

# Evaluations of Phenyl Acrylic Derivatives as UV-curable Optical Materials with High Refractive Index

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## **Introduction**

UV-curable formulations using acrylic compounds have been applied to the manufacturing process of various optical materials, such as prism sheets for liquid crystal displays (LCD), adhesives, optical fibers, lenses, and so on, because they are suitable materials to obtain plastic articles with complicated shape or high precision in high productivity as well as their excellent optical properties<sup>1)-5)</sup>.

Although the importance of UV-curable formulations in these fields increases, it is getting hard to satisfy required properties using current commercial acrylates due to rapid progress of essential performance in electro optics, and the development of new practical materials for optical applications have been desired.

The new materials for optical applications require high curability, excellent compatibility with other ingredients, odorless, and durability such as heat resistance, and light resistance, as well as optimization of refractive index, and transmittance. When we direct our attention to conventional polymeric materials, we can enumerate the polymers with high refractive index, such as poly ethylene terephthalate (PET), polycarbonate (PC), and polystyrene<sup>6), 7)</sup>. Although they have been already applied to various optical applications, they are not utilizable as UV-curable materials. Although polyols bearing PET and PC may be able to be introduced to acrylic oligomers, such as urethane acrylates and polyester acrylates, they will show poor compatibility with other ingredients. On the contrary, styrene monomer can be blended well with many types of acrylates and methacrylates, and the formulation with low viscosity can be obtained, but neither its low curing rate nor strong odor are permissible to manufacture polymeric materials industrially. Recently, nanocomposites using inorganic particles have been paid attention as optical materials as another method, and they have been applied to varnishes<sup>8)</sup>, and thermosetting resins<sup>9), 10)</sup>. But it is difficult to achieve high transmittance enough to be applied to optical materials in many cases due to light scattering or absorption at visible rays, then optical communications utilizing

higher wavelength are expected as one of their potential applications.

With regard to acrylic derivatives, although phenoxyethyl acrylate, alkoxyated bisphenol A diacrylate, and bisphenol A epoxy acrylates are applied to electro optics, the adjustable refractive index range of the formulation based on them is narrower than other conventional plastics. In some articles, alkoxyated fluorene diacrylate have been reported to give a transparent polymer with high refractive index and small anisotropy<sup>11), 12)</sup>. It is expected to be a useful UV-curable material for optical films and coatings, however, the obtained formulations tend to be highly viscous at room temperature due to fluorene structure. Then the acrylic derivatives which exhibit both high refractive index and low viscosity are still required.

From these view points, we have been examining the utility of phenyl acrylic derivatives. We have prepared a series of phenyl acrylic derivatives to evaluate their liquid properties as reactive diluents with high refractive index, curing properties, and physical properties of resulting cured films.

Moreover, we have tried to clarify the effects of an ethoxy unit on optical properties, curability, and practical durability taking *o*-phenylphenyl ester by way of example.

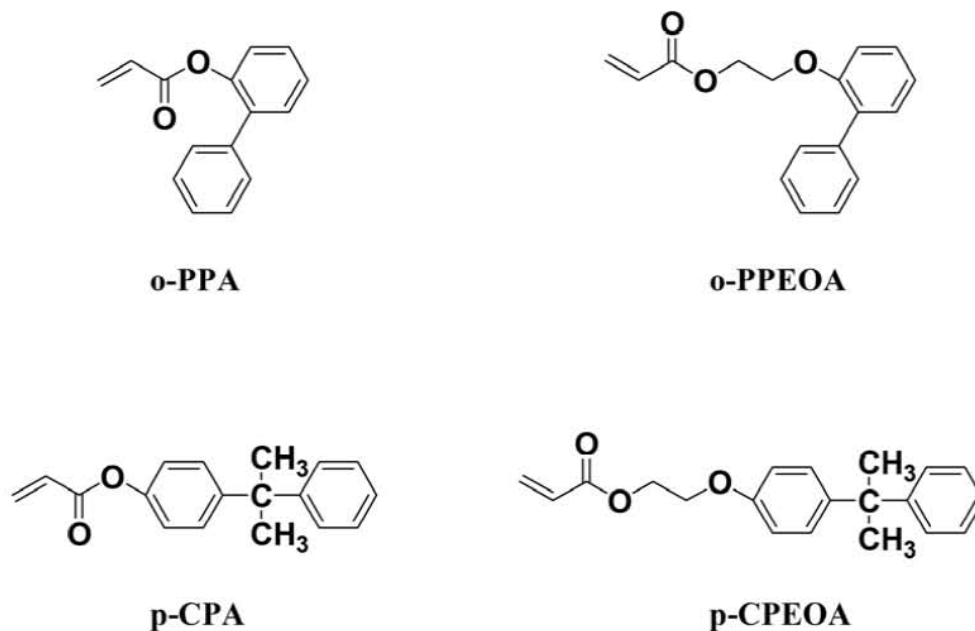


Figure 1. Chemical structure of phenyl acrylic derivatives.

