Note

N – 비닐프탈이미딘과 말레산 무수물의 자유라디칼 공중합

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Free Radical Copolymerization of N-Vinylphthalimidine and Maleic Anhydride

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INTRODUCTION

Many papers have been published on the mechanistic and kinetic studies of free radical initiated 1:1 alternating copolymerizations[1,2]. It now appears to be generally accepted that alternating copolymerizations proceed through competitive propagations of classical terminal carrier radicals and donor-acceptor, charge-transfer complexes[3].

We could recently analyze kinetically the free radical 1:1 alternating copolymerization between diethyl α-phenylvinyl phosphate and maleic anhydride[4]. It was assumed that the propagations occurred via a mixed mechanism of the classical terminal model and 1:1 charge-transfer polymerization, which has been earlier proposed by Seiner and Litt[5].

As a part of our continued efforts to establish a structure-reactivity relationship of vinyl monomers in free radical initiated copolymerizations, we have conducted a study on copolymerization between N-vinylphthalimidine and maleic anhydride. According to Murata[6] N-vinylphthalimidine is expected to be a good π-donor monomer with the e value of –1.80. Moreover, hydrolysis of N-vinylphthalimidine copolymers is expected to result in very interesting structures containing pendant amino and carboxylic acid groups.

In additon, we also determined the formation constant of the 1:1 charge-transfer complex between the two comonomers. Foster[7] modified the conventional Benesi-Hildebrand equation in such a way that the degree of change in the chemical shift, before and after complexation, can be utilized for the determination of the complex formation constant, K_c^{AD}:

$$\frac{\Delta}{[D]} = -\Delta \cdot K_c^{AD} + \Delta_o^{AD} \cdot K_c^{AD}$$

In the above equation Δ represents the observed change in the chemical shift of an olefinic proton of the acceptor before and after complexation and Δ_o^{AD} stands for the difference between the chemical shifts of the pure donor and the pure complex. This equation shows that if one plot the value of $\Delta/[D]$ vs. that of Δ, one should obtain a straight line whose slope corresponds to K_c^{AD}.
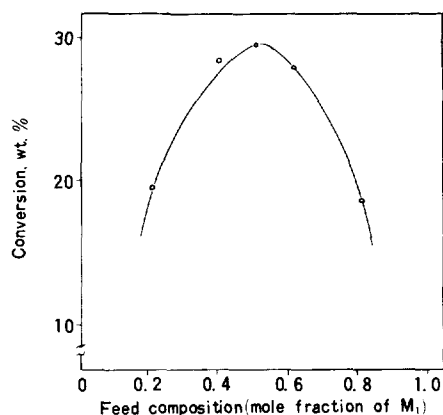
RESULTS AND DISCUSSION

Copolymerizations were conducted at varying feed compositions and the results are summarized in Table 1. The data in the table point two impor-

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Table 1. Copolymerization of N-Vinylphthalimidine (M_1) and Maleic Anhydride (M_2)*

Exp. No.	Feed Composition		Conversion wt.%	Copolymer Composition	
	$M_1:M_2$, g	Mole Fraction of M_1		N Content, wt.%	Mole Fraction of M_1
1	4.240:0.654	0.80	18.7	5.38	0.49
2	3.543:1.457	0.60	27.8	5.39	0.49
3	3.093:1.907	0.50	29.6	5.47	0.50
4	2.596:2.403	0.40	27.4	5.45	0.50
5	1.442:3.558	0.20	19.5	5.39	0.49
6	0:5.0	0	0	0	0

*Copolymerized in DMF for 4 hours at 60°C using 0.1 wt.% benzoyl peroxide as an initiator.

Fig. 1. Monomer feed compositon vs. copolymerization rate.

Table 2. Change of Chemical Shift of the Olefinic Proton in Maleic Anhydride After Mixed with N-Vinylphthalimidine*

[D], mole/1	Δ, H_z	Δ/[D], H_z/mole/1
0.125	5.2	41.3
0.250	9.5	38.1
0.500	16.6	33.2
0.750	22.8	30.4

*The concentration of the acceptor, maleic anhydride, was kept constant at 0.0250 mole/1. Spectral data were obtained in DMSO at 21°C.

tant observations: 1) compositions of all of the copolymers obtained were basically the same and were of equimolar in the comonomer contents and 2) conversion was highest at the equimolar feed.

Since maleic anhydride is unable to undergo polymerization under the reaction condition employed in the present investigation, it can be concluded that the copolymers obtained were of 1:1 alternating consequence.

As far as the dependence of copolymerization rate on the feed composition is concerned, it was very often observed in many 1:1 alternating copolymerizations that the rate was maximum at the 1:1 equimolar feed. Such observations were taken by many researchers as an indication that 1:1 donor-acceptor complex between the comonomer pair is participating in propagation steps. However, as mentioned above in the introduction, it seems to be more reasonable to assume that a mixed mechanism is operating in propagations. Un-

fortunately, detailed kinetic analysis for the present comonomer pair is not yet available.

We have determined the formation constant, K_c^{AD}, of the 1:1 charge-transfer complex between N-vinylphthalimidine (π-donor) and maleic anhydride (π-acceptor) by measuring the change in the chemical shift of the protons in the latter before and after complexed with the former (see Figure 1).

