Determination of Molecular Weights of High Molecular Weight Poly(ethylene Oxide)s by Means of a Quick Cloud Point Titration Method

INTRODUCTION

High molecular weight ($M_v > 1 \times 10^6$ g/mol) poly(oxyethylene)s, hereafter referred to as POE's, suffer an easy degradation both in the solid state as well as in solution.[1,2] This fact complicates a quick and precise determination of its degrees of polymerization. Methods such as light scattering and ultracentrifugation[3] are too cumbersome for routine industrial practice. The same concerns the viscometric determination due to the lack of stability of POE's and high viscosities of its solutions.

The present note describes a simply procedure for the estimation of molecular masses of high molecular weight POE's by means of the cloud point titration method. Contrary to many other polymers the microstructure of the POE chains does not depend on the synthesis method, thus rendering the cloud composition titrations feasible for determining of the average molecular weights M_{av}.

Most of the relationships for cloud point titrations were established empirically, and only recently it was shown that some of these relations were compatible with theoretical approaches.[4]

Basing on the following empirical relationship between volume fraction Φ_3^i of the precipitant and the polymer mass concentration c_2^i at the point of incipient phase separation, i.e.,

$$\Phi_3^i = A' - B_\phi \ln c_2^i \tag{1}$$

Elias[4] derived the equation

$$\Phi_3^i = A - B_\phi \ln \Phi_2^i \tag{2}$$

where A' and B_ϕ = constants for the system solvent "1"/polymer "2"/precipitant "3" for a given temperature and molecular weight; $\Phi_2^i = c_2^i \rho_2$ denotes the volume fraction of the solute at the point of incipient phase separation; $A = A' - B_\phi \ln \rho_2$ means a constant parameter which denominates the volume fraction Φ_3^i of the precipitant in a theta mixture. $A' = A$ if the polymer density $\rho_2 \approx 1$.

As the slope B_ϕ decreases with increasing polymerization degrees,[5] it can be utilized to gain information about the molecular weight of the polymer. Contrary to B_ϕ the quantity A' is assumed to be molecular weight independent.[6] This fact has been evidenced, beside others, on low molecular weight poly(oxyethylene)s. Nevertheless, the main difficulty exists in establishing of the exact relationship between B_ϕ and the average molecular weight M_{av}. There are two functions which have been proposed empirically either by Elias,[7]

$$B_\phi = B_\phi^0 + D \cdot M_{av}^{-m} \tag{3}$$

or by Mathieson,[8]

$$(B_\phi)' = (B_\phi^0)' - m \cdot \log M_{av} \tag{4}$$

where B_ϕ^0 and $(B_\phi^0)'$ and D = constants; $(B_\phi)' = \log B_\phi$ if $B_\phi \gg B_\phi^0$.

Much controversy emerged around the numerical value of m. Some investigations indicated figures between 1 and 0.5 with a tendency toward the value of 0.5. These findings were empirical, and only Talamini and Vidotto[9] showed on the basis of the Flory–Huggins theory that m should be around 0.6. The value of 0.61 is claimed to be indeed in accordance with experimental data for some systems.[4]

The aim of our investigations was to check the applicability of eqs. (1), (3), and (4) to solutions of high molecular weight POE's in order to derive relations for determining molecular weights by means of cloud composition titrations.

It is to notify that the high molecular weight POE's differ in many respects in behavior from those with lower M_{av} values. Relying on eqs. (1) and (3) the possibility should exist to determine the molecular weight from cloud composition titrations.

TABLE I
Polymers POE I–V[a]

