

Mixing of ethylene oxide and propylene oxide oligomers: 1. Enthalpy and volume changes

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Calorimetry and dilatometry have been used to determine the enthalpy and volume changes on mixing oligomers of ethylene oxide ($\bar{M}_n < 600$) and propylene oxide ($\bar{M}_n < 2025$). The mixing of α,ω -hydroxy-oligomers is markedly affected by end-group interactions. The enthalpies of mixing of α,ω -methoxy-oligomers are determined predominantly by differences in chain-segment interaction energies and surface areas. The volumes of mixing of α,ω -methoxy-oligomers can be explained only by accounting additionally for slight differences in their liquid properties.

INTRODUCTION

The thermodynamics of mixing of polymers is a subject of interest on two counts. There is the technological importance of polymer blends and block copolymer systems and the consequent need to have some knowledge of the parameters which determine their equilibrium states. Secondly there is the intrinsic interest in systems in which the enthalpy and non-combinatorial entropy changes on mixing predominate in determining the equilibrium state^{1,2}. Our own interest in mixtures of poly(ethylene oxide) and poly(propylene oxide) stems from our work with their block copolymers³.

The range of experimental methods which can be successfully applied to the study of polymer mixtures is limited, particularly if the introduction of a common solvent is avoided. The problems have been discussed by Koningsveld *et al.*². The chief problem is the high viscosity of polymeric liquids. Here we follow those (see for example ref 2) who have used mixtures of oligomers as model systems. Moreover in our case we have a direct interest in mixtures of oligomers since block copolymers of ethylene oxide and propylene oxide are usually⁴ of fairly low molecular weight.

In this paper we look in some detail at the enthalpy and volume changes on mixing ethylene oxide and propylene oxide oligomers. In a subsequent paper⁵ we report on equilibrium phase separation in similar systems.

EXPERIMENTAL

Materials

We denote the various oligomers by a prefix E or P (ethylene oxide or propylene oxide), by a number (molecular weight, \bar{M}_n) and by a suffix H or M (hydroxy- or methoxy-end-group).

The α,ω -hydroxy-oligomers were obtained from a variety of commercial sources: diethylene glycol (E106H) and triethylene glycol (E150H) from BDH Chemicals Ltd, dipropylene glycol (P134H) from Koch-Light and Co. Ltd, and the higher oligomers from the sources quoted in Table 1. The molecular weights of the higher oligomers were checked by gel permeation chromatography (g.p.c.; see ref 5 for ex-

perimental details) and vapour pressure osmometry: comparisons with standard samples served to show that the molecular weights quoted by the suppliers were sufficiently accurate for our purposes. All samples had narrow molecular weight distributions: the ratios \bar{M}_w/\bar{M}_n determined by g.p.c. were less than 1.05. All samples were dried for two weeks or more under high vacuum (<1 Pa) at 20° – 40°C : this treatment reduced the water content (Karl Fischer) to less than 0.1% by wt.

The α,ω -hydroxy-oligomers were methoxylated by a modified Williamson ether synthesis described in the Appendix to this paper. Infra-red spectroscopy, elemental analysis and end-group analysis were used to confirm a conversion of hydroxy- to methoxy-end-groups of more than 99.7%. The molecular weight distributions, as determined by g.p.c., were essentially unchanged by the methoxylation process.

Picnometry

Specific volumes at 30°C of the oligomers were measured by means of small (1 to 2 cm³) picnometers to an accuracy of about ± 0.002 cm³/g.

Calorimetry

Enthalpies of mixing were measured by means of an LKB Model 10700-2 batch microcalorimeter fitted with glass mixing cells (total volume 6 cm³) and maintained at $30^\circ \pm 0.1^\circ\text{C}$. In an experiment the cells were dried thorough-

Table 1 Specific volumes (v_{sp} , cm³/g) at 30°C

Sample	v_{sp}	Sample	v_{sp}
E300H ^a	0.896	E300M	0.963
E600H ^b	0.893	E600M	0.933
P250H ^c	(0.996)	P250M	(1.074)
P425H ^d	1.000	P425M	1.047
P750H ^a	1.002	P750M	1.023
P1000H ^a	1.003	P1000M	1.023
P1500H ^a	1.004	P1500M	1.015
P2025H ^e	1.007	P2025M	1.012

Sources: ^aShell Chemical Co. Ltd; ^bHoechst Chemicals Ltd; ^cDow Chemical Co. Ltd; ^dBDH Chemicals Ltd; ^eKoch-Light Co. Ltd

