

Melt and One-Pot Solution Synthesis of Thermally Stable, Organosoluble and Photocurable Acidic Polyimides

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Abstract

Polyimides are well known for their high chemical and thermal stability. However, a few polyimide samples have been reported which are completely soluble in such environmentally friendly and common organic solvent as propyleneglycol monomethyl ether acetate (PGMEA). In this work thermally stable, organosoluble and photocurable acidic polyimides were synthesized by simple and cost effective one-pot solution method. They polyimides obtained by this method showed much higher thermal stability (1 wt% loss temperature 345°C) than melt polymerized polyimides owing to the photocrosslinking reactions by the terminal double bonds.

Keywords

Polyimide, Melt Polymerization, One-Pot Solution Polymerization, Thermal Stability, Organosoluble Polyimide, Photocurable Polyimide

1. Introduction

Polyimides are widely used in electronic devices [1], battery separators [2] and gas adsorption [3] due to the chemical inertness and superior thermal stability [4]. Besides these applications, polyimides of relatively lower molecular weight can be served as thermal stabilizers or binder polymers in photoresists to be developed by basic aqueous solutions. Therefore, the organosolubility and acidity (usually represented by phenolic -OH and/or carboxyl groups) of polyimides are becoming important. Most thermally stable polyimides are made from aromatic diamines and dianhydrides which hinder their solubility in a common organic

solvent, among which only small parts of them are soluble in polar solvents such as NMP, DMAc and THF [5]. Photocuring not only gives a way for the polyimide to serve as a binder polymer in typical photoresists, but also reinforces the overall thermal stability to a great extent. Polyimides which have substituents like acrylate or methacrylate, *i.e.*, photocurable polyimides have been utilized in gate insulators for thin-film transistors [6] and 3D printing process [7] [8].

In this work, we report the melt and one-pot solution syntheses of acidic organosoluble and photocurable new polyimides and analyzed their thermal stability before and after UV curing for potential application in areas such as photoresist binder polymer or thermal stabilizer developable with aqueous base.

2. Experimental

2.1. Materials

All the reagents and solvents were purchased from commercial sources and used directly in the experiments without further purification. Abbreviations of the compounds are as following: 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride (6FDA); 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (MCDA); 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BF6); 2,2'-bis(3-amino-4-hydroxy-phenyl)-hexafluoropropane (AH6); 3,5-diaminobenzoic acid (DAB); 5-aminoisophthalic acid (AIPA); 4-amino benzoic acid (4-AB); 3-amino benzoic acid (3-AB); glycidyl methacrylate (GMA); Pentaerythritoltriacrylate (PETA); 3,5-Di-tert-4-butylhydroxytoluene (BHT); tetrabutylphosphonium bromide (TBPB); dimethyl acetamide (DMAc); propyleneglycolmonomethyl ether acetate (PGMEA).

2.2. Syntheses of Polyimides

2.2.1. Melt Polymerization

Typical reaction scheme: Certain molar ratio of dianhydrides, diamines and monoamine powders were well mixed by a mortar in a metal cup and then the metal cup was placed into 240 °C electric oven with N₂ gas flowing for certain reaction time. Afterwards, the metal cup was taken out of the oven, cooled down in N₂ atmosphere to room temperature and the resulting polyimides were recovered and pulverized to fine particles (Figure 1 and Figure 2).

2.2.2. Solution Polymerization

One-pot solution polymerization of SAM intermediate and SAMG polyimide.

MCDA 30 wt% solution (10 mmol) in DMAc was added into 30 wt% AH6 (9 mmol) and AIPA (2 mmol) solution of DMAc under ice bath and stirred for 1 h. Then the temperature was raised up to 45 °C and stirred for 23 h, followed by stirring at 130 °C for 24 h to afford **SAM** which was used directly in the next step without further purification. To the DMAc solution of **SAM** was added 30 wt% GMA (4 mmol), BHT (0.02 mmol) and TBPB (0.04 mmol) in DMAc solutions.

