The pressure–volume–temperature properties of polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) and poly(propylene glycol) as a function of molecular weight

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The pressure–volume–temperature (*PVT*) properties of a number of polymer liquid samples as a function of molecular weight have been investigated. The polymers studied included polyethylene (PE), poly(dimethyl siloxane) (PDMS), poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG). The properties of the end-groups and their effect on the density, compressibility, thermal pressure coefficient and expansivity as a function of their concentration are discussed. The specific volume exhibits a clear $1/M_n$ dependence for those molecules with weakly interacting end-groups, i.e. PE and PDMS. The specific volume is found to be independent of M_n for PEG and PPG, which can hydrogen-bond to each other. The data sets have been compared using equation-of-state theories.

(Keywords: *PVT* properties; polymer liquids; molecular weight; polyethylene; poly(dimethyl siloxane); poly(ethylene glycol); poly(propylene glycol); end-groups)

INTRODUCTION

The change in density as a function of pressure, temperature and molecular weight is an important fundamental material property. Thermodynamic properties such as the expansivity, compressibility and pressure coefficient $(dP/dT)_V$, can be calculated once this is known. Other equilibrium optical, electrical and material properties such as the refractive index, dielectric coefficient, glass transition temperature and surface tension are also functions of the density.

The density is a function of molecular weight for polymer liquids. A 20% change in the density is typical for changes in the degree of polymerization from 10 to 1000. This change in the density with molecular weight can be thought of as due to a change in the concentration of end-groups with molecular weight. The end-group segments are assumed to have different molar volumes from the main-chain segments. The molar volume of the end-group is determined by the size of the end-group and the fact that the end-groups have more degrees of freedom than the main-chain mers.

In this paper we describe the pressure–volume–temperature (*PVT*) properties, as a function of molecular weight, for four polymers, polyethylene (PE), poly(dimethyl siloxane) (PDMS), poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG). We interpret the results in terms of the concentration of end-groups and their composition.

THEORY

Equation-of-state theories can be used to characterize *PVT* data. In their simplest application they provide fitting functions[1]. The physical properties of the polymer are then represented by three or more reduction parameters. The limitation in the use of equations of state lies in their inability to describe the *PVT* data to within the experimental accuracy except for very restricted temperature and pressure domains.

A class of equations of state called cell models have been particularly useful in describing the thermodynamic properties of polymer systems. The Flory, Orwoll and Vrij[2] (FOV) theory can be derived in the context of the cell model formalism, developed by Lennard-Jones and Devonshire[3] to describe the properties of small molecular liquids. The N polymer molecules are divided into r mers, with each mer occupying one cell. The connectivity of the polymer is taken into account by assuming that each mer has $3c$ degrees of freedom, where c is a constant less than one. The FOV theory does not give as accurate a description of *PVT* data as other theories such as the cell model[4] or the modified cell model[5]. It is, however, one of the most commonly used, and when making comparisons between different polymers will give qualitatively the same picture.

Details of the derivation of the FOV equation of state and its application to mixtures are presented in detail elsewhere[6]. The equation of state has the following form:

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - 1) - 1/\tilde{T}\tilde{V} \tag{1}$$

Equation (1) is written in terms of reduced pressure, temperature and volume variables $\tilde{P}$, $\tilde{T}$ and $\tilde{V}$. The reduction variables P^*, T^* and v^* are defined as follows:

$$\tilde{T} = Tck/\varepsilon^* = T/T^* \tag{2}$$

$$\tilde{P} = Pv^*/ckT^* = P/P^* \tag{3}$$

$$\tilde{V} = v/v^* = v_{sp}/v_{sp}^* \tag{4}$$

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where ε^* is the characteristic interaction energy per mer, v^* is the hard-core mer volume and v_{sp}^* is the hard-core specific volume. The parameters r, v^*, ε^* and c are the microscopic parameters of the model. The relationships between these microscopic parameters and the reduction parameters P^*, T^* and v_{sp}^*, which specify the macroscopic physical properties of the system, are:

$$Nrv^* = Mv_{\mathrm{sp}}^* \tag{5}$$

$$Nr\varepsilon^* = MP^*v_{\mathrm{sp}}^* \tag{6}$$

$$Nrc = MP^*v_{\mathrm{sp}}^*/kT^* \tag{7}$$

where M is the molecular weight of the molecule, N is the number of molecules and r is the number of mers per molecule. In the case of a polydisperse polymer sample, these equations apply as long as the same average is used for r and M.

Let us assume that the effect of molecular weight on some property Γ is simply a volume-fraction average of that property between the main-chain mers and the end-group mers. Then, within the context of the cell model, we can write the following expression for the dependence or Γ on r or the molecular weight:

$$\Gamma(r) = \Gamma_1\phi_1 + \Gamma_2\phi_2 \tag{8}$$

where ϕ_i and Γ_i are the volume fraction and value of Γ for each component mer, respectively. If we denote by v_1 and v_2 the volumes of the main-chain and end-group mers, respectively, then ϕ_1 and ϕ_2 take the following form:

$$\begin{aligned} \phi_1 &= 1/(1 + 2v_2/rv_1) \\ \phi_2 &= 1/(1 + rv_1/2v_2) \end{aligned} \tag{9}$$

where we have assumed that there are two end-groups attached to each chain. In the limit where r is large, we can expand these expressions. Using equation (5) we can write equation (8) in the form:

$$\begin{aligned} \Gamma(M_{\mathrm{n}}) = \Gamma_1 &- (2V_2/M_{\mathrm{n}}v_{1\mathrm{sp}})(\Gamma_1 - \Gamma_2) \\ &+ (2V_2/M_{\mathrm{n}}v_{1\mathrm{sp}})^2(\Gamma_1 - \Gamma_2) + \ldots \end{aligned} \tag{10a}$$

where V_2 is the molar volume of the end-group mers, M_{n} is the number-average molecular weight of the polymer chain and $v_{1\mathrm{sp}}$ is the specific volume of the main-chain mers. Keeping the lowest-order term one obtains the well known relation:

$$\Gamma(M_{\mathrm{n}}) = \Gamma_\infty - \alpha/M_{\mathrm{n}} \tag{10b}$$

where Γ_∞ is the value of $\Gamma(M_{\mathrm{n}})$ at infinite molecular weight and α is a constant. Using equations (10a,b) we can estimate the value of M_{n} for which we start to see deviations from linearity in equation (10b). To do this we simply ask when the third term in equation (10a) becomes of the order of a tenth of the second term, for example, i.e. when $2V_2/M_{\mathrm{n}}v_{1\mathrm{sp}} = 0.1$. The theory implies that we should see deviations from equation (10b) when the molar volume of the chain is of the order of 10 times that of the end-groups.