Polymer	$c_2 \times 10^3$ (g/cm³)	Vol_3 (cm³)	$Vol_1 + Vol_3$ (cm³)	$\Phi_3^1 \times 10^2$	$c_2^i \times 10^4$ (g/cm³)	$A' \times 10$	$B_\phi \times 10^2$
POE I	1.50	61.36	86.36	71.05	4.34	5.95	1.49
$M_v = 1.25 \times 10^6$ g/mol	1.25	62.50	87.50	71.43	3.57		
	1.00	63.71	88.71	71.82	2.82		
	0.75	64.89	89.89	72.19	2.09		
	0.50	66.02	91.02	72.53	1.37		
POE II	1.50	51.31	76.31	67.24	4.91	5.44	1.71
$M_v = 1.80 \times 10^6$ g/mol	1.25	52.40	77.40	67.70	4.04		
	1.00	53.69	78.69	68.23	3.18		
	0.75	55.00	80.00	68.75	2.34		
	0.50	56.99	81.99	69.51	1.52		
POE III	1.50	41.18	66.18	62.22	5.67	4.58	2.23
$M_v = 2.81 \times 10^6$ g/mol	1.25	42.40	67.40	62.91	4.64		
	1.00	43.65	68.65	63.58	3.64		
	0.75	44.96	69.96	64.26	2.68		
	0.50	46.09	71.09	64.83	1.76		
POE IV	1.50	38.05	63.05	60.35	5.95	4.36	2.28
$M_v = 3.10 \times 10^6$ g/mol	1.25	38.96	63.96	60.91	4.89		
	1.00	40.20	65.20	61.66	3.83		
	0.75	41.68	66.68	62.51	2.81		
	0.50	42.90	67.90	63.18	1.84		
POE V	1.50	33.50	58.50	57.23	6.41	3.89	2.56
$M_v = 3.74 \times 10^6$ g/mol	1.25	34.97	59.97	58.31	5.21		
	1.00	36.02	61.02	59.03	4.10		
	0.75	37.31	62.31	59.88	3.01		
	0.50	38.45	63.45	60.60	1.97		

[a] With viscometrically determined molecular masses M_v, initial polymer concentration c_2, volume of precipitant Vol_3 used to develop the first stable cloud point in a volume $Vol_1 = 25$ cm³ of the POE chloroform solution, volume fraction of the precipitant at the point of incipient phase separation c_2^i, quantity A' from eq. (1), slope coefficient B_ϕ of the Φ_3^1 vs. ln c_2^i relationship according to eq. (1).
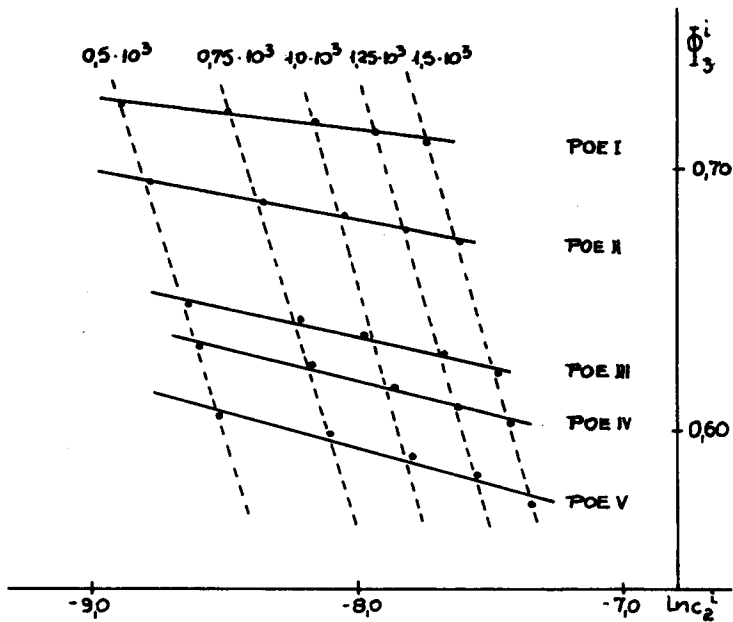
Fig. 1. Extrapolation plot of the volume fraction of the precipitant at the point of incipient phase separation Φ_3^i vs. logarithm of the polymer concentration c_2^i (g/cm^3) at the point of incipient phase separation for constant molecular weight (——) or for constant initial concentration (- - -) of the appropriate POE I–V.

