Practical and Theoretical Molecular Weights in Polyaddition Reactions of Ethylene and Propylene Oxide

AMABILE PENATI, *Istituto di Chimica Industriale Politecnico, 20133 Milano, Italy,* CARLO MAFFEZZONI and ENRICO MORETTI, *Pressindustria S.p.A., 20046 Biassono, Milano, Italy*

Synopsis

The addition reactions of ethylene oxide and/or propylene oxide catalyzed by KOH and initiated with compounds containing free hydroxyls are followed by secondary reactions which vary the expected molecular weight. By using ethylene oxide, diols are formed and by using propylene oxide, both diols and unsaturated monofunctional compounds are formed. These products are usually characterized by their hydroxyl number. The average molecular weight is found by taking into consideration the starter functionality only. There are often some behavioral differences among similar products owing to the different quantity and chain length of the secondary products contained therein. The secondary products are analyzed and the quantity of the secondary products were determined from the hydroxyl number values and from the unsaturation of reagents and products. In the case of monofunctional adducts using the calculation method, the results have been experimentally confirmed.

INTRODUCTION

The addition reactions of ethylene oxide (EO) and propylene oxide (PO) catalyzed by KOH and initiated with compounds containing free hydroxyls have taken on significant industrial importance in the last decade. When EO is polymerized, in addition to the expected product, other products, with different molecular weights are formed; this is due to the oxide polyaddition, both with the humidity present and with the catalyst itself, producing polyoxyethyleneglycols (PEG).[1,2]

While analytical methods are known to determine the PEG amount present with a monofunctional EO adduct,[3-5] as well as a calculation method based on the hydroxyl number,[6] analytical and calculation methods are not known to determine the amount of PEG in the presence of adducts with higher functionality. Polyoxypropyleneglycols (PPG) are formed during the PO adducts preparation and, furthermore, an oxide isomerization occurs, which produce an unsaturated compound (allyl alcohol). The latter compound can initiate new chains with the formation of unsaturated, monohydroxyl functionalized compounds.[2,7-10] The relative importance of these secondary reactions depends on the reaction conditions. Their effect on the hydroxyl analysis is only apparent when the adduct reaches a certain molecular weight. In the case of adducts with EO that are initiated with ethylene glycol, the difference between the theoretical molecular weight, estimated from the reacted EO, and the practical molecular weight, obtained from the hydroxyl number[11] is apparent after the molecular-weight exceeds about 1500 (Fig. 1).

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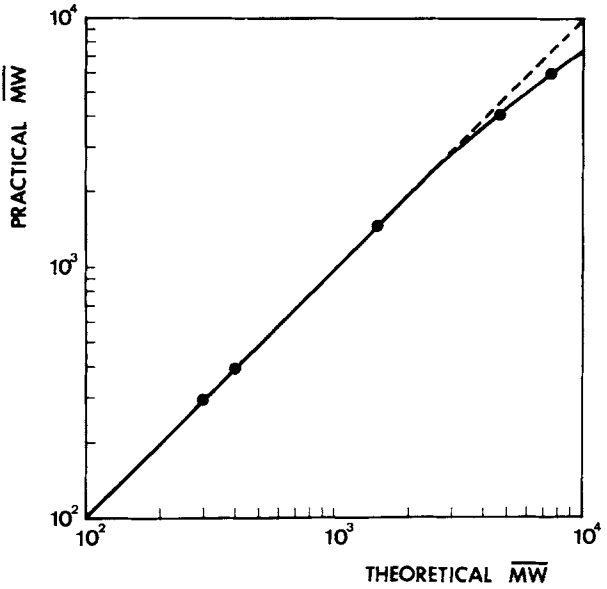

Fig. 1. Theoretical vs. practical molecular weights in ethylene glycol/ethylene oxide reaction; reaction temp. = 160–180°C.

