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A tunable mixture solvent for poly(ε-caprolactone): Acetone + CO_2

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Abstract

We report on a tunable, versatile solvent system for poly(ε-caprolactone) (PCL). It is shown that acetone + carbon dioxide mixtures are efficient solvents for this biodegradable polymer. Phase behavior and volumetric properties of PCL + acetone + CO_2 mixtures were determined in a variable-volume view cell. Effect of temperature (323–398 K), pressure (0.1–50 MPa), polymer concentration (1–20 wt%), polymer molecular weight (14k and 65k) and carbon dioxide concentration (0–60 wt%) on the liquid–liquid (L–L) phase boundaries and the densities was explored. Complete miscibility of mixtures with polymer concentrations up to 20 wt% could be achieved in the fluid mixtures containing up to 50 wt% carbon dioxide at modest pressures (5–40 MPa). The solutions all showed LCST-type phase behavior. Comparisons with literature data on the miscibility pressures in other solvent mixtures such as dimethyl ether + carbon dioxide or chlorodifluoromethane + carbon dioxide show that complete miscibilities of PCL in acetone + carbon dioxide mixtures are achievable at much lower pressures.

The mixture densities were in the range 0.58–1.20 g/cm^3. Mixtures with carbon dioxide content more than 20 wt% showed higher sensitivity and larger change in density with pressure. Densities of the polymer solutions were found to increase significantly with PCL concentration. The densities of solutions with different polymer molecular weights were close to each other, with the lower molecular weight polymer samples showing slightly higher densities.

A unique contribution of the present paper is the comparison of compressibility and expansivity of the solutions with the corresponding properties of the solvents. Analysis of the data shows that the compressibilities of PCL solutions are lower than that of the acetone + carbon dioxide solvent mixture at temperatures lower than 373 K. At around 373 K, compressibilities become equal to each other and a switchover is observed at higher temperatures. The difference in the isothermal compressibility of the polymer solution and the solvent decreases with pressure, but reaches a plateau value for pressures greater than 25 MPa. Compared to their solvent mixture, the polymer solutions display a higher isobaric expansivity at the same pressure.

Keywords: Poly(ε-caprolactone); Acetone; Carbon dioxide

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1. Introduction

Poly(ε-caprolactone) is a semi-crystalline polymer that shows a high degree of miscibility with a number of different polymers such as polycarbonate and poly(vinyl chloride) [1]. As such, it is of great importance in polymer blend applications. It is one of those polymers that shows complete miscibility in all proportions with polycarbonate. Blends of PCL with polystyrene, even though not compatible, lead to blends with co-continuous phase morphologies when phase compositions are at around 50 wt% [2].

Polycaprolactone is a biodegradable polymer and as such it is of great importance also in drug delivery systems and biomedical applications such as tissue engineering [3–8]. In drug delivery systems, PCL functions either as a biodegradable polymer matrix or as an encapsulating agent for the drug particles [3–5], while in tissue engineering, it is used in constructing scaffolds including composites with inorganic particles, fibers, or sintered ceramic matrices [6–8]. In all these applications, physical properties such as crystallinity, morphology, microstructure, and mechanical properties play important roles. The degree of crystallinity of the polymer, for example, determines

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Table 1
Liquid–liquid (L–L) demixing pressures (*P*) at different temperatures (*T*) for poly(ε-caprolactone) (Mw = 14k and 65k) solutions in acetone + carbon dioxide mixtures

T (K)	*P* (MPa)
PCL (14k)	
PCL (1 wt%) + acetone (59 wt%) + CO_2 *(40 wt%)*	
334.5	10.0
338.9	11.3
347.6	13.0
352.9	15.0
359.0	16.0
363.1	18.0
368.5	19.5
374.0	23.0
379.3	24.5
383.6	26.0
388.5	26.8
394.1	27.3
398.0	28.0
PCL (5 wt%) + acetone (55 wt%) + CO_2 *(40 wt%)*[a]	
340.0	17.8
343.5	18.8
348.8	20.8
351.0	21.3
354.6	22.3
358.6	23.2
361.1	23.5
364.6	24.8
368.8	25.5
372.3	26.7
PCL (10 wt%) + acetone (50 wt%) + CO_2 *(40 wt%)*	
325.1	4.9
330.1	6.8
337.7	9.1
342.5	10.5
347.5	11.9
352.8	12.7
356.8	14.7
363.5	16.7
369.3	18.4
374.0	19.5
380.2	21.1
384.9	22.4
389.0	23.3
394.5	24.7
399.4	26.0
PCL (20 wt%) + acetone (40 wt%) + CO_2 *(40 wt%)*	
354.6	7.1
359.9	9.2
363.9	10.8
368.0	14.9
378.1	16.5
383.3	18.1
388.6	20.3
393.3	21.3
PCL (5 wt%) + acetone (45 wt%) + CO_2 *(50 wt%)*	
323.1	18.5
328.1	19.8
334.0	20.8
339.5	21.8
344.8	23.8
348.0	24.5
352.5	24.8
359.1	27.8
364.0	28.8
369.6	30.5
375.4	31.8
PCL (10 wt%) + acetone (40 wt%) + CO_2 *(50 wt%)*	
324.0	24.6
328.9	26.0
333.0	27.3
338.4	28.6
342.6	30.0
347.5	31.4
354.1	33.0
356.1	33.3
364.3	35.9
PCL (65k)	
PCL (10 wt%, 65k) + acetone + CO_2 *(40 wt%)*	
323.9	10.8
329.1	11.9
333.6	13.0
338.9	14.3
344.9	15.8
355.4	21.0
359.4	21.3
369.5	23.5
374.3	24.5
378.5	25.0
383.1	26.1
390.5	27.6
399.0	29.8

[a] Note: the L–L phase boundary data for the 5 wt% PCL (Mw = 14k) solution in acetone (55 wt%) + carbon dioxide (40 wt%) mixture had been reported in our earlier publication [20].

the rate of its degradation and the rate of release of the drugs that are contained within the polymer matrix [9].

Various methods are available to process polymers or polymer + drug composites. Processing PCL in supercritical fluids especially in carbon dioxide is a more recent technique that is attracting more and more attention [10–15]. Preparation of controlled release drugs and generation of microcellular foams are among the growing areas [15,16]. However, the solubility of PCL in high-pressure CO_2 is fairly low [17] which limits its potential for a wider range of applications. Addition of a co-solvent is an approach to improve the dissolving power of carbon dioxide and relax some of the limitations. Several publications have already appeared on the phase behavior of PCL in dimethyl ether (DME) + CO_2 and chlorodifluoromethane (HCFC-22) + CO_2 mixtures [18a,b] and also in mixtures of carbon dioxide with dichloromethane or chloroform [19]. Limited solubility information has been reported also in connection with extractability of PCL from PCL + PMMA blends using acetone + CO_2 mixtures [15].

Recently, we reported on the density and viscosity of 5 wt% PCL solutions in acetone or in acetone + CO_2 mixtures containing 1, 2, 4, and 40 wt% carbon dioxide [20]. The density measurements were made in the high-pressure viscometer. We have also reported recently on the volumetric properties and viscosities of acetone + carbon dioxide mixtures and

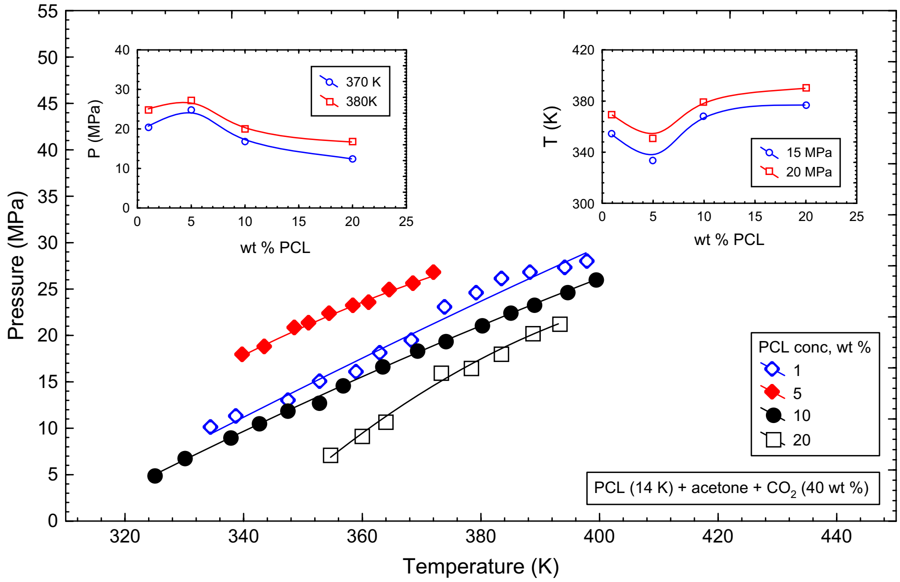

Fig. 1. Demixing pressures for PCL (Mw = 14k) solutions in acetone + CO_2 containing 40 wt% CO_2 at different polymer compositions. The insets are *T*-composition and *P*-composition diagrams generated from the *P*–*T* data at 15 and 20 MPa, and 370 and 380 K, respectively.

