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Synthesis and thermodynamics properties of poly(ethylene oxide) prepared in diphenylzinc-water

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ABSTRACT

Poly(ethylene oxide) (PEO) samples, obtained using diphenylzinc-water as initiator, have been used to determine some characteristics of this polymer. The unperturbed dimensions of PEO have been obtained by the application of various theoretical treatments to viscometry measurements carried out in a good solvent. The following relationship between intrinsic viscosity and weight average molecular weight has been obtained $[\eta]/dL.g^{-1} = 3.99x10^{-4}M_w^{0.69}$.

INTRODUCTION

Investigations of the properties of dilute polymer solutions have long been of interest, both as a practical means of characterizing polymers and as a means of elucidating the thermodynamic and conformational properties of macromolecules.In this paper we describes the polymerization of ethylene oxide (EO) in benzene solution initiated by the diphenylzinc-water system. Dilute solution properties of PEO have been measured by viscometry; MHS expresion have been determined in benzene at 298 K.

The values of the unperturbed dimensions, $<s^2>_o/M$, solvent-polymer interaction parameters (B and χ_1) and conformational parameter, σ, have been computed by applying the theories of Flory-Fox, Kurata-Stockmayer, Stockmayer-Fixman, Cowie-Bohdanecky and Berry. The unperturbed mean-square radius of gyration, $<s^2>_o$ is one of the two basic molecular parameters, which represents short-range interactions in the chain, and from which valuable information concerning the chain structure is obtained.

EXPERIMENTAL PART

Ethylene oxide (BDH puriss) was dried over calcium oxide, fractionally distiled, and stored in a sealed ampoule over calcium oxide in the absence of air. Benzene was purified by conventional methods, and finally distiled from sodium wire and stored over calcium oxide, in the absence of air.

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Diphenylzinc (Ventron Corp.) was purified by bulb-to-bulb fractional distillation at 10^{-5} mm Hg, and stored in calibrated ampoules, provide with a break seal.

Polymerization experiments were carried out in benzene solution at 333 K in vials filled using a vacuum line technique (RABAGLIATI, GARBAN 1985; RABAGLIATI, BRADLEY 1984). Polymerization vessels were pumped on the vacuum line for 12-14 hours before use. The diphenylzinc solution in benzene and the required amount of water were transferred by syringe but ethylene oxide and benzene used as solvent, were distiled under vacuum from calibrated tubing connected to the vacuum line. The reaction mixtures were degassed to 10^{-5} mm Hg, then the vessel were sealed off and placed in the thermostat bath for the required length of time. Polymerization were termined by addition of benzene and a small excess of methanol over that required to precipitate the cata-lyst. Catalyst residues were removed centrifugally, and the poly-mers were isolated by freeze-drying.

The ^{1}H NMR samples were prepared by dissolving 13 to 20 mg of polymer in 0.40 mL of 2H-chloroform or benzene and measured at 313 K with a Varian T-60 Spectrometer using tetramethylsilane (TMS) as an internal standard. TMS was distiled under vacuum and stored over calcium oxide.

IR spectra were taken on a Perkin Elmer 377 or on a Aculab-2 spectrophotometer. The polymer were normally sampled as thin films on NaCl disks.

GPC was performed with a Waters Associates model 200 apparatus, operated at 313 K and equipped with five columns connected in serie and packed with styragel 10^3, 10^2, 50, 10 and 6 nm for the high molecular weight polymers. Chloroform was used as solvent and the instrument was calibrated with polystyrene samples of known molecular weights.

A Ubbelohde viscometer was used (KATIME, RAMIRO VERA 1972). The temperature of the bath was regulated to ±0.05°. Kinetic energy corrections were applied, although often they were very small. Fluctuation of the temperature was less than ±0.02°. The $[\eta]$ was obtained by double extrapolation of η_{sp}/c and $\ln \eta_r/c$ to zero concentration. $[\eta]$ values were expressed in $dL.g^{-1}$.