In the case of PO adducts (reactions with glycerine or propylene glycol), the difference between the theoretical and practical value appears with molecular weights of about 1500 and 1000, respectively (Figs. 2 and 3). The difference at lower molecular weights, obtained with PO in comparison with EO, depends on the unsaturated monofunctional compound formation. These adducts, like the

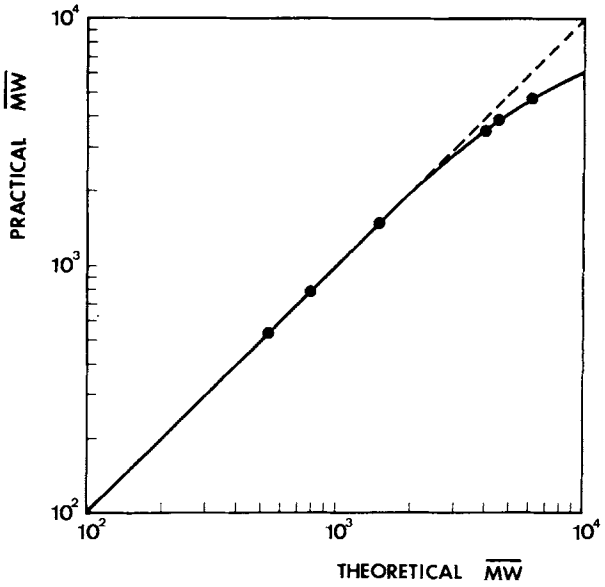

Fig. 2. Theoretical vs. practical molecular weights in glycerine/propylene oxide reaction; reaction temp. = 120–125°C.

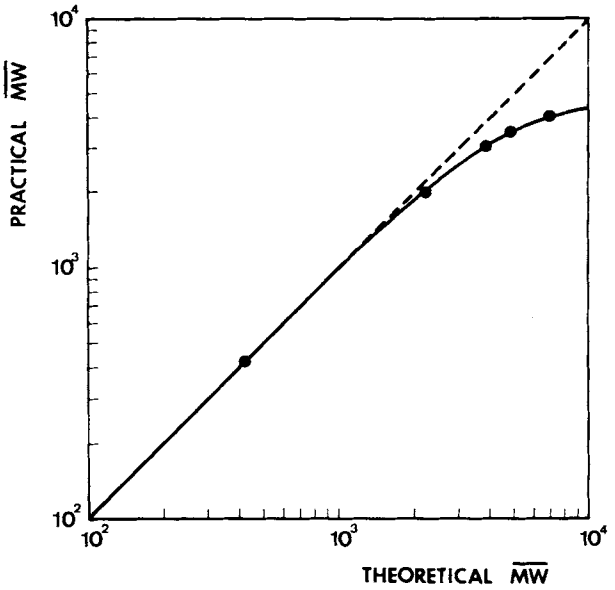

Fig. 3. Theoretical vs. practical molecular weights in propyleneglycol/propylene oxide reaction; reaction temp. = 120–125°C.

surface-active and the polyether polyols, are classified on the basis of hydroxyl number, and the practical molecular weight is calculated using the starter functionality. The aim of this work is to determine the quantity of secondary products and to estimate their true molecular weight from the reaction data and from the ethoxylated or propoxylated products analyses.

THEORETICAL

Reactions with Ethylene Oxide

When a starter, having a functionality f, is ethoxylated, besides the desired adduct, certain diols with different molecular weights[1] originated by the water present and by the catalyst KOH are obtained. Experiments showed that, under reaction conditions, the diol formation is delayed with respect to the chain formation of the adduct. At the end of the reaction if the ethoxylated chains of the adduct contain m units of EO for each OH group of the starter, the diol chains will contain $(m - y)$ units of EO:

(a) $R - (OH)_f + fm\ CH_2—CH_2 \xrightarrow{K^+} R - [O—(CH_2—CH_2—O)_m - H]_f$

(b) $H_2O + 2\,(m - y)\ CH_2—CH_2 \xrightarrow{K^+}$

$$H - (O—CH_2—CH_2)_{m-y}—O—(CH_2—CH_2—O)_{m-y}\ H$$

Thus, from a generic starter having a molecular weight MW_s ($\overline{MW}_s$ if a partially ethoxylated starter is used) the average molecular weights of the adducts $\overline{MW}_a$ and of the diols $\overline{MW}_d$ which accompany it, will be the following:

$$\overline{MW}_a = MW_s + fm\ MW_{EO} \quad (1)$$

$$\overline{MW}_d = 2(m - y)\ MW_{EO} + MW_{H_2O} \quad (2)$$

The diol molecular weight is always related to the previous formula if they originated from water or KOH. The molecular weights of these products are usually determined by the hydroxyl number NOH[11]:

$$\overline{MW} = \frac{56{,}100 \cdot f}{NOH} \quad (3)$$

In the absence of secondary reactions, the hydroxyls do not change during the reaction; and the following relation is satisfied:

$$NOH_a \cdot W_a = NOH_s \cdot W_s \quad (4)$$

When diols are formed, the hydroxyl balance assumes the expression for a final product of hydroxyl number NOH_f having weight W_f:

$$NOH_f \cdot W_f = NOH_a \cdot W_a + NOH_d \cdot W_d \quad (5)$$

where NOH_d is the hydroxyl number of the diols having weight W_d. Considering Eqs. (3) and (4), Eq. (5) can be written:

$$NOH_f W_f = NOH_s W_s + 2 \cdot 56{,}100 \cdot m_d \quad (6)$$

From this equation it is possible to calculate m_d, i.e., the number of moles of diol formed.

