CHAPTER 6

THERMAL ANALYSIS OF HYDROGENATED POLYMER

The term thermal analyses is frequently used to define all methods in which investigations are made of a material property that changes as a function of temperature. Thermal analyses refers to conventional methods such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA). Some methods, such as DTA and DSC are specially designed to monitor the thermal properties of material under enthalpy or entropy changes. Whereas others i.e. DMTA measure the dynamic mechanical properties of a sample (storage modulus, loss tangent) while the temperature is changed. Thermogravimetric analysis (TGA) monitors weight losses as the temperature is increased. Weight losses occur as the result of driving off volatile components and the degradation of polymer at high temperature (Campbell and White, 1989).

The advantages of thermal analyses over other analytical methods can be summarized as follows: (i) the sample can be studied over a wide temperature range using various temperature programs (ii) almost any physical form of sample (solid, liquid, or gel) can be accommodated using a variety of sample vessels or attachments (iii) a small amount of sample (0.1 μg – 10 mg) is required (iv) the atmosphere in the vicinity of the sample can be standardized (v) the time required to complete an experiment ranges from several minutes to several hours and (vi) thermal analyses instruments are reasonably priced.

Hydrogenation reduces the degree of unsaturation in the diene polymers and leads to significant changes on the chemical, physical and mechanical properties of the hydrogenated diene polymers (McManus and Rempel, 1995; Singha et al., 1997a: 309-367). Some researchers have employed thermal analyses to investigate the thermal properties of hydrogenated polymers. Doi et al. (1986) investigated the thermal properties of hydrogenated polybutadiene in the presence of RhCl(PPh$_3$)$_3$ by using differential scanning calorimetry (DSC). The degradation temperature of hydrogenated natural rubber using RhCl(PPh$_3$)$_3$ increases with the degree of hydrogenation (Singha, 1998). Hydrogenated nitrile rubbers resulting from nitrile

butadiene rubber hydrogenation in the presence of $RhCl(PPh_3)_3$ have improved low temperature resistance and improved tensile stress properties (Bhattacharjee et al., 1991). The resistance to oxidation as well as improved thermal stability of hydrogenated NBR have been reported (Kubo, 1993). Cassano et al. (1998) studied the thermal stability of hydrogenated polybutadiene and the heat fusion increases as the degree of hydrogenation increases from 0 to 89% conversion. Charmondusit (2001) reported on the thermal properties of NR and hydrogenated NR and showed that the high temperature properties of hydrogenated NR are much better than NR.

The purpose of this chapter is to consider the thermal properties of hydrogenated synthetic cis-1,4-polyisoprene (HCPIP) and hydrogenated natural rubber (HNR). The differential scanning calorimetry (DSC) provided the low temperature properties of the polymer (glass transition temperature, T_g). The thermal degradation of elastomer samples was investigated using thermogravimetric analysis (TGA).

6.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a technique that is used to determine the glass transition temperature (T_g) of elastomers. The glass transition is a phenomenon observed in amorphous polymers. In other words, the glass transition temperature is a property of the polymer. The state of polymer whether it is glassy or rubbery depends on whether its application temperature is above or below its glass transition temperature (Rosen, 1993).

The low temperature properties of hydrogenated polyisoprene (HCPIP), hydrogenated natural rubber (HNR), hydrogenated natural rubber latex (HNRL), polyisoprene (CPIP), natural rubber (NR) and natural rubber latex (NRL) were investigated. The DSC thermogram of the natural rubber, polyisoprene and their hydrogenated products are presented in Figure 6.1 – 6.3. The glass transition temperature (T_g) of the rubber sample was determined from the middle point of the incline portion of the DSC curve. The results summarized in Table 6.1 show that the glass transition temperatures of hydrogenated products were closed to those of starting polymers. This suggests that the hydrogenated polymers still show the amorphous properties. This is consistent with the investigation of properties of hydrogenated natural rubber (Charmondusit, 2001; Singha, 1998) and synthetic polyisoprene (Lal and Mark, 1986). However, some hydrogenated NRL has a T_g in the range of –11 to $3^{\circ}C$, which is much higher than the T_g of NRL because of gel