RESULTS AND DISCUSSION

From the M-$[\eta]$ data in Table 1 for PEO the following relationship was obtained: $[\eta] = 3.99\times10^{-4}M^{0.69}$. The uncertainties are $\pm0.03\times10^{-4}$ in K and ±0.01 in the exponent a. The obtained values of K and a MHS parameters agree very well with the values obtained by Allen et al.(1967)

Table 1. Intrinsic viscosity of PEO measured in benzene.

$M_w.10^{-5}$	1.52	1.93	3.70	5.12	5.67	7.01	10.49	14.20	15.70	39.40
$[\eta]$	1.43	1.68	2.62	3.28	3.52	4.06	5.36	6.60	7.06	13.29

Values of K_θ and hence the unperturbed dimensions, $\langle s^2\rangle_o/M$, and the long-range interaction parameter B of the PEO are also obtainable from several extrapolation procedures. The most relevant theories used in this paper are the following:

Flory-Fox (FF). It is based on the assumption that $\alpha_\eta^3 = [\eta]/[\eta]_\theta$ and Flory's theory of exclude volume; in terms of polymer/solvent interaction parameter B, it can be written as

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0.857K_\theta^{2/3}\Phi_o B\frac{M}{[\eta]} \qquad (1)$$

where B is a parameter characteristic of the polymer/solvent interaction and given by $B = \beta/m_o^2$ where β is the so-called binary cluster integral and mo the molecular weight of a chain segment, Φ_o is the Flory-Fox viscosity constant for theta solvents, with theoretical value 2.87×10^{21} mol^{-1} (KIRKWOOD, RISEMAN 1948), for homogeneous flexible polymers in good solvents (FLORY 1953). The result of plotting $[\eta]^{2/3}M^{-1/3}$ against $M.[\eta]^{-1}$ should be a linear graph, having a intercept equal to $K_\theta^{2/3}$ from which the unperturbed dimensions can be evaluated. Figure 1 shows the FF plot for PEO in benzene at 298. The values of K_θ obtained by this equation is 2.42×10^{-3} $dL.g^{-1}$. The value of parameter B obtained from the slope is 1.63×10^{-27} $cm^3.mol^2.g^{-2}$ and the polymer/solvent interaction parameter χ_1 is 0.36. This theory holds well in the vicinity of theta temperature, but normally fails in good solvents.

Kurata-Stockmayer (1955) (KS). It is based on KSR model (1960) of an ellipsoid for expansion coefficient, and assumes that α_η and α have the same functional form; the final equation is

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K_\theta^{2/3} + 0.363\Phi_o B g(\alpha_\eta)\frac{M^{2/3}}{[\eta]^{1/3}} \qquad (2)$$

where the parameter B is related to interaction parameter χ_1 by

$$B = \frac{v^2(\frac{1}{2} - \chi_1)}{V_1 N_A} \qquad (3)$$

and

$$g(\alpha_\eta) = 8\alpha_\eta^3/(1 + 3\alpha_\eta^2)^{3/2}$$

v is the partial specific volume of polymer, V_1 is the molar volume of the benzene (89.3 cm^3/mol) and N_A is the Avogadro number. The parameter B is also a measure of solvent quality for a polymer. Thus, at the theta temperature, B is zero and χ_1 will be 0.5; in a good solvent, in which polymer/solvent interactions are great, χ_1 will be < 0.5; as that χ_1 decreases for increasing polymer/solvent interactions meaning that we are for from the theta temperature.