The increase in weight of the starter during polymerization is due to the reacted EO and the water which formed the diols. If m_t is the total moles of EO reacted, the following material balance exist:

$$W_f - W_s = m_t MW_{EO} + m_d MW_{H_2O} \quad (7)$$

The following relation is a mass balance for the reacted EO:

$$m_t = m_s \cdot f \cdot m + m_d \cdot 2(m - y) \quad (8)$$

where m_s is the moles of starter. With m_d [eq. (6)] and values for y, it is possible to obtain m, i.e., the EO units per chain of product and $(m - y)$, the EO units per chain of diol. From these data and eqs. (1) and (2), the molecular weight of the adduct $\overline{MW}_a$ and of the diols $\overline{MW}_d$ can be determined. By knowing the molar fractions, it is possible to calculate the weight percent of adduct and diols and the true average molecular weight of the product.

Reactions with Propylene Oxide

When PO is used instead of EO, the PO isomerization to allyl alcohol, which can initiate monofunctional chains,[2,7-10] decreases the molecular weight of the product:

(c) $CH_2\text{—}CH\text{—}CH_3 \longrightarrow CH_2{=}CH - CH_2OH$ (O)

(d) $CH_2{=}CH - CH_2OH + (n - x_i - 1)\ CH_2\text{—}CH\text{—}CH_3 \xrightarrow{K^+}$ (O)

$$CH_2{=}CH - CH_2 - O - (CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - O)_{n-x_{i-1}} - H$$

The moles of unsaturated monofunctional chains m_i with an average molecular weight $\overline{MW}_i$, can be analytically determined.[11] If n are the units of PO in the adduct chain, the unsaturated chains will contain $(n - x_i)$ units of PO and the diols chain will contain $(n - x_d)$ of PO. Thus, the following relationships exist:

$$\overline{MW}_a = MW_s + fn MW_{PO} \tag{9}$$

$$\overline{MW}_i = (n - x_i)\, MW_{PO} \tag{10}$$

$$\overline{MW}_d = 2(n - x_d)\, MW_{PO} + MW_{H_2O} \tag{11}$$

The hydroxyl number results in the following relation:

$$NOH_f \cdot W_f = NOH_s W_s + 56.100\, m_i + 2 \cdot 56{,}100\, m_d \tag{12}$$

Eqs. (7) and (8) now assume the form:

$$W_f - W_s = n_t\, MW_{PO} + m_d\, MW_{H_2O} \tag{13}$$

$$n_t = m_s fn + m_i(n - x_i) + m_d \cdot 2(n - x_d) \tag{14}$$

where n_t is the total number of moles of reacted PO.

Equation (14) yields the n units of PO contained in the adduct chains, the $(n - x_i)$ of PO contained in unsaturated chains, and the $(n - x_d)$ of PO in diols chains by assigning a value to x_i and x_d parameters. From this data and from eqs. (9)–(11) the molecular weight of the adduct $\overline{MW}_a$, of the unsaturated compounds $\overline{MW}_i$ and of the diols $\overline{MW}_d$ can be obtained. From known molar fractions, it is possible to calculate the weight percent of adduct, diols, and unsaturated compounds and, in the end, the true average molecular weight of the product.

Co-Addition of Ethylene Oxide and Propylene Oxide

In reacting a starter with EO and PO simultaneously,[12] the resultant product will contain m units of EO and n units of PO. The monofunctional unsaturated chains will be shorter and contain $(n - x_i)$ units of PO and $(m - y_i)$ of EO, while the diol chains will contain $(n - x_d)$ of PO and $(m - y_d)$ of EO. We will obtain three average molecular weights:

$$\overline{MW}_a = MW_s + fn MW_{PO} + fm MW_{EO} \tag{15}$$

$$\overline{MW}_i = (n - x_i)\, MW_{PO} + (m - y_i) MW_{EO} \tag{16}$$

$$\overline{MW}_d = 2[(n - x_d)\, MW_{PO} + (m - y_d) MW_{EO}] + MW_{H_2O} \tag{17}$$

The equation for the hydroxyl balance is the same as eq. (12).