formation in the products. This may be due to the effects of crosslinking that restricts chain mobility and causes an increase in the apparent T_g. Completely hydrogenated CPIP yields the alternate ethylene-propylene copolymer. The glass transition temperature of random ethylene-propylene copolymer (EPM) is in the range of –9 to –60°C depending upon the comonomer content (Mani et al., 1994). The standard EPDM (ethylene/propylene = 50/50, diene = 9.5%) shows T_g at –44.6°C which is higher than hydrogenated polymer product (Hinchiranan). It is interesting that synthetic *cis*-1,4-polyisoprene, natural rubber and natural rubber latex show the same T_g value, therefore the non-rubber components present in the NR have no effect on the T_g. This agrees well with the observations by Loadman (1985) for different grades of NR. However, a very small variation in T_g may be observed due to the presence of *trans* isomers in synthetic polyisoprene. Sircar (1997) reported that T_g of common NR isomers (CPIP, balata, gutta-percha, synthetic *trans*-1,4-polyisoprene) obtained from the midpoint of DSC thermogram lies over a narrow range of temperature from about –70 to –63°C.

Table 6.1: DSC and TGA Results of Elastomers

Polymer	Hydrogenation (%)	T_g (°C)	T_{id} (°C)	T_{max} (°C)
CPIP	0	-59	361	386
HCPIP-1	46	-58	385	410
HCPIP-2	69	-58	404	444
HCPIP-3	97	-57	426	453
NR	0	-62	357	380
HNR-1	69	-59	397	441
HNR-2	80	-58	431	460
HNR-3	98	-57	439	468
NRL	0	-60	340	378
HNRL-1	12	-58	351	387
HNRL-2	53	-58	408	443
HNRL-3	99	-57	412	453
EPDM[a]	-	-45	453	471

