CHAPTER 4

RESULTS ON THERMAL STUDIES OF POLY(ε-CAPROLACTONE) COMPLEXES

4.1 Introduction

In order to understand the transport property of the polymer electrolyte, it is also important to investigate the thermal properties. In this work, Differential Scanning Calorimetry (DSC) analysis was used to correlate the glass transition temperature, T_g , melting point, T_{m} and the degree of crystallinity to the ionic conductivity of the polymer electrolytes. It has been well established that crystalline and amorphous phases co-exist in most of the polymeric materials. PCL is one of the semi crystalline polymers exhibiting both the glass transition and melting transition [Fonseca *et al.*, 2007].

At T_{g}, a step transition of endothermic reaction will be observed in the DSC trace. This is the characteristic of an amorphous structure, indicating a transition from disordered glassy solid (brittle amorphous) into a more rubbery solid. There are three temperature values: onset, midpoint and endset. In this work, the midpoint is taken as T_{g} and it is calculated from the peak maximum in the first derivative of heat flow, using TA Universal Analysis software.

On the other hand, a broad endothermic peak shall be obtained, showing the crystalline melting. Within the onset and endset temperature, the peak temperature is taken as T_m. T_m is a thermal property of a crystalline structure, phase transition from solid (ordered structure) to liquid (disordered structure).

4.2 Thermal Studies of PCL-NH_4SCN system

These thermal analyses were performed using a DSC instrument (Perkin Elmer DSC 8000). The samples were heated to 80 °C at a heating rate of 20 °C/min (isothermal hold for 10 minutes), cooling down to -90 °C at a cooling rate of 20 °C/min and then heated again to 90 °C at 20 °C /min under dry nitrogen atmosphere. The second heat data is used to analyze the T_g, T_m and ΔH_m. High heating rate was used in order to observe clearer T_g signal.

Fig. 4.1 illustrates the thermal behavior of pure PCL and of PCL containing 10, 20, 26 and 32 wt.% NH_4SCN while inset shows the magnified thermograms indicating T_m. Fig. 4.2 is the magnified thermograms of the complexes, showing T_g. The DSC results are also tabulated in Table 4.1.

The addition of salt to the polymer solution during the preparation stage resulted in the formation of polymer-salt complexes and a change in the crystalline nature of the sample. Fig. 4.1 inset shows an endothermic peak indicating the first-order transition temperature or melting point of pure PCL at 56 ºC. This is attributed to the melting of crystalline PCL that reflects the presence of uncomplexed crystalline phase. Fonseca *et. al*. (2006b) also obtained a similar result with T_m at 55.7 °C.

