TABLE V
Analysis of Methyl Ester of Polymeric and Degraded Fractions

Fatty acid	Fractions			
	C (8.1)[1]	D (13.0)	E (10.4)	F (5.6)
A*	+	0.64	0.53	++
B*	0.42	0.36	0.44	1.2
C*	0.34	0.45	0.30	0.40
D*	....	.....		++
E*	....	0.32	+	....
F*	....		+	....
$C_{15:0}$	....	1.2	....	0.9
Azelaic†	....	++	....	1.4
$C_{16:0}$	10.8	10.0	9.9	10.7
$C_{16:1}$	5.3	4.2	3.1	1.0
Sebacic†	2.9	2.1	0.6	2.1
$C_{18:0}$	1.9	1.4	1.7	1.8
$C_{18:1}$	25.7	29.1	28.2	28.7
$C_{18:2}$	52.6	50.1	55.1	51.7

* Unidentified.
† Tentatively identified by retention time and internal standards.
[1] Figures in parenthesis indicate values in per cent of the fraction.
+ Indicates trace.
++ Indicates less than 0.1.

compounds marked A,B and E in Table V suggests the presence of short chain, unsaturated, branched acids (910 cm^{-1}). Compound B also shows an OH group. Dibasic acids tentatively identified by internal standards could not be obtained for further chemical analysis. $C_{16:0}$ and $C_{18:1}$ acids in these fractions gave remarkably broad peaks. This in itself was an indication that the compounds were not pure. Appearance of palmitoleic acid seems anomalous and no explanation is available at this time.

Fractionation into urea adduct forming fatty acids and non-adduct forming material. Fraction C,D, E and F were subjected to fractionation with urea. The procedure used was essentially the same as described by Bhalerao and Mahon (3) except that 1–2 g samples were saponified for 2 hr to ensure complete saponification. Under the conditions of urea fractionation used, all $C_{16:0}$ (palmitic) acid forms an adduct. Eight to 13% of the compound reported as $C_{16:0}$ by GLC in fractions C,D,E and F did not form an adduct. These compounds have the same relative retention time as $C_{16:0}$ under the conditions of GLC used in this study. Work on these fractions is being continued and will be reported later.

ACKNOWLEDGMENT

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The Preparation of a Series of Molecularly Homogeneous Para-*t*-Octylphenoxypoly(ethoxy)ethanols

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Abstract

Multi-gram quantities of the first ten members of a series of para-(1,1,3,3-tetramethylbutyl)-phenoxypoly(ethoxy)ethanols (p-*t*-OPE_n) have been prepared. Analytical and physical data indicate that each of these materials is composed of greater than 95% of a single molecular species.

Introduction

THE BASE-CATALYZED addition of ethylene oxide to alkylphenols is the most common method of preparation of a group of nonionic surface active materials, the alkylphenoxypoly(ethoxy)ethanols. This type of reaction leads to products having a Poisson distribution (1–5) of molecular species. The popular terms "E number" or "E_n" refer to the average number of ethylene oxide units attached to the alkylphenol in the product mixture. Thus an oxyethylated p-*t*-octylphenol having an average of five mole of ethylene oxide and a Poisson distribution of molecular weights can be called *p-t*-octylphenol-E_5 (p-*t*-OPE_5). An interesting subject is the comparison of the physical and surface active properties of such materials with those of materials having the same E_n, but consisting of a single molecular species. Such a comparison has been made possible in these laboratories by the synthesis of multi-gram quantities of the first 10 members of a series of essentially molecularly homogeneous p-*t*-OPE_n's and has been reported by Crook and co-workers (6). The synthesis and purification of these materials represent, respectively, extensions of the work of Gingras and Bayley (7), who have described the synthesis of molecularly homogeneous p-*t*-OPE_7 by the reaction of hexaoxyethylene glycol with p-*t*-octylphenyl-β-chloroethyl ether and of Kelly and Greenwald (5), who obtained very small quantities of a number of substantially homogeneous p-*t*-OPE_n's by tedious chromatographic separation of the components of normal p-*t*-$OPE_{9.7}$, prepared by the addition of ethylene oxide to recrystallized p-*t*-octylphenol.

Experimental

A. *Synthetic*

1. *Normal p-t-OPE_n.* The following preparation of p-*t*-$OPE_{8.94}$ is typical.

