Limiting Viscosity Number and Molecular Weight Measurements on Poly-(1,2-cyclohexene oxide)[*]

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Limiting viscosity number and molecular weight data are reported for fractions of poly(1,2-cyclohexene oxide) in benzene and toluene. The following relationship was found at 35°C

$$|\eta| = 3{\cdot}5\times 10^{-5} M_n^{0{\cdot}83} \text{ for } 20\,000 < \overline{M}_n < 500\,000$$

Molecular dimensions in solutions were determined by using the Kurata–Stockmayer–Roig and Stockmayer–Fixman treatments. The characteristic ratio $\overline{r_0^2}/M$ *was found to be* $0{\cdot}35\times 10^{-16}$ *and* $0{\cdot}39\times 10^{-16}$ *cm*^{2} *by the two methods respectively. The conformational parameter* σ *of the polymer has been compared with the values calculated for other linear polyethers.*

THE behaviour of a macromolecule is determined by the structural parameters such as bond length, bond angles and hindrances to free rotation. The end-to-end r.m.s. distance $\overline{r^2}$ characterizes its spatial configuration. In a θ-solvent, where the excluded volume effect is zero, this distance corresponds to the unperturbed value $\overline{r_0^2}$. If a θ-solvent is not available the unperturbed distance may be obtained from intrinsic viscosity and molecular weight determinations in a good solvent by various methods of extrapolation.

The aim of the present investigation is to calculate the $\overline{r_0^2}$ value for poly(1,2-cyclohexene oxide) which is a polymer of special interest because of its characteristic structure with a ring in the repeat unit. The spatial configuration of this polymer may be usefully compared with that of other polyethers having in the chain backbone the sequence $(CH_2{-}CHR{-}O)_n$.

EXPERIMENTAL

Material

The poly(1,2-cyclohexene oxide) studied in this work was prepared either by irradiating the liquid monomer with γ-rays[1] or by using triethylaluminium as catalyst[2].

Fractionation

The polymer was fractionated from a benzene solution of about 1 g/100 ml by the addition of methanol at 25°C[3]. Ten or more fractions of about 0·2 to 0·3 g were obtained.

Viscosity

Viscosity measurements were carried out in an Ubbelohde viscometer in a constant temperature bath controlled to ±0·01 deg. C.

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Molecular weight

The molecular weight was determined by osmometry. The osmotic pressure measurements were carried out with a high speed membrane osmometer (Mechrolab, Model 502). All measurements were made at 35°C in toluene.

RESULTS AND DISCUSSION

The results of the viscosity and molecular weight measurements have been plotted in *Figure 1*. From these data, by a least squares treatment the following expression for the Mark–Houwink relation is obtained

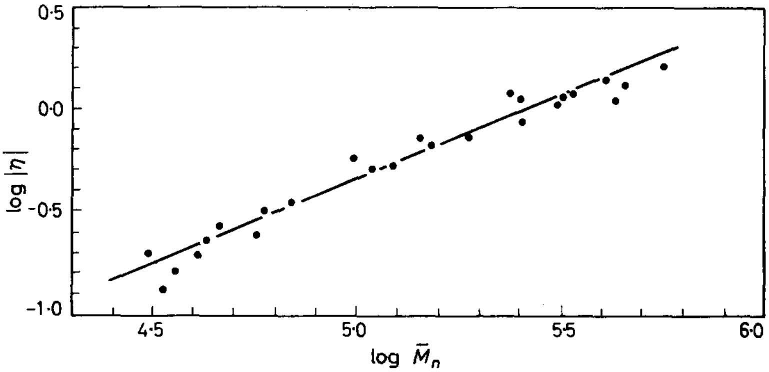

Figure 1—A log/log plot of $|\eta|$ versus $\bar{M}_n$ for poly(1,2-cyclohexene oxide) fractions at 35°C in toluene

$$|\eta| = 3{\cdot}5 \times 10^{-5} \bar{M}_n^{0{\cdot}83}$$

This equation has been found to be valid at 35°C, within experimental error for benzene and toluene solutions of the polymer. The values of $|\eta|$ were determined from the relations:

$$\eta_{sp}/c = |\eta| + k' |\eta|^2 c$$

and

$$[\ln \eta/\eta_0]/c = |\eta| - \beta |\eta|^2 c$$

In *Table 1* typical values of k' and β in benzene are reported.