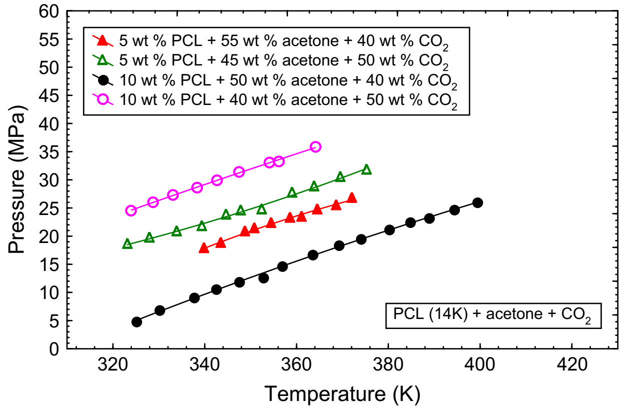

Fig. 2. Demixing pressures for 5 and 10 wt% PCL (Mw = 14k) solutions in acetone + CO_2 containing 40 or 50 wt% CO_2.

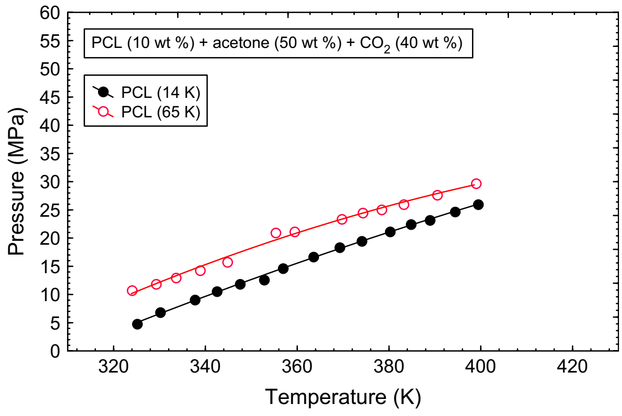

Fig. 3. Demixing pressures for 10 wt% PCL solutions in acetone + CO_2 containing 40 wt% CO_2 for different polymer molecular weights (Mw = 14k and 65k).

demonstrated the consequence of interplay of specific interaction of CO_2 with the C=O group in acetone molecule [21]. In this paper, we report a more complete picture of the phase behavior and volumetric properties for the PCL solutions in acetone + CO_2 mixture at 323, 348, 373, and 398 K and at pressures up to 50 MPa over a wider range of polymer and carbon dioxide concentrations. Specifically, we present data for 1, 5, 10, 20 wt% PCL solutions in acetone + carbon dioxide mixtures containing 5, 10, 20, 40, 50, and 60 wt% carbon dioxide. Volumetric properties of the polymer solutions are analyzed in terms of the isothermal compressibility and isobaric expansivity and compared with the solvent properties. The results are interpreted in terms of the changes in the relative degree of interaction of CO_2 with the C=O group in acetone molecules *versus* C=O groups in the PCL chains. This is the first time that a complete comparison of the compressibility and the

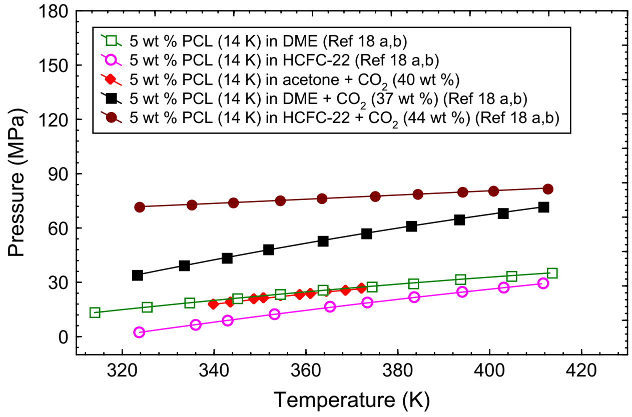

Fig. 4. Variation of demixing pressure with temperature for 5 wt% PCL (Mw = 14k) solutions in DME, HCFC-22, acetone + carbon dioxide (40 wt%), DME + carbon dioxide (37 wt%), and HCFC-22 + carbon dioxide (44 wt%) mixtures. (The data for systems other than acetone + CO_2 are from literature [18].)

Table 2
Density data for 5 wt% PCL (Mw = 14k) solution in acetone at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
323.4	6.9	0.8802
323.5	14.0	0.8893
323.5	20.9	0.8981
323.5	27.8	0.9062
323.5	34.8	0.9140
323.5	41.8	0.9204
323.4	48.5	0.9266
348.9	7.3	0.8495
348.9	14.2	0.8609
348.5	20.9	0.8704
348.8	27.9	0.8799
348.9	34.8	0.8889
348.8	41.7	0.8965
348.8	48.5	0.9039
373.3	7.1	0.8191
373.1	14.1	0.8324
373.1	21.0	0.8444
373.1	27.9	0.8546
373.2	35.1	0.8645
373.2	42.0	0.8735
373.0	48.6	0.8817
398.3	7.5	0.7890
398.3	14.1	0.8020
398.3	21.2	0.8162
398.2	28.0	0.8285
398.4	35.0	0.8397
398.4	41.8	0.8491
398.4	48.6	0.8581

expansivity of a polymer solution is made with its corresponding solvent mixture.

The results show that the mixtures of acetone, which is a good manufacturing practice (GMP) solvent, with carbon dioxide provide new opportunities for processing of poly(ε-caprolactone) at relatively low pressures. Compared with other solvent + carbon dioxide systems such as DME, HCFC-22, acetone + carbon dioxide mixtures as shown in the present paper indeed offer the lowest processing pressures.

2. Experimental

2.1. Materials

Poly(ε-caprolactone) samples were purchased from Scientific Polymer Products (Ontario, NY). The experiments have been conducted with samples with two different molecular weights, one with Mw = 14,300 and PDI = 2.3 and the other with Mw = 65,000 and PDI = 1.8. Acetone (Burdick & Jackson) with purity of 99.5% and CO_2 (Airgas) with a minimum purity of 99.9% were used without further purification.

2.2. Determination of demixing pressures and densities

In the present study the phase boundaries and densities were both determined using a variable-volume view cell following the procedures described in our earlier publications [20]. After the polymer and solvent mixtures with known amounts are loaded in the cell, the pressure and temperature are adjusted to achieve complete miscibility. The phase boundary is then determined by decreasing the pressure at a given temperature while recording the transmitted light intensity, or visually observing the cell content through two sapphire windows. To generate complete phase boundaries in the *P*–*T* domain additional experiments were conducted at different temperatures. The densities of the solutions were calculated from the total mass loaded and the inner volume of the cell at a given *T*/*P* condition.

3. Results and discussion

3.1. Phase behavior

Phase behavior of the PCL + acetone and PCL + acetone + CO_2 mixtures were studied for two different molecular weights in the temperature range from 323 to 398 K and at pressures up to 35 MPa. For the low molecular weight polymer solution, we explored polymer concentrations in the range from 1 to 20 wt%. The carbon dioxide concentrations in the solutions were in the range from 0 to 60 wt%. For the high molecular weight polymer sample we explored miscibility condition only for 10 wt% solutions in acetone (50 wt%) + carbon dioxide (40 wt%) mixtures. In the *P*–*T* range that was studied, both polymers were completely miscible in pure acetone for all compositions tested.

For PCL (Mw = 14k) solutions in acetone + carbon dioxide mixtures, at carbon dioxide levels of 5, 10, 20 wt%, complete miscibility conditions were readily achieved. In the temperature range studied, liquid–liquid (L–L) phase separation was observed only for the mixtures containing 40 and 50 wt% carbon dioxide. In solutions containing 60 wt% carbon dioxide, complete miscibility could not be achieved.

The L–L demixing pressures are presented in Table 1 and in Figs. 1–3. The data show that PCL can be easily dissolved at relatively high concentrations (up to 20 wt%) at modest pressures and temperatures even at high carbon dioxide levels. In these figures, the region above each curve is the homogeneous, one-phase region. The demixing pressures increase with temperature, which is typical of systems that show LCST-type phase behavior. The insets in Fig. 1 show the pressure–composition (*P*–*x*) and temperature–composition (*T*–*x*) diagrams that were generated from constant temperature cuts at 370 and 380 K, and from constant pressure cuts at 15 and 20 MPa, respectively, from the *P*–*T* data. Increasing the temperature shifts the demixing pressures to higher values. Increasing the pressure shifts the demixing temperatures to higher values. It should be noted that in the *P*–*x* diagrams, the region above each curve corresponds to the homogeneous one-phase regions, while in the *T*–*x* diagrams, homogeneous regions are the regions below each curve.

