

CHAPTER 9

HIGH-PRESSURE SOLUTION BLENDING OF POLY (ϵ -CAPROLACTONE) WITH POLY (METHYL METHACRYLATE) IN ACETONE + CARBON DIOXIDE

Having determined the miscibility of PCL or PMMA in acetone + CO₂ mixtures, we explored the miscibility of blends of these polymers in this mixed solvent. We determined the liquid-liquid phase boundaries, and generated information on demixing pressures at different temperatures. Blends were prepared by first bringing the system to homogenous conditions, and then by imposing a pressure quench. This is a unique polymer system showing the large shift in demixing pressures to bring about complete miscibility. Pressures are much larger than the pressures needed for complete miscibility of component polymers. Furthermore, the DSC data show that presence of PMMA influences the crystallization and melting transitions of PCL.

9.1 Introduction

Polymer solution blending in high-pressure carbon dioxide or in fluid mixtures of carbon dioxide with an organic solvent is of continuing interest, and several publications have already appeared (Kiran, 1994; Lee and Shine, 1994; Han et. al., 2000; Mawson et. al., 1997; Duarte et. al., 2006). Specifically, the blends of poly (methyl methacrylate) and poly (ethyl

methacrylate) were prepared from solutions in Freon-22 via rapid expansion of supercritical solutions (Lele and Shine, 1994). The blends of isotactic polypropylene and poly (ethylene-co-butene) copolymers were also prepared in solutions of propane by rapid expansion (Han et. al., 2000). The blends of polycarbonate with poly (styrene-co-acrylonitrile) were prepared from solutions in tetrahydrofuran (THF) by precipitation with carbon dioxide or heptane as antisolvents (Mawson et. al., 1997). Blends of PCL with PMMA have been prepared from solutions in dichloromethane by precipitation with carbon dioxide (Vega-Gonzalez et. al., 2004).

The interest in the blends of poly (ϵ -caprolactone) (PCL) stems from its biodegradability and their potential use in biomedical applications. It is used as a matrix for controlled- release drug system (Xie et. al., 2006; Wu et. al., Lin and Yu, 2001) or as materials for scaffolds for tissue engineering (Reignier and Huneault, 2006; Sarkar et. al., 2006). In biomedical application, the advantages of using PCL are linked to its slow degradation and the degradation products being neutral. Because of its low glass transition temperature along with its biodegradability, blends of PCL with other polymers have also been of interest. It is used to lower the T_g of another polymer or enhance the degradation for environmental remediation. Indeed, blends of PCL have been reported at ambient pressures with poly (hydroxyl ether of bisphenol A) (De Juana and Cortazar, 1993), poly (vinyl methyl ether), poly (styrene-co-acrylonitrile) (Men and Strobl, 2003), polypropylene (Balsamo and Gouveia, 2004), poly (L-lactic acid) (Tanaka et. al., 2006), poly (butylene terephthalate) (Di Lorenzo et. al., 2007), tetramethyl polycarbonate (Madbouly, 2007) and polypyrrole (Corres et. al., 2006).

PCL has also been explored as compatibilizer for polymer blends such as bisphenol polycarbonate with styrene-acrylonitrile copolymer (Deanin and Vale, 2000).

In contrast to PCL which is semicrystalline, poly (methyl methacrylate) (PMMA) is an amorphous polymer with a wide range of utilization areas such as impact resistant substitute for glass, and also as materials for medical implants such as replacement intraocular lenses, bone cements, and dentures. Its blends have therefore been extensively studied. Among the recent publications are its blends with poly (vinylidene fluoride) (Lin et. al., 2006; Ma et. al., 2007), poly (L-lactic acid) (Hirota et. al., 2006; Yao et. al., 2007), poly (vinyl chloride) (Zhuo et. al., 2007; Agari et. al., 2007; Aouachria and Belhaneche-Bensemra, 2006), poly (ethylene terephthalate) (Al-Mulla and Shaban, 2007; Al-Mulla, 2007), polystyrene (PS) (Kailas and Bertrand, 2006), poly (styrene-co-acrylonitrile) (Prusty et. al., 2007) and poly (ethylene oxide) (Okerberg and Marand, 2007).

Studies on blending of PCL with PMMA have been of special interest not only because of their potential biomedical applications or environmentally desirable attributes, but also because of the possibility of specific intermolecular interactions arising from the ester groups in the backbone of the PCL molecules with the ester groups in the side group in PMMA molecules. The specific interactions between carbonyl group (C=O) in PCL and PVC (Coleman and Zarian, 1979), poly (bisphenol A carbonate) (Varnell et. al., 1981), and poly (hydroxyl ether of bisphenol A) (Coleman and Moskala, 1982) have been reported.

For solution blending, information on phase behavior of polymer mixtures is needed. This type of information is however very limited especially for high pressure solutions. The phase behavior of polyethylene + polypropylene blends in pentane (Kiran, 1994) and the phase behavior of the blends of isotactic polypropylene and poly (ethylene-co-butene) copolymers in propane have been reported (Han et. al., 2000). Studies on blends of semi-crystalline polymers with amorphous, glassy polymers are of additional interest in that the glassy polymers can alter the crystallization of the semi-crystalline polymers. Generally, the presence of a glassy component leads to a crystallization depression of the crystallizable component due to either a reduction in chain mobility, or a dilution of the crystallizable component at the growth front, or due to a change in the free energy of nucleation (Ajili and Ebahimi, 2007; Madbouly, 2007). In the presence of an amorphous component, lamellar thickness, crystal inter-phase, and spherulitic growth rate of the crystallizable component are altered (Madbouly, 2007). How these features are altered in dense fluids is not presently known.

In the present study, PMMA/PCL blends were prepared from their solutions in acetone + carbon dioxide mixtures at high pressures. The properties of this mixture solvent have been discussed in the previous chapters (Chapter 7; Liu and Kiran, 2007). We have also reported on the phase behavior, viscosity, and density of PMMA solutions and PCL solutions in this mixture solvent at high pressures (Chapters 8 and 9; Liu et. al., 2006; Liu and Kiran, 2006). We now extend phase behavior information from individual polymer solutions to the solutions of PCL + PMMA blends.

9.2 Experimental

9.2.1 Materials

The polymers were purchased from Scientific Polymer Products (Ontario, NY). The molecular weight (M_w) and polydispersity (PDI) of the PCL sample were 14,300 and 2.3, respectively. Two PMMA samples ($M_w = 15,000$, PDI = 1.8; and $M_w = 540,000$, PDI = 2.8) were used. Acetone (Burdick & Jackson) with purity of 99.5 % and CO₂ (Airgas) with a minimum purity of 99.9% were used without further purification.

9.2.2 Determination of liquid-liquid phase boundary

A variable-volume high-pressure view cell, described in Chapter 6 (Liu and Kiran, 2006; 2007), were used to prepare the PCL/PMMA blends and to determine the liquid-liquid (L-L) phase boundary for the polymer blends in acetone + carbon dioxide mixtures at high pressures. After the polymers and the solvent with known amounts were loaded, complete miscibility was achieved by adjusting the temperature and pressure. The L-L demixing pressure was 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. The pressure-temperature phase diagram was generated by repeating this demixing pressure determination at different temperatures.

9.2.3 Preparation of PCL/PMMA blends

To prepare polymer blend from high pressure fluid or fluid mixtures, temperature, pressure, and/or composition quenches can be used to induce solid-fluid (S-F) phase separation or S-F

separation after the liquid-liquid (L-L) separation. The importance of the quench path has been discussed in an earlier study (Zhang and Kiran, 2006). In the present study, the polymer blend preparation involved two steps. These are illustrated in Figure 9.1. The first step is the depressurization at a given temperature to cross the liquid-liquid phase boundary. The second step is the further depressurization and cooling to ambient temperature. Typically, in the first stage, the pressure was decreased from 20 MPa to around 6-7 MPa at a rate of 10 MPa/min. After holding this solution at the lower pressure (6-7 MPa) but still at the initial temperature of the solution (348 K) for 30 mins with stirring, the system was completely depressurized by full discharge. The polymer blends discharged were collected in a beaker and the fraction of acetone solvent that was not removed with expanding carbon dioxide, was evaporated by placing the samples in vacuum (0.05 Torr) for 72 hours at room temperature. Either powders or films were formed depending upon the composition of the blends. Film formation was enhanced in blends that contained higher fraction of PMMA. The polymer blends were then further characterized by DSC scans (in the temperature range from -50 to +150 °C) and FTIR (using KBr disks with about 3mg polymer samples).

9.3 Results and discussion

9.3.1 Liquid-liquid phase boundary

The liquid-liquid (L-L) phase boundaries were determined for 10 wt % PMMA ($M_w = 15,000$; $M_w = 540,000$), 10 wt % PCL ($M_w = 14,300$), and 10 wt % (PMMA + PCL) blends. In the blends the total polymer concentration was kept as the same as in the pure component polymer solutions. In these solutions, the concentrations of acetone and carbon dioxide were

maintained at 50 wt % and 40 wt %, respectively. For the blend solutions of PCL with low- M_w PMMA ($M_w = 15,000$), the PCL concentrations were 2.5, 5.0, and 7.5 wt % (with PMMA concentrations being 7.5, 5.0 and 2.5 % respectively). The PCL concentration were 5.0 wt % for the blend solutions with the high- M_w PMMA ($M_w = 540,000$). The phase boundaries of these polymer solutions are shown in Figures 9.2 through 9.4. The demixing pressures are given in Table 9.1.

Figure 9.2 shows the liquid-liquid phase boundaries for the 10 wt % PCL ($M_w = 14,300$), 10 % PMMA ($M_w = 15,000$) and 10 wt % (PCL +PMMA) blends with PCL/PMMA mass ratios of 25/75, 50/50, and 75/25, respectively. PCL solution shows higher L-L demixing pressures than the PMMA solution at the same temperatures. All the blends display higher L-L demixing pressures than their corresponding individual polymer. Among these blends, even though the differences are slight, the 50/50 PCL/PMMA blend shows the highest demixing pressures and the 25/75 PCL/PMMA blend displays the lowest demixing pressures. In all the solutions, at a given pressure, two phase regions are entered when temperature is increased.

Figure 9.3 shows the L-L phase boundaries of 10 wt % PCL ($M_w = 14,300$), the higher molecular weight PMMA ($M_w = 540,000$), and their 50/50 blend solutions in acetone + carbon dioxide mixture. The solution of the high molecular weight PMMA shows higher demixing pressures than those of the pure PCL solution. However, once again, the 50/50 PCL/PMMA blend shows higher demixing pressures than its corresponding PCL or PMMA solutions. Figure 9.4 shows that the solution of the 50/50 blend of high molecular weight PMMA ($M_w = 540,000$) with PCL displays higher demixing pressures than those of the

50/50 low molecular weight PMMA ($M_w = 15,000$) blend solution. The observation of higher demixing pressures in polymer blend solutions compared to their component solutions has been observed in other polymer systems such as blends of polyethylene and polypropylene in pentane (Kiran, 1994).

9.3.2 Polymer blend characterizations

A. DSC results. The DSC scans were carried out at 10 K/min from -50 to + 150 °C. Both the initial heating and cooling scans were generated. Figure 9.5a shows the first heating scans for the original PMMA samples. The T_g 's are displayed at around 80 and 120 °C respectively. Figure 9.5b shows the melting transition in original PCL. A double melting peak is noted. The primary melting transition is observed at 54.5 °C. Figure 9.5c is the first heating scan for the 75/25 PCL/PMMA blend. It is also a doublet but the primary peak is at a slightly lower temperature of 54 °C. Figure 9.5d is the heating scan for 50/50 blend. The doublet is still observed, and the primary peak is still at a lower temperature at around 53 °C. With this sample with greater amount of PMMA in the blend, T_g was noted at around 100 °C. The heating scan for the 25/75 blend is shown in Figure 9.5e. Here, the doublet peaks (around 51 and 55 °C) are more distinct and equally strong, and a T_g around 90 °C is noted. Figure 9.5f is the scan for the 50/50 blend with the higher molecular weight PMMA. A T_g around 105 °C is noted along with the doublet melting peak from PCL. Figure 9.6 is a comparative plot of all the first heating scans for ease of comparisons. The y-axes are the specific heats (per gram). The figure is instructive in showing the reduction in heat of melting (area under the melting curve) as one moves from pure PCL to blends with less amount of PCL.

Figures 9.7 a-e show the cooling scans immediately after the first heating scans. The peaks are the crystallization peaks. The 50/50 (Figure 9.7d) and the 25/75 (Figure 9.7e) PCL/PMMA blends show multiple crystallization peaks. Two distinct peaks are at near 0 and 20 °C, in between there appears to be additional peaks that are better resolved in the 25/75 blend. Figure 9.7f shows the cooling scan for the 50/50 blend with the higher molecular weight PMMA sample. The cooling scans for all the polymers are compared in Figure 9.8. The heats of crystallization values were assessed from the peak areas. The transition temperatures and the heats of crystallization and melting are shown in Table 9.2. The heat of crystallization and melting values show some differences. The values decrease ingoing from pure PCL to the blend with the lower PCL content as they showed. The heat of crystallization data suggests PCL compositions in the blends to be 67, 36, and 14 wt %, as compared to 75, 50, and 25 wt % initial mixture compositions loaded into the view cell. The lower heats of crystallization may be due to the compositional effect, or influence of PMMA in retarding the crystallization of PCL in the blends. Further analysis using the heats of melting data suggests blend composition of 67, 42, and 13 wt %. For the high molecular weight PMMA blends, both the heats of melting and crystallization lead to 40 wt % PCL in blends.