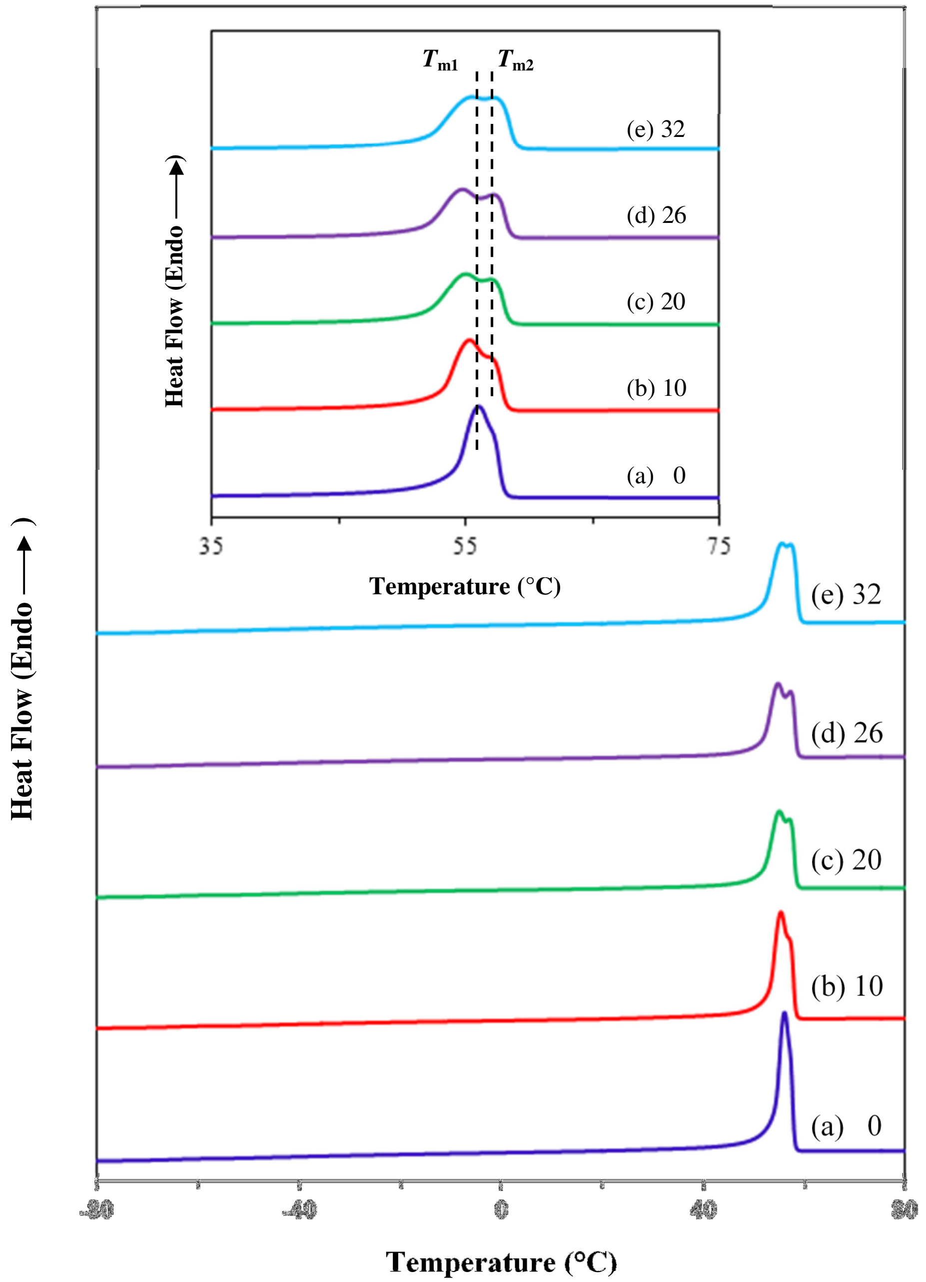

Fig. 4.1 DSC thermograms of PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN. Inset shows the magnified thermograms indicating T_m.

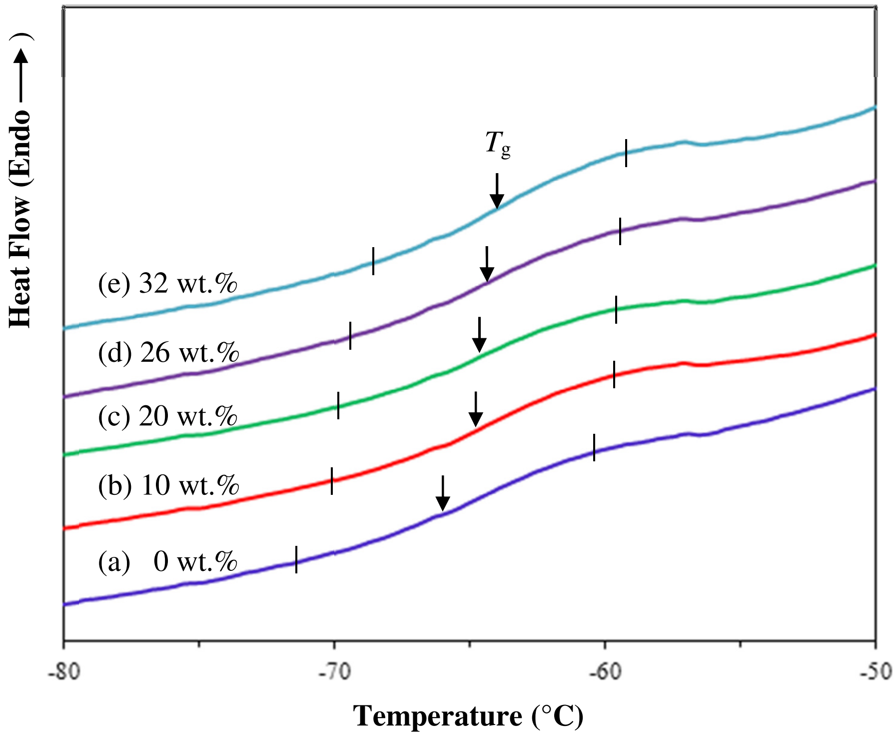

Fig. 4.2 Magnified DSC thermograms of PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN, showing T_g.