If n_t and m_t are the total reacted moles of PO and EO the following expression is obtained:

$$W_f - W_s = n_t\, MW_{PO} + m_t\, MW_{EO} + m_d\, MW_{H_2O} \tag{18}$$

If $n_t = R\, m_t$, with R the molar PO/EO ratio, eq. (18) may be written as:

$$W_f - W_s = m_t(R\, MW_{PO} + MW_{EO}) + m_d\, MW_{H_2O} \tag{19}$$

and the material balance in terms of moles will have the following form:

$$n_t + m_t = m_t(1 + R) = m_s f(m + n) + m_i[(n - x_i) + (m - y_i)] + m_d \cdot 2[(n - x_d) + (m - y_d)] \tag{20}$$

It is easier to operate with the partial balance equations for EO and PO:

$$n_t = m_s f n + m_i(n - x_i) + m_d \cdot 2(n - x_d) \quad (21)$$

$$m_t = m_s f m + m_i(m - y_i) + m_d \cdot 2(m - y_d) \quad (22)$$

Having calculated m_d from the hydroxyl balance, using eqs. (21) and (22), by tabulating the values of m and n in functions of x_i, x_d, y_i, and y_d and choosing the opportune $(x_i + y_i)$ and $(x_d + y_d)$ values, it is possible to obtain the three molecular weights. The distribution of EO and PO units, the weight percent of the components, and the true average molecular weight of the product are also obtained.

Method Limitations

As this calculation method is based on the hydroxyl number test, it is necessary to take into consideration the errors made in this determination which can be as high as ±0.5. These experimental errors result in an uncertainty in the calculation of the moles of diol formed. It has been experimentally proven that the influence of this error is very important for small diol molar fractions in the final product. It decreases when its molar fraction grows. In contrast this experimental error has little influence in y or x and m and n determination and therefore, in the average molecular weight values. Where this error is more critical, these variations will be examined.

EXPERIMENTAL

Oxyalkylation Plant Description

The reactions investigated in this study were conducted with a particular process developed by Pressindustria Co. (Fig. 4). The reaction is carried out in a special gas–liquid contactor where the starter is in a liquid phase, moving as a piston flow through a gaseous oxide atmosphere. As a result, a rapid reaction occurs without large increases in temperature and pressure. A predeterminated starter quantity is charged together with the catalyst. A portion of the water present is removed by heating the reactor content under vacuum. The system is then purged with N_2 to remove traces of oxygen; oxide is then fed to the reactor, where it instantly vaporizes. After having fed the fixed quantity of oxide, the product undergoes a short cooking phase and then is cooled and discharged from the reactor. The reaction heat is removed by a heat exchanger.

Reagents Used

The starters were: nonylphenol, pure at 98% having a max. H_2O content of 0.1%; glycerine, pure at 98% having a max. H_2O content of 0.2%; pure ethylene glycol having a max. H_2O content of 0.3%; pure propylene glycol having a max. H_2O content of 0.2%. The catalyst used was solid KOH in chip or tablet form with a titrate on the dry substance of 99.5% and a water content of 10% max. Excluding ethylene glycol the starter and catalysts were stripped before reaction to a water quantity less than 0.05%. The ethylene oxide used was at 99.9%, with a water content of 0.03%. The propylene oxide used was at 99.85%, with a water content of 0.05%.

