

감광성 수지에 관한 연구(제 9 보).
Naphthoquinone-1, 2-diazide-5-sulfonyl Esters의 합성

沈 貞 燮 · 姜 斗 煥

서울대학교 工科大学 工業化學科
(1974. 9. 19 접수)

Studies on Photosensitive Polymers(IX).
Syntheses of Naphthoquinone-1, 2-diazide-5-sulfonyl Esters
with Backbone Resins

Jyong Sup Shim and Doo Whan Kang

Department of Chemical Technology, College of Engineering,
Seoul National University, Seoul, Korea

(Received Sept. 19, 1974)

요 약. 감광성 관능기를 갖는 중합체. 이를테면 polyglyceryl phthalate(PG), bisphenol A-epichlorohydrin 축중합체(BE) 및 polyvinyl alcohol(PVA)의 naphthoquinone-1, 2-diazide-5-sulfonyl esters(PGND, BEND 및 PVAND)를 합성하였다. 빙점강하법으로 측정한 모체수지들의 분자량은 PG의 경우 650~1200, BE는 780~1320이었다. PG, BE 및 PVA를 naphthoquinone-1, 2-diazide-5-sulfonyl chloride로 ester화시켜 얻은 PGND, BEND 및 PVAND는 적외선 흡수 spectra 및 원소분석등으로 확인하였다. PGND, BEND 및 PVAND의 원소분석의 계산치와 실측치가 잘 일치하고 있는 점으로 보아 모체수지인 PG, BE 및 PVA의 중합도는 ester화 된 경우에도 변하지 않는다는 것을 알 수 있었다.

ABSTRACT. Polymers with photosensitive functional groups, the naphthoquinone-1, 2-diazide-5-sulfonyl esters(PGND, BEND and PVAND) of polyglyceryl phthalate(PG), bisphenol A-epichlorohydrin polycondensate(BE) and polyvinyl alcohol(PVA), were prepared. The molecular weights of the starting materials were determined by the cryoscopic method, i.e., in the range of 650~1200 for PG and 780~1320 for BE. PGND, BEND and PVAND were prepared by esterification of PG, BE and PVA with naphthoquinone-1, 2-diazide-5-sulfonyl chloride, and the replacements of such a functional groups were confirmed by the infrared absorption spectra and elemental analyses. The good agreement between the observed values of elemental analyses (PGND, BEND and PVAND) and the calculated values, indicated that the degree of polymerization did not change in the course of esterification of PG, BE and PVA.

INTRODUCTION

Many studies on the decomposition of diazo

compounds,¹⁻⁴ intermediates of dyestuffs, by thermal or photochemical reactions have been reported in recent years. *o*-Quinonediazides⁵⁻⁶ are

usually insoluble in water, and decomposed to carbonium ion by light exposure, to cyclic diazoketones by Wagner-Meerwein rearrangement, and then to indene carbonic acid, which is soluble in aqueous alkali solution by hydrolysis with water.

o-Quinonediazides used as photosensitive materials for plate making have attracted attention as positive-positive type. There are few patents on the preparation of the light sensitive compounds by using *o*-quinonediazides such as 2,3,4-trioxybenzophenone-*bis* (naphthoquinone-1,2-diazide-5,5-sulfonyl ester)⁷, naphthoquinone-1,2-diazide-5-sulfanilide⁸, and diallyl ester⁹ derived from naphthoquinone-1,2-diazide sulfonic acid and aminoisophthalic acid. However, there were no reported attempts to obtain the photodegradative polymers by introducing *o*-quinonediazide into the polymers, except a patent¹⁰ on the esterification of novolak resin with photoseensitive group.

This type of photosensitive materials based on novolak ester, i.e., Azoplate-Shipley AZ series (U.S.A.) has been commercialized.

