b) 20 mol% PNP contents

It has been concluded that the degassing of organic compounds under UHV is remarkably effective for obtaining good optoelectronic materials especially under strong light irradiation conditions.

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