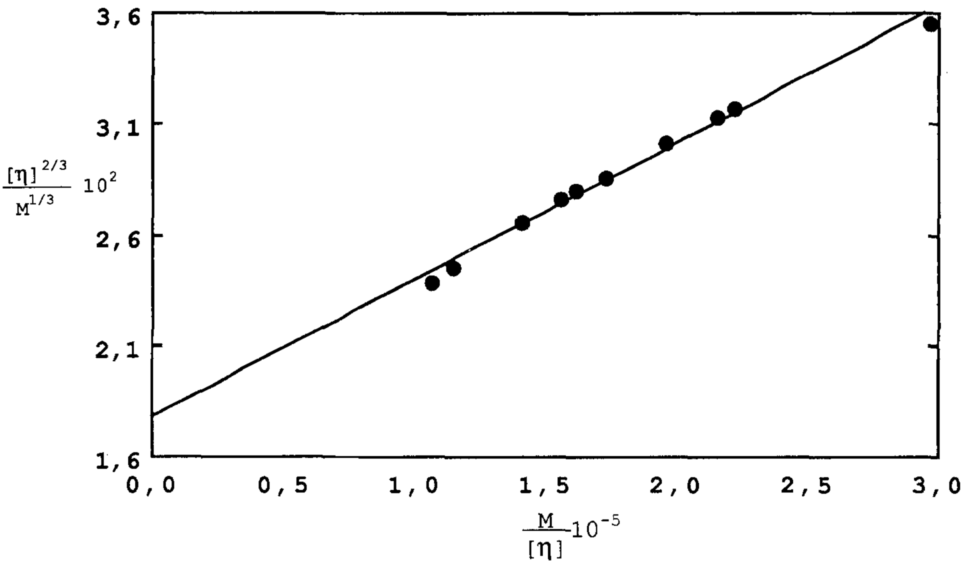

Figure 1. The FF plot for PEO in benzene at 298 K.