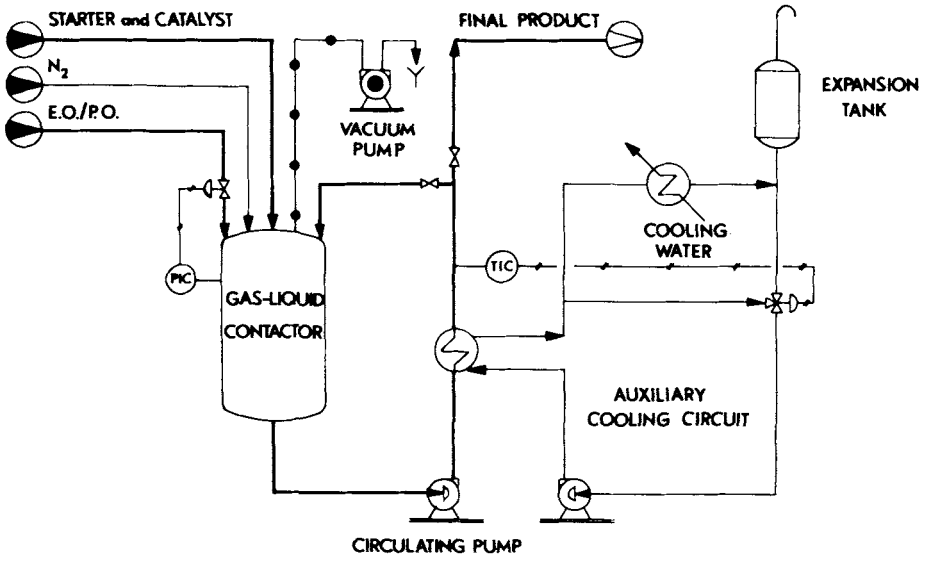

Fig. 4. Pressindustria oxyalkylation plant process used for experimental tests: vol = 140 liter total.

Hydroxyl Number Determination

Free OH groups were acetylated at 98°C for 1 hr with acetic anhydride in pyridine. After the H_2O addition and cooling, the acetic acid formed was titrated with alcoholic KOH, and the difference from a blank test conducted in parallel was calculated for the mg KOH/g of sample, which per definition, is the NOH, hydroxyl number.

Unsaturation Determination

This method is based on the treatment of double bonds present in the sample with a methanolic solution of mercury acetate. Subsequently, this system is titrated with alcoholic KOH in the presence of phenolphthalein and NaBr. From the difference between the analysis and a blank test, the KOH mequiv/g of sample due to the unsaturation was calculated.

Weibull Determination Method of PEG in Monofunctional Adducts

This method is based on the partition, at 35°C, of the polyethyleneglycols and the adduct between ethyl acetate and sodium chloride solution. The polyglycols are then extracted from the sodium chloride solution with chloroform and weighed after the solvent evaporates (the amount of sodium chloride in the residual is also determined).

APPLICATION OF METHOD

Example One

The starter was 12 kg of nonylphenol ($f = 1$) with $NOH_s = 250.5$. After EO addition, the product weighed 84 kg and had $NOH_f = 36.5$. $MW_s = 224$ and $m_s = 53.57$ [eq. (3)]. Since the hydroxyl number determination involves an error of ±0.5 applying eq. (6) results in $m_d = 0.535 \pm 0.375$ and from eq. (7), $m_t = 1636.15 \pm 0.15$. Since NOH_f is 36, substitution into eq. (8) results in

$$m = \frac{0.32y + 1636.3}{53.89}$$

which yields the values in Table I, for $NOH_f = 36.5$:

$$m = \frac{1.07y + 1636.15}{54.64}$$

which yields the values also shown in Table I, for $NOH_f = 37$:

$$m = \frac{1.82y + 1636}{55.39}$$

values which are also shown in Table I. The corresponding PEG percentages are reported as a function of y (Fig. 5). From the Weibull method, a PEG content of 1.8% was found with $NOH_d = 55$. By considering the experimental error ±0.5, we obtain [eq. (3)] a PEG molecular weight of 2040 ± 19.

By now applying eq. (2) and inserting the m values as a function of y for the different values of NOH_f we obtain: with $NOH_f = 36$, $y = 7.43 \pm 0.21$; with $NOH_f = 36.5$, $y = 7.11 \pm 0.21$; and with $NOH_f = 37$, $y = 6.75 \pm 0.21$.

The intersection, with the straight line at 1.8% of PEG (Fig. 5), is obtained when the NOH_f value is 36.78. With $NOH_f = 36.78$ we obtain 6.9 for y; 29.1 for m; 1540 for $\overline{MW}_a$; 2042 for $\overline{MW}_d$; and 1.8 for the weight percent of d. Therefore,

TABLE I
Values for m Found by Substitution in eq. (8)

y	m	$\overline{MW}_a$	$\overline{MW}_d$
	$m = (0.32y + 1636.3)/53.89$		
5	30.39	1561	2252
10	30.42	1562	1815
15	30.45	1564	1378
20	30.48	1565	940
25	30.51	1566	503
	$m = (1.07y + 1636.15)/54.64$		
5	30.04	1546	2221
10	30.14	1550	1790
15	30.24	1555	1359
20	30.34	1559	928
25	30.43	1563	496
	$m = (1.82y + 1636)/55.39$		
5	29.70	1531	2192
10	29.86	1538	1566
15	30.03	1545	1341
20	30.19	1552	915
25	30.36	1560	490

