

Polymerization by the Active Species Produced from the Charge Transfer Complex. IV. Phototerpolymerization of *N*-Vinylpyrrolidone, Maleic Anhydride and Methyl Methacrylate

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It was found by us that the photo and thermal polymerizations of methyl methacrylate (MMA) were largely accelerated in the presence of both amide and maleic anhydride (MAH) and the acceleration was more effective in air than in *vacuo*. Besides, it was assumed that the radical species initiating the polymerization of MMA was produced *via* the complex between amide and MAH.¹⁾

As *N*-vinylpyrrolidone (VPD) is an amide containing a vinyl group, it probably interacts with MAH, as a result the complex may participate in polymerization as a monomer unit. Therefore, it is expected that the terpolymerization of VPD, MAH, and MMA is induced by the VPD-MAH complex.

The mixture of VPD and MAH turned yellowish and then pink or scarlet upon UV irradiation. The spectra of the solutions of VPD and MAH in 1,2-dichloroethane are shown in Fig. 1. The results suggest a complex formation between VPD and MAH.

The composition of the VPD-MAH complex was determined by the continuous-variation method,

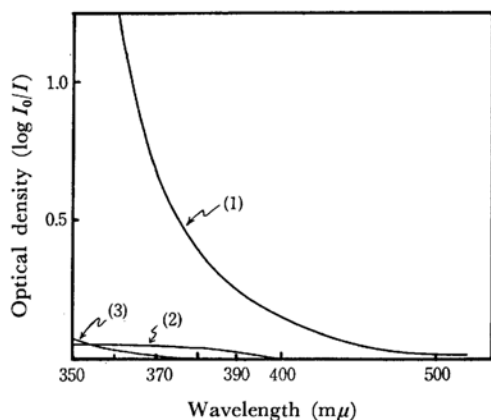


Fig. 1. Absorption spectra of the complex between VPD and MAH.

- (1) VPD 1.185 mol/l + MAH 0.069 mol/l
- (2) VPD 1.185 mol/l
- (3) MAH 0.069 mol/l
(solvents, 1,2-dichloroethane)

1) H. Tamura, M. Tanaka and N. Murata, to be published.

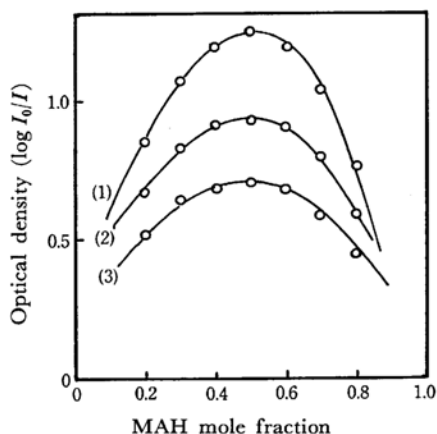


Fig. 2. The continuous variation method of VPD-MAH complex. VPD 0.404 mol/l, MAH 0.400 mol (solvent, chloroform)
(1) 360 mμ (2) 365 mμ (3) 370 mμ

TABLE I. PHOTOPOLYMERIZATION OF VPD, MAH, AND MMA AT 30°C IN AIR (polymerization time, 3 hr)

Experimental number	VPD (mol/l)	MAH (mol/l)	MMA (mol/l)	Polymer yield (g)
1	3.75	0.41	5.62	0.421***
*2	3.75	0.41	0	0.120
3	3.75	0	5.62	0.047
*4	0	0.41	5.62	0
**5	3.75	0.41	5.62	0.290

* The total volume was maintained at 5 ml by employing benzene instead of MMA or VPD.

** Polymerization was carried out for 2 hr using AIBN (2×10^{-2} mol/l) as the initiator.

*** The polymerization in the dark was almost negligible.

the results shown in Fig. 2 were obtained. The curves reached a maximum at the 0.5 mol fraction of MAH, and it was estimated that a 1:1 complex was formed between VPD and MAH.

The polymerization of the VPD-MAH-MMA system was induced, in fact, without any initiator, the results of the photopolymerization are shown in Table I,