

## A High Hydroxyl Group Content Found in High Molecular Weight Fractions of Poly(oxyethylene Glycol)

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### Synopsis

The results of a fractionation of high molecular weight poly(oxyethylene glycol) with the mixture benzene-isooctane are presented. The fractions are characterized by gel permeation chromatography (GPC), infrared spectroscopy, viscometry, and dialysis. A high hydroxyl content was found for the higher fractions, which is not compatible with a linear polyoxyethylene glycol molecule with hydroxyl endgroups. The presence of hydroxyl groups on the chain is improbable. The dialysis of the higher fractions in  $\text{CCl}_4$  and toluene shows that a surprising amount passes through the dialysis bag. The possibility of degradation of the polymer is considered. However, GPC analysis of the products of the dialysis suggest that the high molecular weight is made up of aggregates of middle-sized molecules and low molecular weight ones, held together by hydrogen bonding between hydroxyl and ether groups. Some results of a fractionation in water with the lower critical solubility temperature at  $99^\circ\text{C}$ . are given.

### INTRODUCTION

Although much work has been done on low molecular weight polyoxyethylene glycol (POE), very little has been published on the solution properties of high molecular weights since the extensive work of Bailey et al.<sup>1</sup> on unfractionated POE. The low molecular weight material is obtained by anionic polymerization which gives molecular weights lower than  $\approx 40,000$ . Higher molecular weights can be obtained by using as catalysts complex counterions derived from zinc or aluminum alkyls and alkoxyis. We believe that a reason for lack of work on high molecular weight POE is that its composition is not quite clear.

Our preliminary work with the unfractionated material showed a very large polydispersity. We have therefore analysed fractions which reveal another surprising feature of the polymer: the highest fractions with the largest  $[\eta]$  appear to have the highest hydroxyl content which is not consistent with a linear POE molecule with hydroxyl endgroups.

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## APPARATUS

### Viscometers

We used a four bulb viscosimeter of the Ubbelohde type, the capillary of which was 1 m. long and 1 mm in diameter; the shear rate could be varied from  $\simeq 130 \text{ sec.}^{-1}$  to  $\simeq 30 \text{ sec.}^{-1}$ ; the relative viscosities were extrapolated to zero gradient but the correction was never found greater than 1%. In some instances, we found a positive shear rate effect which we attributed to incomplete solubility of the polymer. These points were disregarded; the presence of a small negative shear gradient was a check on the dissolution.

### Gel Permeation Chromatography

The Waters apparatus was used with tetrahydrofuran as solvent. The molecular weights were calculated using the calibration established for low molecular weights. The solutions of the unfractionated samples and of the higher fractions were clear but left between 30 and 50% of the polymer on the filter. Thus, the molecular weights obtained by GPC are too low for the fractions; the GPC curves are, however, informative concerning the low molecular weight content of the fractions.

### Infrared Spectroscopy

We used a Perkin-Elmer 125 with NaCl windows: measurements were made at room temperature using a fan to avoid the heating of the cell by the beam. The cells had a 1-cm. path length. The  $\text{CCl}_4$  solvent was carefully distilled following standard procedures; when left over  $\text{P}_2\text{O}_5$ , it gave  $\simeq 5\%$  absorption at  $1710 \text{ cm.}^{-1}$  (Fig. 3). The polymer was dried in a vacuum oven during 10 hours at  $\simeq 30^\circ\text{C}$ . before being dissolved.

### Dialysis

The dialysis bags were of the usual type. They were cleaned as recommended in boiling aqueous solution of  $\text{CaCO}_3$  and rinsed in water and isopropanol before being used in toluene. The dialyses were carried out during 44–72 hr., depending on the temperature and concentration. The membrane was known to be permeable to molecular weights lower than 5000. The polymer outside and inside the dialysis bag was analysed by GPC. The solvents were distilled just before the dialysis; no anti-oxidant was added.

