PVT Measurements for Mixtures of Poly(ethylene glycol methyl ether) with Poly(ethylene glycol) from 298 K to 338 K and Pressures up to 30 MPa

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PVT properties were measured for fractionation cuts of poly(ethylene glycol methyl ether)-350, poly(ethylene glycol)-200, poly(ethylene glycol)-600, and their blends at temperatures from 298 K to 338 K and pressures up to 30 MPa. Excess volumes were found to be negative in blending poly(ethylene glycol)s with poly(ethylene glycol methyl ether). The pressure effect on the liquid densities was represented accurately by the Tait equation, which was used to calculate isothermal compressibilities for the oligomers and the oligomeric blends. Both the Flory−Orwoll−Vrij and the Schotte equations of state were employed to correlate the experimental specific volumes. Accurate results were obtained from these two equations.

Introduction

Volumetric properties of polymers are needed in polymer processing and are also useful for development of polymer equations of state. While the investigators frequently focused the *PVT* measurements on high molecular weights (10^4 g·mol^{-1} or greater) polymers, the studies on oligomers have received less attention. Dee et al. (1992) studied the *PVT* properties for various polymer liquids, including polyethylene, poly(dimethyl siloxane), poly(ethylene glycol) (PEG), and poly(propylene glycol) (PPG) at the temperature range of room temperature to 250 °C and pressures up to 200 MPa. The experimental results were presented graphically together with the determined characteristic parameters of the Flory−Orwoll−Vrij (FOV) equation of state for each polymer liquid. The densities (or specific volumes) of aqueous PEGs and of oligomeric propylene glycols have been measured by Muller and Rasmussen (1991) and Sandell and Goring (1971) at atmospheric pressure. Recently, extensive *PVT* properties of polymers have also been compiled by Zoller and Walsh (1995). In the present work, *PVT* data were measured for poly(ethylene glycol methyl ether)-350 (PEGME-350), PEG-200, PEG-600, and the blended mixtures of PEGME-350 with PEG-200 or PEG-600 at temperatures from 298.15 K to 338.15 K and pressures up to 30 MPa. These new experimental results further provide information on the volumetric behavior of the oligomeric blends in response to the effects of temperature, pressure, and composition.

Experimental Section

The fractionation cuts of PEGME-350, PEG-200, and PEG-600 were purchased from Aldrich Chemical Co. (United States). Their number average molecular weights (M_n) were claimed approximately (350, 200, and 600) g·mol^{-1}, respectively. The apparatus used in the present study is the same as that described by Chang and Lee (1995). Liquid mixture samples, prepared by mass to an accuracy of ±0.001 in mole fraction, were delivered into a high-pressure densimeter (DMA-512, Anton Paar) via a hand pump (model-2426-801, Ruska). Pressure in the measuring cell was manipulated by the hand pump and monitored by a pressure transducer (model-PDCR 330, 0−40 MPa, Druck) with a digital indicator (model-DPI 261, Druck). The accuracy of pressure measurements was better than ±0.75%. A thermostatic bath with circulating silicon oil maintained the temperature of the measuring cell to within ±0.03 K. A precision digital thermometer (model-1506, Hart Scientific) incorporated with a thermistor probe measured the temperature to an accuracy of ±0.02 K. The oscillation period (t_i) of sample i in the vibrating U tube was displayed by a DMA-60 processing unit (Anton Paar), which was converted into density (ρ_i) via

$$\rho_i = A(t_i^2 - B) \tag{1}$$

where A and B are apparatus parameters determined by using the literature *PVT* data of two calibration fluids: pure water (Haar et al., 1984) and dry nitrogen (Vargaftik, 1975). The calibration was made at each temperature of interest over (0.1−30) MPa. Parameter A decreases linearly with increasing both pressure and temperature. The calibration reproduced water densities with an average absolute deviation of 0.01% over the entire calibrated conditions. The accuracy of density measurements was estimated to be ±0.0001 g·cm^{-3}.