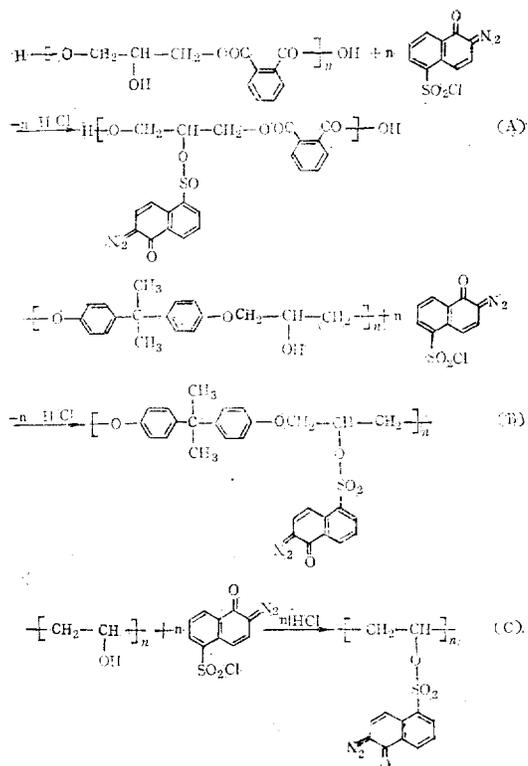
We have prepared the photosensitive polymers introducing *o*-quinonediazide into the backbone resins like polyglyceryl phthalate(PG), bisphenol A and epichlorohydrin polycondensate(BE), and polyvinyl alcohol(PVA) in order to investigate their photosensitivities. They were synthesized by esterification of naphthoquinone-1,2-diazide-5-sulfonyl chloride(NDSC) with PG(A), BE(B) and PVA(C)—PGND(ester for PG with NDSC), BEND(ester for BE with NDSC) and PVAND(ester for PVA with NDSC). They may also be called PGND-1,2..., BEND-1,2..., and PVAN D-1,2... according to the types of the backbone resins used such as PG-1,2..., BE-1,2..., and PVA-1,2... The numbers denote the molecular weight of the backbone resins.

EXPERIMENTAL

Synthesis of Naphthoquinone-1,2-diazide-5-sodium sulfonate (NDSS) and its Chlorinated Derivative

Cupric Sulfate, 2-amino-1-naphthol-5-sulfonic acid, sodium nitrite and chlorosulfonic acid were reagent grades and used without further purification. Acetone of the commercial-grade was redistilled.

Preparation of NDSS. Sodium salt of naphthoquinone-1,2-diazide-5-sulfonic acid was prepared according to the method of Reverdin¹¹. Twenty eight grams of 30% aqueous cupric sulfate solution was added to 47.8g(0.2mole) of 2-amino-1-naphthol-5-sulfonic acid dissolved in 200ml distilled water. After adding of 12g of sodium nitrite, the solution was stirred vigorously for 60 minutes at 4~5 °C. The resulting yellowish brown reaction mixture was acidified with 10 ml of 0.1 N HCl and NDSS was separated by salting out with 10 g of sodium chloride. The crude



NDSS was washed two times with methanol and then dried in vacuum to give 54.8 g (yield 85 %) of yellowish needles, m. p. 144~146 °C (lit.¹¹, m. p 145 °C).

Anal. Found: C, 44.25; H, 1.86; N, 10.29; Calcd. for $C_{10}H_5N_2O_4SNa$: C, 44.11; H, 1.84; N, 10.33 %

Chlorination of NDSS. Into a three-necked round bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser was placed 210 g (1.80 mole) of chlorosulfonic acid and 16.3 g (0.06 mole) of NDSS was added to it. The mixture was then heated at 65~67 °C for 4 hours, cooled to 20 °C, and then poured onto crushed ice. The precipitate was separated by filtration. After washing with cold water, dried at 20~25 °C under the reduced pressure. It was purified by dissolving it in 200 ml of acetone, precipitating it in the cold distilled water, followed by filtration. The final product was dried in vacuum to give 13 g (yield 82 %) of yellowish solid, m p 147~148 °C (lit.¹² 148 °C).

Preparation of Backbone Resins

Polyglyceryl Phthalate (PG). Phthalic anhy-

dride and glycerine were reagent grades and used without further purification. Methanol of the commercial-grade was redistilled.