Figure 9.9 is a rare diagram displaying the actual crystallization data and L-L demixing conditions in a common plot for a blend system prepared from high-pressure solutions displaying LCST-type behavior. These types of diagrams for high-pressure polymer solutions are not common in the literature yet would be of great significance in providing direct information on the temperature below which the system must be quenched to bring about solid-fluid (S-F) phase separation when homogeneous solutions are expanded. To further

highlight this point, a generalized diagram is included as an insert. In the present of solvents it is possible that the crystallization curve may be slightly shifted to lower temperatures. Along the direction of arrows, phase separation will occur upon either increasing or decreasing temperature. What is important to realize is that the nature of the phase separation will be different along the paths that accompany an increase or a decrease in temperature. Starting from homogeneous conditions, increasing the temperature leads to L-L phase separation, but lowering the temperature leads to S-F phase separation.

B. FTIR tests. Figures 9.10 and 9.11 show the FTIR spectra for the original PCL and the original low-molecular weight PMMA ($M_w = 15,000$) samples. The characteristic bands are noted in each figure. In the PCL spectrum, the bands in the range $2867\text{-}2947\text{ cm}^{-1}$ are assigned to $-\text{CH}_2$ stretching, the band at 1727 cm^{-1} is assigned to the C=O carbonyl stretching, the band at 1295 cm^{-1} is assigned to C-O and C-C stretching in the crystalline phase, and the band at 1241 cm^{-1} is assigned to asymmetric COC stretching (Elzein et. al., 2004). The band at 1295 cm^{-1} has been used in the literature to investigate the crystallinity change in PCL (Elzein et. al., 2004). In the PMMA spectrum, the bands in the range $2854\text{-}2998\text{ cm}^{-1}$ are assigned to C-H stretching, the band at 1730 cm^{-1} is assigned to the C=O carbonyl stretching, and the band at 1148 cm^{-1} is assigned to $-\text{OCH}_3$ stretching (Ramesh et. al., 2007).

Figure 9.12 show the IR spectra of the blends. Figure 9.13 shows the spectra along with the pure PCL and PMMA. Figure 9.14 is an expansion of the region from $600\text{ to }2000\text{ cm}^{-1}$ which shows the changes in the band at 1295 cm^{-1} . This band corresponding to the C-O and

C-C stretching in the crystalline phase shows a decrease with addition of glassy PMMA to PCL and disappears in the pure PMMA spectrum. The transformation from PCL to PMMA can be easily followed.

The IR spectra further confirm the formation of PCL + PMMA blends. It should be noted that no new bands were observed, suggesting there are no specific interactions between PCL and PMMA.

9.4 Summary and conclusions

For the first time miscibility boundaries for blends of PCL and PMMA in acetone + carbon dioxide mixtures have been determined. These PCL blend solutions in acetone + carbon dioxide mixture show LCST-type phase behavior. The solutions of polymer blends display higher demixing pressures than the solutions of component polymers PMMA and PCL. The DSC studies show the melting and crystallization peaks associated with PCL, and in some of the blends the T_g associated with PMMA, suggesting these blends are microphase separated blends. The FTIR spectra confirm the formation of polymer blends. No new bands are observed in the PCL + PMMA blends, suggesting that there are no intermolecular specific interactions. The changes in the band at 1295 cm^{-1} confirm the changes (decrease) in overall crystallinity upon addition of PMMA, which is also observed in the DSC tests.

Table 9.1 Demixing pressures at different temperatures for 10 wt % PCL ($M_w = 14,300$), PMMA ($M_w = 15,000$ or $540,000$), and their blend solutions in acetone + carbon dioxide mixtures.

Temperature (K)	Pressure (MPa)
<i>PCL ($M_w = 14,300$) (10 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)</i>	
325.0	4.9
330.0	6.8
337.6	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
380.1	21.1
384.9	22.4
389.0	23.3
394.5	24.7
399.4	26.0
<i>PMMA ($M_w = 15,000$) (10 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)</i>	
347.1	10.5
352.0	11.5
356.0	13.0
360.3	14.0
366.5	15.4
370.0	16.5
374.8	18.0
380.4	19.0
385.4	21.0
390.0	22.0
393.3	23.0
399.1	24.5
<i>PCL ($M_w = 14,300$) (2.5 wt %) + PMMA ($M_w = 15,000$) (7.5 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)</i>	
341.1	10.5
347.0	12.6
353.4	14.3
358.0	15.7
363.3	17.2
368.5	18.6
374.1	20.3

379.5	21.7
384.9	23.2
390.9	24.5
395.3	25.4
400.8	27.0

PCL ($M_w = 14,300$) (5 wt %) + PMMA ($M_w = 15,000$) (5 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)

326.1	7.5
333.1	9.7
337.4	10.9
343.8	13.0
347.5	14.3
354.8	16.0
359.8	17.3
365.5	19.2
370.1	20.4
375.5	22.0
380.6	23.0
384.9	24.2
390.4	25.6
394.3	26.4
400.6	27.8

PCL ($M_w = 14,300$) (7.5 wt %) + PMMA ($M_w = 15,000$) (2.5 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)

328.0	7.1
332.8	8.5
339.0	10.5
344.0	12.2
351.5	14.5
356.1	15.8
362.3	17.5
369.0	19.5
374.1	20.6
377.4	22.0
379.4	22.4
384.6	23.8
389.8	24.9
394.6	26.1
401.0	27.6

PMMA ($M_w = 540,000$) (10 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)

330.0	15.5
335.5	17.0
340.5	18.5
348.3	20.0
353.1	22.0
359.0	23.5
365.4	24.5
370.1	25.5
376.0	27.0

381.9	28.5
386.6	29.5
391.9	30.5
396.4	32.5
400.4	34.0

PCL ($M_w = 14,300$) (5 wt %) + PMMA ($M_w = 540,000$) (5 wt %) + acetone (50 wt %) + carbon dioxide (40 wt %)

352.3	23.0
356.5	24.0
363.3	26.0
367.6	27.0
372.8	29.0
373.4	29.3
378.8	30.5
384.0	32.0
389.5	34.0
395.1	35.0
400.1	37.0

Table 9.2 Melting and crystallization temperatures, and heat of melting and crystallization for PCL ($M_w = 14$ K) and its blends with PMMA ($M_w = 15$ K or 540 K)

Polymer or polymer blends	Cooling Scan		Heating Scan	
	<i>Heat of Crystallization *</i> (J/g)	<i>Crystallization Temperature**</i> (°C)	<i>Heat of Melting *</i> (J/g)	<i>Melting Temperature**</i> (°C)
PCL (14 K)	78	28	84	54.5, 57
PCL(14 K) / PMMA (15 K)				
75 / 25	52	27	57	54, 57
50 / 50	28	-22, 2, 18, 24	36	53, 57
25 / 75	11	0, 8, 12, 20	11	51, 55
PCL(14 K) / PMMA (540 K)				
50 / 50	30	30, 32.5	35	53, 56

* Peak areas are based on total peak area including all peaks.

** Transition temperatures are included only for the major peaks that are distinct.

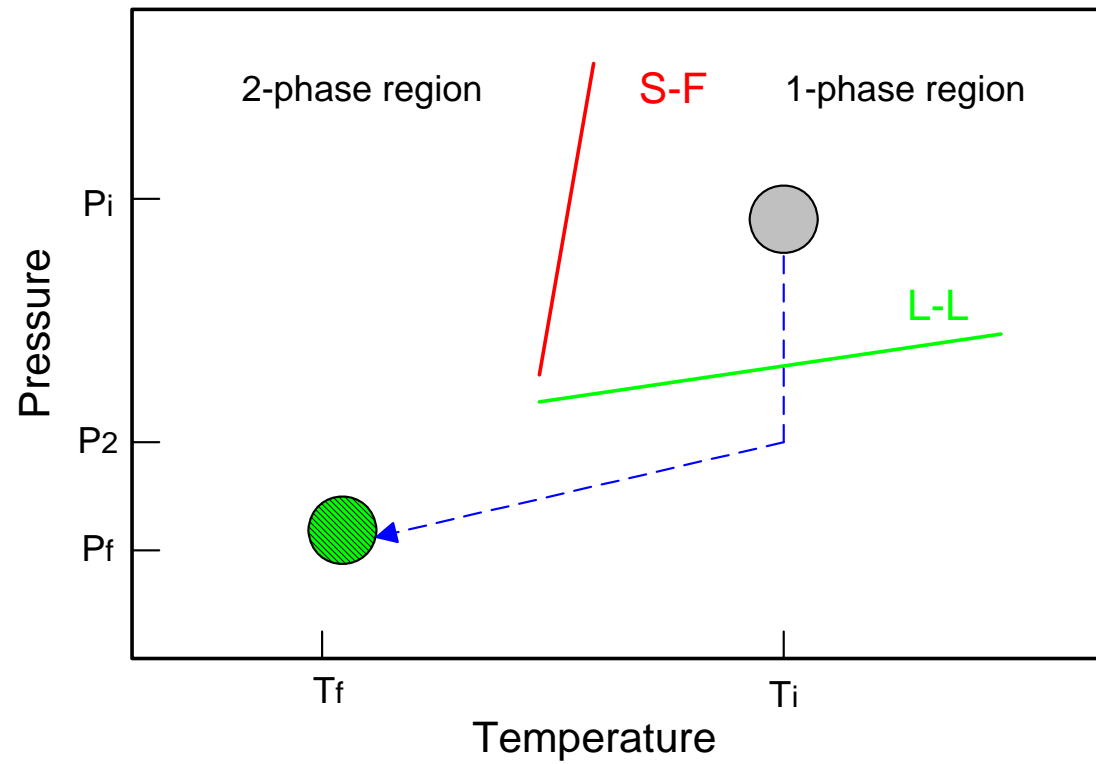


Figure 9.1 The schematic of phase separation process in forming the blends.

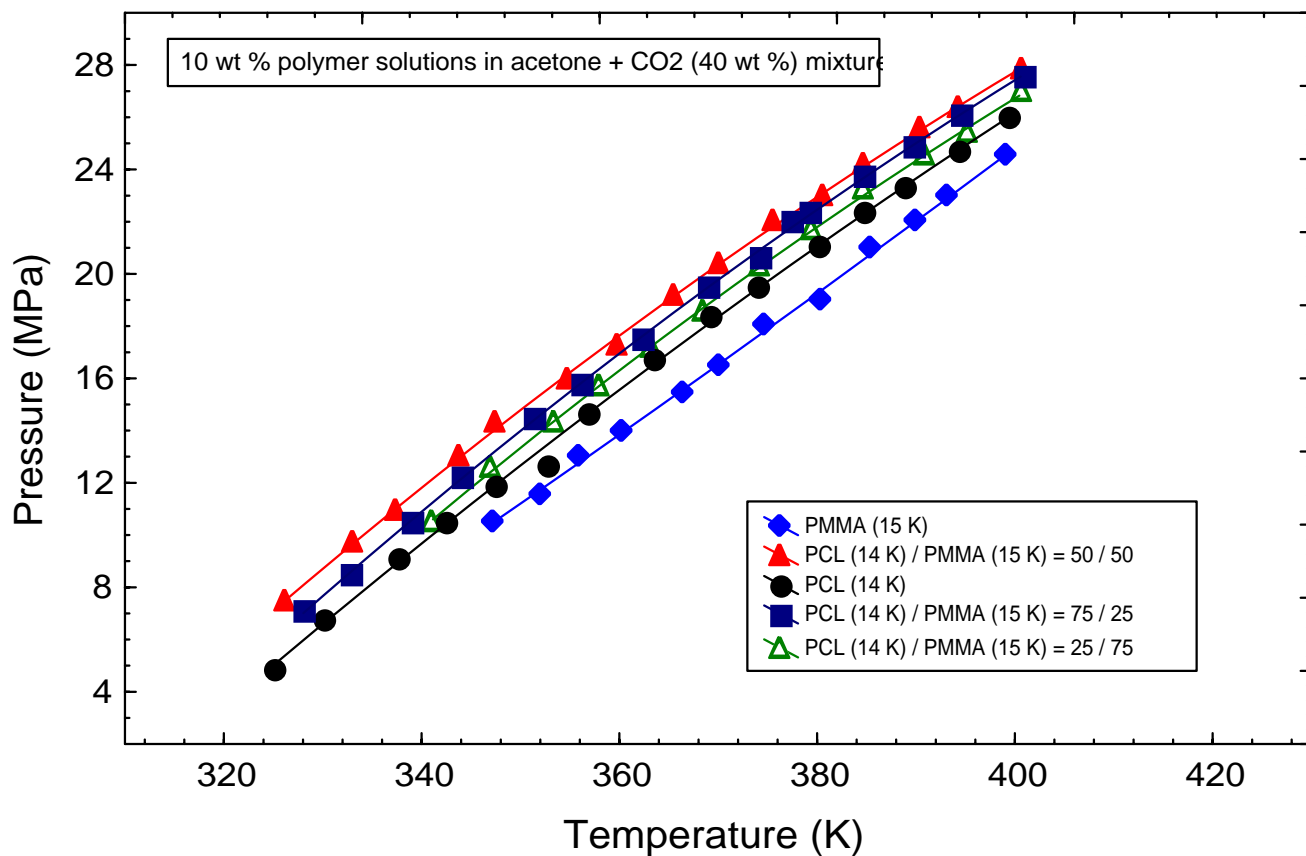


Figure 9.2 Variation of demixing pressure with temperature for 10 wt % PCL, PCL / PMMA blends, and PMMA (15 K) solutions in acetone (50 wt %) + carbon dioxide (40 wt %) mixture. Molecular weight: $M_w = 14,000$ (PCL); $15,000$ (PMMA).