Table 4.1
DSC results of PCL-NH_4SCN complexes added with 0 to 32 wt.% NH_4SCN

PCL:NH_4SCN ratio	T_g (°C)	T_m (°C) Peak 1	Peak 2	ΔH_m (Jg^{-1})
100:0	-66.0	56.0	-	96.4
90:10	-64.7	55.3	57.1	88.5
80:20	-64.6	55.0	57.1	79.0
74:26	-64.3	54.7	57.2	78.1
68:32	-63.9	55.5	57.3	86.3

When 10 wt.% salt is accommodated into the polymer matrix, the melting is observed to begin from lower temperature achieving a melting peak at 55.3 °C. This melting peak continues to decrease to 55.0 °C and 54.7 °C at 20 and 26 wt.% salt respectively. Similar finding was reported in the literature for other polymer–salt system. When $NiBr_2$ was added to PEO, Cai *et al*. (1992) observed a decreased melting temperature for all PEO-$NiBr_2$ compositions. T_m was also observed to reduce by Fonseca and co-workers (2006b) up to 12 wt.% of salt in PCL-$LiClO_4$ system. According to literature [Sperling, 1986; Choi *et al*., 2007], this lowering of T_m was a common finding in many polymers with impurities and might be caused by thermodynamic depression as a result of the reduction in chemical potential [He *et al*., 2004]. In this work, the incorporated salt is believed to act as impurities to lower the T_m of PCL.

Closer inspection shows that the melting peak of the 10 wt.% salt sample is broadened and a weak shoulder appears at ~57 °C. This shoulder becomes more prominent at 20 wt.% salt onwards. Since the melting temperature of the ammonium salt is 149.6 °C, way beyond 57 °C, the existence of this second peak is attributed to the melting of PCL-NH_4SCN complex phase.

Other literature has reported that the splitting of the melting peak is attributed to the melting of two different types of crystal phases (perfect crystal phase and imperfect crystal phase) [Fonseca *et al*., 2007]. These double T_m peaks were depicted as pure PEO phase and PEO-salt complex phase in many different PEO-based systems such as PEO-$NiBr_2$ system reported by Huq and Farrington (1998) and PEO-NH_4ClO_4 system investigated by Dey *et al*. (2008). In the present work, the complexation between PCL and NH_4SCN should be supported by T_g analysis in the following section and FTIR result in chapter 6.

All PCL-salt systems shown in Fig. 4.2 exhibited a single T_g indicating that no microphase separation occurs in this system. T_g of pure PCL is found to be ~-66 ºC. This is in reasonable agreement with T_g of -65 ºC reported by Fonseca *et. al*. (2007). This glass transition temperature is observed to increase gradually with increasing salt concentration from -66.0 °C to -63.9 °C in 68 wt.% PCL-32 wt.% NH_4SCN sample.

The T_g increasing trend confirms that complexation has occured between the polymer host and the incorporating salt. Idris *et al*., (2001) reported an increase of T_g with increasing salt concentration in the modified natural rubber-based PE added with $LiCF_3SO_3$. Similar behavior was observed by Cruickshank *et al.* (1995) in the PEG-based system added with various salts which includes $LiCF_3SO_3$, $LiClO_4$, $NaClO_4$, $LiBF_4$ and $NaBF_4$. The interaction between PCL and NH_4SCN is also expected to disturb the polymer chain orderly crystalline matrix.

The area under the curve for the melting endothermic is associated to the crystallinity of the sample. The enthalpy of melting is displayed in Table 4.1. For pure PCL, ΔH_m^0 is observed as high as 96.4 Jg^{-1}. ΔH_m drops to 88.5, 79.0 and 78.1 Jg^{-1} at 10, 20 and 26 wt.% salt before it bounds back to 86.3 Jg^{-1} at 32 wt.%. The relative degree of crystallinity, χ_C of the sample is then estimated as shown in Fig.4.3.