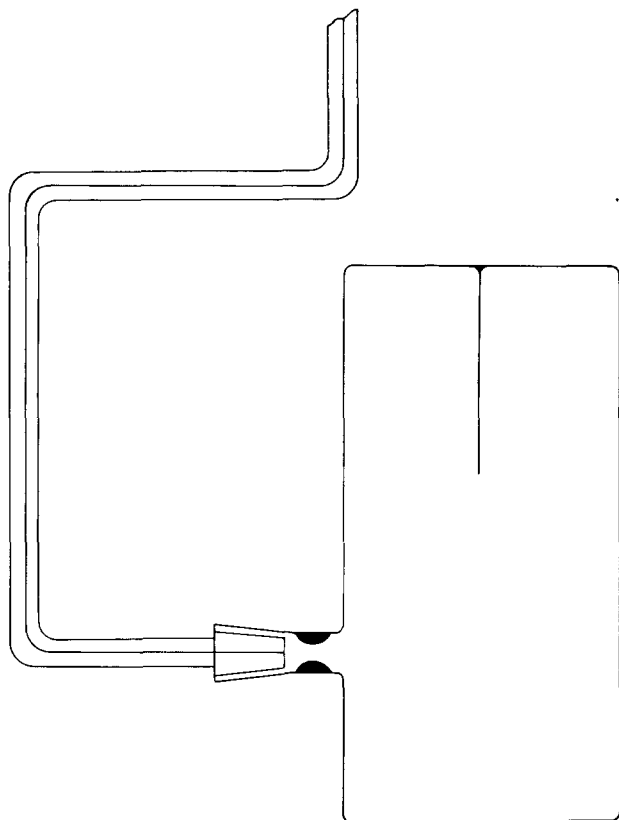


Figure 1 The mixing dilatometer. Springs retaining the B10/19 joint are not shown

ly before syringing in the two oligomers in the required proportions, the exact proportions being determined by weighing the syringes. The reference cell was filled with the same weight of a mixture of oligomers of a similar composition. Mixing was by a programmed sequence of rotation of the drum housing the cells. The sequence was repeated until no further heat flow could be detected: up to 30 such sequences were used for the most viscous systems. The volume of oligomers used (total of 2 to 5 cm³) usually produced a heat flow of 5 to 10 J. This heat flow was recorded as a voltage/time curve (3 mV range), the calibration being by Joule heating of the reference cell to produce peaks of similar size to those found in the experiments. Frictional heating during rotation was always less than 0.1 J: corrections were made where necessary. The major source of uncertainty was due to shifts in the baseline, which might amount to ± 0.2 J. We estimate an overall uncertainty in our results of ± 0.05 J/g.

Dilatometry

Volumes of mixing were measured by means of a mixing dilatometer similar to that described by Kershaw and Malcolm⁶. The apparatus is shown in Figure 1. The capillary was 0.4 mm internal diameter Veridia tubing. In an experiment the cylindrical cell (volume ~ 40 cm³) was filled under high vacuum with clean mercury. Syringes, fitted with flexible extensions, were used to introduce the oligomers on either side of the partition. The exact weights of oligomers were determined by weighing the syringes. The dilatometer was then assembled, taking care to exclude air bubbles and to avoid mixing, and placed in a water bath held at $30^\circ \pm 0.01^\circ\text{C}$. The height of the mercury meniscus, relative to a scribe mark, was read by means of a catheto-

meter (to ± 0.02 mm). The dilatometer was removed from the bath and the contents mixed by repeated tilting. Then it was returned to the bath and the meniscus height re-measured. This mixing procedure was repeated several times. The volumes of oligomers used (total of 5 to 10 cm³) resulted in volume changes of up to 10 mm³, i.e. meniscus movements of up to 10 cm. It was expected that the changes in pressure, due to the meniscus movement, might cause small changes in volume of the glass cell; to avoid errors from this source the apparatus was calibrated by filling with mercury alone and then measuring the meniscus height after expelling small weighed amounts of mercury. In this way it was shown that the apparent volume changes required a correction amounting to 6%. Correction was made for settling of the B10/19 capillary joint during the mixing process; this could amount to about 0.05 cm³. We estimate an overall uncertainty in our results of 0.02 mm³/cm³.

RESULTS

Specific volumes (v_{sp}) at 30°C are listed in Table 1: the values for P250H and P250M were estimated by linear extrapolation of the specific volumes of the other oligomers (see Figure 2).

Enthalpy changes on mixing (Δh_m , J/cm³) are shown in Figure 3 for various values of the volume fraction of the ethylene oxide oligomer (ϕ_1). Mixtures involving P1000H were incompletely miscible at 30°C. We have used the volumes of the pure components before mixing to calculate Δh_m and ϕ_1 : the volume changes on mixing are very small (see Table 2) and so the differences between these quantities and those defined for the mixture are negligible.

Volume changes on mixing (Δv_m) were measured only for $\phi_1 = 0.5$: values are listed in Table 2 together with the corresponding enthalpy change (taken from Figure 3 for $\phi_1 = 0.5$).

Enthalpy changes on mixing equal volumes of oligomers of the same chemical type but of different molecular weight are listed in Table 3.

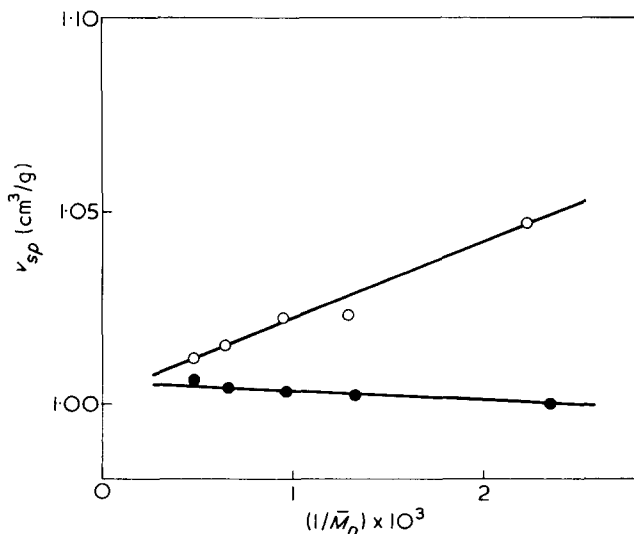


Figure 2 Specific volume (v_{sp}) versus reciprocal molecular weight ($1/\bar{M}_n$) for α,ω -methoxy- (○) and α,ω -hydroxy-oligomers (●) of propylene oxide