Fig. 2 displays the effect of carbon dioxide concentration on the demixing pressure for 5 and 10 wt% polymer solutions in mixtures with 40 and 50 wt% carbon dioxide. As the carbon

Table 3
Density data for the 5 wt% PCL (Mw = 14k) solutions in acetone + CO_2 mixtures containing 5, 10, 20 wt% CO_2 at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)	Temperature (K)	Pressure (MPa)	Density (g/cm^3)	Temperature (K)	Pressure (MPa)	Density (g/cm^3)
PCL (5 wt%, 14k) + acetone (90 wt%) + CO_2 (5 wt%)			*PCL (5 wt%, 14k) + acetone (85 wt%) + CO_2 (10 wt%)*			*PCL (5 wt%, 14k) + acetone (75 wt%) + CO_2 (20 wt%)*		
325.0	7.2	0.8929	324.2	7.2	0.8969	322.8	7.2	0.9254
325.0	14.0	0.9023	324.1	14.3	0.9076	322.8	14.2	0.9315
324.8	21.0	0.9113	324.2	21.2	0.9170	322.8	21.0	0.9377
324.8	27.8	0.9188	324.2	27.9	0.9261	322.7	28.0	0.9420
324.7	34.8	0.9243	324.2	34.8	0.9337	322.8	34.9	0.9438
324.7	41.7	0.9379	324.3	41.7	0.9410	322.8	41.8	0.9520
324.7	48.5	0.9379	324.3	48.6	0.9485	322.7	48.7	0.9649
348.2	7.6	0.8586	348.6	7.1	0.8651	348.5	7.4	0.8923
348.2	14.1	0.8694	348.6	14.3	0.8781	348.5	14.2	0.9020
348.2	21.0	0.8790	348.5	21.2	0.8894	348.4	21.1	0.9144
348.2	27.8	0.8878	348.6	28.3	0.9009	348.4	28.1	0.9247
348.1	34.8	0.8961	348.6	34.8	0.9080	348.3	34.9	0.9337
348.1	41.9	0.9040	348.7	41.9	0.9169	348.5	42.1	0.9418
348.1	48.7	0.9109	348.8	48.6	0.9249	348.6	48.7	0.9494
373.4	7.2	0.8252	372.9	7.0	0.8317	373.9	7.3	0.8486
373.3	14.1	0.8389	372.7	14.6	0.8476	373.8	14.4	0.8642
373.3	21.0	0.8502	372.7	21.3	0.8611	373.8	21.1	0.8784
373.2	28.0	0.8616	372.8	28.1	0.8728	373.8	28.0	0.8921
373.2	34.8	0.8709	372.8	34.9	0.8831	373.8	35.0	0.9034
373.2	41.8	0.8796	372.8	41.9	0.8930	373.8	41.8	0.9139
373.2	48.5	0.8877	372.8	48.8	0.9020	373.7	48.8	0.9235
398.7	7.4	0.7906	399.3	7.3	0.7927	398.3	7.0	0.8036
398.7	14.4	0.8075	399.5	14.4	0.8114	398.4	14.1	0.8265
398.8	21.3	0.8217	399.4	21.3	0.8275	398.4	21.2	0.8453
398.8	28.1	0.8332	399.5	28.2	0.8417	398.5	28.1	0.8608
398.7	35.2	0.8452	399.5	35.1	0.8535	398.5	35.1	0.8744
398.7	41.7	0.8546	399.3	41.8	0.8646	398.6	41.9	0.8860
398.6	48.6	0.8636	399.2	48.7	0.8760	398.7	48.8	0.8974

dioxide content is increased, the demixing pressure increases. The shift in pressure with increased carbon dioxide content for 5 wt% solution is only about 5 MPa, however, for the 10 wt% solution the shift is much greater with an increase of 25 MPa in the demixing pressures.

Fig. 3 compares the results for the different molecular weight (14k and 65k) samples. The demixing pressures are shown for 10 wt% PCL solution containing 40 wt% carbon dioxide. The 65k sample requires about 5 MPa higher pressures to achieve complete dissolution.

There have been two recent publications from other laboratories in which phase boundaries have been reported for PCL in other solvent mixtures [18,19]. One of these studies reports data for PCL with molecular weight of 14,000 (which is the same as the molecular weight of one of the samples used in the present study) in dimethyl ether (DME) and chlorodifluoromethane and their mixtures with carbon dioxide [18a,b]. For the 5 wt% polymer solutions we could compare the data for the pure solvents and for the fluid mixtures containing about 40 wt% carbon dioxide. The results are shown in Fig. 4. The figure demonstrates the effectiveness of acetone + carbon dioxide mixtures as a solvent for PCL. Miscibility is achieved at much lower pressures compared to the other solvent mixtures. While in pure DME and HCFC-22, a pressure of 10–15 MPa is required to achieve miscibility, in pure acetone PCL is completely miscible at all pressures. While in DME + carbon dioxide mixtures complete miscibility requires 30–60 MPa and in HCFC-22, a pressure of 70–110 MPa is needed, in acetone + carbon dioxide mixtures complete miscibility is achieved at much lower pressures at around 15 MPa. The effectiveness of acetone + CO_2 mixtures as a tunable solvent for PCL offers new possibilities for processing of PCL from low, moderate or relatively high concentrations at modest pressures, providing an alternative path for formation of particles, fibers, porous materials, membranes or blends. We will be reporting on blend formation in a future article.

3.2. Volumetric properties: density

Densities of PCL + acetone and PCL + acetone + carbon dioxide mixtures have been determined at 323, 348, 373, and 398 K at a pressure of up to 50 MPa. They are presented in Tables 2–9.

Figs. 5 and 6 represent the variation of density for one of these solutions [5 wt% polymer solution of PCL (Mw = 14k) in acetone (85 wt%) + CO_2 (10 wt%)] (see Table 3) as a function of pressure and temperature. The smooth variations are typical of the behavior of solutions in homogeneous one-phase regions. Fig. 7 is a similar diagram for a solution with higher

Table 4
Density data for the 1 wt% PCL (Mw = 14k) solutions in acetone (59 wt%) + CO_2 (40 wt%) mixture at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
323.1	7.4	0.8959
323.1	14.4	0.9154
323.2	21.1	0.9311
323.2	28.1	0.9445
323.2	34.8	0.9505
323.2	41.7	0.9509
323.2	48.8	0.9513
348.1	7.3	0.7312
348.1	13.9	0.8597
348.1	21.2	0.8865
348.1	28.3	0.9050
348.2	35.1	0.9206
348.2	42.0	0.9352
348.1	48.9	0.9468
373.8	8.8	0.7779
373.8	14.1	0.8084
374.0	21.3	0.8376
373.9	28.2	0.8605
373.9	34.8	0.8801
373.9	41.9	0.8974
374.0	48.7	0.9127
398.2	8.3	0.5673
398.5	13.9	0.7279
398.5	21.0	0.7836
398.5	28.1	0.8172
398.5	35.0	0.8406
398.6	42.1	0.8613
398.6	48.8	0.8796

Table 5
Density data for the 5 wt% PCL (Mw = 14k) solutions in acetone (55 wt%) + CO_2 (40 wt%) mixture at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
323.0	7.2	0.9203
323.2	14.1	0.9383
323.1	21.1	0.9555
323.0	28.1	0.9705
322.8	34.8	0.9838
322.7	42.3	0.9963
322.7	48.7	1.0046
348.0	7.0	0.8276
348.1	14.2	0.8600
347.8	21.0	0.9062
347.8	28.1	0.9248
347.7	35.1	0.9412
347.8	41.8	0.9556
347.7	48.8	0.9685
372.0	7.5	0.7059
372.5	14.6	0.8018
372.4	21.0	0.8495
372.5	28.0	0.8780
372.3	35.3	0.9009
372.4	41.9	0.9180
372.5	47.6	0.9334
399.2	8.7	0.5713
398.8	14.3	0.7369
398.5	21.1	0.7963
398.2	27.8	0.8304
398.1	35.2	0.8564
397.9	42.1	0.8772
398.2	49.4	0.8958

CO_2 content [10 wt% polymer solution of PCL (Mw = 65k) in acetone (50 wt%) + CO_2 (40 wt%)] (see Table 9) which shows the variation of density in both the homogeneous and the phase-separated regions. The figure includes the liquid–liquid phase separation points (shown with "+" symbol) that were determined from the phase boundary measurements (Fig. 3). In Fig. 7, along a given isotherm, the pressures to the left of the phase separation points correspond to the non-homogeneous phase-separated region, and pressures to the right correspond to the homogeneous regions. It is interesting to note that as the L–L phase boundary is crossed density does not display an immediate discontinuity or a sharp change. In this figure, along the 348 K isotherm, we have also included the density data that were obtained at small pressure intervals at lower pressures. Even though, at pressures near the L–L phase separation point the density changes were smooth and continuous, at lower pressures at around 10 MPa, the density shows a sharp variation with a small change in pressure. This is indicative of the formation of a vapor phase. The L–L–V phase boundary which typically occurs at lower pressures than that for the L–L phase boundary has been reported in the literature for some other binary mixtures of biodegradable polymers such as poly(L-lactide) (L-PLA), poly(D,L-lactide) (D,L-PLA), or poly(D,L-lactide-*co*-glycolide) (D,L-PLG) in chlorodifluoromethane (HCFC-22) [22], and recently for poly(ε-caprolactone) in carbon dioxide + dichloromethane or chloroform solutions for a sample with Mw = 122,400 [19] as well.