EXPERIMENTAL

The poly(ethylene oxide)s were prepared by means of a calcium amide catalyzed solution precipitation polymerization in the same way as described earlier.[2] The molecular weights M_v were calculated from the relation[3]

$$[\eta](cm^3 \cdot g^{-1}) = 2.84 \times 10^{-2} M_v^{0.683} \tag{5}$$

by determining the intrinsic viscosity on 0.1N HCl water solutions. The chloroform solutions of the POE's were filtered through a 0.65 μm Millipore filter. The cloud titrations were carried out by determining the cloud points visually in a thermostated flask containing 25 cm^3 of the appropriate chloroform solution with the following concentrations: $c_2 = 0.5 \times 10^{-3}, 0.75 \times 10^{-3}, 1.0 \times 10^{-3}, 1.25 \times 10^{-3}, 1.50 \times 10^{-3}$ g/cm^3. The nonsolvent n-hexane was admitted through a burette graduated on 0.01 cm^3. Both the chloroform and n-hexane were preliminary purified by rectification until reaching the refractometric purity $\pm$ 0.0002. The titrations were carried out at 19 $\pm$ 0.2°C until the first stable cloud point developed. Using the least squares relationship, the straight lines were extrapolated to zero point at the abscissa, thus yielding the parameter A'. From the slopes, the slope coefficients were determined.

RESULTS AND DISCUSSION

The high molecular weight POE's I–V show in the range of its molecular masses $M_v = 1.25 \times 10^6$–3.74 $\times 10^6$ g/mol a straight line Φ_3^i vs. c_2^i relationship fitting the equation $\Phi_3^i = A' - B_\phi \ln c_2^i$ when submitted to cloud composition titrations with n-hexane as precipitant and chloroform as solvent in the concentration range $c_2 = 0.5 \times 10^{-3}$–1.5 $\times 10^{-3}$ g/cm^3 (see Table I and Fig. 1).

According to expectations the slope coefficient B_ϕ depends markedly on the molecular weights of the POE's (see Fig. 2 and Table I).

The equation proposed by Elias, $B_\phi = B_\phi^0 + D \cdot M_v^{-m}$ can be regarded to be compatible with the experimental established relation between B_ϕ and the viscometrically determined weight average M_v. The numerical values for the quantities B_ϕ^0, D, and m were derived on the ground of the data
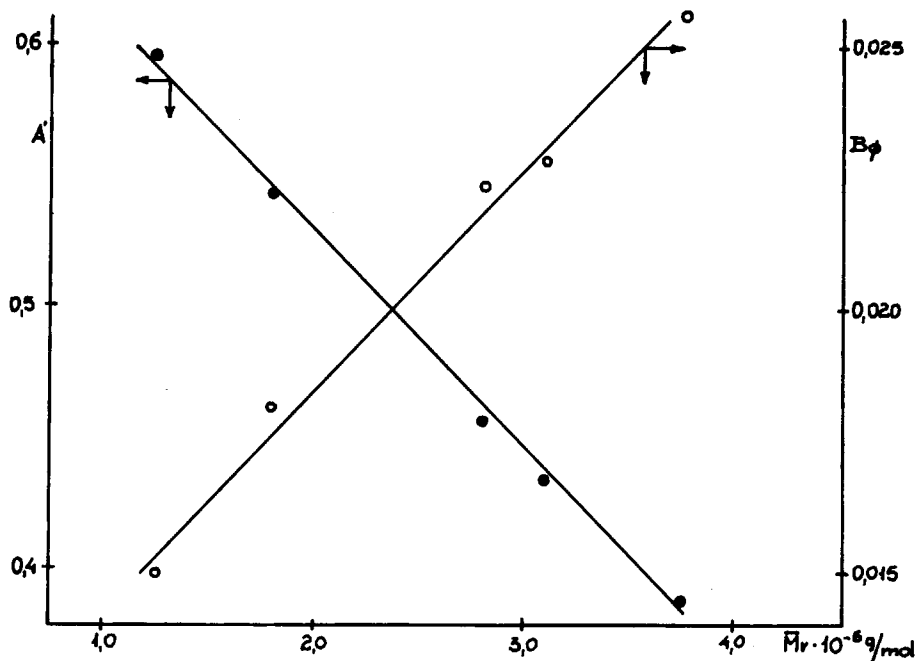
Fig. 2. Plot of the slope coefficient B_ϕ (O) as well as of the quantity A' (●) from eq. (1) vs. viscometrically determined molecular mass M_v for poly(ethylene oxide) samples of Table I.

gathered in Table I and illustrated in Fig. 2. The least squares relationship provides the equation

$$B_\phi = 9.461 \times 10^{-3} + 4.363 \times 10^{-9} \cdot M_v \tag{6}$$

where $9.461 \times 10^{-3} = B_\phi^0$, $4.363 \times 10^{-9} = D$, and $-1 = m$.