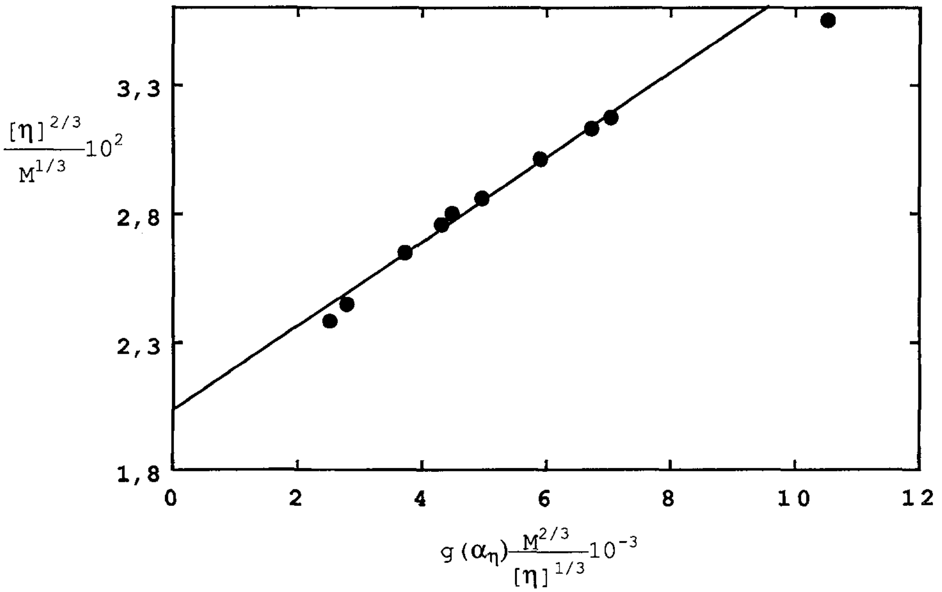

Figure 2.The KS plot for PEO in benzene at 298 K

To apply the equation of KS, an iterative procedure is required. We may first plot $[\eta]^{2/3}M^{-1/3}$ against $M^{2/3}[\eta]^{-1/3}$, ignoring the functional $g(\alpha_\eta)$ and finding an approximate value of K_θ which permits us to evaluate $[\eta]_\theta$, α_η and $g(\alpha_\eta)$. Then using this result, we may replot $[\eta]^{2/3}M^{-1/3}$ against $g(a_\eta)M^{2/3}[\eta]^{-1/3}$, and find an improved value of K_θ parameter. subsequent re-plotting gives an accurate K_θ value. The convergence of this procedure is fairly rapid. Example of this plot is shown in Figure 2. It is observed that the KS plot lead to a much more reliable estimate of K_θ than FF. The K_θ value obtained from the intercept is $2.91\text{x}10^{-3}$ dL/g; that together with Equations (10-11) yields $<s^2>o/M = 16.90\text{x}10^{-18}$ $cm^2.mol.g^{-1}$. From the slope we have obtained the value of parameter $B = 1.75\text{x}10^{-27}$ $cm^3.mol^2.g^{-2}$ and $\chi_1 = 0.35$. However, some data deviate from linearity, especially the polymers of high molecular weights.

Stockmayer-Fixman(SF). A much simpler modification has been proposed by BURCHARD (1961) and STOCKMAYER Y FIXMAN (1964). Numerically very close to the above,

$$\frac{[\eta]}{M^{1/2}} = K_\theta + 0.51\Phi_o BM^{1/2} \qquad (4)$$

It has been pointed out (KATIME, ROIG 1973) that the correct estimate of K_θ will be obtained if result for $M > 10^6$ g/mol are omited. In our case, the samples of low molecular weights ($1.52\text{x}10^5$ and $1.93\text{x}10^5$ g/mol) and the higher molecular weight $3.94\text{x}10^6$ g/mol show deviations in the BSF.

The application of this method to the present data is illustrated in Figure 3, from which $K_\theta = 2.95\text{x}10^{-3}$ $dL.g^{-1}$ and hence $<s^2>_o/M = 16.97\text{x}10^{-18}$ cm^2. The SF plot is also seen to yield accurate estimated of K_θ. The value of parameter B was $1.75\text{x}10^{-27}$ $cm^3.mol^2.g^{-2}$ and $\chi_1=0.35$.

Cowie-Bohdanecky (1965,1966) (CB). Based on a semiempirical equation of Krigbaum (1955) and the Flory-Orofino theory (1957) of second virial coefficient:

$$\frac{[\eta]}{M^{1/2}} = (\Phi(\varepsilon)/\Phi_o)K_\theta + 0.9166(\Phi(\varepsilon)/\Phi_o)K_\theta k^{7/10}M^{7/20} \qquad (5)$$

In this equation, k and $\Phi(\varepsilon)$ are defined, respectively, as (17):

$$k = 0.33B[M/<r^2>_o]^{3/2} = 0.33B\Phi_o/K_\theta \qquad (6)$$

$$\Phi(\varepsilon) = \Phi_o(1 - 2.63\varepsilon + 2.86\varepsilon^2) \qquad (7)$$

where ε is related to the exponent, a, of the MHS equation as $\varepsilon = (2a-1)/3$. We have found for ε the value 0.1247, and so, $\Phi(\varepsilon)/\Phi_o = 0.7165$. Figure 4 show the CB plot, from which we have obtained the values $K_\theta = 3.35\text{x}10^{-3}$ $dL.g^{-1}$, $B = 4.81\text{x}10^{-27}$ $cm^3.mol^2.g^{-2}$ and $\chi_1 = 0.10$.

Berry (18) proposed the following equation

$$\frac{[\eta]^{1/2}}{M^{1/4}} = K_{\theta}^{1/2}(1 + 0.42\Phi_0 BM[\eta]^{-1}) \qquad (9)$$

Figure 5 shows the Berry plot. From intercept we have found that $K_{\theta} = 2.50\times10^{-3}$ dL/g and from the slope $B = 1.88\times10^{-27}$ $cm^3.mol^2\ g^{-2}$ and $\chi_1 = 0.34$.