Table 1. Viscosity data in benzene at 35°C

$\|\eta\|$ dl g^{-1}	k'	β	$\|\eta\|$ dl g^{-1}	k'	β
1·60	0·405	0·135	0·88	0·208	0·208
1·49	0·326	0·181	0·73	0·375	0·113
1·34	0·334	0·118	0·64	0·209	0·209
1·12	0·402	0·120	0·61	0·310	0·161
0·98	0·286	0·171	0·51	0·370	0·192

The values of the molecular weight were obtained from the osmotic pressure data plotted according to the equation

$$(\pi/c)^{1/2}=(RT/\overline{M}_n)^{1/2}+bc$$

The second virial coefficient is given by the following relation

$$A_2=2b/\overline{M}_n\,[1/(\pi/c)_{c=0}]^{1/2}$$

From the slope and the intercept of the linear plots of $(\pi/c)^{1/2}$ versus concentration a value of $A_2=2{\cdot}0\times10^{-4}$ cm^3 g^{-2} mole is obtained.

The Flory–Fox plot[4] of the data according to the equation

$$|\eta|^{2/3}/M^{1/3}=K^{2/3}+K^{5/3}C_TM/|\eta|$$

should lead to the determination of $K=\Phi\,(\overline{r_0^2}/M)^{3/2}$ where Φ is the universal constant, and $\overline{r_0^2}$ is the mean-square end-to-end distance for the unperturbed chain. This plot is shown in *Figure 2*. The data are well fitted by a straight line but the intercept on the ordinate axis is negative.

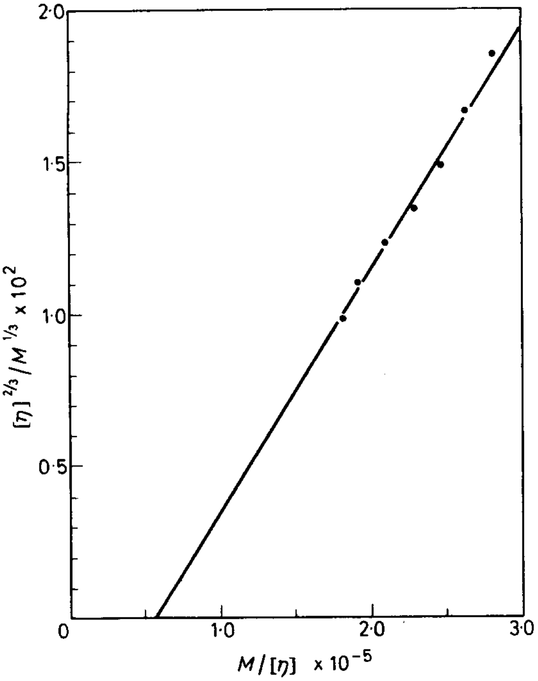

Figure 2—Flory–Fox plot for poly(1,2-cyclohexene oxide) fractions at 35°C in toluene

The Flory–Fox treatment has been found to fail for many polymeric systems and may lead to erratic values of K particularly in good solvents. Kurata, Stockmayer and Roig[5] and more recently Stockmayer and Fixman[6] have proposed a different treatment to evaluate the unperturbed distance from viscosity data. The expressions proposed by these authors yield substantially the same results.

The data have been reported in *Figure 3* according to the Kurata, Stockmayer and Roig method applying the following equation

$$|\eta|^{2/3}/M^{1/3} = K^{2/3} + 0{\cdot}363\,\Phi B\,\{g(\alpha_\eta)\}\,M^{2/3}/|\eta|^{1/3}$$

where B is the measure of polymer–solvent interaction, Φ the Flory–Fox constant and $\{g(\alpha_\eta)\} = 8\alpha_\eta^3(3\alpha_\eta^2+1)^{-3/2}$. The K obtained from the intercept is $5{\cdot}3\times10^{-4}$.. From this value and assuming $\Phi = 2{\cdot}5\times10^{21}$, $\overline{r_0^2}/M = 0{\cdot}35 \times 10^{-16}$ cm².