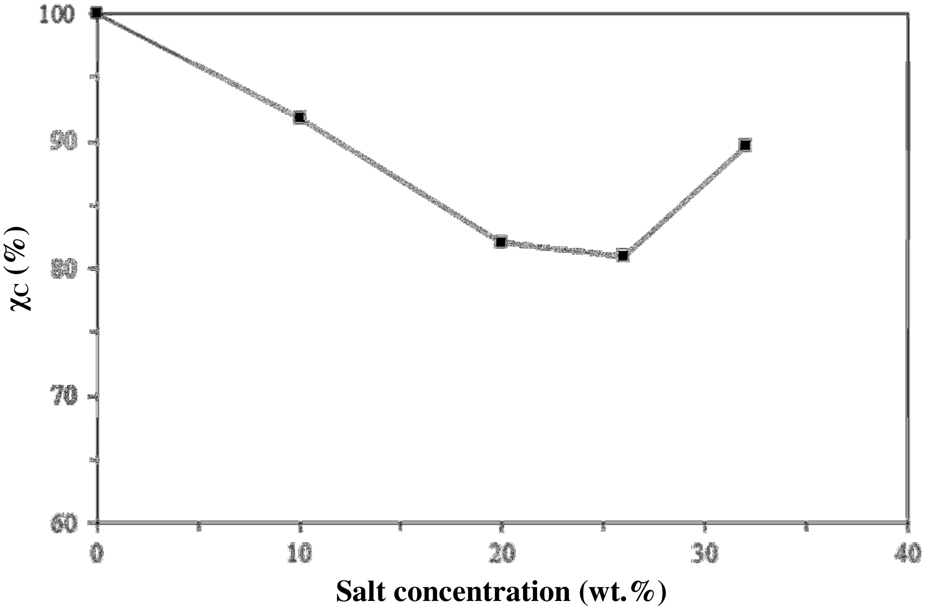

Fig. 4.3 Relative degree of crystallinity as a function of salt content for PCL-NH_4SCN films added with 0 to 32 wt.% NH_4SCN.

χ_C of PCL-salt complexes is found to decrease to 91.8 % compared to pure unsalted PCL sample when 10 wt.% NH_4SCN salt is added. The crystalline fraction reduces continuously to 82.0 % at 20 wt.% salt and reaches a minimum value of 81.0 % at 26 wt.% salt. However, salt concentration at 32 wt.% shows an increase of crystallinity to 89.6 %. Since the amorphous content is often reported to be the high conducting phase in a polymer electrolyte system [Kumar and Sekhon, 2002], the highest conducting sample is expected to be that with 26 wt.% salt incorporated in the polymer. This will be confirmed later in Section 7.2.

The general trend of reduction in crystalline fraction and T_m can be attributed to the inhibition of crystallization by the dissolved ions. As more salt is interacted with PCL, it disrupts the order of polymer chain and thus suppresses the crystalline phase of the polymer.

4.3 Thermal studies of PCL-NH_4SCN-EC system

These thermal analyses were performed with TA Instruments DSC-Q200. The samples were heated to 80 ^oC at a heating rate of 10 ^oC/min (isothermal hold for 10 minutes), cool down to -90 °C at a cooling rate of 40 °C/min and then heated again to 90 °C at 10 °C /min under dry nitrogen atmosphere. The second heat data is used to analyze the T_g, T_m and ΔH_m.

It must be mentioned that the cooling rate for this system is higher than PCL-NH_4SCN system and the heating rate is lower. Therefore, the melting enthalpy of PCL-NH_4SCN-EC systems is expected to be lower than PCL-NH_4SCN systems as described in Section 4.2. Nevertheless, the calculation of the relative degree of crystallinity, χ_C shall not be affected since ΔH_m^0 in equation 3.2 is taken as the melting enthalpy of pure PCL membrane that was measured by the corresponding instrument and system. All samples in each system had gone through the same controlled thermal history (first heating scan) to compare T_g, T_m and ΔH_m relatively.

Fig. 4.4 presents the thermal behavior of pure EC, pure PCL and PCL-NH_4SCN-EC complexes added with 10 to 50 wt.% EC. On the other hand, Fig. 4.5 and 4.6 show the magnified thermograms, indicating T_g and T_m. The DSC results are depicted in Table 4.2.