## Experimental

### Materials

o-Phenyl acrylate (o-PPA) and p-cumylphenyl acrylate (p-CPA) were synthesized by reaction of acryloyl chloride with their corresponding phenols, and then the obtained acrylates were purified to remove residual phenol, acrylic acid, and catalyst by column chromatography.

o-Phenoxyethyl acrylate (o-PPEOA) and p-cumylphenylethyl acrylate (p-CPEOA) are commercially available from Toagosei Co., Ltd. They were purified by column chromatography to remove residual alcohol, acrylic acid, and catalyst. Methyl methacrylate was purchased from Wako Chemical Co., and purified by vacuum distillation. 1-Hydroxy cyclohexyl phenyl ketone (HCPK) was purchased from Ciba, and used as received.

### Photo-DSC measurement

Heat of photopolymerization was studied using a DSC (TA Instruments Q100 differential scanning calorimeter) modified with a medium pressure mercury lamp. Approximately 1mg of sample was placed in the pan to give uniform thickness of film. The samples were allowed to equilibrate at 25°C for 3 minutes before UV-irradiation. The UV intensity was adjusted to 2.8mW/cm<sup>2</sup> at 365 nm.

### Refractive index measurement

Refractive index ( $n_D^{25}$ ) of monomers and cured films were determined using Abbe refractometer. 2-Bromonaphthalene was used as a contact liquid when refractive index of cured films was measured, and measurement was conducted quickly so as to prevent deviation of refractive index which caused by permeation of 2-bromonaphthalene into cured films.

### General procedures to obtain films

The formulations were prepared by mixing acrylic monomers and photoinitiator at 40°C. Once photoinitiator dissolved in monomers, the formulations were cooled down to 25°C. UV-irradiation was conducted using a medium pressure mercury lamp, and UV-exposure dose was adjusted by changing the speed of the conveyor.

### Thermal analysis

Thermo gravimetry was conducted using a TG/DTA 220 (Seiko Instruments Inc.). Approximately 10mg of samples was placed in the pan. The rate of heating was 20°C a minute. Differential scanning calorimetry was conducted using a RDS220 (Seiko Instruments Inc.) to determine glass transition temperature of the obtained polymers. Approximately 6mg of samples was placed in the pan. At first, the sample was cooled down to -50°C at the rate of 30°C a minute, and then heated to 200°C at the rate of

10°C a minute.

## Results and Discussion

Phenyl acrylic derivatives showed lower viscosity compared with the corresponding phenoxyethyl ones as well as their higher refractive index as shown in Table 1. This feature will benefit the formulations to achieve the optical materials manufactured by a minute process such as prism sheets, nanoimprints, and so on.

Furthermore, the introduction of phenyl groups into acrylic esters did not cause the increase of specific gravity, while the introduction of halogen atoms necessarily leads to higher specific gravity<sup>13)</sup>.

**Table 1. Physical properties of phenyl acrylic derivatives**

Properties		o-PPA	p-CPA	o-PPEOA	p-CPEOA
Monomer	Refractive Index ( $n_D^{25}$ )	1.583	1.565	1.578	1.552
	Viscosity(mPa*s) 25°C	90	95	130	155
	Specific Gravity	1.122	1.084	1.136	1.097
	Ames Test	Negative	Negative	Negative	Negative
Cured Film	Tg (DSC)	66°C	58°C	30°C	19°C
	Refractive Index ( $n_D^{25}$ )	1.619	1.593	1.612	1.577
	Specific Gravity	1.215	1.153	1.221	1.164
	Shrinkage (%)	7.6	6.0	7.0	5.7

Photo-curability of o-PPA and p-CPA has been investigated calorimetrically by photo-DSC. Although their DSC profiles were very similar when photo-curing was conducted in a nitrogen atmosphere, the enthalpy of o-PPA was found out to be less declined in an air atmosphere compared to that of p-CPA as shown in Figure 2 and Figure 3.

