Resins from Formaldehyde. 103.[1] Reaction of Naphthalene with Aqueous Formaldehyde Solution*

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(Received March 7, 1974)

The reaction of naphthalene(N) with formaldehyde(F) was carried out in dioxane or an acetic acid/water solution, using sulfuric acid as the catalyst. The rate of the consumption of F is proportional to $[N]^{1.12}[F]^{1.05}[H_2SO_4]^{1.05}$. The activation energies and entropies of the reaction of N, α- and β-naphthyl carbinol(NC) with F were estimated to be 21.4, 15.3, and 16.0 kcal/mol and −19.1, −36.2, and −33.2 e.u., respectively. The reaction products were isolated and their structures were identified as α-NC, αα′-, αβ′-dinaphthylmethane, three- and four-nuclear compounds, which are linked to each other with methylene or methylene ether bonds at the α- or β-positions; identified was done by means of the IR, NMR, and UV spectra, molecular-weight measurements, elemental analysis, and thin-layer chromatography. In addition to the compounds described above, acetyl esters were obtained when the reaction was carried out in the presence of acetic acid. The reactivities of the α-position of N and its derivatives was larger than those of the β-position. Moreover, the resin formation from N and F was studied by means of gel-permeation chromatography. On the bases of these results, the reaction route of N with F to resin was deduced.

Almost seventy years ago, Bohn[2] found that the condensation resin of naphthalene(N) with formalin gave a resinous matter which could be used as a drying oil. According to his patent, when the molar ratio of formaldehyde(F) to naphthalene becomes larger, the resulting resin has a larger molecular weight, a large melting point, and a lower oxygen content. The resin was assumed to be composed of compounds with methylene linkages.

A German patent[3] in 1918 described that the reaction product of N with F was white resin and could be dissolved in acetone, benzene, solvent naphtha, carbon tetrachloride, and carbon disulfide. In 1962, Imoto *et al.*[4] studied kinetically the reactions of N and methylnaphthalene with F in the presence of perchloric acid, using acetic acid as the solvent.

The present paper will deal with acid-catalyzed reaction of N with an aqueous F solution in dioxane or acetic acid. Moreover, some intermediate compounds to resinous matter were isolated; the reaction mechanism will be discussed.

Experimental

Materials. N of a special grade was purified by sublimation. Formalin containing 41.51% of F and less than 0.8% of methanol, supplied by the Mitsubishi Gas Chemical Co., Ltd., was purified in order to remove the formic acid by passing it through an ion-exchange resin column.

Five kinds of authentic compounds (α-NC, β-NC, αα′-DNM, αβ′-DNM, and ββ′-DNM) were synthesized according to the scheme shown in Fig. 1. Their melting points and their R_f values in thin-layer chromatography (tlc) are listed in Table 1. A thin-layer chromatogram on silica gel (Wakogel B5F) was activated by heating at 130 °C for a period of 4 hr.

Measurement of the Reaction Rate. N or its derivative was dissolved in dioxane. After adding 5 N-sulfuric acid, the measuring flask was warmed at a definite temperature,

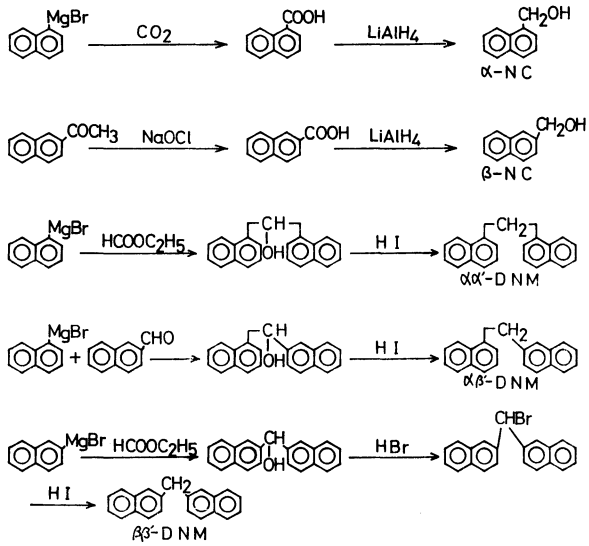


Fig. 1. Syntheses of authentic compounds.