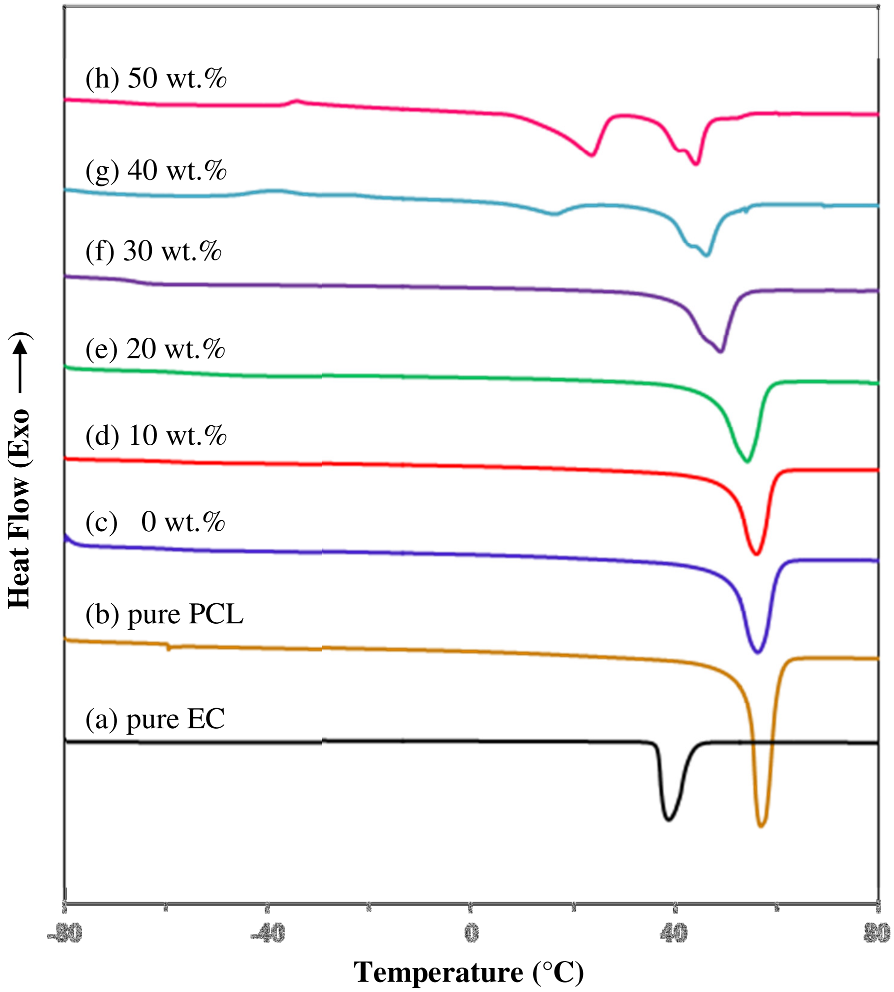

Fig. 4.4 DSC thermograms of pure EC, pure PCL and PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC.

Table 4.2
DSC results of pure PCL and PCL-NH_4SCN-EC complexes added with 0 to 50 wt.% EC

	EC content, (wt.%)	T_g (°C)	T_m (°C)			ΔH_m (Jg^{-1})
			Peak 1	Peak 2	Peak 3	
Pure PCL		-59.8	57.0	-	-	60.4
PCL-NH_4SCN-EC complexes	0	-59.7	56.4	-	-	49.6
	10	-59.9	56.1	-	-	39.5
	20	-56.9	54.3	-	-	38.9
	30	-66.0	49.0	46.2	-	32.4
	40	-76.1	46.3	43.0	17.0	28.0
	50	-	44.1	40.8	23.8	23.4