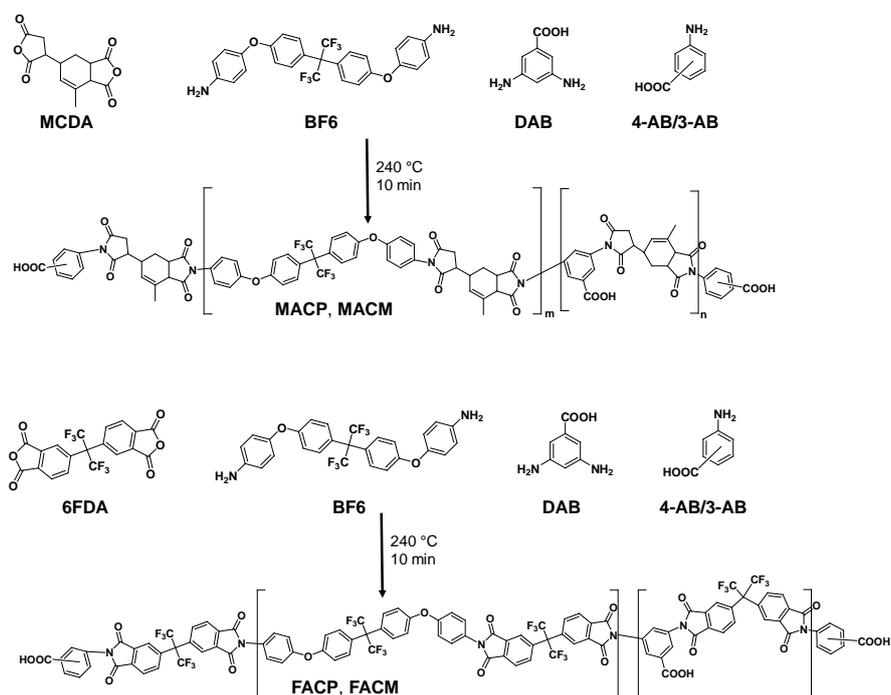


Figure 1. Synthesis of MACP (M) and FACP (M) series polyimides by melt polymerization.

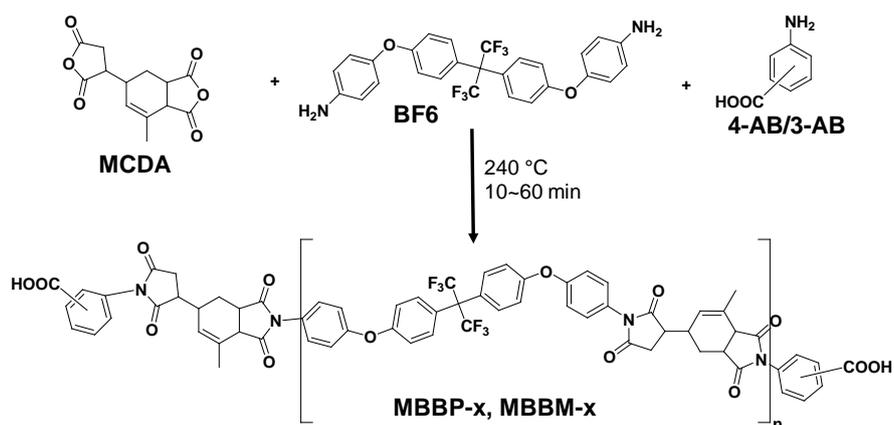


Figure 2. Synthetic scheme of MBBP and MBBM series polyimides by melt polymerization.

The mixture solution was stirred at 90 °C for 3 h to afford SAMG which was used in the test without further purification (Figure 3).

One-pot solution polymerization of PAMG and MAMG series polyimides.