Table 1. Melting point and R_f value of naphthalene derivatives

Compounds	mp (°C) Found	mp (°C) Lit	R_f value[a]
Naphthalene (N)	79.5—80.5	80.2	0.6
α-Naphthylcarbinol (α-NC)	60—61.5	59.5—60[6]	0.1
β-Naphthylcarbinol (β-NC)	80.5—81.5	80—80.5[6]	0.1
α,α′-Dinaphthylmethane (α,α′-DNM)	105—105.5	107—108,[8] 109[9]	0.6
α,β′-Dinaphthylmethane (αβ′-DNM)	94.5—95.5	96[9]	0.6
β,β′-Dinaphthylmethane (ββ′-DNM)	91.5—92.5	93[9]	0.6

a) Benzene–carbon tetrachloride mixture (1: 1) was used as a solvent

an F solution at the same temperature was added, and the solution was diluted to exactly 50 ml with dioxane. The time thirty seconds after the mixing in of F was considered as the starting point of the reaction. An aliquot portion (3 ml) of the reaction mixture was taken up from time to time and quenched with a sufficient volume of a 0.5 M–NaOH solution to neutralize the above mixture. The concentration of the remaining unreacted F was determined by means of the sodium-sulfite method.

Fractionation of the Reaction Product. The reaction products were fractionated by column chromatography and tlc. The R_f values of tlc were obtained by using benzene–CCl_4 (1:1 in vol.) as the developing solvent. The three kinds of DNM showed almost the same R_f values of tlc as that of N. Accordingly, when the separation of DNM from N by tlc was carried out, the chromatogram was allowed to stand under an atmosphere at room temperature for about 20 hr in order to sublime the N. The spot of tlc was determined by the UV-fluorescence method or by coloration with iodine.

Molecular Weights. The molecular weights were determined by the vapor-pressure osmometer (VPO) method at 37 °C, using benzene as the solvent.

Results and Discussion

Kinetics of the Reaction of Naphthalene with Formaldehyde. At first, a kinetic experiment was conducted on the rate of the reaction of N with F in a dioxane–water mixture (1:1) at 80 °C in order to derive the rate equation.

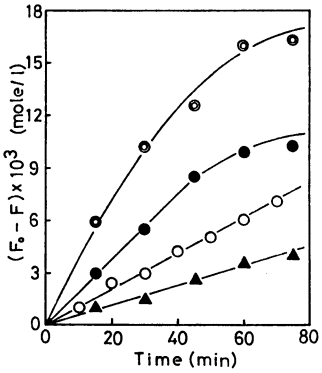


Fig. 2. $[N]_0$ *vs.* consumed [F] at 80 °C. $[F]_0=0.0568$ mol/l, $[H_2SO_4]=0.483$ mol/l, $[N]_0$ ▲: 0.0250 mol/l, ○: 0.0500 mol/l, ●: 0.0750 mol/l, ◎: 0.100 mol/l
solvent: dioxane–water (80:20 in vol)

When the concentration of N was varied from 0.0250 to 0.100 mol/l, while the initial concentrations of F and sulfuric acid were kept at 0.0568 and 0.483 mol/l respectively, the consumption of F increased linearly with the reaction time, as is shown in Fig. 2.

When the F and catalyst concentrations were changed, linear relationships were also obtained between the consumption of F and the reaction time. In addition, the dependence of the initial concentration on the rate was drawn (Fig. 3).

From this figure, the rate equation of the reaction of N with F in aqueous dioxane in the presence of sulfuric acid was concluded to be as follows:

$$R_0 = -\mathrm{d[F]/d}t = k[\mathrm{N}]_0^{1.12}[\mathrm{F}]_0^{1.05}[\mathrm{H_2SO_4}]^{1.05} \qquad (1)$$

