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YAG Laser-induced Polymerization of Monomers Containing Metal Ions

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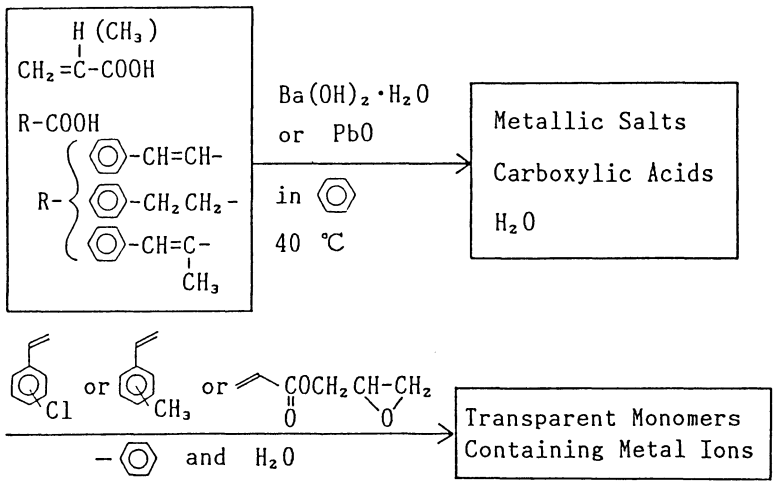
YAG laser irradiation onto a film of transparent monomers containing Ba^{2+} or Pb^{2+} on a glass slide caused polymerization in thin film conditions. The refractive indices of polymers formed by the laser irradiation are about 0.02 higher than those of polymers formed by heating. This could be attributed to the structure with high density.

As laser has temporal and spatial coherence, it is used in microprocessing. Moreover, laser beams are monochromatic and powerful, so that they induce unusual chemical reactions.[1] As for laser-induced polymerization, it was reported that the high speed curing[2] and the polymerization via two-photon absorption occurred.[3] But there are few examples of effective polymerization by laser.

We attempted YAG laser (λ=1064 nm) irradiation onto monomers containing metal ions. Some monomers polymerized in thin film conditions. The refractive indices of the polymers formed by the laser irradiation were higher than those of the polymers formed by heating. Formation of a refractive index distribution is needed for optical waveguides. If this distribution could be obtained by laser irradiation, the technique is very convenient and useful. So we studied possible causes of the higher refractive indices of polymers formed by YAG laser irradiation.

Monomer mixtures are prepared as are shown in Scheme 1.[4] Acrylic acid or methacrylic acid was mixed in benzene with cinnamic acid, 3-phenylpropionic acid, or α-methylcinnamic acid. Barium hydroxide or lead oxide was added during heating at 40 °C over several hours. Then, vinyl monomer such as chlorostyrene, methylstyrene, or glycidyl methacrylate was added to the mixture. Benzene and water were removed by vacuum distillation, leaving a transparent monomer mixture.



Scheme 1.

We used a pulsed or a constant wave YAG laser. The conditions of laser irradiation were as follows : for the pulsed laser, intensity 2-25 J/pulse; irradiation number, 50-300 pulses; pulse width, 9 ms; repetition rate, 2 pulses/s: for the constant wave laser, intensity, 10-25 W; irradiation time 10-1000 s. The monomers containing metal ions were coated on glass slides by about 0.5 mm thickness. A lens was put in the beam path and the sample was placed near its focal point. The monomers on the laser-irradiated region polymerized as a film of a few hundred nm thick. This region was circular, and it was larger than the cross-section of laser beam.

Refractive indices of polymers formed by YAG laser irradiation were measured by an ellipsometer. The results are summarized in Table 1. The values are 1.615-1.646, and higher than those of polymers formed by heating.

The infrared spectra of polymers were examined in order to elucidate the reason for the higher refractive indices (Fig. 1). The spectra of Fig. 1 are for the sample No. 1 listed in Table 1. There are obvious differences between the spectrum of polymer by YAG laser irradiation and that of polymer by heating. Absorption peaks at 1680 cm^{-1} and 1315-1280 cm^{-1} attributed to ν(C=O) and ν(C-O) of carboxylic acid dimers, respectively, were seen for the monomer and the polymer by heating, but not for the polymer by laser irradiation.

It is considered that the differences in infrared spectra are related to the higher refractive indices. Based on the spectra, posibilities of decarboxylation, vaporization of carboxylic acids, or reconfiguration of molecules and ions by laser irradiation could be proposed.

