

CHAPTER 6

RESULTS FROM THERMAL STUDIES BY TGA

6.1 Introduction

The thermal studies of PEMA/PVdF–HFP–LiTf, PEMA/PVdF–HFP–LiTf–EC, PEMA/PVdF–HFP–LiTf–PC, PEMA/PVdF–HFP–LiTf–BMII and PEMA/PVdF–HFP–LiTf–BMITf polymer electrolyte systems are presented in this chapter. By obtaining the onset decomposition temperature of the polymer electrolyte components, we can determine the thermal stability of the polymer electrolyte samples.

6.2 Solid PEMA/PVdF–HFP–LiTf Polymer Electrolyte System

Table 6.1 tabulates the decomposition temperatures of PEMA, PVdF–HFP, thermograms LiTf, EC, PC, BMII and BMITf obtained from literature. Figure 6.1 depicts the TGA of PEMA, PVdF–HFP and S–0 samples whereby the labels **I**, **II**, **III** and **IV** represent the different components present in the polymer(s).

Table 6.1 TGA decomposition temperatures of PEMA, PVdF–HFP, LiTf, EC, PC, BMII and BMITf

Sample	Decomposition temperature, T_d (°C)	References
PEMA	229, 264, 344	Costache et al. (2006)
PVdF–HFP	420–470	Gnana Kumar et al. (2009)
LiTf	450	Ramesh and S.–C. Lu (2011)
PC	below 100	Kim et al. (2006)
EC	100–150	Ye et al. (2007)
BMII	265	Ngo et al. (2000)
BMITf	409	Tokuda et al. (2004)

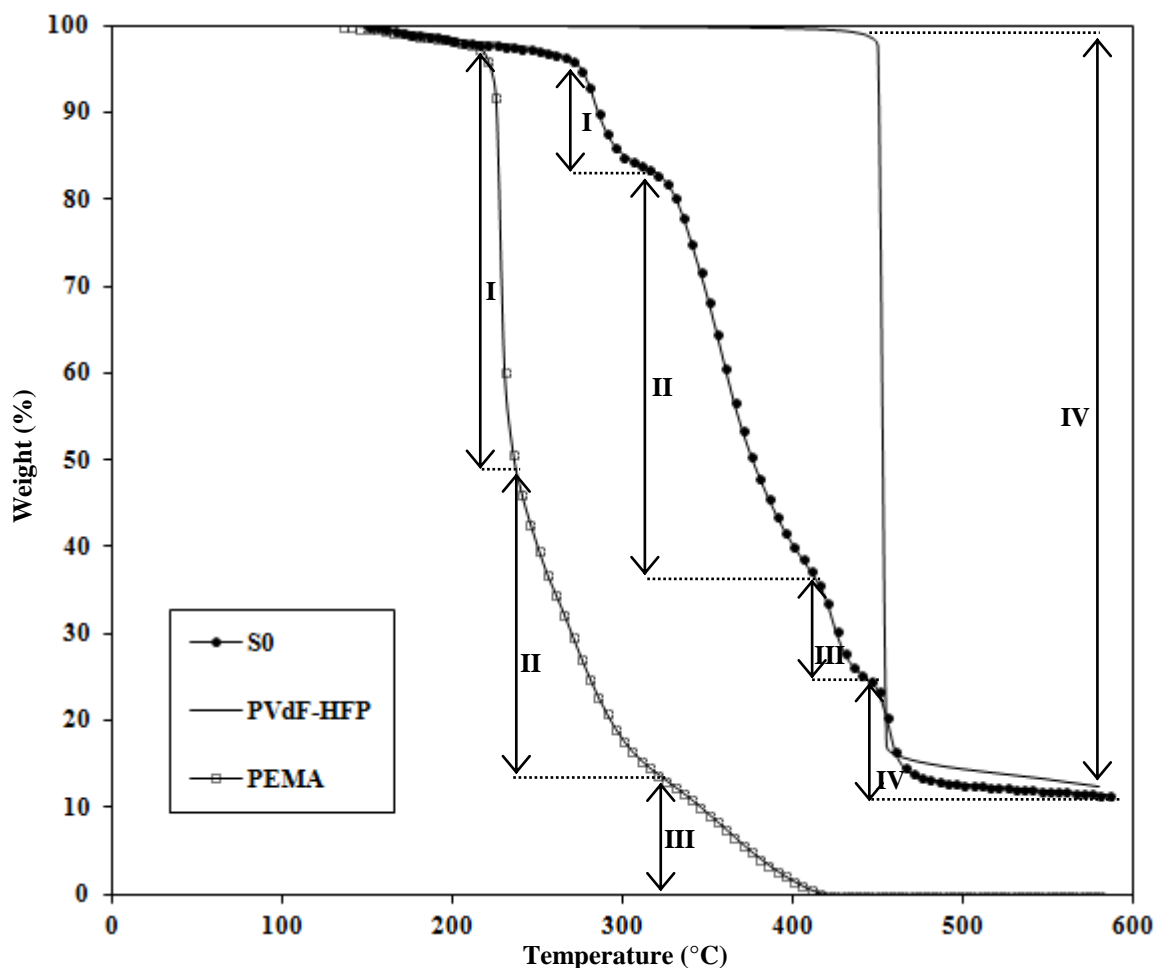


Figure 6.1 TGA plots of PEMA, PVdF-HFP and S-0

For PEMA film sample, three decomposition steps labeled as **I**, **II** and **III** attributable to different mechanisms were observed as opposed to two decomposition stages as reported in several literatures [Kashiwagi et al., 1986; Inaba et al., 1988; Kashiwagi and Inaba, 1989; Manring, 1991]. The TGA curve obtained for PEMA in our work is similar to that reported for poly(methyl methacrylate) (PMMA) [Costache and co-workers, 2006] which also displayed three decomposition stages. A three-stage decomposition is reported to occur for PMMA prepared by free radical polymerization [Hirata et al., 1986]. Similarity in the chemical structure of PEMA with that of PMMA allows the decomposition mechanisms of the latter to be used for comparison.

From Figure 6.1, the major weight loss of PEMA film (Region **I**) which started at 229 °C is attributed to the breaking of weak head-to-head linkages [Kandare et al., 2006; Ouaad et al., 2013]. In head-to-head linkages, monomer units are attached in a way that some of the monomers are oriented opposite to the remainder of the polymer chain. In the case of PEMA, the head and tail sections of the polymer correspond to the $\text{CH}_3\text{-COOC}_2\text{H}_5$ and CH_2 groups respectively. Hence, head-to-head linkages would pair the $\text{CH}_3\text{-COOC}_2\text{H}_5$ groups side-by-side along the polymer chain causing the C-C linkages between the two bulky groups to be weak due to large steric hindrance.

The second step (Region **II**) of PEMA decomposition was observed at 264 °C and is attributed to the scission at the vinylidene ($\text{C}=\text{CH}_2$ -) chain-end units which exist due to termination by disproportionation. Disproportionation is one of the termination process which converts free radicals into end products. Scission at the vinylidene chain-end units involves the homolytic cleavage of the second C-C bond (called β) to the vinyl group to form a radical. Homolytic bond cleavage is a process where the electron pair comprising a bond is split, causing the bond to break. The final decomposition step (Region **III**) of PEMA at 344 °C is the result of the random scission of the polymer backbone [Kashiwagi et al., 1986]. Random scission refers to breaking of bonds that occur at random locations in the polymer chains, which is a very common mechanism for polymer decomposition. Random scission occurs by homolysis of the C-C bonds to produce free radicals along the polymer backbone.

Figures 6.2 (a) to (c) depicts the mechanism for the three stages of decomposition of PEMA. From Figure 6.1, it can be observed that PEMA is completely decomposed around 425 °C leaving no solid residue or char. This is because volatile ethyl methacrylate (EMA) monomers are formed as the sole product.