3.2.1. Influence of polymer concentration on density

Fig. 8 displays the variation of density with pressure for three different concentrations of PCL (Mw = 14k) in acetone + CO_2 (40 wt%) mixtures at 373 K (see Tables 5, 7 and 8). The density shows a significant increase with increasing polymer concentration. Such a large change in density with polymer concentration was not observed in the poly(methyl methacrylate) (PMMA) solutions in mixtures of acetone and CO_2 [23]. The larger change in the density with increasing PCL concentration may arise from an increase in interaction of CO_2 with PCL which is discussed later in the paper in connection with compressibilities.

3.2.2. Influence of CO_2 concentration on density

Effect of CO_2 concentration is illustrated in Fig. 9 for a 5 wt% PCL (Mw = 14k) solution containing 0, 5, 10, 20, 40, 50, 60 wt% CO_2 at 348 K (see Tables 2, 3, 5 and 6). For all mixtures, densities increase with pressures as expected. At low carbon dioxide concentrations (lower than 20 wt%), the mixture densities always increase with CO_2 concentration. At high carbon dioxide concentrations (greater than 20 wt%), the densities at pressures below 25 MPa decrease with increasing CO_2 content from 40–50 to 60 wt%, while at pressures greater 25 MPa the densities increase with increasing CO_2 content. This density crossover arises from the density of carbon dioxide being lower than that of acetone at low

Table 6
Density data for the 5 wt% PCL (Mw = 14k) solutions in acetone + CO$_2$ mixture containing 50 and 60 wt% CO$_2$ at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)	Temperature (K)	Pressure (MPa)	Density (g/cm^3)
PCL (5 wt%, 14k) + acetone (45 wt%) + CO$_2$ (50 wt%)			*PCL (5 wt%, 14k) + acetone (35 wt%) + CO$_2$ (60 wt%)*		
323.0	7.5	0.8365	323.8	7.3	0.8777
322.9	14.1	0.9372	323.7	14.3	0.9347
322.7	21.4	0.9578	323.8	21.3	0.9587
322.5	27.8	0.9745	323.9	28.1	0.9861
322.7	34.7	0.9895	323.8	35.0	1.0035
322.9	41.8	1.0041	323.9	41.9	1.0177
323.0	48.8	1.0157	323.8	48.9	1.0352
348.8	7.6	0.6692	347.9	8.4	0.6493
348.8	13.9	0.8168	347.8	13.8	0.7506
348.9	21.2	0.8976	347.5	20.9	0.8952
349.0	28.0	0.9210	347.4	27.9	0.9268
348.9	34.8	0.9402	347.5	34.7	0.9520
348.8	41.7	0.9565	347.5	41.8	0.9743
348.7	48.5	0.9720	347.5	48.6	0.9925
373.6	8.5	0.7591	372.6	10.5	0.5899
373.8	14.6	0.8126	372.6	14.4	0.7455
373.8	21.2	0.8471	372.7	21.5	0.8287
373.9	28.0	0.8746	372.9	28.2	0.8716
374.0	35.1	0.8971	372.9	35.1	0.9044
374.1	42.1	0.9166	372.9	41.8	0.9290
374.4	48.9	0.9329	373.0	48.7	0.9493
398.6	9.7	0.6158			
399.2	14.5	0.7356	398.1	13.9	0.5904
398.9	21.2	0.7863	398.8	21.7	0.7445
398.9	28.1	0.8233	399.0	28.3	0.8055
398.9	35.1	0.8510	398.9	35.1	0.8481
399.1	41.8	0.8736	398.7	41.9	0.8811
398.7	48.7	0.8925	398.7	48.8	0.9075

Table 7
Density data for the 10 wt% PCL (Mw = 14k) solutions in acetone (50 wt%) + CO$_2$ (40 wt%) mixture at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
323.5	7.6	1.0080
323.5	14.0	1.0306
323.8	20.9	1.0457
323.8	27.8	1.0635
323.6	34.7	1.0796
323.5	41.6	1.0866
323.5	48.8	1.0866
348.0	7.2	0.8521
348.4	14.7	0.9716
348.6	20.8	0.9932
348.6	27.8	1.0139
348.7	34.9	1.0340
348.6	42.0	1.0528
348.6	48.9	1.0689
372.8	7.3	0.8128
373.3	14.2	0.9076
373.4	21.1	0.9422
373.5	28.5	0.9700
373.7	35.1	0.9871
374.1	42.1	1.0046
373.3	48.8	1.0208
397.8	8.5	0.7017
398.1	14.4	0.8292
398.0	20.7	0.8849
397.8	27.6	0.9190
398.1	35.1	0.9464
398.0	41.8	0.9648
398.1	49.0	0.9819

pressures, but becoming higher at high pressures. The density crossover is a common observation for mixtures of carbon dioxide and an organic solvent [24]. Fig. 9 indicates a greater sensitivity of density to pressure especially for pressures less than 30 MPa for mixtures with high carbon dioxide contents.

3.2.3. *Influence of polymer molecular weight on density*

Densities of 10 wt% PCL solutions with Mw = 14k and 65k were also compared at a given temperature. Even though not shown graphically, the densities were of similar magnitude but the lower molecular weight polymer solutions displayed consistently higher densities than solutions of higher molecular weight polymer samples (see Tables 7 and 9).

3.3. *Isothermal compressibility and isobaric expansivity: polymer solutions versus solvent mixtures*

The isothermal compressibility (k_T) and isobaric expansivity (β) which are defined by the following equations

$$k_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T \tag{1}$$

$$\beta = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p \tag{2}$$

are important thermodynamic parameters of a given system that are extremely valuable in the development of models. To our knowledge no prior work has been reported in which systematic comparisons of the compressibility and expansivity of polymer solutions and their corresponding solvent mixtures have been presented. With the extensive density data that we have generated, we have made such comparisons and the results are presented below for two solutions with different CO$_2$ contents. In calculations of the values of isothermal compressibility, the density–pressure data at a given temperature were fitted by a function of the form given in Eq. (3):

$$\rho = ap^2 + bp + c + d/p \tag{3}$$

where ρ and p are density and pressure. a, b, c, and d are parameters, which are determined from the optimal fitting. The $(\partial\rho/\partial p)_T$ was calculated from this function and thus the values of the isothermal compressibility were obtained. Isobaric expansivities were calculated following a similar procedure, by fitting the density–temperature data to a function similar to Eq. (3) but expressed in terms of T.

Table 8
Density data for the 20 wt% PCL (Mw = 14k) solutions in acetone (40 wt%) + CO_2 (40 wt%) mixture at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
323.0	7.0	1.1453
322.9	14.3	1.1679
322.8	21.1	1.1857
322.9	28.0	1.2038
322.9	34.9	1.2227
322.9	41.7	1.2357
322.8	48.3	1.2488
349.3	7.5	0.9851
349.2	13.9	1.0893
349.2	21.1	1.1204
349.3	28.1	1.1453
349.1	34.9	1.1651
349.1	41.8	1.1835
349.1	48.8	1.1993
373.2	7.2	0.9776
373.2	14.2	1.0328
373.2	21.3	1.0668
373.3	27.9	1.0914
373.3	34.9	1.1146
373.2	41.7	1.1356
373.2	48.5	1.1536
397.9	8.0	0.7219
398.3	14.4	0.9443
398.3	21.1	0.9978
398.4	28.2	1.0335
398.5	34.9	1.0607
398.5	41.9	1.0930
398.4	48.6	1.1137

3.3.1. Solutions containing 10 wt% CO_2

Figs. 10 and 11 show the isothermal compressibility and isobaric expansivity for a 5 wt% polymer (14k) solution, and its corresponding polymer-free mixture solvent containing ~90 wt% acetone and ~10 wt% carbon dioxide. The data for the solvent mixture were generated from the density data for acetone + CO_2 mixtures presented in our previous study [21]. As shown in Fig. 10, both the polymer solution and the solvent display a decrease in isothermal compressibility with pressure and an increase with temperature as would be expected, even though the dependence on pressure is weak. At 398 K the polymer solution surprisingly displays compressibilities higher than those of the solvent. At lower temperatures the compressibilities for the solution are smaller than those for the solvent. At 373 K, they display comparable isothermal compressibilities. These trends in compressibility are intriguing since one would not have *a priori* expected an increase in compressibility upon addition of polymer molecules to a solvent. The observed trends can, however, be rationalized in terms of changes in the specific interactions in the system. The specific interactions between carbon atom in carbon dioxide and carbonyl group in acetone or in PCL have been predicted from *ab initio* calculations [25,26] and confirmed with spectroscopic measurements [27,28]. These interactions lead to associations between carbon dioxide and acetone or PCL molecules, which have been discussed in detail in our previous publication [21]. The present observation on lowered

Table 9
Density data for the 10 wt% PCL (Mw = 65k) solutions in acetone (50 wt%) + CO_2 (40 wt%) mixture at high pressures