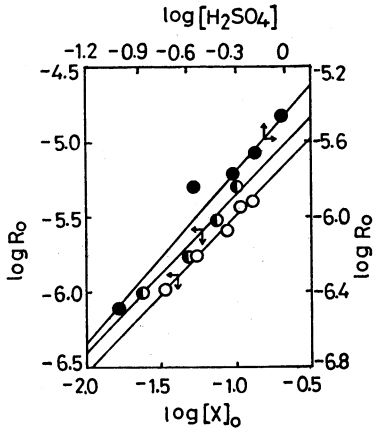


Fig. 3. Dependence of initial concentration on reaction rate.
○: X=N, $[F]_0=0.0568$ mol/l, $[H_2SO_4]=0.483$ mol/l, $[N]_0=0.0250$—0.100 mol/l
◐: X=F, $[N]_0=0.0500$ mol/l, $[H_2SO_4]=0.438$ mol/l, $[F]_0=0.0341$—0.1363 mol/l
●: $[F]_0=0.0568$ mol/l, $[N]_0=0.500$ mol/l, $[H_2SO_4]=$ 0.0966—0.966 mol/l
Solvent: dioxane–water (80:20 in vol) Temp: 80 °C

Equation (1) agreed well with Eq. (2), which was formerly[4] obtained by the acidic reaction of N with F carried out in acetic acid by one of the present authors (M. Imoto). Moreover Eq. (2) is a usual rate equation for the acidic reaction of F with many phenolic compounds and aromatic hydrocarbones.

$$-\mathrm{d[F]/d}t = k[\mathrm{N}]_0[\mathrm{F}]_0[\mathrm{H_2SO_4}] \qquad (2)$$

By using Eq. (2), the average value of the rate constant, k, at 80 °C was calculated to be 1.29×10^{-3} $l^2\,mol^{-2}\,s^{-1}$.

Reactivities of Naphthalene and its Derivatives with Formaldehyde. As has been mentioned above, F was concluded to react with N in the presence of sulfuric acid according to Eq. (2). This equation can be also applied to the N derivatives which may be generated as intermediates during the so-called addition-condensation of N with F to from naphthalene-resin.

The reaction was carried out at 80 °C in aqueous dioxane, keepting the initial concentrations of N or its derivatives, F and, H_2SO_4 constant at 0.0500, 0.0568, and 0.483 mol/l respectively.

The experiments to determine the rate constant, k, were repeated twice. The averages of k listed in Table 2 were thus obtained. From the results shown in

Table 2. Reactivities of naphthalene and its derivatives.
$[N]_0$ or [N derivatives]$_0=0.0500$ mol/l, $[F]_0=0.0568$ mol/l, $[H_2SO_4]=0.483$ mol/l; 80 °C
solvent: dioxane–water (80:20 in vol)

Compounds	$k\times10^3$ (l^2/mol^2 s)
N	1.24
α-NC	1.21
β-NC	2.01
αα′-DNM	1.61
αβ′-DNM	3.65
ββ′-DNM	4.62

Table 2, it can be concluded that the α-position of N is more reactive than the β-position. These results are explicable with reactive parameters calculated by means of the molecular-orbital method.

Estimations of E_a and ΔS^* on the Acidic Reactions of Naphthalene and its Carbinols with Formaldehyde. The rate constants of the reaction of N, α-NC, and β-NC with F in aqueous dioxane were determined at 80 °C; they are listed in Table 2. Similarly, the values of the rate constants at 60, 70, and 90 °C were determined. Arrhenius plots were thus drawn, as is shown in Fig. 4. From these lines, the overall activation energies (E_a) and entropies (ΔS^*) were calculated; they are listed in Table 3.

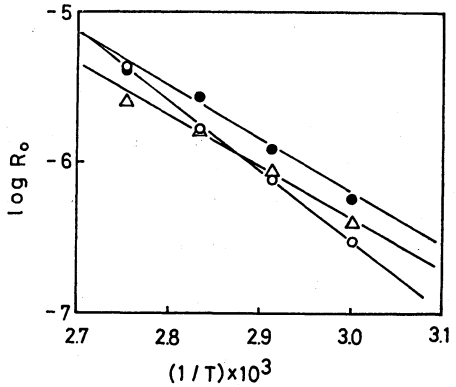


Fig. 4. Arrhenius plots of the reaction of F with N, α-NC and β-NC in aqueous dioxane. ○: N, △: α-NC, ●: β-NC

Table 3. E_a and ΔS^*

Compounds	E_a (kcal/mol)	ΔS^* (80 °C) (e.u.)
N	21.4	−19.1
α-NC	15.3	−36.2
β-NC	16.0	−33.2

The E_a of the reaction of N with F was estimated to be 21.4 kcal/mol. One of the present authors (M. I.) has formerly reported that the activation energies of the reactions of phenol, cresols, and their polynuclear compounds with F were generally close to 23 kcal/mol.[11] It is interesting that the value of 21.4 kcal/mol obtained in the case of naphthalene was also close to 23 kcal/mol.

