Graft-copolymerization of *N*-Vinyl Phthalimide to Polyethylene by γ-Ray Radiation[1]

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Although the works of polymerization and copolymerization of *N*-vinyl imides initiated by radical catalysts have been reported by many workers, the ones initiated by radiation have been counted just two,[2,3] and the studies of graft-copolymerization of *N*-vinyl imides have not been able to find at all.

On the other hand, we have been studing in a series of aminobutadienes, in which the reactivity differences among 1-phthalimido-1, 3-butadiene, 1-succinimido-1, 3-butadiene, *N*-vinyl phthalimide (VPI) and *N*-vinyl succinimide in radical copolymerization were already discussed.[4]

The present paper deals the studies on the graft-copolymerization of VPI to polyethylene (PE) by γ-radiation, the treatment of the obtained graft-copolymer with amine and the dyeing characteristics of our products by several dyes.

Experimental

Materials. *N-Vinyl Phthalimide (VPI).* VPI was prepared *via* β-hydroxyethyl phthalimide obtained by the condensation of monoethanolamine with phthalic acid and the succeeding pyrolysis of its acetate; pale yellow needles melting at 85—86°C (lit., mp 86,[5,6] 85.5—86°C[7,8]).

Polyethylene (PE) Films. Yukalon film (Mitsubishi Petrochemical Co. Ltd., thickness 0.05 mm) as high pressure method PE and Hizex film (Mitsui Petrochemical Co. Ltd., thickness 0.04 mm) as low pressure method PE were chosen. These PE films were washed with water, immersed in a large amount of chloroform for about ten days to extract the impurity and dried under vacuum.

N, N'-Dimethyl Formamide (DMF). DMF was dried over anhydrous sodium sulfate and then purified by the repeated distillations; bp 53—53.5°C/23 mmHg.

Radiation Source. Radiation source was γ-ray from Cobalt-60 (1000 Ci) and the dose rate was measured by a Toshiba Dosimeter Model RCD-43101.

Graft-copolymerization Procedure. In a glass tube, required amounts of PE film, VPI and DMF were placed. In this experiment, PE film must be immersed thoroughly in monomer solution. The tube was sealed under nitrogen atmosphere. Graft-copolymerization by γ-radiation was carried out for a given time at 25—28°C. After the copolymerization, the film was immersed in a large amount of chloroform for a week at room temperature to remove homopolymer and monomer. The resulting grafted film was dried under vacuum and then weighed to determine the grafting ratio.

Reaction of Grafted Film with Amine. Grafted film was immersed in a large amount of amine and reacted for a given time at a constant temperature. After the reaction, the film was washed with methanol and dried under vacuum.

Dyeing Method. Grafted film and its amine-treated film were dyed by several dyes such as direct, acid, basic and dispersed dyes according to the prescriptions shown in Table 1. Dyeing bath was heated in boiling water for 1 hr. After finishing, these films were immersed in

TABLE 1. THE PRESCRIPTIONS FOR DYEING BY THE SEVERAL DYES

i) Direct Dye	
Nippon Sky Blue[a]	500 mg
Sodium Chloride	1.0 g
Water	25 m*l*
ii) Acid Dye	
Xylene Fast Blue PR[b]	300 mg
Sulfuric Acid Solution (10 vol%)	1.5 m*l*
Water	30 m*l*
iii) Basic Dye	
Methylene Blue FZ conc.[c]	500 mg
Water	25 m*l*
iv) Dispersed Dye	
Samaron Blue 3GL[d]	500 mg
Nonion N-1000 Solution (2%)	1.5 m*l*
Water	25 m*l*

a) C. I. Direct Blue 15.
b) C. I. Acid Blue 129.
c) C. I. Basic Blue 9.
d) Dispersed dye for polyester fibres.

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1) Presented by K. Murata at the Hiroshima Meeting of the Chemical Society of Japan, Hiroshima, November, 1965.

2) G. Hardy, K. Nyitrai, J. Vorga and N. Fedorova, *J. Polymer Sci.*, **C2**, 923 (1965); G. Hardy, K. Nyitrai, G. Kovacs and N. Fedorova, *Magy. Kem. Folyoirat*, **69**, 441 (1963).

3) G. Hardy, J. Vorga and G. Nagy, *Makromol. Chem.*, **85**, 58 (1965); *Magy. Kem. Folyoirat*, **71**, 171 (1965).

4) K. Murata and A. Terada, This Bulletin, **39**, 2494 (1966).

5) M. Bachstez, *Ber.*, **46**, 3087 (1913).

6) U. S. Pat. 2276840.

7) T. Yoshida and H. Hirakawa, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **55**, 83 (1952).

8) S. Akiyoshi, K. Yanagi and T. Matsuda, *ibid.*, **59**, 658 (1956).

0.25% cleaning material solution for 30 min at 80—85°C, washed with water and then dried in air.

Results and Discussion

Graft-copolymerization. Graft-copolymerization of VPI to PE films was carried out by γ-radiation. The relationships between grafting ratio and irradiation time in Yukalon-VPI and Hizex-VPI systems are shown in Fig. 1, in which the induction periods are not observed and the saturation phenomena are observed in both cases. These phenomena are explained to be caused by the decrease of the monomer concentration with the increase of irradiation time, because homopolymerization of VPI simultaneously takes place in the same system. Grafting ratio of Yukalon-VPI system is bigger than that of Hizex-VPI system. This fact is suggested that the crystallinity of PE is related to the grafting ratio.