Temperature (K)	Pressure (MPa)	Density (g/cm^3)
PCL (10 wt%, 65k) + acetone (50 wt%) + CO_2 (40 wt%)		
322.5	6.9	0.9833
322.7	14.1	0.9991
322.9	21.2	1.0085
323.1	28.0	1.0113
323.3	35.0	1.0118
323.3	41.8	1.0119
323.3	48.8	1.0121
349.1	4.6	0.6119
349.1	4.9	0.6439
349.1	5.0	0.6591
349.0	4.9	0.6764
348.6	4.8	0.6950
348.6	5.0	0.7126
348.5	5.0	0.7339
348.5	5.2	0.7562
348.6	5.3	0.7819
348.9	5.4	0.8077
348.9	6.2	0.8436
349.1	6.8	0.8836
349.1	8.5	0.9142
349.1	11.7	0.9447
349.2	14.8	0.9617
349.2	21.0	0.9816
349.1	27.9	1.0006
349.0	34.8	1.0066
349.1	41.9	1.0090
349.3	48.6	1.0110
374.8	6.9	0.8115
374.8	14.1	0.8982
374.8	21.1	0.9266
374.5	27.9	0.9498
374.5	34.8	0.9698
374.2	41.7	0.9864
374.4	48.8	1.0007
398.9	7.9	0.6958
399.2	14.4	0.8112
399.0	21.0	0.8760
398.5	27.8	0.9049
398.5	35.0	0.9266
398.8	42.0	0.9464
398.7	48.5	0.9641

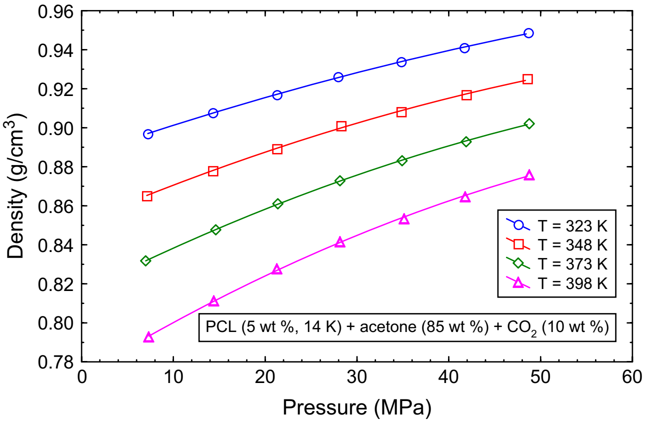

Fig. 5. Variation of density with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + 10 wt% CO_2 at 323, 348, 373, and 398 K.

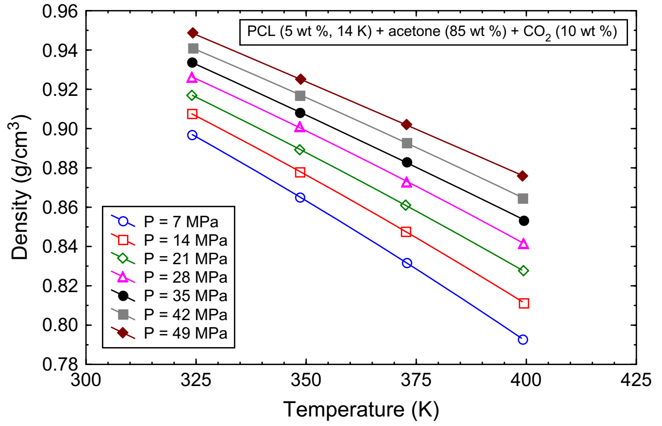

Fig. 6. Variation of density with temperature for 5 wt% PCL (Mw = 14k) solution in acetone + 10 wt% carbon dioxide at 7, 14, 21, 28, 35, 42, and 49 MPa.

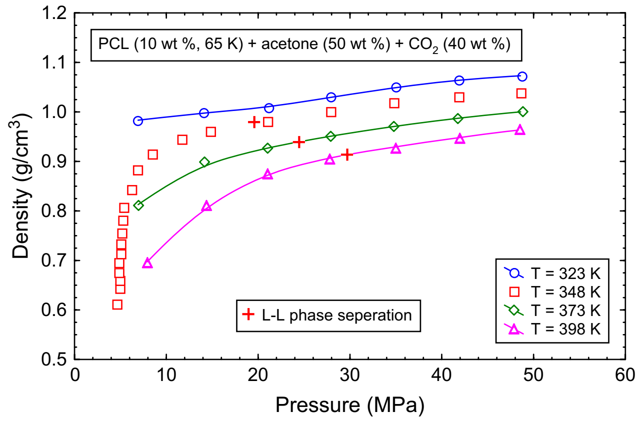

Fig. 7. Variation of density with pressure for 10 wt% PCL (Mw = 65k) solution in acetone + 40 wt% carbon dioxide at 323, 348, 373, and 398 K. (The liquid–liquid phase separation points are shown with symbol "+").

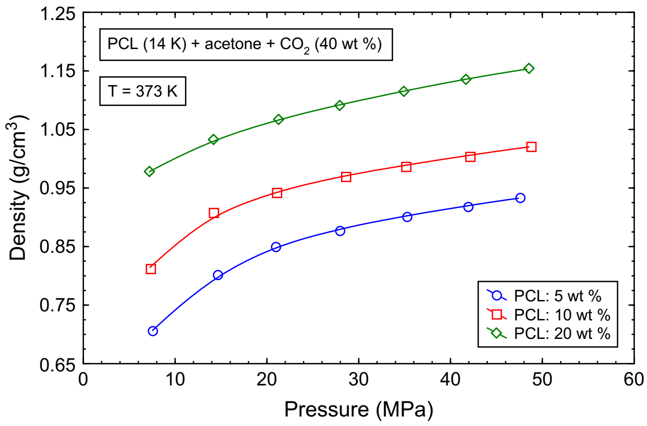

Fig. 8. Variation of density with pressure for mixtures of PCL (Mw = 14k) + acetone + CO$_2$ (40 wt%) containing 5, 10, and 20 wt% PCL at 373 K.

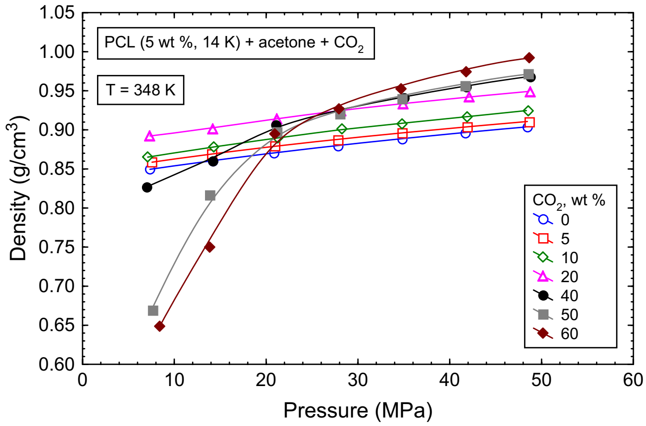

Fig. 9. Variation of density with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixtures containing 0, 5, 10, 20, 40, 50, 60 wt% CO$_2$ at 348 K.

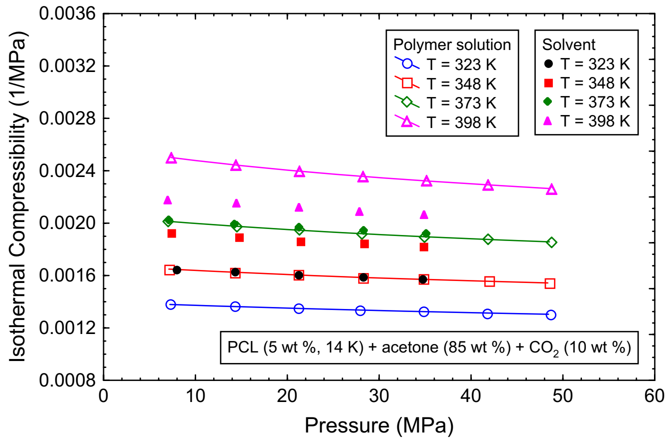

Fig. 10. Variation of isothermal compressibility with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 10 wt% CO$_2$ and the polymer-free solvent mixture acetone + carbon dioxide (~10 wt%) at 323, 348, 373, and 398 K.

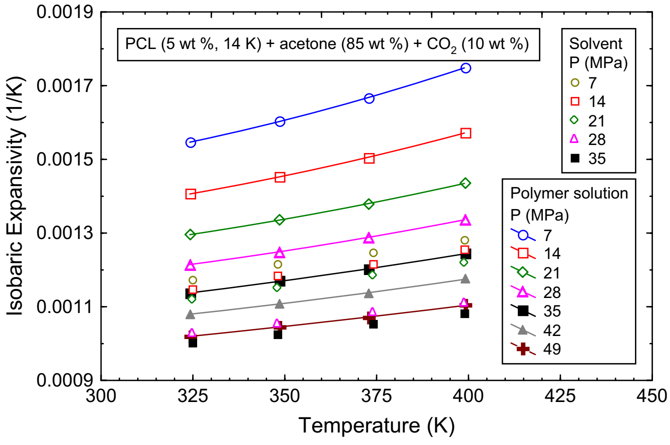

Fig. 11. Variation of isobaric expansivity with temperature for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 10 wt% CO$_2$ at 7, 14, 21, 28, 35, 42, and 49 MPa and the polymer-free solvent mixture acetone + carbon dioxide (~10 wt%) at 7, 14, 21, 28, 35 MPa.