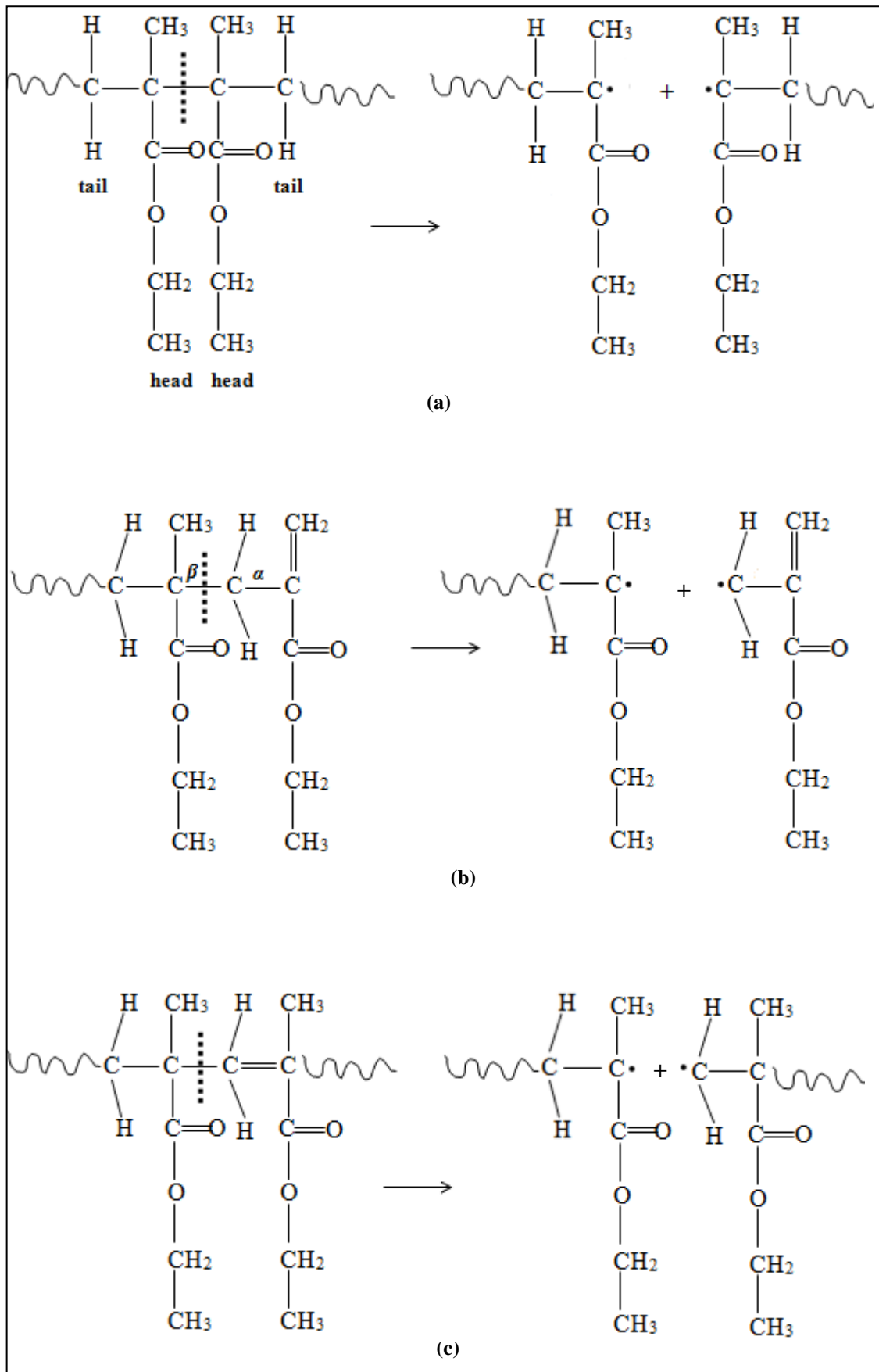


Figure 6.2 Decomposition of PEMA through (a) head-to-head linkage scission, (b) scission at vinylidene chain-end units and (c) random scission

Polymethacrylates i.e. PMMA and PEMA tend to decompose into their monomers [Czech and Pelech, 2010] as shown in Figure 6.3. All radicals produced from the different scission mechanisms of PEMA will undergo depropagation and termination to produce EMA monomers.

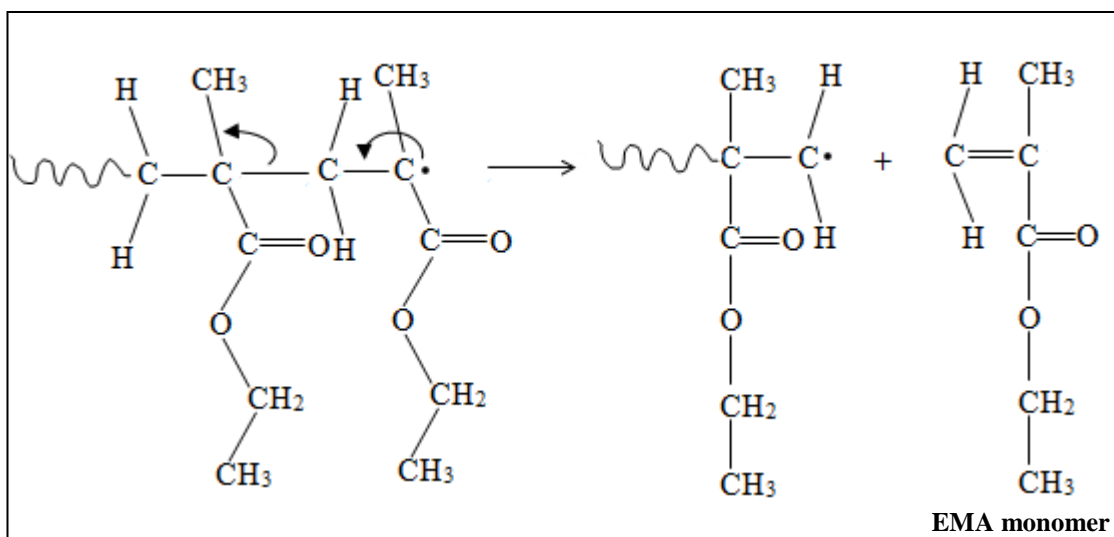


Figure 6.3 Formation of EMA monomers by depropagation and termination of all radicals

On the other hand, PVdF–HFP manifested only one decomposition point at 449 °C (decomposition step labeled as **IV**) which occurs by random scission [Wu and Feng, 1995]. The high decomposition temperature of PVdF–HFP is caused by the presence of strong C–F, C–C and C–H bonds which are due to high–energy fluorine atoms and the formation of strong van der Waals forces between H and F atoms [Banks, 1970]. At 580 °C, only about 12.2 wt.% of solid residue remained. The solid residue is the carbonaceous char of PVdF–HFP.

Figure 6.4 shows the decomposition of PVdF–HFP by random scission. In random scission, three steps occur, namely initiation, propagation and termination. During initiation, breakage of bonds occurs at random positions. Hence, two different

pathways *a* and *b* are shown here to illustrate resultant products that can be obtained if the bonds break at locations *a* and *b* as shown in Figure 6.4.