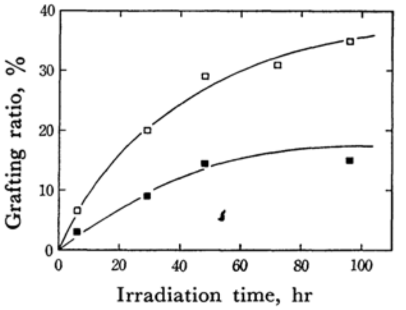

Fig. 1. Graft-copolymerization of VPI in DMF at 25—28°C: monomer concentration 1.01 mol/kg; dose rate 1.1×10^5 R/hr; (□) Yukalon-VPI system; (■) Hizex-VPI system.

The relationships between the initial rate of graft-copolymerization by one point method and the dose rate are shown in Fig. 2. The rate of graft-copolymerization in Yukalon-VPI and Hizex-VPI systems are proportional to the 0.60th order of the dose rate.

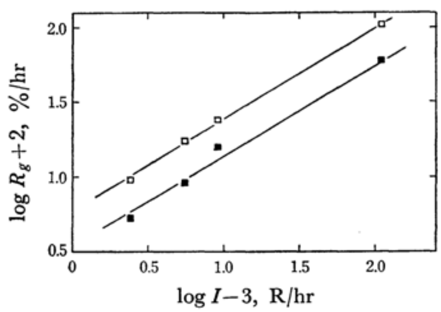

Fig. 2. Relationships between the dose rate (I) and the rate of graft-copolymerization (R_g) in DMF at 25—28°C: monomer concentration 1.01 mol/kg; (□) Yukalon-VPI system; (■) Hizex-VPI system.

Each of these grafted films dyed by dispersed dye was observed the section by a microscope, from which these films were found to be dyed homogeneously, in spite of the small affinity of DMF to PE. This fact shows that the affinity to PE increases with grafting, because homopolymer of VPI is easily soluble in DMF. Accordingly, the diffusion of VPI into PE does not retard the rate of these graft-copolymerizations.

These results lead us to induce that the termination mechanism in these graft-copolymerizations is mainly bimolecular mode which is essentially identical to the homogenous radical polymerizations of many vinyl compounds.

Reaction of Grafted Film with Amine. It was reported that VPI could react easily with alkyl and aryl amines at room temperature and gave *N*-alkyl- and *N*-aryl-*N'*-vinyl phthalamides by ring-opening of phthalimido group in VPI.[9] The reaction of grafted film with *n*-propylamine was carried out at room temperature, and the process of this reaction was traced by infrared spectra. The intensity of absorption bands at

TABLE 2. DYEING CHARACTERISTICS OF THE GRAFTED FILMS AND THE TREATED PRODUCTS WITH AMINES[a)]

Sample		Direct dye	Acid dye	Basic dye	Dispersed dye
Yukalon		−	−	−	−
Yukalon irradiate[b)]		−	−	−	−
Hizex		−	−	−	−
Hizex irradiate[b)]		−	−	−	−
Yukalon-VPI	(5%)		−		+
	(6%)	−		−	2+
	(10%)		−		2+
	(13%)	−		−	
	(20%)		−		3+
	(31%)		−		4+
	(35%)	−		−	
Hizex-VPI	(4%)	−		−	
	(6%)		−		+
Yukalon-VPI (10%)-[c)] n-PrNH$_2$			2+		3+
Hizex-VPI (9%)-[c)] n-PrNH$_2$			2+		3+
Hizex-VPI (6%)-[d)] $Et_2NCH_2CH_2NH_2$			3+		5+

a) −: This symbol shows that the sample is not dyeable.
+—5+: These symbols show the degrees of dyeing characteristics, qualitatively.
b) These samples were irradiated for 96 hr in DMF by γ-radiation of 1.1×10^5 R/hr.
c) These samples were heated in *n*-propylamine for 24 hr at 50°C.
d) This sample was heated in β-diethylaminoethylamine for 24 hr at 100°C.

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[9] K. Kato, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **83**, 313 (1962).

1770 and 1710 cm^{-1} due to carbonyl of phthalimido group becomes gradually weak with the lapse of reaction time. On the other hand, the intensity of absorption bands at 1640 and 1540 cm^{-1} due to amido group becomes strong with the lapse of reaction time, but the ring-opening reaction of grafted film is very slow and takes for about four months to be completed. When the above mentioned reaction was carried out at high temperature, the reaction is still slow, but almost completed within 24 hr at 100°C.

From these results, the phthalimido group in the grafted film was found to be difficult in reaction with amine. These amine-treated films were colorless and their external appearances were not changed.

Dyeing of Grafted Film and Its Amine-treated Film. These films were dyed by direct, acid, basic and dispersed dyes. The results are shown in Table 2, in which Yukalon-VPI and Hizex-VPI grafted films are not dyeable by direct, acid and basic dyes. However, by dispersed dye, these grafted films can be dyed well and the increase of grafting ratio improves the dyeing characteristics.

The treated products of these grafted films with *n*-propylamine became more easily dyeable than the originals by dispersed dye and especially by acid dye, because they have many amido groups. Also the grafted film treated by β-diethylaminoethylamine shows the good dyeing characteristic to acid and dispersed dyes, as it arises many tertiary amino groups in addition to amido groups.

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