The Chromatographic Separation of Polyoxyethylene Nonylphenyl Ether

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Studies of the properties of polyoxyethylene derivatives, prepared by the addition of ethylene oxide to molecules already containing active hydrogen, have long been confused by the fact that such preparations have always resulted in mixtures. Mayhew and Hyatt¹⁾ obtained a narrow range of molecular species by distillation in a centrifugal molecular distillation still. Several other workers²⁾ have studied fractionation by means of molecular distillation. Also, chromatographic separation has been applied by Kelly³⁾.

In these studies, it has been found that the distribution of molecular weight was close to the theoretical distribution curve proposed by Flory⁴⁾. He assumed that all steps in the reaction of the ethylene oxide sequence are kinetically identical, and his results showed a Poisson's distribution. On the other hand, the products of relatively low molecular weight polyoxyethylene derivatives have been shown by means of vacuum fractional distillation not to agree with Flory's distribution⁵⁾.

Regarding the assumption of the kinetic identity of all steps as an oversimplification, Weibull and Nycander⁶⁾ have suggested a compromissed treatment for the reaction of an alcohol with ethylene oxide. They have proposed that all hydroxyl groups bound to an oxyethyl group have an equal ability to add ethylene oxide, this ability differing, however, from that of the parent alcohol. This has led to the following equations:

$$v = c\ln\frac{n_{00}}{n_0} - (c-1)\left(1-\frac{n_0}{n_{00}}\right) \qquad (1)$$

$$\frac{n_i}{n_{00}} = \frac{c^{i-1}}{(c-1)^i}\left\{\frac{n_0}{n_{00}} - \left(\frac{n_0}{n_{00}}\right)^c \times \sum_{j=0}^{i-1}\frac{1}{j!}\left[(c-1)\ln\frac{n_{00}}{n_0}\right]^j\right\} \qquad (2)$$

where

N_i = molecule with i added ethylene oxide molecules

m = number of moles of ethylene oxide consumed

n_{00} = number of moles of the starting material

n_0 = number of moles of the surviving starting material

n_i = number of moles of N_i in reaction product

k_i = rate constant for the reaction of N_i with ethylene oxide

k_0 = rate constant for the reaction of the starting material with ethylene oxide

$c = k_i/k_0$ = distribution constant

$v = m/n_{00}$ = average number of moles of ethylene oxide per mole of the starting material.

Since the polyoxyethylene derivatives are not thermostable, fractional distillation is not suitable for separation of the products; also, complete separation by distillation is not possible in the presence of many components.

For fractionation of this type, there are several attractive features of column chromatography. This method was used in the present preparation of polyoxyethylene nonylphenyl ether in order to provide data on the distribution of products for comparison with the theoretical equations mentioned above.

Experimental

Materials.—The nonylphenol (produced by the General Aniline and Film Co., Ltd.) was purified by distilling it with a Widmer column at 138～139°C/2.5 mmHg (hydroxyl value 249.8).

Ethylene oxide with a quoted minium purity of 99% was used.

The polyoxyethylene derivatives of nonylphenol were prepared by blowing ethylene oxide gas into nonylphenol in presence of metallic sodium as a catalyst; the amount of sodium was 0.1% by weight of the nonylphenol.

The reaction temperatures of 190, 140 and 100°C (±2°C), were selected. The products were neutralized with sulfuric acid, freed of water under vacuum, and then filtered through filter paper.

The properties of the polymers obtained by the reaction are shown in Table I.

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1) R. L. Mayhew and R. C. Hyatt, *J. Am. Chemist's Soc.*, **29**, 375 (1952).

2) J. V. Karabinos and E. J. Quinn, ibid., **33**, 223 (1956). L. M. Kushner, W. D. Hubbard and A. S. Doan, *J. Phys. Chem.*, **61**, 371 (1957).

3) J. Kelly and H. L. Greenwald, ibid., **62**, 1096 (1958).

4) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).

5) K. Nagase and K. Sakaguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kagyo Kagaku Zasshi*), **63**, 588 (1960); A. N. Wrigley, A. J. Stirton and E. Howard, *J. Org. Chem.*, **25**, 439 (1960).

6) B. Weibull and B. Nyoander, *Acta Chem. Scand.*, **8**, 847 (1954).