A mixture of 50.0 g (0.243 m) of p-*t*-octylphenol which had been recrystallized four times from heptane (mp 85–86C; congealing pt. 84.8C) and 0.3 g (0.013 g atom) sodium metal in a tared ethylene oxide reaction flask was

flushed with nitrogen and then stirred and slowly heated to 80–90C under a slight positive pressure while hydrogen was evolved. When the evolution of hydrogen ceased, an ethylene oxide addition flask containing 100.3 g (2.19 m + 4 g excess) was attached to the system and the temp was raised to 170–180C. The ethylene oxide was vaporized into the reaction flask at this temperature. After the addition of ethylene oxide was complete, the system was filled with nitrogen, cooled, and weighed. There was a weight increase of 95.6 g. The product was neutralized with 50% sulfuric acid, digested with 5% water, stripped for 4 hr at 90–100C/10–20 mm, and filtered with Celite 545.

Calculations and Analyses:

Mole OP = 0.243
Mole E.O. = 2.17
Mole E.O./mole OP = 8.94
Cloud Point = 60.0C; % Ash = nil;
% H_2O = 0.22; OH No. = 95.2
(theory = 93.6).

2. *Intermediates (Table I).*

a. *p-t-Octylphenol.* Commercial octylphenol was recrystallized four times from heptane to a constant mp (85–86C).

b. *"Polyethylene glycol monochlorides."* A stirred mixture of 150 g (1.86 m) 2-chloroethanol and 1.4 ml BF_3 etherate, in an ethylene oxide addition flask, was flushed well with nitrogen and then three times with ethylene oxide. There was then added 355 g ethylene oxide at 30–40C during 2 hr. The reaction was strongly exothermic at the beginning, becoming less exothermic as the reaction progressed. The mixture was stirred an additional one-half hr, neutralized with 30 g 12% aqueous sodium carbonate, stirred another one-half hr, stripped free of water, and filtered through Celite 545. The filtered product was distilled at 0.25 mm with no fractionating column and the material distilling up to 210C was collected and allowed to stir overnight with 25 ml 20% aqueous sodium carbonate solution. This mixture was then treated with carbon black, stripped, filtered and distilled. Three fractions were collected.

Fraction	br, °C/mm Hg	Principal Component
1	up to 135/0.6	"tetraethylene glycol monochloride"
2	135–165/0.6	"pentaethylene glycol monochloride"
3	165–200/0.6	"hexaethylene glycol monochloride"

Each of these fractions was treated with sodium carbonate and carbon black and redistilled one or more times to give 25–50 g portions of single molecular species "polyethylene glycol monochlorides." Gas chromatographic analysis of the "tetraethylene glycol monochloride" showed a single peak. The "pentaethylene glycol monochloride" chromatogram showed a second small peak which corresponded to contamination by about 1% "hexaethylene glycol monochloride" and the "hexaethylene glycol monochloride" chromatogram showed only a single broad peak.

c. *"Polyethylene glycol dichlorides."* *Bis*(2-chloroethyl)ether ("Chlorex") and 1,2-*bis*(2-chloroethoxy)ethane were obtained by repeated distillation of commercially available materials. *Bis*[2-(2-chloroethoxy)-ethyl] ether (8) was redistilled several times.

d. *Hexaoxyethylene glycol.* The procedure of Fordyce et al. (9) was used to prepare hexaoxyethylene glycol from diethylene glycol and "Chlorex" which had been first purified by several distillations through a 10-plate Oldershaw column. Constant boiling fractions were used. The product was also distilled several times through the same column.

e. *"p-t-OPE_n Chlorides."* The preparation of molecularly homogeneous "p-*t*-OPE_2 chloride" is typical of the procedure used to prepare "p-*t*-OPE_n chlorides."

A mixture of 290 g (2.03 m) of redistilled "Chlorex," 98 g (0.475 m) recrystallized p-*t*-octylphenol, and 50 g (0.625 m) of 50% aqueous sodium hydroxide solution was refluxed for 4 hr and allowed to stand overnight. There was added 75 ml water and the mixture was thoroughly stirred. The resulting layers were separated. The organic layer was diluted with toluene and washed with water until the wash water was no longer basic. The organic material was distilled to give 102 g distillate, bp 130–180C/0.5 mm. The distillate was redistilled and a center, product fraction of 66 g "p-*t*-OPE_2 chloride," bp 153C/0.35 mm was obtained.