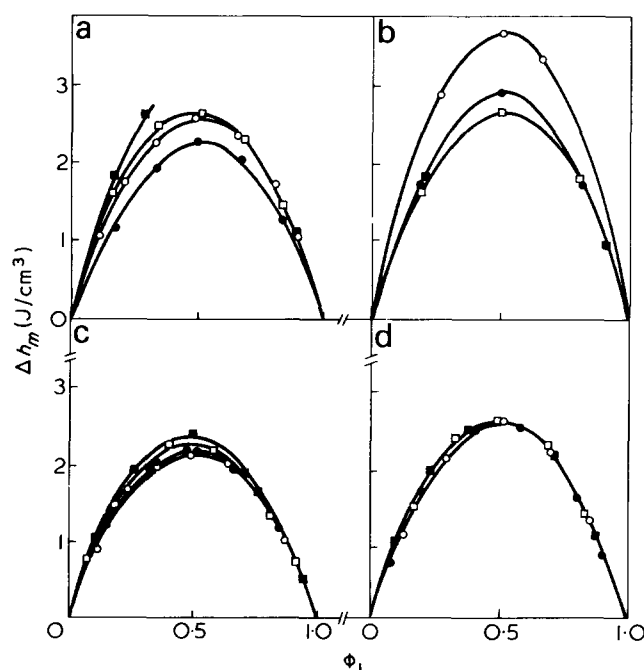


Figure 3 Enthalpy of mixing (Δh_m) versus volume fraction of ethylene oxide oligomer (ϕ_1). The data are for mixtures of α,ω -hydroxy-oligomers of propylene oxide with (a) E300H and (b) E600H, and for mixtures of α,ω -methoxy-oligomers of propylene oxide with (c) E300M and (d) E600M. The propylene oxide oligomers are represented by P250 (\circ), P425 (\bullet), P750 (\square), P1000 (\blacksquare)

Table 2 Enthalpy and volume changes on mixing equal volumes of oligomers at 30°C

Mixture	Δh_m (J/ cm ³)	Δv_m (mm ³ / cm ³)	Mixture	Δh_m (J/ cm ³)	Δv_m (mm ³ / cm ³)
E300H/P250H	2.7	-0.31	E300M/P250M	2.15	-0.27
E300H/P425H	2.3	-0.88	E300M/P425M	2.23	-0.26
E300H/P750H	2.7	-1.02	E300M/P750M	2.33	+0.27
			E300M/P1000M	2.35	+0.29
E600H/P250H	3.7	-0.18	E600M/P250M	2.65	-0.47
E600H/P425H	2.9	-0.58	E600M/P425M	2.65	-0.34
E600H/P750H	2.7	-0.53	E600M/P750M	2.65	+0.03
			E600M/P1000M	2.69	+0.08

DISCUSSION

It is apparent from our data that the properties of the hydroxy-ended oligomers and their mixtures are very much influenced by the end-group. We can point to the difference in the molecular weight dependence of specific volume between the hydroxy- and methoxy-ended oligomers (Figure 2); to the irregularities in the dependence of Δh_m at $\phi_1 = 0.5$ on molecular weight (Table 2 and Figure 3); and to the large enthalpies of mixing observed for hydroxy-ended oligomers of the same type (Table 3). These effects are due to the hydrogen bonding interaction of the hydroxy-group with the ether oxygen of the oligomer chains and with other hydroxy-end-groups. This complication is avoided by the use of methoxylated polymers (compare the enthalpies of mixing found for hydroxy- and methoxy-ended oligomers which are recorded in Table 3). Consequently we concentrate, in subsequent discussion, on the mixing of the methoxy-ended oligomers. A convenient starting point for discussion is the Flory-Huggins⁷ model of the mixture, which is based upon a quazi-lattice model of the liquid state.

Flory-Huggins approximation

In its most general form the Flory-Huggins expression for the free energy of mixing can be written² for 1 mole of segments:

$$\frac{\Delta G_m}{RT} = \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2 \quad (1)$$

where

$$\chi = \chi_0 + \chi_1 \phi_1 + \chi_2 \phi_1^2 + \dots \quad (2)$$

and r_1 and r_2 are the chain lengths of the oligomers expressed in segments. The choice of segment size is arbitrary. We take the specific volume of poly(ethylene oxide) of high molecular weight to be 0.894 cm³/g and use:

$$\Delta H_m = 44 \times 0.894 \Delta h_m = 39.3 \Delta h_m$$

Taking each term in χ to be linearly dependent on $1/T$ leads to:

$$\chi_0 = \chi_{0,1} + \chi_{0,2}/T \quad (3)$$

$$\chi_1 = \chi_{1,1} + \chi_{1,2}/T \quad (4)$$

etc., and so to an expression for the enthalpy of mixing per mole of segments:

$$\frac{\Delta H_m}{R} = \phi_1 \phi_2 (\chi_{0,2} + \chi_{1,2} \phi_1 + \chi_{2,2} \phi_1^2 + \dots) \quad (5)$$