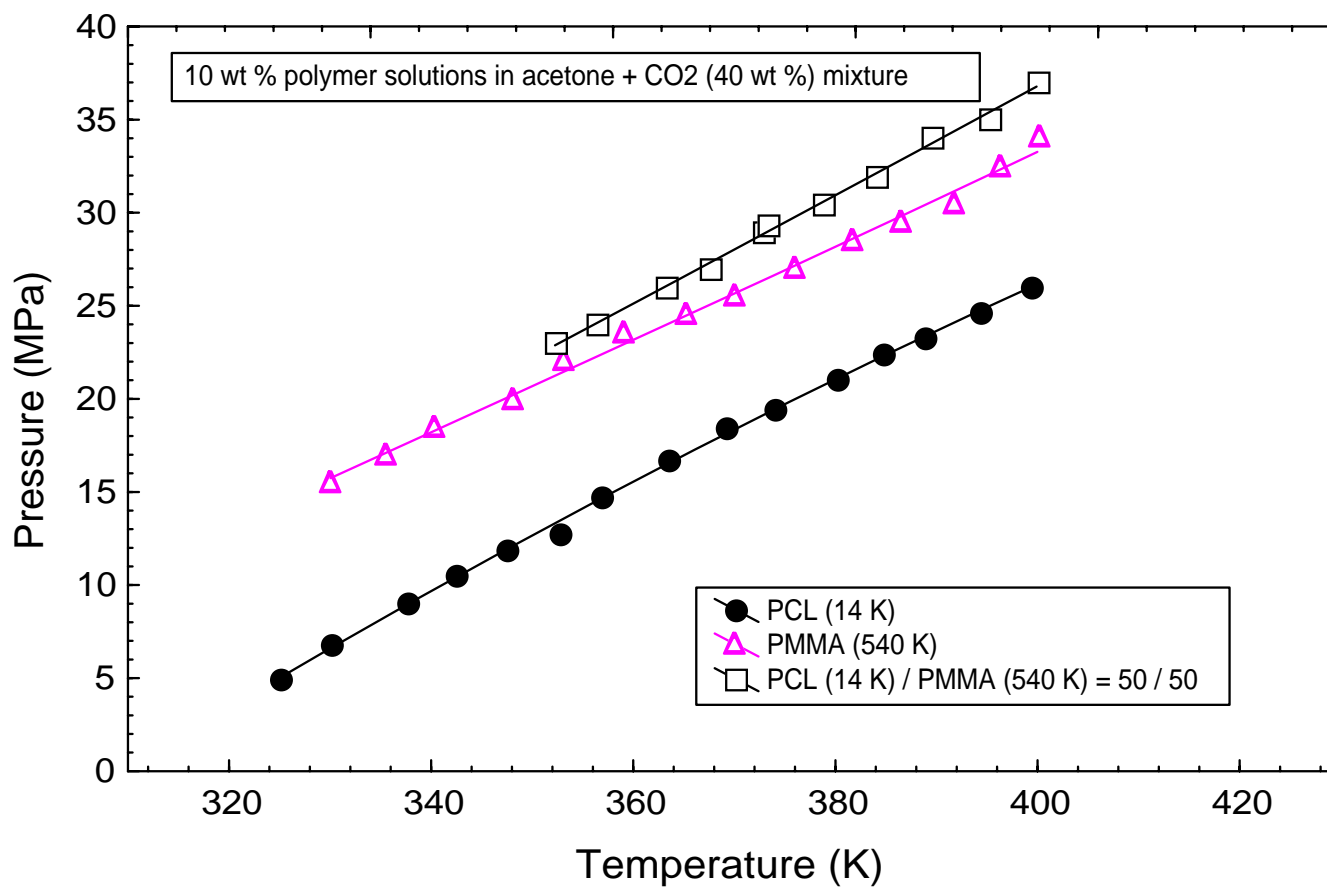


Figure 9.3 Variation of demixing pressure with temperature for 10 wt % PCL (14 K), PCL (14 K)/ PMMA (540 K) blend, and PMMA (540 K) solutions in acetone (50 wt %) + carbon dioxide (40 wt %) mixture.

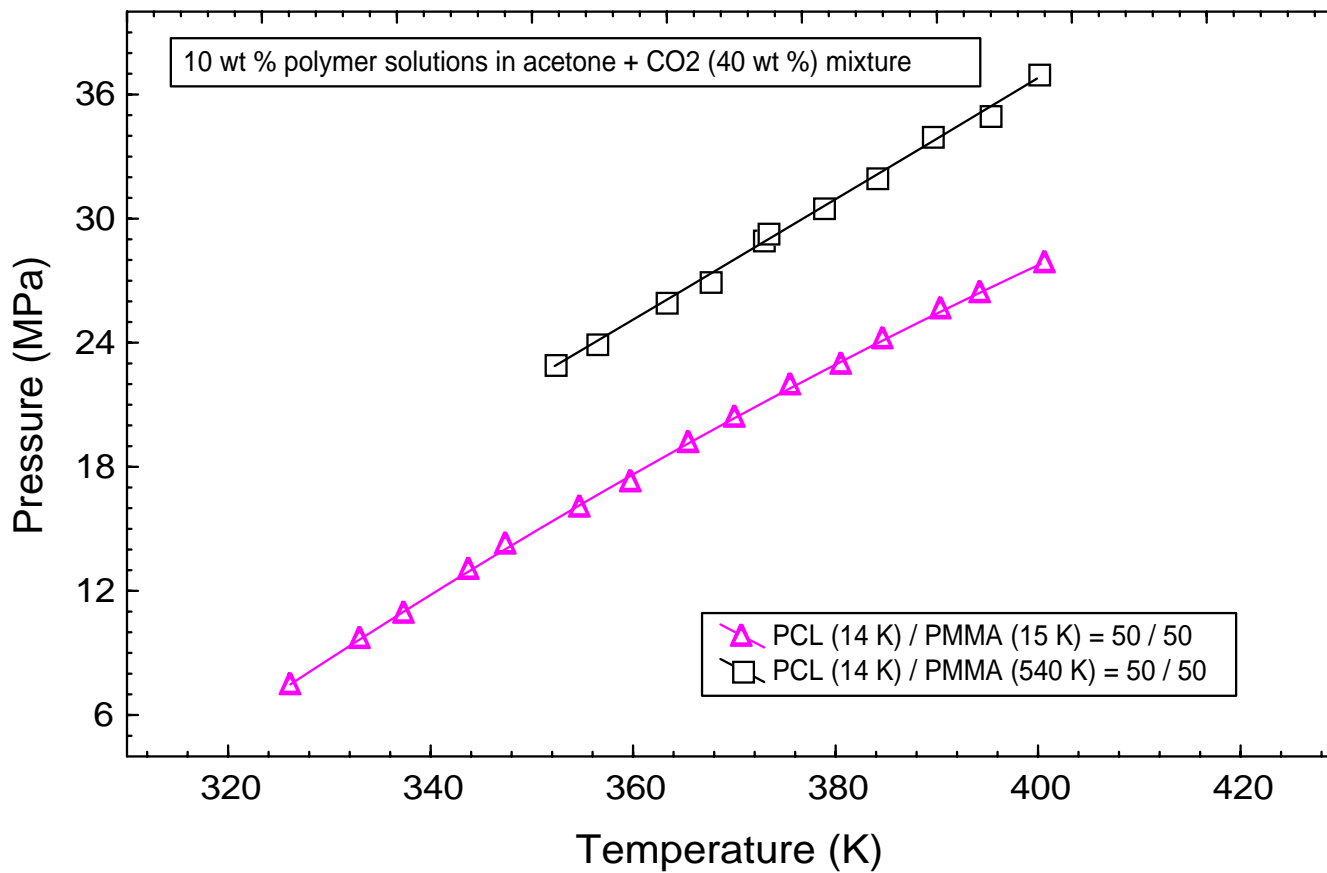


Figure 9.4 Variation of demixing pressure with temperature for solutions of 5 wt % PCL (14 K) + 5 wt % PMMA (15 K) and 5 wt % PCL (14 K) + 5 wt % PMMA (540 K) in acetone (50 wt %) + carbon dioxide (40 wt %) mixture.

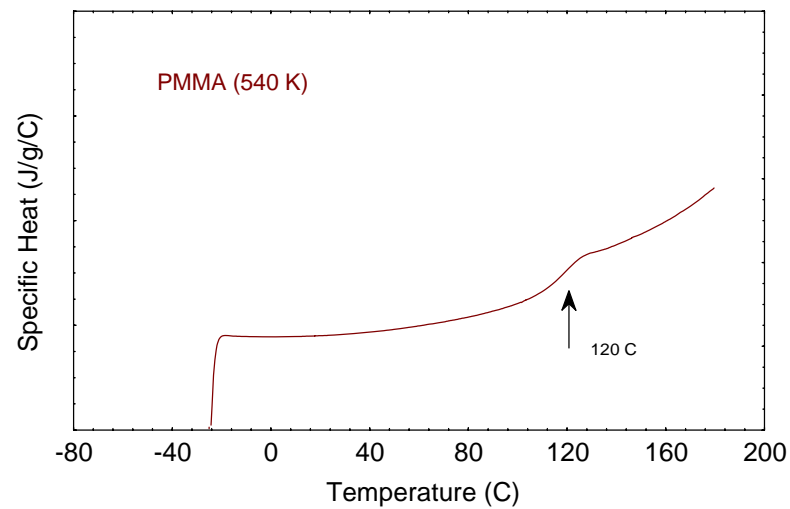
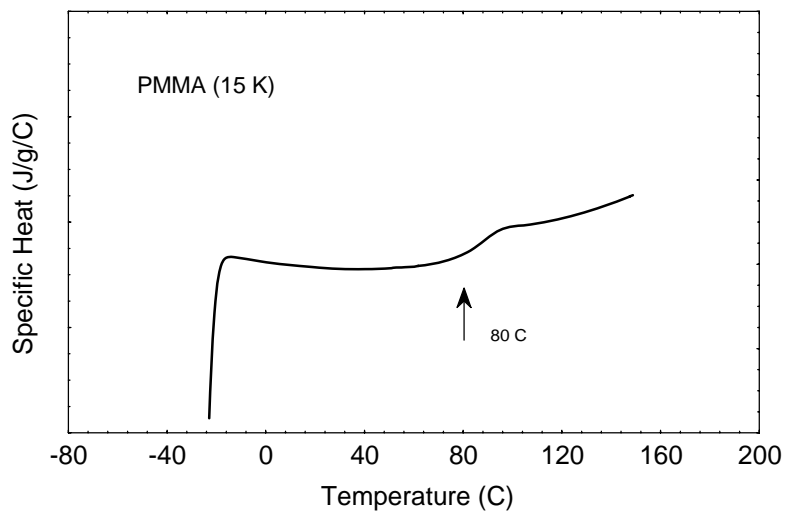


Figure 9.5a First heating scans for original PMMA samples ($M_w = 15,000$ and $540,000$). The heating rates are 10 K/min . The glass transition temperatures are indicated by the arrows.

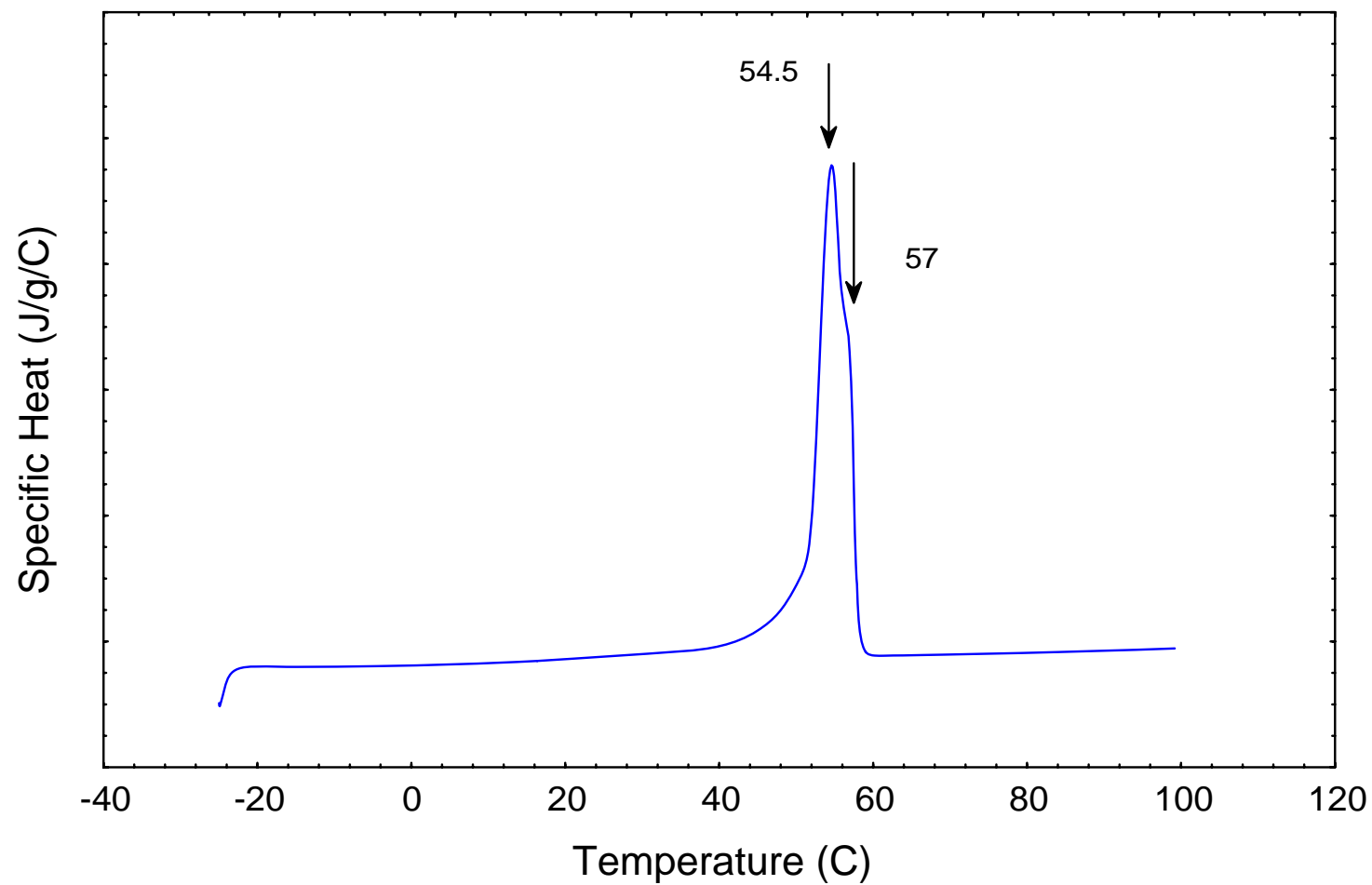


Figure 9.5b First heating scan for original PCL samples ($M_w = 14,000$). The heating rate is 10 K/min. The doublet peaks represent the melting transitions.