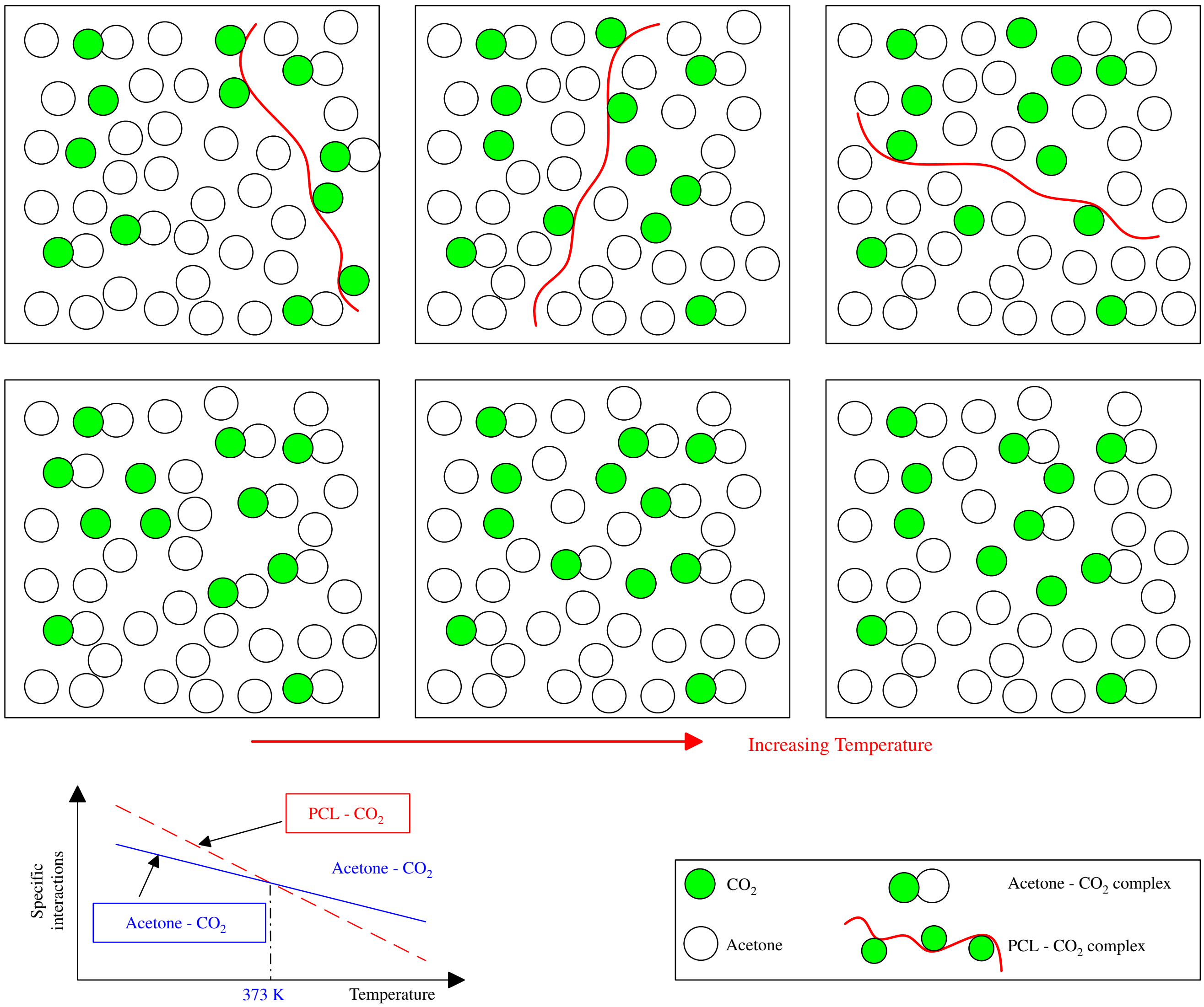

Fig. 12. Schematic diagrams for intermolecular interactions in the PCL solutions (top row) and acetone + carbon dioxide solvent mixture (second row) at different temperatures. Acetone–CO_2 interactions are stronger than PCL–CO_2 interactions at lower temperatures which undergo a reversal at a crossover temperature at around 373 K.

compressibility can be rationalized if one were to recognize that the interactions between CO_2 and acetone or CO_2 and PCL are favored at low temperatures, but weakened at low pressures. The results shown in Fig. 10 would suggest that the PCL–CO_2 interactions are stronger than acetone–CO_2 interactions at the lower temperatures and acetone–CO_2 interactions are stronger at the higher temperatures, and that these two interactions are almost identical at 373 K.

Fig. 12 is a cartoon illustrating the changes in the intermolecular interactions for the PCL solution in acetone + carbon dioxide mixtures (top figures) and in the solvent mixture itself (lower figures) at different temperatures. Carbon dioxide and acetone molecules are shown as circles, acetone molecules being the larger circles. Association between CO_2 and acetone is depicted as overlapping circles. Association of CO_2 with PCL is illustrated as CO_2 circles attached to the polymer chain backbone. In each row, temperature increases along the direction of the arrow from left to right. As illustrated in the figure, in the polymer solution or in the solvent mixture, both PCL–CO_2 and acetone–CO_2 associations are decreased as the temperature is increased, which release the "bound" CO_2 to produce "free" carbon dioxide. This increase in "free" carbon dioxide in the mixture results in an increase in the isothermal compressibility. At lower temperatures, the interaction of PCL with carbon dioxide becomes stronger than that for acetone–carbon dioxide interactions, resulting in more "bound" carbon dioxide molecules and thus reducing its compressibility compared to that of the solvent. At higher temperatures, the stronger acetone–carbon dioxide interaction results in more "free" CO_2 molecules and thus higher compressibilities for the polymer solution. At 373 K, these interactions appear to become comparable, leading to comparable compressibilities.

Fig. 12 includes also a schematic representation of the variation of the interactions of PCL–carbon dioxide and acetone–carbon dioxide with temperature illustrating the crossover at 373 K. In this figure, the PCL–CO_2 interactions

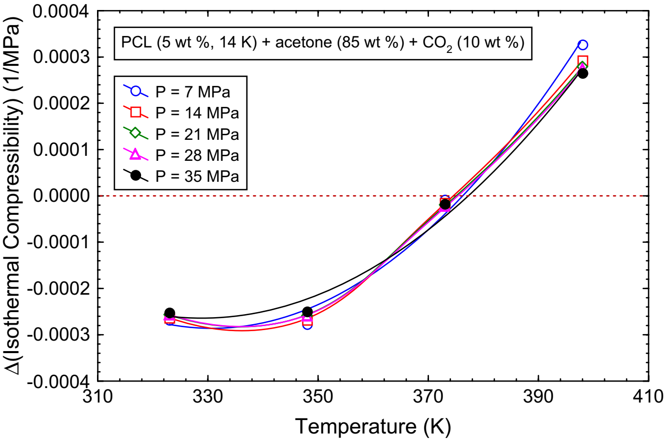

Fig. 13. Variation of isothermal compressibility difference between 5 wt% PCL (Mw = 14k) solution in acetone + 10 wt% carbon dioxide and the polymer-free solvent mixture acetone + carbon dioxide (∼10 wt%) with temperature at 7, 14, 21, 28, and 35 MPa.

are specifically shown as more sensitive to temperature. This can also be deduced from Fig. 11 which shows that the isobaric expansivities show an increase with temperature and a decrease with pressure for both the polymer solution and the solvent. However, the polymer solution displays higher expansivities than those of the corresponding solvent at the same pressure, suggesting that the PCL–CO_2 interaction is indeed more sensitive to temperature than acetone–CO_2 interaction. The crossover in compressibility is further demonstrated in Fig. 13 which shows the variation in the difference in compressibility of the solution and the solvent with temperature at different pressures. At all pressures, the difference increases from negative to positive values with an inversion temperature at around 373 K. The pressure in the range studied appears to have no major influence.

Fig. 14 demonstrates the variation of the difference in isobaric expansivity between the solution and the solvent with pressure at different temperatures. At all temperatures, the polymer solutions display higher isobaric expansivities than the solvent. The difference decreases with pressure and appears to reach a plateau value at about 25 MPa and remains unchanged for higher pressures.