PG was prepared by the method of Kienle.¹³ In the case of PG-1, 148g (1 mole) of phthalic anhydride and 96 g (1 mole) of 95% glycerine were charged to a 500 ml of four-necked round bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser and a nitrogen in-let tube, and heated to 199~203 °C under a stream of nitrogen. At 20 minutes intervals, a 1~2 g sample of the melt was taken out by means of a suction tube and immediately poured onto a glass plate. After cooling to room temperature the acid number of the sample was determined. The condensation was continued for a given time until the acid number reach 33. The colourless transparent PG-1 was purified by dissolving it in acetone and precipitating it in a 5 to 1 solution of methanol. After separation, it was washed with methanol, and dried in vacuum to give a white powder PG-1. Other PG resins were prepared by a method similar to that used to obtain PG-1, and the preparation conditions, molecular weight of the products, melting point,

Table 1. Polymerization of Phthalic anhydride with Glycerine and Bisphenol A with Epichlorohydrin.

Exp. No.	Product	Materials		Conditions		Acid Value	Yield (%)	m p (°C)	Mol. wt.	Solvent*
		(mol)	(mol)	Temp. (°C)	Time (min.)					
		Phthalic anhydride	Glycerine							
1	PG-1	1	1	199~203	300	33	70	96~104	1200	Ac, Dx, Py
2	PG-2	1	1	198~200	260	34	65	87~93	1120	"
3	PG-3	1	1	204~208	230	30	31	85~90	850	"
4	PG-5	1.5	1	185~190	190	36	38	70~74	650	"
5	PG-4	1	1	190~194	210	35	52	80~85	720	"
		Bisphenol A	Epichlorohydrin							
6	BE-1	1.3	1.6	89~92	120		72	78~84	1320	Ac, Dx, Mk, Ch
7	BE-3	1.3	1.3	80~87	90		52	64~68	820	"
8	BE-2	1.0	1.5	93~97	120		68	67~72	950	"
9	BE-4	1.5	2.0	96~101	70		40	55~59	780	"

*Ac: Acetone, Ch: Chloroform, Dx: Dioxane, Mk: Methyl, Ethyl Ketone, Py: Pyridine

and solubility, etc. were summarized in *Table 1*.

The yields indicate the percentage of the amount of product to the total amount of reactants after a reprecipitation. The molecular weights of PG and BE resins are the average molecular weights determined by the cryoscopic method using acetone as a solvent.

Bisphenol A-Epichlorohydrin Polycondensate (BE). Bisphenol A of reagent grade was recrystallized from dilute acetic acid solution, and epichlorohydrin of commercial-grade was redistilled at 110 °C under 760 mmHg.

BE was prepared by Wegler's method.¹⁴ In the case of BE-1, 296.4 g (1.3 mole) of bisphenol A and 738 g of 10 % NaOH solution were charged to a 2 l four-necked round bottom flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser, and then heated to 45°C with vigorous stirring. One hundred and forty eight grams (1.6 mole) of epichlorohydrin was added to the solution. The temperature was raised to 89~92 °C over a period of 20 minutes and then kept constant for 100 minutes. The clear aqueous upper layer was carefully siphoned off, and the resin was slurred by vigorous stirring with 300 ml of distilled water. After settling, the aqueous layer was again siphoned off. This washing procedure was repeated several times until the washing water became neutral. After separation, the resin was dried at 60 °C under 23~30 mmHg, and the crushed BE resin was purified by dissolving it in 200 ml of acetone and precipitating it in a 5 to 1 solution of methanol. As a result, a white syrupy condensate was precipitated. After a reprecipitation, it was washed with methanol twice and dried to give a white powder BE-1. Other BE resin were prepared using a method similar to that used to obtain BE-1, and the preparation conditions, molecular weight of the

products, melting point, and solubility, etc. were summarized in *Table 1*.

Esterification of PG, BE and PVA with NDSC

Esterification was carried out according to the method of Shim and Kikuchi.¹⁵ In the case of the esterification of PG-1, 10 g of PG-1 and 26 ml of purified pyridine were placed in a three-necked round bottom flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a calcium chloride tube, and refluxed for one hour. After the addition of an additional 10 ml of pyridine, the reactant was cooled to 40° C, and then 11g of NDSC was added to the solution. This reaction was carried out for 6 hours at 53~55 °C. The reaction product was purified by dissolving it in 4 times of acetone, filtering through the glass fiber, and then precipitating it in a large amount of distilled water to give a yellowish syrupy ester. After washing the precipitate with distilled water, it was dried in a vacuum.