## EXPERIMENTAL

### Material

The POE was Union Carbide Polyox WSR 5M<sub>1</sub> sent to us by Dr. J. A. Faucher. According to Dr. Faucher, this sample was essentially the same except for molecular weight, as the better known WSR 35 and WSR 205,

and was prepared using a modified calcium amide catalyst along the lines described in the patent of Bailey and Hill (U.S. Patent 3,062,755 of Nov. 6, 1962). We have made some viscosity and infrared measurements on two other samples, WSR 5M<sub>3</sub> and WSR 5L<sub>1</sub>. The polymer was purified by dissolving in boiling CCl<sub>4</sub> and was reprecipitated by pouring into an excess of hexane; viscosities measured before and after the purification on the three samples showed the operation had not altered the molecular weights.

The low molecular weight POE 28,000 used together with its fractions, for infrared calibration, was prepared using KOH as a promoter. There was no catalyst left on the chain. The good agreement obtained in the determination of  $M_n$  by vapour pressure osmometry and by hydroxyl determination (acetylation in pyridine) shows there are only two terminal hydroxyls per chain.

### Measurements of Unfractionated Sample WSR 5M<sub>1</sub>

Its intrinsic viscosity at 25°C. was 2.45 dl./g. in water and 2.35 in benzene; using any of the three published viscosity relations<sup>1-3</sup> we found  $M_n = 318,000$  in water and  $M_v = 313,000$  in benzene.<sup>3,4</sup>  $M_w$  obtained by light scattering in water was  $390,000 \pm 50,000$ ; GPC measurements (Fig. 1) showed the sample to be highly polydisperse, there being a peak at 4000 and  $M_n = 8,500$ . The  $M_w$  value of 94,000 is too low, as discussed above. End-group analysis showed  $M_n = 14,000$ , confirming the large polydispersity.

### Fractionation

We followed the procedure of Price and Booth,<sup>4</sup> adding successive amounts of isooctane to a dilute solution of the polymer in benzene at 65°C.

## RESULTS ON THE FRACTIONS

### Viscometry

Table I gives the intrinsic viscosities of the nine fractions. One notices the first three fractions amount to 50% of the total weight. We give, in the third column of Table I, the  $M_v$  values calculated from Price and Booth's relation.<sup>4</sup> Actually, as F<sub>6</sub>, F<sub>7</sub>, F<sub>8</sub>, and F<sub>9</sub> were completely soluble in THF, their intrinsic viscosity was calculated from the GPC  $M_w$  value and this relation.

### Gel Permeation Chromatography

The results are shown in Table I and Figures 1 and 2 where the GPC curves are plotted on a logarithmic scale for  $M$ . The incomplete solubility of the polymer is reflected by the difference between  $M_v$  and  $M_w$  in Table I. One sees (Fig. 1) that F<sub>2</sub> ( $M_n = 95,000$ ) is less soluble than M<sub>1</sub> ( $M_n = 8500$ ) but does not show a pronounced peak around 3500; F<sub>3</sub> shows a

TABLE I  
Intrinsic Viscosities of Fractions (Benzene-Isocetane) in Benzene at 25°C.

Fract. no.	%	[ $\eta$ ], dl./g.	Mol. wt. <sup>a</sup> $M_v$ ( $\times 10^{-3}$ )	GPC mol. wt.	
				$M_w$ ( $\times 10^{-3}$ )	$M_n$ ( $\times 10^{-3}$ )
1	19.7	3.95	685	200 <sup>b</sup>	100
2	19.4	3.80	645	190 <sup>b</sup>	95
3	11.6	1.70	195	97 <sup>b</sup>	31.5
4	9.1	0.87	74	34 <sup>b</sup>	19
5	9.7	0.45	20.3	18.5	9.7
6	13.5	0.32 <sup>c</sup>		9.1	6.5
7	4.3	0.15 <sup>c</sup>		5.7	4.8
8	10.4	0.11 <sup>c</sup>		3.8	3.4
g	2.0			3.7	2.4
$M_1$		2.35	313	94	8.5

<sup>a</sup>  $M_v$  from [ $\eta$ ] and the relation of Price and Booth.<sup>4</sup>

<sup>b</sup> Fractions partially soluble in the THF.