If the end-groups have more degrees of freedom, then we expect that their molar volume will have different temperature and pressure dependences than those of the main-chain mers. This implies that the end-groups will have a higher compressibility and expansivity. Based on this argument we expect to see deviations from equation (10b) in properties such as the specific volume at higher molecular weights as we lower the pressure or increase the temperature. This is indeed what we observe in the case of PE and PDMS, as we will show below. In the case where the end-group is constrained by the presence of a hydrogen bond to another polymer, we expect the number of degrees of freedom of the end-group to be comparable to those of the main-chain mers. Under these circumstances we might expect that the physical size of the end-group dominates the dependence of the specific volume on molecular weight. For PEG and PPG with hydroxy end-groups we observe that the specific volume is independent of molecular weight. This implies that the enhanced mobility of the end-groups is the principal factor determining the molecular-weight dependence of such equilibrium properties as the specific volume.

EXPERIMENTAL

Materials

The linear hydrocarbons, obtained from Alfa Products, were specified as 99% pure, and were used as supplied. All of the polymer samples were obtained from Polysciences. They were dried overnight in a vacuum oven before use. The properties of the materials used are shown in *Table 1*. Some of the PPG samples were treated

Table 1 Properties of polymers

Polymer	M_{n}[a]	$M_{\mathrm{w}}/M_{\mathrm{n}}$	Density at 22°C (g cm^{-3})
$C_{11}H_{24}$	156.3		0.740[g]
$C_{14}H_{30}$	198.4		0.760[g]
$C_{16}H_{34}$	226.4		0.770[g]
$C_{24}H_{50}$	338.7		0.933
$C_{36}H_{74}$	507.0		0.948
$C_{44}H_{90}$	619.2		0.956
Polyethylene 1000	1100[b]	1.07[b]	0.956
Polyethylene 2000	2100[b]	1.09[b]	0.974
High-density PE	28 000[b]	4.5[b]	0.949
Poly(dimethyl siloxane)	340[c]	1.01[f]	0.850[g]
	770[c]	1.13[f]	0.916[g]
	2600[c]	1.5[f]	0.953
	5200[c]	1.86[f]	0.957
	7830[c]	2.2[f]	0.960
	68 000[c]	3.3[f]	0.966
	187 000[c]	8.0[f]	0.966
Poly(propylene oxide)	400	1.3[f]	1.004
	1025[d]	1.7[f]	1.003
	2000	1.3[f]	0.999
	4000	1.7[f]	0.999
dimethyl ether	400		0.960
dimethyl ether	1000		0.972
dimethyl ether	2000		0.990
Poly(ethylene oxide) 300	302[e]	1.18[f]	1.123[g]
600	692[e]	1.06[f]	1.124[g]
1540	1470[e]	1.16[f]	1.215
	18 500		1.212
	100 000		1.207
monomethyl ether	350		1.091[g]
monomethyl ether	750		0.929[h]
dimethyl ether	600		1.072[g]
dimethyl ether	1000		0.944[h]

[a] Unmarked molecular weights are manufacturers' quotation
[b] G.p.c. relative to polyethylene standards
[c] M_{w} by viscosity, then adjusted by $M_{\mathrm{w}}/M_{\mathrm{n}}$
[d] Bimodal from g.p.c.
[e] Vapour-phase osmometry
[f] G.p.c. relative to polystyrene standards
[g] S.g. bottle
[h] S.g. bottle at 60°C, since sample melts in the vicinity of room temperature

to substitute methoxy groups on the end of the chains. The procedure used was as described previously[7].

PVT *measurements*

Densities of the liquid polymers were measured using a specific-gravity bottle. The densities of the solid polymers were measured at 25°C and atmospheric pressure using an autopycynometer (Micromeritics). The changes in density as a function of temperature and pressure were measured using a *PVT* apparatus, which has been fully described elsewhere[8]. It consists of a sample cell containing about 1–1.5 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows on changing temperature or pressure is used to calculate the volume change of the sample cell. In the isothermal mode, volume readings are obtained at fixed pressure intervals (usually 10 MPa) at a constant temperature. After measurements along an isotherm, the temperature is increased by 8–10°C and the process is repeated. The absolute accuracy of the device is 10^{-3} to $2 \times 10^{-3}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$; however, volume changes as small as 10^{-4} to $2 \times 10^{-4}\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ can be resolved. A version of the *PVT* apparatus is available as a complete instrument from Gnomix Research, Boulder, Colorado, USA.

Solid samples may be loaded directly into the cell prior to filling with mercury, and the weight of the cell along with the known densities assures a good air-free fill. For liquid samples the cell must first be filled with mercury, a known weight of mercury is removed and replaced by the sample, and the final weight used as a check. This latter procedure is more difficult and more prone to error owing to poor fills.

RESULTS

The polymers we studied can be classified into two distinct categories. The first category involves those polymers (PE, PDMS) whose end-groups can be assumed to be polymer segments or mers that have more degrees of freedom than the main-chain segements. In the second category (PEG, PPG) we have those polymers whose end-groups can hydrogen-bond to other polymer segments. The formation of these hydrogen bonds reduces the effective number of degrees of freedom of these end-groups to the extent that they exhibit bulk static properties similar to the main-chain segments.