TABLE I. PROPERTIES OF THE POLYOXYETHYLENE DERIVATIVES OF NONYLPHENOL

Reaction temp., °C	Hydroxyl value	Refractive index n_{D}^{25}
100	182.5	1.5057
140	179.9	1.5050
190	177.8	1.5050

Apparatus.—The diameter and the length of the column were 3.5 and 75 cm. respectively. The column was packed with silicic acid up to a height of 50 cm. Silicic acid (Mallinckrodt A. R., 100 mesh powder, suitable for chromatographic analysis) was used as supplied. A spectrophotometer (Hitachi Model EPU-2) was used for the spectrophotometric measurements.

Procedure.—The gel ratio was 160 : 1. The development was carried out by applying the mixture of chloroform and acetone (95 : 5, 85 : 15 volume ratio). A solvent system of benzene and methanol was examined for this purpose, but the results were not satisfactory. In each case, 1.000 g. of the sample was used. The flow rate was adjusted to 20 cc. per 13 min., and portions were collected with a volumetric fraction collector. An aliquot of 3 cc. was taken from every 20 cc. fraction, and the solvent was evaporated in a vacuum desiccator. The absorbance of the chloroform solution was measured at the wavelength of 277 mμ by a spectrophotometer.

Results and Discussion

A typical elution curve is plotted in Fig. 1. The figure shows that the chromatographic separation of polyoxyethylene nonylphenyl ether was satisfactory. A very small peak was observed in the fraction, at $26\sim32$ of Fig. 1; this seems to come from a trace of impurity. This will be evident from the following tests.

a) The OCH_2CH_2OH group was not detected.

Following the procedure indicated by Feigl[7], the sample was treated with periodic acid, but no aldehyde was detected.

b) No phenolic OH was detected.

No coloration was observed when a diazonium sulfanilic acid solution was sprayed on filter paper spotted with the samples. The evidence described above suggests that the trace of impurity was not nonylphenol derivatives, but no further investigation was made. The amount of the impurity was at any rate, less than 1%.

The materials eluted from each peak were collected and weighed by microbalance. The molar absorptivities of each peak were calculated from the absorbance of the 0.01% chloroform solution at 277 mμ and were assumed the molecular weight.

If this assumption is right, each molar absorptivity should agree well with that of nonylphenol, because the absorption at 277 mμ originates from the phenyl radical. The numbers of the polymerized oxyethylene radicals for each peak were thereby determined. These results showed no nonylphenol survived in the reaction.

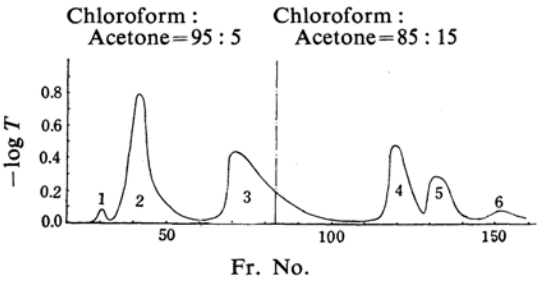

Fig. 1. Chromatogram (reaction temp. 190°C).

This fact shows that the ethylene oxide addition of nonylphenol was selective and that ethylene oxide reacted with nonylphenol completely in the first step.

The weights of all the peaks are shown in Table II. These results show that a high rate

TABLE II. WEIGHT OF THE PEAKS SEPARATED BY THE CHROMATOGRAPHY

Peak No.	Reaction temp. 100°C		Reaction temp. 140°C		Reaction temp. 190°C	
	Wt., g.	Converted total wt.*	Wt., g.	Converted total wt.*	Wt., g.	Converted total wt.*
1	0.00537	0.00634	0.00543	0.00649	0.00858	0.01009
2	0.27230	0.32127	0.21433	0.25597	0.21655	0.25466
3	0.38373	0.45749	0.36016	0.43014	0.33155	0.38990
4	0.13103	0.15466	0.16803	0.20063	0.16730	0.19674
5	0.03544	0.04182	0.05612	0.06702	0.07083	0.08329
6	0.00724	0.00854	0.01424	0.01701	0.01482	0.01728
Acetone elute	0.00103		0.02231		0.04517	
	$\sum$ wt. = 0.99115		$\sum$ wt. = 0.99957		$\sum$ wt. = 0.99713	

* Weight × 20/17

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7) F. Feigl, "Spot Tests in Organic Analysis", Elsevier, New York (1956), p. 189.

of recovery should be obtained by adding the fraction eluted with acetone to the separate sample.