[a]The ethylene-propylene copolymer (EPDM) has the ratio of ethylene/propylene as 50/50 (Hinchiranan).
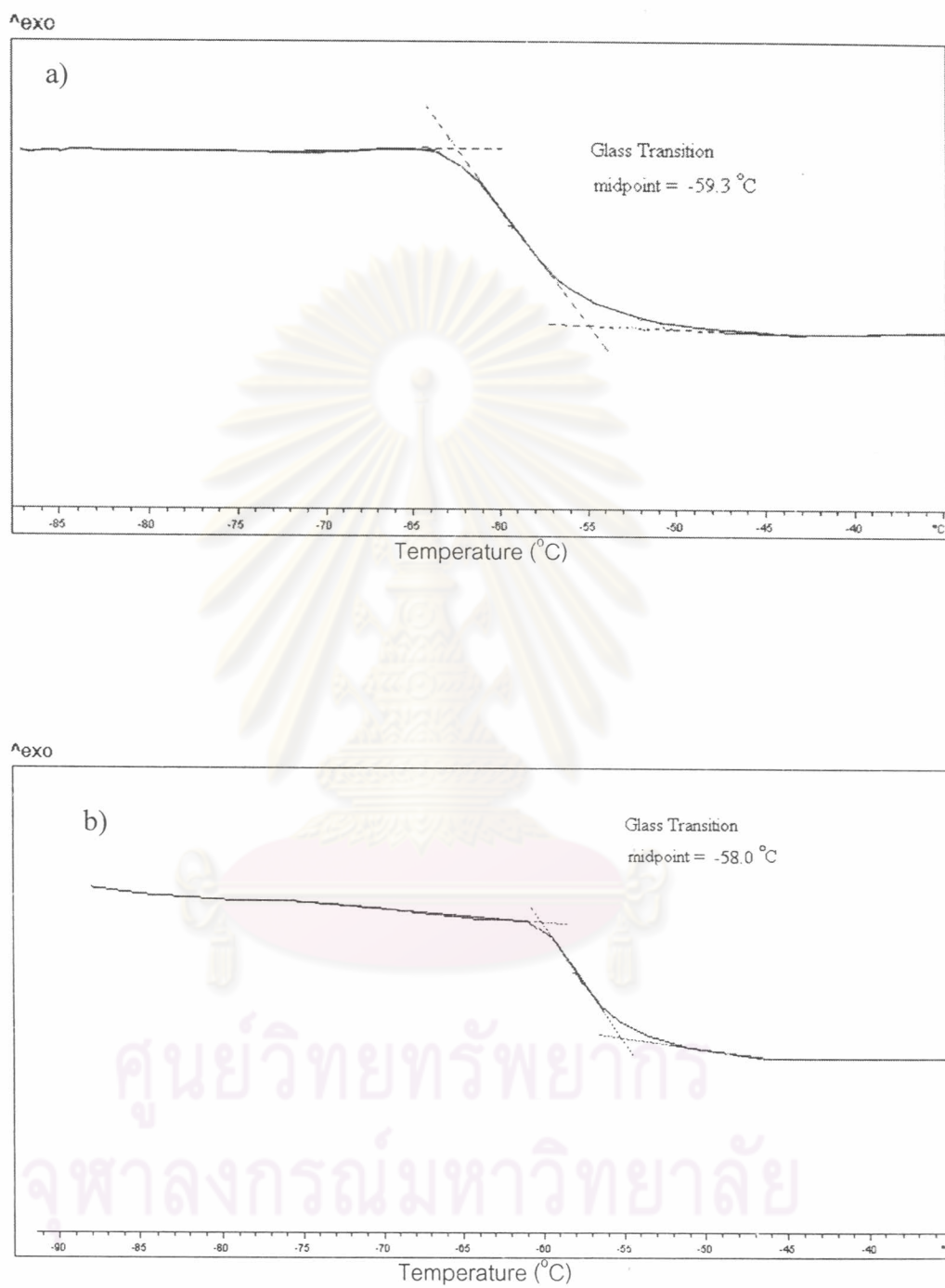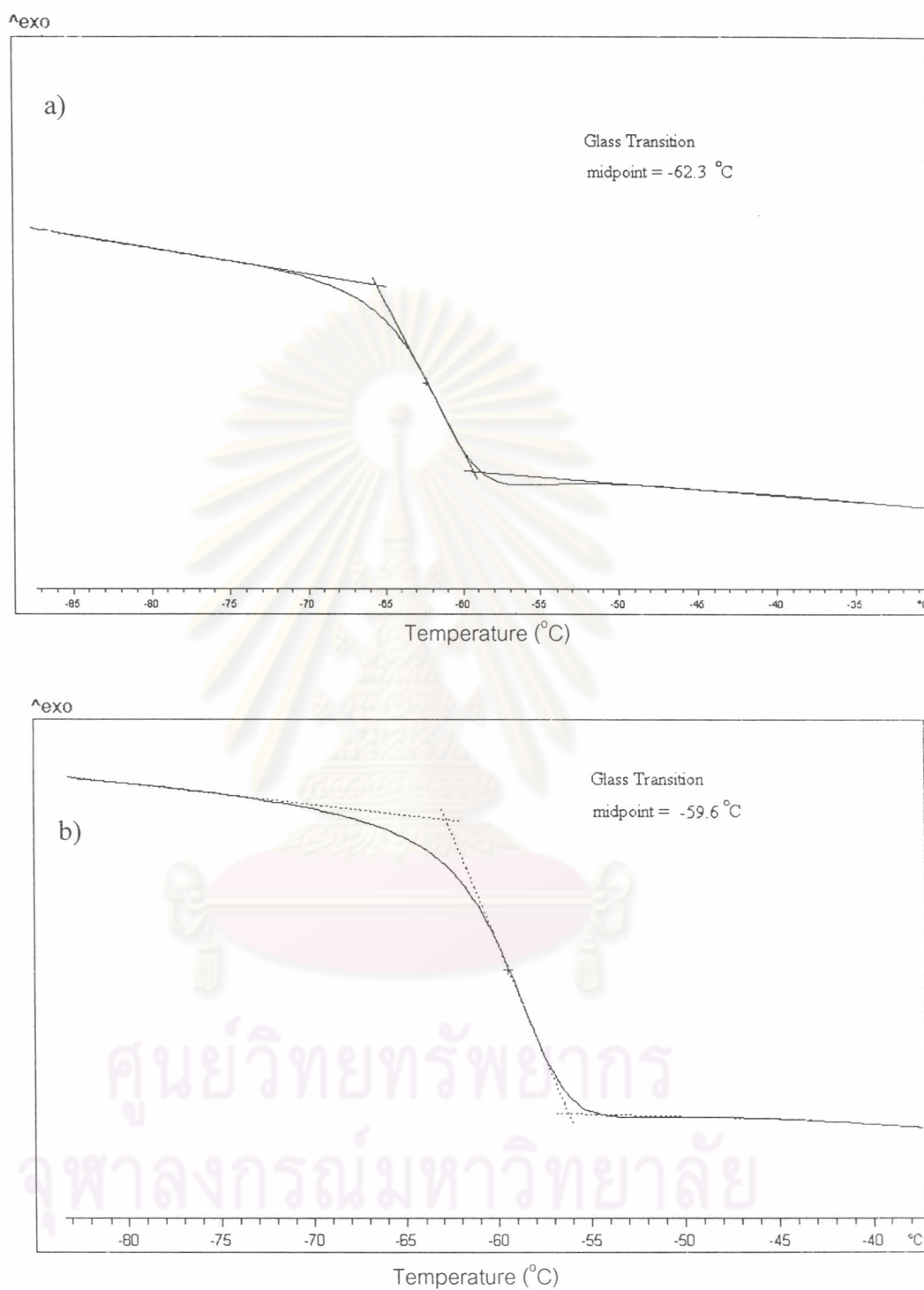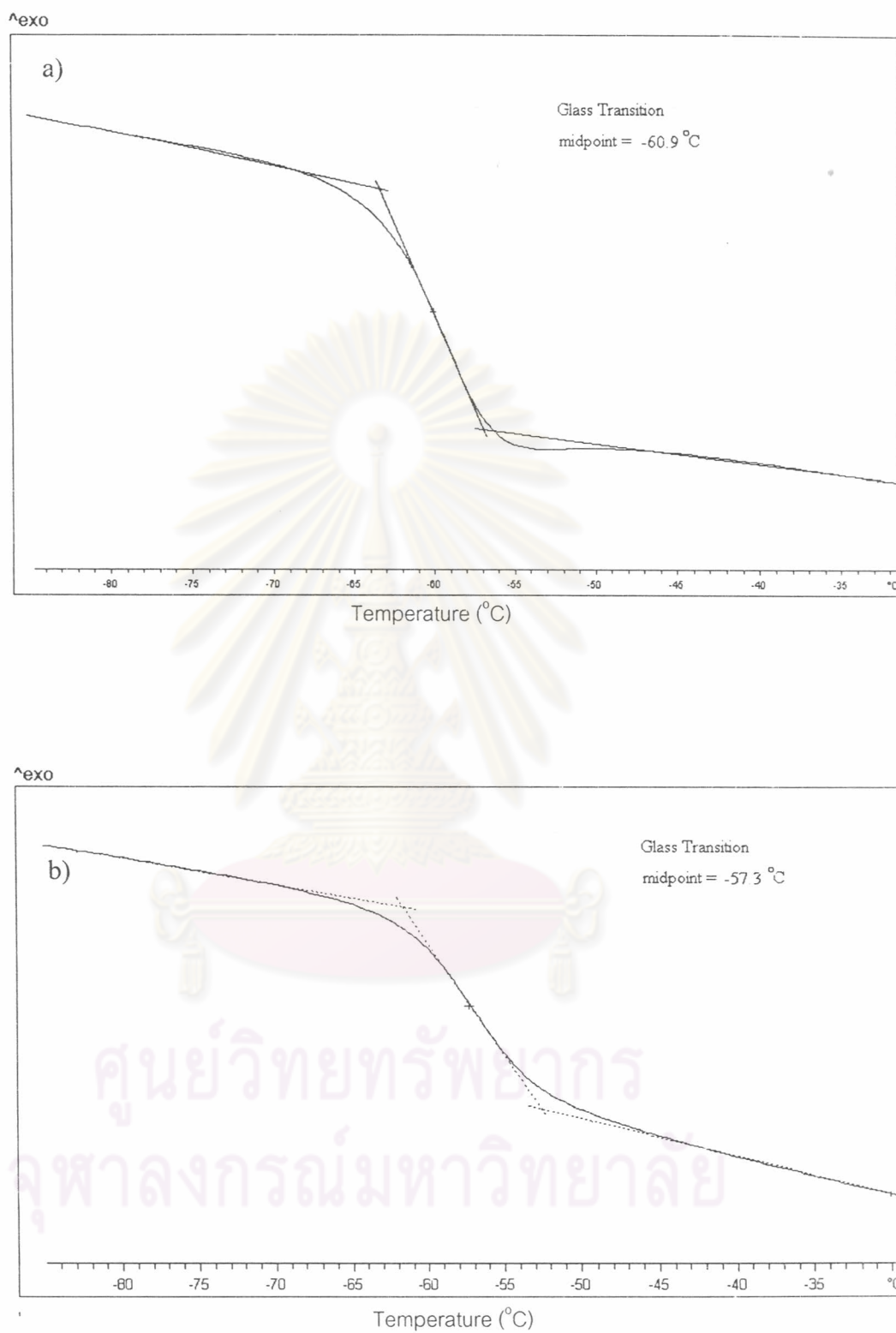
Figure 6.1: DSC thermograms of rubber samples a) CPIP b) HCPIP (53% hydrogenation).