MCDA powder (5 mmol) was added into PGMEA solution of AH6 (4 mmol) and 4-AB (2 mmol) with an overall concentration of 25 wt%. The mixture was stirred at RT for 1 h, at 45 °C for 23 h followed by 130 °C for 24 h. After cooling, to the mixture was added 25 wt% of GMA (2 mmol) in PGMEA, BHT (0.01 mmol) and TBPB (0.02 mmol). The solution was stirred at 90 °C for 3 h to afford

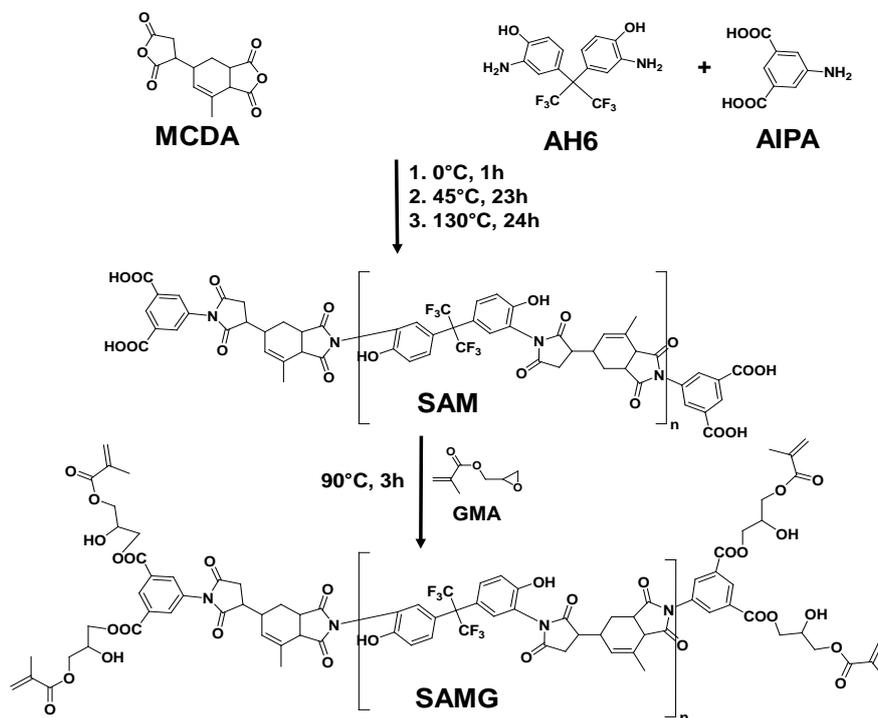


Figure 3. Synthetic scheme of SAMG polyimide.

PAMG which was used without further purification. MAMG was synthesized using 3-AB instead of 4-AB with the same scheme (Figure 4).

2.3. Evaluation of Thermal Stability with Thermogravimetric Analysis (TGA)

For a TGA test of solution polyimide sample (without UV curing), the solution was spin-coated on glass substrates, pre-baked (110°C, 100 s) and subjected to post-cure (250°C, 30 min). After cooling, the film on glass substrates was scratched off as powder for TGA test.

For the TGA test of UV-cured polyimide samples, photoinitiator (SPI-03, 3 wt%) was added in the polyimide solution; and the solution was spin-coated on glass substrates, pre-baked (110°C, 100 s), UV exposed (80 mJ) and subjected to post-cure (250°C, 30 min). After cooling, the film on glass substrates was scratched off as powder for TGA test.

3. Results and Discussions

3.1. Melt Polymerization of Polyimides

In our previous work we used various combinations of dianhydrides, diamines and monoanhydrides to synthesize polyimides soluble in common organic solvents (PGMEA) by melt polymerization [9]. It was found that the polyimide (FTAP-1) obtained by the combination of dianhydride with $-\text{CF}_3$ groups (6FDA), diamine with $-\text{CF}_3$ groups (AH6) and monoanhydride (PEPA) monomers as shown in Figure 5 exhibited good solubility in PGMEA solvent.