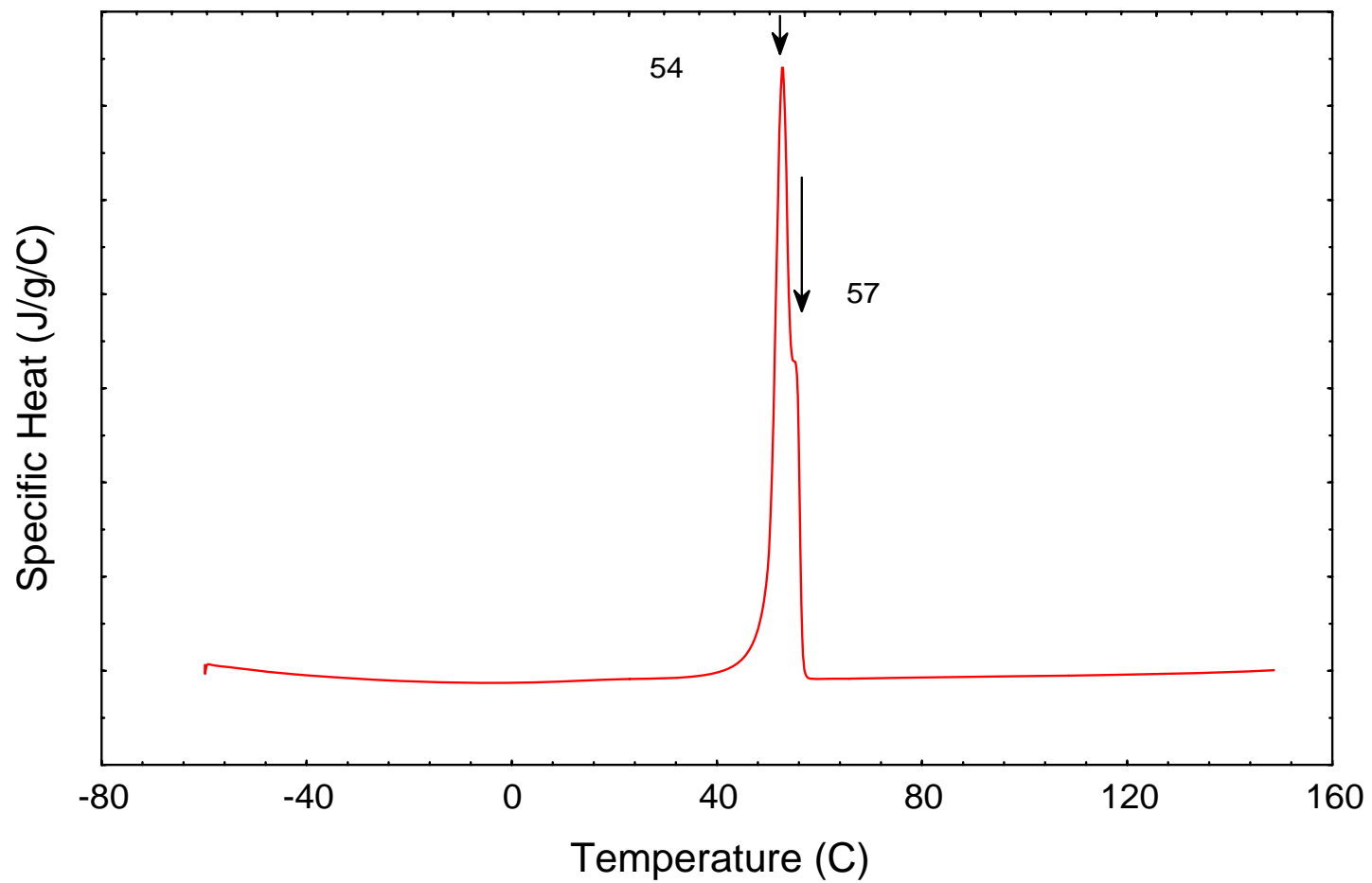


Figure 9.5c First heating scan for 75/25 PCL (14 K)/PMMA (15 K) blend. The heating rate is 10 K/min. The doublet peaks represent the melting transitions.

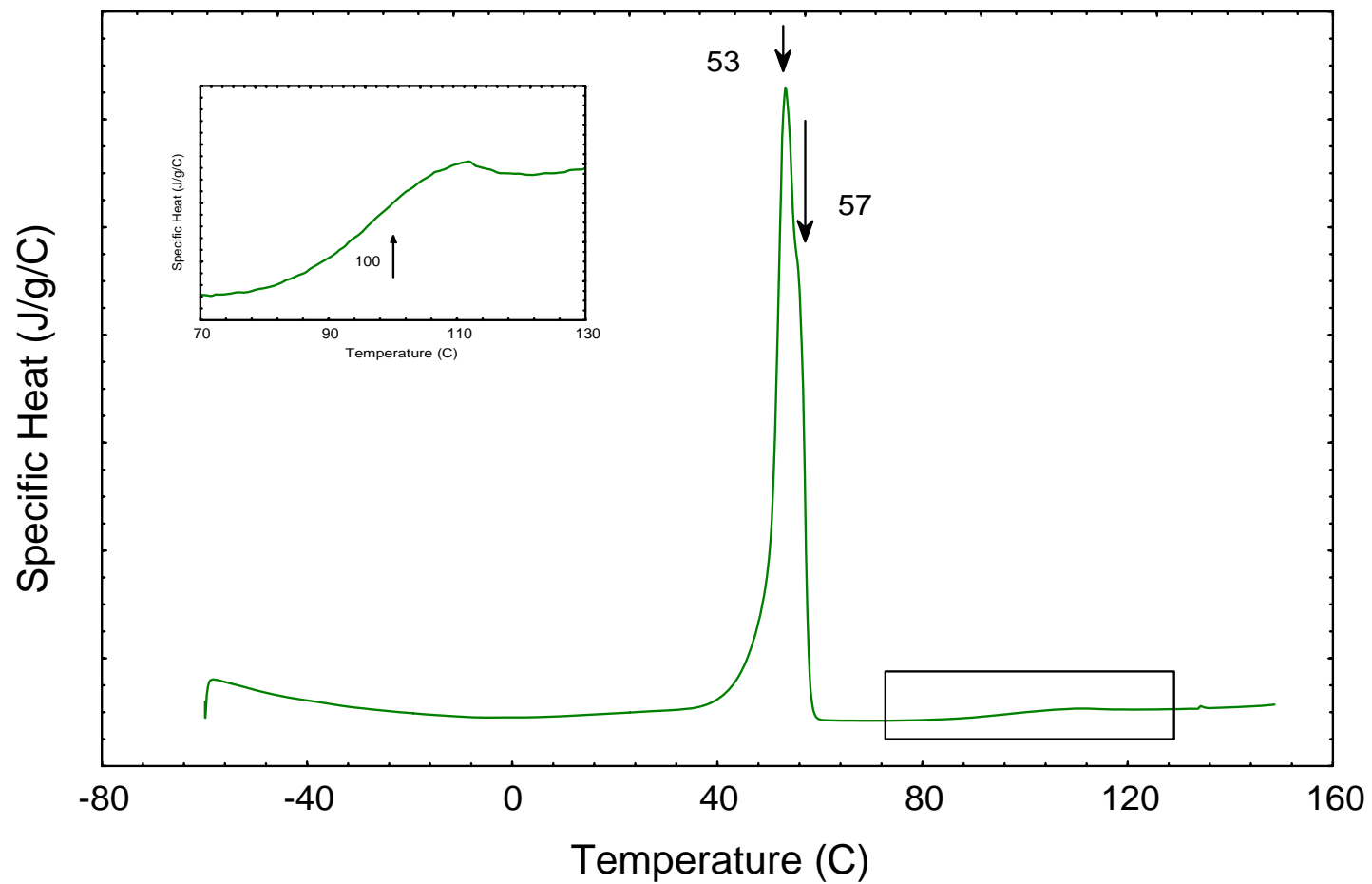


Figure 9.5d First heating scan for 50/50 PCL (14 K)/PMMA (15 K) blend. The heating rate is 10 K/min. A T_g is suggested at around 100 °C in the enlarged insert.

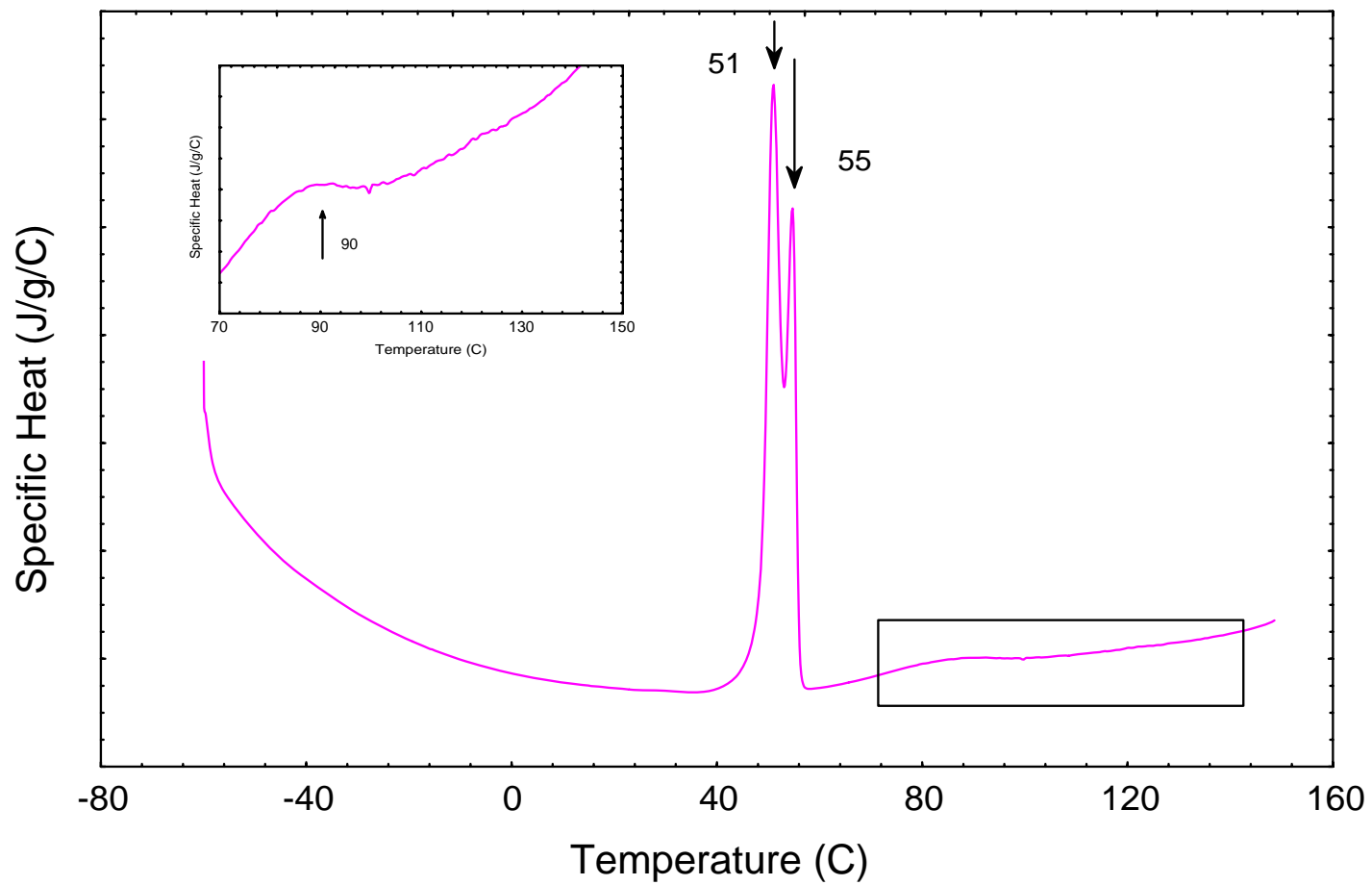


Figure 9.5e First heating scan for 25/75 PCL (14 K)/PMMA (15 K) blend. The heating rate is 10 K/min. The enlarged insert indicates a T_g at around 90 °C.