Results and Discussion

Table 1 lists the experimental densities (ρ) and calculated isothermal compressibilities (κ_T) of PEGME-350, PEG-200, and PEG-600. The density of PEG-600 measured by this study is 1.1212 g·cm^{-3} at 298 K and 0.1 MPa. It is in a good agreement with that of Sandell and Goring (1971)

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Table 1. Experimental Density and Calculated Isothermal Compressibility for PEGME-350, PEG-200, and PEG-600

	T = 298.15 K		T = 318.15 K		T = 328.15 K		T = 338.15 K	
P (MPa)	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})
				PEGME-350				
0.1	1.0839	4.907	1.0669	5.507	1.0582	5.617	1.0500	5.925
5	1.0864	4.700	1.0697	5.269	1.0611	5.432	1.0530	5.710
10	1.0888	4.506	1.0725	5.043	1.0639	5.255	1.0560	5.507
15	1.0913	4.328	1.0752	4.856	1.0667	5.909	1.0588	5.319
20	1.0936	4.164	1.0777	4.656	1.0694	4.935	1.0616	5.144
25	1.0959	4.012	1.0802	4.482	1.0719	4.789	1.0642	4.980
30	1.0981	3.871	1.0826	4.322	1.0745	4.653	1.0668	4.826
				PEG-200				
0.1	1.1200	4.067	1.1040	4.534	1.0961	4.701	1.0880	4.938
5	1.1222	3.939	1.1064	4.388	1.0985	4.545	1.0906	4.753
10	1.1244	3.816	1.1088	4.249	1.1010	4.398	1.0932	4.578
15	1.1266	3.700	1.1111	4.119	1.1034	4.260	1.0956	4.416
20	1.1286	3.592	1.1134	3.996	1.1057	4.130	1.0980	4.265
25	1.1306	3.490	1.1156	3.822	1.1079	4.009	1.1003	4.124
30	1.1325	3.394	1.1177	3.773	1.1102	3.894	1.1025	3.933
				PEG-600				
0.1	1.1212	4.172	1.1048	4.590	1.0962	4.883	1.0883	5.126
5	1.1234	4.055	1.1072	4.466	1.0988	4.726	1.0910	4.946
10	1.1257	3.942	1.1097	4.346	1.1014	4.577	1.0936	4.775
15	1.1279	3.836	1.1120	4.233	1.1039	4.437	1.0962	4.615
20	1.1300	3.735	1.1144	4.126	1.1063	4.306	1.0987	4.567
25	1.1321	3.640	1.1167	4.024	1.1086	4.183	1.1011	4.327
30	1.1341	3.549	1.1189	3.928	1.1109	4.066	1.1034	4.197

(1.1223 g·cm^{-3}). Tables 2 and 3 give the experimental ρ and calculated κ_T for PEGME-350 + PEG-200 and PEGME-350 + PEG-600, respectively. The isothermal densities at a given composition were correlated with the Tait equation

$$\frac{\rho - \rho_0}{\rho} = C \ln\left(\frac{D + P}{D + 0.1}\right) \tag{2}$$

where ρ_0 is the density at 0.1 MPa. The optimized values of C and D were obtained by fitting the Tait equation to the density data with the following objective function (π)

$$\pi = [\sum_{k=1}^{n} |\rho_{k,\mathrm{calc}} - \rho_{k,\mathrm{expt}}|/\rho_{k,\mathrm{expt}})]/n \tag{3}$$

where n is the number of data points. $\rho_{k,\mathrm{calc}}$ and $\rho_{k,\mathrm{expt}}$ represent the calculated and the experimental densities for the kth point, respectively. Table 4 presents the calculated results including the values of C, D, and π. The Tait equation appears to correlate accurately the isothermal densities over the entire pressure range. The tabulated isothermal compressibility was calculated with the following equation

$$\kappa_T = \frac{-1}{\mathrm{V}}\left(\frac{\partial V}{\partial P}\right)_{T,x} = \frac{V_0}{V}\left(\frac{C}{D + P}\right) \tag{4}$$

where V is the molar volume, V_0 is the molar volume at 0.1 MPa, and the constants C and D are parameters of the Tait equation.