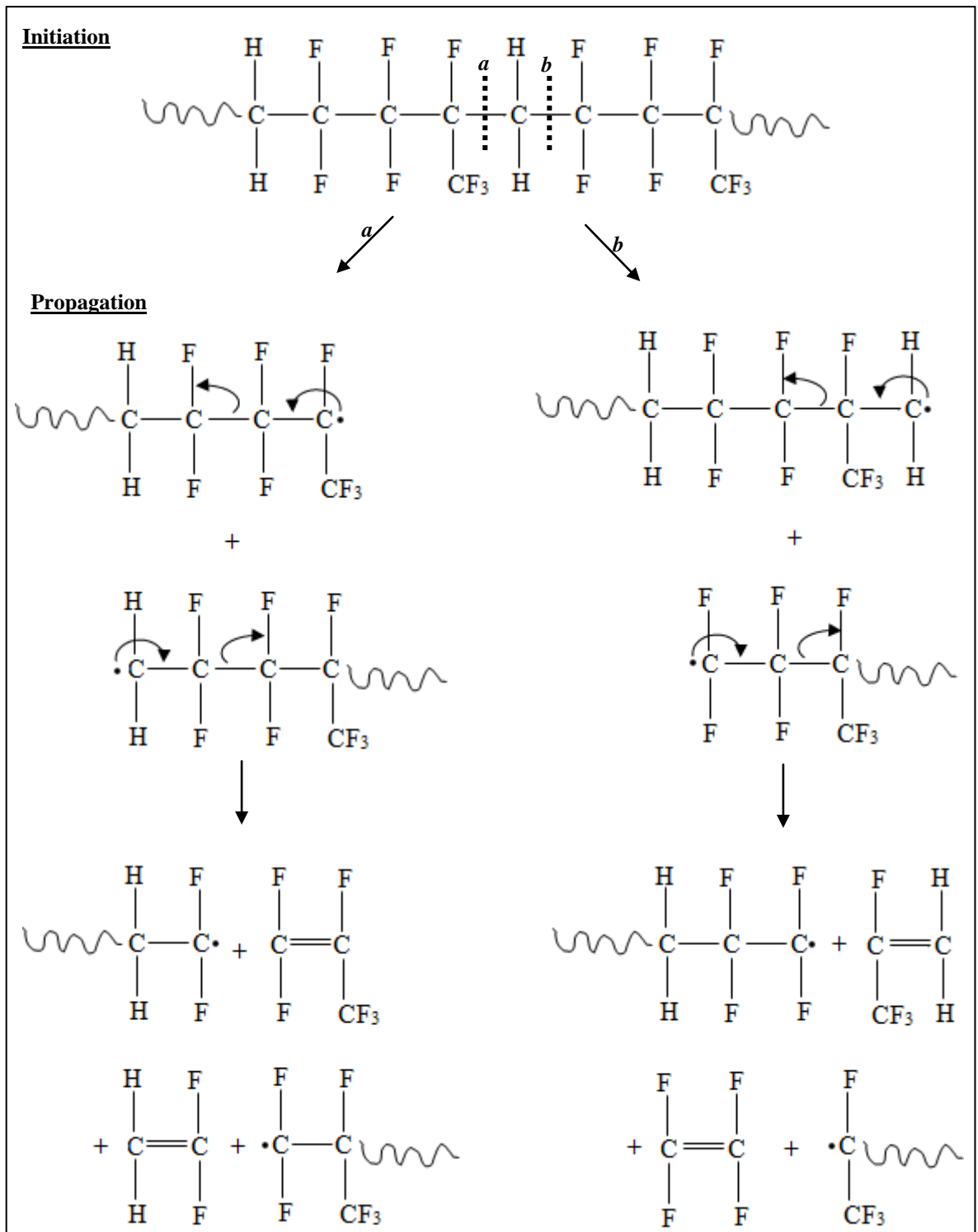


Figure 6.4 Decomposition of PVdF–HFP by random scission by different pathways *a* and *b*

Initiation is then followed by propagation whereby non-radical compounds and radicals are formed. The radical products obtained from the propagation step further

breaks down to form more non-radical compounds. Any radicals left at the end of propagation undergo termination by combining with each other to form non-radical species.

In the PEMA/PVdF–HFP blend (S–0) sample, the first weight loss (1.2 %) could be attributable to the loss of moisture introduced into the sample during loading. The weight loss pertaining to PEMA in the polymer blend is observed to occur at higher temperatures: 268 °C (**I**), 328 °C (**II**) and 413 °C (**III**), while the decomposition temperature of PVdF–HFP maintained at 446.6 °C (**IV**). Hence, the addition of PVdF–HFP to PEMA to form PEMA/PVdF–HFP polymer blend increased the thermal stability of the polymer system to 268 °C. Figure 6.5 illustrates the decomposition of LiTf upon heating. Figure 6.6 depicts the TGA plots of PEMA/PVdF–HFP blend added with various LiTf contents. It is well known that lithium salts are hygroscopic and is the reason of 12.7 % weight loss observed from 44 °C to 131°C for LiTf. The main decomposition due to LiTf structure occurred at 440 °C.

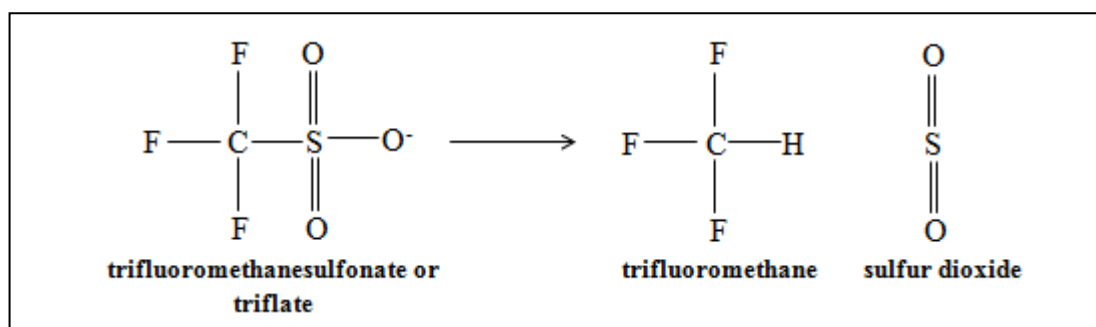


Figure 6.5 Decomposition of LiTf [Taken from Ohtani et al., 2008]

PEMA started to decompose at lower temperatures: T_d for stage **I** decreased from 268 °C to about 256–260 °C in the polymer blend–LiTf samples. The second decomposition due to PEMA (**II**) exhibited higher T_d for S–10 and S–20 ($\Delta=19$ to 23 °C) and then decreased for S–30 and S–40 samples ($\Delta=8$ to 15 °C). The third

decomposition of PEMA (III) occurred at lower temperatures for all LiTf-added samples: about 25 to 31 °C lower than original T_d at 413 °C.