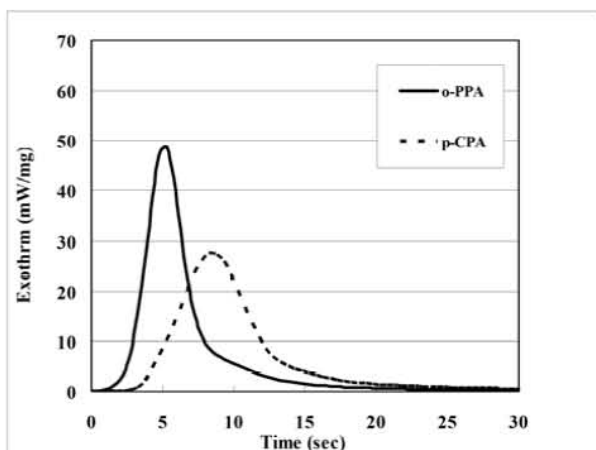


Figure 2. Photo-DSC curves for the curing of o-PPA and p-CPA. HCPK: 2wt%, UV-intensity; 2.8mW/cm<sup>2</sup>, in an air atmosphere.

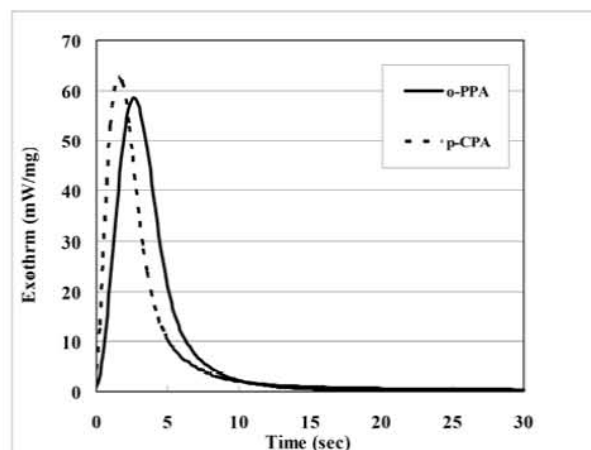
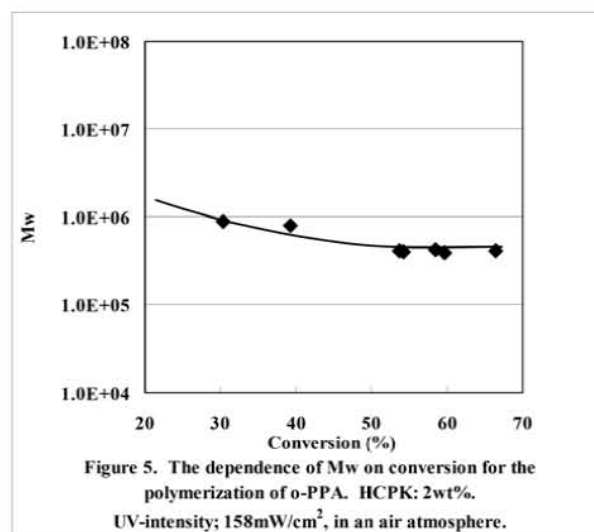
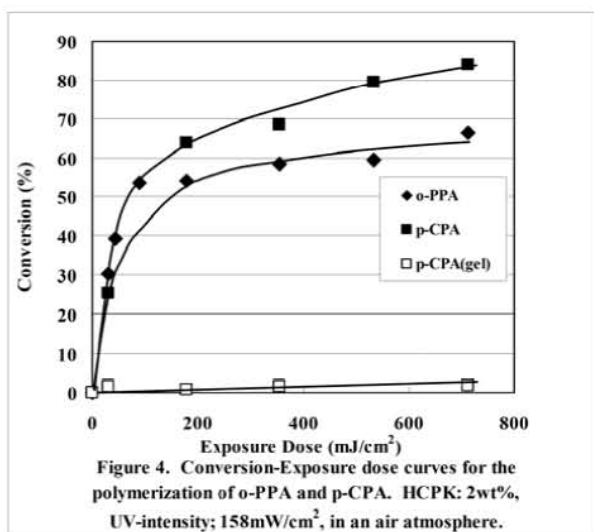


