

## Poly( $\epsilon$ -caprolactone)/poly(vinyl methyl ether) blends: miscibility by calorimetric measurements

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### Abstract

The miscibility of the poly( $\epsilon$ -caprolactone)/poly(vinyl methyl ether), PCL/PVME system, is investigated by differential scanning calorimetry. Thermal analysis results indicate that the system is semicrystalline/amorphous and the PCL degree of crystallinity is influenced significantly by the composition of the mixture as well as by the thermal treatment. The two polymers form blends containing a single amorphous miscible phase over the entire composition range as evidenced by the constant presence of a single glass transition temperature,  $T_g$ . A phase separation process occurs when the blends are heated just above the melting point of PCL, giving a lower critical solution temperature (LCST) behaviour. © 1998 Elsevier Science B.V.

*Keywords:* Polymer blends; Calorimetry; PCL; PVME

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### 1. Introduction

Differential scanning calorimetry (DSC) is commonly used to study the miscibility of polymer blends. The usefulness of this technique originates from the possibility of examining physical phenomena such as glass transition, melting and crystallisation.

The observation of a single, composition-dependent, glass transition temperature,  $T_g$ , between those of the pure components is normally taken as evidence of miscibility [1–3]. On the contrary, immiscible polymer blends should exhibit two individual  $T_g$ s.

In amorphous blends such appearances may be used to follow the phase separation process, but in blends with one crystallizable component it may be difficult

to monitor a similar evolution. The possibility of observing two distinct  $T_g$ s depends not only on the  $T_g$  difference between the polymers but also on the position of the exothermic and endothermic peaks, the extent of the crystallinity in the system and the final difference in composition between the separated phases.

Instead of looking for changes of  $T_g$ s, it might be possible to follow the phase separation process by examining the crystallisation and melting phenomena. Thus, the aim of the work is to investigate the miscibility of poly( $\epsilon$ -caprolactone) and poly(vinyl methyl ether) [4].

### 2. Experimental

The polymers used in this study were purchased from Aldrich-Chemie. Poly( $\epsilon$ -caprolactone) had a

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nominal  $\bar{M}_w = 85\,000\text{ g mol}^{-1}$  and  $\bar{M}_n = 48\,000\text{ g mol}^{-1}$ . Poly(vinyl methyl ether), supplied as a 50 wt.% water solution, was dried under vacuum at 323.15 K for at least 48 h. The intrinsic viscosity of PVME in butanone gave  $\bar{M}_v = 32\,500\text{ g mol}^{-1}$ . The two polymers were not subjected to further purification procedures.

Blends were prepared by solvent casting: appropriate amounts of PCL and PVME were mixed and dissolved in toluene (Aldrich-Chemie), yielding a 5 wt.% solution. The solvent was completely removed first air drying at room temperature for a week and then vacuum drying at 343 K for 48 h.

Thermal transition of the blends were examined with a Mettler TA3000 differential scanning calorimeter. A heating rate of 20 K/min and a cooling rate of 300 K/min were used. In each test, the as-cast sample was heated from room temperature to 373.15 K and then left for 1 min with the purpose of eliminating the effects of previous thermal histories and of ensuring complete melting of PCL crystals. A first heating scan was recorded. Subsequently, the sample was quenched to 153.15 K and then heated to 373.15 K. In the second scan, the glass transition temperature was determined from the midpoint of the change in the specific heat,  $\Delta c_p$ .

In order to investigate the phase separation, this scanning procedure was repeated so that a series of scan were obtained with different annealing temperatures,  $T_a$ , and annealing times,  $t_a$ .

The degree of crystallinity of PCL was determined calculating both exothermic and endothermic heats and assuming a 100% crystalline heat of fusion of 136.08 j/g.