The parameter A' (as well as Φ_3^θ) should be according to older measurements reported in the literature practically independent of the molecular weight, whereas more accurate recent investigations indicate a slight molecular weight dependence of this quantity.[4] Contrary to these statements, however, it was found that in the case of high molecular weight POE's an even stronger dependence of A' on the molecular weight exists than in the instance of the appropriate B_ϕ dependence (see Fig. 2 and Table I).

Unexpectedly, the relation between A' and M_v appeared to be linear too according to the equation

$$A' = Q + PM_v = 0.696 - 8.318 \times 10^{-8} \cdot M_v \tag{7}$$

where Q = const and P = slope of the straight line relationship.

Due to linearity of both the B_ϕ vs. M_v as well as A' vs. M_v relations, the following formula can be derived by combining eqs. (6) and (7) under the instance that $-m = 1$:

$$M_v = \frac{\Phi_3^i - Q + B_\phi^0 \ln c_2^i}{P - D \cdot \ln c_2^i} \tag{8}$$

This formula enables us to determine the molecular weight from a single cloud composition titration. The precondition, however, is to determine the quantities represented in eq. (8) for a given initial polymer concentration c_2.

Besides the Φ_3^i vs. c_2^i linear relationship at constant molecular weights (see Fig. 1), there are similar Φ_3^i vs. c_2^i relations refering to constant c_2 values (see Fig. 1—dotted lines). For this relation the following equation does comply:

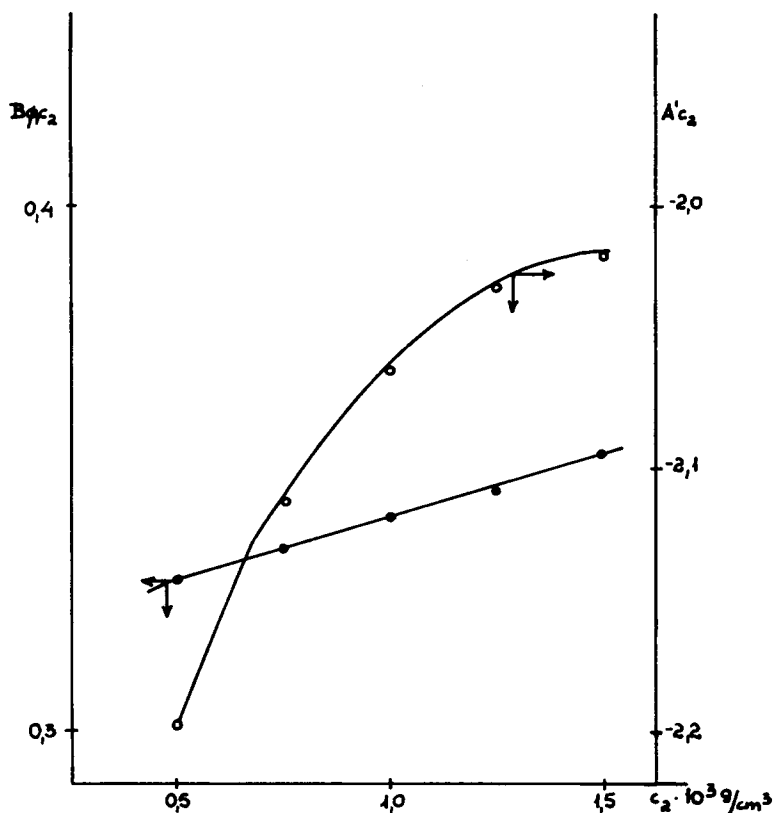$$\Phi_3^i = A'_{c2} - B_{\phi,c2} \cdot \ln c_2^i \tag{9}$$

Fig. 3. Plot of the slope coefficient B_{ϕ,c_2} (●) as well as of the quantity A'_{c_2} (○) from eq. (1) vs. the initial polymer concentration c_2 for poly(ethylene oxide) samples of Table I.

for c_2 = const and $M_v \neq$ const, where A'_{c_2} and $B_{\phi c_2}$ = constants for the system solvent "1"/polymer "2"/precipitant "3" for a given temperature and initial polymer concentration c_2.