<sup>c</sup> [ $\eta$ ] calculated from the relation of Price and Booth<sup>4</sup> and the GPC  $M_w$  values.

maximum at  $M = 75,000$  and another smaller one at 3500. Figure 2 shows similar GPC curves for  $F_4$ ,  $F_5$ , and  $F_6$ . One can conclude from the GPC curves, as well as from the viscosities, that the fractionation has been effective, although a very small amount of low molecular weight material has been left in all the fractions. As the low molecular weight of the lower fractions can be obtained from low molecular weight POE with a narrower

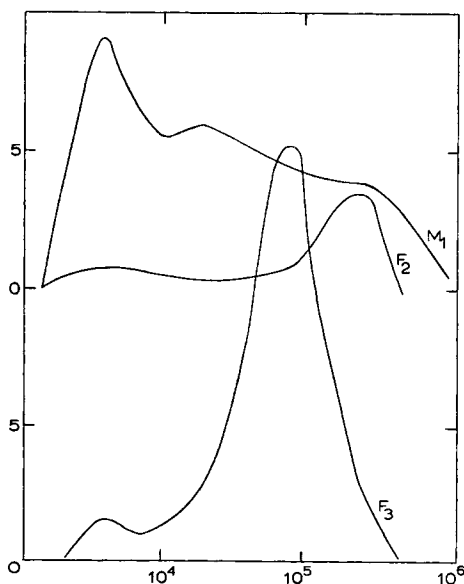


Fig. 1. GPC curves of fractions  $F_2$  and  $F_3$  and unfractionated  $M_1$ . Relative concentration of molecular weight  $M$  versus  $M$  on a log scale.

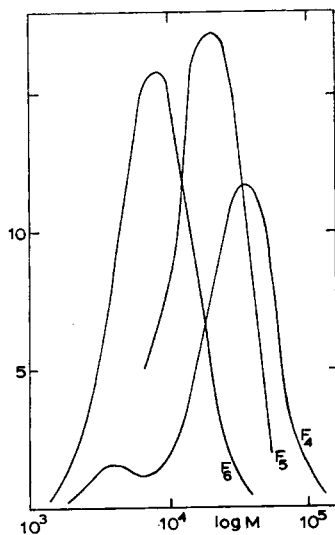


Fig. 2. GPC curves of fractions  $F_4$ ,  $F_5$ , and  $F_6$ . Relative concentration of molecular weight  $M$  versus  $M$  on a log scale.

distribution, we pursued the study only of the higher fractions by infrared spectroscopy and endgroup analysis.

### Infrared Spectroscopy

The bands associated with the hydroxyl groups are situated between  $3500\text{ cm}^{-1}$  and  $3700\text{ cm}^{-1}$ . The  $\text{CCl}_4$  solutions of POE show three bands

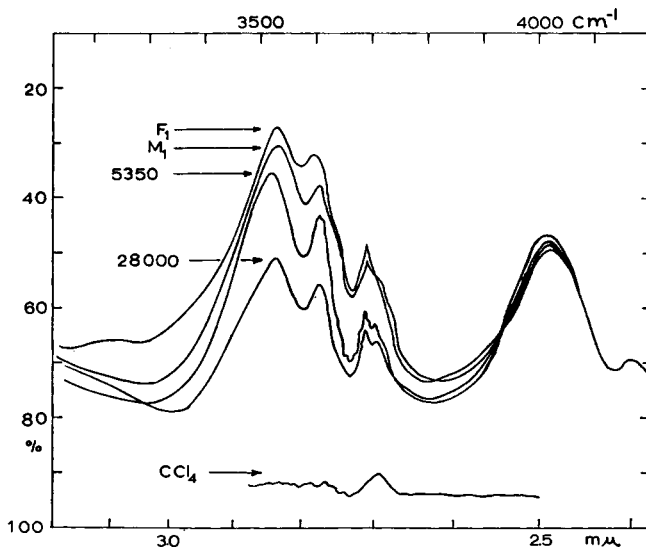


Fig. 3. Infrared spectra of four samples of POE in  $\text{CCl}_4$  at the same concentration (1.5%). Two of high molecular weight,  $M_1$  and  $F_1$ ; two of low molecular weights 5,350 and 28,000; at the bottom, noncompensated  $\text{CCl}_4$ , cell thickness 1 cm.