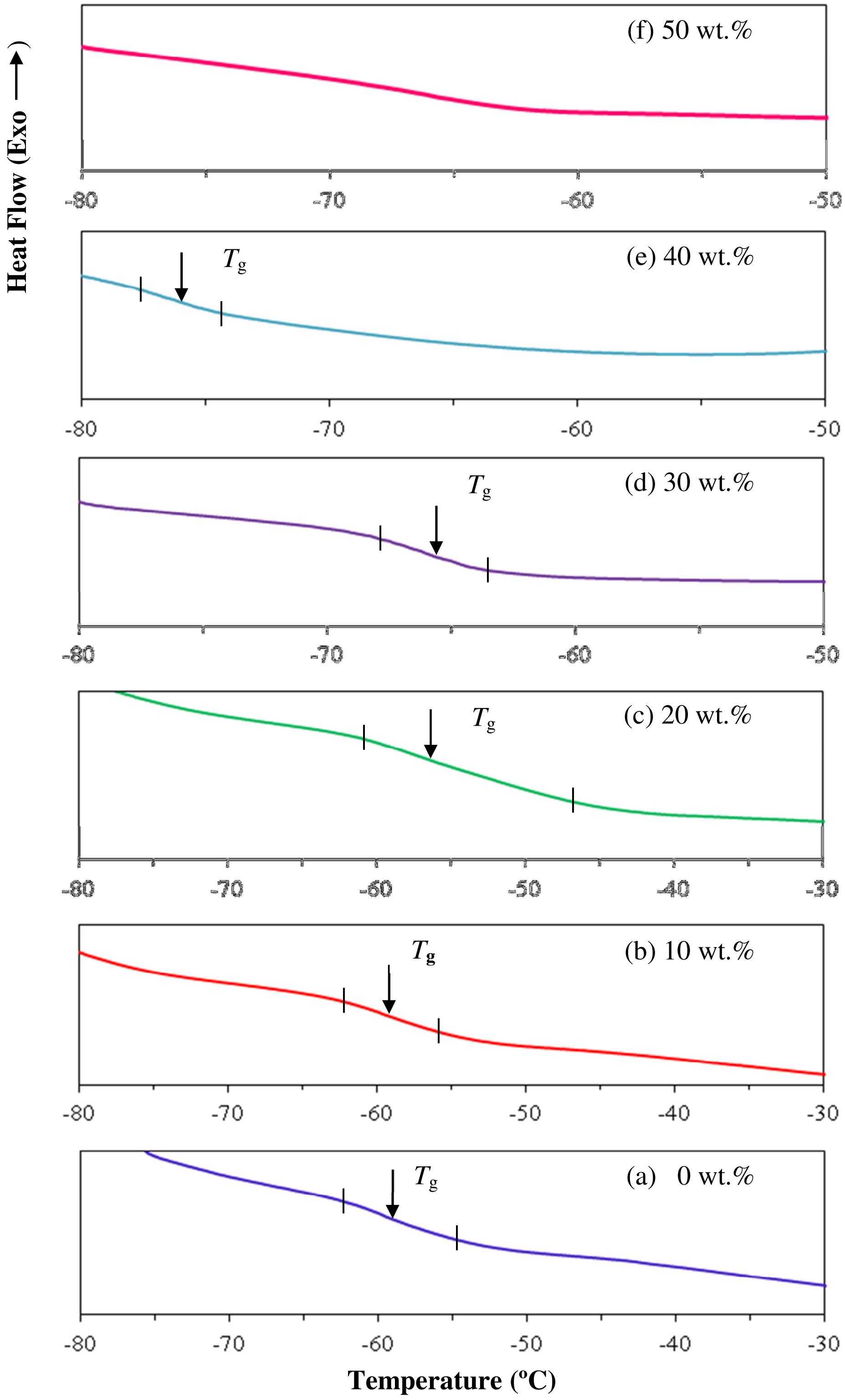

Fig. 4.5 Magnified DSC thermograms of PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC, showing T_g.