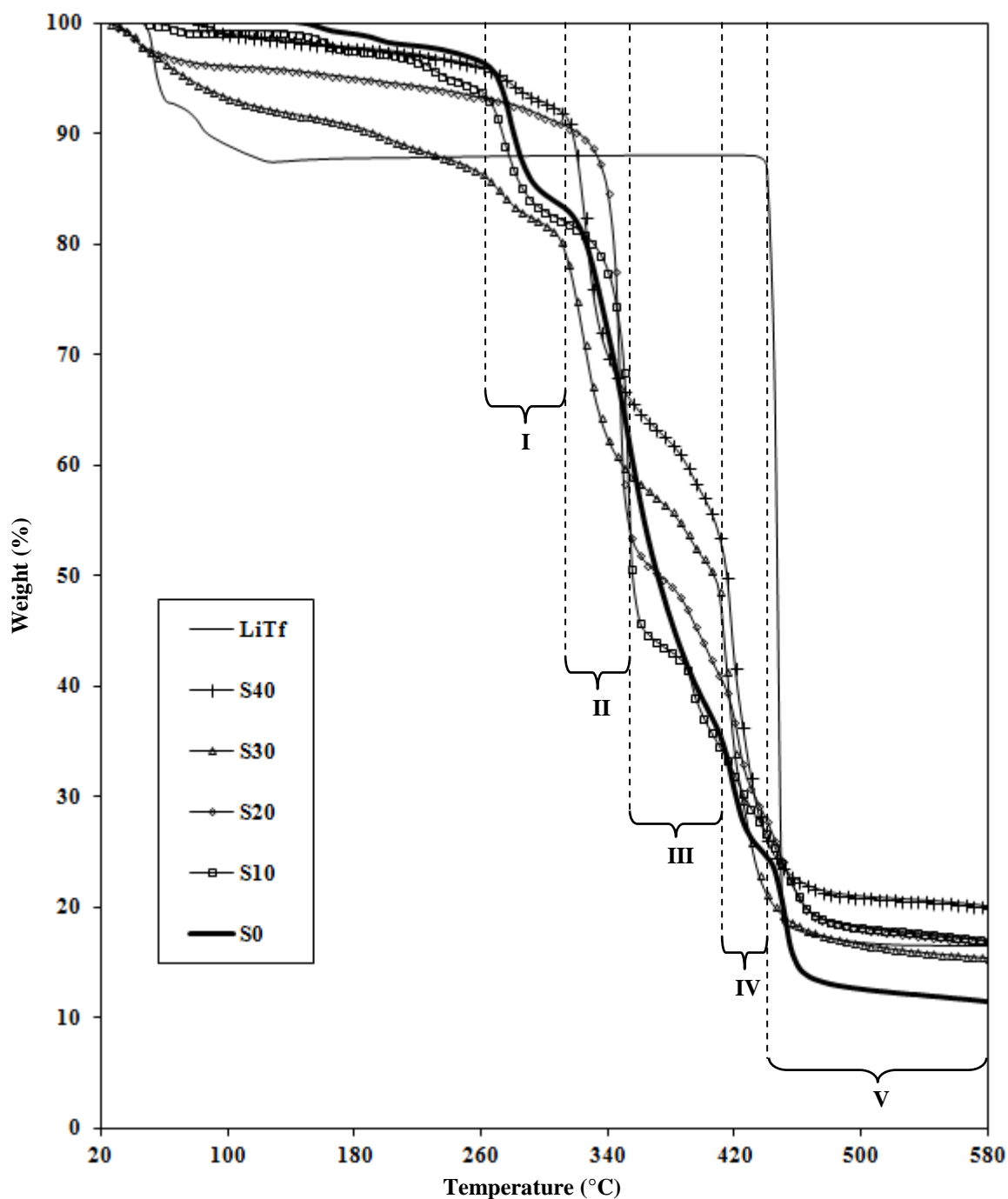


Figure 6.6 TGA plots of PEMA/PVdF-HFP-LiTf polymer electrolytes

The onset T_d of PVdF-HFP in the polymer blend-LiTf samples also decreased by 29 to 36 °C from 447 °C. The T_d of LiTf was observed to increase slightly from 440

°C to 443 and 441 °C in S–10 and S–20 samples, respectively. In S–30 and S–40, the T_d of LiTf was lowered to 417 and 431 °C, respectively. Overall, the addition of LiTf into PEMA/PVdF–HFP blend tends to decrease the T_d of the samples, the lowest T_d being 416 °C.

Table 6.2 Decomposition temperatures of PEMA/PVdF–HFP–LiTf polymer electrolytes (Value in bracket represents wt.% lost in the stage)

Sample	Decomposition temperature, T_d (°C)				
	PEMA		PVdF–HFP	LiTf	
	I	II	III	IV	V
PEMA	229 (62.7)	264 (22.7)	344 (13.3)	–	–
PVdF– HFP	–	–	–	449 (86.1)	–
S–0	268 (15.2)	328 (45.7)	413 (12.9)	447 (13.4)	–
LiTf	–	–	–	–	440 (71.2)
S–10	256 (20.5)	347 (32.8)	388 (6.2)	411 (7.5)	443 (15.0)
S–20	258 (4.8)	351 (41.2)	386 (3.8)	418 (11.9)	441 (12.4)
S–30	259 (5.8)	313 (24.9)	382 (5.6)	412 (20.5)	417 (15.1)
S–40	260 (3.0)	320 (31.7)	387 (5.3)	416 (24.3)	431 (14.2)

6.3 Plasticized PEMA/PVdF–HFP–LiTf Polymer Electrolyte Systems

6.3.1 PEMA/PVdF–HFP–LiTf–EC System

TGA curves of various PEMA/PVdF–HFP–LiTf–EC samples are shown in Figure 6.7.

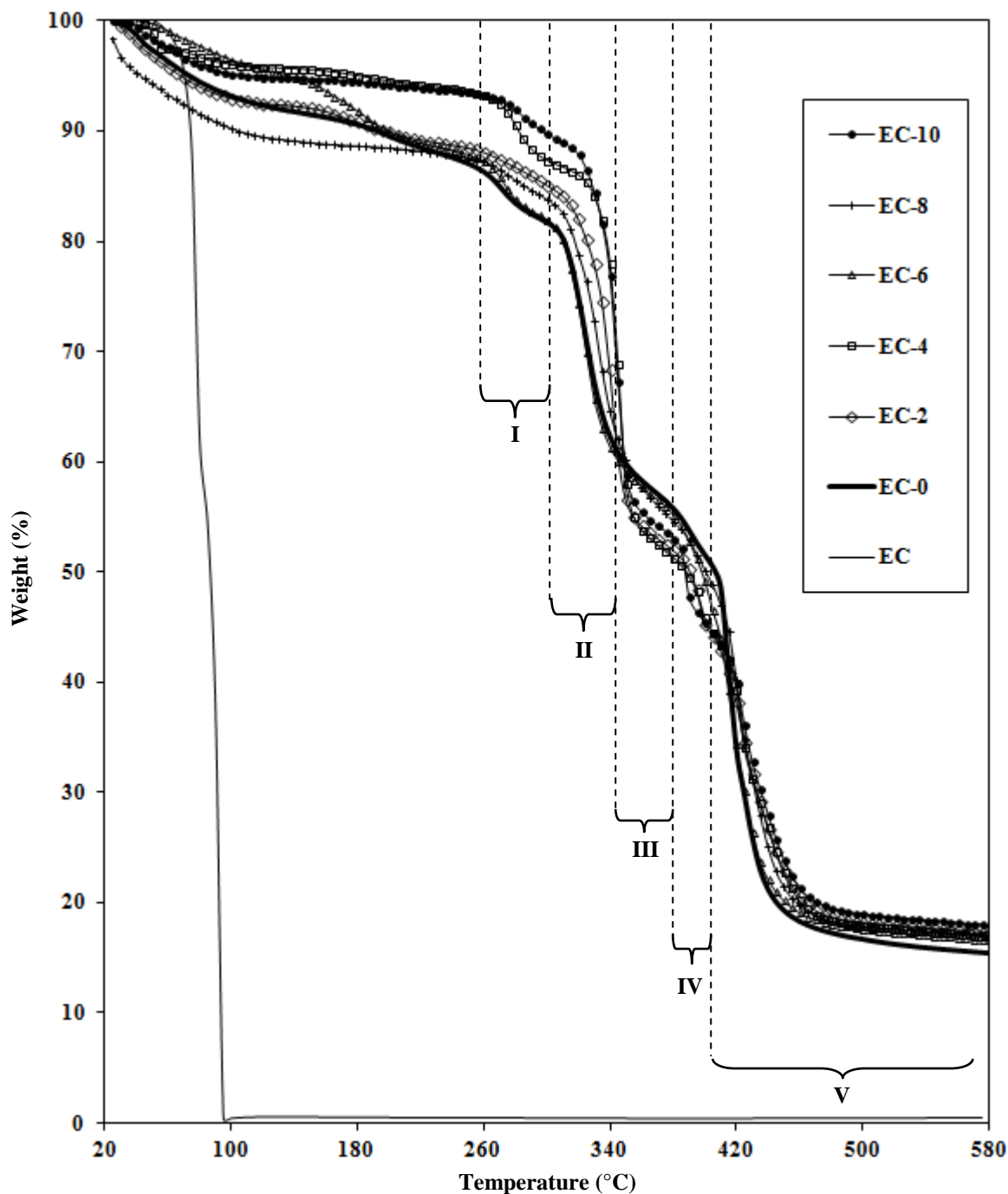


Figure 6.7 TGA plots of PEMA/PVdF-HFP-LiTf-EC polymer electrolytes

The T_d of EC can be observed at 89.3 °C. Nearly all of EC decomposed below 100 °C by vaporization into the gaseous state leaving nearly zero solid residue. Upon the incorporation of EC into the optimized PEMA/PVdF-HFP-LiTf (70:30) composition, changes in the T_d of the polymer electrolytes were observed. The T_d for stage I of PEMA increased from 259 °C before addition of EC to 264.1 and 269.1 °C in

EC-2 and EC-4 respectively. In EC-6 and EC-8, the T_d decreased to 263.3 and 255.4 °C, respectively. In EC-10 sample, the T_d increased to 271 °C. The T_d for stage **II** of PEMA also showed similar pattern whereby EC-2 and EC-4 samples showed increased T_d at 331 and 338.7 °C respectively as compared to that of EC-0 at 313 °C.