The weight percentages of all the peaks are shown in Table III. In this Table, C was calculated by applying Weibull's equation (1). "The number of the starting material" was calculated on the basis of nonylphenyloxyethanol.

TABLE III. DISTRIBUTIONS OF THE WEIGHT PERCENTAGE

Reaction temp.		190°C	140°C	100°C
Oxyethylene, $\bar{P}$		2.04	2.00	1.85
Peak No.	No. of oxyethylene			
2	1	25.5	25.6	32.1
3	2	39.5	43.0	45.8
4	3	20.5	20.1	15.4
5	4	7.1	6.7	4.2
6	5	3.1	1.7	0.9
Acetone elute		3.4	2.3	1.0
Peak No. 1		0.9	0.6	0.6
C		0.66	0.61	0.58

The results of these experiments may be compared with Poisson's and Weibull's distributions.

Poisson's distribution as proposed by Flory[4] (weight):

$$W_x = \frac{M_x}{M+44v} \mathrm{e}^{-v} \frac{v^i}{i!} \qquad (3)$$

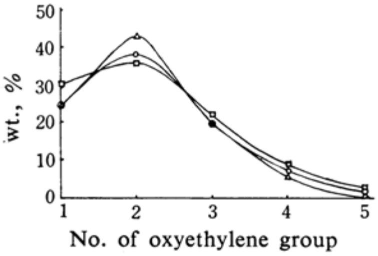

Fig. 2. Weight distribution (reaction temp. 190°C).

-○- Experimental
-△- Weibull's distribution
-□- Poisson's distribution

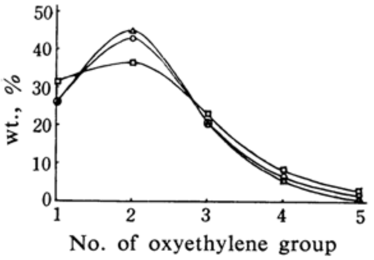

Fig. 3. Weight distribution (reaction temp. 140°C).

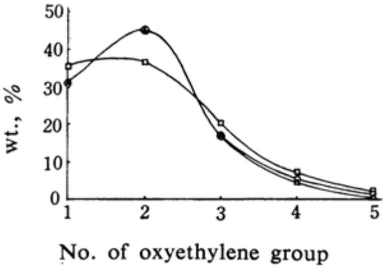

Fig. 4. Weight distribution (reaction temp. 100°C).

Distribution (weight) based on Weibull's formula.

$$W_x = \frac{M_x}{M+44v} \cdot \frac{c^{i-1}}{(c-1)^i} \left\{ \frac{n_0}{n_{00}} - \left(\frac{n_0}{n_{00}}\right)^c \times \sum_{j=0}^{i-1} \frac{1}{j!} \left[(c-1) \ln \frac{n_{00}}{n_0} \right]^j \right\} \qquad (4)$$

where

M = molecular weight of the starting material
M_x = molecular weight of the product of chain length x units.
W_x = weight fraction of the product of chain length x units

The results indicated in Figs. 2, 3 and 4 show that distribution in these cases agreed better with Weibull's distribution than with Poisson's.

With the increase of the reaction temperature, however, a considerable difference was observed.

Also, these figures show that the lower the reaction temperature, the narrower the distribution of molecular weights.

Summary

Polyoxethylene nonylphenyl ether can be separated with respect to the unit of the oxyethylene radical by applying the chromatographic method, using silicic acid as the adsorbent and a chloroform-acetone mixture as the eluent. Nonylphenol was allowed to react with ethylene oxide in the mole ratio of 1:2 in the presence of metallic sodium as a catalyst at the three different temperatures of 190, 140 and 100°C.

The chromatographic method was applied to the reaction products, and it was shown that the distribution became somewhat narrower at the lower reaction temperature.

A comparison of these results with the theoretical distributions proposed by Flory and by Weibull indicated significant agreement with the latter but a discrepancy with the former. However, when the temperature was rather high, the agreement with the Weibull formula was not good.

Similarly, polyoxyethylene nonylphenyl ether having more than two oxyethylene units could be separated by this method. When $\bar{P}=10.3$, 14 peaks was obtained from a chromatogram.

The separation and recovery by this method were considerably better than the distillation method, and a better understanding of the distribution of molecular weights was obtained.

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