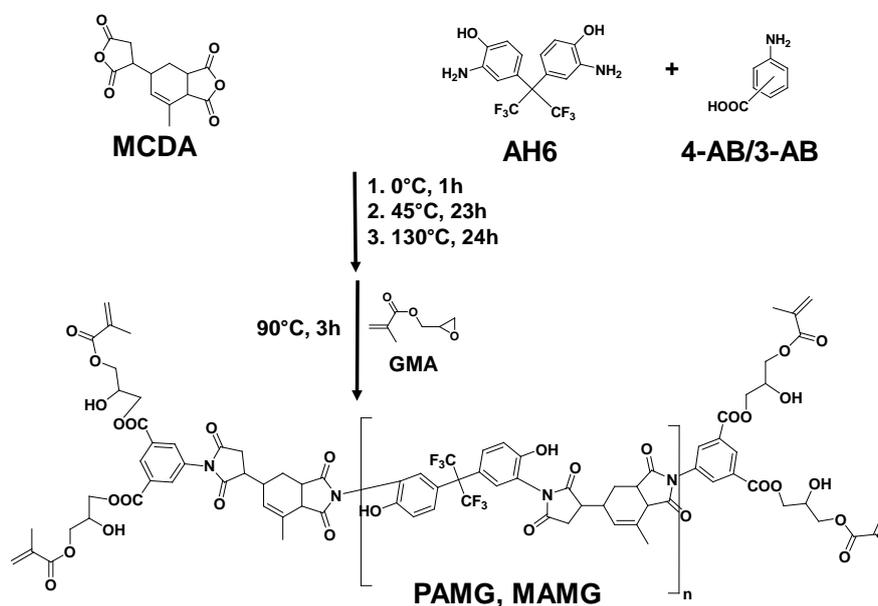


Figure 4. Synthetic scheme of PAMG and MAMG series polyimides.

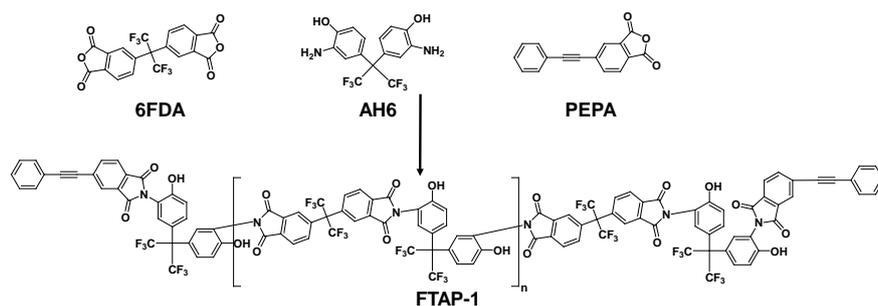


Figure 5. The structures of polyimide (FTAP-1) obtained from 6FDA, AH6 and PEPA monomers.

The PGMEA soluble polyimide (**FTAP-1**), however, could be obtained only at the melt polymerization condition at 240°C for a short reaction time of 10 min, thus resulting in low molecular weight polyimides. When the melt polymerization temperature was above 240°C or the time was over 10 min, the polyimides obtained showed insolubility in PGMEA. This result could be attributed to the cross-linking reaction between the synthesized **FTAP-1** polyimides through the dehydration of phenolic –OH groups in the AH6 units.

One plausible synthesis of polyimide by melt polymerization to avoid the problem of **FTAP-1** is shown in **Figure 1** with the reaction condition given in **Table 1**. In this case we used MCDA and 6FDA as dianhydride monomers, BF6 and DAB (diaminobenzoic acid) as diamine comonomers and 4-AB (4-aminobenzoic acid) or 3-AB (3-aminobenzoic acid) as monoamines to control the molecular weight of the resulting polyimides as well as maintain certain acidity by –COOH groups. In these melt polymerizations, in contrast to the previous polyimides, the monoamines (4-AB or 3-AB) were used to give polyimides with carboxyl terminal groups. The carboxyl groups will also be present in the main chain of

Table 1. The synthetic conditions of polyimides and their solubility in organic solvents.

Sample	Dianhydride (mmol)	Diamines (mmol)	Monoamine (mmol)	Condition	30% PGMEA	30% DMAc
MACP	MCDA (5)		4-AB (2)		X	O
MACM		BF6 (1)	3-AB (2)	240°C	X	O
FACP	6FDA (5)	DAB (3)	4-AB (2)	10 min	X	O
FACM			3-AB (2)		O	O

the polyimides with the use of DAB co-monomer which will increase the solubility of the resulting polyimides in the PGMEA solvent. However, only the polyimide (**FACM**) exhibited solubility in PGMEA solvent up to 30 wt%. This result of low solubility in PGMEA could be explained to be due to the intermolecular charge transfer complex (CTC) formation among the imide units linked by less sterically hindered major DAB co-monomers as shown in **Figure 6**.