Basing on the data assembled in Table I and illustrated in Figure 1 the following equations were derived by means of the least squares relationship:

$$\Phi_3^i = -2.019 - 0.353 \cdot \ln c_2^i \qquad \text{for } c_2 = 1.5 \times 10^{-3} \text{ g/cm}^3 \qquad (10)$$

$$\Phi_3^i = -2.030 - 0.346 \cdot \ln c_2^i \qquad \text{for } c_2 = 1.25 \times 10^{-3} \text{ g/cm}^3 \qquad (11)$$

$$\Phi_3^i = -2.062 - 0.341 \cdot \ln c_2^i \qquad \text{for } c_2 = 1.00 \times 10^{-3} \text{ g/cm}^3 \qquad (12)$$

$$\Phi_3^i = -2.112 - 0.335 \cdot \ln c_2^i \qquad \text{for } c_2 = 0.75 \times 10^{-3} \text{ g/cm}^3 \qquad (13)$$

$$\Phi_3^i = -2.197 - 0.329 \cdot \ln c_2^i \qquad \text{for } c_2 = 0.50 \times 10^{-3} \text{ g/cm}^3 \qquad (14)$$

Taking into account the dependence of the Φ_3^i vs. $\ln c_2^i$ relationship both on the molecular weight as well as on the initial polymer concentration c_2, it is advisable to replace the quantity $\ln c_2^i$ in eq. (8) by the ratio $(A'_{c_2} - \Phi_3^i)/B_{\phi,c_2}$ taken from eq. (9).

As a consequence the following formula is derived:

$$M_v = \frac{\Phi_3^i(B_{\phi,c_2} - B_\phi^0) - Q \cdot B_{\phi,c_2} + B_\phi^0 \cdot A'_{c_2}}{P \cdot B_{\phi,c_2} - D \cdot A'_{c_2} + D \cdot \Phi_3^i} \qquad (15)$$

In order to determine the molecular weight by a single cloud point titration, it is necessary to fix the initial polymer concentration at one of the levels ascribed to eqs. (10)–(14) and to take the quan-

tities A_{c_2} and B_{ϕ,c_2} appropriately from these equations. Then the quantities D, Q, and P should be taken from eqs. (6) and (7), respectively. If $c_2 = 1.50 \times 10^{-3}$ g/cm³, eq. (15) can be written as

$$M_v = \frac{(0.344\Phi_3^i - 0.265) \times 10^8}{0.463\Phi_3^i - 2.055} \tag{16}$$

Principally it is possible to utilize any concentration c_2 in the range between 0.50×10^{-3} and 1.5×10^{-3} g/cm³, taking the appropriate A_{c_2}' and B_{ϕ,c_2} quantities from Figure 3, which shows the A_{c_2}' vs. c_2 and B_{ϕ,c_2} vs. c_2 relationships based on eqs. (10)–(14).

It should be noted that the $B_{\phi,c}$ vs. c_2 relationship is linear too with the slope coefficients growing proportionally to the increasing c_2 concentrations. This fact is a consequence of increasing polymer–polymer interaction. The relation A_{c_2}' vs. c_2, however, is not a linear one.

The described cloud point titration method has been tested by utilizing eq. (16) (i.e., at $c_2 = 1.5 \times 10^3$ g/cm³) for POE's ranging in weight average molecular masses between $M_w = 1 \times 10^6$ and $M_w = 4 \times 10^6$ g/mol. The deviations in the results did not exceed 10% limit.

Based on theoretical considerations, the method is restricted to unbranched polymers with unchanging microstructure.

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