The decomposition temperature, T_d of stage **III** of PEMA was increased in all EC-containing samples although the samples showed a decreasing T_d trend with increasing EC contents; EC-2 exhibited T_d at 393.4 °C, which was 11.4 °C higher than 382 °C for the unplasticized sample, and EC-10 exhibited T_d at 386.2 °C. The T_d of PVdF-HFP was increased from 412 °C to between 414.9 and 418 °C in all EC-containing samples except for EC-6; EC-6 exhibited lower T_d at 402.9 °C. The decomposition of LiTf occurred at higher temperatures from 417 °C to between 424.4 and 437.5 °C in EC-added samples. The TGA data for EC-plasticized samples are listed on Table 6.3. Overall, PEMA/PVdF-HFP-LiTf-EC polymer electrolytes are thermally stable up to around 250 °C.

Table 6.3 Decomposition temperatures of PEMA/PVdF-HFP-LiTf-EC polymer electrolytes (Value in bracket represents wt.% lost in the stage)

Sample	Decomposition temperature, T_d (°C)					
	EC	PEMA			PVdF-HFP	LiTf
		I	II	III	IV	V
EC	89.3 (95.5)	–	–	–	–	–
EC-0	–	259 (5.8)	313 (24.9)	382 (5.6)	412 (20.5)	417 (15.1)
EC-2	–	264.1 (3.4)	331 (32.6)	393.4 (8.5)	415.2 (13.1)	435.3 (14.0)
EC-4	–	269.1 (7.3)	338.7 (34.7)	392.4 (8.4)	418.4 (14.4)	437.5 (12.4)
EC-6	–	263.3 (5.3)	313.3 (25.4)	390.1 (9.6)	402.9 (15.8)	424.4 (15.0)
EC-8	–	255.4 (4.2)	319.9 (29.7)	389.2 (4.9)	414.9 (18.7)	433.9 (14.2)
EC-10	–	271 (5.7)	336.3 (35.0)	386.2 (8.9)	418.0 (13.8)	437.5 (13.6)

6.3.2 PEMA/PVdF–HFP–LiTf–PC System

The TGA curves of PC–added PEMA/PVdF–HFP films studied are depicted in Figure 6.8. Evaporation of PC is observed to begin at 94 °C and decomposition of PC is completed at around 110 °C.

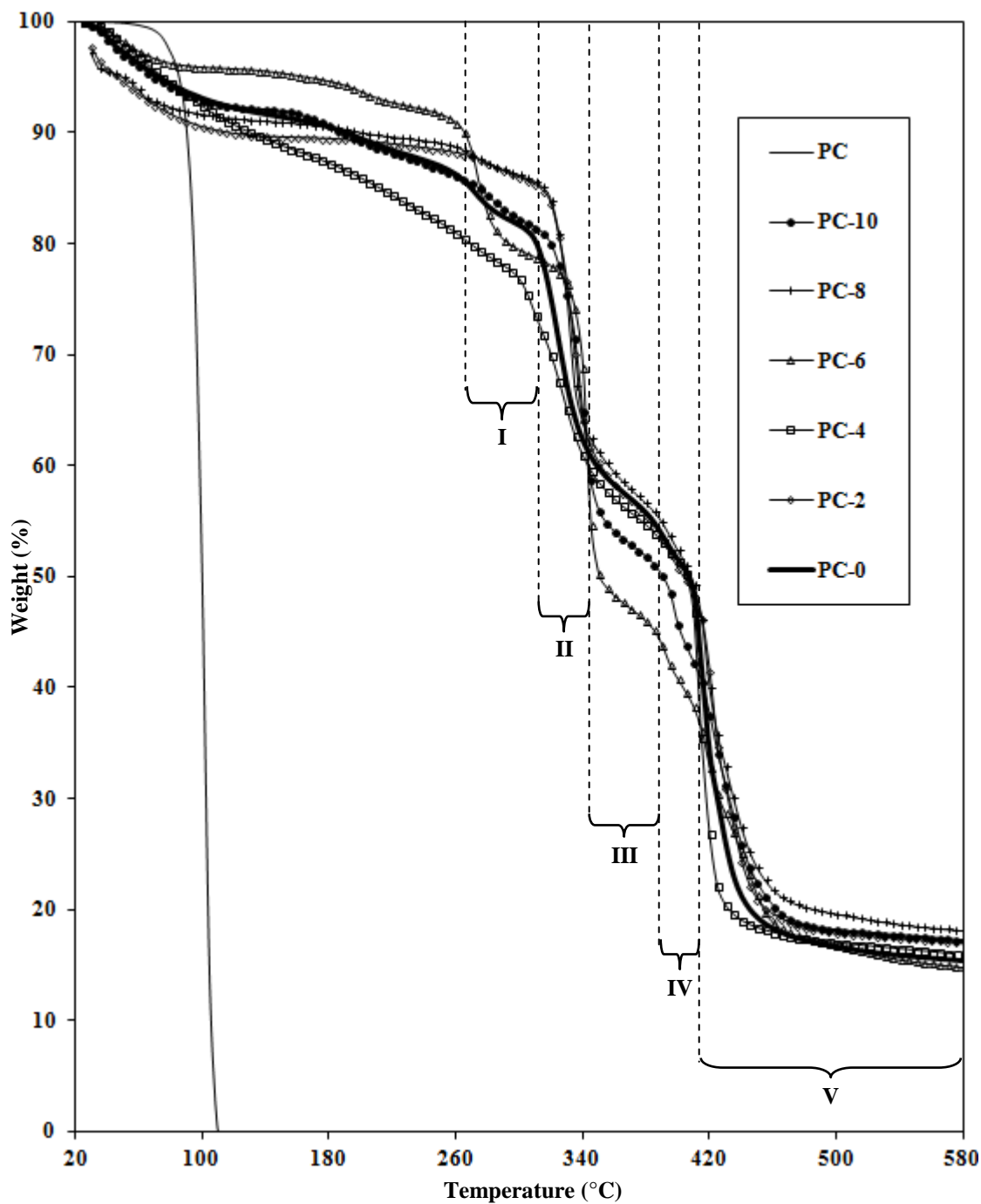


Figure 6.8 TGA plots of PEMA/PVdF–HFP–LiTf–PC polymer electrolytes

The first decomposition of PEMA (stage I) did not show significant change from 259 °C for the samples added with PC except for PC-6 and PC-10 which was increased to 266 and 269 °C. In the PC-added samples, the second stage (stage II) of decomposition of PEMA occurred at higher temperatures at 325 to 337 °C as compared to original 313 °C before addition of PC. Similar observation was recorded for the T_d of stage III of PEMA which increased from 382 °C to between 385 and 393 °C after the addition of PC.

As for the T_d of PVdF-HFP, it was found to occur at higher temperatures of 417 and 416 °C in PC-2 and PC-10 samples, respectively; the T_d did not show significant change in PC-4, PC-6 and PC-8 samples which diverted around 1 or 2 °C from the original T_d at 412 °C in PC-0. The decomposition of LiTf moieties occurred at higher temperatures in the PC-containing samples at around 432 to 436 °C as compared to 417 °C in PC-0. The T_d values and wt. % loss of each component in PEMA/PVdF-HFP-LiTf-PC system are listed in Table 6.4.

Table 6.4 Decomposition temperatures of PEMA/PVdF-HFP-LiTf-PC polymer electrolytes (Value in bracket represents wt.% lost in the stage)

Sample	Decomposition temperature, T_d (°C)					
	PC	PEMA			PVdF-HFP	LiTf
		I	II	III	IV	V
PC	94 (100.0)	–	–	–	–	–
PC-0	–	259 (5.8)	313 (24.9)	382 (5.6)	412 (20.5)	417 (15.1)
PC-2	–	256.0 (3.5)	325 (29.6)	387 (6.6)	417 (19.0)	432 (13.8)
PC-4	–	260 (9.8)	331 (22.8)	385 (3.6)	412 (16.3)	435 (15.2)
PC-6	–	266 (3.5)	337 (13.4)	386 (31.6)	413 (7.0)	436 (15.2)
PC-8	–	259 (3.0)	325 (29.2)	388 (4.9)	411 (19.9)	433 (14.4)
PC-10	–	269 (5.8)	330 (29.1)	393 (10.1)	416 (12.0)	432 (13.7)

Overall, the addition of PC did not increase the onset decomposition temperature of PEMA/PVdF–HFP–LiTf system from 259 °C; the PC–based polymer electrolytes are stable up to 256 °C.