Figure 6.2: DSC thermograms of rubber samples a) NR b) HNR (69% hydrogenation).

Figure 6.3: DSC thermograms of rubber samples a) NRL b) HNRL (99% hydrogenation).

6.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used as a method to assess the thermal stability of the polymer samples by monitoring the change in the mass of sample, which occurs as the temperature is increased at a constant rate. Polymers when heated under nitrogen normally degrade by breaking down to smaller fragments, which subsequently volatilize. The high temperature degradation of hydrogenated polyisoprene (HCPIP), hydrogenated natural rubber (HNR), hydrogenated natural rubber latex (HNRL), polyisoprene (CPIP), natural rubber (NR) and natural rubber latex (NRL) was studied. The TG curves are shown in Figure 6.4 – 6.6. Under nitrogen, there is no weight loss up to $300^{o}C$ indicating stability of the material over this temperature range. The weight loss occurs between $300 – 450^{o}C$, due to the loss of volatile matter absorbed by the polymer. The initial decomposition temperature (T_{id}) was determined from the intersection of two tangents at the onset of the decomposition temperature. The maximum decomposition temperature (T_{max}) was calculated from the peak maxima of the derivative of the TGA curves.

Decomposition temperature, T_{id} and T_{max} of rubber and hydrogenated samples are shown in Table 6.1. It is apparent that both T_{id} and T_{max} increased as the degree of hydrogenation increased. Similar thermal properties behavior of hydrogenated products, was observed by Singha (1998) and Charmondusit (2001), for synthetic polyisoprene and natural rubber hydrogenation. Hinchiranan reported T_{id} and T_{max} of standard EPDM to be higher than those of completely hydrogenated NR. From the thermal analysis of NBR and HNBR, T_{id} as well as T_{max} increases with decreasing carbon - carbon double bond content (Bhattacharjee, 1991). Therefore, the high temperature properties of all elastomers are improved upon hydrogenation. This may be due to the fact that in polyisoprene there is electron withdrawal from the α-methylene carbon by double bonds. When the concentration of these double bonds is decreased, the attack on the α-methylene group by O_2 is also reduced.
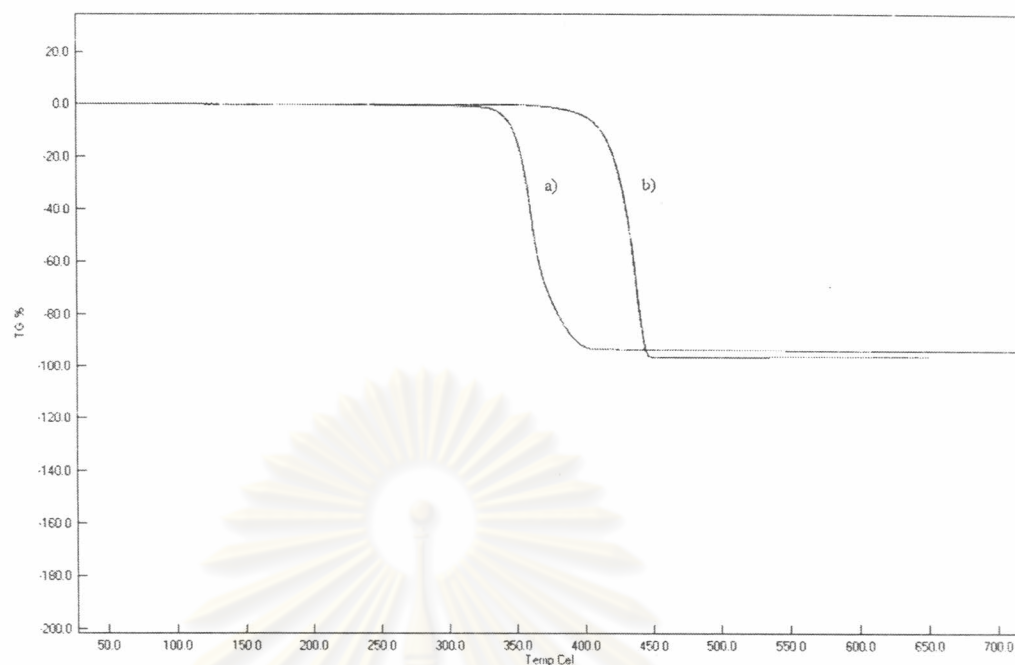
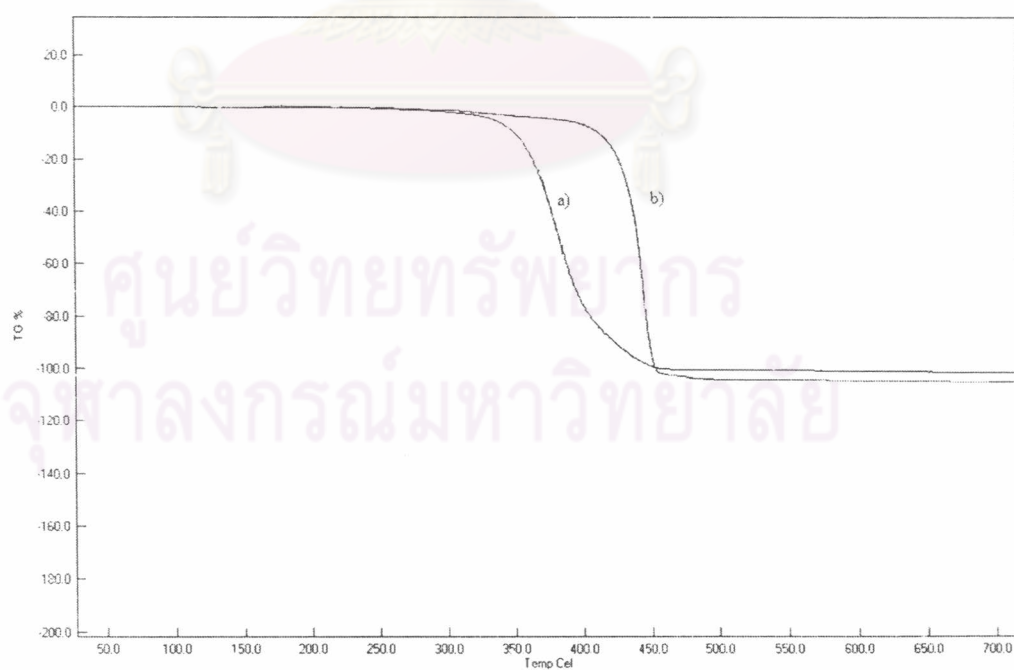Figure 6.4: TG curves of a) CPIP b) HCPIP (97% hydrogenation).