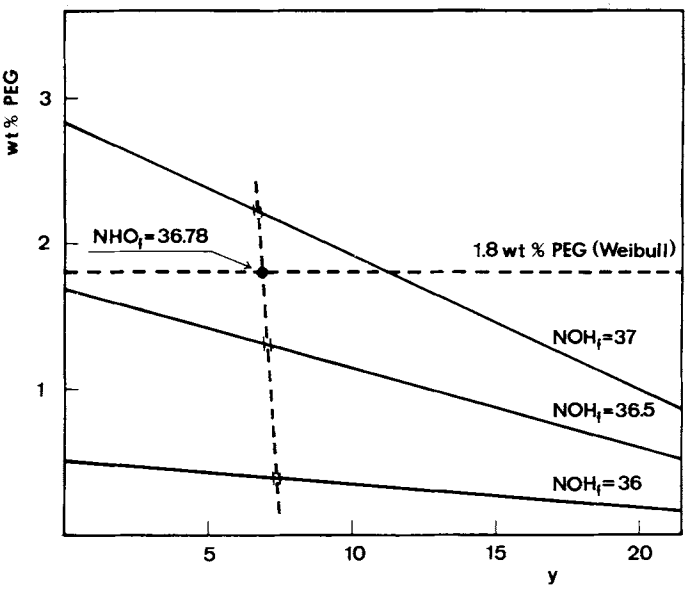

Fig. 5. PEG wt % vs. y values with respect to NOH_f variations, relevant to Example One.

we can determine the y value. While the practical molecular weight is 1537, the true molecular weight of product is, actually, 1547.

Example Two

The starter was 16 kg of product already partially ethoxylated with functionality $f = 2$ and $NOH_s = 74$. After the addition of EO, the product weighed 50.2 kg and $NOH_f = 26.7$. $\overline{MW}_s = 1516$ and $m_s = 10.55$ [eq. (3)]. It was found [eq. (6)] that $m_d = 1.39$ and from the eq. (7) $m_t = 776.7$. Equation (8) gives the expression:

$$m = \frac{2.78y + 776.7}{23.88}$$

which, with y values of 5, 10, 15, 20, 25, and 30, yields m values of 33.11, 33.69, 34.27, 34.85, 35.44, and 36.02. The molecular weights $\overline{MW}_a$ and $\overline{MW}_d$, in the function of y are reported in Figure 6, together with the weight percent of diols. In order to value what is y (Fig. 6), we utilize Figure 7, which reports the PEG percent from ethoxylation tests of monofunctional products versus the EO chain length, independent of the actual reaction. There is a good correlation between the chain length and PEG content, since PEG is principally originated from the humidity present in the EO. We can estimate that the value of y is most probably between 5 and 6. The practical molecular weight corresponds to the true molecular weight because both the adduct and the byproduct have the same functionality.

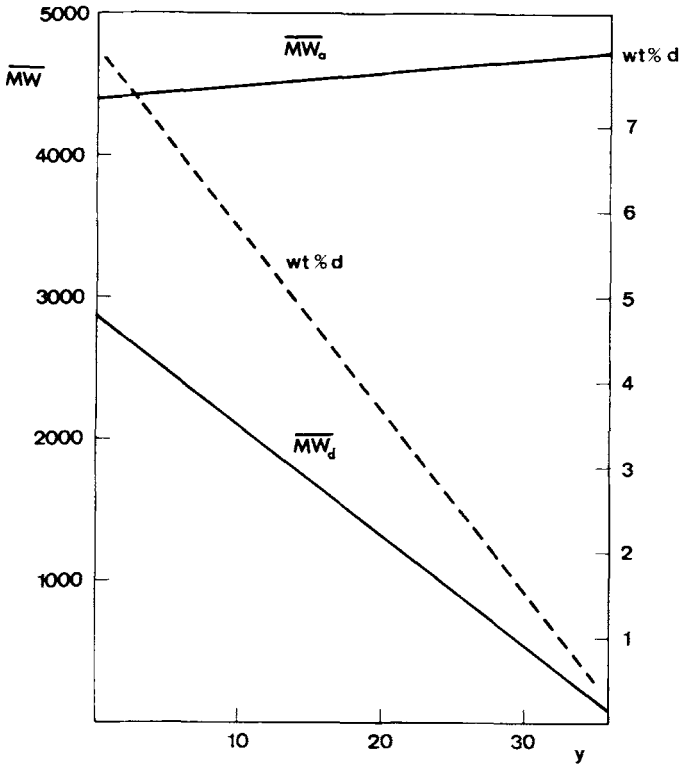

Fig. 6. $\overline{MW}_a$, $\overline{MW}_d$, and diols wt % value (PEG in this case) vs. y relevant to Example Two.