While the pressure dependence of isothermal densities obeys the Tait equation, the isobaric densities decrease linearly with the increase of temperature for PEGME-350, PEG-200, PEG-600, and the oligomeric blends as shown in Figure 1. It is also found that the excess volumes of PEGME-350 + PEG-200 and PEGME-350 + PEG-600 are negative, ranging from −0.12 cm^3 mol^{-1} to 0.0 cm^3 mol^{-1}, under the experimental conditions, implying that volume contraction occurs when blending PEG with PEGME. However, the effects of temperature and pressure on the excess volumes are not clearly seen because the effects are almost in the same order of the magnitude of the experimental uncertainty (±0.05 cm^3 mol^{-1}).

PVT Data Correlation with Equations of State

PVT data of polymers are useful for model development of correlation methods needed in polymer processing. The specific volumes obtained in the present work were correlated by two polymer equations of state (EOS): the Flory−Orwoll−Vrij (FOV) (1964) and the Schotte (1982). These EOS were expressed as follows.

The FOV EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{\bar{V}^{1/3} - 1} - \frac{1}{\bar{T}\bar{V}} \tag{5}$$

The Schotte EOS:

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{RT^*}{P^*MV^*}\left(1 - \frac{1}{\bar{V}^{1/3}}\right) + \frac{1}{\bar{V}^{1/3} - 1} - \frac{2}{\bar{T}\bar{V}} \tag{6}$$

where $\bar{P} = P/P^*$, $\bar{V} = V/V^*$, and $\bar{T} = T/T^*$. The model parameters P^*, V^*, and T^* are characteristic pressure, specific volume, and temperature, respectively, which were determined by fitting the EOS to experimental *PVT* data. Table 5 lists the calculated results for PEGME-350, PEG-200, and PEG-600. These tabulated values of characteristic properties were also employed to calculate the specific volumes of the oligomeric blends via the following mixing rules (Schotte, 1982)

$$V^*_{\mathrm{m}} = \left[M_{\mathrm{m}}\left(\frac{\Psi_1}{M_1V^*_1} + \frac{\Psi_2}{M_2V^*_2}\right)\right]^{-1} \tag{7}$$

$$T^*_{\mathrm{m}} = \frac{P^*_{\mathrm{m}}}{\dfrac{\Psi_1P^*_1}{T^*_1} + \dfrac{\Psi_2P^*_2}{T^*_2}} \tag{8}$$

and

$$P^*_{\mathrm{m}} = \Psi_1^2\,P^*_1 + \Psi_2^2\,P^*_2 + 2\Psi_1\Psi_2P^*_{12} \tag{9}$$

Table 2. Experimental Density and Calculated Isothermal Compressibility for PEGME-350 (1) + PEG-200 (2)