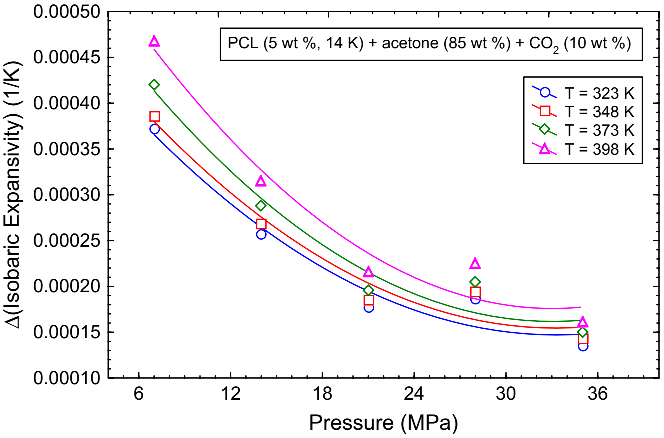

Fig. 14. Variation of isobaric expansivity difference between 5 wt% PCL (Mw = 14k) solution in acetone + 10 wt% carbon dioxide mixture and the polymer-free solvent mixture acetone + carbon dioxide (∼10 wt%) with pressure at 323, 348, 373, and 398 K.

3.3.2. Solutions containing 40 wt% CO_2: isothermal compressibility

Fig. 15 shows the variation of the isothermal compressibility with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% carbon dioxide and the corresponding polymer-free mixture solvent containing ∼42% CO_2. The inset is an enlargement of the low compressibility region which also shows the *P*/*T* conditions leading to L–L phase separation in the mixture. Data to the left of these phase-separated points (illustrated with "+" symbol) correspond to homogeneous single-phase conditions. Unlike the results shown in Fig. 10 for mixtures containing 10 wt% CO_2, the compressibility for these solutions shows a stronger dependence on pressure. The polymer solution now displays a higher compressibility than the solvent at low pressures, while the solvent shows higher compressibility at high pressures, leading to a switchover in the compressibility between the polymer solution and the solvent. This switchover is not due to phase separation as the phenomenon is observed in the homogeneous one-phase region for the system. It is simply a consequence of the high concentration of carbon dioxide in this polymer solution. It should be pointed out that the compressibility switchover suggests stronger acetone–CO_2 interactions at low pressures and stronger PCL–CO_2 interactions at high pressures. A more direct comparison of the results for the 10 and 40 wt% CO_2 cases is presented in Fig. 16 which shows that increasing CO_2 content results in an increase in the compressibility.

Fig. 17 compares the compressibility for 5 and 10 wt% polymer solutions. No significant differences are observed. Fig. 18 shows the compressibilities for 10 wt% PCL solutions for Mw = 14k and 65k samples. The effect of the molecular weight is negligible in this molecular weight range.

3.3.3. Solutions containing 40 wt% CO_2: isobaric expansivity

Fig. 19 shows the variation of isobaric expansivity with temperature at different pressures for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% carbon dioxide and its corresponding solvent. Comparison with Fig. 11 shows that even though the carbon dioxide concentration is increased from 10 to 40 wt%, the polymer solution still displays higher expansivities than the solvent. Fig. 20 provides a more direct comparison for these solutions and shows that the increasing CO_2 concentration leads to an increase in the expansivity.

Fig. 21 shows the variation of isobaric expansivity with temperature for the 5 and 10 wt% polymer solutions for the 14k sample. The expansivity of polymer solutions with higher polymer concentration appears to be lower. The difference becomes smaller at higher pressures. Fig. 22 shows the expansivities are similar for solutions with different molecular weight

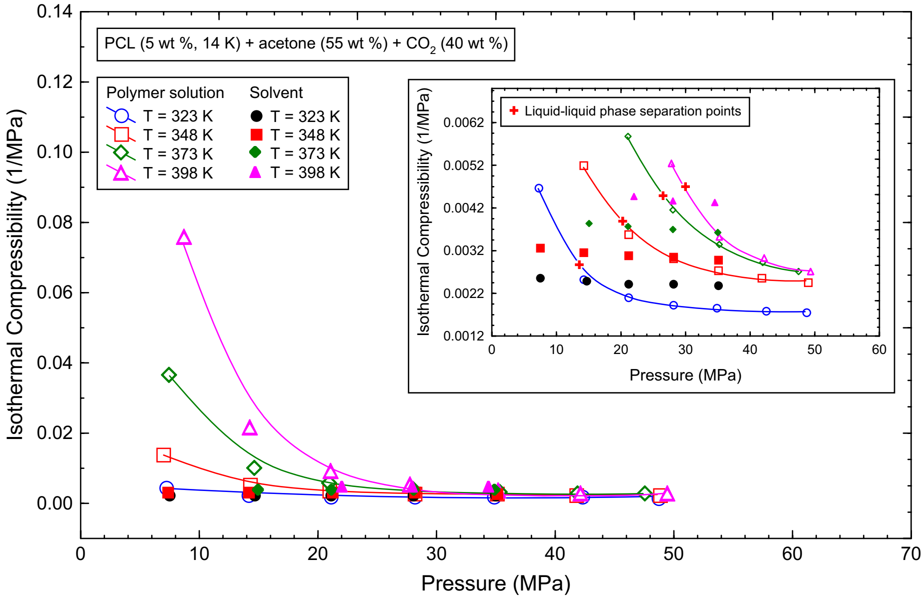

Fig. 15. Variation of isothermal compressibility with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ and the polymer-free solvent mixture acetone + carbon dioxide (~42 wt%) at 323, 348, 373, and 398 K.

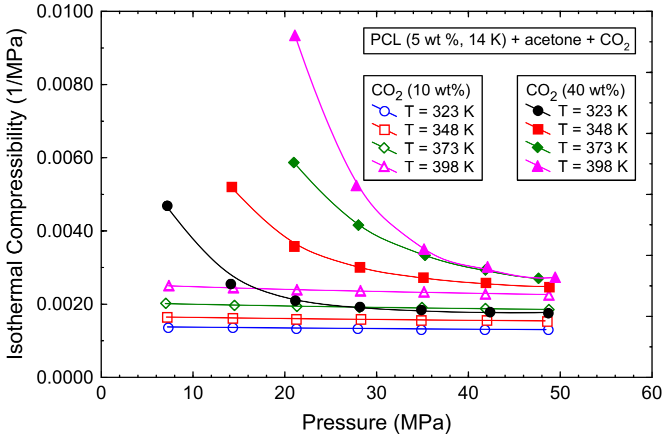

Fig. 16. Variation of isothermal compressibility with pressure for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 10 and 40 wt% CO$_2$ at 323, 348, 373, and 398 K.

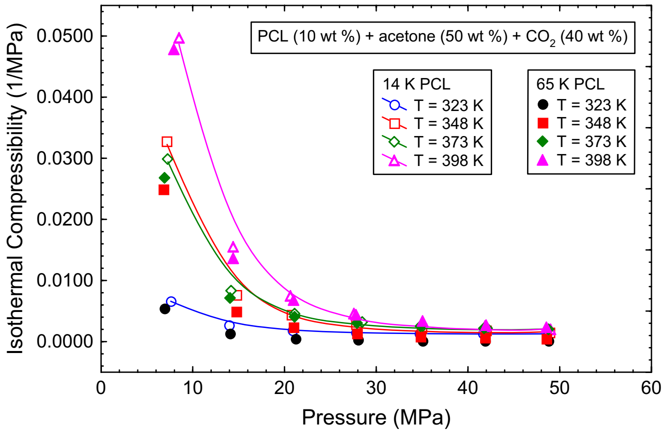

Fig. 18. Variation of isothermal compressibility with pressure for 10 wt% PCL solutions in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ with two different molecular weights of 14k and 65k at 323, 348, 373, and 398 K.

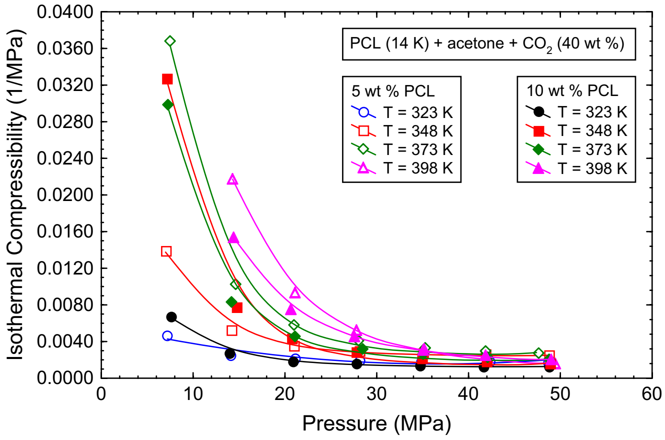

Fig. 17. Variation of isothermal compressibility with pressure for 5 and 10 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ at 323, 348, 373, and 398 K.