The characteristics of the PE samples used are shown in *Table 1*. A typical *PVT* data set is shown in *Figure 1* for $C_{44}H_{90}$ (C44). *Figure 2* shows the temperature dependence of the specific volume for a number of PE oligomers at 0.1 MPa. A change in the density of the order of 20% occurs as a function of molecular weight in the range $11 < DP < 200$. The inset in *Figure 2* shows the dependence of the specific volume on $1/M_n$. A linear dependence over this molecular-weight range at lower temperatures is apparent. At higher temperatures a deviation from a linear dependence is observed, which in the context of the model discussed above would be interpreted as an increase in the molar volume of the end-group to the extent that the third term in equation (10a) is non-negligible. *Figure 3* shows the specific volume of the same samples at 20 MPa. The inset shows the dependence of the specific volume on molecular weight at different temperatures. At the higher pressures

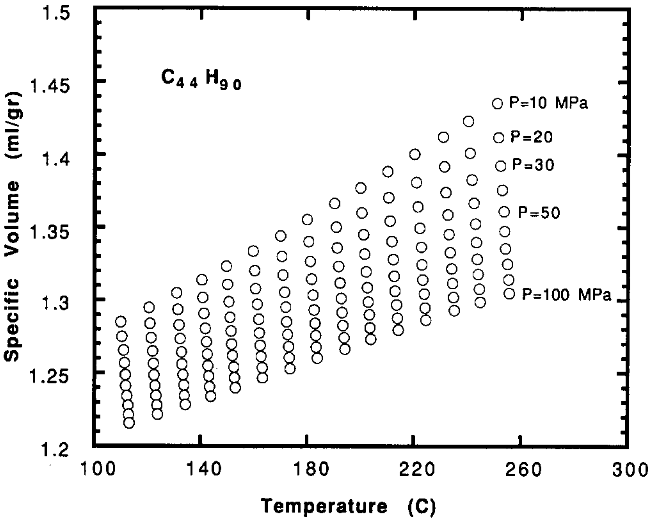

Figure 1 The specific volume as a function of temperature for C44. The data for pressures from 10 to 100 MPa are shown in 10 MPa increments

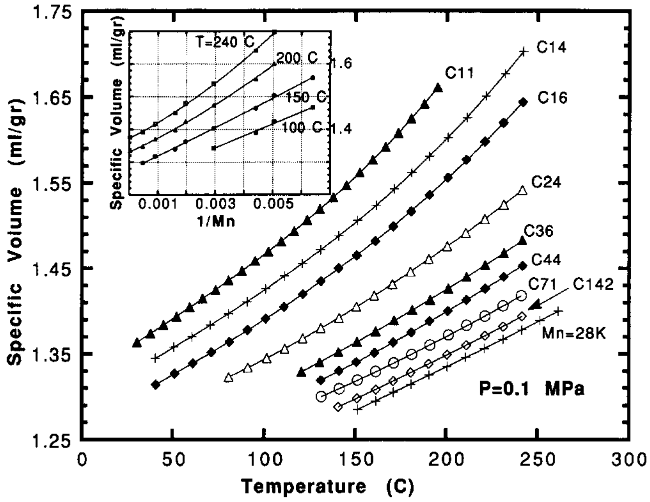

Figure 2 The specific volume at atmospheric pressure for PE oligomers plotted *versus* temperature. The inset shows the specific volume at this pressure as a function of $1/M_n$ for the temperatures indicated

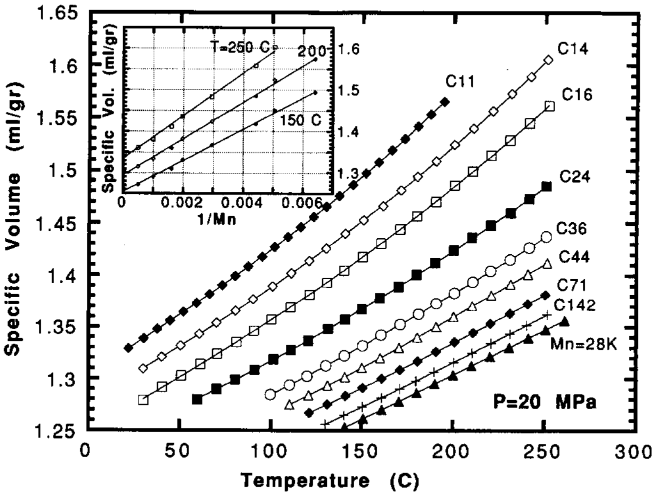

Figure 3 The specific volume at $P = 20$ MPa for PE oligomers plotted *versus* temperature. The inset shows the specific volume at this pressure as a function of $1/M_n$ for the temperatures indicated

we observe a clear linear dependence over all the temperatures shown.

Figure 4 shows a plot of the compressibility and thermal pressure coefficients at atmospheric pressure. As the density increases with increasing molecular weight, the physical properties of the samples approach limiting values as the concentration of end-groups decreases. These curves were generated using the equation of state. The equation of state was fitted to low-pressure *PVT* data. Pressure and temperature ranges were chosen so that the equation of state provided fits to the experimental data to within the experimental accuracy of the data. Then the equation of state was used to generate the compressibility, thermal pressure coefficient and expansivity of the liquid in that temperature range. The equation of state is used to smooth experimental noise and hence reduce the scatter in the computed derivatives of the *PVT* data.

The characteristics of the PDMS samples used in the study are shown in *Table 1*. *Figure 5* shows the specific volume at a pressure of 0.1 MPa for the differing molecular-weight samples. Once again we see that a 20% change in specific volume occurs in this system over the range of $4 < DP < 50$. As in the case of PE, the specific volume has a linear dependence on $1/M_n$ as shown by the inset in *Figure 5*. *Figure 6* shows the compressibility and thermal pressure coefficient for the same samples shown in *Figure 5*. The molecular-weight dependence is similar to that observed for the PE samples. The properties approach their asymptotic values as the concentration of end-groups decreases.