π-donor π-acceptor
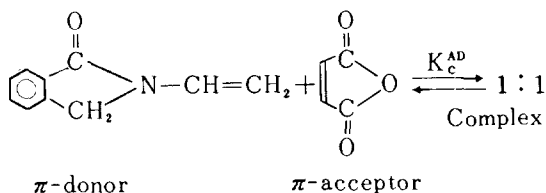
The experimental results are tabulated in Table 2 and the data are represented in Figure 2. The value of K_c^{AD} obtained from the slope of the figure is 0.70 1/mole. This value is significantly higher than 0.25 1/mole of styrene-maleic anhydride pair[8]. This indicates that N-vinylphthalimidine is much better π-donor than styrene in
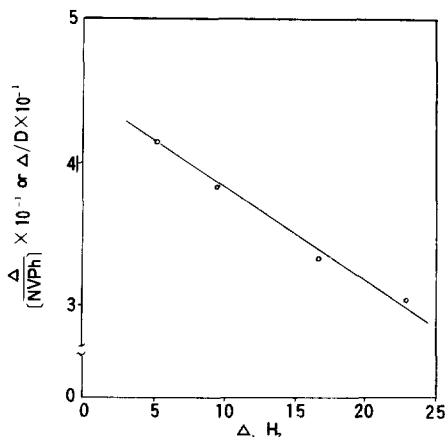
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Fig. 2. Determination of K_c for the systen N-vinyl-phthalimidine-maleic anhydride, $K_c = 0.70$ l/mole, $\Delta = \delta_A - \delta$ is the difference between the chemical shifts of the acceptor protons in uncomplexed form, δ_A, and in complexing media, δ.


complexation with maleic anhydride. This is in complete line with the fact that the e-value of the former, -1.80^6 is much lower than that (-0.80) of styrene.

EXPERIMENTAL

Synthesis of N-Vinylphthalimidine N-Vinylph-thalimidine was prepared from phthalide and ethanolamine following the procedure described by Murata[6]: The structure of the monomer was confirmed by its IR spectrum, m.p. (61-62°C) and elemental analysis.

Determination of the Formation Constant of Charge-Transfer Complex The formation constant, K_c^{AD}, of the charge-transfer complex between N-vinylphthalimidine and maleic anhydride was determined in DMSO at 21°C using the Foster equation. The concentration of maleic anhydride was fixed at 2.5×10^{-2} mole/1 and that of N-vinylphthalimidine was varied from 12.5×10^{-2} mole/1 to 75.0×10^{-2} mole/1. NMR spectral analysis was performed on a Brucker FT Spectrometer WP 80 SY.

Copolymerization Desired amounts of N-vinylphthalimidine and maleic anhydride were
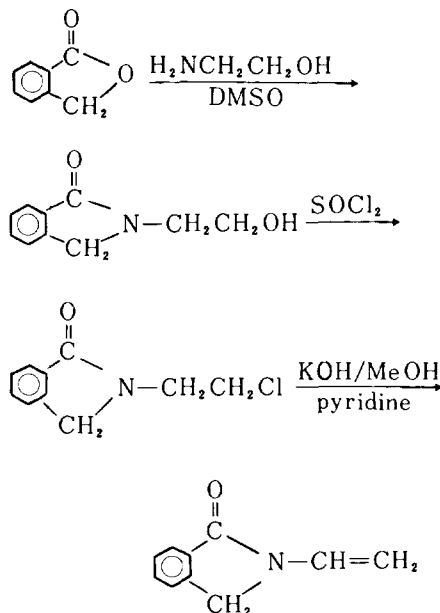
dissolved in N,N-dimethylformamide. The overall concentration of the two monomers was 50 wt.%. To the solution was added 0.1 wt.% of benzoyl peroxide (based on the total monomer mixture) and the mixture was degassed by the usual freeze and thaw cycles using a vacuum line. Finally the polymerization tubes were filled with nitrogen and placed in a water bath at 60.0 ± 0.1°C. After 4 hours of polymerization, the tubes were immersed in a dry ice-acetone bath, followed by the transfer of the frozen mixture into diethyl ether containing 1% by weight of hydroquinone. The precipitate was then separated by centrifugation and the polymers were purified by solution-precipitation cycles using acetone and diethyl ether. The copolymers thus obtained were dried under vacuum at 50°C.

REFERENCES

1. K. Dodgson and J.R. Ebson, *Europ. Polym. J.,* **13**, 791 (1977).

2. M.L. Hellensleben, *Makromol. Chem.,* **144**, 267 (1970).

3. M. Yoshimura, H. Mikawa, and Y. Shirota,

Macromolecules, **11,** 1085 (1978).

4. J.-I. Jin and H.-K. Shim, *Polymer J.(Japan),* **15,** 683 (1983).

5. J.A. Seiner and M. Litt, *Macromolecules* **4,** 308 (1971).

6. K. Murata, *Bull. Chem. Soc. Jap.,* **46,** 1752 (1973).

7. R. Foster and C.A. Fyfe, *Trans. Faraday Soc.,* **61,** 1626 (1965).

8. P.D. Bartlette and K. Nozaki, *J. Am. Chem. Soc.,* **68,** 1495 (1946).