Therefore, melt polymerization of polyimides were attempted without DAB co-monomer as shown in **Figure 2** utilizing MCDA as dianhydride, BF6 as diamine and 4-AB or 3-AB as monoamines. The resulting polyimides **MBBP** and **MBBM** were all soluble in PGMEA up to 30 wt% as shown in **Table 2**. It was also noted the **MBBP** and **MBBM** polyimides could be melt polymerized at 240°C up to 60 min in the electric furnace. These difference in melt polymerization and solubility in PGMEA compared to the previous **FTAP-1** in **Figure 5**, and **MACP (M)** and **FACP (M)** polyimides in **Figure 1** could be explained by exchange of AH6 diamine monomer with BF6, and elimination of DAB co-monomer. In the **MBBP** and **MBBM** polyimides no cross-linking reaction could occur due to the absence of phenolic -OH groups thus melt polymerization time could be extended up to 60 minutes. The improved solubility of **MBBP** and **MBBM** could be also explained by less CTC formation by removing DAB units which could make CTC easier than BF6 diamine monomer due to less steric hindrance. The higher molecular weights of **MBBM** than **MBBP** may be explained by close melting points of MCDA/BF6/3-AB than MCDA/BF6/4-AB set of monomers thus promoting the melt polymerization to occur under more homogeneous state during short period of time as shown in **Table 2**.

The FT-IR analyses of **MBBP-3** and **MBBM-3** polyimides in **Figure 7** exhibited all the typical imide linkages as carbonyl group stretching (1712 cm^{-1}), aromatic -C=C- (1502 cm^{-1}) and aryl-aryl ether C-O stretching ($1171 - 1246\text{ cm}^{-1}$) while the other characteristic absorption peaks were observed at different points corresponding to the chemical groups in **MBBP-3** and **MBBM-3**.

3.2. Solution Polymerization of Polyimides

In order to further enhance the thermal stability of polyimides while retaining the solubility in organic solvent, we tried to synthesize double bond containing polyimides and to proceed UV curing. We utilized one-pot solution polymerization

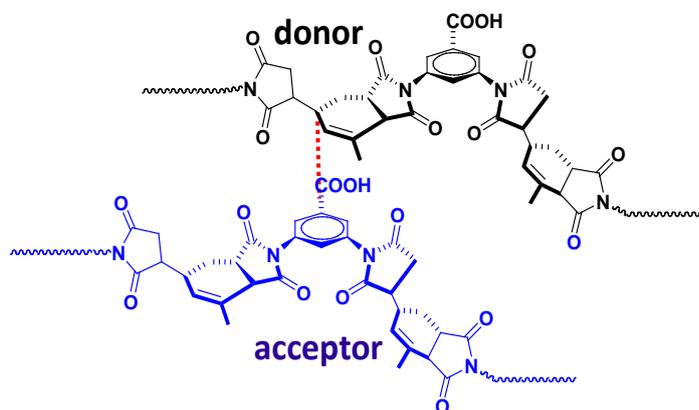


Figure 6. The schematic diagram of charge transfer complex formation by polyimides.

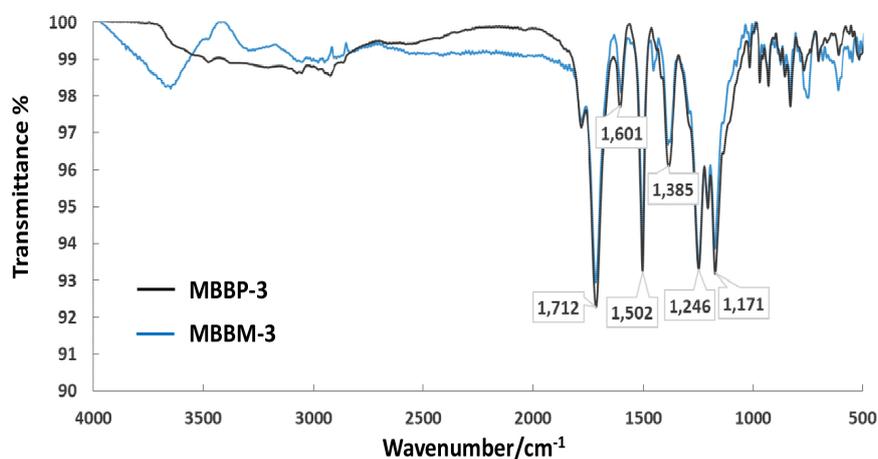


Figure 7. The FT-IR spectra of **MBBP-3** and **MBBM-3** polyimides.