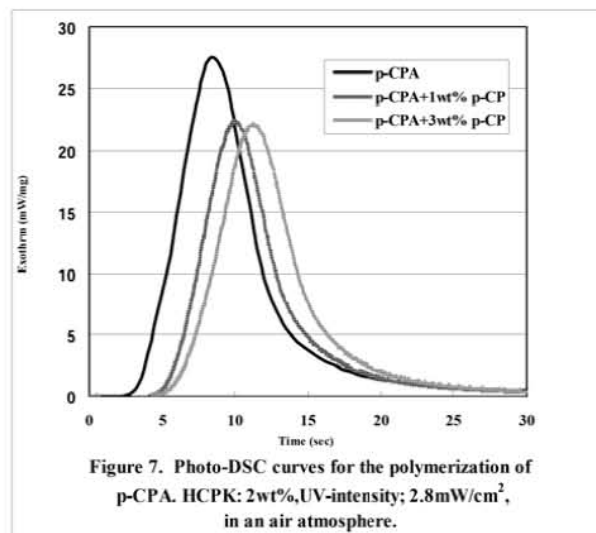
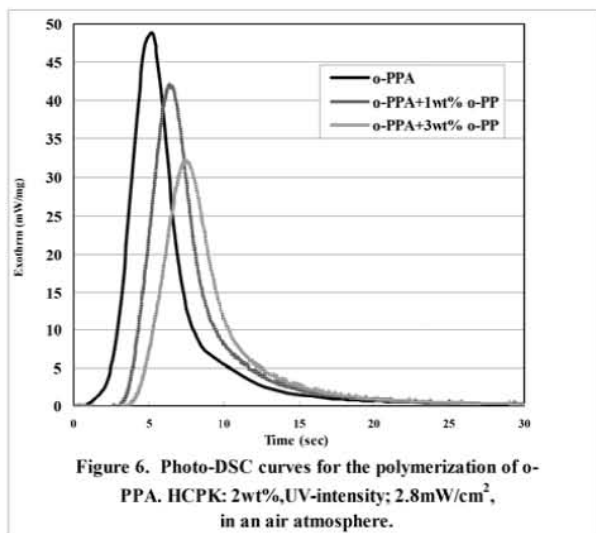
Figure 3. Photo-DSC curves for the curing of o-PPA and p-CPA. HCPK: 2wt%, UV-intensity; 2.8mW/cm<sup>2</sup>, in a N<sub>2</sub> atmosphere.

This phenomenon might be explained by Tromsdorff effect which was caused by hydrogen abstraction and sequent cross-linking during photo-curing<sup>14</sup>).

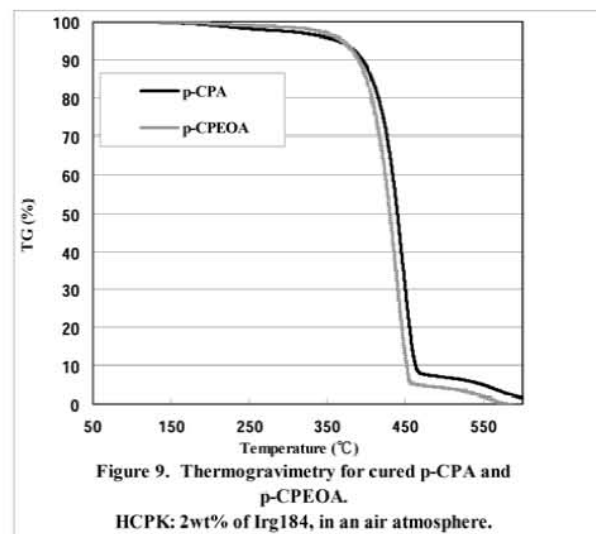
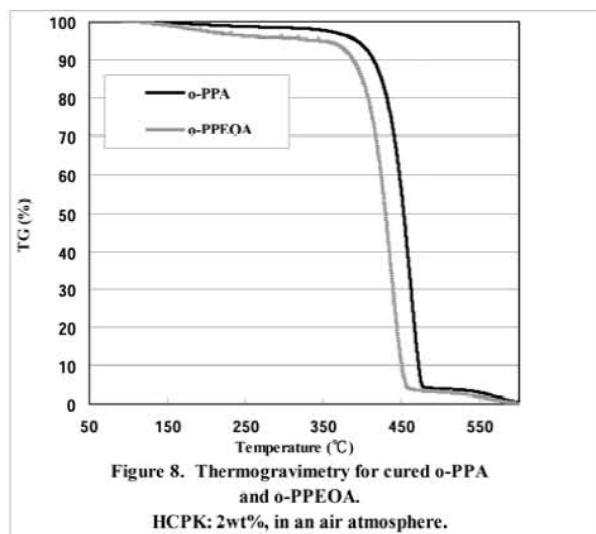
The influence of cross-linking reaction upon final conversion was examined by the measurement of gel fraction of their cured film, but significant Tromsdorff effect had not been seen in the polymerization of o-PPA and p-CPA either as shown in Figure 4. Unexpectedly, soluble polymer could not be obtained in the polymerization of p-CPA due to gelation at very low conversion. According to the dependence of weight average molecular weight of the obtained polymer on conversion, the influence of cross-linking reaction which was caused by hydrogen abstraction had not been seen in the polymerization of o-PPA as shown in Figure 5.