### 3. Results and discussion

Fig. 1 displays several scans of PCL, PVME and their blends: the constant presence of a single, composition dependent, glass transition temperature suggests miscibility between poly( $\epsilon$ -caprolactone) and poly(vinyl methyl ether). It is evident from the melting endotherms that PCL is partially crystalline in the mixture even at low concentration. Under the experimental conditions used, pure PCL and PCL-rich blends readily crystallise during quenching and no further crystallisation occurs during the heating scan. An increase of PVME amount in the system gradually leads to a larger presence of amorphous PCL at low temperature, but crystallisation takes place upon heating as evidenced by an exothermic peak. In PVME-

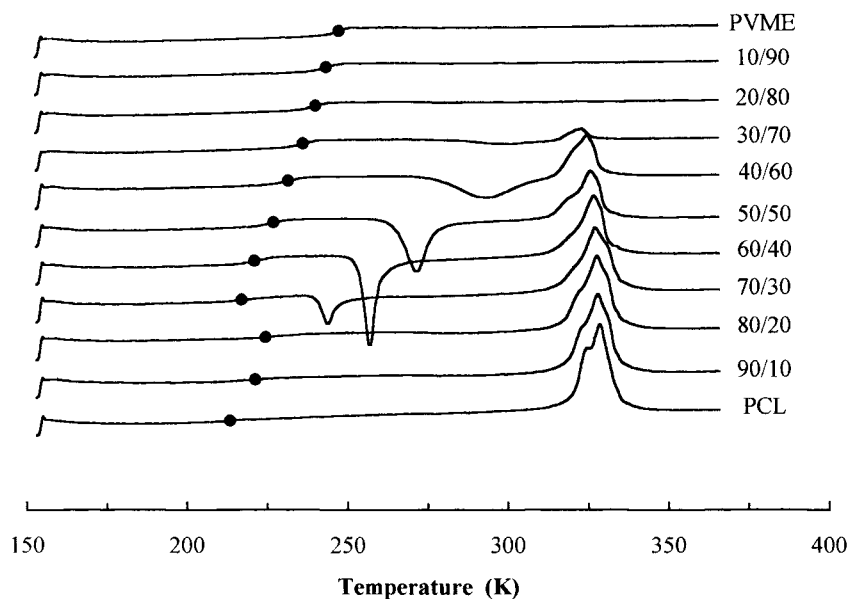


Fig. 1. DSC scans of PCL, PVME and their blends.

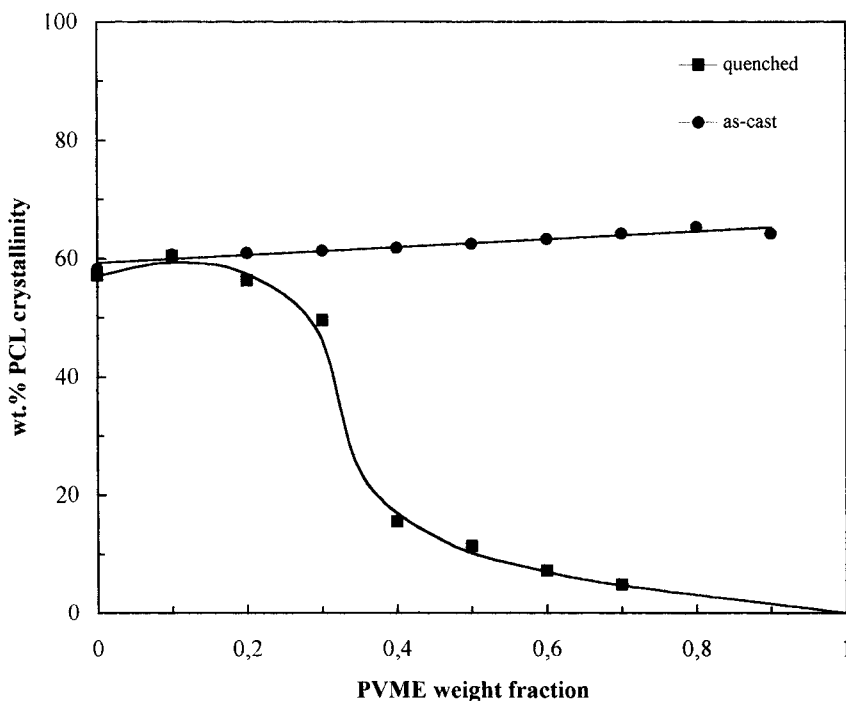


Fig. 2. Weight percent PCL crystallinity obtained from as-cast (●) and quenched (■) samples.

rich blends, the melting endotherm does not appear following either quenching to low temperature or heating.