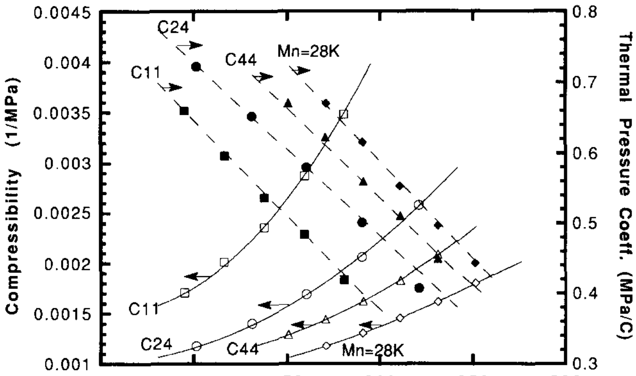

Figure 4 The compressibility and thermal pressure coefficient plotted as functions of temperature at atmospheric pressure for the indicated PE samples

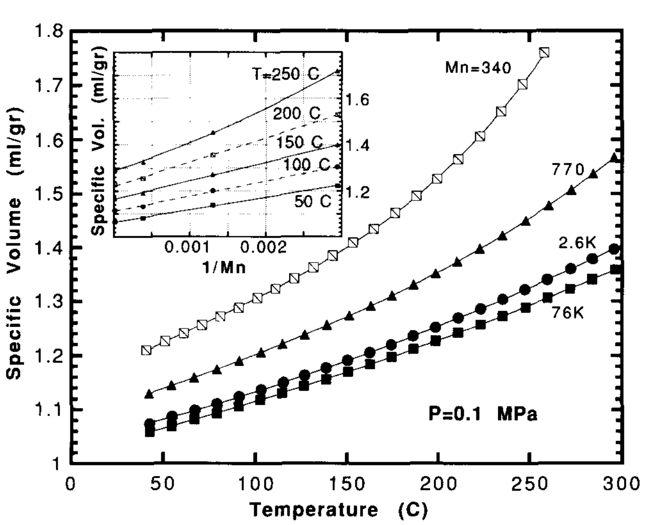

Figure 5 The specific volume at atmospheric pressure for the indicated PDMS samples plotted *versus* temperature. The inset shows the specific volume at this pressure as a function of $1/M_n$ for the temperatures indicated

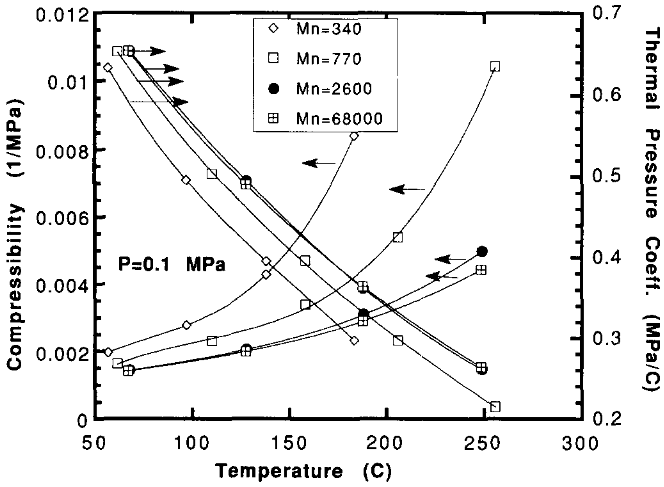

Figure 6 The compressibility and thermal pressure coefficient plotted as functions of temperature at atmospheric pressure for the indicated PDMS samples

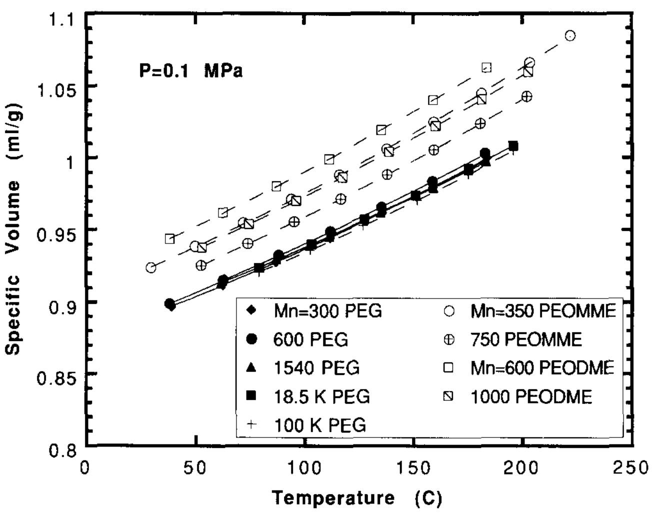

Figure 7 The specific volume at atmospheric pressure for the indicated PEG, PEOMME and PEODME samples plotted *versus* temperature

Table 1 shows the characteristics of the PEG samples used. Some of the samples used have end-groups that cannot form hydrogen bonds. These are the samples labelled PEG dimethyl ether (PEODME) and PEG monomethyl ether (PEOMME), respectively, indicating the nature and number of the end-groups used to cap these polymers. The PEODME polymer cannot form hydrogen bonds with its neighbours via its end-groups. *Figure 7* shows a plot of the specific volume at 0.1 MPa as a function of the temperature for the PEG, PEOMME and PEODME samples listed in *Table 1*. The obvious observation is that the density is not a strong function of the molecular weight for the PEG samples[9]. In fact, the equilibrium physical properties of all the PEG samples are remarkably similar, as shown in *Figure 8*. This strongly suggests that the end-groups form hydrogen bonds with other molecules so that all of the samples