	$T = 298.15$ K		$T = 318.15$ K		$T = 328.15$ K		$T = 338.15$ K	
P (MPa)	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})
				$x_1 = 0.900$				
0.1	1.0861	4.888	1.0691	5.350	1.0606	5.620	1.0523	5.872
5	1.0886	4.680	1.0719	5.161	1.0635	5.420	1.0553	5.652
10	1.0911	4.485	1.0746	4.983	1.0664	5.230	1.0582	5.443
15	1.0935	4.307	1.0772	4.817	1.0691	5.054	1.0610	5.250
20	1.0959	4.142	1.0798	4.662	1.0718	4.890	1.0638	5.071
25	1.0981	3.990	1.0823	4.517	1.0743	4.736	1.0664	4.904
30	1.1003	3.849	1.0847	4.381	1.0768	4.592	1.0690	4.748
				$x_1 = 0.800$				
0.1	1.0885	4.746	1.0715	5.255	1.0631	5.502	1.0547	5.806
5	1.0910	4.582	1.0742	5.085	1.0660	5.321	1.0576	5.594
10	1.0935	4.427	1.0769	4.922	1.0688	5.149	1.0606	5.395
15	1.0959	4.282	1.0795	4.770	1.0715	4.988	1.0634	5.209
20	1.0982	4.147	1.0821	4.627	1.0741	4.837	1.0661	5.037
25	1.1004	4.020	1.0846	4.493	1.0766	4.695	1.0687	4.875
30	1.1026	3.901	1.0870	4.367	1.0791	4.562	1.0712	4.725
				$x_1 = 0.700$				
0.1	1.0912	4.707	1.0743	5.181	1.0658	5.438	1.0574	5.735
5	1.0936	4.543	1.0770	5.019	1.0686	5.261	1.0604	5.521
10	1.0961	4.388	1.0797	4.864	1.0714	5.092	1.0633	5.318
15	1.0985	4.244	1.0822	4.718	1.0740	4.934	1.0660	5.130
20	1.1008	4.109	1.0848	4.582	1.0766	4.785	1.0687	4.956
25	1.1030	3.982	1.0872	4.453	1.0791	4.646	1.0713	4.793
30	1.1051	3.863	1.0896	4.332	1.0817	4.515	1.0738	4.641
				$x_1 = 0.580$				
0.1	1.0946	4.640	1.0779	5.109	1.0695	5.358	1.0612	5.620
5	1.0970	4.474	1.0805	4.936	1.0723	5.179	1.0641	5.418
10	1.0995	4.317	1.0832	4.771	1.0750	5.009	1.0669	5.227
15	1.1018	4.171	1.0857	4.617	1.0777	4.850	1.0697	5.049
20	1.1041	4.035	1.0881	4.472	1.0802	4.702	1.0723	4.884
25	1.1062	3.907	1.0905	4.337	1.0827	4.562	1.0748	4.729
30	1.1084	3.788	1.0929	4.211	1.0852	4.431	1.0773	4.584
				$x_1 = 0.500$				
0.1	1.0972	4.605	1.0804	5.070	1.0721	5.273	1.0639	5.557
5	1.0996	4.428	1.0830	4.898	1.0748	5.097	1.0667	5.349
10	1.1020	4.261	1.0857	4.735	1.0775	4.930	1.0696	5.153
15	1.1043	4.107	1.0882	4.582	1.0801	4.774	1.0722	4.971
20	1.1065	3.963	1.0906	4.439	1.0827	4.628	1.0749	4.802
25	1.1087	3.830	1.0930	4.306	1.0851	4.490	1.0774	4.644
30	1.1108	3.705	1.0954	4.180	1.0876	4.362	1.0799	4.497
				$x_1 = 0.400$				
0.1	1.1007	4.484	1.0843	4.948	1.0758	5.184	1.0677	5.448
5	1.1031	4.332	1.0869	4.789	1.0785	5.012	1.0705	5.255
10	1.1055	4.188	1.0894	4.637	1.0812	4.848	1.0733	5.072
15	1.1077	4.053	1.0919	4.494	1.0837	4.695	1.0760	4.902
20	1.1099	3.927	1.0943	4.361	1.0862	4.551	1.0786	4.743
25	1.1121	3.809	1.0967	4.235	1.0887	4.417	1.0811	4.594
30	1.1142	3.697	1.0990	4.117	1.0910	4.290	1.0835	4.455
				$x_1 = 0.300$				
0.1	1.1047	4.410	1.0883	4.848	1.0801	5.038	1.0719	5.330
5	1.1070	4.258	1.0908	4.700	1.0828	4.883	1.0747	5.142
10	1.1093	4.112	1.0934	4.558	1.0854	4.735	1.0774	4.964
15	1.1116	3.977	1.0958	4.425	1.0879	4.596	1.0800	4.797
20	1.1138	3.851	1.0981	4.299	1.0904	4.465	1.0826	4.642
25	1.1159	3.733	1.1005	4.181	1.0928	4.342	1.0850	4.497
30	1.1179	3.622	1.1028	4.070	1.0951	4.225	1.0874	4.362
				$x_1 = 0.200$				
0.1	1.1091	4.337	1.0928	4.745	1.0847	4.995	1.0766	5.253
5	1.1114	4.185	1.0953	4.608	1.0873	4.829	1.0794	5.054
10	1.1137	4.041	1.0978	4.477	1.0899	4.671	1.0820	4.866
15	1.1160	3.906	1.1002	4.353	1.0924	4.523	1.0846	4.692
20	1.1181	3.781	1.1026	4.236	1.0948	4.385	1.0871	4.530
25	1.1202	3.663	1.1049	4.125	1.0971	4.255	1.0895	4.380
30	1.1222	3.553	1.1071	4.021	1.0994	4.133	1.0918	4.239
				$x_1 = 0.100$				
0.1	1.1142	4.185	1.0983	4.606	1.0901	4.774	1.0821	5.043
5	1.1164	4.051	1.1007	4.467	1.0926	4.633	1.0847	4.863
10	1.1187	3.924	1.1032	4.334	1.0952	4.498	1.0873	4.692
15	1.1208	3.805	1.1055	4.209	1.0976	4.371	1.0898	4.533
20	1.1229	3.692	1.1078	4.092	1.1000	4.251	1.0923	4.385
25	1.1250	3.587	1.1100	3.981	1.1023	4.138	1.0946	4.247
30	1.1270	3.487	1.1122	3.876	1.1045	4.031	1.0969	4.117