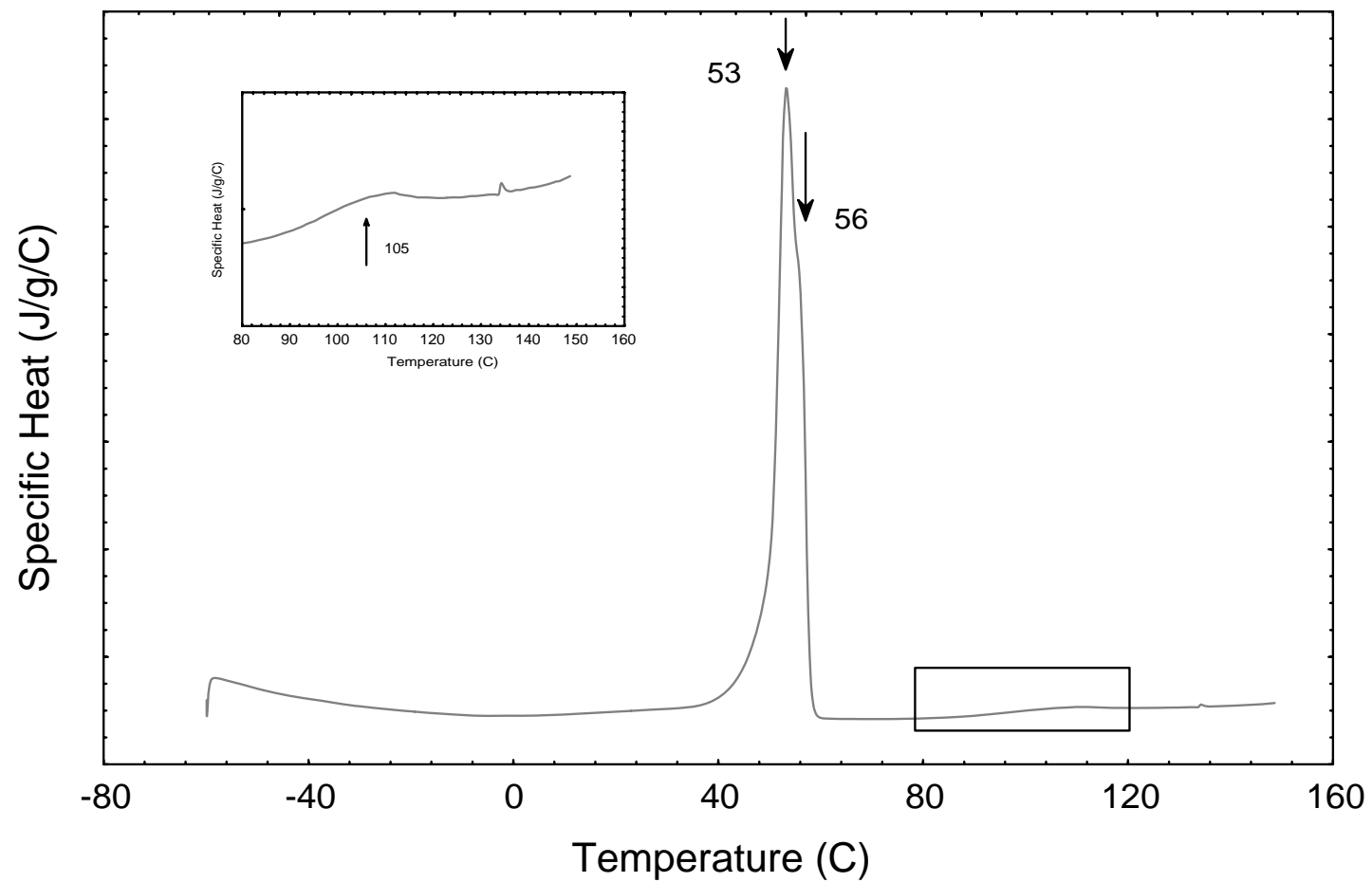


Figure 9.5f First heating scan for 50/50PCL (14 K)/PMMA (540 K) blend. The heating rate is 10 K/min. A T_g is detected at around 105 °C.

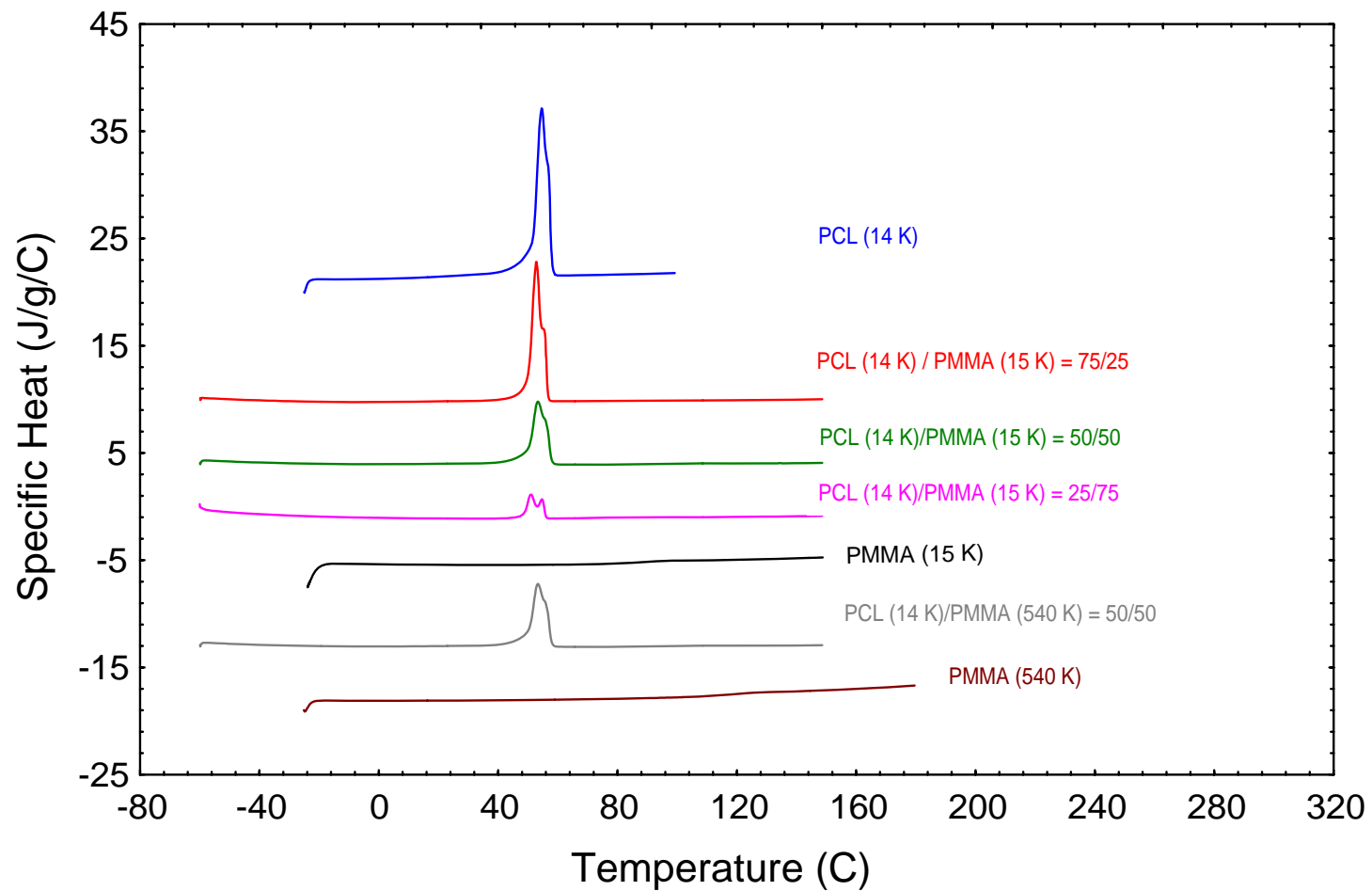


Figure 9.6 Comparative of DSC scans (first heating scans) for PCL ($M_w = 14$ K), PMMA ($M_w = 15$ K), PMMA ($M_w = 540$ K) and their blends.

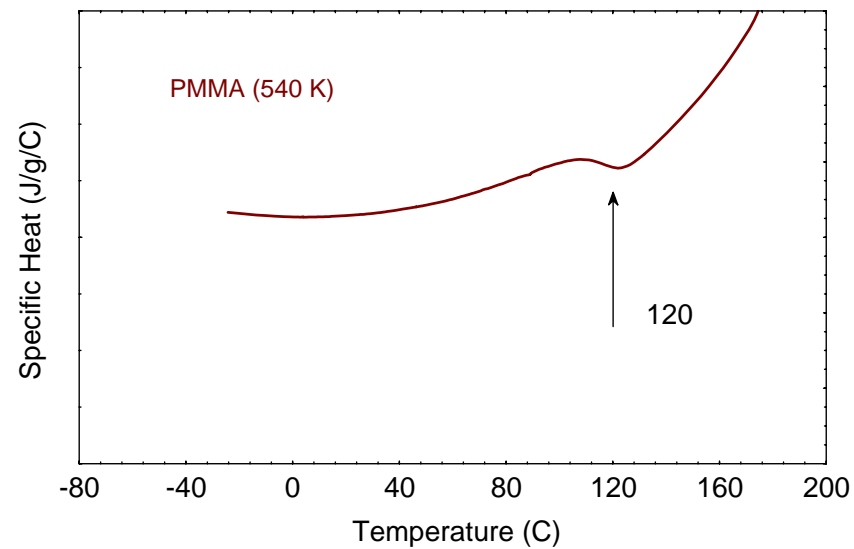
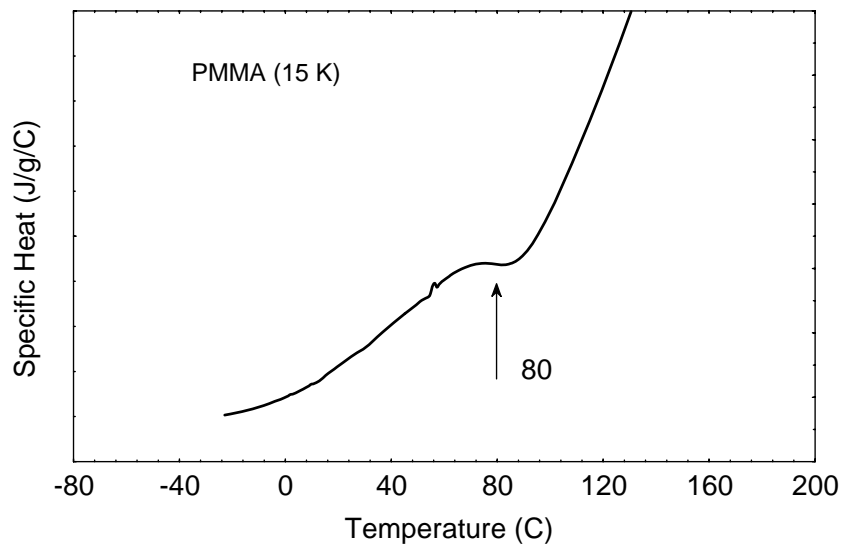


Figure 9.7a First cooling scans for the original PMMA samples ($M_w = 15$ K and 540 K) showing the T_g 's. The cooling rate is 10 K/min.

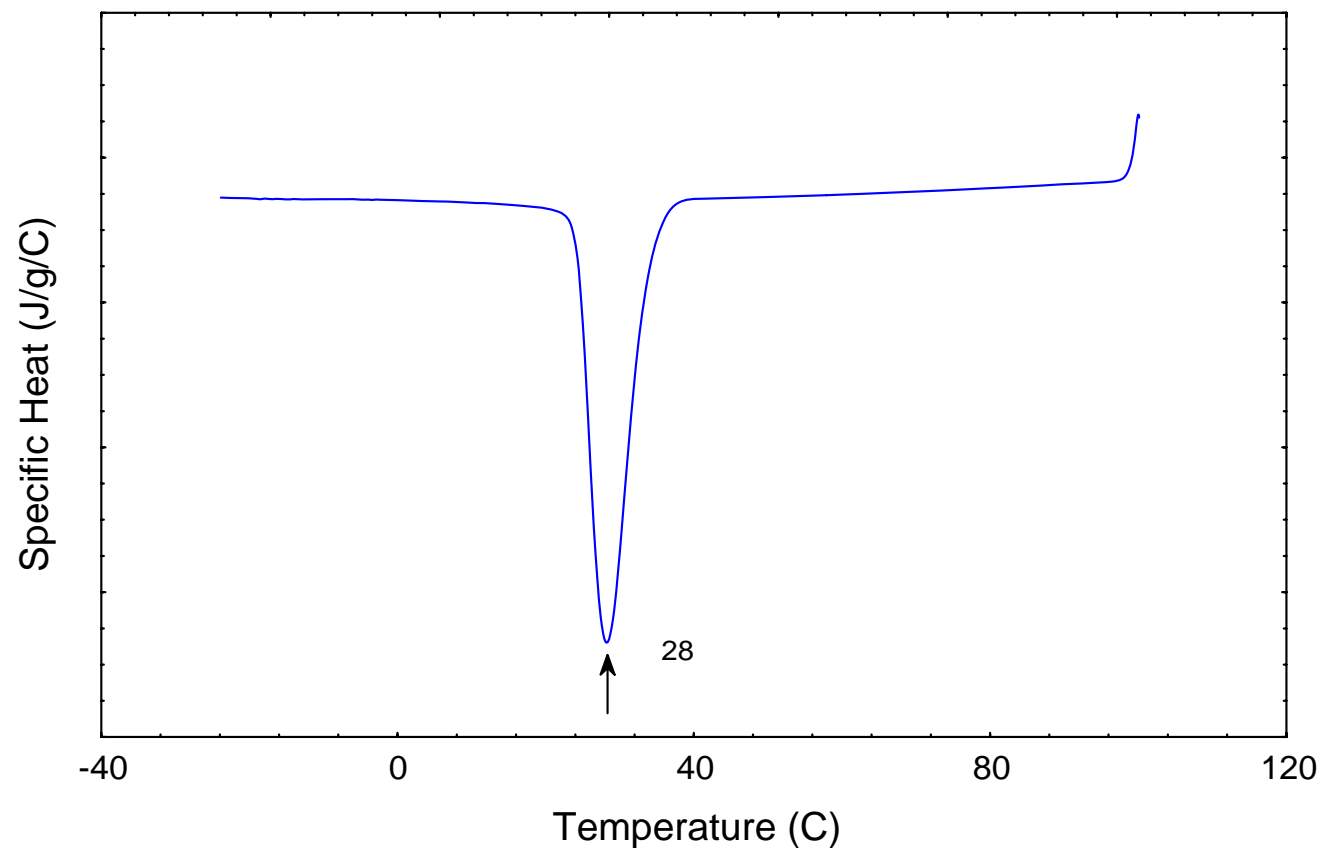


Figure 9.7b First cooling scans for the original PCL samples ($M_w = 14$ K). The cooling rate is 10 K/min.