3. *Molecularly Homogeneous p-t-OPE_n (Table II).*

a. *n = 1–3.* Three-hundred and seventy-eight g of a mixture of p-*t*-OPE_2, p-*t*-OPE_3 and p-*t*-OPE_4 prepared from recrystallized p-*t*-octylphenol and ethylene oxide as described above was distilled through a 10-plate Oldershaw column at 0.55 mm, using a $^3/_{10}$ reflux ratio.

Fraction No.	br, °C	Wt, g
1	133–144	23
2	144–161	9
3	161–170	70
4	170–192	19
5	192–200	75
Residue		180

Fractions 1 and 2 were combined and redistilled through the same column at the same reflux ratio to give 14 g of single species p-*t*-OPE_1, br 134–135C/0.55 mm. Gas chromatographic analysis indicated a purity of 98–99%, the impurity being p-*t*-octylphenol. No p-*t*-OPE_2 was observed.

Fraction No. 3 was redistilled through the same column at the same reflux ratio to give 42 g of single molecular species p-*t*-OPE_2, br 160–161C/0.45 mm. Gas chromatographic analysis showed only a single component.

Fraction No. 5 was redistilled through the same column at the same reflux ratio to give 38 g of single molecular species p-*t*-OPE_3,

TABLE I
Intermediates[a]

Material	Emp. form	mr, °C or br, °C/mm Hg	% C		% H		% Cl		Hydroxyl No.	
			Found	Calc	Found	Calc	Found	Calc	Found	Calc
p-*t*-Octylphenol[b]	$C_{14}H_{22}O$	85–86[c]	81.67	81.49	10.82	10.75	.....	.....	268.8	271.9
"Tetraethylene glycol monochloride"	$C_8H_{17}O_4Cl$	126–127/0.65	45.31	45.18	8.23	8.06	16.89	16.67	.....	.....
"Pentaethylene glycol monochloride"	$C_{10}H_{21}O_5Cl$	152–153/0.50	46.90	46.78	8.24	8.25	13.78	13.81	.....	.....
"Hexaethylene glycol monochloride"	$C_{12}H_{25}O_6Cl$	180–182/0.65	48.35	47.91	8.59	8.38	11.39	11.79	.....	.....
bis(2-chloroethyl) ether	$C_4H_8OCl_2$	74/12	33.69	33.59	5.59	5.64	49.82	49.58	.....	.....
1,2-*bis*(chloroethoxy)ethane	$C_6H_{12}O_2Cl_2$	109–110/9	38.31	38.52	6.34	6.47	38.39	37.91	.....	.....
bis[2-(2-chloroethoxy)-ethyl]-ether	$C_8H_{16}O_3Cl_2$	105–106/0.25	41.55	41.57	7.05	6.98	30.50	30.68	.....	.....
Hexaoxyethylene glycol	$C_{12}H_{26}O_7$	191–194/0.35	51.04	51.05	9.18	9.28	.....	.....	394.9	397.4
"p-*t*-OPE$_1$ chloride"	$C_{16}H_{25}OCl$	129–130/0.60	72.00	71.48	9.29	9.37	12.44	13.19	.....	.....
"p-*t*-OPE$_2$ chloride"	$C_{18}H_{29}O_2Cl$	153/0.35	69.04	69.10	9.24	9.34	11.32	11.33	.....	.....
"p-*t*-OPE$_3$ chloride"	$C_{20}H_{33}O_3Cl$	182/0.50	67.52	67.30	9.29	9.32	10.01	9.93	.....	.....
"p-*t*-OPE$_4$ chloride"	$C_{22}H_{37}O_4Cl$	201/0.25	66.14	65.89	9.11	9.30	8.91	8.84	.....	.....

[a] After purification.
[b] Recrystallized four times from heptane.
[c] Congealing point = 84.8C.

br 191–192C/0.45 mm.

b. $n = 4$–6. The preparation of single molecular species p-*t*-OPE$_4$ is typical.

To a stirred homogeneous mixture of 28.8 g (0.140 m) of p-*t*-octylphenol which had been recrystallized 4 times from heptane (mp 85–86C) and 30.8 g (0.145 m) redistilled "tetraethylene glycol monochloride," br 126–127C/0.65 mm was added 12.0 g (0.150 m) 50% sodium hydroxide solution. The mixture exothermed to 55C and was then heated at reflux (100–105C) for 4 hr, cooled, and diluted with 60 ml water and 200 ml toluene. The resulting layers were separated and the upper layer was washed with water until the wash water was neutral. The organic layer was distilled to give 34 g single molecular species p-*t*-OPE$_4$, br 222–223C/0.55 mm. Gas chromatographic analysis indicated the product was free of p-*t*-octylphenol and "tetraethylene glycol monochloride."

c. $n = 7$–10. The general procedure of Gingras and Bayley (7) was employed for the preparation of p-*t*-OPE$_{7-10}$ from hexaoxyethylene glycol and "p-*t*-OPE$_1$ chloride," "p-*t*-OPE$_2$ chloride," "p-*t*-OPE$_3$ chloride" and "p-*t*-OPE$_4$ chloride," respectively.