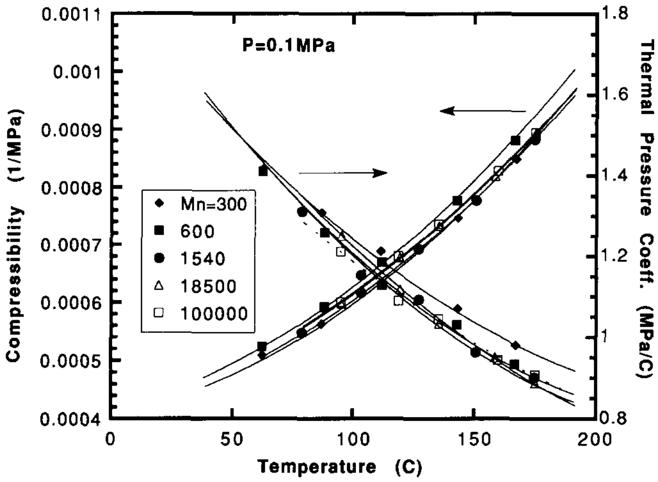

Figure 8 The compressibility and thermal pressure coefficient plotted as functions of temperature at atmospheric pressure for the indicated PEG samples

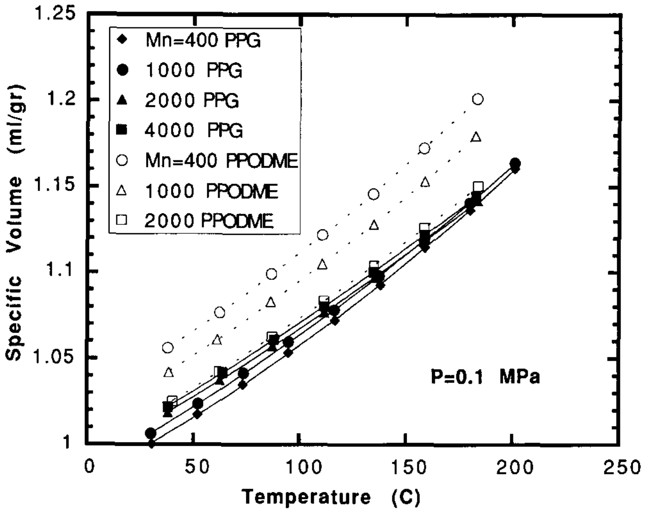

Figure 9 The specific volume at atmospheric pressure for the indicated PPG and PPODME samples plotted *versus* temperature

have the equilibrium properties of PEG in the limit of high M_n. Also shown in *Figure 7* are the 0.1 MPa data for the PEOMME and PEODME samples. We observe that these samples have higher specific volumes and that the specific volume is a function of the molecular weight. This is expected since we have end-groups that do not bond to other molecules, and which we expect to have higher degrees of freedom. Thus, the behaviour of these liquids is similar to that exhibited by the PE and PDMS samples.

Table 1 shows the characteristics of the PPG samples used. Some of the samples used have end-groups that cannot form hydrogen bonds. These are the samples labelled PPO dimethyl ether (PPODME), indicating the nature of the end-group used to cap the polymer. *Figure 9* shows the specific volume as a function of temperature at 0.1 MPa. As in the case of PEG, the density of the PPG samples is a weak function of the molecular weight. Here again we must suspect that the end-groups hydrogen-bond to each other to form an effective infinite-molecular-weight molecule. Although the densities of the various samples do not change appreciably over the temperature range shown, one can observe a change in the expansivity. *Figure 10* shows the compressibility and thermal pressure coefficient for these samples. As with the PEG samples, we observe that the compressibility is independent of the molecular weight, and the thermal pressure coefficient shows a weak dependence on M_n. *Figure 9* also shows the specific volumes of the PPODME samples. These polymers have end-groups that do not form hydrogen bonds with other molecules. They exhibit behaviour similar to the PE and PDMS samples, as was the case with the PEODME samples.

In fitting the equation of state to the data, we choose a temperature domain for which each sample was in a liquid state over that temperature range. A limited pressure and temperature domain was chosen so that the equation of state fits the measured data to within the experimental accuracy. The equation of state can therefore be used as an interpolation function and to predict the density at atmospheric pressure. The reduction parameters obtained from the non-linear least-squares regression fitting procedure will have errors due to the experimental errors associated with measuring the density of a given sample and to the extreme sensitivity of some of the fitting parameters to small changes in the measured data. In particular P^* is very sensitive to small systematic errors in the data. Such errors can arise due to the presence of air in the sample, for example. The systematic errors associated with the measuring apparatus should be the same for each sample, and hence their effects are not manifested in the reduction parameters as a function of the molecular weight. If one uses data from different sources, however, one can observe differences in the reduction parameters due to small differences in the systematic errors associated with the different experimental procedures.

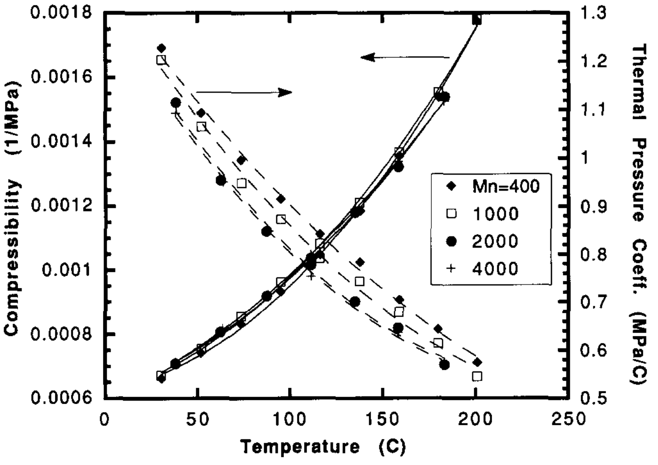

Figure 10 The compressibility and thermal pressure coefficient plotted as functions of temperature at atmospheric pressure for the indicated PPG samples

Figures 11, 12 and *13* show the reduction parameters P^*, v^*_{sp} and T^* as measured for the samples discussed above. The reduction parameters are plotted as a function of $1/M_n$. It is possible to give them molecular significance according to equations (2), (3) and (4), though one should beware of reading too much into this interpretation since this depends on the model on which the equation of state is based having physical reality. Qualitatively, however, the trends do make sense.