In Figure 4 we plot the experimental enthalpies of mixing as $\Delta H_m/R\phi_1\phi_2$ versus ϕ_1 . The results are well represented by straight lines, i.e. are consistent with:

$$\frac{\Delta H_m}{R} = \phi_1 \phi_2 (\chi_{0,2} + \chi_{1,2} \phi_1) \quad (6)$$

It is clear from Figure 4 that $\chi_{0,2}$ and $\chi_{1,2}$ vary from mixture to mixture. In order to investigate this variation further

Table 3 Enthalpy changes on mixing equal volumes of oligomers at 30°C

Mixture	Δh_m (J/cm ³)	Mixture	Δh_m (J/cm ³)
E106H/E300H	-1.11		
E106H/E600H	-0.55		
E150H/E200H	0.06		
E150H/E300H	0.31		
E150H/E400H	0.59		
E150H/E600H	1.07		
E200H/E300H	0.11		
E200H/E400H	0.30		
E200H/E600H	0.58		
E300H/E600H	0.21	E300M/E600M	0.02
P134H/P250H	-0.05		
P134H/P1000H	~0.9		
P250H/P425H	0.27		
P250H/P750H	1.04		
P250H/P1000H	1.34	P250M/P1000M	0.00
P425H/P750H	0.26		
P425H/P1000H	0.45	P425M/P1000M	-0.01
P425H/P2025H	0.95		
		P750M/P1000M	-0.06

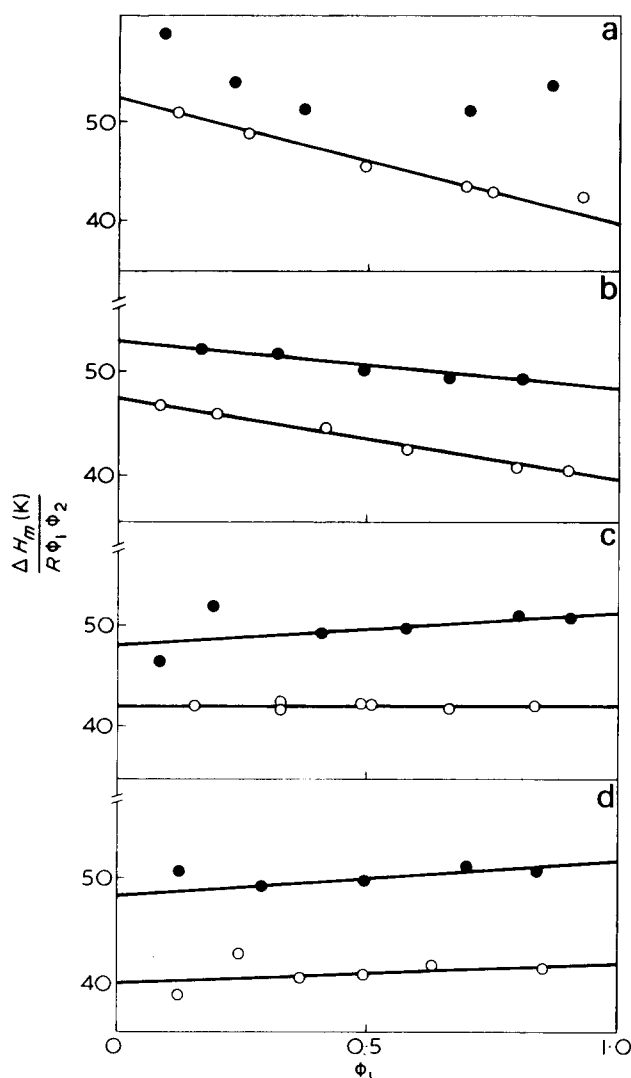


Figure 4 Enthalpy of mixing ΔH_m (J/mol) plotted as $\Delta H_m/R\phi_1\phi_2$ versus ϕ_1 . The data are for E300M (○) and E600M (●) mixed with the α,ω -methoxy-oligomers of propylene oxide: (a) P1000M; (b) P750M; (c) P425M; (d) P250M

we refine the model for the mixture along the lines suggested by Orwoll and Flory⁸.

Orwoll and Flory have explained the mixing of n-alkanes of differing chain length by accounting for the differing properties of the component liquids and the differing interactions of midchain and end-segments. Unfortunately the liquid properties of the α,ω -methoxy oligomers of ethylene oxide and propylene oxide are not well known and so a detailed application of theory is not possible. However, we can take advantage of the fact that the liquid properties of the oligomers are all similar, so that equation of state contributions to the enthalpy of mixing will be small compared to contributions arising from the interchange of contacts. We find it convenient to use the notation of Flory^{8,9}, particularly in anticipation of our later discussion of the volume changes on mixing.