Fig. 2 shows the degree of crystallinity for as-cast samples and quenched samples, expressed in % w/w of PCL as a function of the concentration of the amorphous component. The as-cast blends always have higher PCL crystallinity than the corresponding quenched ones and the addition of PVME seems to increase the PCL crystallisation. In effect, the PCL crystallinity found in the as-cast samples may be viewed as the 'quasi-equilibrium' crystallinity at room temperature and, moreover, since the  $T_g$  of the amorphous component is much lower than the PCL melting temperature,  $T_m$ , the amorphous regions remain mobile throughout and do not hamper the crystallisation process. In contrast, the PCL crystallinity in the quenched samples shows a marked reduction at ~30% w/w PVME composition and decreases towards zero at high PVME content. Such different behaviour depends on kinetic factors: because the crystallisation is governed by the degree of undercooling and the resistance to segmental motions, this

process may be limited by quenching upon adding to the system an amorphous diluent that tends to decrease the temperature gap ( $T_m - T_g$ ) and, then, restrict crystallisation [5].

Due to the presence of crystallinity, the composition of the amorphous phase is different from the overall blend composition. Assuming that this system consists of two phases, a crystalline PCL phase and an homogeneous mixed amorphous PCL/PVME phase, it appears necessary to calculate the real weight fraction of the components in the mixed amorphous phase at the time when each sample passes through the  $T_g$  region.

Fig. 3 shows how the glass transition temperature depends on the correct weight fraction of PVME.

Actually, crystallinity in PCL-rich blends seems to affect also the measured glass transition temperatures: the restrictions on segmental motion that the crystalline regions place on the amorphous regions appears to increase the energy requirements for the transition and, thereby, to raise  $T_g$ s. However, because of the low degree of crystallinity, the  $T_g$  data obtained from blends containing 50% w/w or more PVME, may

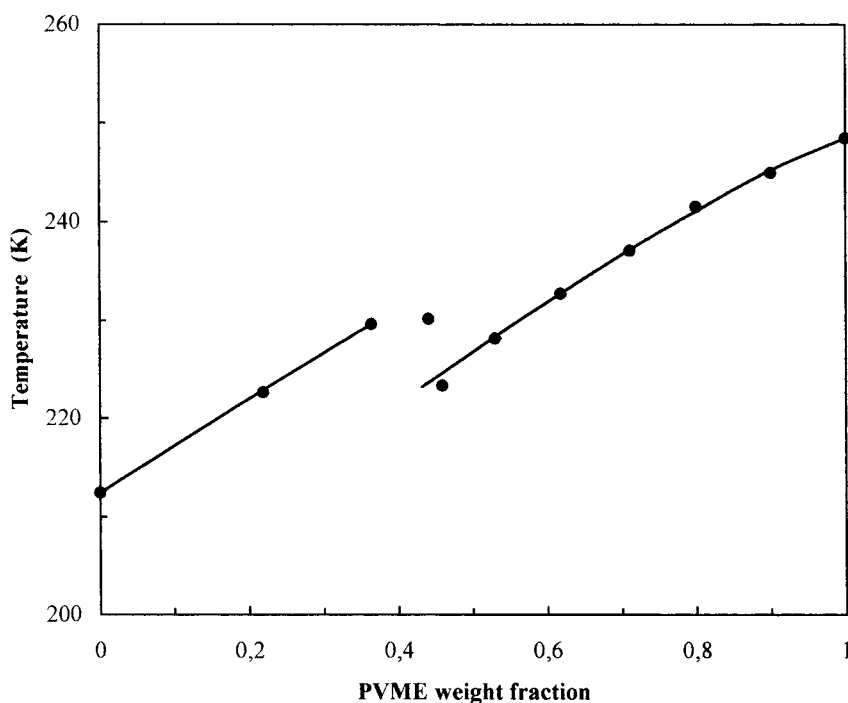


Fig. 3. Glass transition temperatures for PCL/PVME blends as a function of overall blend composition.

be correlated equally well, assuming the variations in value within experimental error.

Several theoretical equations have been proposed to explain the  $T_g$ -composition behaviour of binary polymer blends [3]. In the expression proposed by Utracki [6] and derived from the more general Couchman–Karasz equation [7]:

$$\ln T_g = \frac{\omega_1 \ln T_{g_1} + k\omega_2 \ln T_{g_2}}{\omega_1 + k\omega_2} \quad (1)$$

$T_g$  is the glass transition temperature of the blend,  $\omega_i$  is the weight fraction of the  $i$ -th component and  $k = \Delta c_{p_2} / \Delta c_{p_1}$ , where  $\Delta c_{p_i}$  is the difference in specific heat between the liquid and glassy state at  $T_{g_i}$ . The  $k$  parameter is often taken as an adjustable parameter but it is preferred to use a fixed value calculated from experimental data of  $\Delta c_{p_i}$ . In the simple two phase model, this variation is expected to be directly proportional to the amount of amorphous material. Thus, the  $\Delta c_p$  value for PCL is normalised by the mass of amorphous material in the semicrystalline polymer, yielding a  $k$  parameter of 1.33. A trial and error determination is employed to fit glass transition data

for blends and, then, to extrapolate a value of 202.85 K for  $T_g$  of amorphous PCL. The results are depicted in Fig. 4.