The E_a and ΔS^* of the reaction of F with NC were found to be smaller than those with N. This may be a result of the activation of the cationic attack on the naphthalene nucleus and the intermolecular hydrogen bond by the introduction of the CH_2OH group into N.

Isolation of Initial Products of the Reaction of Naphthalene with Formaldehyde. Various amount of glacial acetic acid, 12.8 g of N, 5.4 g of 41.51% formalin, and 5 g of 18M-sulfuric acid were mixed thoroughly and warmed (Table 4). After the reaction time has elapsed, the mixture was neutralized with a sodium hydroxide solution and extracted with benzene. The extract was washed repeatedly with water, concentrated to about 100 ml, and then distilled by steam. The unreacted N was then distilled off, and the residue was extracted with benzene. The separation of the components in the extract was carried out by column chromatography, using carbon tetrachloride–benzene (5:1) as the eluent.

Fraction I: Fraction I in Table 4 was fractionated once more into five portions by column chromatography, using the above solvent. The first portion (i) has the largest R_f-value, while the fifth portion (v) has the smallest R_f-value.

Fraction (i): Repeated recrystallizations from an equivolume mixture of benzene and methanol gave needle crystals; mp 104.5—107 °C; R_f of tlc 0.6 (benzene–CCl_4 1:1 in vol.). Mixing with an authentic sample of αα′-DNM showed the same mp, without any depression. IR (KBr disk) 2925, 2875 cm^{-1} (CH_2); NMR (CCl_4) τ 5.16 (s, Ar–CH_2–Ar).

Found: C, 93.81; H, 5.70%; mol wt, 265. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.10%; mol wt, 268.

Fraction (ii): The powder-like crystals were collected by recrystallization from a benzene–methanol mixture; mp 94.5—95.5 °C; R_f of tlc 0.6. No depression of the mp was observed after mixing with an authentic sample of αβ′-DNM. IR (KBr disk) 2925, 2875 cm^{-1} (CH_2); NMR (CCl_4) τ 5.46 (s, Ar–CH_2–Ar).

Found: C, 94.02; H, 5.79%; mol wt, 263. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%; mol wt, 268.

An alternative reaction of N with F under the conditions shown for Experiment No. 2 in Table 4 was carried out. Fractions (I-i) and (I-ii) were thus isolated. They were distilled under a vacuum (bp 258—265 °C/10 mmHg) and fractionated by recrystallization from a benzene–methanol mixture into αα′-DNM and αβ′-DNM. The quantity of αα′-DNM was assumed to be larger by 15—20 times than that of αβ′-DNM.

Fraction (iii): Repeated fractional recrystallizations from diethyl ether gave powder-like crystals as the most difficultly soluble fraction: mp 137—140 °C; R_f of tlc 0.6; IR (KBr disk) 2925, 2875 cm^{-1} (CH_2); NMR (CCl_4) τ 5.20 (s, Ar–CH_2–Ar–CH_2–Ar).

Found: C, 94.27; H, 5.64%; mol wt, 405. Calcd for $C_{32}H_{24}$: C, 94.08; H, 5.92%; mol wt, 408.

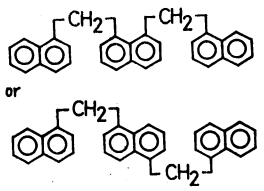
The absorptions due to the methylene group at 2925 and 2875 cm^{-1} very much resembled that of αα′-DNM,

Table 4. Fractionation of reaction products of naphthalene with formaldehyde

Exp. No.	N (g)	F (g)	Acetic acid (ml)	Temp (°C)	Unreacted N (g)	Fractions from column chromatography (g)				
						I	II	III	IV	V
						R_f 0.6	0.4	0.25	0.2	0
1	12.8	5.4	200	90	4.7[a]	6.1	—	0.1	1.8	—
2	12.8	12.0	150	100	4.8[a]	6.3	0.04	0.04	1.6	0.4

a) Including the portion of R_f 0—0.1 of the column chromatography.