TABLE II  
 Molecular Weight Values

Fract. no.	Endgroup anal. $M_n$	Infrared <sup>a</sup> $M_n$			GPC $M_n$
		(1)	(2)	(3)	
F <sub>1</sub>	1,420	1,900	1,170	3,250	100,000
F <sub>2</sub>	1,980				95,000
F <sub>3</sub>	4,100	2,040			31,500
M <sub>1</sub>	14,250	3,280		3,600	8,500
1 <sub>1</sub>			1,930	4,000	5,940
1 <sub>2</sub>			2,350	5,500	9,400
1 <sub>3</sub>			4,800	5,150	23,000
Fraction of mol. wt.					
28,000					

<sup>a</sup> (1) By calibration with GPC values on fractionated, low molecular weights 1<sub>1</sub>, 1<sub>2</sub>, and 1<sub>3</sub>. (2) With  $\epsilon = 13$  and 26 m.<sup>2</sup>/mole. (3) With  $\epsilon = 36$  m.<sup>2</sup>/mole.

characteristic of the polymer, whatever the origin, and the molecular weight of the POE; a band at 4017 cm.<sup>-1</sup> is proportional to the quantity of polymer present. Figure 3 shows the spectra at about the same concentration (1.5%) of four samples: two of high molecular weight, M<sub>1</sub> and F<sub>1</sub>, and two of low molecular weight, 5350 and 28,000. To compare the samples, we draw on the same graph log  $I_0/I$  versus  $c$  for each sample from 0.2 to 2% and compare the slopes of the straight lines so obtained.

Table II gives the various  $M_n$  values for the fractions found, using the technique detailed in the Appendix. The surprising result is the high hydroxyl content of the higher fractions. F<sub>1</sub> contains more hydroxyls than F<sub>3</sub> and M<sub>1</sub>. The lowest hydroxyl content is found in low molecular weight POE (28,000). Repetition on polymer which had been dried longer gave similar results. The same trend was found for the 3525 and 3605 cm.<sup>-1</sup> bands.

The low molecular weight POE 28,000 and the high molecular weights are prepared by different catalysts; the great similarity of the infrared bands of the two make it very unlikely that the source of the bands is a hydroxyl-bearing catalyst in the case of the high molecular weight polymer, except if the catalyst happened to be a low molecular weight POE. A high hydroxyl content in the unfractionated polymer is not peculiar to WSR 5M<sub>1</sub>. We have also run infrared absorption spectra versus concentration for 5L<sub>1</sub> and 5M<sub>3</sub>; the spectra are quite similar and the hydroxyl amounts are of the same order of magnitude.

### Hydroxyl Endgroup Analysis

To confirm the results of the IR spectra, we made a hydroxyl determination using the perchlorite method.<sup>5</sup> Table II gives the results for three fractions and the initial polymer; the  $M_n$  values were calculated, allowing two hydroxyl groups per chain. The hydroxyl determination is independent of the presence of water when carried out in the correct conditions.

The hydrochloric acid produced by the reaction of the phosgene with water is eliminated by a nitrogen current before the polymer perchlorite is hydrolysed; on the suggestion of the authors of the method, we let the nitrogen current pass overnight instead of four hours; on F<sub>2</sub> we have found similar  $M_n$  values in the two cases.

These two methods confirm the finding that the hydroxyl content of the higher fractions is higher than for the lower fractions or the initial sample. The value of  $M_n$  found by GPC is of a different order from that obtained from infrared and endgroup analysis.