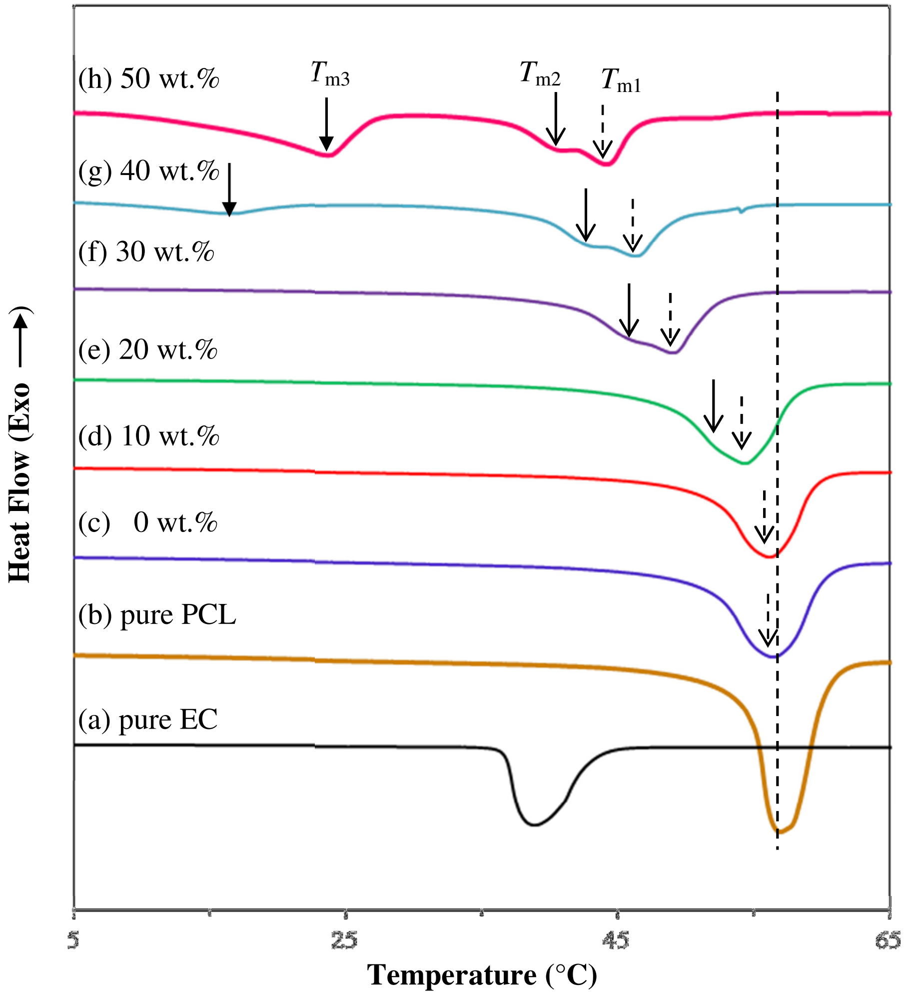

Fig. 4.6 Magnified DSC thermograms of PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC, showing T_m.

The addition of EC into the polymer-salt complexes has changed the crystallization nature of the sample. Fig. 4.6(a) and (b) show endothermic peaks indicating crystalline melting of pure EC and pure PCL at 36.7 °C and 57.0 °C, respectively. 0 wt.% EC (the highest conducting PCL-NH_4SCN film before adding EC) in Fig. 4.6(c) displays a single melting peak at 56.4 ºC.

When 10 wt.% EC is introduced, T_m is observed to shift from 56.4 °C to 56.1 °C. The melting temperature keeps decreasing to 54.3 °C and 49.0 °C with increase of

EC content to 20 wt.% and 30 wt.%, respectively. This reduction of T_m reflects that the PCL and EC are miscible in the melting state.

Moreover, the endothermic peak at 30 wt.% EC becomes broader and a second melting peak at 46.2 °C appears as a shoulder. EC content beyond 30 wt.% displays multiple endothermic peaks as shown in Fig.4.5(f) and (g). The lowest melting temperature was recorded for the system containing 50 wt.% EC. This lowering of T_m and multiple peaks are commonly observed in literature [Jiang *et al.*, 1997; Bhide and Hariharan, 2007] for plasticized polymer electrolyte system. According to literature, the appearance of multiple melting peaks is a result of electrolyte aggregates of polymer segments of different chain length [Jiang *et al.*, 2007] or occurrence of recrystallization during melting [Barbosa *et al.*, 2010]. In this work, multiple T_m could be attributed to new PCL-EC complex phases of different chain length of PCL segments. The interaction between PCL and EC would be studied in FTIR chapter.

Refer to Table 4.2, the T_g of pure PCL obtained by this instrument is -59.8 °C. No big changes of T_g is observed until addition of 20 wt.% EC into the polymer electrolyte system. A moderate drop of T_g value to -56.9 °C is found at 20 wt.% EC. Drastic decrease of T_g is only apparent from 30 wt.% EC onwards. T_g, the glass transition temperature reduces from -56.9 to -66.0 and -76.7 °C at 30 wt.% and 40 wt.% EC, respectively. Upon addition of 50 wt.% EC and beyond, T_g is believed to fall outside the lower limit temperature window of the instrument.

Since T_g is a measure of the chain ability to rotate about the chain bonds, a decrease of T_g means the polymer backbone becomes more flexible [Bandara *et al.*, 1998; Kumar and Sekhon, 2002; Wang *et al.*, 2005c]. Thus, the lowering T_g is a representative of increase in polymer segmental motion which could assist the ionic motion and results in conductivity enhancement. As such it is interesting to look at the electrical studies in chapter 7.

The enthalpy of melting, ΔH_m is calculated from the area under the melting peak as presented in Table 4.2. The melting enthalpy for pure PCL membrane is 60.4 J g^{-1}. The PCL-NH_4SCN sample before adding EC (0 wt.% EC) records a value of 49.6 J g^{-1}. This enthalpy of melting continue to reduce to 39.5, 38.9, 32.4 and 28.0 J g^{-1} at EC concentration 10, 20, 30 and 40 wt.%, respectively. The minimum ΔH_m is 23.4 J g^{-1} when EC concentration is 50 wt.%. The calculated relative degree of crystallinity, χ_C is shown in Fig.4.7.