B. Purification of Molecularly Homogeneous p-t-OPE$_{1-10}$. The first five members were distilled as described previously. p-*t*-OPE$_6$ was first distilled and then purified by chromatography on silicic acid and p-*t*-OPE$_{7-10}$ were purified by chromatography on silicic acid. The following description of the purification of p-*t*-OPE$_8$ is typical.

Reagents:

Silicic Acid—Mallinckrodt, "Suitable for Chromatographic Analysis by the Method of Ramsey and Patterson." Analytical Reagent-100 mesh.

Celite 545—Washed with chloroform.

Alumina—Merck Reagent "Suitable for Chromatographic Analysis."

Chloroform—B. & A. U.S.P. prepurified over alumina.

Acetone—Baker Reagent prepurified over alumina.

Methanol—Baker Reagent prepurified over alumina.

Benzene—Baker Reagent prepurified over alumina.

Ottawa Sand—Washed with chloroform.

Procedure:

A column measuring 38 x 2 in. was packed over a 1-in. layer of Ottawa sand with a slurry of 300 g silicic acid and 150 g Celite 545 in benzene. The column was charged with 50 g crude homogeneous p-*t*-OPE$_8$ in an equal volume of benzene. When the liquid surface had reached the top of the silicic acid, the sides of the column were washed down with 50 ml benzene. This procedure was repeated twice and then the column was filled with benzene. One-hundred ml fractions were collected and evaporated until a total of 15.5 g water insoluble material had been eluted with 1.5 l benzene. The first visible yellow band had stalled about ¾ of the way down the column. The column was then charged with chloroform and another 2.0 g water insoluble material was eluted with 1.2 l chloroform. The first colored band moved lower and was partially eluted with the chloroform. A 50% by volume mixture of acetone and chloroform was charged to the column and was visibly followed down the column. One-hundred ml fractions of this mixture were collected and on evaporation gave the following weights of materials.

TABLE II
Purified p-*t*-OPE$_n$ (Single Molecular Species)

E No. (n)	Emp. form	br, °C/mm Hg	OH No.		Mole wt[a]		n_D^{25}	% C		% O	
			Found	Calc	Found	Calc		Found	Calc	Found	Calc
1	$C_{18}H_{28}O_2$	134–135/0.55	223.8[c]	224.1	251	250	1.5124	76.72	76.75	10.28	10.47
2	$C_{18}H_{30}O_3$	160–161/0.45	187.5[c]	190.5	300	294	1.5080	73.41	73.43	10.27	10.27
3	$C_{20}H_{34}O_4$	191–192/0.45	162.3[c]	165.7	339	339	1.5037	70.75	70.97	10.06	10.12
4	$C_{22}H_{38}O_5$	222–223/0.55	147.3[c]	146.7	371	382	1.5002	69.29	69.08	9.85	10.01
5	$C_{24}H_{42}O_6$	225–227/0.30	129.1[c]	131.5	410	427	1.4972	67.56	67.57	9.88	9.92
6	$C_{26}H_{46}O_7$	250–253/0.30[b]	.....	119.2	454[c]	471	1.4945[c]	66.49[c]	66.35	9.80[c]	9.85
7	$C_{28}H_{50}O_8$	.....	.....	108.9	526	515	1.4919	65.47	65.34	9.64	9.79
8	$C_{30}H_{54}O_9$	.....	98.8[d]	100.3	542	559	1.4907	64.59	64.49	9.79	9.74
9	$C_{32}H_{58}O_{10}$	.....	89.3[d]	93.2	602	603	1.4896	63.78	63.76	9.75	9.70
10	$C_{34}H_{62}O_{11}$	.....	87.5[d]	86.8	643	647	1.4878	63.09	63.13	9.57	9.66

[a] Determined spectroscopically using a Beckman DK-2 spectrophotometer. Wavelength of maximum absorbance = 275.5 mμ. E max. = 1.33 x 10^3 in water for E$_{7-10}$ and 1.66 x 10^3 in isooctane for E$_{1-6}$ (5).
[b] Before chromatographic purification.
[c] Determined chemically.
[d] Determined by IR method of Hilton (10).
[e] After chromatographic purification.