Enthalpy of mixing

We assume that the oligomers under consideration have identical reduced volumes, pressures and temperatures so that the energy of mixing arises only from interchange of

segment contacts. We distinguish four types of segment and denote these:

	Component	Midchain segment	End segment
Poly(ethylene oxide)	1	A	B
Poly(propylene oxide)	2	C	D

Let ψ and σ represent segment and site fractions in the pure components. Thus ψ_A is the segment fraction of mid-chain segments in component 1, and:

$$\sigma_A = \psi_A s_A / (\psi_A s_A + \psi_B s_B) \quad (7)$$

is the corresponding site fraction: s being the number of contact sites per segment. Similarly we let ϕ and θ represent segment and site fractions in the mixture. Thus ϕ_1 and θ_1 are the segment and site fraction of component 1, while $\phi_1 \psi_A$ and $\theta_1 \sigma_A$ are the corresponding segment and site fractions of midchain segments of component 1. We note that within our assumptions segment and volume fractions are identical.

Following Flory *et al.*⁹ we write the van der Waals energy per contact as $-\eta/\nu$. Thus we have for N_A segments of pure A in volume ν a total van der Waals interaction energy of:

$$E_{AA} = -N_A s_A \eta_{AA} / 2\nu \quad (8)$$

For a mixture, the interchange energy per contact is written, for example for A and B segments, as:

$$\Delta \eta_{AB} / 2\nu = (\eta_{AA} + \eta_{BB} - 2\eta_{AB}) / 2\nu \quad (9)$$

Assuming random mixing of segments we have for N_1 segments of component 1 in volume ν a van der Waals energy in excess of that for the corresponding numbers of pure segments A and B equal to:

$$E_{11} = (N_1 s_1 / 2\nu) \sigma_A \sigma_B \Delta \eta_{AB} \quad (10)$$

with similar equations for component 2 and the mixture, i.e.:

$$E_{22} = (N_2 s_2 / 2\nu) \sigma_C \sigma_D \Delta \eta_{CD} \quad (11)$$

$$E_{12} = (N s / 2\nu) [\theta_1^2 \sigma_A \sigma_B \Delta \eta_{AB} + \theta_2^2 \sigma_C \sigma_D \Delta \eta_{CD} + \theta_1 \theta_2 (\sigma_A \sigma_C \Delta \eta_{AC} + \sigma_A \sigma_D \Delta \eta_{AD} + \sigma_B \sigma_C \Delta \eta_{BC} + \sigma_B \sigma_D \Delta \eta_{BD})] \quad (12)$$

In these equations:

$$N = N_1 + N_2 \quad (13)$$

$$s = \phi_1 s_1 + \phi_2 s_2 \quad (14)$$

$$s_1 = \psi_A s_A + \psi_B s_B \quad (15)$$

$$s_2 = \psi_C s_C + \psi_D s_D \quad (16)$$

We can therefore write the change in van der Waals energy on randomly mixing the two components as:

$$\begin{aligned} \Delta E_m &= E_{12} - E_{11} - E_{22} \\ &= (Ns/2\nu)\theta_1\theta_2[-\sigma_A\sigma_C\Delta\eta_{AB} - \sigma_C\sigma_D\Delta\eta_{CD} \\ &\quad + \sigma_A\sigma_C\Delta\eta_{AC} + \sigma_A\sigma_D\Delta\eta_{AD} + \sigma_B\sigma_C\Delta\eta_{BC} \\ &\quad + \sigma_B\sigma_D\Delta\eta_{BD}] \end{aligned} \quad (17)$$

which we write as:

$$\Delta E_m = (Ns/2\nu)\theta_1\theta_2\Delta\eta_{12} \quad (18)$$

or as

$$\Delta E_m = (Ns_1\Delta\eta_{12}/2\nu)\phi_1\theta_2 \quad (19)$$

For small external pressures the energy change on mixing approximates the enthalpy change on mixing. Thus we write, for 1 mole of segments:

$$\Delta H_m = (Ls_1\Delta\eta_{12}/2\nu)\phi_1\theta_2 \quad (20)$$

where ν is the volume containing 1 mole of segments. This can be rearranged to:

$$\Delta H_m = \frac{\phi_1\phi_2(Ls_1\Delta\eta_{12}/2\nu)}{1 + \phi_1\left(\frac{s_1}{s_2} - 1\right)} \quad (21)$$

which, for $s_1/s_2 \approx 1$, can be written:

$$\Delta H_m = \phi_1\phi_2 \left(\frac{Ls_1\Delta\eta_{12}}{2\nu} \right) \left[1 - \phi_1 \left(\frac{s_1}{s_2} - 1 \right) \right] \quad (22)$$

whence, comparing equations (6) and (22):

$$\chi_{0,2} = \frac{1}{R} \left(\frac{Ls_1\Delta\eta_{12}}{2\nu} \right) \quad (23)$$

and

$$\chi_{1,2} = \frac{1}{R} \left(\frac{Ls_1\Delta\eta_{12}}{2\nu} \right) \left(1 - \frac{s_1}{s_2} \right) \quad (24)$$

Values of s_1/s_2 can be calculated from $\chi_{0,2}$ and $\chi_{1,2}$: the results are collected together in Table 4.