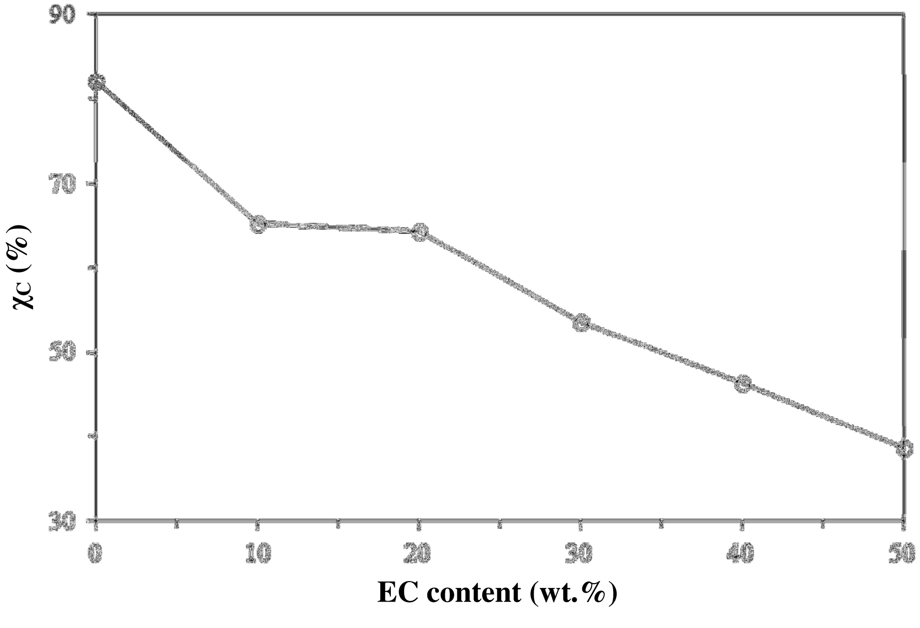

Fig. 4.7 Relative degree of crystallinity as a function of EC content for PCL-NH_4SCN-EC films added with 0 to 50 wt.% EC.

Fig. 4.7 shows that the addition of EC results in the monotonous reduction of χ_C. This implies that the 50 wt.% EC sample is the most amorphous samples among the PCL-NH_4SCN-EC system. It seems that EC molecules are trapped into the PCL matrix and interrupt polymer-polymer interaction either by occupying or increasing inter and intra-chain separations [Bandara *et al*., 1998]. This disrupts the original polymer orderly crystalline structure [Kuila *et al*., 2007], causing more entanglement of polymer chains and increase the amorphous domain. Referring to Pan *et al*. (2007), the highest conducting sample gives the lowest value of χ_c in PEO-$LiClO_4$-TiO_2 polymer electrolyte system. Therefore, sample containing 50 wt.% EC is expected to be the highest conducting sample, which will be verified and discussed in detail in chapter 7.

4.4 Summary

For PCL-NH_4SCN system:

- When more NH_4SCN is added to PCL-salt films, T_m of PCL reduces and the DSC endothermic band for all samples becomes broader. Second melting peak appears prominently on samples containing 20 wt.% salt onwards, which can be attributed to a new crystalline phase of PCL-NH_4SCN complex.

- The glass transition temperature is observed to increase gradually with increasing NH_4SCN concentration. This indicates interaction between PCL and NH_4SCN. The complexation between PCL and NH_4SCN shall be verified in the FTIR chapter.

- The area under the melting peak (melting enthalpy) is found to reduce with addition of salt until a minimum at 26 wt.% salt. This implies that a PCL-

NH_4SCN complex with 26 wt.% salt is the most amorphous sample. Therefore, the most conducting sample for this system is expected to be at 26 wt.% salt and will be verified using electrochemical impedance spectroscopy in Chapter 7.

For PCL-NH_4SCN-EC system:

- T_m reduces with increasing EC content and multiple peaks are observed from 30 wt.% EC onwards. These multiple T_m could be attributed to new PCL-EC complex phases. The PCL-EC interaction would be studied in FTIR chapter.

- Massive decrease of glass transition temperature is apparent upon addition of 30 wt.% EC onwards. This shows that the polymer segments are easier to move to assist ionic motion.

- From analysis of the relative degree of crystallinity, the sample containing 50 wt.% EC is the most amorphous sample among the PCL-NH_4SCN-EC complexes. Thus, the 50 wt.% EC sample should exhibit the highest conductivity. This will be studied in chapter 7.

How do these DSC results contribute to better understanding of the morphology and structural studies? This will be dealt in next chapter.