BE, and PVA (viscosity average DP, 1400; saponification value, 80 %) obtained from Nippon Gosei Kagaku Co. Ltd., were esterified according to the procedure similar to that of PG-1. Esterification conditions, melting points, the degree of esterification, etc. of PG, BE, and PVA with NDSC were summarized in *Table 2*.

Determination of Acid and Esterification Values

Determination of Acid Value. One gram of the sample was placed in a 250 ml Erlenmeyer flask with 75 ml of acetone, and then stirred until the sample was dissolved. The solution was titrated with 0.1N KOH solution using alcoholic phenolphthalein solution as an indicator. The blank test was run on the solvent (acetone). The acid value was determined as follows:

$$AV = \frac{(T-B) \times f \times 0.1 \times 56.11}{W}$$

Table 2. Esterification of PG, BE, and PVA with NDSC.

Exp. No.	Products	Reaction Materials			Reaction Conditions		EV (%)	Yield (%)	m p (°C)
		Backbone Resins(g)	NDSC (g)	Pyridine (ml)	Temp. (°C)	Time (hr.)			
1	PGND-1	PG-1 10	11	36	53~55	6	86	60	83~89
2	PGND-2	PG-2 10	12	35	54~57	6	80	56	80~87
3	PGND-3	PG-3 5	10	20	52~56	6	78	54	78~84
4	PGND-4	PG-4 5	7	20	51~57	6	82	52	76~81
5	BEND-1	BE-1 10	11	35	51~56	6	79	62	97~107
6	BEND-2	BE-2 10	12	35	56~58	6	76	56	98~105
7	BEND-3	BE-3 5	10	20	53~56	6	75	52	98~103
8	PVAND-1	PVA-1 10	12	30	5~8	6	61*	55	94~102
9	PVAND-2	PVA-2 5	10	20	5~9	6	60*	54	96~101

*Estimated from the consideration of the data of the saponification value of PVA.

AV : acid value, T : milliliters of 0.1N KOH solution required for the titration of sample and solvent, B : milliliters of 0.1N KOH solution required for the titration of solvent, f : factor of 0.1N KOH solution and W : weight of sample in grams.

Determination of Esterification Value. One gram of sample was placed in a 250 ml of Erlenmeyer flask with 20 ml of 0.1 N alcoholic KOH solution, and refluxed for 3 hours. After cooling the above solution to room temperature, it was titrated with 0.1 N HCl solution using alcoholic phenolphthalein solution as an indicator. The blank test was run on 0.1N alcoholic KOH solution. The esterification value was determined as follows:

$$EV = \frac{(B-T) \times f \times 0.1 \times 56.11}{W} - A$$

EV : esterification value, B : milliliters of 0.1 N HCl solution required for blank test, T : milliliters of 0.1 N HCl solution required for back titration, f : factor of 0.1N HCl solution, W : weight of sample in grams and A : acid value for the sample.

ANALYTICAL METHODS

Infrared Spectra. Beckman IR-4 infrared spectrophotometer was used for the study. The

measurements were made at room temperature using the pressed potassium bromide disk (conc. 5%) technique.

Elemental Analyses. The backbone resins of PG-1, BE-1 and PVA-1, and the esters of PG

ND-1, BEND-1 and PVAND-1 were analyzed by the Coleman Carbon and Hydrogen Analyzer, and the Coleman Nitrogen Analyzer.

RESULTS and DISCUSSION

Preparation of PG and BE. PG and BE were prepared as a backbone resin, in order to synthesize the photosensitive polymers, by introducing the photosensitive group through the reaction of secondary hydroxyl group of backbone resins with NDSC. The preparation of PG has been well documented, and the authors followed the method of Kienle¹³. The reaction was carried out at the relatively low temperature of 200°C¹⁶ as shown in Table 1, in order to keep secondary hydroxyl group unreacted on the backbone resin of PG, since the photosensitive side chain has to be introduced later by reacting the remaining secondary hydroxyl group with NDSC. Also, the reaction was carried out with equimolar ratio of phthalic anhydride to glycerine, since it has known¹⁷ that the ester of the backbone resin with

a higher degree of polymerization was superior in photosensitivity.