The hard-core volumes, v^*_{sp}, can be compared with the van der Waals volumes tabulated in the literature. If one computes the effect of the end-groups, one would predict

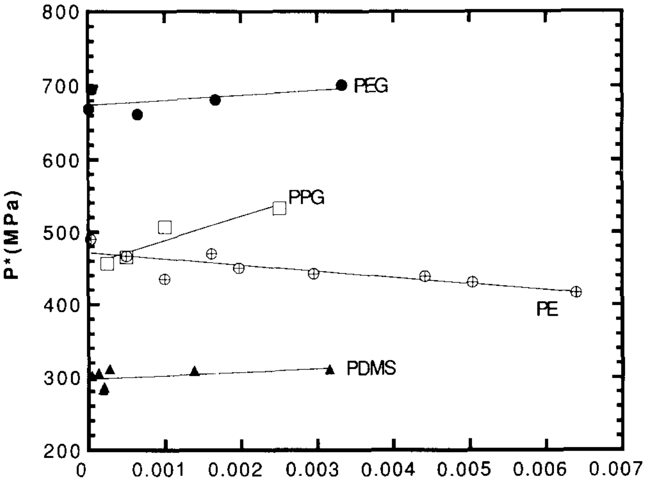

Figure 11 The values of P^* for the different polymer samples plotted as functions of $1/M_n$ for the FOV model. The pressure range used for each polymer was 0–40 MPa. The temperature ranges used for PE, PDMS, PEG and PPG were 150–210°C, 125–175°C, 75–130°C and 100–150°C, respectively

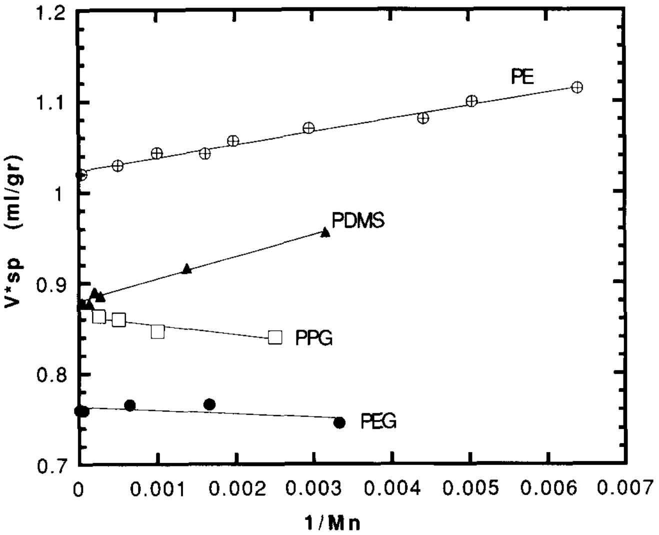

Figure 12 The values of v_{sp}^* for the different polymer samples plotted as functions of $1/M_n$ for the FOV model

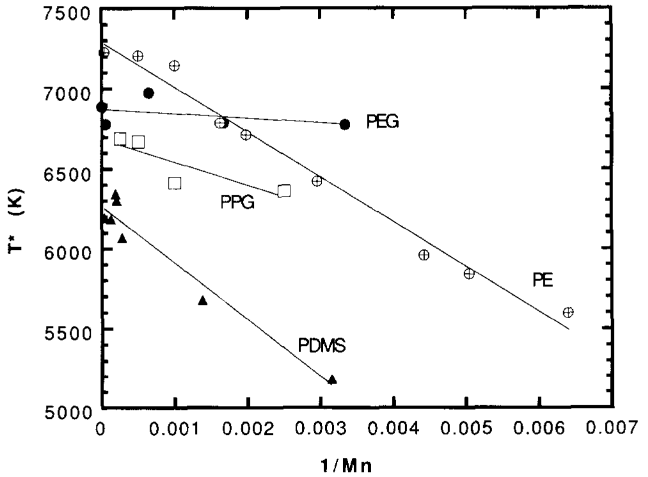

Figure 13 The values of T^* for the different polymer samples plotted as functions of $1/M_n$ for the FOV model

a difference of approximately 7% for the volumes of PE over the range of molecular weights studied, compared to an observed 10%. For PEG, PPG and PDMS the values are predicted to be relatively flat, in contradiction to our observations.

The P^* values are expected to scale with the squares of the solubility parameters, which are calculable from group contributions tabulated in the literature[10]. For PE we observe an approximate 13% difference in P^* over the range studied. This is close to that predicted by the tabulation of Fedors[10], though contributions of hydrocarbons are very scattered between various authors and some would predict a shift in the opposite direction. All systems would predict higher P^* values as observed for lower-molecular-weight PEG and PPG due to the polar OH groups. Data are not presented for PDMS.

The T^* values show the strongest variation with molecular weight. Since the dependence of P^* is very much less, it follows from equations (2) to (7) that this must be associated with a larger value of c, the degrees of freedom per mer, for lower-molecular-weight species. This has also been observed in the case of polystyrene oligomers and interpreted as increased freedom in chain ends or the addition of the three translational degrees of freedom to the vibrational degrees present in each mer[11]. The fact that PEG does not show this effect is perhaps attributable to very strong hydrogen bonding of the terminal OH groups (which may be to the main-chain ether groups rather than to each other). The PPG exhibits similar behaviour but the effect is not so pronounced or clear.

CONCLUSIONS

The thermodynamic properties of polymer liquids are of practical and scientific importance. Properties such as the density, compressibility, expansivity and thermal pressure coefficient of a number of polymer liquids were presented.

The change in the density and other physical properties with molecular weight can most simply be accounted for by the properties of the end-groups of the polymers. We showed that, for the case of PE and PDMS, a clear $1/M_n$ dependence is observed in the density as the concentration of end-groups decreases. If the end-groups were allowed to form hydrogen bonds, we saw that the $1/M_n$ dependence was not observed. In the case of PEG, which forms a strong bond, we observed that the physical properties of the liquid samples were independent of molecular weight at atmospheric pressures. Similar properties were observed for the PPG samples. Capping the end-groups of the PPG and PEG samples so that they could no longer form hydrogen bonds with their neighbours resulted in the return of a molecular-weight dependence of the liquid properties.