Table 3. Experimental Density and Calculated Isothermal Compressibility for PEGME-350 (1) + PEG-600 (2)

	$T = 298.15$ K		$T = 318.15$ K		$T = 328.15$ K		$T = 338.15$ K	
P (MPa)	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})	ρ (g·cm^{-3})	$10^4\kappa_T$ (MPa^{-1})
				$x_1 = 0.900$				
0.1	1.0899	4.762	1.0729	5.189	1.0644	5.464	1.0559	5.776
5	1.0924	4.592	1.0756	5.048	1.0673	5.299	1.0589	5.573
10	1.0949	4.432	1.0783	4.912	1.0701	5.141	1.0618	5.381
15	1.0972	4.282	1.0809	4.784	1.0728	4.993	1.0646	5.202
20	1.0996	4.143	1.0834	4.662	1.0754	4.853	1.0673	5.037
25	1.1018	4.012	1.0859	4.547	1.0779	4.721	1.0699	4.878
30	1.1040	3.890	1.0883	4.437	1.0804	4.596	1.0725	4.731
				$x_1 = 0.800$				
0.1	1.0953	4.703	1.0782	5.113	1.0698	5.362	1.0614	5.664
5	1.0977	4.522	1.0809	4.959	1.0726	5.198	1.0642	5.459
10	1.1001	4.351	1.0835	4.810	1.0754	5.040	1.0671	5.265
15	1.1025	4.193	1.0861	4.671	1.0780	4.893	1.0699	5.085
20	1.1048	4.047	1.0886	4.540	1.0806	4.754	1.0726	4.917
25	1.1070	3.910	1.0910	4.417	1.0831	4.622	1.0752	4.761
30	1.1092	3.783	1.0934	4.300	1.0856	4.499	1.0776	4.614
				$x_1 = 0.700$				
0.1	1.0998	4.602	1.0830	4.985	1.0745	5.271	1.0662	5.554
5	1.1021	4.435	1.0857	4.849	1.0773	5.108	1.0690	5.362
10	1.1046	4.276	1.0882	4.718	1.0800	4.953	1.0719	5.179
15	1.1069	4.129	1.0908	4.595	1.0826	4.808	1.0746	5.010
20	1.1092	3.992	1.0932	4.478	1.0852	4.671	1.0772	4.851
25	1.1114	3.864	1.0956	4.367	1.0876	4.542	1.0798	4.703
30	1.1135	3.744	1.0980	4.261	1.0901	4.420	1.0822	4.563
				$x_1 = 0.600$				
0.1	1.1040	4.643	1.0870	4.859	1.0787	5.193	1.0702	5.529
5	1.1064	4.381	1.0896	4.740	1.0814	5.036	1.0731	5.315
10	1.1088	4.228	1.0921	4.625	1.0841	4.886	1.0759	5.113
15	1.1111	4.085	1.0947	4.515	1.0871	4.746	1.0786	4.927
20	1.1133	3.952	1.0971	4.411	1.0892	4.611	1.0812	4.754
25	1.1155	3.828	1.0995	4.312	1.0917	4.485	1.0837	4.593
30	1.1176	3.711	1.1018	4.217	1.0941	4.367	1.0862	4.443
				$x_1 = 0.500$				
0.1	1.1075	4.504	1.0907	4.834	1.0824	5.117	1.0740	5.398