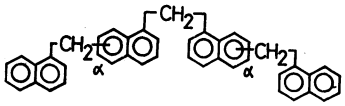
but the different absorption appeared at about 800 cm^{-1}. By this absorption in IR and a singlet signal due to protons of CH_2 in NMR, it was considered that this compound has a symmetrical structure. Accordingly, it may be concluded that this crystal is a three-nuclear compound linked with methylene groups at the α-positions, as is shown below.



Fraction (iv): Powder-like crystals were obtained by repeated reprecipitations from a benzene solution with methanol; mp 214—220 °C; R_f of tlc 0.6; IR (KBr disk) 2925, 2875 cm^{-1} (CH_2): NMR (CCl_4) 5.15 (s, Ar–CH_2–Ar–CH_2–Ar–CH_2–Ar–CH_2–Ar).

Found: C, 93.27; H, 5.91%; mol wt, 526. Calcd for $C_{43}H_{32}$: C, 94.12; H, 5.88%; mol wt, 549.

From the data of IR and NMR, this fraction was assumed to be composed mainly of the four-nuclear compound, linked with CH_2 groups at the α-positions.



Fraction (v): Repeated reprecipitations from benzene and methanol gave the following five fractions; the mps ranged between 120 and 190 °C, and the R_f values between 0.6 and 0.5; IR (KBr disk) 2925, 2875 cm^{-1} (CH_2).

Found: (a) C, 93.64; H, 5.81%; mol wt, 524; (b) C, 93.38; H, 5.70%; mol wt, 548; (c) mol wt, 649; (d) C, 93.81; H, 5.69%; mol wt, 683; (e) C, 93.16; H, 5.49%; mol wt, 869.

Fraction II: This fraction was obtained as a viscous liquid, with an R_f value of about 0.4. Repeated reprecipitations from benzene and methanol gave a white powder. It started to melt at 78 °C without showing any definite temperature. The IR spectrum has signals at 1730 cm^{-1} (C=O) and 1225 cm^{-1} (C–O), showing that the fraction is composed of an acetylester of NC or DNM.

Found: C, 88.30; H, 6.35%.

Fraction III: This fraction was also assumed to be an ester: mp>117 °C, R_f 0.25. Signals of IR agreed with those of the acetic ester.

Found: C, 89.22; H, 5.58%.

Fraction IV: Fraction IV (R_f 0.2) was a highly viscous liquid. It was purified by reprecipitation from benzene and methanol, and then fractionated by column chromatography, using carbon tetrachloride and chloroform as the solvents. The most abundant fraction was purified by the reprecipitation method, using carbon tetrachloride and methanol. A white powder was thus obtained; mp 142—164 °C; R_f 0.2; IR: 1730 cm^{-1} (C=O), 1225 cm^{-1} (C–O).

Found: C, 90.32; H, 5.63%; mol wt, 600. Calcd for $C_{46}H_{36}O_2$: C, 89.00; H, 5.85%; mol wt, 621.

$C_{46}H_{36}O_2$ corresponds to an acetate of the four-nuclear methylol compound.

Fraction V: A viscous liquid was obtained as a fraction with an R_f value of 0.0—0.06. Reprecipitation from a benzene solution with methanol gave the following three fractions.

Found: (i) C, 88.02; H, 5.40%; mol wt, 790, (ii) C, 86.63; H, 5.38; mol wt, 874, (iii) C, 85.09; H, 5.46; mol wt, 1028.

The oxygen contents of these fractions were very large, and it was assumed from, the IR spectra that oxygen existed as an acetate group or as a dimethylene ether group.

Fraction having R_f of 0.1: In another experiment, the reaction product of N with 41.51% formalin under the same conditions as an Exp. No. 2 in Table 4 was distilled under a vacuum. The fraction boiling at 150—170 °C/15 mmHg was again fractionated by column chromatography, using carbon tetrachloride as the solvent. A fraction with an R_f value of 0.1 was recrystallized from a carbon tetrachloride–methanol solution (1 : 1 in vol.) to give needle crystals: mp 60.5—61.5 °C. IR (KBr disk) 3350, 1000 cm^{-1} (OH), 2925, 2875 cm^{-1} (CH_2).