### Dialysis of the Fractions

The high GPC and viscosity molecular weights and the high hydroxyl content found on the fractions are not compatible with a linear POE molecule having hydroxyls at the end. To obtain more information on the composition of the polymer, we have dialysed the fractions and the non-fractionated samples. This should indicate whether the high molecular weight material is in fact an aggregate containing smaller molecules.

**Conditions of the Dialysis.** A 1% solution in toluene was dialysed at room temperature, the outside solvent being slowly stirred. The volume of the outside solvent was about fifteen times that of the solution; it was changed once during the dialysis. Under these conditions of concentration and temperature, the dialysing solution crystallizes slowly. The polymer extracted from the precipitated crystals and from the solution are kept separate. For this reason we have the initial F<sub>1</sub> divided in three: the precipitate of high molecular weight, P, the solution of smaller weight, S, and the dialysate, D. The variation of the quantity of P relative to that of S could be due to a change of room temperature between dialyses. This, however, does not affect the results, as will be seen in the GPC curves.

TABLE III  
Results of Dialysis.

Fract. no.	% <sup>a</sup>	[ $\eta$ ]	$M_v$	GPC mol. wt.		Solubility, %	
				$M_w$	$M_n$	Before dial.	After dial.
F <sub>1</sub> , 1%	P 48	3.2	492,000	205,000	52,300		50
	S 23	1.9	233,000	84,000	6,500	10	75
	D 29	0.11		4,000	3,200		100
F <sub>1</sub> , 0.1%	P 12						
	S 68	1.7	195,000	116,000	12,000	10	82
	D 20						100
F <sub>3</sub> , 1%	P 11						
	S 69			60,000	15,900	54	100
	D 20						100
F <sub>1w</sub>	P 31			132,000	50,000		45
	S 16	0.65	47,000	30,600	6,000	39	100
	D 53						100

<sup>a</sup> P, S, D: polymer in precipitate, solution, and dialysate, respectively.

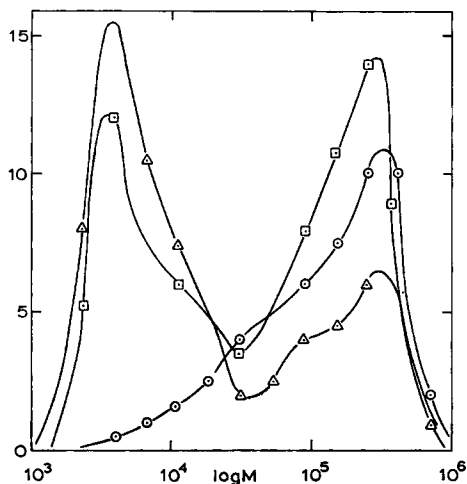


Fig. 4. GPC curves of dialyzed fractions in toluene: (○) F<sub>1</sub>, 1%, precipitate; (△) F<sub>1</sub>, 1%, solution; (□) F<sub>1</sub>, 0.1%, precipitate and solution.

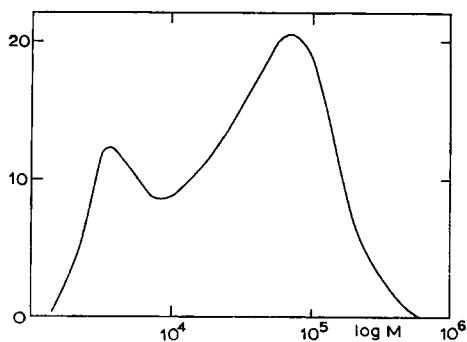


Fig. 5. GPC curve of F<sub>3</sub>, dialyzed solution, in toluene.

The polymer was recuperated by evaporating the solution under a 15 mm. vacuum and at  $\approx 40^\circ\text{C}$ . The dried deposit was dissolved in  $\text{CCl}_4$  and reprecipitated by hexane, the ratio of solvent to precipitant being about one to eight.