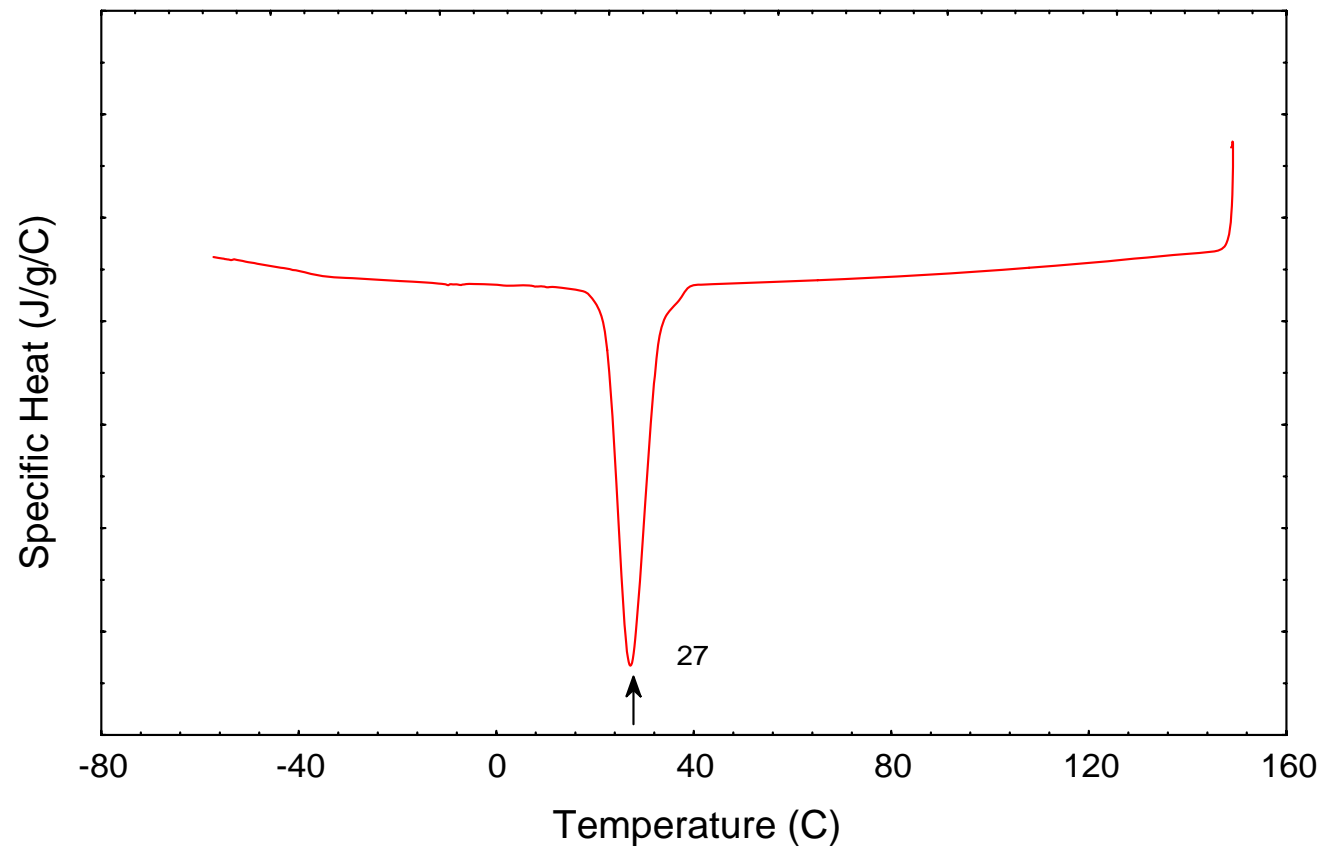


Figure 9.7c First cooling scans for the 75/25 PCL (14 K)/PMMA (15 K) blend sample. The cooling rate is 10 K/min.



Figure 9.7d First cooling scans for the 50/50 PCL (14 K)/PMMA (15 K) blend sample. The cooling rate is 10 K/min.

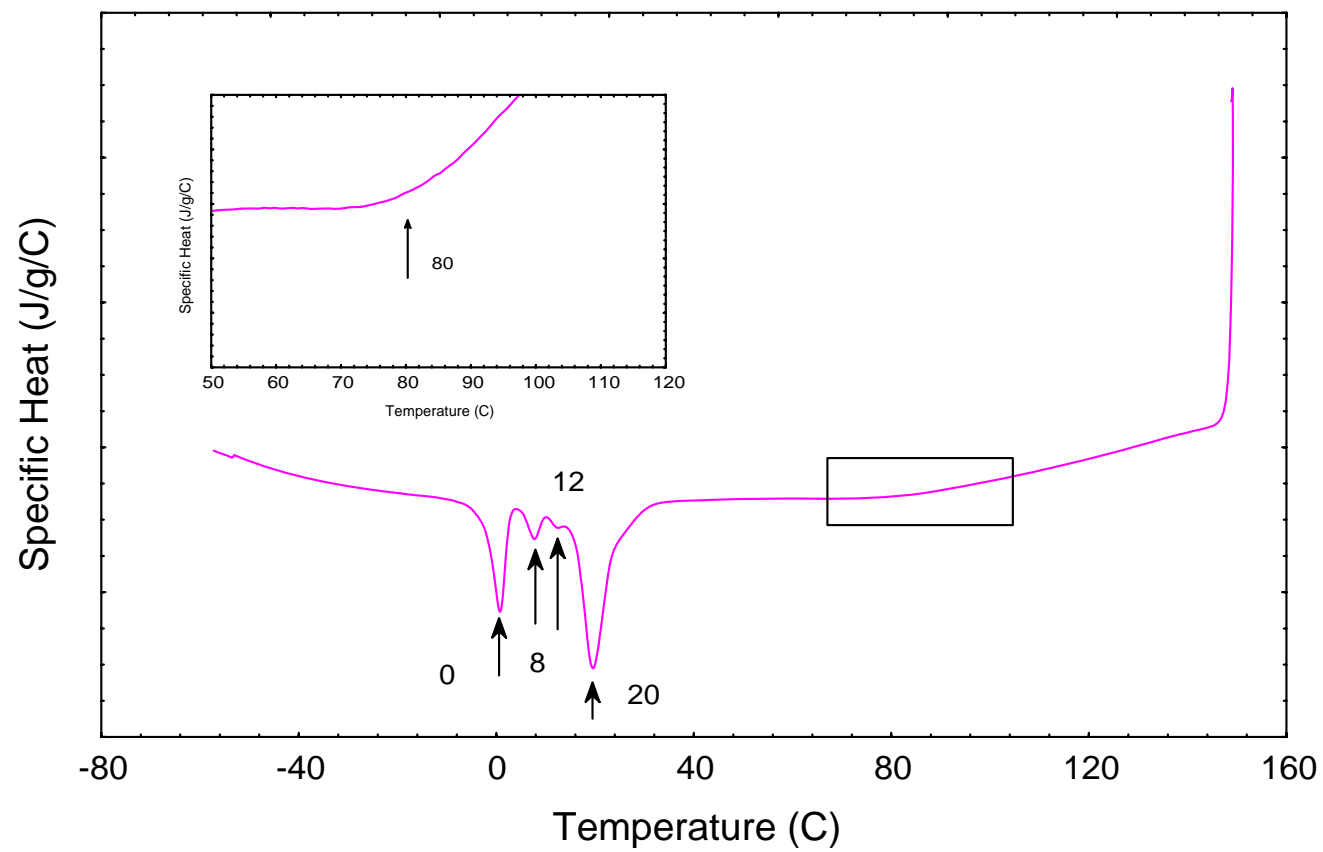


Figure 9.7e First cooling scans for the 25/75 PCL (14 K)/PMMA (15 K) blend sample. The cooling rate is 10 K/min.

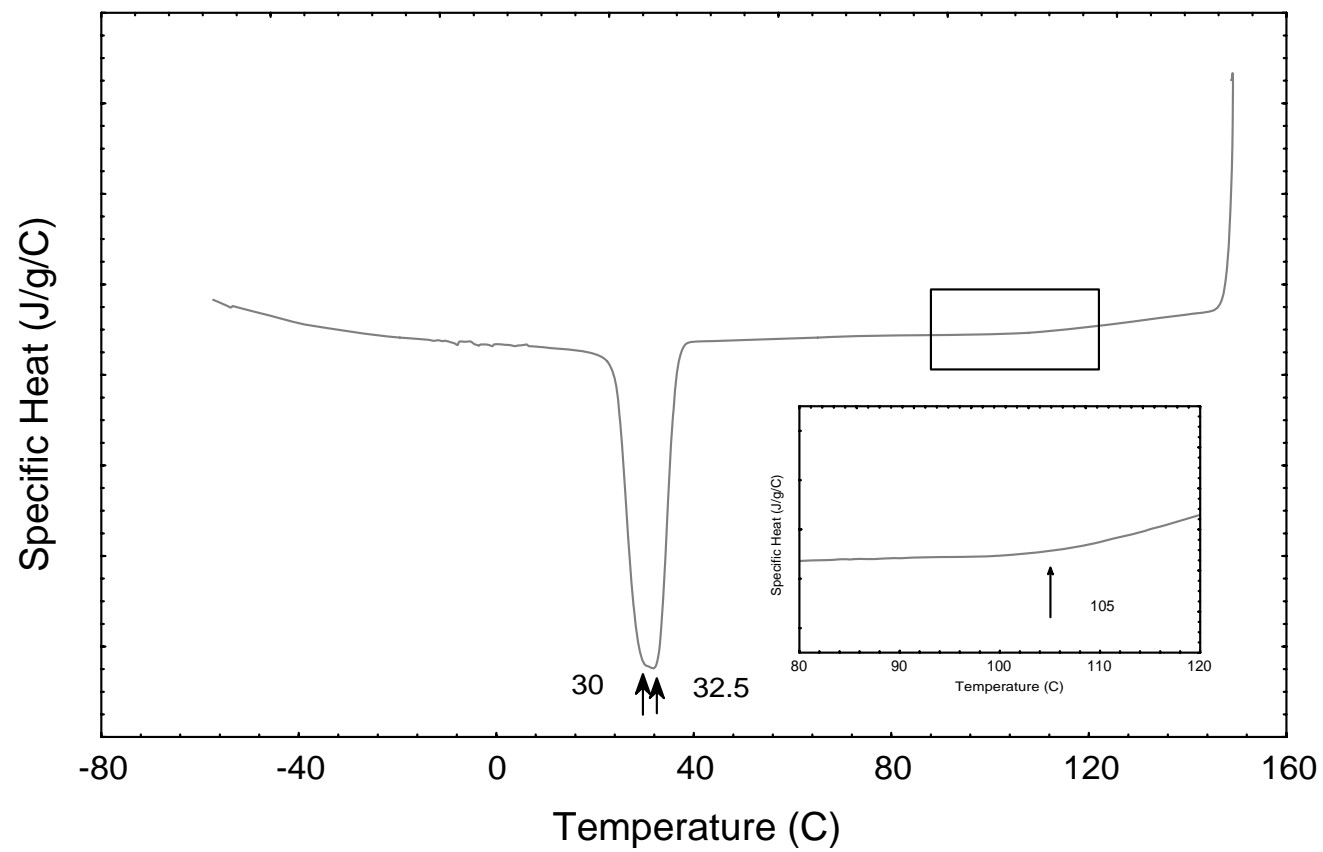


Figure 9.7f First cooling scans for the 50/50 PCL (14 K)/PMMA (540 K) blend sample. The cooling rate is 10 K/min.