6.4 Ionic Liquid Based PEMA/PVdF–HFP–LiTf Polymer Electrolyte Systems

6.4.1 PEMA/PVdF–HFP–LiTf–BMII System

Figure 6.9 illustrates the TGA plots of PEMA/PVdF–HFP–LiTf–BMII polymer electrolyte films. The ionic liquid, BMII was shown to decompose at 247 °C in a single step. Upon incorporation into the optimized PEMA/PVdF–HFP–LiTf composition, the decomposition peak belonging to BMII could not be observed in the TGA plots. The T_d of BMII may have shifted from its original temperature, and most probably masked by the first decomposition stage I of PEMA.

Earlier work by Chan and co-workers (1977) reported that nucleophilic attack by the halide anion occur at the N–position of the BMI^+ to produce haloalkanes and 1–alkylimidazoles in ionic liquids containing halide anions. A nucleophilic attack occurs when a nucleophile containing free pair of electrons, which in this case is I^- donates an electron pair to form a bond with an electrophile, the methyl and butyl groups in BMII.

Ohtani et al. (2008) studied the thermal decomposition behavior of BMICl , another imidazolium halide ionic liquid. From Ohtani and co-workers' (2008) findings, chloromethane, 1–butene, 1–chlorobutane, 1–methylimidazole and 1–butylimidazole were produced upon pyrolysis of BMICl . Hence, it is suggested that BMII decomposes through a C–N bond cleavage at an alkyl group by the nucleophilic attack of iodide ion into methyl iodide (CH_3I), 1–butyl iodide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$), 1–butene ($\text{CH}_2=\text{CH}-$

CH₂CH₃), 1-methylimidazole and 1-butylimidazole. Figure 6.10 shows the schematic diagram of thermal decomposition pathways of BMII.