5	1.1099	4.342	1.0933	4.699	1.0851	4.957	1.0769	5.203
10	1.1123	4.190	1.0958	4.569	1.0877	4.804	1.0796	5.018
15	1.1146	4.047	1.0982	4.447	1.0903	4.660	1.0823	4.846
20	1.1168	3.915	1.1007	4.331	1.0928	4.525	1.0849	4.686
25	1.1190	3.791	1.1030	4.221	1.0952	4.398	1.0873	4.536
30	1.1211	3.675	1.1054	4.117	1.0976	4.278	1.0898	4.396
				$x_1 = 0.400$				
0.1	1.1109	4.441	1.0941	4.829	1.0858	5.097	1.0775	5.281
5	1.1133	4.285	1.0967	4.684	1.0885	4.921	1.0802	5.106
10	1.1156	4.137	1.0992	4.545	1.0912	4.755	1.0829	4.939
15	1.1179	3.998	1.1017	4.414	1.0937	4.600	1.0856	4.783
20	1.1201	3.870	1.1041	4.291	1.0962	4.455	1.0881	4.637
25	1.1222	3.749	1.1064	4.175	1.0986	4.319	1.0906	4.500
30	1.1243	3.636	1.1087	4.065	1.1009	4.192	1.0930	4.371
				$x_1 = 0.300$				
0.1	1.1140	4.387	1.0972	4.771	1.0890	5.023	1.0807	5.237
5	1.1163	4.235	1.0999	4.634	1.0916	4.859	1.0835	5.062
10	1.1186	4.091	1.1023	4.503	1.0942	4.703	1.0862	4.895
15	1.1209	3.956	1.1048	4.379	1.0968	4.557	1.0888	4.740
20	1.1231	3.831	1.1071	4.262	1.0993	4.420	1.0913	4.594
25	1.1252	3.713	1.1094	4.151	1.1016	4.291	1.0938	4.457
30	1.1273	3.603	1.1117	4.046	1.1039	4.170	1.0962	4.329
				$x_1 = 0.200$				
0.1	1.1170	4.323	1.1003	4.695	1.0920	4.960	1.0837	5.193
5	1.1194	4.177	1.1028	4.571	1.0946	4.799	1.0864	5.019
10	1.1216	4.037	1.1053	4.452	1.0972	4.645	1.0891	4.852
15	1.1239	3.907	1.1077	4.338	1.0997	4.501	1.0917	4.697
20	1.1261	3.785	1.1101	4.231	1.1021	4.366	1.0942	4.552
25	1.1282	3.671	1.1124	4.129	1.1045	4.239	1.0967	4.416
30	1.1302	3.563	1.1146	4.032	1.1068	4.119	1.0990	4.288
				$x_1 = 0.100$				
0.1	1.1193	4.268	1.1028	4.641	1.0945	4.906	1.0863	5.135
5	1.1216	4.127	1.1053	4.514	1.0970	4.747	1.0890	4.956
10	1.1238	3.992	1.1077	4.390	1.0997	4.596	1.0917	4.786
15	1.1261	3.867	1.1101	4.274	1.1022	4.454	1.0942	4.627
20	1.1282	3.749	1.1124	4.164	1.1046	4.321	1.0967	4.479
25	1.1303	3.638	1.1147	4.059	1.1069	4.196	1.0991	4.340
30	1.1324	3.534	1.1170	3.960	1.1092	4.079	1.1015	4.210