Additionally, kinetics in the presence of the phenol was examined calorimetrically to see the effect of small amount of it, although all monomers employed in this study was purified by column chromatography. Figure 6 and Figure 7 show the dependence of phenol on photo-curability, but their difference of polymerization behavior could not be explained by the effect of residual phenol.



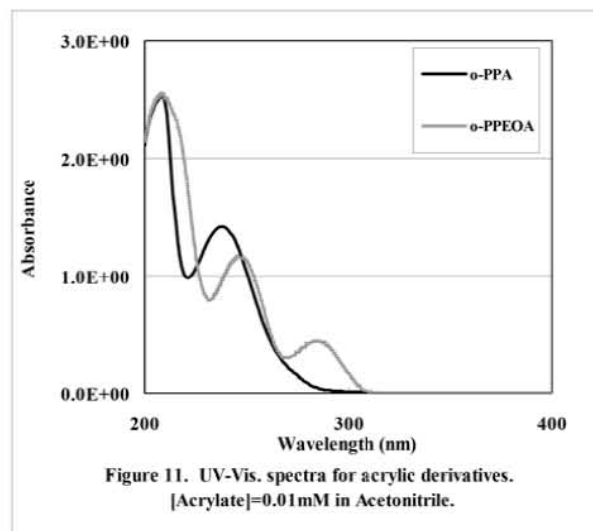
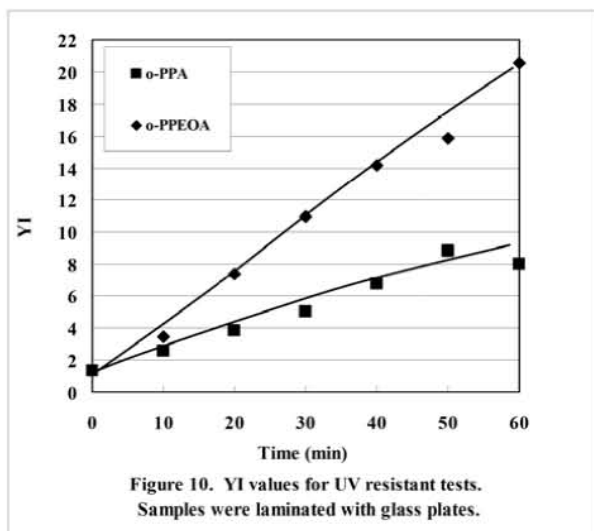
Thermal analysis of the cured film was conducted, and the dependence of their mass change on temperature was shown in Figure 8 and Figure 9. Both o-PPA and p-CPA was found out to show better heat stability than their corresponding phenoxyethyl acrylates. According to DSC measurement, glass transition temperature (T<sub>g</sub>) of them also showed same tendency.



As one of the most important practical properties required as optical materials, yellowing index of cured films after accelerated tests such as heat resistance and UV resistance was examined.

No significant difference was observed after heating, while the yellowing index of o-PPA after UV resistance was lower than that of o-PPEOA as shown in Figure 10.

Figure 11 shows the UV-Vis. absorption of o-PPA and o-PPEOA, and the latter was found out to have specific absorption at higher wavelength. It could influence the UV resistance of the cured film as well as photocurability.



## Conclusions

Major physical and optical properties of phenyl acrylic derivatives were investigated. Phenyl acrylic derivatives not only possessed higher refractive index, but also showed lower viscosity than the corresponding phenoxyethyl ones. The obtained films showed excellent durability enough to apply to the ingredients for optical materials such as prism sheets, nanoimprints, optical coatings, and so on.

Regardless of practical benefits, they have not been widely used for UV-curable materials so far. Further study for commercialization of these materials and the utilization of their benefits for applications are still required.

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