The preparation of BE is well known^{18,19}, and the authors prepared it according to the Wegler's method¹⁴. Structure and molecular weight of the resulting BE resin are strongly influenced by the reaction conditions: A large excess of epichlorohydrin (about 5 moles per mole of bisphenol A) favors the formation of terminal epoxy groups; on the other hand, the molecular weight of the products decreases with increasing epichlorohydrin. Besides the ratio of the reactants, the reaction temperature is also of importance: High temperature promotes secondary reactions such as the hydrolytic cleavage of epoxy groups, which results in the formation of additional hydroxyl groups.

For the purpose of the present study, BE resin containing a secondary hydroxyl group was obtained with reacting a slight excess of epichlorohydrin at the relatively high temperature of about 90 °C.

As shown in Table 1, BE resins having a molecular weight of 950 and 1320 were obtained with reacting at the molar ratio of epichlorohydrin to bisphenol A, 1.50 and 1.23, respectively.

In the infrared spectra of PG-1 (shown in Fig. 1 as dotted line), the absorption band of the hydroxyl group at 3500cm⁻¹ and the secondary hydroxyl group¹⁵ at 1130 cm⁻¹ were observed.

In the infrared spectra of BE-1 (shown in Fig. 2 as dotted line), the absorption band of epoxy ring²⁰ at 1250 cm⁻¹, 910 cm⁻¹ and 830 cm⁻¹, that of secondary hydroxyl group²¹ at 1110cm⁻¹ were observed. The presence of a secondary hydroxyl group in PG-1 and BE-1 is, therefore, confirmed.

Esterification of Backbone Resins. The esterification was carried out according to the conditions specified in Table 2, since it was known that the esterification¹⁵ of PG with cinnamoyl chloride could be applied to the esterifica-

tion of PG, BE and PVA with NDSC.

The infrared spectra of the backbone resins and the esters, PG-1 and PGND-1, BE-1 and BEND-1, and PVA-1 and PVAND-1, are shown in Fig. 1, 2 and 3.

In the spectra of PGND-1 as shown in Fig. 1 (solid line), the absorption band of *o*-quinonediazide²² C=N= at 2210 cm⁻¹ and 2170 cm⁻¹, C=O at 1600 cm⁻¹ and sulfonyl ester —O—SO₂— at 1160 cm⁻¹, were newly observed, while the absorption band of secondary hydroxyl group of PG-1 at 1130 cm⁻¹ was decreased. In the spectra of BEND-1 as shown in Fig. 2 (solid line), the absorption band of *o*-quinonediazide C=N= at 2150 cm⁻¹ and 2220 cm⁻¹, C=O at 1620 cm⁻¹, and sulfonyl ester —O—SO₂— at 1180 cm⁻¹ were newly observed with a slight shift from the original position of PGND-1, while the absorption band of the secondary hydroxyl group of BE-1 at 1110 cm⁻¹ was decreased. Similarly, in the spectra of PVAND-1 (Fig. 3), the absorption band of *o*-quinonediazide C=N= at 2100 cm⁻¹, and 2250 cm⁻¹, C=O at 1610 cm⁻¹, and the absorption band of sulfonyl ester —O—SO₂— at 1150 cm⁻¹ were newly observed with a slight shift from the original position, while the absorption band of secondary hydroxyl group of PVA-1 at 1100 cm⁻¹ was decreased.

The results of the elemental analyses of the PG-1, PGND-1, BE-1, BEND-1, PVA-1 and PVAND-1 are summarized in Table 3.

In the Table 3, the observed values of the elemental analyses of backbone resins and esters are in good agreement with the calculated values.

From the results of elemental analyses and infrared absorption spectra, the esterification method and the determination of the degree of esterification presented by the authors could be justified, and also, we could conclude that the degree of polymerization did not change in the course of esterification of PG, BE and PVA.