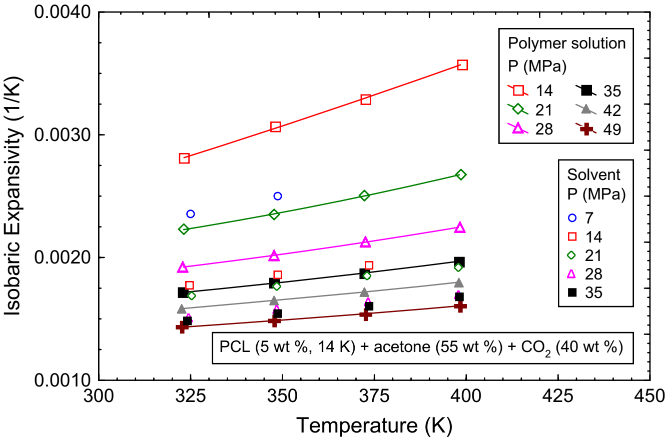

Fig. 19. Variation of isobaric expansivity with temperature for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ at 14, 21, 28, 35, 42, and 49 MPa and for the polymer-free solvent acetone + carbon dioxide (42 wt%) at 7, 14, 21, 28, and 35 MPa.

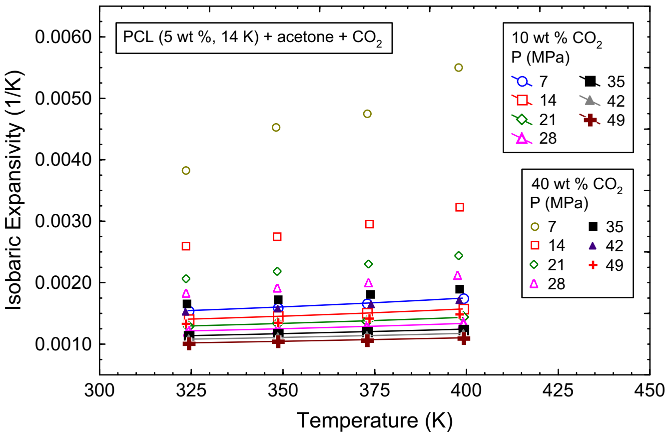

Fig. 20. Variation of isobaric expansivity with temperature for 5 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 10 and 40 wt% CO$_2$ at 7, 14, 21, 28, 35, 42, and 49 MPa.

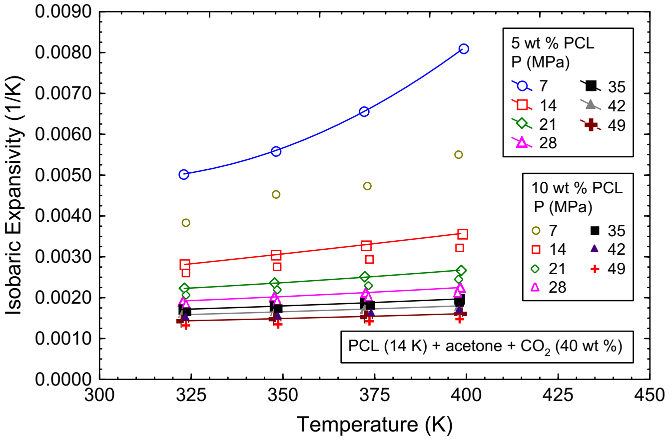

Fig. 21. Variation of isobaric expansivity with temperature for 5 and 10 wt% PCL (Mw = 14k) solution in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ at 7, 14, 21, 28, 35, 42, and 49 MPa.

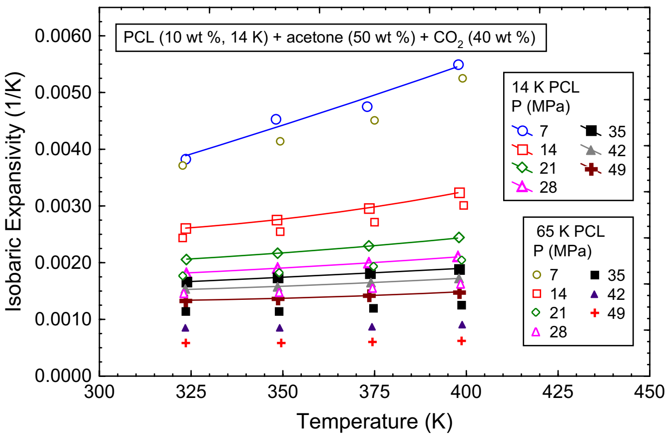

Fig. 22. Variation of isobaric expansivity with temperature for 10 wt% PCL solutions in acetone + carbon dioxide mixture containing 40 wt% CO$_2$ with two different molecular weights of 14k and 65k at 7, 14, 21, 28, 35, 42, and 49 MPa.

polymer samples with values being slightly lower for the higher molecular weight systems.

4. Conclusions

The present study has shown that mixtures of acetone + carbon dioxide are effective solvents for poly(ε-caprolactone). Complete miscibility for 1–20 wt% PCL solutions could be achieved in the fluid mixtures containing up to 50 wt% carbon dioxide at modest pressures (5–40 MPa), which are much lower than other organic solvent + carbon dioxide mixture solvents reported in the literature.

The mixture densities show higher sensitivity to pressure as the carbon dioxide content is increased. An increase in polymer concentration results in a significant increase in the mixture density, while the effect of polymer molecular weight is negligible. The isothermal compressibilities of the solutions become higher than that of the corresponding solvent with increasing temperature suggesting that the PCL–CO$_2$ interactions are weaker than acetone–CO$_2$ interactions at high temperatures. The polymer solutions were observed to always show higher expansivity than those of their solvents. The increase in carbon dioxide concentration leads to higher compressibility and expansivity while an increase in polymer concentration results in no apparent change in compressibility and lower expansivity. The polymer molecular weight shows negligible effects on both compressibility and expansivity.

References

[1] Shabana HM, Olley RH, Bassett DC, Jungnickel BJ. Polymer 2000;41:5513–23.
[2] Sarazin P, Favis BD. Polymer 2005;46:5966–78.
[3] Xie JW, Marijnissen JCM, Wang CH. Biomaterials 2006;27:3321–32.
[4] Wu BM, Borland SW, Giordano RA, Cima LG, Sachs EM, Cima MJ. Journal of Controlled Release 1996;40:77–87.
[5] Lin WJ, Yu CC. Journal of Microencapsulation 2001;18:585–92.
[6] Reignier J, Huneault MA. Polymer 2006;47:4703–17.
[7] Sarkar S, Lee GY, Wong JY, Desai TA. Biomaterials 2006;27:4775–82.
[8] Peroglio M, Gremillard L, Chevalier J, Chazeau L, Gauthier C, Hamaide T. Journal of the European Ceramic Society 2007;27:2679–85.
[9] Vandamme ThF, Ngombo Mukendi JF. International Journal of Pharmaceutics 1996;145:77–86.
[10] Busby AJ, Zhang JX, Roberts CJ, Lester E, Howdle SM. Advanced Materials (Weinheim, Germany) 1995;17:364–7.
[11] Cotugno S, Di Maio E, Mensitieri G, Iannace S, Roberts GW, Carbonell RG, et al. Industrial and Engineering Chemistry Research 2005;44:1795–803.
[12] Elvira C, Fanovich A, Fernandez M, Fraile J, San Roman J, Domingo C. Journal of Controlled Release 2004;99:231–40.
[13] Vega-Gonzalez A, Domingo C, Elvira C, Subra P. Journal of Applied Polymer Science 2004;91:2422–6.
[14] Reverchon E, Della Porta G, De Rosa I, Subra P, Letourneur D. Journal of Supercritical Fluids 2000;18:239–45.
[15] Domingo C, Vega A, Fanovich MA, Elvira C, Subra P. Journal of Applied Polymer Science 2003;90:3652–9.
[16] Xu Q, Ren X, Chang Y, Wang J, Yu L, Dean K. Journal of Applied Polymer Science 2004;94:593–7.
[17] Byun HS, Lee DH, Lim JS, Yoo KP. Industrial and Engineering Chemistry Research 2006;45:3366–72.
[18] (a) Park JY, Kim SY, Byun HS, Yoo KP, Lim JS. Industrial and Engineering Chemistry Research 2006;45:3381–7;

(b) Park JY, Kim SY, Byun HS, Yoo KP, Lim JS. Industrial and Engineering Chemistry Research 2006;45:6092.
[19] Kalogiannis CG, Panayiotou CG. Journal of Chemical and Engineering Data 2006;51:107–11.
[20] Liu K, Kiran E. Journal of Supercritical Fluids 2006;39:192–200.
[21] Liu K, Kiran E. Industrial and Engineering Chemistry Research 2007;46:5453–62.
[22] Lee JM, Lee BC, Lee SH. Journal of Chemical and Engineering Data 2000;45:851–6.
[23] Liu K, Schuch F, Kiran E. Journal of Supercritical Fluids 2006;39:89–101.
[24] Pöehler H, Kiran E. Journal of Chemical and Engineering Data 1997;42:379–83.
[25] Nelson MR, Borkman RF. Journal of Physical Chemistry A 1998; 102:7860–3.
[26] Danten Y, Tassaing T, Besnard M. Journal of Physical Chemistry A 2002;106:11831–40.
[27] Blatchford MA, Raveendran P, Wallen SL. Journal of Physical Chemistry A 2003;107:10311–23.
[28] Cabaco MI, Danten Y, Tassaing T, Longelin S, Besnard M. Chemical Physics Letters 2005;413:258–62.