Table 2. Molecular weights and thermal stabilities of **MBBP** and **MBBM** polyimide series.

Compound Code	Reactants (mmol)	Reaction Time/min	GPC M_w	1% WLT/ $^{\circ}$ C (TGA) ^a	5% WLT/ $^{\circ}$ C (TGA)	PGMEA solubility
MBBP-1	MCDA (5)	10	4993	275	400	All soluble up to 30 wt%
MBBP-2	$T_m = 172^{\circ}$ C - 176° C	20	4562	326	398	
MBBP-3	AH6 (4) $T_m = 243^{\circ}$ C	30	4745	338	411	
MBBP-4	4-AB (2)	40	3486	235	391	
MBBP-6	$T_m = 188^{\circ}$ C	60	4238	252	391	
MBBM-1	MCDA (5)	10	4121	287	383	
MBBM-2	$T_m = 172^{\circ}$ C - 176° C	20	5348	318	385	All soluble up to 30 wt%
MBBM-3	AH6 (4) $T_m = 243^{\circ}$ C	30	6428	346	400	
MBBM-4	3-AB (2)	40	4983	266	385	
MBBM-6	$T_m = 178^{\circ}$ C - 180° C	60	3694	285	364	

^aWLT: weight loss temperature.

for the synthesis of photocurable polyimides since double bonds undergo thermal cross-linking at melt polymerization temperature.

As shown in **Figure 3**, we first synthesized the intermediate **SAM** using MCDA as dianhydride, AH6 as diamine and AIPA as monoamine monomer in DMAc solvent. In the second step the carboxyl groups of the **SAM** intermediate were converted to methacrylate groups to give final product **SAMG** polyimides with two double bonds at both terminal which could be cured by UV exposure after spin coating and soft bake on the substrate.

The FT-IR chart of **SAMG**, **PAMG** and **MAMG** polyimides in **Figure 8** showed similar peaks as **MBBP** and **MBBM** polyimides (**Figure 7**) since both series of polymers shared the same main-chain polyimide scaffold. In case of these 3 polyimides, the peaks around 1200 cm^{-1} were shrunk due to the absence of aryl-aryl ether.

Since the **SAMG** polyimide was prepared in the DMAc solvent which is known as a carcinogen to human, we tried to synthesize polyimide in environmentally friendly PGMEA solvent by using one-pot reaction method. We used the same MCDA and AH6 as dianhydride and diamine monomer but replaced AIPA with 4-AB (or 3-AB) as monoamine monomer. This was due to the solubility difference of 4-AB/3-AB monomers with AIPA monomer; the former had high solubility in PGMEA, while the latter was not soluble in PGMEA. One-pot solution polymerization of **PAMG** and **MAMG** polyimides are shown in **Figure 4** in which the intermediate is omitted since it was used directly in the second step. These **PAMG** and **MAMG** polyimides were obtained with 4-AB and 3-AB as monoamines, respectively. The GPC molecular weights of **SAMG** (2578 g/mol) and **MAMG-3** (2475 g/mol) were similar as shown in **Figure 9**.

3.3. Thermal Stability Tests

We first checked the thermal stability of the **MBBP** and **MBBM** polyimides, which were synthesized by melt polymerization method. As shown in **Table 2** of the **MBBP** and **MBBM** series polyimides, **MBBP-3** and **MBBM-3** exhibited the highest thermal stability as shown by 1 wt% and 5 wt% loss temperatures (1 WLT and 5 WLT) of the samples (**Figure 10**). The high thermal stability of **MBBP-3** and **MBBM-3** may be explained by the characteristics of the melt polymerization. As the melt polymerization time increased from 10 min to 30 min the conversion of melt polymerization could increase, thus improving the thermal stability, however after 30 min the partial degradation of polyimide may occur due to the accumulated heat in the electric oven leading to both low Mw and low thermal stability of the polyimides.