Fig. 5 displays a series of scans obtained from blends containing 30 wt.% PCL for various annealing temperatures. It can be noticed that the PLC melting peak gradually increases with  $T_a$ . This indicates that a phase separation process occurs (lower critical solution temperature (LCST) behaviour): one phase is enriched in PVME whereas the other one is depleted of PVME, leading to the crystallisation and melting of PCL during the heating scan. Phase separation depends not only on the annealing temperature but also on the annealing time. As evidenced in Fig. 6, the melting peak increases with  $t_a$  and the lower  $T_a$ , the longer time is necessary to the phase separation to extend.

In Fig. 7, the scan refer to blends containing 70 wt.% PCL annealed at different temperatures. These shows how the exothermic peak gradually decreases with an increase of  $T_a$ , until the curve becomes similar to that of pure PCL. Moreover, it is evident that such phase separation also influences

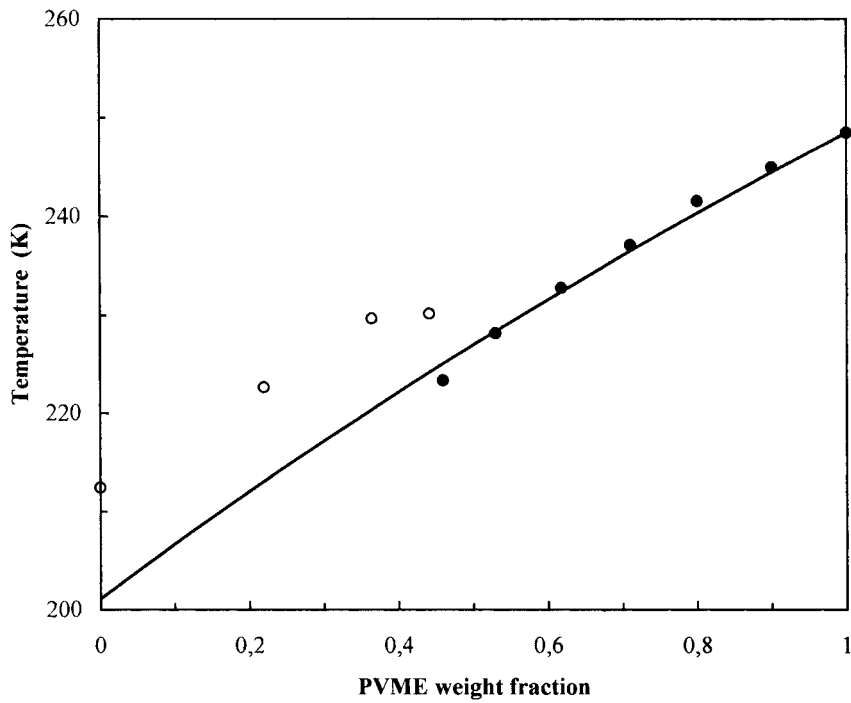


Fig. 4. Glass transition temperatures for PCL/PVME blends as a function of amorphous phase composition. The line is plotted according to the Utracki equation ( $k=1.33$ ) and is fitted to (●) experimental data.