**Results of the Dialysis.** These are shown in Table III and Figures 4 and 5. The columns give the percentage of the different parts with their intrinsic viscosities in benzene and the molecular weights as calculated.<sup>4</sup> We also give the  $M_w$  and  $M_n$  values obtained by GPC and the solubility in THF before and after dialysis. In Figures 4 and 5, as in Figures 1 and 2, the abscissa corresponds to the volume of eluent or to  $M$  on a log scale. In this representation, the relative amounts of any two molecular weights cannot be directly estimated from their relative areas below the curve, as would be the case with  $M$  as abscissa. For instance, in Figure 4, the amount of low molecular weight polymer at 3500 is only a few per cent of the total.



The first interesting result is the large amount of polymer (between 20 and 30%) which passes through the dialysis membrane. (The conditions here are of course different from those in the above GPC determination.) To be sure of the effect of the stirring, we subjected an identical solution during 36 hr. to a much higher shear gradient than in the case of the dialysis. In this case, the magnetic stirrer was directly inside the solution turning at about the same speed as in the large volume of the outside solvent of the dialysis. The viscosity of the recuperated polymer had diminished by only 12%. On the other hand, if we add the viscosities of S, P and D after the dialysis, the total viscosity would have decreased by a factor of two. The second point is that the overall solubility of the dialysed products has increased. Figure 4 shows the GPC curves of P and S. For S, there are two peaks at 360,000 and 3500 molecular weight with some high molecular weight left in the solution, while the P fraction does not show any peak at 3500. The other curve shows the dialysis of  $F_1$  in dilute solution where P and S are mixed, and the two peaks are in good agreement with the 1% results.

The dialysis of  $F_3$  gives about the same picture (Fig. 5). The two peaks seen in the nondialysed sample (Fig. 1) exist at the same molecular weights 75,000 and 3500 as in the dialysed one but the proportion of low molecular weight has increased considerably. The overall solubility has increased from 50 to near 100%.

We have carried out the same experiment in  $CCl_4$  in order to be sure that the dialysis did not depend on the solvent.

### Fractionation in Water at 100°C. under $N_2$

Before we knew of the work of Price and Booth on the benzene isooctane system, we performed a fractionation at the LCST in water<sup>1-6</sup> which lies at 99°C. for the high molecular weight. This temperature is higher than the melting point of the POE and one very easily obtains two liquid phases in equilibrium. The polymer-rich phase could be collected at the bottom of the container. The various parts of the apparatus in glass, stainless steel and Teflon were under nitrogen to avoid degradation. The GPC results of the dialysis of the first fraction are mentioned in Table III. They are quite similar to those for the comparable fraction obtained using the procedure.<sup>4</sup>

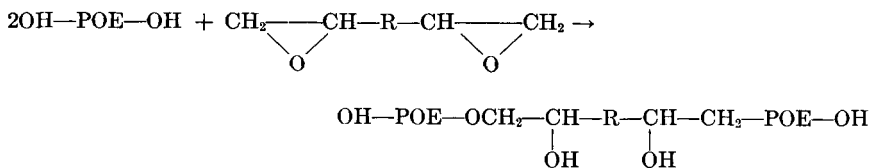
### Comments on the Dialysis Results and the High Hydroxyl Content of the Polymer

The results of the dialysis and the hydroxyl content of the higher fractions would suggest two possible explanations:

- (1) Hydroxyls along the POE chain of the high molecular weights.
- (2) Aggregates of middle and low molecular weights (the two peaks seen on the GPC curves) held together by hydrogen bonds.

These two possibilities will now be discussed beginning with (1) which seems to us less likely.

**Hydroxyls on the Chain.** Bush et al.,<sup>5</sup> developing the phosgene method for hydroxyl determination, tested it on low molecular weight POE. For molecular weights 1000, 3000, and 6000, they found good agreement with other  $M_n$  determinations. On the other hand, for molecular weight 20,000 Carbowax (Union Carbide) they found  $M_n = 6000$ . They explained this high hydroxyl content by the way this polymer is prepared, i.e., from two 6000 molecular weight molecules bonded together by a diepoxide such as:



In this way, one sees that high molecular weight POE so synthesized would have the same hydroxyl content as the initial POE used. A constant hydroxyl content, whatever the molecular weight, is not at variance with the present experimental facts; the  $F_1$ ,  $F_3$ ,  $M_1$  hydroxyl contents are of the same order of magnitude. To explain the actual value, the initial POE should be low, around 3500. The higher fractions would be, as in normal cases, the higher molecular weights.