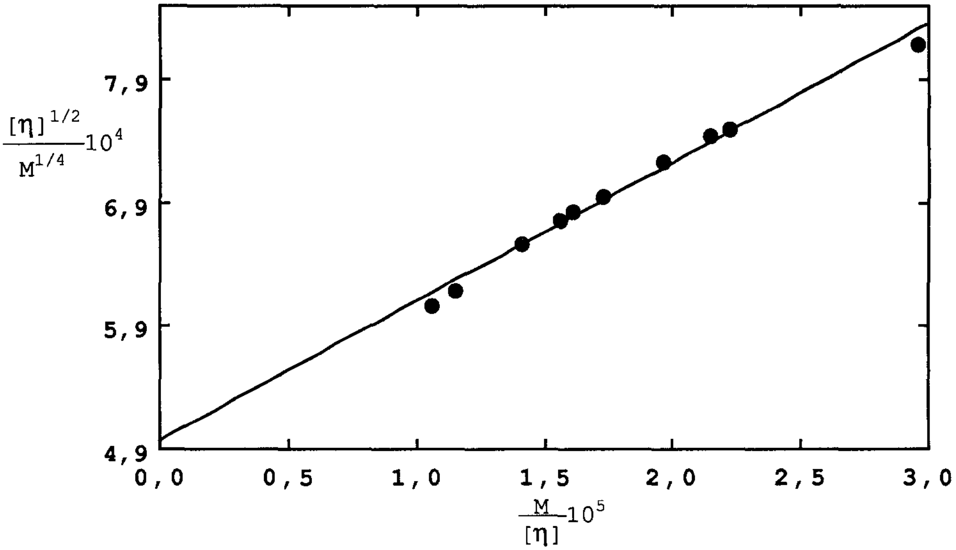

Figure 3. The SF plot for PEO in benzene at 298 K.