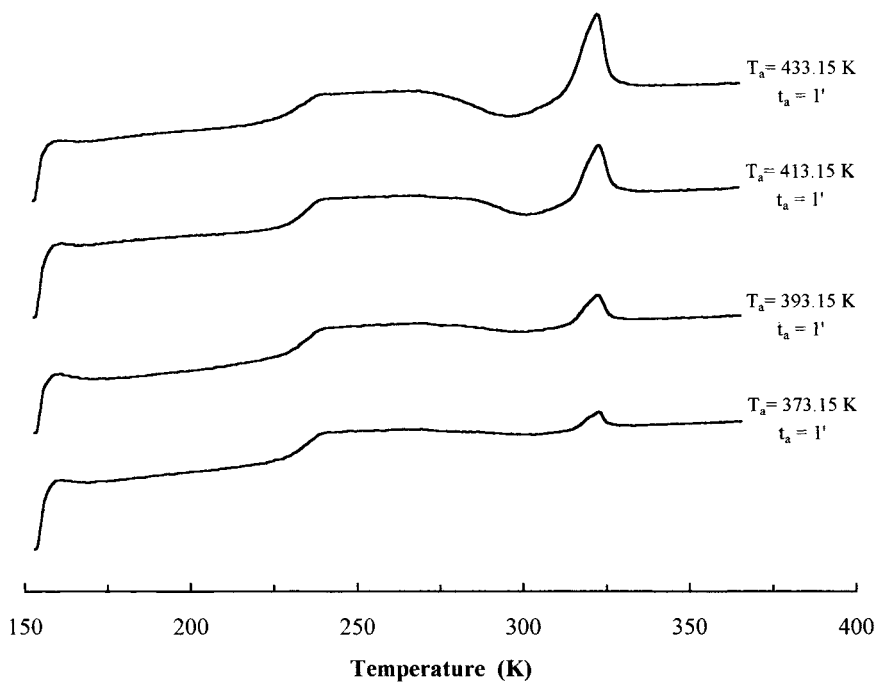


Fig. 5. DSC scans of PCL/PVME containing 30 wt.% PCL for various annealing temperatures ( $T_a$ ) and the same annealing time ( $t_a$ ).

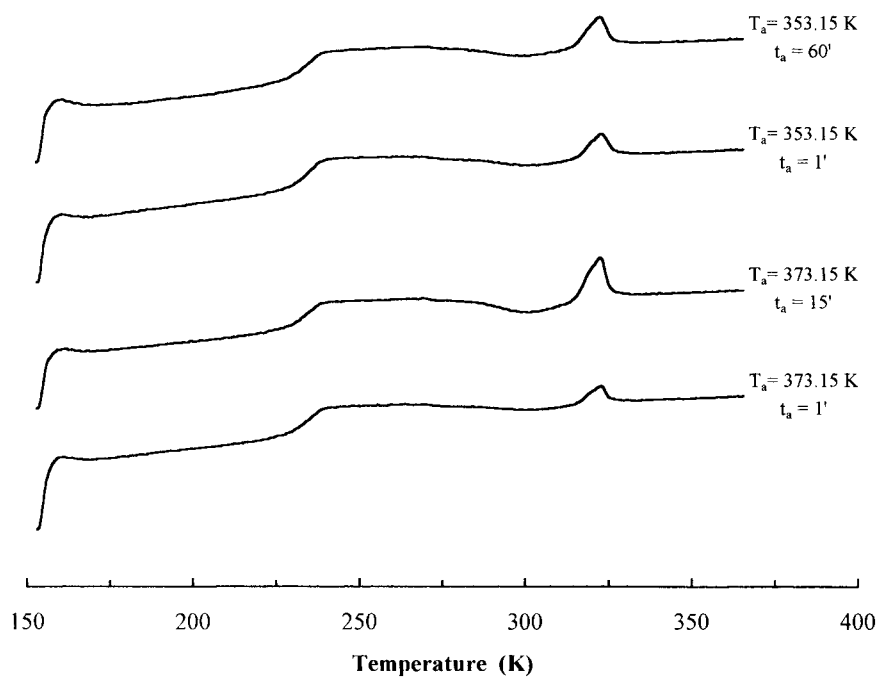


Fig. 6. DSC scans of PCL/PVME containing 30 wt.% PCL for various annealing temperatures ( $T_a$ ) and annealing times ( $t_a$ ).