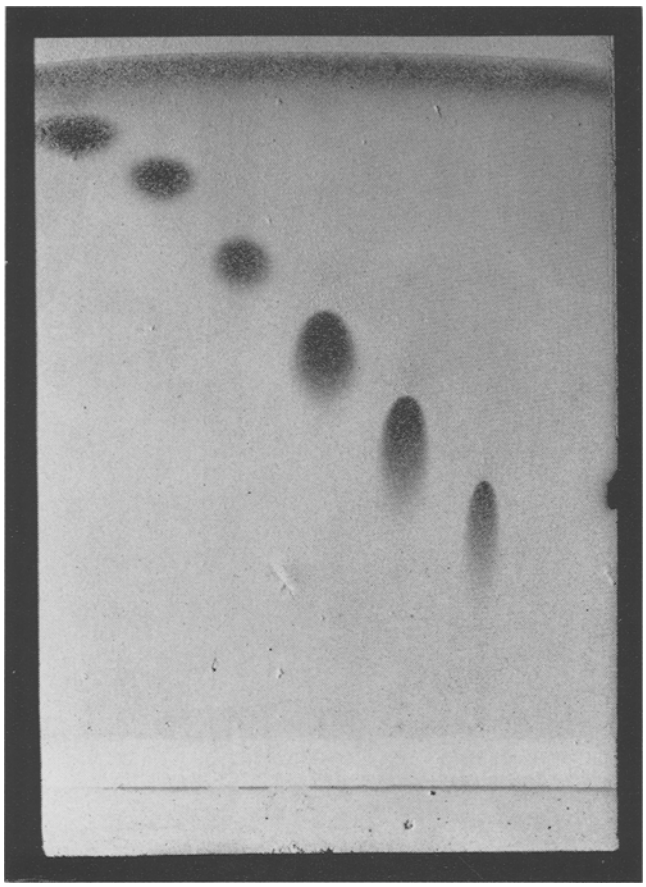

FIG. 1. TLC of molecularly homogeneous p t-OPE$_{1-6}$.

Fraction No.	Wt, g	Cloud Point, °C
1	5.1	<0
2	5.2	21
3	4.2	34
4	2.8	38.5
5	1.6	44
6	0.7	45
7	0.5	46

These fractions were combined and rechromatographed as follows:

A column measuring 18 x 1⅜ in. was packed over glass wool and Ottawa sand with a slurry of 110 g silicic acid in chloroform and then charged with the combined fractions described previously in the same manner as the original column had been charged. Eluted chloroform was collected and evaporated to give a total of 0.6 g water insoluble material. The column was then charged with 5% by volume of methanol in chloroform and 50 ml fractions were collected and evaporated to give the following weights of materials.

Fraction No.	Wt, g	Cloud Point, °C
1	1.6	0
2	1.9	0
3	3.0	27
4	2.9	....
5	2.8	34
6	2.5	....
7	1.0	....
8	0.8	26

FIG. 2. TLC of molecularly homogeneous p t-OPE$_{6-10}$.

Fractions 3–7 were combined and rechromatographed in the same column using 100 g silicic acid for packing and chloroform as the solvent. Fifty-ml portions were collected and evaporated and the cloud point of the eluted adsorbate measured. A total of 1.3 l chloroform was used to elute approximately 2.5 g material which came off with most of the broad visible yellow color band. The cloud points of the fractions gradually rose to 40C. Ten per cent by volume of methanol in chloroform was then charged to the column and 9.8 g material was eluted from the column. This material had a cloud point of 51.0C. It was dissolved in about 25 ml chloroform and allowed to stand over the weekend in contact with 1–2 g carbon black.

A final chromatographic purification was carried out by the same procedure on the same column using 70 g silicic acid and 800 ml chloroform to separate a total forerun of 2.8 g in 25–50 ml fractions of eluate. The cloud point of the eluted adsorbate in these fractions rose from 37–51.7C. A 10% by volume mixture of methanol in chloroform was used to elute another 6.3 g of product having a cloud point of 51.7C. The product was filtered through a small sintered glass filter, stripped for 8 hr at 90–100C/0.5 mm and then stored under nitrogen.