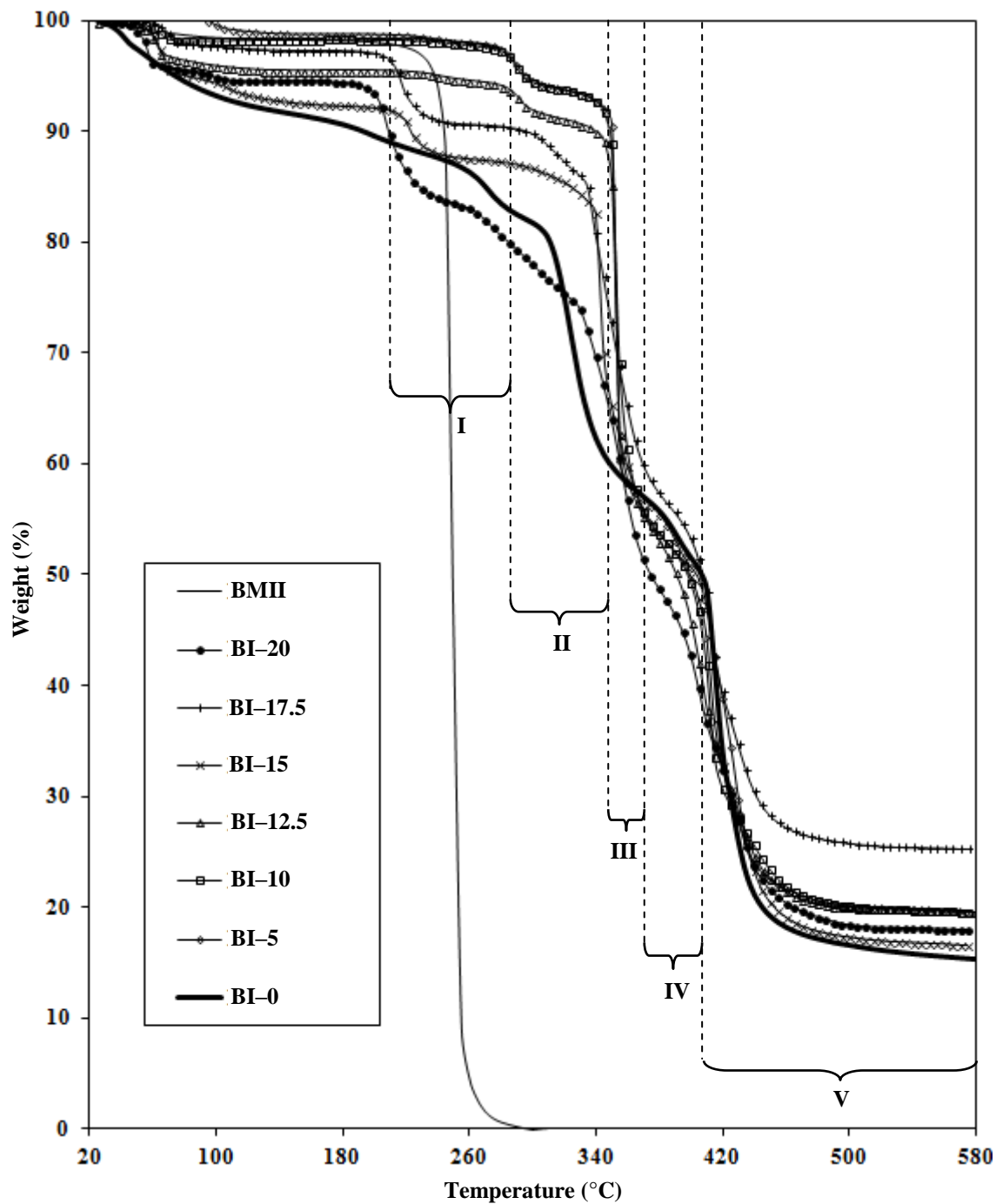


Figure 6.9 TGA plots of PEMA/PVdF-HFP-LiTf-BMII polymer electrolytes

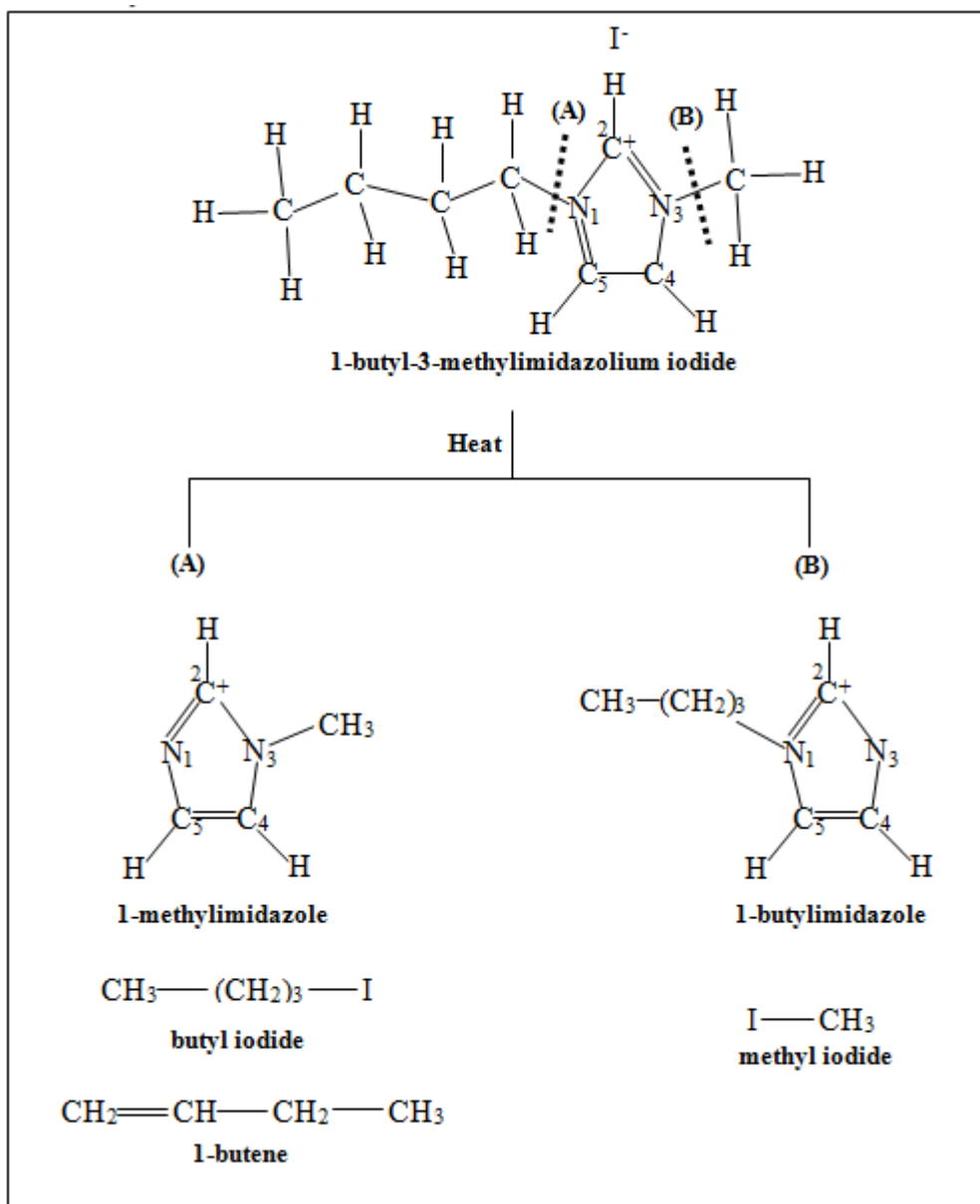


Figure 6.10 Thermal decomposition pathways of BMII

The T_d value for the first decomposition stage of PEMA (labeled **I**) was observed to increase from 259 °C to 281 °C upon the addition of 5 wt.% BMII. With increasing BMII contents, the T_d showed a decreasing trend; the T_d value was lowered to 279 and 276 °C in BI-10 and BI-12.5, respectively, which is still higher than the T_d of BI-0. Above 12.5 wt.% BMII content, the T_d for stage **I** of PEMA showed drastic decrease to 217, 211 and 202 °C for BI-15, BI-17.5 and BI-20, respectively; the onset decomposition temperature is even lower than that of BI-0 by about 42 to 57 °C. The TGA data of BMII-added polymer electrolytes are listed in Table 6.5.

The T_d of stage **II** and **III** of PEMA was observed to increase upon the incorporation of 5 wt.% BMII into the optimized polymer blend–salt composition from 313 to 353 °C and from 382 to 383 °C, respectively. Above that BMII content, the decomposition for stage **II** and **III** occurred at lower temperatures. For BI–10 and BI–12.5 samples, only one T_d , instead of two decomposition peaks, was observed at 351 and 350 °C, respectively. The presence of only one T_d for both decomposition stages could be due to the overlap of the decomposition peaks which are difficult to be resolved. In samples added with 15 wt.% of BMII and above, the T_d of stage **II** and **III** of PEMA decreased continually with increasing ionic liquid content.

Table 6.5 Decomposition temperatures of PEMA/PVdF–HFP–LiTf–BMII polymer electrolytes (Value in bracket represents wt.% lost in the stage)

Sample	Decomposition temperature, T_d (°C)					
	BMII	PEMA			PVdF– HFP	LiTf
		I	II	III	IV	V
BMII	247 (97.8)	–	–	–	–	–
BI–0	–	259 (5.8)	313 (24.9)	382 (5.6)	412 (20.5)	417 (15.1)
BI–5	–	281 (5.2)	353 (36.9)	383 (6.0)	408 (11.1)	423 (20.1)
BI–10	–	279 (4.4)	351 (40.8)	–	407 (26.0)	425 (7.5)
BI–12.5	–	276 (4.4)	350 (37.5)	–	396 (21.3)	426 (12.7)
BI–15	–	217 (4.8)	342 (34.6)	357 (7.2)	409 (21.9)	428 (12.5)
BI–17.5	–	211 (6.7)	338 (8.6)	346 (21.5)	408 (19.1)	428 (11.9)
BI–20	–	202 (10.7)	265 (8.5)	338 (26.7)	397 (15.3)	423 (15.3)

The decomposition of PVdF–HFP shown as stage **IV** was observed to decrease from 412 °C in BI–0 to between 396 and 409 °C when incorporated with BMII up to 20 wt.%.

On the other hand, the T_d due to LiTf (stage **V**) were found to be slightly higher at between 423 and 428 °C in the BMII-added samples as compared to that at 417 °C of BI-0 sample. Overall, the BMII-added samples are thermally stable up to 200 °C.

6.4.2 PEMA/PVdF-HFP-LiTf-BMITf System

TGA plots of BMITf-containing PEMA/PVdF-HFP-LiTf films are depicted in Figure 6.11. BMITf was observed to begin decomposition at 377 °C in a single step.

Ohtani and co-workers (2008) who carried out thermal decomposition of BMITf ionic liquid reported 1-butylimidazole, 1-methylimidazole, 1-butene, *cis*-2-butene and *trans*-2-butene as decomposition products due to the imidazolium cation. Trifluoromethane (CF₃H) and sulfur dioxide (SO₂) were also observed as decomposition products of the triflate anion. Figure 6.12 shows the decomposition mechanisms of BMITf.

After BMITf was added into PEMA/PVdF-HFP-LiTf (70:30) system, the T_d of BMITf could not be observed. The BMITf-bearing moieties may have decomposition close to that of PVdF-HFP chains. The T_d of PVdF-HFP increased from 412 °C to 419 °C in BT-10, and then decreased continually with increasing BMITf contents to 384 °C in BT-60.

Upon the introduction of BMITf into the optimized polymer blend-salt composition, the onset decomposition temperature of stage **I** due to PEMA increased from 259 to 294 °C. All BMITf-added samples only exhibited one T_d for the decomposition of stages **II** and **III** of PEMA between 336 °C and 355 °C. The T_d due to

LiTf was found to be increased from 417 °C to between 430 °C and 436 °C in the BMITf-containing samples. The TGA results for PEMA/PVdF-HFP-LiTf-BMITf system are listed in Table 6.6. Overall, the thermal stability of BMITf-incorporated samples was increased to above 275 °C.