Since we are unable to present all the *PVT* data for each sample, we present in *Table 2* in the Appendix the reduction parameters of the modified cell model, which will enable the interested reader to reconstruct the data to within the experimental accuracy of the original data. The modified cell model was used in order to use the largest pressure–temperature range so that the *PVT* properties of a sample can be characterized by as few sets of reduction parameters as possible. Using these parameters one can calculate the specific volume to within 10^{-3} ml g^{-1} over the pressure and temperature range quoted in the Appendix. First derivatives of the data can also be calculated. However, it is not a useful exercise to try to extract second derivatives from the data owing to the systematic errors introduced by the fitting procedure and the systematic errors present in the original data.

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APPENDIX

The modified cell model[4] was found to provide a good description to polymer liquid PVT data sets. The form of the equation is shown below:

$$\tilde{P}\tilde{V}/\tilde{T} = \tilde{V}^{1/3}/(\tilde{V}^{1/3} - \delta) - (2/\tilde{T}\tilde{V}^2)(A - B/\tilde{V}^2) \quad \text{(A1)}$$

where $\tilde{P}$, $\tilde{T}$ and $\tilde{V}$ are the reduced pressure, temperature and volume as defined in equations (2), (3) and (4) above. The parameters A, B and δ have the values 1.2045,

Table 2 The reduction parameters of the modified cell model

Polyethylene

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
C11, $M_n = 156.3$					
37.2	89.9	467.7	1.13053	4126.2	0.064
94.5	147.7	441.8	1.14033	4200.9	0.043
151.5	190.8	423.3	1.15014	4300.8	0.044
C14, $M_n = 198.4$					
39.8	92.7	490.6	1.11759	4320.2	0.069
100.4	154.1	459.5	1.12706	4414.8	0.034
160.6	214.4	429.5	1.14035	4527.0	0.066
1220.7	246.1	388.2	1.15953	4650.5	0.046
*C*16, $M_n = 226.4$					
40.0	83.4	504.6	1.09390	4344.6	0.149
90.3	134.1	475.7	1.10273	4444.8	0.051
139.9	183.6	450.2	1.11340	4549.0	0.028
189.9	235.1	415.4	1.12842	4668.0	0.066
C24, $M_n = 338.7$					
80.0	134.7	482.2	1.10407	4958.8	0.173
140.5	193.6	479.1	1.10149	4906.2	0.072
199.6	245.5	419.5	1.12256	5104.1	0.084
C36, $M_n = 507.0$					
99.5	143.8	524.5	1.07870	5020.3	0.119
150.2	194.6	490.8	1.08814	5139.4	0.105
200.3	245.9	438.2	1.10505	5322.2	0.057
C44, $M_n = 619.2$					
109.9	153.2	511.5	1.07353	5202.4	0.099
159.7	204.0	505.5	1.07394	5196.6	0.069
210.2	244.9	450.7	1.09263	5411.8	0.066

Poly(ethylene glycol) *continued*

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
C78, $M_n = 1100$					
130.9	164.2	502.1	1.07319	5470.1	0.118
170.5	204.6	479.4	1.07875	5546.4	0.149
210.5	245.0	452.9	1.08658	5642.6	0.109
C150, $M_n = 2100$					
140.0	174.5	527.2	1.05799	5485.3	0.078
179.3	214.4	499.7	1.06534	5589.4	0.055
220.4	244.3	460.8	1.07823	5764.9	0.072
C2000, $M_n = 28\,000$					
150.7	184.0	545.2	1.04782	5484.7	0.032
189.9	224.5	506.5	1.05910	5651.2	0.064
230.2	265.8	452.8	1.07714	5907.5	0.043

Poly(dimethyl siloxane)

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
$M_n = 340$					
40.2	73.1	373.9	0.95877	3726.5	0.068
80.0	114.0	341.7	0.97331	3864.9	0.055
120.4	156.0	323.3	0.98412	3962.1	0.068
164.2	202.8	302.0	0.99880	4074.0	0.161
$M_n = 770$					
41.8	81.2	384.0	0.90786	4011.4	0.100
90.8	129.6	351.0	0.92227	4191.3	0.065
138.3	177.9	326.5	0.93556	4339.7	0.071
185.9	225.9	289.0	0.95579	4525.0	0.062
234.6	276.8	255.0	0.97724	4699.4	0.099
$M_n = 2600$					
41.9	93.8	387.0	0.88951	4312.3	0.141
103.0	153.3	355.6	0.90384	4534.6	0.091
162.0	214.4	311.8	0.92463	4796.3	0.066
222.2	275.9	269.8	0.94801	5055.7	0.078
$M_n = 5200$					
42.3	93.0	379.7	0.89329	4471.9	0.155
102.0	153.3	332.7	0.91150	4771.7	0.076
162.1	214.7	300.4	0.92737	4995.2	0.107
223.5	274.5	257.3	0.95031	5271.4	0.059
$M_n = 7830$					
42.6	92.0	376.0	0.89176	4491.4	0.133
101.9	154.2	337.1	0.90839	4766.2	0.124
163.6	213.6	312.8	0.92128	4960.7	0.081
221.7	276.6	274.1	0.94284	5230.4	0.101
$M_n = 68\,000$					
41.5	92.6	386.0	0.87853	4339.5	0.068
102.0	153.4	349.8	0.89509	4607.2	0.093
162.3	213.7	310.1	0.91516	4883.2	0.079
221.6	275.5	266.6	0.93934	5176.3	0.076
$M_n = 187\,000$					
42.1	92.9	382.6	0.88085	4386.7	0.139
102.0	153.7	347.8	0.89597	4628.8	0.066
161.9	214.5	311.9	0.91443	4883.6	0.102
221.8	275.5	269.5	0.93826	5174.5	0.069

Poly(ethylene glycol)