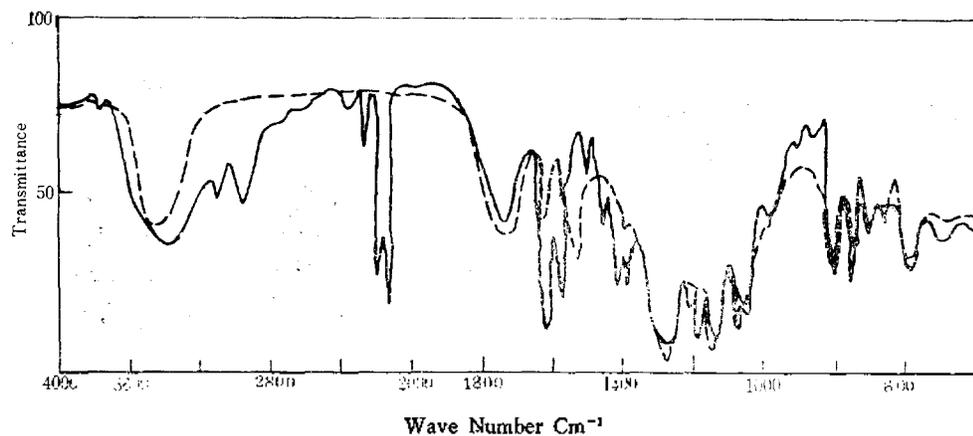


Fig. 1. IR spectra of PG-1 and PGND-1 (solid line:PGND-1, dotted line:PG-1).

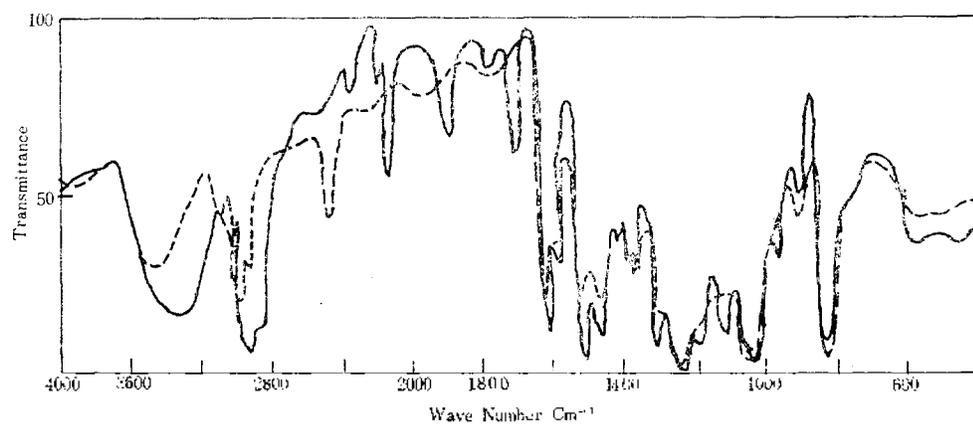


Fig. 2. IR spectra of BE-1 and BEND-1 (solid line: BEND-1, dotted line: BE-1).

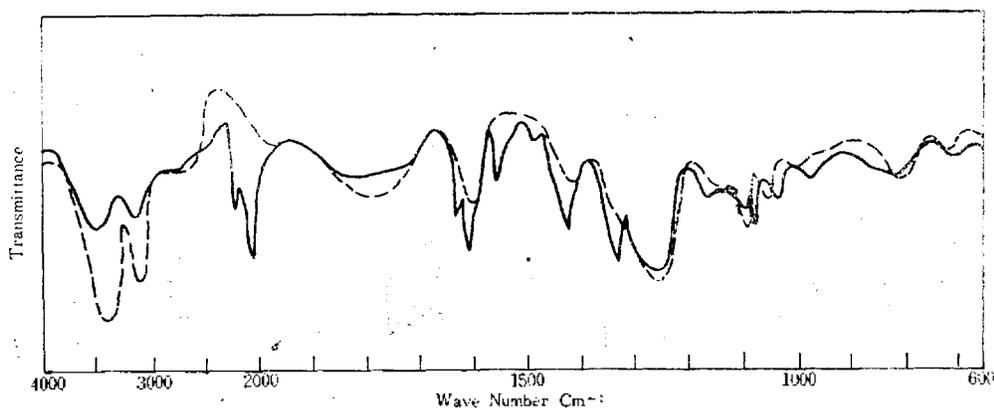


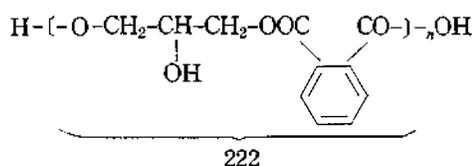
Fig. 3. IR spectra of PVA-1 and PVAND-1 (solid line: PVAND-1, dotted line: PVA-1).

Table 3. Elemental analyses for PG-1, PGND-1, BE-1, BEND-1, PVA-1, and PVAND-1.