Table 4. Results of Density Correlation with the Tait Equation

	PEGME-350 (1) + PEG-200 (2)			PEGME-350 (1) + PEG-600 (2)		
x_1	C	D (MPa)	$10^4\pi^a$	C	D (MPa)	$10^4\pi^a$
			$T = 298.15$ K			
1.0	0.051 62	105.1	0.30	0.051 62	105.1	0.30
0.900	0.051 02	104.3	0.29	0.059 31	124.4	0.08
0.800	0.061 08	128.6	0.06	0.054 32	115.4	0.18
0.700	0.060 15	127.7	0.05	0.056 29	122.2	0.17
0.600[b]	0.057 70	124.3	0.05	0.056 79	124.9	0.10
0.500	0.053 29	115.6	0.19	0.055 99	124.2	0.06
0.400	0.058 92	131.3	0.13	0.056 20	126.5	0.05
0.300	0.056 76	128.6	0.06	0.056 50	128.7	0.14
0.200	0.055 17	127.1	0.08	0.056 81	131.3	0.12
0.100	0.058 55	139.8	0.05	0.057 56	134.8	0.23
0.0	0.057 38	141.0	0.11	0.065 98	158.0	0.04
			$T = 318.15$ K			
1.0	0.056 23	102.0	0.20	0.056 23	102.0	0.20
0.900	0.066 98	125.1	0.14	0.083 30	160.4	0.17
0.800	0.071 20	135.4	0.09	0.074 24	145.1	0.11
0.700	0.072 68	140.2	0.12	0.080 13	160.7	0.15
0.600[b]	0.066 32	129.7	0.35	0.086 51	177.9	0.22
0.500	0.066 01	130.1	0.19	0.076 14	157.4	0.21
0.400	0.067 81	137.0	0.08	0.070 92	146.8	0.10
0.300	0.069 96	144.2	0.12	0.073 28	153.5	0.22
0.200	0.072 55	152.8	0.19	0.078 17	166.4	0.27
0.100	0.067 71	146.9	0.10	0.074 17	159.7	0.18
0.0	0.062 57	137.9	0.06	0.0747 3	162.7	0.26
			$T = 328.15$ K			
1.0	0.074 35	132.3	0.12	0.074 35	132.3	0.12
0.900	0.069 28	123.2	0.12	0.079 01	144.5	0.28
0.800	0.073 35	133.2	0.18	0.076 52	142.6	0.16
0.700	0.073 08	134.3	0.17	0.075 12	142.4	0.18
0.600[b]	0.070 62	131.7	0.06	0.075 25	144.8	0.80
0.500	0.069 65	132.0	0.06	0.071 89	140.4	0.21
0.400	0.068 75	132.5	0.07	0.065 45	128.3	0.11
0.300	0.072 13	143.1	0.09	0.067 96	135.2	0.24
0.200	0.066 38	132.8	0.25	0.067 27	135.5	0.11
0.100	0.071 37	149.4	0.09	0.067 01	136.5	0.13
0.0	0.063 15	134.2	0.06	0.067 34	137.8	0.11
			$T = 338.15$ K			
1.0	0.071 63	120.8	0.21	0.071 63	120.8	0.21
0.900	0.068 51	116.6	0.12	0.071 97	124.5	0.23
0.800	0.069 96	120.4	0.20	0.068 71	121.2	0.09
0.700	0.067 28	117.2	0.14	0.070 53	126.9	0.20
0.600[b]	0.068 68	122.1	0.22	0.0628 8	113.6	0.11
0.500	0.065 36	117.5	0.08	0.065 63	121.5	0.12
0.400	0.067 61	124.0	0.19	0.069 95	132.3	0.17
0.300	0.066 47	124.6	0.21	0.086 9	131.6	0.13
0.200	0.061 23	116.5	0.18	0.068 03	130.9	0.24
0.100	0.062 36	123.6	0.08	0.064 85	126.2	0.10
0.0	0.058 29	117.93	0.12	0.064 29	125.31	0.13

