Densities, Viscosities, Refractive Indices, and Heat Capacities of Poly(propylene glycols) or Poly(ethylene glycol)−Poly(propylene glycol)−Poly(ethylene glycol)-*block*-Copolymers + 2-Methyltetrahydrofuran at (298.15 and 313.15) K and at Atmospheric Pressure

Fabio Comelli,*,† Adriana Bigi,‡ Daniele Vitalini,§ Katia Rubini,‡ and Romolo Francesconi‡

Istituto per la Sintesi Organica e la Fotoreattività (ISOF-CNR), via Gobetti 101, I-40129 Bologna, Italy, Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy, and Istituto di Chimica e Tecnologia dei Polimeri (ICTP-CNR), viale Andrea Doria 6, I-95125 Catania, Italy

Densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, for the binary mixtures containing two poly(propylene glycols) (M_n = 1335 and M_n = 2004) and two *block*-copolymers [poly(ethylene)−poly(propylene)−poly(ethylene)] (M_n = 1220 and M_n = 2280) + 2-methyltetrahydrofuran were determined at (298.15 and 313.15) K and at atmospheric pressure using an Anton Paar density meter, a Schott-Geräte AVS viscometer, an Abbe refractometer, and a Perkin-Elmer differential scanning calorimeter. Volume variations, ΔV, and deviations of the dynamic viscosities, $\Delta\eta$, were obtained at these temperatures and are negative for all mixtures. Experimental data were fitted to the Redlich−Kister equation, and the adjustable parameters and the standard deviations between experimental and calculated values were estimated. Conclusions were qualitatively discussed in terms of molecular interactions.

Introduction

This paper is part of a series of studies[1–3] we are carrying out on thermodynamic and bulk properties of binary mixtures containing polyethers with oxyethylene and oxypropylene repetitive units, terminated by hydroxylic groups at both ends. Here, we present experimental data of densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, of the binary systems containing poly(propylene glycols) (PPG) or *block*-[poly(ethylene glycol)−poly(propylene glycol)−poly(ethylene glycol)]copolymers (COP) + 2-methyltetrahydrofuran (MTHF) at (298.15 and 313.15) K and at atmospheric pressure. PPGs at low molecular weights are liquids, mostly insoluble in water, and used to suppress foaming in industrial processes and for making polyurethanes, resins, hydraulic fluids, and various other materials. COPs are amphiphilic copolymers, which have been extensively studied as a potential drug delivery vehicle due to its excellent biocompatibility and environmentally friendly behavior.[4] These copolymers are commercially available (under the name of "pluronic" or "poloxamer") and are widely applied as emulsifiers, wetting agents, solubilizers, etc.[5] MTHF, a cyclic ether with a CH_3 group closed to the O atom, has been chosen for the present study because its properties have been the subject of considerable interest due to its versatility as a solvent. On mixing with COPs, ether molecules should perturb the network of inter- and intramolecular H bonds in the polymers. Previous investigations on similar mixtures showed that the degree of interaction between the components depends on the mass of the polymer.[6,7] The aim of this paper is to determine the extent and type of interactions between components at two temperatures in the liquid states. PPGs and COPs were chosen with similar molecular weights (M_n) to have a useful comparison between the behaviors of the two kinds of polymers. To our knowledge, no data are reported in the literature on these mixtures.

Experimental

Materials. All products were from Aldrich and were used as received. The poly(propylene glycols) show molecular weights M_n =1200 and M_n =2000 and are named as PPG1 and PPG2, respectively. In the same way, copolymers with molecular weight M_n = 1100 and M_n = 1900 are named as COP1 and COP2, respectively. MTHF, anhydrous, analytical grade +99 %, was degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy) before use and dried over molecular sieves (Fluka, type 4Å) to remove any traces of moisture. The purities of this compound were corroborated by using a Hewlett-Packard G.CX. model 5890 supplied by an HP (cross-linked 5 % ME siloxane) capillary column, and the obtained values complied with purchaser specifications.

Experimental values of densities, ρ, dynamic viscosities, η, refractive indices, n_D, and heat capacities, C_p, of the pure liquids are compared with available literature data[8–13] in Table 1.

H NMR Analysis. H NMR spectra were obtained on an AC 200 F Bruker spectrometer interfaced with an Aspect 3000 computer using the Bruker DISR 90 acquisition software. Samples were dissolved in $CDCl_3$, and the chemical shifts were expressed in parts per million by comparison with the signal of TMS used as an internal standard.

MALDI-TOF Mass Spectrometric Analysis. MALDI-TOF mass spectra of the copolymer samples were acquired by a Voyager DE-STR instrument (from PerSeptive Biosystem) with delayed extraction (20 kV applied after 233 ns with a potential gradient of 2545 $V\cdot mm^{-1}$) and detection in reflection mode. The instrument was

---

* Corresponding author. E-mail: comelli@isof.cnr.it. Tel.: +39-051-2094326. Fax: +39-051-2094325.

[†] ISOF-CNR.

[‡] Università degli Studi.

[§] ICTP-CNR.

10.1021/je800005q CCC: $40.75

Table 1. Densities, ρ, Dynamic Viscosities, η, Refractive Indices, n_D, and Heat Capacities, C_p, of Pure Components and Comparison with Literature Values

		ρ/g·cm^{-3}		η/mPa·s		n_D		C_p/J·g^{-1}·K^{-1}	
component	T/K	this paper	lit.	this paper	lit.	this paper	lit.	this paper	lit.
PPG1	298.15	1.00079		176.619		1.4503		2.09828	
	313.15	0.98900		80.367		1.4446		2.15022	
PPG2	298.15	1.00007		323.571		1.4511		1.97225	
	313.15	0.98854		147.745		1.4448		2.02836	
COP1	298.15	1.01856		170.295		1.4533		1.89442	
	313.15	1.00667		79.396		1.4470		1.93581	
COP2	298.15	1.05747		360.679		1.4608		2.02783	
	313.15	1.04567		174.291		1.4549		2.06600	
MTHF	298.15	0.84800	0.8481[a]	0.473	0.473[b]	1.4057	1.40508[c]	1.79953	
	313.15	0.83238	0.83365[d]	0.416	0.41[e]	1.3967		1.87020	1.87577[f]

[a] Ref.[8] [b] Ref.[9] [c] Ref.[10] [d] Ref.[11] [e] Ref.[12] [f] Ref[13] (converted in J·g^{-1}·K^{-1}).