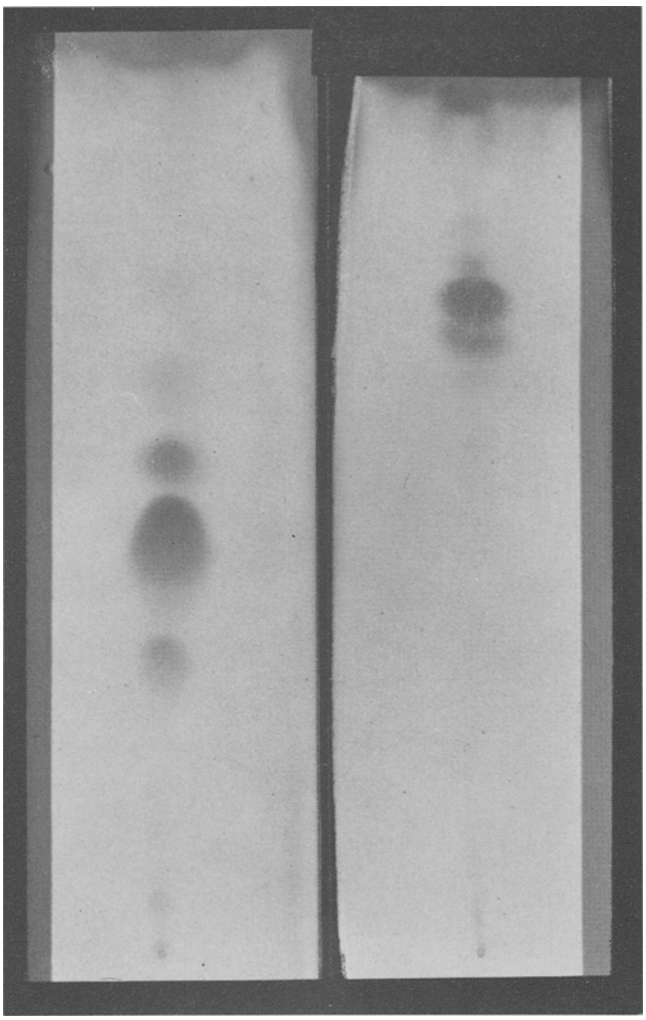

FIG. 3. TLC of molecularly homogeneous p-*t*-OPE_5 containing 5% each of molecularly homogeneous p-*t*-OPE_4 and p-*t*-OPE_6, and of molecularly homogeneous p-*t*-OPE_8 containing 5% of molecularly homogeneous p-*t*-OPE_9.

C. Thin Layer Chromatography of Molecularly Homogeneous p-t-OPE$_n$'s (Figures 1–3). Thin layer plates 300 μ thick were prepared from a water slurry of Camag Silica Gel containing 5% calcium sulfate and were activated at 110C for 4 hr before use. Molecularly homogeneous p-*t*-OPE_n samples of 50 μg were applied to the plates approximately ½ in. from one end. In separate experiments samples were diluted with 5% of various other molecularly homogeneous p-*t*-OPE_n and applied to the plates in the same manner to determine the limit of detection of impurities. Solvent systems used were 40% acetone/60% benzene (v/v) for plates of p-*t*-OPE_1 through p-*t*-OPE_6 and 60% acetone/40% benzene (v/v) for plates of p-*t*-OPE_6 through p-*t*-OPE_{10}. The plates were then dried at 60C for 10 min, sprayed with a 3% aqueous potassium permanganate solution and heated at 60C until spots developed. Excess permanganate was removed by developing the plates with water.

Discussion

A. Synthetic.

1. Normal p-t-OPE$_n$. "E numbers" of a series of p-*t*-OPE_n (n = 2–10) with normal Poisson molecular distribution, prepared from recrystallized p-*t*-octylphenol by standard oxyethylation procedure, were calculated both by weight increase and from hydroxyl number of the product. The small differences (Fig. 4 and Table III) reflect the inherent inaccuracies in weighings and hydroxyl number determinations and the presence of small amounts (<0.1%) water introduced to the system with the ethylene oxide during the oxyethylation. The noticeable effect of the latter is to raise the hydroxyl number and consequently lower the apparent "E number" as a result of the formation of small quantities of polyethylene glycols. The first member of the series, p-*t*-OPE_1, was not prepared since it should be nearly identical with molecularly homogeneous p-*t*-OPE_1. Miller et al. (3) have shown that in base-catalyzed oxyethylations of phenol, the phenol is first exclusively converted to phenoxyethanol (PE_1) before any subsequent monomer additions ("chaining") occur.