To explain the dialysis results and in particular the 30% dialysable polymer, one would have to invoke a chain degradation which would, through the hydroxyls, cut the chain in 3500 molecular weight sections. The maintenance of the high molecular weight peak at the same value before and after dialysis is also difficult to interpret. One would have expected one large peak rather than two. The great similarity between the hydroxyl bands of low and high molecular weight POE (Fig. 3) is not in favour of having, in the first case, primary alcohols and, in the second case, secondary ones, although intramolecular bonding between these hydroxyls and the ether groups could reduce the difference between bands due to primary and secondary alcohols. Finally, one finds several references where a direct determination has shown that a high hydroxyl content does not exist (as with a Dow Corning POE of 20,000 molecular weight<sup>7</sup> or with a material of 400,000 molecular weight prepared using an Al alkoxide catalyst<sup>8</sup>). A high hydroxyl content has not been suggested in the case of Polyox.<sup>1</sup>

**Aggregates.** The hypothetical aggregates would be due to hydrogen bonding between hydroxyl and etheroxide groups, which are known to interact strongly. The association would have to be very stable, but this could be due to a cooperative effect. In the solvent-nonsolvent mixture used for fractionation, the aggregates would have to survive and even be separated according to their size; when dissolved in THF, only a very small proportion of the aggregates of the higher fractions dissociate and go

through the filters; the dialysis, allowing for the escape of the low molecular weights, favours the dissociation.

The dialysis results show that in a 0.1% solution, 1% of the total polymer is of very low molecular weight. One might expect the same amount of low molecular weight material in any dilute solution experiment such as our viscometric and light scattering determinations at concentrations as low as 0.1%. However, this amount of dissociated polymer would probably have a negligible effect on the usual type of measurements. It is usually accepted<sup>9</sup> that intrinsic viscosities are not sensitive to association and that light scattering is not much affected by the presence of low molecular weight material.

We think the hypothesis of aggregates of small molecular weights ( $\approx 3500$ ) with higher molecular weights is more likely than that of hydroxyls on the chain for the following reasons: (1) it would explain the polymer going through the dialysis bag without invoking a degradation which does not occur when the polymeric solution is stirred with a higher shear gradient, (2) it would be more consistent with the fact that the maximum of the GPC curve does not change after the dialysis; the maximum should be displaced towards lower molecular weights in case of random scission, and (3) the presence of endgroup hydroxyls rather than secondary ones would be more consistent with the fact that the hydroxyl region of the infrared spectra shows the same bands for the high and low molecular weight polymers, the latter being known to contain only terminal hydroxyl groups.

The presence of these aggregates is not in contradiction with the ability of this nonfractionated high molecular weight POE to associate strongly<sup>10</sup> with polyacrylic acid to form an insoluble compound. There are still many ether groups not utilized by the hydroxyls. The density of interacting groups presumably creates the difference of solubility and stability in the two cases. The observed increased solubility of the dialysed samples may be explained by the departure of many low molecular weight molecules. This reduces the number of interacting groups inside the polymer aggregate and then favours the interaction with the solvent.

However, more information is undoubtedly needed to decide finally between the two possibilities of aggregation of low molecular weights and of hydroxyl groups along the chain.

## Appendix

### Semiquantitative Evaluation of the Hydroxyl Content

(1) We have used three fractionated, low molecular weight POE, called 1<sub>1</sub>, 1<sub>2</sub>, and 1<sub>3</sub>, whose molecular weights  $M_n$ , as determined by GPC, were 5400, 9400, and 23,000. The  $M_w/M_n$  of these samples lies between 1.07 and 1.2.  $\log I_0/I$  at 3525  $\text{cm}^{-1}$  is plotted against  $1/M_n$ ; the line determined by these three points, for evaluating  $1/M_n$  for the higher fractions, was used. Column 1 of the IR results in Table II gives the values found.