Found: C, 83.21; H, 6.08%. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37%.

No depression of mp was shown upon mixing with an authentic sample. Accordingly, this crystal may be concluded to be α-naphthyl carbinol.

Formation of Two-nuclear Dimethylene Ether Compound from β-Naphthyl Carbinol. A solution of 2 g of β-NC in 25 ml of dioxane was heated at 100 °C for 22 hr in the presence of 10 ml of 5 M-sulfuric acid. After the reaction, the mixture was extracted with benzene, washed with water, and then neutralized with an 1 M-NaOH solution. The benzene was evaporated almost completely. The residue, diluted with carbon tetrachloride was then submitted to column chromatography. A fraction with an R_f value of 0.35 was recrystallized from a mixture of carbon tetrachloride and petroleum ether. Needle-like crystals were thus obtained; mp 123—125.5 °C (121—123 °C[12]).

Found: C, 88.58; H, 6.23%; mol wt, 292. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%; mol wt, 298.

From the IR and NMR results, the fraction was concluded to be di-β-naphthylmethylene ether.

Formation of Dinaphthylmethane from Naphthylcarbinol and Naphthalene. Formation of αα′-DNM: α-NC, N, and sulfuric acid were dissolved in acetic acid. Their concentrations were 0.0500, 0.0500, and 0.483 mol/l respectively. After the solution has been warmed at 80 °C for 5 hr, αα′-DNM was isolated from the reaction mixture by column chromatography in a yield of 20 wt% of the α-NC. The αα′-DNM thus isolated was confirmed by comparing its UV spectrum with that of an authentic sample: λ_{max}=285 nm (ε=16200). *Formation of αβ′-DNM*: β-NC was reacted with N in a way similar to that used in the case of α-NC. The yield of αβ′-DNM isolated was about 10 wt%. Its identity as αβ′-DNM was confirmed by studing the UV spectrum: λ_{max}=273 nm (ε=14400).

Assumed Route for the Reaction of Naphthalene with

Formalin to Resin. As has been mentioned above, α-NC, αα′-DNM, αβ′-DNM, and three- and four-nuclear compounds, which are all linked to each other with methylene bonds, predominantly in the positions of α, were isolated. Thus, it was concluded that the formation reaction of naphthalene-formaldehyde resin is also included in the so-called "addition-condensation" reaction. First, NC, especially α-NC, is generated by the reaction of N with F; then NC is condensed with N to give αα′-dNM. These two reactions occur laternatively in preparing a higher nuclear compound. Accordingly, the reaction route may be shown as in Fig. 5.

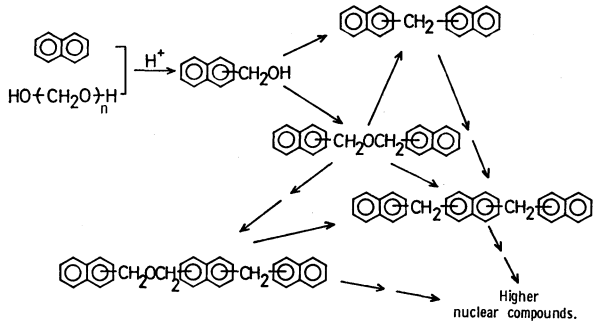


Fig. 5. Reaction route of naphthalene with formaldehyde in acidic medium

Studies of the Resin Formation from Naphthalene and Formaldehyde by Gel-permeation Chromatography. Calibration curve for GPC-analysis: Separation was carried out by means of the apparatus of Waters' Associates, GPC 501, using tetrahydrofuran (THF) as the solvent. The injected samples had an average concentration of 0.1—0.5 wt%. The two columns used were 4 ft long and 1/2 in. in diameter, and were packed with polystyrene gels whose porosities were 100 and 60 Å respectively.