The question remains as to whether the values of $\chi_{0,2} = Ls_1\Delta\eta_{12}/2\nu R$ and s_1/s_2 are meaningful. Both are complex quantities (see equations 15–18). Neither the accuracy of the data nor the sophistication of the theory warrant their quantitative reduction to simpler terms. However, we can make two encouraging observations.

(a) A rough double extrapolation of s_1/s_2 to the limit of two infinite chains leads to a value near 1.1. This is consistent with the value of 1.08 estimated¹⁰ from the dimensions of the two chains in helical conformation.

(b) We expect the major contribution to $\Delta\eta_{12}$ to come from the term $\sigma_A\sigma_C\Delta\eta_{AC}$ (equation 17), i.e. from the interaction of midchain segments. Other terms are small because the values of σ for terminal segments are small. For segments of similar shape (similar surface to volume ratio) the product of site fractions is roughly proportional to the product of weight fractions. Values of w_{AWC} (cal-

culated by assigning –OMe groups as end-groups) and of $\chi_{0,2}/w_{AWC}$ are listed in Table 4: as anticipated the latter quantity is approximately constant (at 65K).

The enthalpies of mixing of oligomers of identical chemical structure but differing chain length should, in principle, be simpler to interpret than those for the mixtures, since only one interchange energy ($\Delta\eta_{AB}$ or $\Delta\eta_{CD}$) is involved. However the values of Δh_m obtained for the methoxy-ended oligomers are very small (see Table 3) and so predominance of contributions arising from interchange of contacts can no longer be assumed.

Volume change on mixing

The volume changes on mixing predicted by a theory based only on contributions from interchange of contacts are necessarily positive when the overall interchange energy ($\Delta\eta_{12}$) is positive¹¹. For example use of Flory's theory⁹ with identical reduced volumes, pressures and temperatures for both components and with parameters suitably chosen (see Table 5, calculation 7, for details) leads, for $\phi_1 = 0.5$, to $\Delta h_m = 2.2 \text{ J/cm}^3$ and $\Delta v_m = +1.42 \text{ mm}^3/\text{cm}^3$. These values can be compared with experimental values for E300M/P250M at $\phi_1 = 0.5$ of $\Delta h_m = 2.2 \text{ J/cm}^3$ and $\Delta v_m = -0.27 \text{ mm}^3/\text{cm}^3$ (Table 3). It seems clear that equation of state contributions to Δv_m cannot be ignored.

According to Flory *et al.*⁹ the volume and enthalpy changes on mixing are given, for 1 cm^3 of pure components, by:

$$\Delta v_m = (\bar{v} - \bar{v}_0)/\bar{v}_0 \quad (25)$$

$$\begin{aligned} \Delta h_m &= (v_{sp}^*/v_{sp,0})[\phi_1 p_1^*(\bar{v}_1^{-1} - \bar{v}^{-1}) \\ &\quad + \phi_2 p_2^*(\bar{v}_2^{-1} - \bar{v}^{-1}) + \phi_1\theta_2 X_{12}\bar{v}^{-1}] \end{aligned} \quad (26)$$

Table 4 Parameters for ethylene oxide/propylene oxide oligomer systems

Mixture	$\chi_{0,2}$ (K)	$\chi_{1,2}$ (K)	s_1/s_2	w_{AWC}	$\chi_{0,2}/w_{AWC}$ (K)
E300M/P250M	40	2.0	0.95	0.63	63
E300M/P425M	42	0.0	1.00	0.70	60
E300M/P750M	48	-8.0	1.17	0.75	64
E300M/P1000M	52	-12.0	1.23	0.76	68
E600M/P250M	49	+3.5	0.93	0.70	70
E600M/P425M	48	+3.0	0.94	0.78	62
E600M/P750M	53	-4.0	1.08	0.83	64
E600M/P1000M	~60	—	—	0.85	~70

Table 5 Calculated values of enthalpy and volume changes on mixing. $v_{sp,1} = 0.963 \text{ cm}^3/\text{g}$; $v_{sp,2} = 1.074 \text{ cm}^3/\text{g}$; $X_{12} = 10 \text{ J/cm}^3$; $s_1/s_2 = 0.95$; $T = 30^\circ \text{C}$; $\phi_1 = 0.5$

Calculation	α_1 ($\times 10^4 \text{ K}^{-1}$)	α_2 ($\times 10^4 \text{ K}^{-1}$)	γ_1 (J/cm ³ K)	γ_2 (J/cm ³ K)	Δh_m (J/cm ³)	Δv_m (mm ³ /cm ³)
1	8	10	1.5	1.0	2.06	-2.23
2	8	9	1.5	1.0	2.14	-0.61
3	8	8	1.5	1.0	2.18	+1.13
4	8	7	1.5	1.0	2.17	+3.00
5	8	9	1.5	0.9	2.14	-1.01
6	8	9	1.5	0.8	2.14	-1.45
7	8	8	1.0	1.0	2.18	+1.42