Polymer	Mol. formula	Values for elemental analyses					
		Found(%)			Calculated ^a (%)		
		C	H	N	C	H	N
PG-1	HO-(C ₁₁ H ₁₀ O ₅) _{3.3} H	58.52	4.58		58.56	4.60	
PGND-1 ^b	HO-(C ₂₁ H ₁₄ O ₈ N ₂ S) _{3.3} H	55.25	3.21	5.61	55.31	3.25	5.65
BE-1	-(C ₁₈ H ₂₀ O ₃) _{7.3}	75.31	7.05		75.35	7.04	
BEND-1 ^c	-(C ₂₈ H ₂₄ O ₆ N ₂ S) _{7.3}	67.62	5.24	4.05	67.79	5.27	3.91
PVA-1 ^d	-(C ₂ H ₄ O) _{7.3}	55.21	8.52		54.96	8.58	
PVAND-1 ^e	-(C ₁₈ H ₈ O ₄ N ₂ S) _{7.3}	53.56	3.52	8.69	53.77	3.57	8.87

^a Calculated from the data of the degree of polymerization and the degree of esterification, ^b degree of esterification, 88(mole %); ^c degree of esterification, 79(mole %); ^d saponification value, 80 %; ^e degree of esterification, 61(mole %).

Determination of Molecular Weight for Backbone Resin. As shown in Table 3, the molecular weight estimated from the results of the calculated and found values of the elemental analyses were in good agreement with the molecular weight determined by the cryoscopic method. On the other hand the molecular weight of PG calculated by the acid value was greater than that determined from the cryoscopic method. For example, the molecular weight of PG-1 determined by the cryoscopic method was 1200, but the calculated molecular weight from the acid value by the following equation was 1700.



If the measured acid value is a,

$$\frac{56.11 \times 1000}{222n + 18} = a, \quad n = \frac{56100 - 18a}{222a}$$

Molecular weight,

$$M = 222n + 18 = \frac{56100}{a}$$

In calculating the molecular weight from the acid value, such a difference seems to result from the assumption that the hydroxyl and carboxyl groups are the same in their concentration. There are two possibilities of lowering of the acid value of a polymer owing; (a) Due to the existence of

PG with terminal hydroxyl groups; (b) and the intramolecular esterification of the carboxyl group.

REFERENCES

1. T. Tsunoda and T. Yamaoka, *J. Appl. Polymer Sci.*, **8**, 1379(1964).
2. J. G. Calvert, W. E. Lee and W. W. Malmberg, *J. Amer. Chem. Soc.*, **83**, 1928(1961).
3. *Brit. Pat.*, 1168182(1970).
4. *U. S. Pat.*, 3502470(1970).
5. O. Süss, *Ann. Chem.*, **556**, 65, 86(1944).
6. O. Süss, K. Möller and H. Heiss, *ibid.*, **598**, 123(1956).
7. *Japan Pat.*, 18015(1962).
8. *ibid.*, 1954(1962).
9. *ibid.*, 11222(1966).
10. *ibid.*, 9610(1970).
11. Reverdin and de la Harpa, *Ber.*, **21**, 1401(1888).
12. M. P. Schmidt, O. Süss and *Ger. Pat.*, 865860.
13. R. H. Kienle and A. G. Hovey, *J. Amer. Chem. Soc.*, **61**, 2258(1939).
14. R. Wegler and R. Schmitz-Josten in, *Houben-Weyl*, **14**(2), 462(1963).
15. J. S. Shim and S. Kikuchi, *Kogyo Kagaku Zasshi*, **68**, 387(1965).
16. R. Houwink and K. H. Klaasens, *Kolloid-Z.*, **70**, 329(1935).
17. T. Yoshinaga, E. Kan and S. Kikuchi, *Kogyo Kagaku Zasshi*, **66**, 665(1963).
18. H. A. Newly and E. C. Schokal, *U. S. Pat.*, 2575558(1951).
19. S. O. Greenlee, *U. S. Pat.*, 2694694(1955).

20. Shreve, Heether, Knight and Swern, *Analyt. Chem.*, **23**, 277(1951).
21. Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, **75**, 897(1953).
22. T. Tsunoda, "Photopolymer", p. 162, Technical Association of Graphic Arts of Japan, 1972.