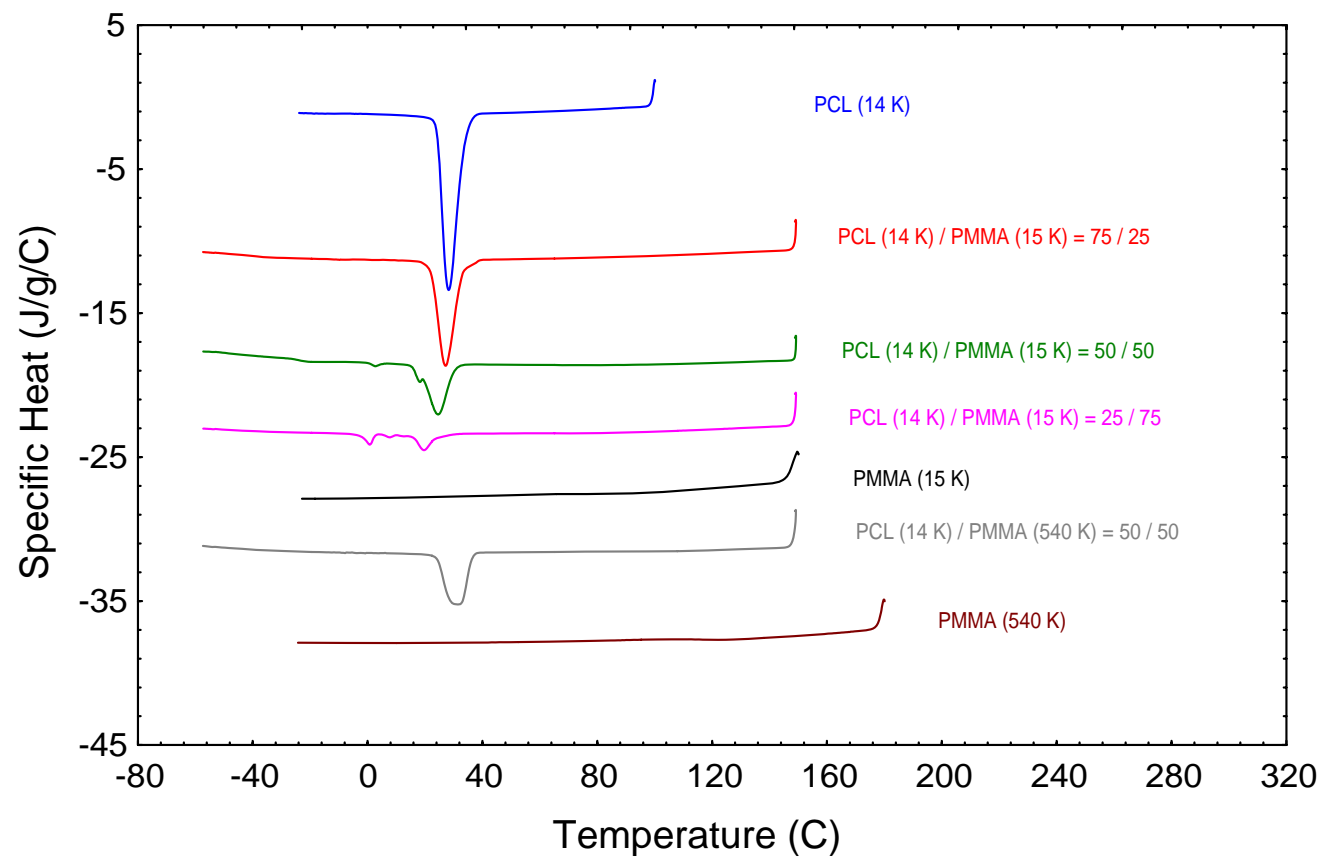


Figure 9.8 Comparative DSC scans (first cooling scans) for PCL ($M_w = 14$ K), PMMA ($M_w = 15$ K), PMMA ($M_w = 540$ K) and their blends.

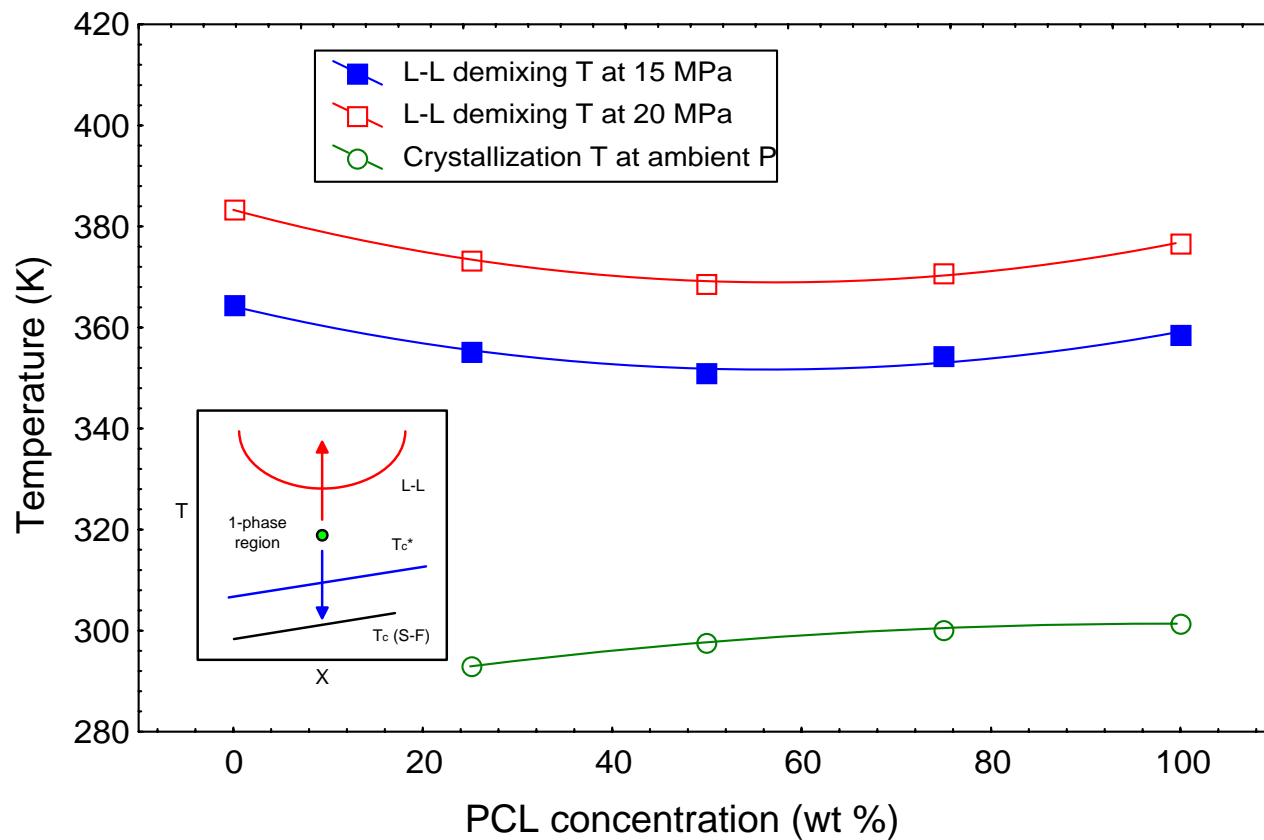


Figure 9.9 Variation of liquid-liquid phase boundary with PCL concentration for PCL ($M_w = 14$ K) + PMMA (15 K) blend (10 wt % total polymer) solutions in acetone (50 wt %) + carbon dioxide (40 wt %) at 15 and 20 MPa. The ambient pressure crystallization temperatures of the PCL + PMMA blends in the absence of solvent are also included. This is depicted as T_c^* in the insert figure. T_c represents the crystallization curve in the presence of solvent fluid. Starting at homogeneous conditions, increasing the temperature leads to L-L phase separation, and lowering the temperature leads to S-F phase separation.

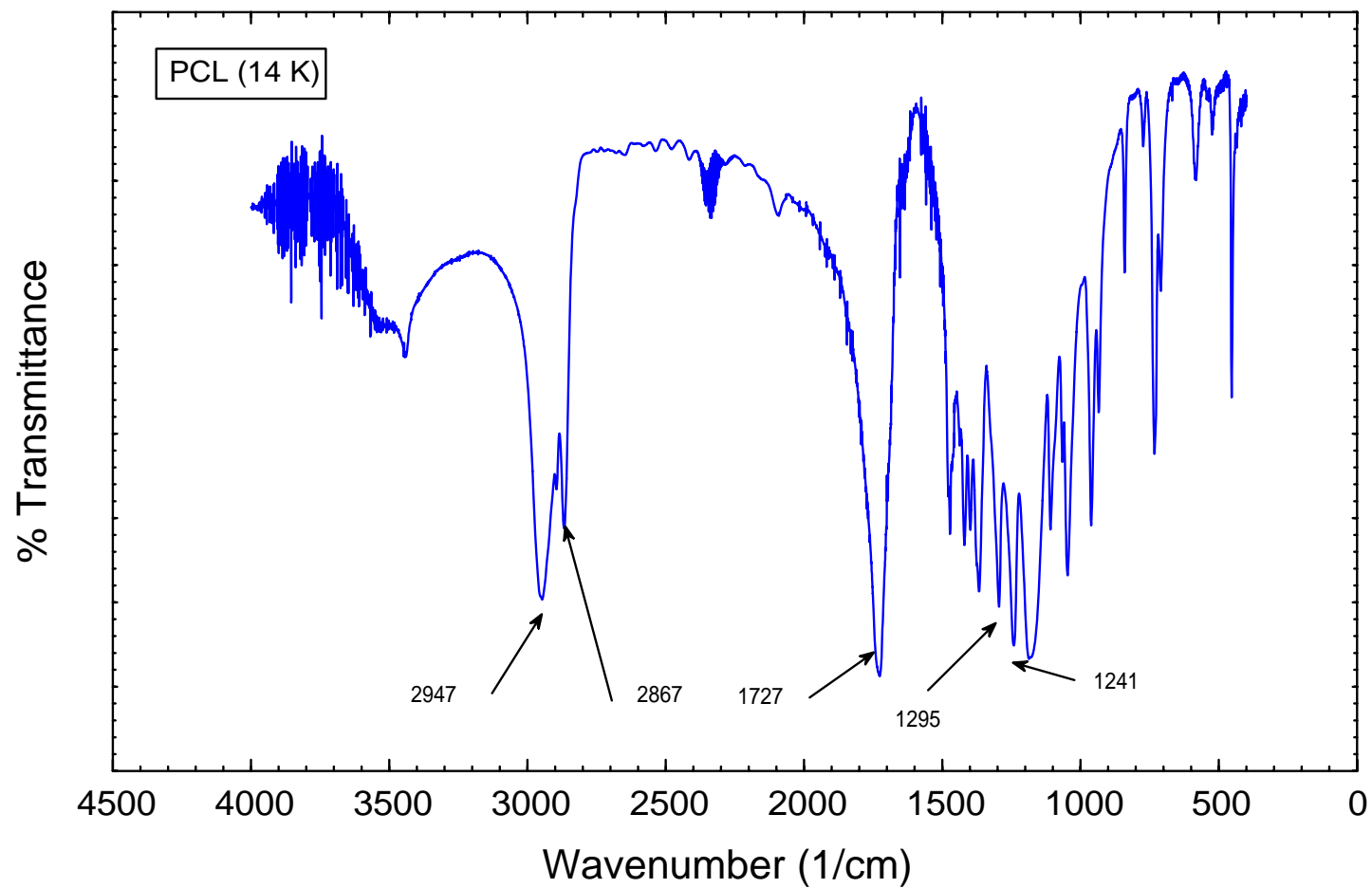


Figure 9.10 FTIR spectrum for original PCL sample.

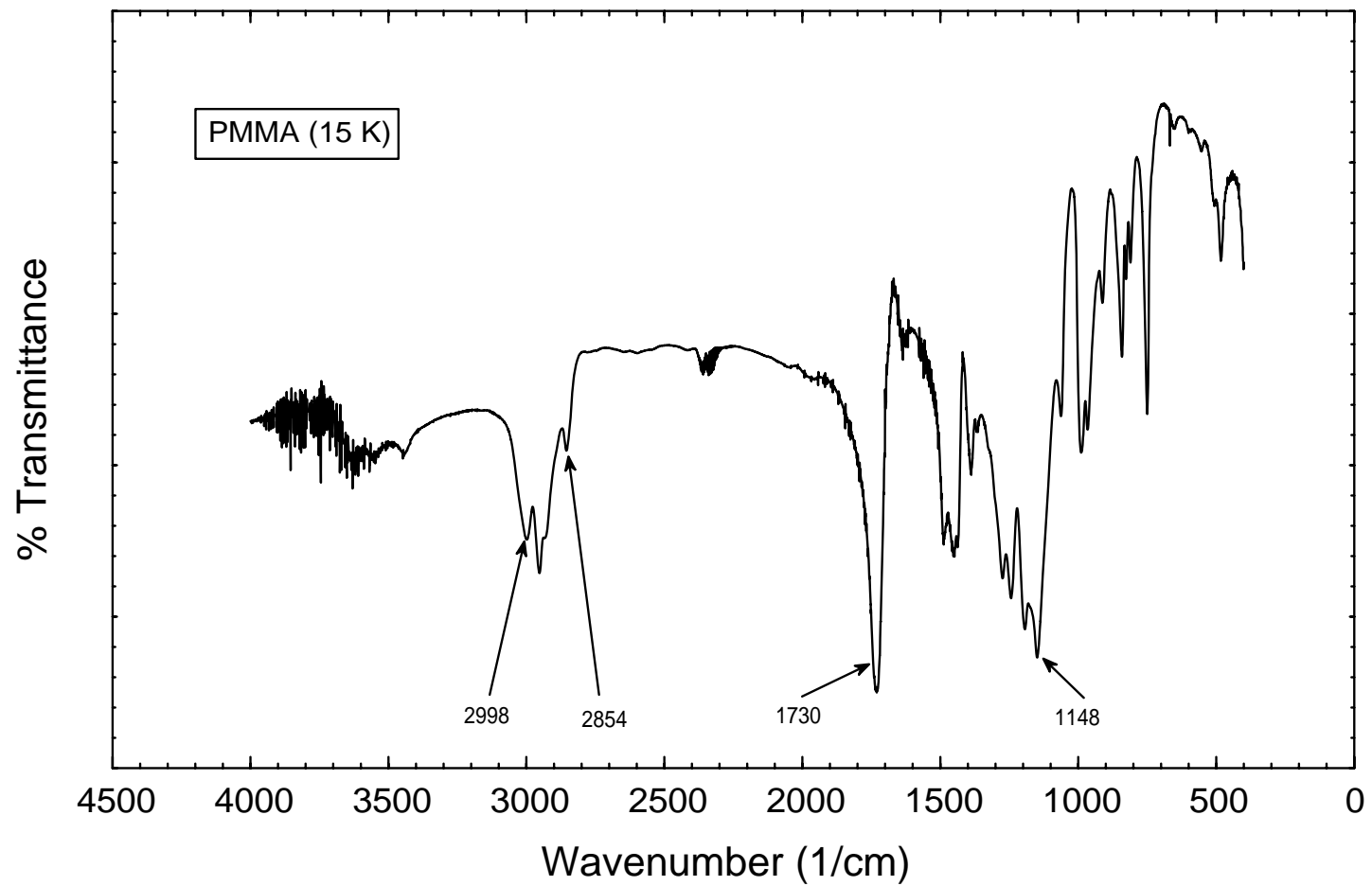


Figure 9.11 FTIR spectrum for original PMMA sample.