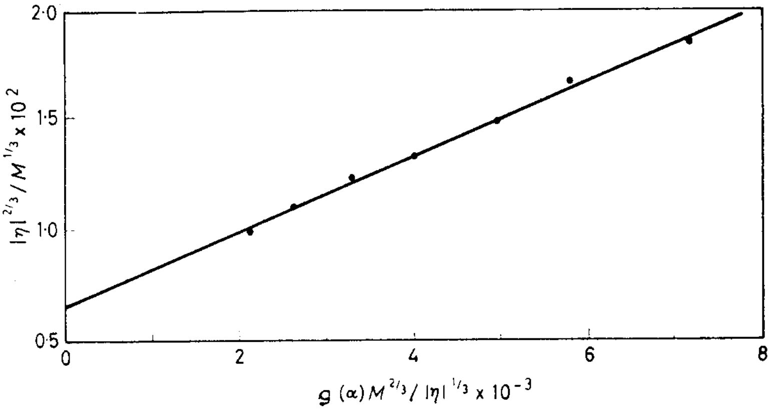

Figure 3—Kurata–Stockmayer–Roig plot for poly(1,2-cyclohexene oxide) fractions at 35 °C in toluene

The Stockmayer–Fixman plot yields a value of $K = 6{\cdot}0\times10^{-4}$ and therefore $\overline{r_0^2}/M = 0{\cdot}39\times10^{-16}$ cm².

The validity of the Kurata, Stockmayer and Roig theory may be tested through the following equation[7] which relates the expansion factor α_η with the molecular weight

$$(\alpha_\eta^3 - \alpha_\eta)\,\{1 + (1/3\alpha_\eta^2)\}^{3/2} = (2^5/3^3)(134/105)\,C_M\Psi(1-\Theta/T)\,M^{1/2}$$

A plot of the left hand term against $M^{1/2}$ yields straight lines passing through the origin for viscosity data at temperatures between 10° and 65°C, as predicted by the equation. A significant change of the limiting viscosity number in benzene was observed with $(\mathrm{d}\,|\eta|/\mathrm{d}T) > 0$, but calculation of the thermodynamic parameters using the above relation proved to be of rather limited accuracy.

The expansion factor α evaluated from K at 35°C in the range of molecular weight between 3 to 50×10^4 varies from 1·28 to 1·90.

The monomeric unit of this polymer is made of two C—O bonds and one C—C bond with a bond length $l_{\mathrm{C-O}} = 1{\cdot}43$ Å and $l_{\mathrm{C-C}} = 1{\cdot}53$ Å and bond angles $\mathrm{C\hat{O}C}$ approximately equal to $\mathrm{O\hat{C}C}$ and of 110°.

The calculation of $\overline{r_f^2} = 2n\,l^2$ from these data yields a value of 12·8 Å² and thus the conformational ratio $\sigma = (\overline{r_0^2}/\overline{r_f^2})^{1/2}$ gives 1·65.

The approximation of the free rotation for the C—C bond is rather crude.

On the other hand by assuming hindered rotations, as actually occurs in the presence of the cyclohexene ring, the calculation would yield a higher value of $\overline{r_f^2}$.

Table 2

Polymer	$\overline{r_0^2}/M \times 10^{16}$	$\sigma=(\overline{r_0^2}/\overline{r_f^2})^{1/2}$	*Ref.*
Poly(ethylene oxide)	0·60	1·44	(8)
Poly(propylene oxide)	0·64	1·70	(9)
Poly(styrene oxide)	0·41	1·95	(10)
Poly(*t*-butyl ethylene oxide)	0·62	2·20	(10)
Poly(1,2-cyclohexene oxide)	0·35	1·65	(This work)

In *Table 2* the conformational ratios of various polyethers are reported. A rough comparison of the data is possible by assuming for all polymers the same value of $\overline{r_f^2}$ calculated for poly(1,2-cyclohexene oxide).

The results indicate that steric hindrance is the main factor which reduces the chain flexibility. The presence of a ring in the backbone would suggest a more rigid structure for poly(1,2-cyclohexene oxide) than that actually found. The calculation of $\overline{r_f^2}$ has been made by assuming free rotation around the bonds and therefore that all configurations are possible. This model yields $\overline{r_f^2}$ lower than the value that may be calculated, more realistically, by excluding some of these conformations. In this latter case the experimental measurements on the real polymer chain indicate that the chain is more flexible than appears from the comparsion of $\overline{r_0^2}$ with $(\overline{r_f^2})_{\text{free rotation}}$. It should be noted finally that the sequence shown in *Table 2* may be altered if the different degrees of tacticity of the polymers are considered.

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