Table 2. Chemical Composition and Average Molecular Weight of the Polymers Used

	$[n + p]$	$[m]$	$[n + p]$	$[m]$	M_n	M_n	M_w	M_w/M_n
polymer	% (Aldrich)	% (Aldrich)	% (our data)	% (our data)	(Aldrich)	(our data)	(our data)	(our data)
PPG 1	0	100	0	100	1200	1335	1374	1.029
PPG 2	0	100	0	100	2000	2004	2062	1.029
COP 1	13[a]	87	19	81	1100	1220	1320	1.080
COP 2	57[b]	43	59	41	1900	2280	2510	1.100

[a] Polymer containing a mass fraction in ethylene glycol of about 0.1. [b] Polymer containing a mass fraction in ethylene glycol of about 0.5.

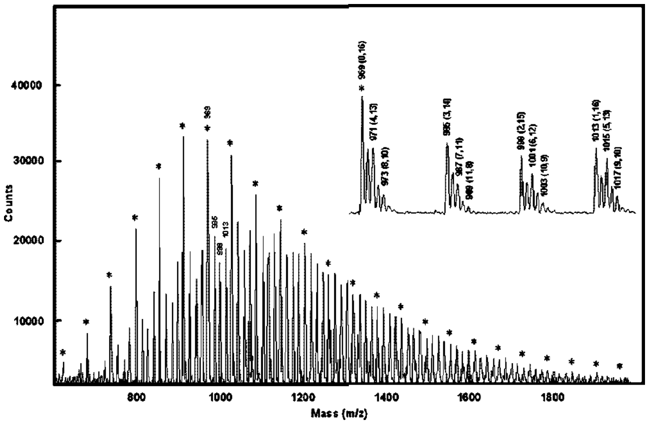

Figure 1. Positive MALDI-TOF mass spectrum of COP1. Peaks due to homopolypropylene glycol are indicated with $*$. In the inset, for each peak due to oligomeric species present in the copolymer, the m/z value and, in parentheses, the number of ethylene glycol (EG) and propylene glycol (PG) units constituting the molecule are indicated.

equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns). The samples were prepared by mixing about 0.1 mmol of polymer and 40 mmol of *trans*-3-indoleacrylic acid (used as a matrix) on the sampler target, using tetrahydrofuran doped with NaCl (as cationizing agent) as a solvent. After instrument calibration, the number average, M_n ($= \Sigma N_i M_i / \Sigma N_i$), and the weight average, M_w ($= \Sigma N_i M_i^2 / \Sigma N_i M_i = \Sigma w_i M_i$), molecular weights were determined using the Grams/386 program (PerSeptive Biosystem) applied on spectra corrected for the offset and the baseline.[14] In the above equalities, N_i is the number of moles of species i, having molecular weight M_i and weight fraction w_i. The polydispersity index was also obtained as the ratio M_w/M_n.

Characterization of Copolymers. Samples used in this work are *block* copolymers having the following general structure

$$\mathrm{HO{-}(-CH_2{-}CH_2{-}O{-})_n{-}[-CH(CH_3){-}CH_2{-}O{-}]_m{-}(CH_2{-}CH_2{-}O)_p{-}H}$$

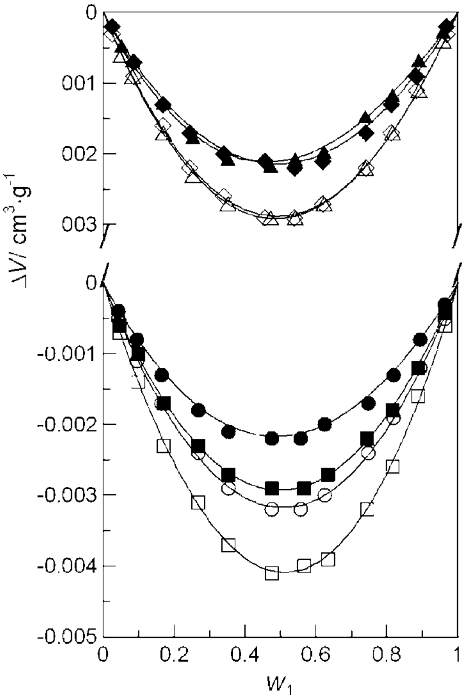

Figure 2. Volume variations, ΔV, for the binary mixtures containing polymers (1) + MTHF (2): ▲,△, PPG1 + MTHF; ◆,◇, PPG2 + MTHF; ●,○, COP1 + MTHF; ■,□, COP2 + MTHF. Full points, T/K = 298.15; open points, T/K = 313.15. Full lines, eq 5.

The relative abundance of EG ($-CH_2-CH_2-O-$) and PG [$-CH(CH_3)-CH_2-O-$] units in each copolymer sample has been achieved by ^{1}H NMR analysis. In the spectra of all samples (omitted for brevity), two clusters of signals are present between (1.16 and 1.11) ppm (due to CH_3 groups of PPG) and between (3.8 and 3.3) ppm (due to CH_2 groups of PPG and PEG and to CH groups of PPG). On the basis of the intensities of these signals, the values of $[n + p]$ (% PEG component abundance) and $[m]$ (% PPG component abundance) have been determined. The results obtained, little different from those indicated by the supplier, are reported in Table 2.