The TGA data of the solution polymerized **SAMG** and **MAMG** polyimides are shown in **Figure 11** and **Figure 12**. The **SAMG** and **MAMG** polyimide solutions were first spin coated without UV photoinitiator (SPI-03) and subjected to TGA analysis of which TGA samples were recorded as **SAMG (a)** and **MAMG (a)** in **Figure 11** and **Figure 12**, respectively. The other samples were spin coated

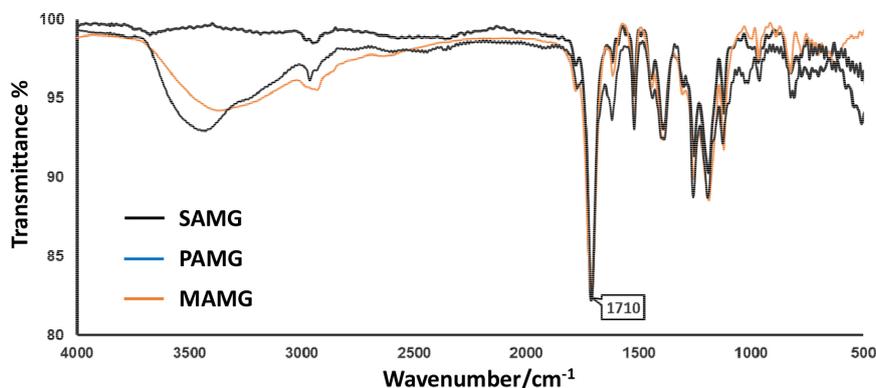


Figure 8. The FT-IR spectrum of **SAMG**, **PAMG** and **MAMG** polyimides.

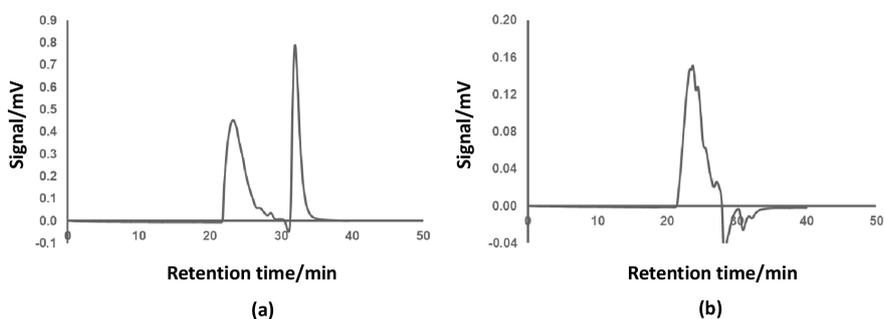


Figure 9. The GPC graphs of (a) **SAMG** and (b) **MAMG-3** polyimides.

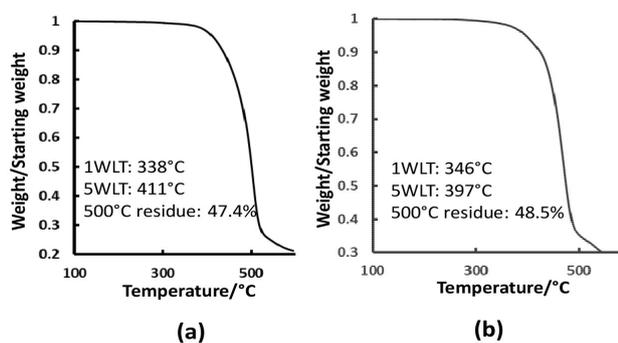


Figure 10. The thermal stability of **MBBP-3** (a) and **MBBM-3** (b) polyimides measured by TGA.

with the **SAMG** and **MAMG** solution containing SPI-03 photoinitiator followed by TGA process to give the thermogram of **SAMG** (b) and **MAMG** (b) in **Figure 11** and **Figure 12**, respectively. The thermal stability of **MAMG** polyimide was higher than that of **SAMG** polyimide while both samples can be crosslinked by thermally or photochemically with photoinitiator. The low thermal stability of **SAMG** compared to the **MAMG** may be due to the incomplete removal of DMAc solvent in the spin coating and soft bake steps compared with PGMEA solvent.