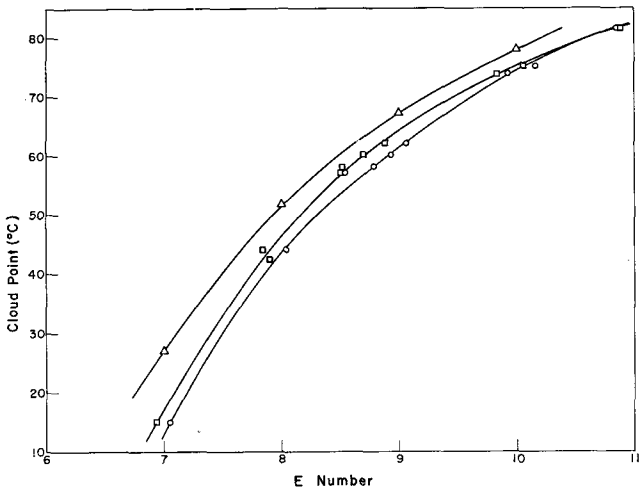

FIG. 4. Cloud point comparison of molecularly homogeneous and normal p-*t*-OPE_{7-10}.

△—Molecularly homogeneous p-*t*-OPE_{7-10}.
□—Normal p-*t*-OPE_n (E No. calc'd. from hydroxyl number.)
○—Normal p-*t*-OPE_n (E No. calc'd from wt increase.)

2. Molecularly Homogeneous p-t-OPE$_{1-10}$. Three synthetic routes were used for the preparation of molecularly homogeneous p-*t*-OPE_{1-10}. The first three members of the series, p-t-OPE_{1-3} were obtained simply by redistillation of fractions isolated by distillation from normal oxyethylated p-*t*-octylphenol. p-*t*-OPE_{4-6} were synthesized by the condensation of recrystallized p-*t*-octylphenol with the appropriate "polyethylene glycol monochloride." The latter were obtained by the BF_3-catalyzed addition of ethylene oxide to ethylene chlorohydrin and were purified by repeated distillations. Distillation of the crude products was sufficient purification to yield high quality p-*t*-OPE_4 and p-*t*-OPE_5, but subsequent purification by chromatography on silicic acid was required for p-*t*-OPE_6. The last four members of the series, p-*t*-OPE_{7-10}, were synthesized by the method of

TABLE III

Normal p-*t*-OPE_n

OH No.	E No.	
	by wt increase	by OH No.
191.5, 190.8	2.00	1.97
164.1, 167.1	2.98	3.00
145.4, 147.7	4.07	4.04
134.3, 133.4	5.01	4.83
119.3, 118.3	6.04	6.04
109.7, 109.9	7.05	6.93

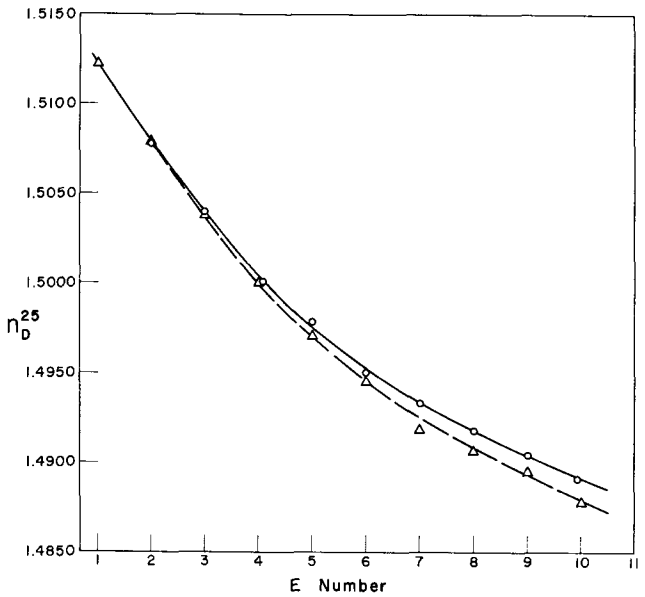

FIG. 5. Refractive index comparison of molecularly homogeneous and normal p-*t*-OPE_{1-10}.

△—Molecularly homogeneous p-*t*-OPE_{1-10}.
○—Normal p-*t*-OPE_{1-10} (E No. calc'd from wt increase.)