The characterization of copolymer samples, to determine both average molecular weight and microstructure, has been at-

Table 3. Densities, ρ, Volume Variations, ΔV, Dynamic Viscosities, η, Deviations in Dynamic Viscosities, $\Delta\eta$, Refractive Indices, n_D, of Poly(propylene glycols) or *block*-Copolymers + MTHF at (298.15 and 313.15) K

w_1	ρ / $g \cdot cm^{-3}$	V / $cm^3 \cdot g^{-1}$	η / $mPa \cdot s$	$\Delta\eta$ / $mPa \cdot s$	n_D	w_1	ρ / $g \cdot cm^{-3}$	V / $cm^3 \cdot g^{-1}$	η / $mPa \cdot s$	$\Delta\eta$ / $mPa \cdot s$	n_D
PPG1 (1) + MTHF (2)											
T/K = 298.15						T/K = 313.15					
0.0504	0.85400	−0.0005	0.567	−8.782	1.4074	0.0504	0.83950	−0.0006	0.486	−3.958	1.3991
0.0815	0.85914	−0.0007	0.640	−14.195	1.4088	0.0815	0.84392	−0.0009	0.548	−6.386	1.4000
0.1690	0.87139	−0.0013	0.910	−29.339	1.4126	0.1690	0.85655	−0.0017	0.756	−13.174	1.4043
0.2519	0.88322	−0.0018	1.289	−43.550	1.4164	0.2519	0.86869	−0.0023	1.057	−19.496	1.4086
0.3515	0.89771	−0.0021	1.953	−60.435	1.4207	0.3515	0.88353	−0.0027	1.565	−26.954	1.4127
0.4708	0.91547	−0.0022	6.646	−76.753	1.4260	0.4708	0.90181	−0.0029	3.281	−34.774	1.4188
0.5403	0.92603	−0.0021	7.778	−87.866	1.4293	0.5403	0.91267	−0.0029	4.171	−39.442	1.4223
0.6223	0.93875	−0.0020	9.145	−100.946	1.4331	0.6223	0.92568	−0.0027	5.322	−44.819	1.4264
0.7393	0.95724	−0.0015	13.823	−116.871	1.4384	0.7393	0.94469	−0.0022	9.561	−49.961	1.4316
0.8150	0.96958	−0.0012	26.933	−117.095	1.4420	0.8150	0.95727	−0.0017	16.953	−48.621	1.4354
0.8893	0.98194	−0.0007	59.386	−97.742	1.4452	0.8893	0.96983	−0.0011	31.976	−39.544	1.4390
0.9578	0.99353	−0.0003	118.873	−50.315	1.4483	0.9578	0.98162	−0.0004	56.831	−20.163	1.4422
PPG2 (1) + MTHF (2)											
T/K = 298.15 K						T/K = 313.15					
0.0254	0.85145	−0.0002	0.533	−8.160	1.4064	0.0254	0.83597	−0.0003	0.458	−3.706	1.3973
0.0847	0.85957	−0.0007	0.721	−27.115	1.4089	0.0847	0.84434	−0.0009	0.609	−12.283	1.4003
0.1670	0.87107	−0.0013	1.088	−53.345	1.4126	0.1670	0.85616	−0.0016	0.929	−24.091	1.4044
0.2433	0.88190	−0.0017	1.131	−78.051	1.4161	0.2433	0.86731	−0.0022	1.320	−34.941	1.4082
0.3398	0.89581	−0.0020	2.564	−107.697	1.4205	0.3398	0.88163	−0.0026	2.049	−48.429	1.4127
0.4551	0.91294	−0.0021	4.605	−142.896	1.4256	0.4551	0.89921	−0.0029	3.969	−63.490	1.4183
0.5388	0.92558	−0.0022	7.274	−167.292	1.4295	0.5388	0.91228	−0.0029	5.431	−74.369	1.4224
0.6187	0.93790	−0.0021	9.839	−190.529	1.4331	0.6187	0.92487	−0.0027	8.337	−83.229	1.4262
0.7396	0.95697	−0.0017	19.816	−219.620	1.4388	0.7396	0.94445	−0.0022	15.088	−94.291	1.4323
0.8121	0.96874	−0.0013	41.050	−221.820	1.4426	0.8121	0.95646	−0.0017	27.035	−93.031	1.4356
0.8837	0.98050	−0.0009	96.523	−189.473	1.4456	0.8837	0.96848	−0.0011	52.354	−78.257	1.4393
0.9686	0.99471	−0.0002	240.517	−72.900	1.4498	0.9686	0.98308	−0.0003	112.308	−30.807	1.4436
COP1 (1) + MTHF (2)											
T/K = 298.15						T/K = 313.15					
0.0423	0.85434	−0.0004	0.552	−7.113	1.4078	0.0423	0.83887	−0.0005	0.487	−3.274	1.3988
0.0938	0.86213	−0.0008	0.681	−15.722	1.4098	0.0938	0.84690	−0.0011	0.565	−7.259	1.4015
0.163	0.87276	−0.0013	0.891	−27.262	1.413	0.1630	0.85780	−0.0017	0.746	−12.543	1.4049
0.267	0.88911	−0.0018	1.361	−44.455	1.4178	0.2670	0.87456	−0.0024	1.105	−20.399	1.4098
0.3525	0.90290	−0.0021	1.978	−58.422	1.4219	0.3525	0.88875	−0.0029	1.611	−26.676	1.4140
0.474	0.92300	−0.0022	3.470	−77.498	1.4275	0.4740	0.90944	−0.0032	2.862	−34.989	1.4200
0.5565	0.93708	−0.0022	5.321	−89.659	1.4317	0.5565	0.92362	−0.0032	3.943	−40.426	1.4244
0.6247	0.94890	−0.002	6.485	−100.076	1.4347	0.6247	0.93596	−0.0030	5.513	−44.242	1.4276
0.7482	0.97104	−0.0017	11.142	−116.395	1.4409	0.7482	0.95850	−0.0024	10.347	−49.164	1.4341
0.8195	0.98414	−0.0013	25.422	−114.221	1.4442	0.8195	0.97183	−0.0019	16.989	−48.152	1.4379
0.8942	0.99813	−0.0008	58.396	−93.928	1.4478	0.8942	0.98605	−0.0012	32.493	−38.545	1.4419
0.9629	1.01132	−0.0003	119.466	−44.523	1.4513	0.9629	0.99938	−0.0005	58.575	−17.888	1.4453
COP2 (1) + MTHF (2)											
T/K = 298.15						T/K = 313.15					
0.0456	0.85613	−0.0006	0.639	−16.273	1.4077	0.0456	0.84071	−0.0007	0.532	−7.819	1.3986
0.0981	0.86559	−0.001	0.936	−34.883	1.4104	0.0981	0.85042	−0.0014	0.736	−16.742	1.4018
0.1713	0.87910	−0.0017	1.221	−60.962	1.4143	0.1713	0.86425	−0.0023	1.041	−29.163	1.4058
0.267	0.89723	−0.0023	2.050	−94.587	1.4193	0.2670	0.88276	−0.0031	1.724	−45.111	1.4111
0.3527	0.91397	−0.0027	3.239	−124.291	1.424	0.3527	0.89989	−0.0037	2.568	−59.179	1.4166
0.4755	0.93876	−0.0029	6.495	−165.266	1.4304	0.4755	0.92529	−0.0041	4.879	−78.219	1.4237
0.5663	0.95779	−0.0029	11.219	−193.227	1.4353	0.5663	0.94467	−0.0040	8.124	−90.751	1.4287
0.632	0.97193	−0.0027	16.990	−211.128	1.4391	0.6320	0.95912	−0.0039	11.764	−98.538	1.4327
0.7441	0.99683	−0.0022	30.998	−237.513	1.4459	0.7441	0.98444	−0.0032	21.651	−108.150	1.4394
0.8145	1.01296	−0.0018	59.237	−234.619	1.45	0.8145	1.00080	−0.0026	36.817	−105.219	1.4436
0.8885	1.03040	−0.0012	125.935	−194.595	1.4542	0.8885	1.01832	−0.0016	69.437	−85.472	1.4484
0.9648	1.04880	−0.0004	263.185	−84.829	1.4587	0.9648	1.03697	−0.0006	131.657	−36.52	1.4530