In these equations subscript 0 refers to the unmixed state. Characteristic quantities (denoted by asterisks) and reduced quantities (denoted by tildes) are related to measurable quantities by, for example for component 1:

$$v_{sp,1}^* = v_{sp,1} / \{1 - \alpha_1 T / [3(1 - \alpha T)]\}^3;$$

$$\tilde{v}_1 = v_{sp,1} / v_{sp,1}^* \quad (27)$$

$$p_1^* = \gamma_1 T \tilde{v}_1^2; \quad \tilde{p}_1 = p / p_1^* \quad (28)$$

$$T_1^* = T \tilde{v}_1^{4/3} / (\tilde{v}_1^{1/3} - 1); \quad T_1 = \tilde{T} / T_1^* \quad (29)$$

where α is the coefficient of thermal expansion, $(1/V)(\partial V/\partial T)_p$, and γ is the thermal pressure coefficient, $(\partial P/\partial T)_V$. Quantities pertaining to the mixture are:

$$v_{sp}^* = w_1 v_{sp,1}^* + w_2 v_{sp,2}^* \quad (30)$$

$$\tilde{v}_0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \quad (31)$$

and \bar{v} , which is obtained from \tilde{v}_0 and \tilde{T}_0 by successive approximations as described by Abe and Flory⁹. The overall interaction parameter X_{12} is given by:

$$X_{12} = s_1 \Delta \eta_{12} / 2v^* \quad (32)$$

The initial data needed for calculation of Δh_m and Δv_m are v_{sp} , α , and γ for each component and X_{12} and s_1/s_2 for the mixture.

As mentioned earlier complete initial data for our systems are not available, and so proper account cannot be taken of the contributions of midchain and end-segments to the liquid properties of the two components and the mixture. However, the data which are available allow a limited discussion of the volume changes on mixing. Specific volumes are listed in Table 1. Values of α and γ will be molecular weight dependent, in the sense that α will decrease and γ increase with an increase in molecular weight. One point of comparison for the two polymers is at high molecular weight ($\bar{M}_v > 10^6$) when end effects are negligible. Values at $T \approx 80^\circ\text{C}$ of $\alpha_1 = 6.7 \times 10^{-4} \text{K}^{-1}$ ¹² and $\alpha_2 = 7.6 \times 10^{-4} \text{K}^{-1}$ ¹³ have been recorded. Values of α and γ measured for α,ω -methoxy-poly(epoxide) oligomers at $T = 30^\circ\text{C}$ are set out below:

	$\alpha \times 10^4 (\text{K}^{-1})$	$\gamma (\text{J}/\text{cm}^3\text{K})$
E400M	7.8 ¹⁴	1.51 ¹⁴
P2025M	7.8 ¹⁴	1.15 ¹⁴

The value of $\alpha_2 = 7.8 \times 10^{-4} \text{K}^{-1}$ for P2025M seems low in comparison with that for the high polymer.

In the light of these data we assume the following values for the system E300M/P250M at 30°C

$$\alpha_1 = 8 \times 10^{-4} \text{K}^{-1}; \quad \gamma_1 = 1.5 \text{J}/\text{cm}^3\text{K}$$

$$\alpha_2 = 8.8 \times 10^{-4} \text{K}^{-1}; \quad \gamma_2 = 1.0 \text{J}/\text{cm}^3\text{K}$$

With $s_1/s_2 = 0.95$ (Table 4) and $X_{12} = 10 \text{J}/\text{cm}^3$ (chosen to fit $\Delta h_m = 2.15 \text{J}/\text{cm}^3$) these values of α and γ , together with specific volumes taken from Table 1, give $\Delta v_m = -2.7 \times 10^{-4}$ at $\phi_1 = 0.5$. We note that variations in α and γ have little effect on Δh_m calculated for given values of

s_1/s_2 and X_{12} , but have a marked effect on Δv_m . This point is illustrated in Table 5. These calculations support our earlier assumption that equation of state contributions to Δh_m are small for our systems.

The results in Table 4 ($s_1/s_2, \chi_{0,2}$) can be used to determine s_1/s_2 and X_{12} for our systems. (X_{12} is almost proportional to $\chi_{0,2}$, via equations (23) and (32) since v_{sp}^* is almost constant in our systems: therefore the value of $X_{12} = 10 \text{J}/\text{cm}^3$ used for E300M/P250M can be used to fix X_{12} for the other systems.) Values of s_1/s_2 and X_{12} are set out in Table 6. Use of these values with constant values of α and γ (as set out above) does not reproduce the pattern of volume changes on mixing found experimentally (see Table 6). However small adjustments to α and γ , in the direction and roughly of the magnitude indicated by measurements on the n-alkanes¹⁶, give values which can be used to calculate a pattern of volume changes similar to those found experimentally (see Tables 2 and 6).

CONCLUSIONS

Liquid oligomers of ethylene oxide and propylene oxide have similar physical properties. Nevertheless a combination of a random conformational entropy change with a van Laar energy change, as in the Flory-Huggins approximation, does not satisfactorily explain the thermodynamic mixing properties. In the case of the α,ω -hydroxy-oligomers we detect important effects attributable to end-group interactions (hydrogen bonding). In the case of α,ω -methoxy-oligomers we find that the Flory-Huggins interaction parameter is concentration dependent: this is attributable to differences in the surface to volume ratios of the two components. In addition we find that the volume changes on mixing α,ω -methoxy-oligomers can be explained only by taking account of the slightly different liquid properties of the two components (in addition to the interchange energy).