Regarding the decarboxylation, it does't seem to occur in this case because removing of oxygen leads to a decrease of refractive index. A refractive index can be estimated roughly from molecular refractivity and molecular volume. Ions, such as carboxylate anions, large polarizability make a refractive index higher. The

Table 1. Refractive indices of polymers by heating and laser irradiation

No.	Monomer components			Refractive index	
	Metal ion	Carboxylic acids	Vinyl monomer	Polymer by heating	Polymer by laser irradiation
1	Ba^{2+}	Cinnamic acid Acrylic acid	Chlorostyrene	1.606	1.635
2	Ba^{2+}	3-Phenyl-propionic acid Acrylic acid	Chlorostyrene	1.581	1.615
3	Pb^{2+}	α-Methyl-cinnamic acid Methacrylic acid	Chlorostyrene	1.626	1.646
4	Pb^{2+}	α-Methyl-cinnamic acid Methacrylic acid	Glycidyl methacrylate	1.580	1.629

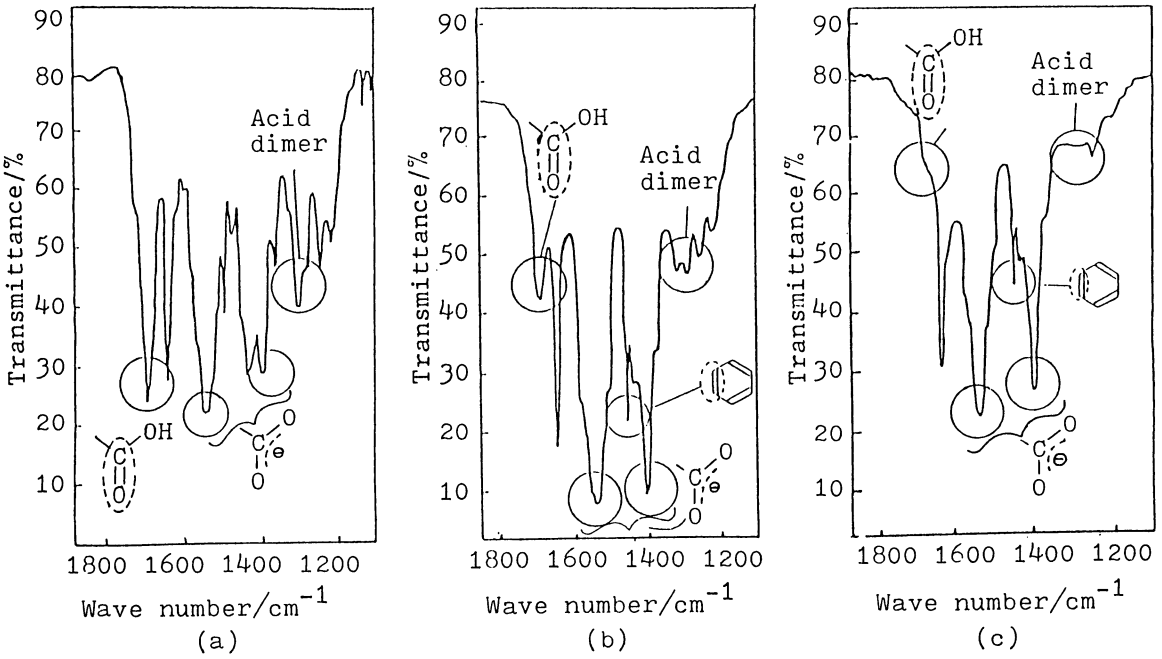


Fig. 1. Infrared spectra of (a) monomer, (b) polymer by heating, and (c) polymer by laser irradiation.

calculated value on the assumption that decarboxylation occurs is 1.604, which is lower than the observed one (1.635).

As for the vaporization of carboxylic acids, it seems to be almost impossible. For the molar quantity of carboxylic acids was five times that of the metal ions in the used monomer, and so it is hard to think that all of carboxylic acids were vaporized by laser irradiation.

It is considered that there is a large probability of the reconfiguration of molecules and ions. It was reported that the reconfiguration occurred in laser annealing.[5] According to this report, electrons are excited in high energy levels and interactions between molecules get weak by laser irradiation, then molecules and ions are easy to move and, consequently, reconfiguration occurs. It is considered that similar phenomena occur in the YAG laser-induced polymerization. Thereupon the infrared spectra were examined in detail, it was found that absorbance by carboxylate anions is strong in the spectrum of polymer by laser irradiation (Table 2). Moreover this polymer is harder than that by heating, and the density of the former is about 1.5 g/cm^3 and that of the latter is 1.3677 g/cm^3. Therefore, it is tentatively concluded that a polymer formed by YAG laser irradiation has a higher refractive index on account of reconfiguration of molecules and ions to a packed structure.

Table 2. Absorbance ratio of carboxylate anion to double bond in benzene ring

	Polymer by heating	Polymer by laser irradiation
Absorbance ratio $D(COO^-)/D(C_6H_6)$	1.648	2.593

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