tempted by MALDI-TOF mass spectrometry. In Figure 1, as an example, the mass spectrum of COP1 is reported.

Unlike COP2, in the spectrum of COP1, a series of peaks at m/z 621 + $n \cdot 58$ (with n = 10 to 33, indicated with $_*$), corresponding to homopropylene glycol oligomers cationized by Na^+, are present with an intensity higher than the expected. Besides, each signal of the mass spectrum is really constituted of a cluster of peaks (see inset of Figure 1) due not only to the isotopic pattern of the different compounds but also mostly to the presence of oligomers of different compositions. So, referring to the inset of Figure 1, on the top of each peak due to an oligomeric component of the copolymer, the m/z value and, in parentheses, the EG, PG composition (in the order: "$n + p$" and "m") are indicated. Considering the whole mass spectrum, about all the oligomers corresponding to the above-reported structure with $0 \le$ "$n + p$" ≤ 15 and $7 \le$ "m" ≤ 33 are detected, and no peaks due to impurities are found. On this basis, COP1 and COP2 can be considered substantially pure.

The average molecular weights, M_w and M_n, of copolymers have been determined, using the Grams/386 program (PerSep-

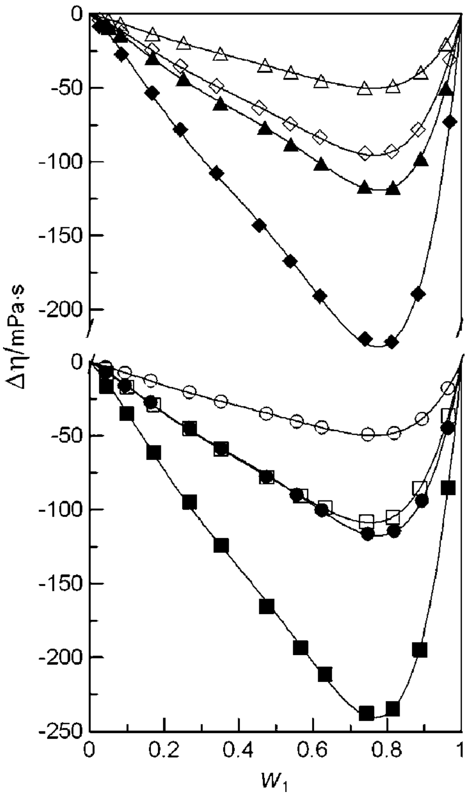

Figure 3. Deviation in viscosity, $\Delta\eta$, for the binary mixtures containing polymers (1) + MTHF (2): ▲,△, PPG1 + MTHF; ◆,◇, PPG2 + MTHF; ●,○, COP1 + MTHF; ■, □, COP2 + MTHF. Full points, T/K = 298.15; open points, T/K = 313.15. Full lines, eq 5.

Table 4. Experimental Liquid Heat Capacities, C^0_p, of Pure Components at Atmospheric Pressure

T/K	PPG1	PPG2	COP1	COP2	MTHF
		C^0_p (J·g^{-1}·K^{-1})			
288.15	2.0496	1.9410	1.8612	1.9753	1.7551
293.15	2.0764	1.9492	1.8750	1.9967	1.7695
298.15	2.0983	1.9723	1.8944	2.0278	1.7996
303.15	2.1117	1.9896	1.9007	2.0413	1.8223
308.15	2.1301	2.0125	1.9164	2.0633	1.8413
313.15	2.1502	2.0284	1.9358	2.0858	1.8702
318.15	2.1705	2.0578	1.9533	2.1155	1.8940
323.15	2.1937	2.0838	1.9733	2.1481	1.9131

tive Biosystem), from the corresponding MALDI mass spectra in the mass range 600 to 2000 (for COP1) and 1000 to 4500 (for COP2). The obtained values, little higher than those given from the supplier, are reported in Table 2.

Data concerning the average molecular weights of two poly(propylene glycol) homopolymer samples, already used in a previous work,[15] are also reported in the table as a reference.