Example Three

The starter, 12 kg of product, has a functionality $f = 3$ and $NOH_s = 286$. After the addition of EO and PO mixture at 10 wt % in EO, the product weighed 88 kg and had a $NOH_f = 44.3$ and an unsaturation content of 0.038 mequiv/g. By applying eq. (3), it was found that $\overline{MW}_s = 588.5$ and $m_s = 20.39$. The unsaturated monofunctional moles equated $m_i = 3.34$. From eq. (12) it was found that $m_d = 2.48$. Being $R = n_t/m_t = 6.83$ from eqs. (18) and (19): $m_t = 172.6$ (EO) and $n_t = 1178.7$ (PO was found). Equation (21) for PO yields:

$$n = \frac{3.34\,x_i + 4.96\,x_d + 1178.7}{69.47}$$

and eq. (22) for EO gives:

$$m = \frac{3.34\,y_i + 4.96\,y_d + 172.6}{69.47}$$

To correlate the x_i, x_d, and y_i, y_d parameters, it is necessary to make some hypotheses. If we insert the values of n in the function of x_i and x_d and the values of m in the function of y_i and y_d into eq. (17), we obtain only one equation which correlates all of the parameters. In order to obtain the diol molecular weight to be introduced in this equation, consider that Figure 7 is valid for this case. Considering the exact average molecular weight of the oxide mixture, we obtain a diol percent of about 5.2%. The true functionality of the product is 2.65, in eq. (3). A molecular weight, equivalent to 5.2% of diols, must be 1845. Therefore, we obtain:

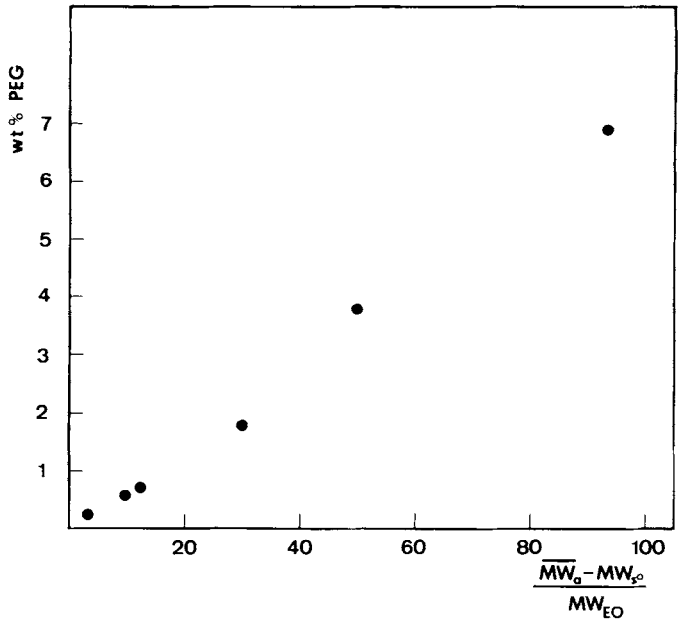

Fig. 7. Experimental values of PEG vs. $(\overline{MW}_a - \overline{MW}_{s^o})/MW_{EO}$ obtained with monofunctional adducts. (MW_{s^o} states initial starter Nonylphenol in this case).

$$1845 = 2\left[\left(\frac{3.34\,x_i + 4.96x_d + 1178.7}{69.47} - x_d\right)58 + \left(\frac{3.34\,y_i + 4.96\,y_d + 172.6}{69.47} - y_d\right)44\right] + 18$$

which rearranged becomes:

$$(58\,x_i + 44\,y_i) - 19.31(58x_d + 44\,y_d) + 3742 = 0$$

Since the oxides mixture is continuously fed, the oxide composition along the chains is constant as is $x_i/y_i = x_d/y_d = R = 6.83$. The previous equation now becomes: $x_i = 19.36x_d - 58.055$. By tabulating we obtain the values shown in Table II. Having previously introduced the hypothesis of a known diol percent, the x_d value changes within a small range, while x_i can vary from 0 to n.

