Polymerization by the Active Species Produced from the Charge Transfer Complex. V. The Thermal Copolymerization of *N*-Vinyl-pyrrolidone and Methyl Methacrylate

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It was previously reported by us[1] that the polymerization of the *N*-vinylpyrrolidone (VPD)-maleic anhydride(MAH)-methyl methacrylate(MMA) ternary system was induced photochemically in air at 30°C without any initiator and that the active species was presumably produced *via* the 1 : 1 complex between VPD and MAH. Furthermore, their polymerizations occurred thermally in air at 70°C.

In the photochemical polymerization, the lack of any one component remarkably lowered the polymer yield, but in the thermal polymerization it was found that the spontaneous copolymerization of VPD and MMA took place simultaneously in air after some induction period and that the copolymerization rate was quite fast, though it was somewhat smaller than that of the ternary system.

Therefore, the following experiments were carried out. The copolymerization of VPD and MMA did not occur at all *in vacuo*. This suggests that oxygen may participate in the reaction of the production of the active species. The copolymers were obtained from mixtures with various ratios of VPD and MMA, and the copolymerization rate was remarkably accelerated by adding a small amount of $ZnCl_2$. Neither VPD nor MMA alone was polymerized under the experimental conditions employed here. The results are shown in Table 1.

TABLE 1. THE SPONTANEOUS COPOLYMERIZATION OF VPD AND MMA AT 70°C

VPD (mol/*l*)	MMA (mol/*l*)	Polymer yield (g) In air (%)*	*In vacuo*
7.50	1.87	0.272 (5.3)	0
6.56	2.81	0.217 (4.3)	0
5.62	3.74	0.419 (8.4)	0
4.68	4.68	0.391 (7.9)	0
**4.68	4.68	2.727 (55.2)	—
3.75	5.62	0.524 (10.7)	0
2.81	6.55	0.221 (4.6)	0
1.87	7.49	0.123 (2.6)	0
***3.75	0	0	—
***0	5.62	0	—

* Weight %-conversion to the total monomer concentration.

** About 0.2 g of $ZnCl_2$ was added to the mixture of VPD and MMA.

*** The total volume was maintained at 5 m*l* employing benzene.

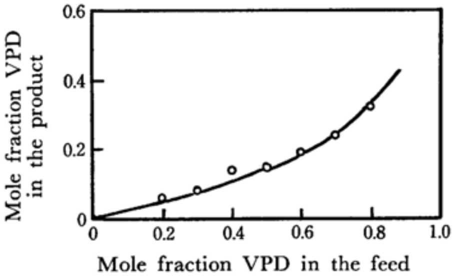

Fig. 1. Composition curve for the VPD-MMA copolymer (in air at 70°C).

It is known that the positive *e*-value of such monomers as MMA and acrylonitrile is elevated by the addition of a Lewis acid such as $ZnCl_2$.[2] Although there is no spectroscopic evidence for thr existence of the VPD-MMA complex, it is possible, judging from these results, that the active species is formed by the reaction of the VPD-MMA complex and oxygen.

The compositions of the copolymers were determined by elemental analysis, while the composition curve for the VPD-MMA copolymer was obtained as is sown in Fig. 1.

The monomer reactivity ratio (M_1=MMA, M_2=VPD) were decided from the Mayo-Lewis plots to be the following: $r_1=4.6\pm0.4$, $r_2=0.02\pm0.02$. The copolymerization of VPD and MMA by a radical initiator (AIBN) at 50°C has already been reported by Bork and Coleman,[3] who obtained the following values: $r_1=4.7\pm0.5$, $r_2=0.005\pm0.05$.

The results we have obtained here are quite consistent with theirs. This suggests that the spontaneous copolymerization of VPD and MMA proceeds by way of a radical mechanism. The details of the study will be reported later.

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[1] H. Tamura, M. Tanaka and N. Murata, This Bulletin, **42**, 3041 (1969).

[2] M. Imoto, T. Otsu and Y. Harada, *Makrmol. Chem.*, **65**, 180 (1963).

[3] J. F. Bork and L. E. Coleman, *J. Polymer Sci.*, **43**, 413 (1960).