Density Measurements. Mixtures were prepared by mass in airtight-stoppered bottles, using a digital balance (Mettler, model AE 160, Switzerland), covering the whole mass fraction range. The whole procedure was described elsewhere.[16] Densities of the liquids were measured by means of a vibrating tube density meter (Anton Paar, model DMA 60/602, Graz, Austria). The temperature inside the vibrating-tube cell was measured by a digital thermometer (Anton Paar, type CTK 100) and was regulated to better than ± 0.01 K using a water circulating bath (Heto, type 01 DBT 623, Birkeròd, Denmark). Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from the literature.[17,18]

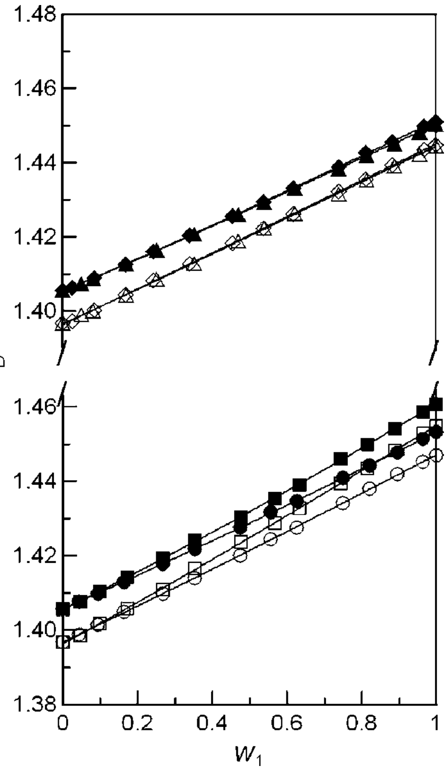

Figure 4. Refractive indices, n_D, vs the mass fraction, w_1, of the binary mixtures containing polymers (1) + MTHF (2): ▲,△, PPG1 + MTHF; ◆,◇, PPG2 + MTHF; ●,○, COP1 + MTHF; ■,□, COP2 + MTHF. Full points, T/K = 298.15; open points, T/K = 313.15. Full lines correspond to a three-parameter polynomial regression.

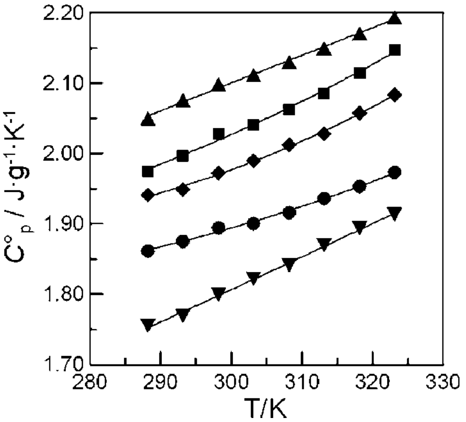

Figure 5. Heat capacities, C^0_p, of pure components in the range (288.15 to 333.15) K. ●,■,▲,◆,▼, Refer to PPG1, PPG2, COP1, COP2, and MTHF, respectively. Full line, eq 4.

The uncertainty in the densities was $\pm\ 1.5 \cdot 10^{-5}$ g·cm^{-3} at 308.15 K. Correspondingly, the uncertainty in the volume variation ΔV is estimated as < 1 %. Before measurements, the apparatus was checked by determining the ΔV using the test mixture benzene + cyclohexane at 298.15 K. Agreement of our results with those of the literature[19] is within 1 %.

Values of ΔV (cm^3·g^{-1}), during mixing of 1 g of mixture, can be obtained by the following equation

$$\Delta V = 1/\rho - w_1/\rho_1 - w_2/\rho_1 \qquad (1)$$

where ρ is the density of the mixture and w_i and ρ_i (i = 1, 2) are the mass fractions and densities of the ith component, respectively. The experimental values for the four binary mixtures PPG or COP + MTHF are listed in Table 3. The curves

Table 5. Experimental Heat Capacities, C_p, for Binary Mixtures Containing Polymers + MTHF

w_1	C_p / $J\cdot g^{-1}\cdot K^{-1}$	w_1	C_p / $J\cdot g^{-1}\cdot K^{-1}$
	PPG (1) + MTHF (2)		
	T/K = 298.15		
0.0763	1.8419	0.5820	1.9625
0.0792	1.8426	0.6250	1.9752
0.1559	1.8609	0.7219	1.9907
0.2771	1.8900	0.8321	2.0356
0.3887	1.9184	0.9203	2.0595
0.5371	1.9533	0.9578	2.0751
	T/K = 313.15		
0.0763	1.9117	0.582	2.0587
0.0792	1.9127	0.625	2.0672
0.1559	1.9438	0.7219	2.0834
0.2771	1.9651	0.8321	2.1098
0.3887	2.0009	0.9203	2.1302
0.5371	2.0403	0.9578	2.1398
	PPG2 (1) + MTHF (2)		
	T/K = 298.15		
0.0455	1.8057	0.5967	1.8850
0.0827	1.8112	0.6343	1.8981
0.2123	1.8258	0.7224	1.9055
0.3228	1.8401	0.8287	1.9302
0.4235	1.8561	0.9257	1.9573
0.5337	1.8768	0.9626	1.9658
	T/K = 313.15		
0.0455	1.8747	0.5967	1.9456
0.0828	1.8800	0.6343	1.9505
0.2123	1.8914	0.7224	1.9715
0.3228	1.9100	0.8287	1.9900
0.4235	1.9251	0.9257	2.0035
0.5337	1.9413	0.9626	2.0182
	COP1 (1) + MTHF (2)		
	T/K = 298.15		
0.0423	1.8057	0.5565	1.8692
0.0938	1.8112	0.6247	1.8801
0.1630	1.8208	0.7482	1.8886
0.2670	1.8354	0.8195	1.8890
0.3525	1.8407	0.8942	1.8921
0.4740	1.8531	0.9629	1.8931
	T/K = 313.15		
0.0423	1.8731	0.5565	1.9163
0.0938	1.8752	0.6247	1.9197
0.1630	1.8838	0.7482	1.9234
0.2670	1.9054	0.8195	1.9246
0.3525	1.9074	0.8942	1.9257
0.4740	1.9091	0.9629	1.9285
	COP2 (1) + MTHF (1)		
	T/K = 298.15		
0.0487	1.8167	0.5509	1.9456
0.0854	1.8252	0.6288	1.9656
0.1640	1.8405	0.7350	1.9852
0.3227	1.8903	0.8014	1.9926
0.4596	1.9246	0.9029	2.0123
0.5338	1.9446	0.9393	2.0151
	T/K = 313.15		
0.0487	1.8856	0.5509	2.0083
0.0854	1.8977	0.6288	2.0103
0.1640	1.9152	0.7350	2.0322
0.3227	1.9524	0.8014	2.0444
0.4596	1.9802	0.9029	2.0567
0.5338	1.9950	0.9393	2.0589

of the volume variations, ΔV, vs the composition of these binary systems at the two experimental temperatures are shown in Figure 2.