[a] π defined as in eq 3. [b] $x_1 = 0.580$ for PEGME-350 + PEG-200.

with

$$\Psi_i = \frac{w_i V_i^*}{w_1 V_1^* + w_2 V_2^*} \tag{10}$$

and

$$P_{12}^* = (1 - \Delta_{12})(P_1^* P_2^*)^{0.5} \tag{11}$$

where Ψ_i, M_i, and w_i stand for the segment volume fraction, the number average molecular weight, and the weight fraction of component i, respectively. Δ_{12}* in eq 11 is a binary interaction constant determined from the *PVT* data for each binary system. The correlated results are reported in Table 6. Both the FOV and the Schotte EOS represent quantitatively the *PVT* behavior of PEGME-350 + PEG-200 and PEGME-350 + PEG-600 with reasonable accuracy over the entire experimental conditions.

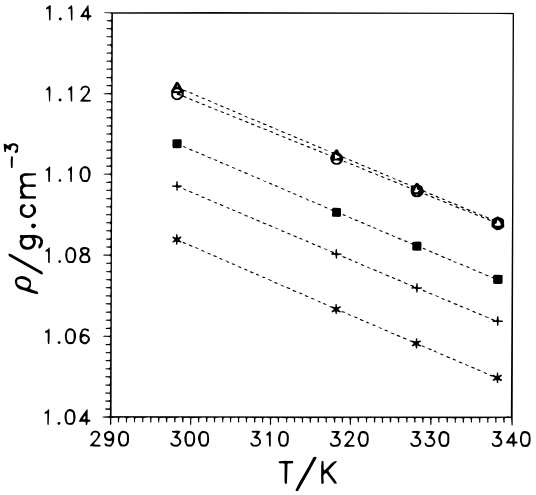

Figure 1. Variations of isobaric density with temperature at 0.1 MPa for PEGME-350 (*); PEG-200 (○); PEG-600 (△); PEGME-350 + PEG-200, $x_1 = 0.5$ (+); PEGME-350 + PEG-600, $x_1 = 0.5$ (□); smooth curves (- - -).

Table 5. Results of Specific Volume Correlation with the Equations of State for "Pure" Compounds

	FOV EOS				Schotte EOS			
compound	P^* (MPa)	T^* (K)	V^* (cm³·g⁻¹)	AAD[a] (cm³·g⁻¹)	P^* (MPa)	T^* (K)	V^* (cm³·g⁻¹)	AAD[a] (cm³·g⁻¹)
PEGME-350	707.2	6122	0.7705	0.000 17	722.9	5395	0.7591	0.000 10
PEG-200	738.2	6541	0.7566	0.000 21	783.3	5728	0.7444	0.000 07
PEG-600	752.4	7549	0.7524	0.000 20	813.4	5490	0.7363	0.000 30

[a] AAD = $(1/n)\sum_{k=1}^{n}|V_{k,\mathrm{calc}} - V_{k,\mathrm{expt}}|$.

Table 6. Results of Specific Volume Correlation with the Equations of State for Polymer Blends

	FOV EOS		Schotte EOS	
mixture (1) + (2)	Δ_{12}	AAD%[a]	Δ_{12}	AAD%[a]
PEGME-350 + PEG-200	−0.0020	0.02	−0.0012	0.01
PEGME-350 + PEG-600	−0.0013	0.03	−0.0028	0.02

[a] AAD% = $(100/n)\sum_{k=1}^{n}|V_{k,\mathrm{cal}} - V_{k,\mathrm{expt}}|/V_{k,\mathrm{expt}}$.

Conclusions

PVT data have been measured for PEGME-350, PEG-200, PEG-600, PEGME-350 + PEG-200, and PEGME-350 + PEG-600 at temperatures from 298 K to 338 K and pressures up to 30 MPa. The results showed that the isobaric densities varied linearly with temperature. The pressure effect on the isothermal densities was represented by the Tait equation, which was used to calculate isothermal compressibilities. Both the FOV and the Schotte EOS were found to correlate accurately the *PVT* data of the oligomers and their blends.

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