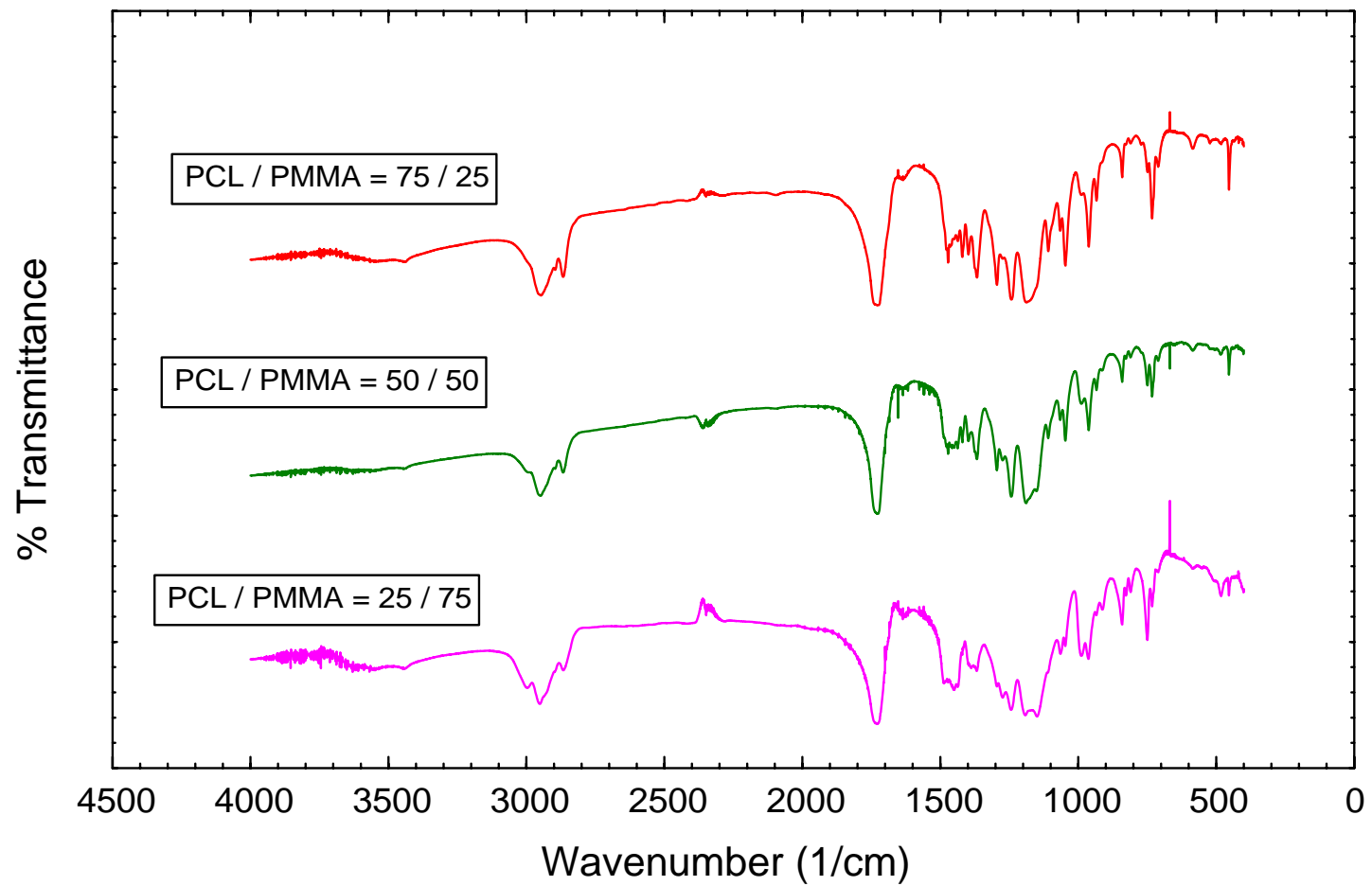


Figure 9.12 Comparison of FTIR spectra for PCL + PMMA blend samples.

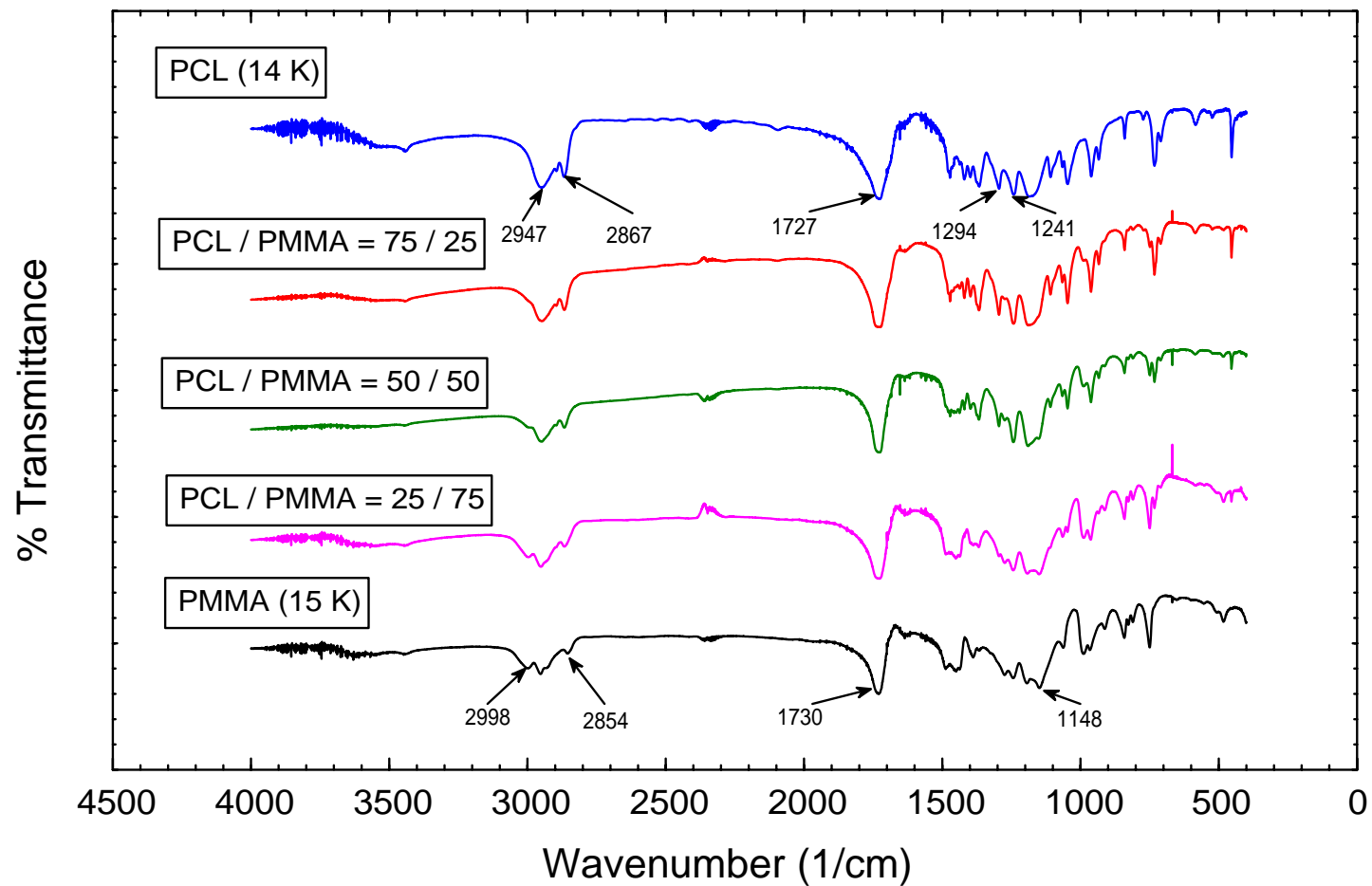


Figure 9.13 Comparison of FTIR spectra for PCL ($M_w = 14$ K), PMMA ($M_w = 15$ K), and their blends.

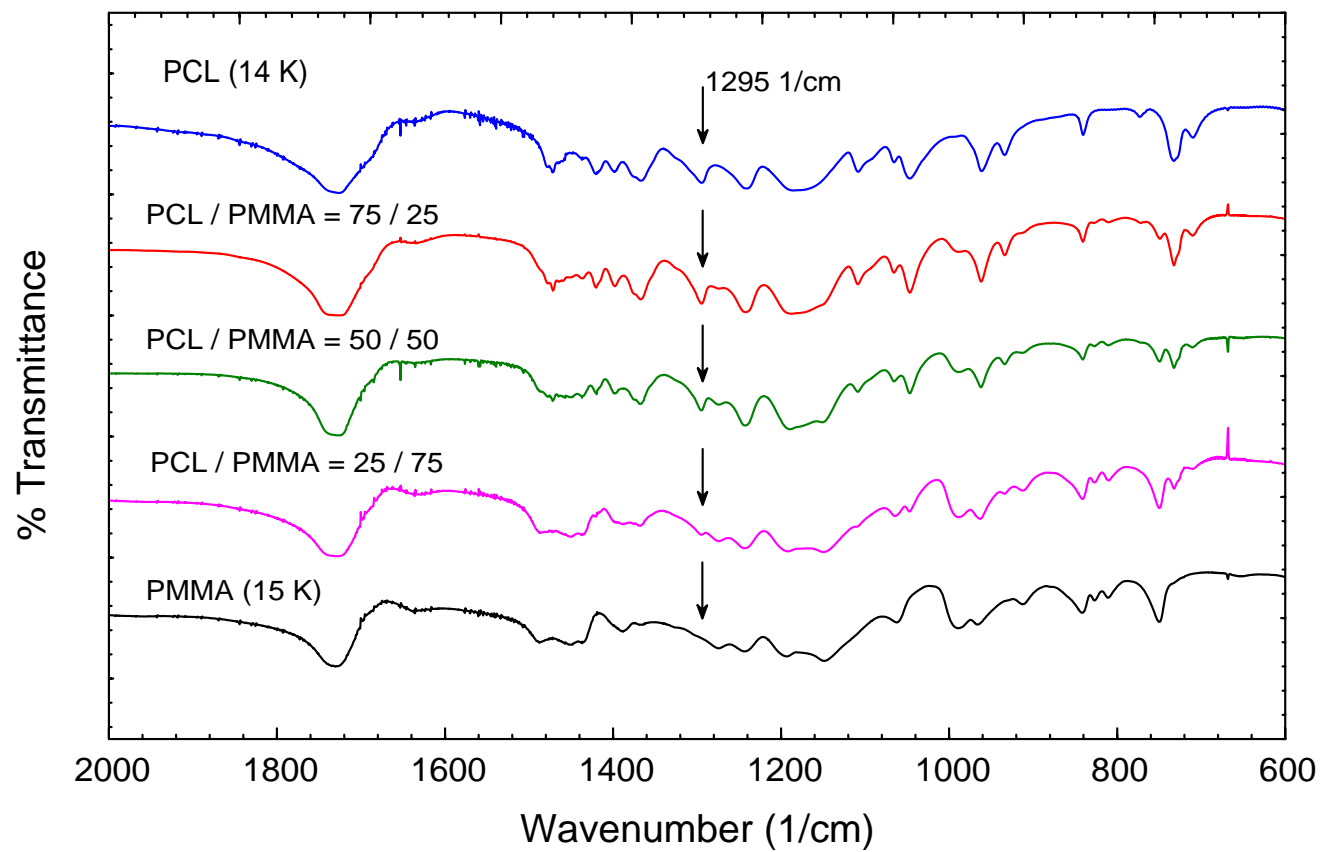


Figure 9.14 Comparison of FTIR spectra for PCL ($M_w = 14$ K), PMMA ($M_w = 15$ K), and their blends in the wavenumber range 600-2000 cm^{-1} . The band at 1295 cm^{-1} is used to characterize the crystallinity of the PCL and its blends with PMMA.