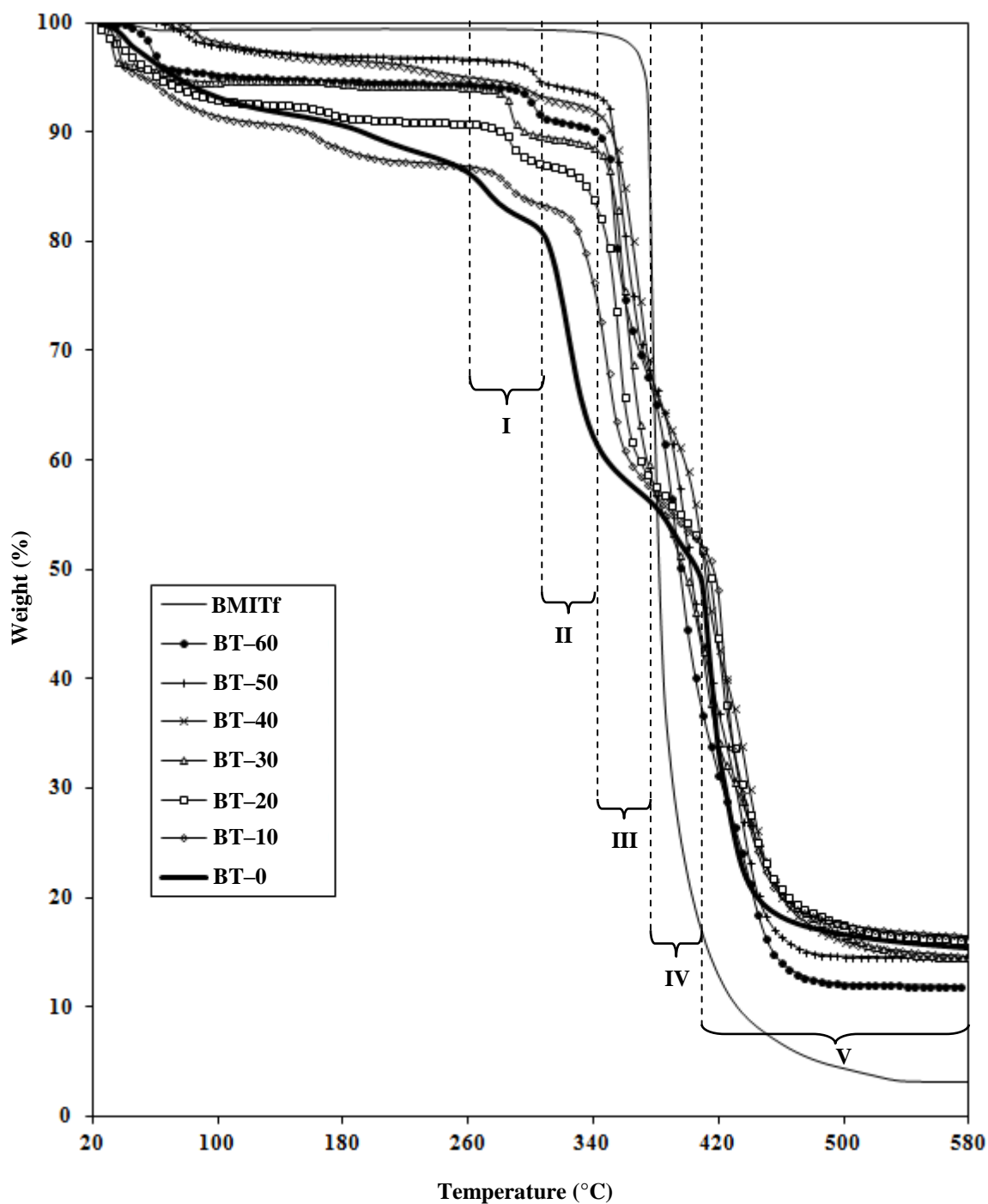


Figure 6.11 TGA plots of PEMA/PVdF-HFP-LiTf-BMITf polymer electrolytes

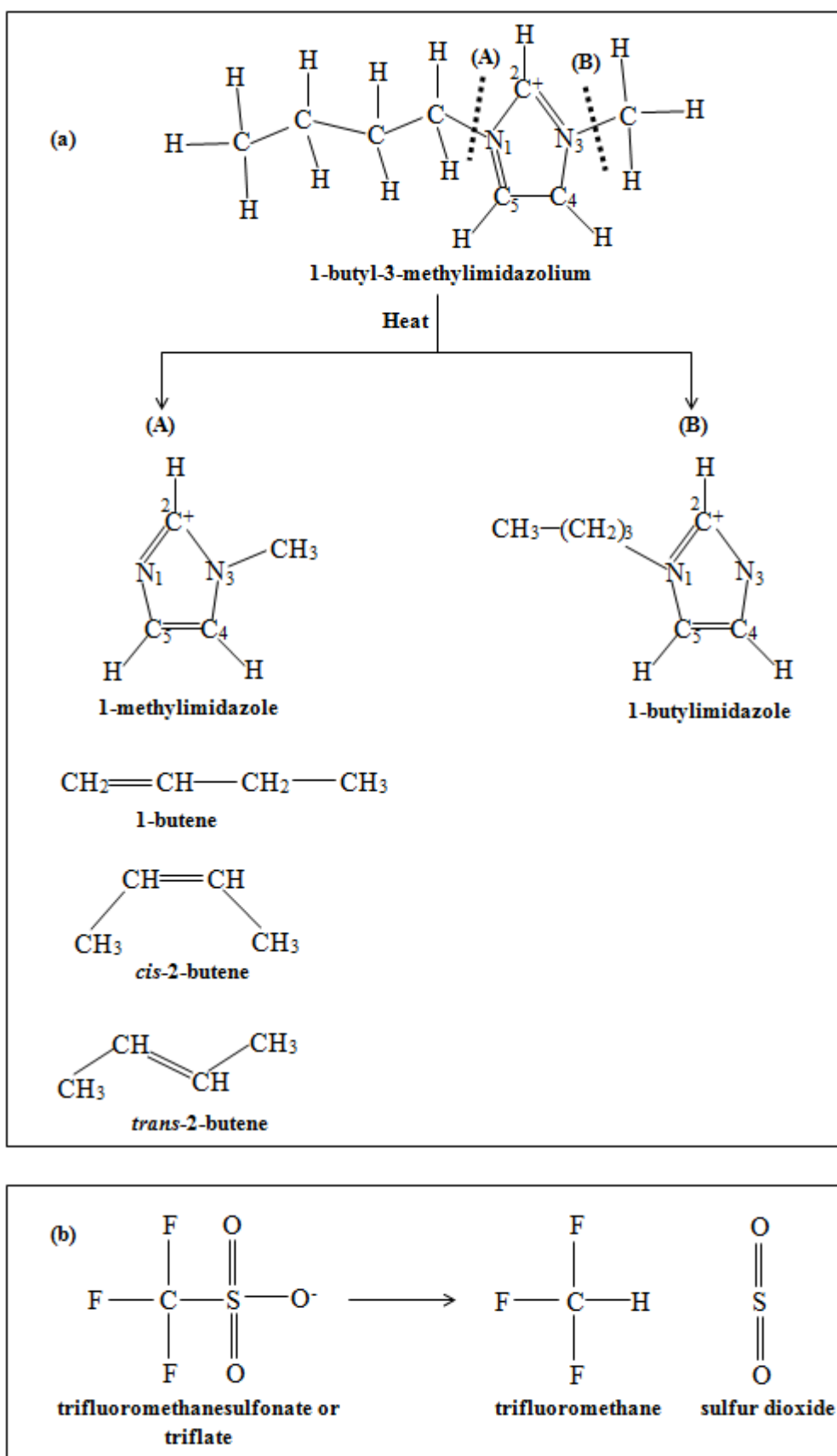


Figure 6.12 Thermal decomposition mechanisms of (a) 1-butyl-3-methylimidazolium and (b) triflate of BMITf [Taken from Ohtani et al., 2008]

Table 6.6 Decomposition temperatures of PEMA/PVdF–HFP–LiTf–BMITf polymer electrolytes (Value in bracket represents wt.% lost in the stage)

Sample	Decomposition Temperature, T_d (°C)					
	PEMA			BMITf	PVdF–HFP	LiTf
	I	II	III			
BMITf	–	–	–	377 (96.1)	–	–
BT–0	259 (5.8)	313 (24.9)	382 (5.6)	–	412 (20.5)	417 (15.1)
BT–10	275 (10.5)	336 (25.2)	–	–	419 (37.1)	–
BT–20	281 (10.0)	348 (31.6)	–	–	414 (23.4)	431 (16.0)
BT–30	284 (4.8)	351 (35.4)	–	–	404 (23.5)	431 (16.0)
BT–40	290 (3.5)	355 (30.0)	–	–	404 (22.8)	431 (25.4)
BT–50	294 (2.8)	352 (27.1)	–	–	391 (29.1)	430 (23.5)
BT–60	294 (3.7)	350 (21.7)	–	–	384 (41.7)	435 (15.6)

6.5 Summary

The thermal stability of the PEMA/PVdF–HFP (70:30) blend, PEMA/PVdF–HFP–LiTf, PEMA/PVdF–HFP–LiTf–EC, PEMA/PVdF–HFP–LiTf–PC, PEMA/PVdF–HFP–LiTf–BMII and PEMA/PVdF–HFP–LiTf–BMITf systems have been determined.

- The thermal stability of the polymer electrolyte systems in terms of onset T_d (provided in bracket) was observed to increase in the following order:
PEMA/PVdF–HFP–LiTf–BMII (202 °C) < PEMA/PVdF–HFP–LiTf–EC (255 °C) \approx PEMA/PVdF–HFP–LiTf (256 °C) = PEMA/PVdF–HFP–LiTf–PC (256 °C) < PEMA/PVdF–HFP–LiTf–BMITf (275 °C)
- The onset decomposition temperature due to PEMA was observed to increase from 229 to 268 °C upon blending with PVdF–HFP. This indicates the role of PVdF–HFP to increase the thermal stability of PEMA.