The monofunctional unsaturated compound may analytically be checked when only a few units of oxide have been added. The unsaturation increases as the reaction proceeds. Therefore, there is a similar trend in the formation and growth of the diols. If x_i and x_d values are similar we obtain $x_i = x_d = 3.19$; $y_i = y_d = 0.47$; $(x_i + y_i) = 3.66$; $(x_d + y_d) = 3.66$; $n = 17.35$; $m = 2.54$; $(n + m) = 19.89$; $\overline{MW}_a = 3943$; wt % $a = 91.4$; $\overline{MW}_i = 908$; wt % $i = 3.4$; $\overline{MW}_d = 1838$; and

TABLE II
Values Obtained from Calculating $x_i = 19.36x_d - 58.055$

x_i	x_d	y_i	y_d	n	m	$n + m$
5	3.26	0.73	0.48	17.44	2.55	19.99
10	3.51	1.46	0.51	17.70	2.59	20.29
15	3.77	2.20	0.55	17.96	2.63	20.59

wt % d = 5.2. The practical molecular weight was 3799 and the true one, 3357.

Fourth Example

Start with 9 kg of product with a functionality of f = 3 and NOH_s = 317.5. After addition of PO, the product weighed 83 kg with NOH_f = 46.9 and an unsaturation content of 0.08 mequiv/g. By applying eq. (3), it is found that $\overline{MW}_s$ = 530 and m_s = 16.98. The total monofunctional unsaturated moles is m_i = 6.64. From eq. (12) it is found that m_d = 5.9 and from eq. (13) n_t = 1274. Equation (14) yields:

$$n = \frac{6.64\,x_i + 11.8\,x_d + 1274}{69.38}$$

If we suppose that $x_i = x_d$, we obtain, for $x_i = x_d$ = 5, 10, 15, respectively, n = 19.69, 21.02, 22.35. Using eqs. (9)–(11), we obtain three average molecular weights as functions of x_i and x_d, (Fig. 8). This figure also gives the weight percent of diols and unsaturated compounds. If, as in the previous case, the delay, i.e., x_d = 3.7, we obtain $\overline{MW}_d$ = 1833 and $\overline{MW}_i$ = 908, with a weight percent of 13% and 7.3%, respectively. While the calculated average molecular weight of the product was 3588, the true average molecular weight is 2811. The true functionality is 2.35, instead of 3.

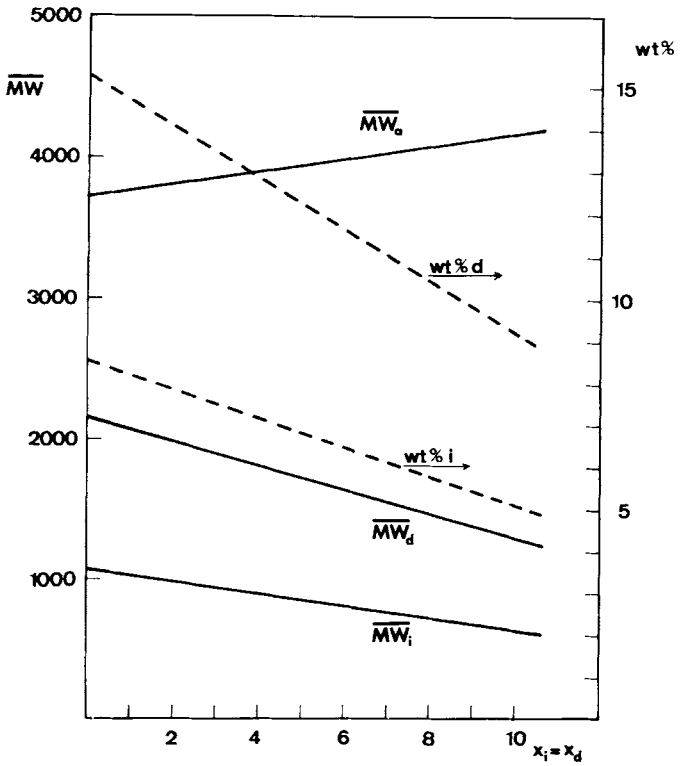

Fig. 8. $\overline{MW}_a$, $\overline{MW}_i$, $\overline{MW}_d$ values and wt % of diols and unsaturated compounds vs. $x_d = x_i$ values relevant to Example Four.

CONCLUSIONS

This work has evaluated the influence of the secondary product on the molecular weight in oxyalkylation reactions. The theoretical calculation methods, were verified by analyzing some typical reactions. In the case of monofunctional adducts, experimental confirmation of the results was possible; with functionalities > 1, the results are probable.

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