(2) Following Langbein's method,<sup>11</sup> we can use known extinction coefficients, respectively 13 and 26  $\text{m}^2/\text{mole}$  for the free and bonded hydroxyls in  $\text{CCl}_4$  (column 2).

In our case it is felt that the absolute determination of the hydroxyl content is only approximate, owing to the high polymer concentration, which makes dubious the use of normal extinction coefficients. Furthermore, the surrounding ether groups can contribute to an increase in the extinction coefficient, since the latter is known to increase by 5, passing from a  $\text{CCl}_4$  to an ether solution.<sup>11</sup> Column 3 is obtained by using  $\epsilon = 36 \text{ m}^2/\text{mole}$  and only the  $3525 \text{ cm}^{-1}$  band. It seems, however, that the infrared method can give rapid comparative information about the hydroxyl content of the POE since, as we see here, the results are supported by other methods, such as the endgroup analysis.

### Identification of the Bands

Langbein attributes the  $3605$  and  $3525 \text{ cm}^{-1}$  bands respectively to "free" and bonded hydroxyls and the  $3695$ – $3705 \text{ cm}^{-1}$  doublet to water. The doublet does not appear at concentrations smaller than  $0.2\%$ . It would be due to water strongly bound to the polymer or to another type of hydrogen bonding. The usual free OH band at  $3640 \text{ cm}^{-1}$  could be displaced owing to the presence of the ether groups, as is the case of butyl alcohol, whose maximum at  $3636 \text{ cm}^{-1}$  in  $\text{CCl}_4$  is displaced to  $3500$  and  $3505 \text{ cm}^{-1}$  in ethyl and butyl ether, respectively.<sup>12,13</sup> On the other hand, vibrations at  $3600$  and  $3511 \text{ cm}^{-1}$  have been found<sup>14</sup> for substituted ethoxyethanol,  $\text{R}-\text{OCH}_2\text{CH}_2-\text{OH}$ , in  $\text{CCl}_4$ . In our case the "free" hydroxyls are possibly in structures similar to the pentagonal chelates suggested by Quivoron and Neel.<sup>14</sup> One is surprised not to find a band characteristic of intermolecular bonding, particularly at concentrations as high as  $2\%$  and with a high hydroxyl content in the solution. Apparently, no intermolecular bond could be seen, either, in solutions of polyoxypropylene,<sup>15</sup> which had concentrations of hydroxyl groups 300 times greater; this might be explained by the polymer chains preventing the hydroxyl endgroups from meeting. There could be some steric hindrance in the polymeric chain, of the kind which exists in branched alcohols: 2,4-dimethyl-3-ethylpentanol<sup>16</sup> in solution shows four fine bands between  $3500$  and  $3640 \text{ cm}^{-1}$  but no intermolecular bands, even when the alcohol is pure. It is possible, too, that the effect of the chain is to lower the frequency of intermolecular vibration and so prevent its observation by interference with the  $\text{CH}_2$  band. However, in the solid state the POE shows one broad band<sup>11</sup> at  $3420 \text{ cm}^{-1}$ , which seems to be due to intermolecular association.

One may add, incidentally, that toward a low molecular weight proton donor the POE behaves like 1,4-dioxane, which may be considered its dimer: if one adds to a dilute solution of *o*-cresol a small amount of 1,4-dioxane or of POE, the free OH peak diminishes, giving in both cases a broad band at  $3380 \text{ cm}^{-1}$ .

I would like to thank Messrs. Kovacs and Pierson for the fractions of POE; Mr. Kohler and Miss Grubisic for the GPC measurements; Mr. Calmé for the endgroup analysis; Mrs. F. Villain who did most of the viscosities and light-scattering experiments.

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