Viscosity Measurements. The kinematic viscosities, ν, were measured with eight Ubbelohde viscometers, to cover the range of temperatures from (298.15 to 313.15) K. A Schott-Geräte automatic measuring unit (model AVS 350), equipped with a thermostat (Lauda, model E 200, Germany) in which the temperature was regulated to within ± 0.01 K, was used for measurements. An electronic stop watch was used to measure the flow times. The capillary diameters of the viscometers, varying from 0.47 mm up to 1.69 mm, were used for kinematic

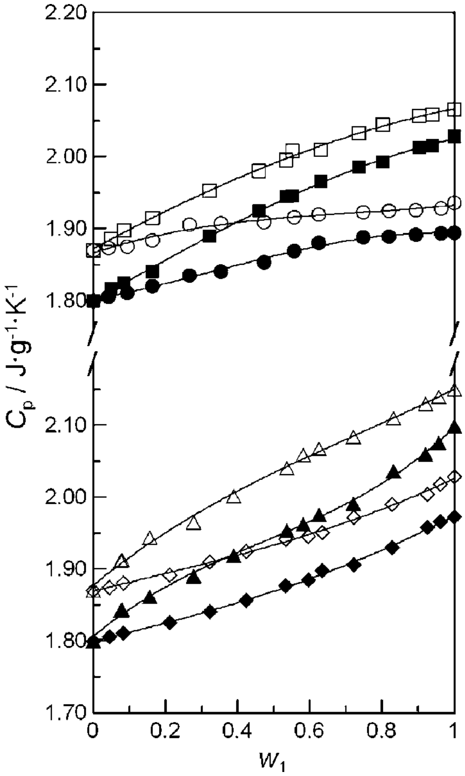

Figure 6. Heat capacities, C_p, for the binary mixtures containing polymers (1) + MTHF (2): ▲,△, PPG1 + MTHF; ◆,◇, PPG2 + MTHF; ●,○, COP1 + MTHF; ■,□, COP2 + MTHF. Full points, T/K = 298.15; open points, T/K = 313.15. Full lines, eq 4.

Table 6. Adjustable Parameters of Equation 4 and Standard Deviation of Pure Components

component	c_0	c_1	c_2	$\sigma(C_p)$ / $J\cdot g^{-1}\cdot K^{-1}$
PPG1	0.806162	0.004672	−0.000001	0.004
PPG2	4.480339	−0.020365	0.000040	0.003
COP1	3.023190	−0.010411	0.000022	0.003
COP2	4.360600	−0.019783	0.000040	0.011
MTHF	0.696216	0.0027701	0.000003	0.004

Table 7. Adjustable Parameters of Equation 4 and Standard Deviation of Polymers (1) + MTHF (2) at (298.15 and 313.15) K

T/K	c_0	c_1	c_2	$\sigma(C_p)$ / $J\cdot g^{-1}\cdot K^{-1}$
		PPG1 (1) + MTHF (2)		
298.15	1.817889	0.229356	0.04044	0.009
313.15	1.881853	0.340404	−0.075423	0.006
		PPG2 (1) + MTHF (2)		
298.15	1.800995	0.0999835	0.071945	0.003
313.15	1.870865	0.095281	0.058395	0.003
		COP1 (1) + MTHF (2)		
298.15	1.797307	0.159818	−0.060186	0.004
313.15	1.869182	0.116455	−0.055784	0.004
		COP2 (1) + MTHF (2)		
298.15	1.798258	0.316575	−0.082958	0.003
313.15	1.871696	0.281739	−0.086509	0.003

Table 8. Adjustable Parameters, a_k, from Equation 5, and Standard Deviations $\sigma(Q)$, from Equation 6, of Polymers + MTHF at (298.15 and 313.15) K

function	T/K	a_0	a_1	a_2	a_3	$\sigma(Q)$
			PPG1 (1) + MTHF (2)			
ΔV/cm^3·g^{-1}	298.15	−0.008781	0.001422			0.000025
	313.15	−0.011654	0.000887			0.000018
$\Delta\eta$/mPa·s	298.15	−323.6321	−311.4590	−440.8366	−329.5845	0.88
	313.15	−146.3578	−135.8509	−161.2827	−108.7958	0.28
			PPG2 (1) + MTHF (2)			
ΔV/cm^3·g^{-1}	298.15	−0.009029	0.000437			0.000024
	313.15	−0.016696	0.000507			0.000028
$\Delta\eta$/mPa·s	298.15	−614.8265	−603.9600	−803.4101	−604.4102	2.12
	313.15	−273.8452	−254.8328	−313.6965	−229.6617	0.84
			COP1 (1) + MTHF (2)			
ΔV/cm^3·g^{-1}	298.15	−0.008958	0.000484			0.000020
	313.15	−0.012804	−0.000391			0.000025
$\Delta\eta$/mPa·s	298.15	−320.2669	−316.6183	−423.1895	−310.2805	1.02
	313.15	−145.0855	−132.5405	−159.5809	−113.6301	0.42
			COP2 (1) + MTHF (2)			
ΔV/cm^3·g^{-1}	298.15	−0.011883	0.000178			0.000018
	313.15	−0.016373	−0.000766			0.000029
$\Delta\eta$/mPa·s	298.15	−679.7327	−643.0457	−811.7889	−597.6598	2.23
	313.15	−322.5113	−292.7688	−332.754	−229.3794	0.80