It is of interest to notice the difference of the TGA residue data at 500 °C of the **MBBP/MBBM** and **SAMG/MAMG** polyimide samples, while the former was in

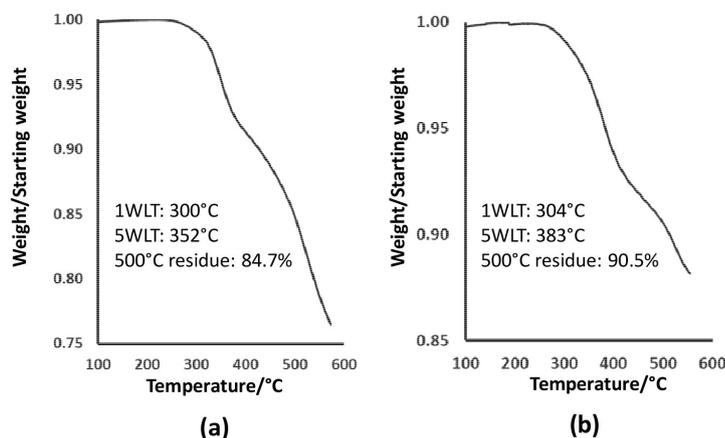


Figure 11. The TGA thermographs of (a) **SAMG** and (b) cured **SAMG**.

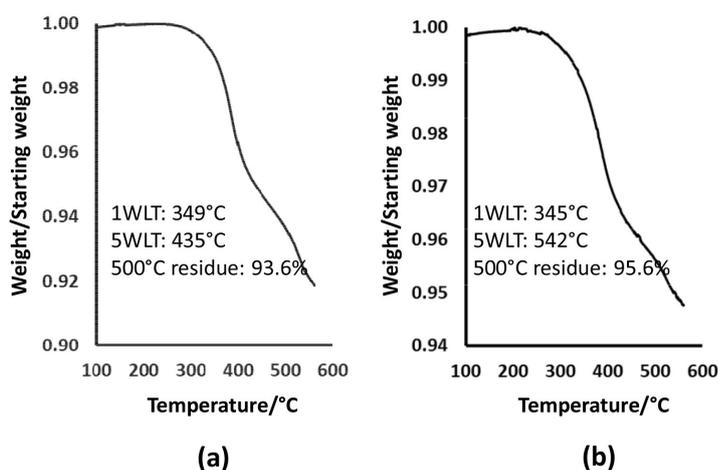


Figure 12. The TGA thermographs of (a) **MAMG** and (b) cured **MAMG**.

the range of 47.4% - 48.5% and the latter, 84.7% - 95.6%. This difference of the TGA 500°C residue data is due to the different synthetic methods, the former by melt polymerization, and the latter by solution polymerization. In the melt polymerization of polyimides the exact stoichiometric balances of the monomers are hard to match compared to the solution polymerization. Another reason is the **SAMG/MAMG** polyimides can be cross-linked by the presence of the terminal double bonds while **MBBP/MBBM** polyimides could not be cross-linked in the absence of double bonds.

4. Conclusion

In this work we reported the melt and one-pot solution synthesis of acidic organosoluble and photocurable new polyimides and analyzed their thermal stability before and after UV curing. In the melt polymerization of **MBBM** and **MBBM** series polyimides high molecular polyimides could be obtained by using BF₆ as diamine monomer which could not undergo thermal crosslinking reaction under melt polymerization conditions. In the solution polymerization of polyi-

mides, the **MAMG** polyimide with two terminal double bonds exhibited higher thermal stability than **SAMG** polyimide with four terminal double bonds. Both **MAMG** and **SAMG** polyimides exhibited higher thermal stability by UV curing which could lead to crosslinking reaction than the same uncured polyimide samples. It was also noted that the UV curing of polyimide samples could enhance the thermal stability to much higher extent than that of melt polymerized polyimides.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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