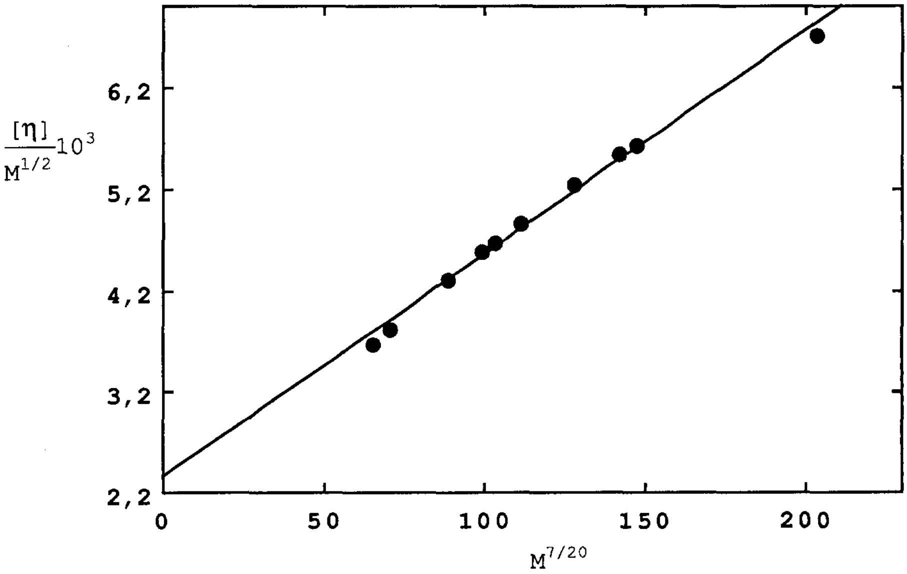

Figure 4. The CB plot for PEO in benzene at 298 K

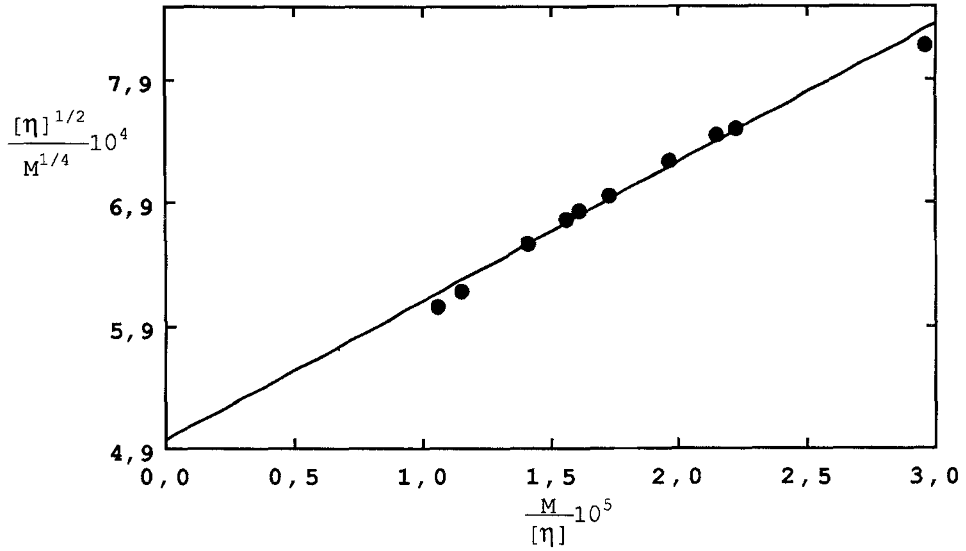

Figure 5.The Berry plot for PEO in benzene at 298 K.

A least squares calculation, by means of an Commodore Amiga 2000 computer gives the results of Table 2. From the mean value of K_θ, the unperturbed dimensions of PEO for the five equations used in this paper, can be calculated from $K_\theta = \Phi_o A^3$, where $A^2 = 6\langle s^2\rangle_o/M$, where $\langle s^2\rangle_o$ is the unperturbed mean square radius of gyration.

Table 2. Comparative data for K_θ parameter, unperturbed dimensions and interaction parameter polymer/solvent for the PEO obtained in benzene using several excluded volume theories.

Extrapolation method	$K_\theta.10^3$ $dL.g^{-1}$	$\langle s^2\rangle_o/M.10^{18}$ $cm^2.mol.g^{-1}$	$B.10^{27}$ $cm^3.mol^2g^{-2}$
Flory-Fox	2.42±0.05	14.88	1.63
Kurata-Stockmayer	2.93±0.05	16.90	1.75
Stockmayer-Fixman	2.95±0.05	16.97	1.75
Cowie-Bohdanecky	3.35±0.05	18.48	4.81
Berry	2.50±0.05	15.20	1.88

The values of the parameters K_θ and B, collected in Table 2, show that most of the procedures employed give results in reasonable agreement. The excluded volume parameter B calculated according to Equation (5) is definitely higher than those obtained by applying the other relationships.

The effect of diminished free rotation about a bond as a result of steric hindrance, σ, is defined as

$$\sigma = \left(\frac{\langle s^2\rangle_o/M}{\langle s^2\rangle_{of}/M}\right)^{1/2} \qquad (10)$$

where $\langle s^2\rangle_{of}$ is the mean square radius of gyration corresponding to completely free internal rotations. By substituting in Equation (10) the data $(\langle s^2\rangle_{of}/M)^{1/2} = 4.88\times10^{-18}$ (PTITSYN, EIZNER, 1960), we find for the steric factor the value 1.86 ± 0.08.

From our data, the K_θ parameter and steric factor is very different to the values obtained by others authors (RITSCHER, ELIAS 1959; SADRON, REMPP, 1958). The reason for these differences is not very clear; may be due to the crystalline character of PEO and also to specific solvent effects. It is necessary to obtain more information about the dependence $[\eta]$-M in other good solvents in order to clarify this question. A strong effect of this kind was reported by Ivin et al. (1962), who studied solution properties of hexene-1-polysulfone. Similar effects were found by Crescenzi and Flory (1964) with poly(dimethylsiloxane), which has a considerably less unperturbed dimension in theta solvents that in good solvents.

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