ranges of (0.5 to 50) mm^2·s^{-1}, respectively. The viscometers were filled with 15 cm^3 of solution for each measurement. The calibration of the viscometers was carried out with double-distilled water and by a standard oil specimen of known viscosity (Petrotest, DIN 51 550). Experiments were repeated at least five times at each temperature for all mixtures, and the results were averaged. The overall uncertainty of viscosity measurements depends on equilibrium temperature, flow time, mole fraction, and calibration fluid. So according to the precision of all experimental instruments, the experimental average relative uncertainties of viscosity were estimated to be ± 0.01 cm^3·s^{-1}. The kinematic viscosities ν/cm^2·s^{-1} were obtained from the equation

$$\upsilon = \eta/\rho = k(t - \theta) \tag{2}$$

where η is the absolute (dynamic) viscosity; ρ is the density; k is the capillary constant; t is the flow time; and θ is the kinetic energy correction. In the whole set of experiments, flow times were maintained > 200 s, by selecting viscometers with appropriate values of k.

Equation 2 and the values of ρ allow calculation of the deviation in viscosity, $\Delta\eta$, from the definition

$$\Delta\eta = \eta - w_1\eta_1 - w_2\eta_2 \tag{3}$$

where η_k is the viscosity of the pure component k and w_k is its mass fraction in the mixture.

Values of $\Delta\eta$ are reported in Table 3 and plotted in Figure 3 against the mass fraction, w_1, of the polymers.

The uncertainty of the viscosity deviations was estimated to be less than 0.02 mPa·s.

Refractive Indices. Refractive indices, n_D (sodium line), were measured to within ± 0.0001 by an Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland). The refractometer was calibrated using distilled water, in accordance with the instrument instructions. Water was circulated into the instrument through a thermostatically controlled bath, whose temperature stability was ± 0.05 K. The refractive index measurements were performed after the liquid mixtures attained a constant temperature in the refractometer cell, as measured by a control thermometer. The procedure was repeated at least five times, and the refractive index was taken as the average of these measurements. Values of the refractive indices, fitted to a three-parameter polynomial, are reported in Table 3 and plotted in Figure 4.

Heat Capacity Measurements. The heat capacity measurements, C_p, were determined by means of a Perkin-Elmer Pyris Diamond DSC differential scanning calorimeter equipped with a model ULSP 90 intracooler. The instrument was calibrated with high-purity standards (indium and cyclohexane) at 5 K·min^{-1}. The temperature was known to within ± 0.1 K. The samples, approximately 10 mg, determined to ± 0.01 mg, were encapsulated in hermetic pans. The heat capacity of the samples was obtained by means of three consecutive DSC runs at a scanning rate of 5 K·min^{-1}: the sample run, the blank run, and the standard sample (sapphire) run.[20] Care was taken to ensure that similar initial and final isotherm levels were reached for all three scans. The heat capacity data were obtained by means of the commercial software supplied by Perkin-Elmer. The estimated uncertainty for repeated data is less than 0.1 %.

The experimental heat capacities, $C_p{}^0$, of pure components, from (288.15 to 323.15) K, vs the temperature T/K, at normal pressure, are listed in Table 4 and represented in Figure 5. The experimental values of the heat capacities, C_p, of mixtures vs the mass fraction, w_1, of polymer are reported in Table 5 and represented in Figure 6. The expression used to fit $C^0{}_p$ as a function of temperature is

$$C^0{}_p = c_0 + c_1(T/\mathrm{K}) + c_2(T/\mathrm{K})^2 \tag{4}$$

An analogous expression is used to fit C_p as a function of w_1: $C^0{}_p$ and (T/K) in eq 4 are substituted by C_p and w_1, respectively.

Values of the parameters c_k (k = 0, 1, and 2) are listed in Tables 6 and 7 and together with the standard deviations $\sigma(C_p)$.

Results

Changes in volume variations, ΔV, and in deviation of viscosities, $\Delta\eta$, with composition can be expressed by the Redlich−Kister equation

$$Q^{\mathrm{E}}_{\mathrm{calcd}} = w_1 w_2 \sum_{k \geq 0} a_k (w_1 - w_2)^k \tag{5}$$

where $Q^{\mathrm{E}}_{\mathrm{calcd}}$ refers to ΔV or $\Delta\eta$. The adjustable parameters a_k were determined by a least-squares method. The corresponding results are reported in Table 8. The tabulated standard deviations, $\sigma(Q^{\mathrm{E}})$, reported in the same table, are defined as

$$\sigma(Q^{\mathrm{E}}) = |\xi_{\mathrm{min}}/(N-n)|^{0.5} \tag{6}$$

with N and n being the number of experimental points and of parameters, respectively, whereas ξ_{min} is the minimum value of the objective function ξ, defined as

$$\xi = \sum_{k=1}^{N} (Q^{\mathrm{E}}_{\mathrm{calcd}} - Q^{\mathrm{E}})^2 \tag{7}$$

and Q^{E} is the experimental value.

Discussion

As can be seen in Figures 2 and 3, all values of both ΔV and $\Delta\eta$ are negative in the entire range of mass fractions. On increasing temperature, the values of ΔV become more negative, whereas $\Delta\eta$ displays an opposite behavior. A similar behavior has also been observed in mixtures of PEGs + 2-methyltetrahydrofuran.[3] However, absolute values of ΔV for mixtures containing PPGs and COPs are much smaller than those for PEGs, whereas absolute values of $\Delta\eta$ show an opposite trend. PPG and COP curves show a similar trend, with absolute values of COP relatively larger than those of PPGs. As reported in a previous paper,[6] mixing of PEGs with MTHF leads to partial disruption of the H-bond configuration of the polymer through the interaction of ether with the polymers. The same will be true for polymers similar to PPG and COP, having terminal OH groups and only a different number of CH_2 inside the chain. However, the presence of side CH_3's along the chain of pure COP and PPG will lead to a very viscous structure if a random coil is assumed for the molecule, containing the CH_3's inside the coil too. This explains the large decrease in the values of $\Delta\eta$ when MTHF disrupts the H-bond configuration of polymers. The absolute values of $\Delta\eta$ are about seven times larger with respect to PEG 400.