Gingras and Bayley (7) from hexaoxyethylene glycol and "p-*t*-OPE_1 chloride," "p-*t*-OPE_2 chloride," "p-*t*-OPE_3 chloride" and p-*t*-OPE_4 chloride" respectively. The latter were synthesized by the condensation of recrystallized p-*t*-octylphenol with ethylene dichloride, *bis* (2-chloroethyl)ether, 1,2-*bis*(2-chloroethoxy) ethane, and *bis*[2-(2-chloroethoxy)-ethyl]ether respectively. p-*t*-OPE_{7-10} were purified by chromatography on silicic acid.

B. Chromatographic Purification of Molecularly Homogeneous p-t-OPE_{6-10}. The successful chromatographic purification of multi-gram quantities of p-*t*-OPE_n materials is apparently as much art as science. It necessitates the use of large columns, large quantities of solvent and considerable patience. The packing of large columns is somewhat more difficult than the packing of smaller columns, and channeling much more difficult to avoid. After a considerable number of exploratory runs a system was eventually evolved which incorporated column overloading and successive rechromatography, but was successful in providing 5–10 g samples of the desired single species nonionics from 50 g initial charges of the crude materials which contained approximately 20-30% of the desired nonionic. The principal impurities in the crudes which had to be separated from the desired products were unreacted hexaoxyethylene glycol, unreacted " p-*t*-OPE_n chloride" and the corresponding p-*t*-OPE_n resulting from reaction of the chloride with water, and either or both of the glycol-α,ω-di(octylphenyl) ethers resulting from a Wurtz type reaction of 2 mole of the "p-*t*-OPE_n chloride" or from the reaction of the "p-*t*-OPE_n chloride" at both ends of the hexaoxyethylene glycol. No effort was made to establish the identity of the latter materials, but chlorine analyses indicated the presence of unreacted "p-*t*-OPE_n chloride." The separation of these materials is somewhat easier than would be the separation of individual species from a normal ethylene oxide reaction product because of greater relative differences in adsorptivity on silicic acid. The experimental section describes the purification of single molecular species p-*t*-OPE_8 since it is typical of all three.

C. Purity of Molecularly Homogeneous p-t-OPE_n. Strong evidence for the purity of the molecularly homogeneous p-*t*-OPE_n's is provided by the agreement, within the experimental limits of error of the various analytical methods, of experimentally determined hydroxyl numbers, molecular weights and elemental analyses with the theoretical values (Table II) coupled with the narrow br for the lower members of the series and the fact that the higher member products were taken from constant cloud point fractions being eluted from the chromatographic purification columns. Further quantitative purity data are provided by TLC (Figs. 1,2,3) which clearly shows that the purity of all the products exceeds 95%.

D. Physical Properties of Molecularly Homogeneous p-t-OPE_n. Figure 4 demonstrates that the cloud points of 1% solutions of molecularly homogeneous p-*t*-OPE_{7-10} in water are about 4–12C higher than those of normal p-*t*-OPE_{7-10}. The difference increases as the "E number" decreases, emphasizing the greater influence on cloud point of the lower members of a mixture of nonionic species.

Figure 5 is a plot of refractive index vs. E number and provides a comparison of single molecular species p-*t*-octylphenol-E_n with p-*t*-octylphenol-E_n of normal distribution. The curvature of both lines is simply a result of greater differences in refractive index between adjacent members of a series at lower E numbers than at the higher E numbers. This is not unexpected when one considers the relative differences in ratio of ethylene oxide (or oxygen) to octylphenol (or hydrocarbon).

The refractive index of normal distribution polymers, RE_x (n_{DRE_x}) is determined by the equation $n_{DRE_x} = N_{RE_1} n_{DRE_1} + N_{RE_2} n_{D\ 2} + N_{RE_3} n_{DRE_3} + \ldots$. Calculations of mole distribution for p-*t*-OPE_n (n = 2–10), based on Flory's equations (2) show that there are more mole with $E_{<n}$ than with $E_{>n}$, but that the difference decreases with increasing E number. Such calculations also indicate that there are fewer species of $E_{<n}$ than of $E_{>n}$. The increasing divergence of the lines with increasing E number in Figure 5 is related to these phenomena.

The differences of two physical properties, cloud point and refractive index, between normal p-*t*-octylphenol-E_n and single molecular species p-*t*-octylphenol-E_n suggest the possibility of differences in other physical properties, particularly those which affect surface active properties of nonionics.

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