Using synthesized authentic samples and fractionated higher-molecular-weight compounds, a calibration curve was prepared. As is shown in Fig. 6, α- and β-Naphthyl carbinols deviated from the line. Such deviations may be due to the increases in the molecular sizes as a results of the loose complexing of naphthyl carbinol with THF.*

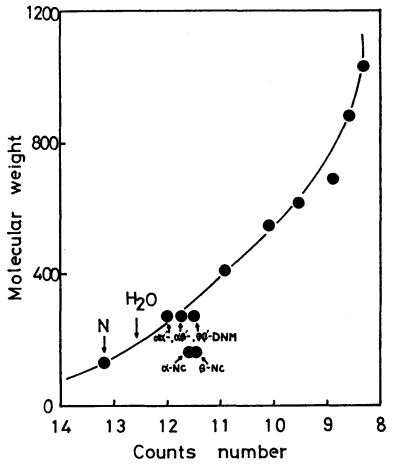


Fig. 6. GPC calibration curve.

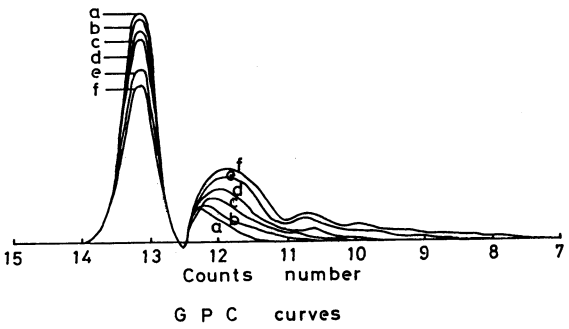


Fig. 7. GPC curves.
Reaction time a: 0 min, b: 30 min, c: 60 min, d: 90 min, e: 150 min, f: 180 min

Change in the GPC-curve of the Reaction Products with Reaction Time: A solution of 19.2 g of N, 9 g of 41.51% formalin, and 7.5 g of 81 M-sulfuric acid in 300 ml of glacial acetic acid was heated at 90 °C. After a definite time, an aliquot of the solution was pipetted

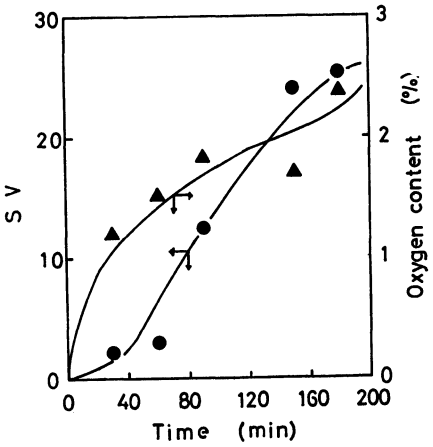


Fig. 8. Saponification values and oxygen contents *vs.* reaction time.

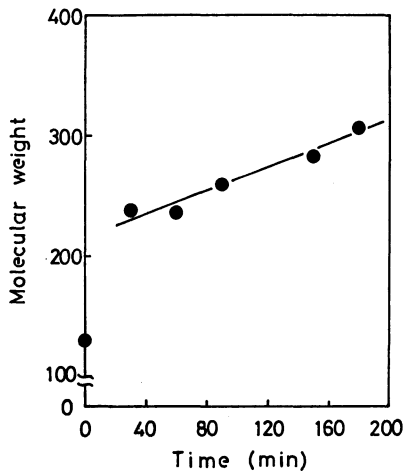


Fig. 9. Molecular weights *vs.* reaction time.

* It had been found that a solution of α- or β-naphthylcarbinol in THF shows a new IR signal of the hydrogen bond at 3420 cm^{-1}.[13]

out, extracted with benzene and carefully washed with water. The benzene layer was then concentrated to almost dryness. The residue was dissolved in THF and used as an injection solution for GPC. The results are shown as Fig. 7. It may be seen that the peak around 13 counts become lower, while the peaks around 12 counts become higher, with the reaction time.

Changes in the Oxygen Contents, Saponification Values and Molecular Weights of the Products with the Reaction Time. The products used for GPC analyses were also submitted to measurements of their oxygen content and saponification value (SV) without and further purification in order to avoid the loss of any components. The oxygen content was estimated by an elemental analysis of the carbon and hydrogen. As the products contained unreacted N, the oxygen contents were not so high as has been expected. The SV was calculated by the usual saponification method, using alcoholic potassium hydroxide in a solvent of benzene–ethanol mixture as the solvent. The molecular weight of the product, after the removal of the unreacted N by steam distillation, was determined by the VPO method, using benzene as the solvent. The results are shown in Figs. 8 and 9.

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