Table 6 Calculated values of the enthalpy and volume changes on mixing: $T = 30^\circ\text{C}$, $\phi_1 = 0.5$

Mixture	s_2/s_1	X_{12} (J/cm^3)	Assumption 1 ^a		Assumption 2 ^b	
			Δh_m (J/cm^3)	Δv_m ($\text{mm}^3/(\text{J}/\text{cm}^3)$)	Δh_m (J/cm^3)	Δv_m ($\text{mm}^3/(\text{J}/\text{cm}^3)$)
E300M/P250M	0.95	10.0	2.2	-2.7	2.2	-2.7
E300M/P425M	1.00	10.5	2.2	-2.5	2.2	-0.5
E300M/P750M	1.16	11.9	2.3	-1.9	2.3	+2.0
E300M/P1000M	1.23	12.9	2.4	-1.3	2.4	+4.4
E600M/P250M	0.93	12.1	2.6	-0.2	2.6	-4.7
E600M/P425M	0.94	12.1	2.6	-0.2	2.6	-2.6
E600M/P750M	1.07	13.2	2.7	+0.1	2.7	-0.3

^aAssumption 1: Values of α and γ constant as set out in text. Values of v_{sp} as in Table 1. ^bAssumption 2: Values of α and γ as set out below. Values of v_{sp} as in Table 1.

Sample	E300M	E600M	P250M	P425M	P750M	P1000M
$\alpha (10^4 \text{K}^{-1})$	8	7.8	8.8	8.7	8.6	8.5
$\gamma (\text{J}/\text{cm}^3\text{K})$	1.50	1.52	1.00	1.01	1.02	1.03

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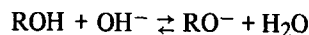
APPENDIX

Methoxylation of α,ω -hydroxy-oligomers of ethylene oxide and propylene oxide

The Williamson ether synthesis may be used to replace the hydroxy-end-groups of polymers by methoxy-groups. The synthesis is based upon the irreversible reaction between an alkoxide ion and an alkyl halide, the alkoxide ion normally being formed by reaction between the hydroxy-group and an alkali metal. However, for low molecular weight polyglycols this procedure is unsatisfactory, since formation of the alkoxide anion is slow and only low conversions are achieved.

The alternative method that we have adopted relies upon reaction between the hydroxy-group and an alkali hydroxide

to generate an equilibrium concentration of the alkoxide ion:



Under the conditions we use the position of equilibrium lies somewhat to the left (e.g. 40% conversion to alkoxide). However, this is unimportant since the equilibrium is rapidly established and subsequent reaction between the alkoxide ion and the alkyl halide is fast and irreversible. Furthermore the rate of hydrolysis of the alkyl halide by the alkali is comparatively low, and all three reactants may be present in the reaction mixture simultaneously.

The following procedure is for methoxylation of E300H, i.e. α,ω -hydroxy-poly(ethylene oxide) of $\bar{M}_n = 300$. The molar ratios, $\text{OH}^-/\text{ROH}/\text{R}'\text{I}$, were maintained in adapting the method to other oligomers.

Powdered potassium hydroxide (500 g, 85% laboratory grade) was stirred with tetrahydrofuran* (1 dm³, refluxed for 12 to 36 h over calcium hydride and distilled) under nitrogen. The flask was cooled in an ice-bath. E300H (100 cm³) was stirred in, and then methyl iodide (70 cm³, general purpose grade) was added from a tap funnel over a period of 15 min. A thick creamy-white precipitate appeared within a few minutes: however stirring was continued for a few hours. The mixture was then filtered through a glass sinter and the filtrate rotary evaporated at a temperature no higher than 40°C. The resulting yellow oil (130 cm³) was diluted with dichloromethane (200 cm³, distilled), and this solution was extracted successively with eight 50 cm³ portions of 10% aqueous sodium carbonate solution and then with 25 cm³ portions of distilled water until the solution was neutral (usually 3 portions). The decolourized organic phase was dried (anhydrous calcium sulphate), filtered and rotary evaporated (<40°C). The liquid product was evacuated (<1 Pa) for 5 to 10 days to remove all traces of solvent. The final yield was about 90 g (75% of theoretical).

The composition of the product was checked by elemental analysis (identical with prediction for E300M, no iodine) and by end-group analysis (phthaloylation in pyridine¹⁸, 99.7 ± 0.5% conversion of -OH to -OMe). Infra-red spectroscopy was used to show that the strong broad band at about 3500 cm⁻¹ due to -OH stretching was virtually absent in E300M. Quantitative assessment of the conversion of -OH to -OMe based upon the band near 3500 cm⁻¹, with the C-H stretching band near 2900 cm⁻¹ used as reference and with the band at 1640 cm⁻¹ used to estimate residual moisture, gave a value of 99 ± 1%.

The molecular weight distribution of E300M, as assessed by vapour pressure osmometry and gel permeation chromatography differed insignificantly from that of E300H. The elution volume in g.p.c. (Styragel columns, tetrahydrofuran solvent) of E300M was higher than that of E300H: this is attributable to negative adsorption of the hydroxy-ended oligomer.

* There has been a report¹⁷ that impure tetrahydrofuran may form an explosive mixture with solid potassium hydroxide, and we have preferred to use chlorobenzene in subsequent work. Use of this solvent has other advantages when the reaction is undertaken with long chain alkyl halides.