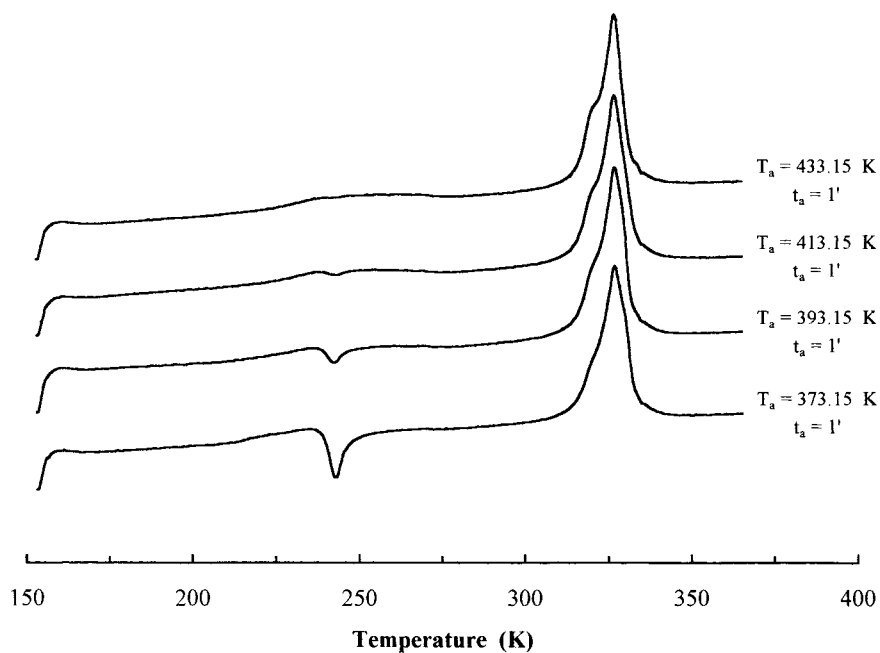


Fig. 7. DSC scans of PCL/PVME containing 70 wt.% PCL for various annealing temperatures ( $T_a$ ) and the same annealing time ( $t_a$ ).

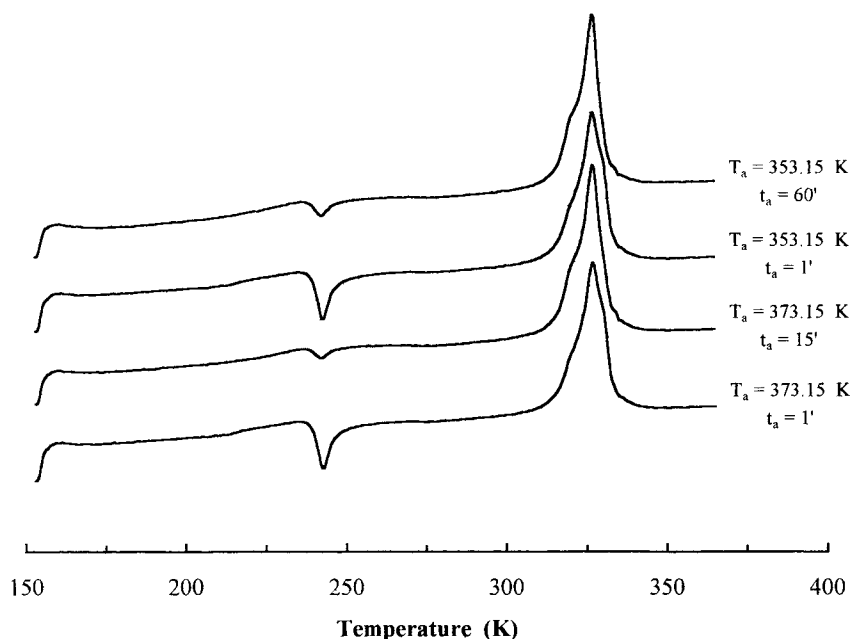


Fig. 8. DSC scans of PCL/PVME containing 70 wt.% PCL for various annealing temperatures ( $T_a$ ) and annealing time ( $t_a$ ).

the shape of the melting peak: the shoulder gradually grows as a result of the melting of PCL crystals formed during quenching. The dependence of this process on annealing time is illustrated in Fig. 8.

#### 4. Conclusions

The system PCL/PVME is clearly semicrystalline and the crystallisation behaviour of PCL in the mixture strongly depends both on the composition and on the thermal treatment.

Though crystallinity appears to influence the measured  $T_g$  values, the blends exhibit a single glass transition over the entire composition range, suggesting miscibility in the amorphous phase. Moreover, the trend can be monitored by Utracki equation using a  $k$  parameter obtained from experimental  $\Delta c_p$  data.

Thermal analysis allows to describe quite well the stability of the amorphous phase. This does not appear to be caused by any chemical specific interactions and the system is found to become unstable when the temperature is raised just above the PCL melting point, according to the presence of a LCST.

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