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
PEG, $M_n = 302$					
38.8	72.0	851.6	0.76576	5180.3	0.180
78.6	105.8	820.6	0.76813	5221.8	0.298
110.8	137.9	813.9	0.76771	5203.1	0.067
142.5	169.7	807.6	0.76768	5197.9	0.074
175.0	194.0	801.7	0.76831	5211.4	0.077
PEG, $M_n = 692$					
38.1	73.7	832.3	0.77723	5036.6	0.054
79.2	114.5	784.3	0.78292	5174.7	0.056
119.3	153.1	771.1	0.78456	5211.5	0.022
157.8	193.5	735.2	0.79047	5330.2	0.023

Poly(ethylene glycol) *continued*

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
PEG, M_n = 1470					
60.8	89.4	832.5	0.78260	5221.2	0.162
94.8	121.7	774.9	0.78957	5403.4	0.147
126.4	153.8	764.8	0.78963	5394.2	0.098
158.0	185.3	727.7	0.79498	5510.5	0.070
PEG, M_n = 18 500					
70.7	97.9	825.5	0.77954	5148.6	0.106
102.5	130.5	779.1	0.78546	5286.8	0.071
134.6	161.8	747.0	0.79064	5400.2	0.050
166.1	194.9	718.9	0.79520	5491.9	0.050
PEG, M_n = 100 000					
70.3	97.4	789.9	0.78145	5270.8	0.069
101.9	129.9	760.6	0.78495	5353.8	0.099
134.3	162.6	769.2	0.78314	5310.2	0.079
166.2	194.5	750.8	0.78659	5383.7	0.052
PEOMME, M_n = 302					
26.6	59.2	847.8	0.78939	4666.3	0.189
63.8	96.4	767.6	0.80020	4915.4	0.089
100.7	133.2	735.2	0.80486	5014.1	0.095
136.7	169.7	733.4	0.80508	5018.3	0.078
173.0	206.6	681.1	0.81504	5180.4	0.073
PEOMME, M_n = 750					
45.1	76.2	819.9	0.78520	4874.6	0.104
80.5	112.1	765.7	0.79227	5042.0	0.090
115.5	147.8	747.5	0.79520	5101.9	0.124
151.1	183.9	708.2	0.80223	5236.7	0.141
186.9	205.3	691.1	0.80578	5301.2	0.153
PEODME, M_n = 600					
38.3	72.9	755.4	0.80706	4799.8	0.073
78.0	113.7	706.7	0.81408	4949.2	0.038
118.4	154.0	682.1	0.81780	5020.3	0.034
157.8	194.7	633.4	0.82671	5170.4	0.041
PEODME, M_n = 1000					
52.3	84.0	786.1	0.79649	4870.2	0.087
88.1	120.3	740.8	0.80217	4991.6	0.043
123.5	156.1	711.6	0.80688	5083.7	0.030
158.8	191.5	674.1	0.81419	5214.8	0.031
194.1	206.3	636.7	0.82192	5343.3	0.021

Poly(propylene glycol)

T_{min}	T_{max}	P^* (MPa)	V^* (ml g^{-1})	T^* (K)	S^2 (MPa^2)
PPG, M_n = 400					
22.6	66.9	641.2	0.85449	4665.9	0.074
72.9	117.3	599.2	0.86192	4814.1	0.027
122.7	166.8	582.5	0.86469	4859.2	0.022
172.2	216.7	528.7	0.87749	5034.8	0.026
PPG, M_n = 1025					
22.1	67.1	626.8	0.86079	4692.8	0.054
73.3	117.0	577.6	0.86845	4842.4	0.027
122.5	166.4	550.8	0.87418	4939.7	0.020
172.0	216.2	502.8	0.88675	5119.4	0.032
PPG, M_n = 2000					
30.1	70.3	596.8	0.87223	4839.8	0.099
70.6	111.7	541.4	0.88244	5057.3	0.031
118.5	158.0	517.0	0.88699	5139.5	0.016
158.7	201.2	485.8	0.89481	5264.9	0.040
PPG, M_n = 4000					
30.2	72.7	591.1	0.87562	4853.5	0.047
73.1	112.0	540.9	0.88452	5041.6	0.036
117.9	158.8	516.5	0.88881	5121.3	0.015
159.3	200.2	476.5	0.90004	5304.9	0.029
PPODME, M_n = 400					
29.9	71.2	552.5	0.89371	4609.8	0.059
71.5	111.0	521.7	0.89957	4711.6	0.022
117.9	157.6	499.4	0.90486	4794.3	0.016
158.1	200.2	461.5	0.91446	4915.7	0.016
PPODME, M_n = 1000					
30.1	68.1	568.5	0.88294	4636.3	0.059
68.6	111.8	527.9	0.89078	4784.6	0.024
118.0	158.1	501.9	0.89687	4885.1	0.004
158.6	199.7	465.8	0.90577	5004.5	0.012
PPODME, M_n = 2000					
30.1	69.3	575.8	0.87480	4799.0	0.079
69.7	112.2	533.9	0.88213	4947.9	0.020
118.4	158.3	505.3	0.88935	5080.8	0.009
158.9	201.5	465.0	0.89937	5233.4	0.033

1.001 and 0.9532, respectively. The only difference between this model and the normal cell model is the value of the parameter δ, which for the cell model has the value 0.8909.

Equation (A1) is fitted to blocks of *PVT* data with 10 < P (MPa) < 100 and for the range of temperatures shown in *Table 2*. The temperature range is selected so that the value of S^2 is of the order of 0.1 and is defined by:

$$S^2 = \sum (P_{data} - P_{fit})^2/(N - 3)$$

where P_{data} is the measured pressure at a given temperature and specific volume, P_{fit} is the pressure predicted by equation (A1) and N is the number of data points. Values of S^2 of the order of 0.1 are equivalent to errors in the specific volume of the order of 1×10^{-3} ml g^{-1}. Therefore, using the parameters in *Table 2* one can reconstruct the original data set with an accuracy of the order of the experimental accuracy of the experimental data. Also shown in *Table 2* are the characteristics of each sample.