The volume variations, ΔV, after mixing are, instead, very small for PPG and COP, when compared with the ΔV values of PEG, if absolute values are considered. This may be due to the larger flexibility of the PPG and COP chain, longer and richer in CH_2 groups than PEG.

Literature Cited

(1) Castellari, C.; Vitalini, D.; Comelli, F.; Francesconi, R. Effect of excess enthalpies on binary mixtures containing propylene glycols and poly(propylene glycols) + dimethyl carbonate at 308.15 K. *Thermochim. Acta* **2004**, *412*, 125–129.

(2) Comelli, F.; Ottani, S. Excess Enthalpies, Densities, Viscosities, and Refractive Indices of Binary Mixtures Involving Some Poly(glycols) + Diethyl Carbonate at 308.15 K. *J. Chem. Eng. Data* **2004**, *49*, 970–975.

(3) Francesconi, R.; Bigi, A.; Rubini, K.; Comelli, F. Molar Heat Capacities, Densities, viscosities, and Refractive Indices of Poly(Ethylene Glycols) + 2-Methyltetrahydrofuran at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **2007**, *52*, 2020–2025.

(4) Xiong, X. Y.; Tam, K. C.; Gan, L. H. Synthesis and aggregation behaviour of Pluronic F127/poly(lactic acid) block copolymers in aqueous solutions. *Macromolecules* **2003**, *36*, 9979–9985.

(5) Rangelov, S.; Dimitrov, P.; Tsvetanov, C. B. Mixed block copolymer aggregates with tunable temperature behaviour. *J. Phys. Chem. B* **2005**, *109*, 1162–1167.

(6) Ottani, S.; Vitalini, D.; Comelli, F.; Castellari, C. Densities, Viscosities, and Refractive Indices of New Mixtures of Poly(ethylene glycols) + Dialkyl Carbonates at 313.15 K. *J. Chem. Eng. Data* **2004**, *49*, 148–154.

(7) Comelli, F.; Ottani, S.; Vitalini, D.; Francesconi, R. A Calorimetric Study of Binary Mixtures Containing Some Glycols and Polyglycols + Anisole at 308.15 K and at Atmospheric Pressure. *Thermochim. Acta* **2003**, *407*, 85–92.

(8) Wang, Z.; Benson, G. C.; Lu, C. Y. B. Excess Enthalpies of 2-Methyltetrahydrofuran + (2,2,4-Trimethylpentane or n-Heptane) + Methylcyclohexane at 25 deg C. *J. Solution Chem.* **2002**, *31*, 771–782.

(9) Ponomarenko, S. M.; Mushtokova, S. P.; Demakhin, A. G.; Faifel, B. L.; Kalmanovich, D. G. Physicochemical Properties and Electonic Structure of Certain Aprotic Solvent. *Zh. Obshch. Khim.* **1995**, *65*, 190–198.

(10) Kobe, K. A.; Ravicz, A. E.; Vohra, S. P. Critical Properties and Vapor Pressures of Some Ethers and Heterocyclic Compounds. *J. Chem. Eng. Data* **1956**, *1*, 50–56.

(11) De Lorenzi, L.; Fermeglia, M.; Torriano, G. Density and Viscosity of i-Methoxy-2-propanol, 2-Methyltetrahydrofuran, α,α,α-Trifluoroethane at Different Temperatures. *J. Chem. Eng. Data* **1996**, *41*, 1121–1125.

(12) Giner, B.; Aldea, M.; Mertin, S.; Gascon, I.; Lafuente, C. Viscosities of Binary Mixtures of Isomeric Butanols or Isomeric Chlorobutanes with 2-Methyltetyrahydrofuran. *J. Chem. Eng. Data* **2003**, *48*, 1296–1300.

(13) Rodriguez, S.; Lafuente, C.; Artigas, H.; Royo, F. M.; Urieta, J. S. Densities, Speeds of Sound, and Isentropic Compressibilities of a Cyclic Ether with Chlorocyclohexane, or Bromocyclohexane at the Temperature 298.15 and 313.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 139–149.

(14) Vitalini, D.; Mineo, P.; Scamporrino, E. Further Application of a Procedure for Molecular Weight and Molecular Weight Distribution Measurements of Polydisperse Polymers from Their Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectra. *Macromolecules* **1996**, *29*, 5285–5289.

(15) Castellari, C.; Vitalini, D.; Comelli, F.; Francesconi, R. Effect of Excess Enthalpies on Binary Mixtures Containing Propylene Glycols and Poly(propylene glycols) + Dimethyl Carbonate at 308.15 K. *Thermochim. Acta* **2004**, *412*, 125–129.

(16) Fermeglia, M.; Lapasin, J. Excess Volumes and Viscosities of Binary Mixtures of Organics. *J. Chem. Eng. Data* **1988**, *33*, 415–417.

(17) Kohlrausch, F. Density of Air. *Prakt. Phys.* **1968**, *3*, 40.

(18) Wagenbreth, H.; Blanke, W. Die Dichte des Wassers im Internationalen Einheitensystem und in die Internationalen Practishen Temperaturskala von 1968; PTB: Mitteilungen, 1971; *6/71*, 412.

(19) Grolier, J. P. E.; Wilhelm, E.; Hamedi, M. H. Molar Heat Capacities and Isothermal Compressibility of Binary Liquid Mixtures: Carbon Tetrachloride + Benzene, Carbon Tetrachloride + Cyclohexane, and Benzene + Cyclohexane. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1282–1290.

(20) O'Neill, M. J. Measurement of specific heat functions by differential scanning calorimetry. *Anal. Chem.* **1966**, *38*, 1331.

Received for review January 03, 2008. Accepted March 17, 2008.

JE800005Q