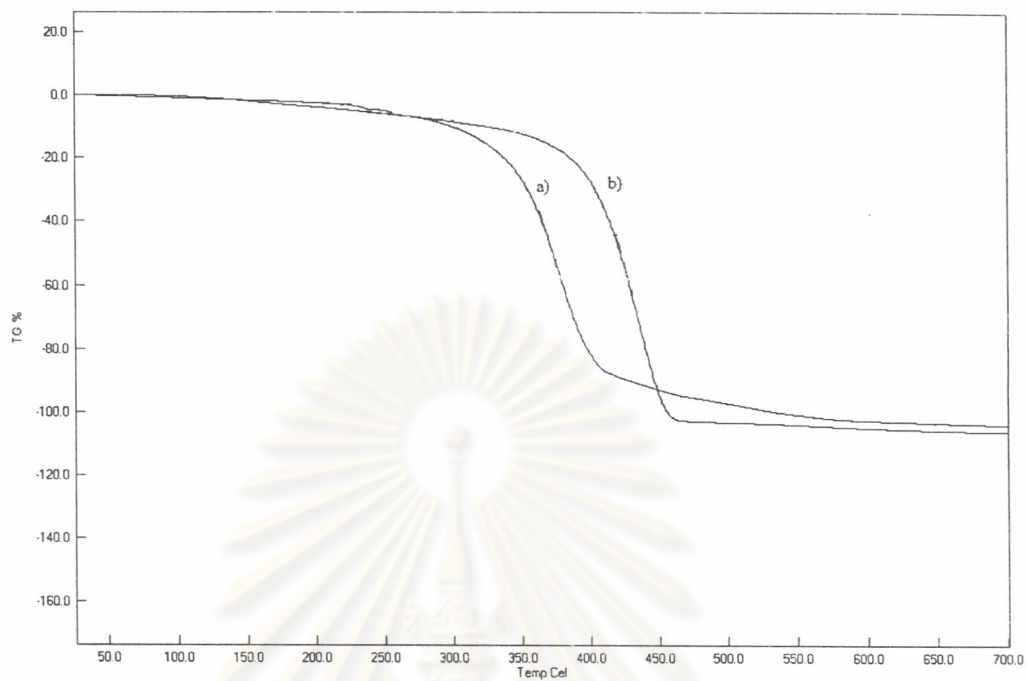
Figure 6.5: TG curves of a) NR b) HNR (98% hydrogenation).

Figure 6.6: TG curves of a) NRL b) HNRL (99% hydrogenation).