

Effect of the Size of the Molecular Mass of Some Amine Groups Modified to Maleic anhydride-alt-1-Octadecene Copolymer on Thermal Stability

Hacıbayram Zengin^{1,a,*}¹ Department of Chemistry, Faculty of Science and Arts, Cumhuriyet University, 58140 Sivas, Türkiye.

*Corresponding author

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ABSTRACT

In this study, 1-octadecene-alt-maleic anhydride (OC-MA) copolymer was synthesized by radical polymerization method. The synthesized copolymer was first time modified with ammonia, methylamine, aniline and hexamethylenediamine reagents in acetone environment. The modified amidic acid derivatives were divided into two parts as quantity. One of these amounts was dried as an amidic acid derivative, and the other was imidized in dimethylformamide environment with constant stirring at 150 °C for 5 hours. Structural characterizations of the obtained samples were determined from the FTIR spectra. Thermal stability was compared from Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) curves. It was established that the modified copolymers were thermally more stable than that of the original OC-MA copolymer. However, it was observed that the size of the molar masses of the reagents participating in the modification reactions showed linear or parabolic increases according to thermal parameter temperature of the decomposition reaction obtained from the TGA and DSC curves.

Keywords: Copolymerization, Radical polymerization, Thermal analysis, Modification.^a hbzengin@cumhuriyet.edu.tr <https://orcid.org/0000-0003-3861-6671>

Introduction

One way to increase the thermal stability of straight chain polymers is to modify them. Polyimides (PI) have been the subject of extensive investigation since the 1960s, owing to their exceptional thermal stability, high mechanical strength, superior chemical resistance, and remarkable electrical properties [1]. Polyamide-imides are usually prepared by three methods; polycondensation of amide group containing dianhydrides or diamines; imide group containing diacids with diamines, trimellitic anhydride with diisocyanates or diamines. First method involves multi-step synthesis of dianhydride or diamine monomers and high temperature imidization [2]. Aromatic polyimides are widely acknowledged as high-performance materials renowned for their outstanding thermal and oxidative stabilities, as well as their excellent electrical and mechanical properties over prolonged periods of use. However, their rigid structure and strong intermolecular interactions render them difficult to process, presenting challenges such as poor thermoplastic flow and solubility, thereby limiting their widespread application. To address these processing issues, various strategies have been explored, including the incorporation of flexible units such as -NHCO-, -O-, and -SO₂-, some of which have been successfully commercialized [3]. Superior polymers are increasingly sought after in cutting-edge technologies such as microelectronics, semiconductors, and composites. Polyimides are frequently favored for these high-temperature applications, serving as coating materials

and insulators for electronic components, thanks to their commendable thermal stability, excellent planarization, superior processability, and elevated glass transition temperature [4]. Cross-linking polymers brings about versatility to the polymer's mechanical properties and processing behavior [5]. In order to increase the heat resistance of a polymer, it is necessary to modify it. The thermal attributes of polymeric materials are widely recognized as their foremost defining features. TGA enjoys broad utilization due to its straightforward methodology and the valuable insights offered through a basic thermogram. The thermal endurance of polymer blends and alloys has undergone comprehensive examination [6-11]. Over time, driven by its relevance across diverse sectors within the polymer industries. Maleic anhydride serves as a valuable intermediary in organic synthesis, finding utility in crafting biologically potent compounds and serving as building blocks for polymerization processes [12]. Within a maleic anhydride (MA) molecule, one can find a conjugated bond alongside an electron-withdrawing carboxyl group. Hence, despite its resistance to polymerization under heat alone, maleic anhydride (MA) readily undergoes copolymerization with electron-donor monomers like 1-octadecene and vinyl acetate [13-14]. The presence of anhydride groups within the polymer chain endows this copolymer with high reactivity, facilitating its application across diverse fields. Copolymers of maleic anhydride (MA) frequently serve as compatibilizers in polymer blends [15-16]. Polyimides are

synthesized through the imidization process of polyamic acids, which are formed by the reaction of an anhydride with an amine or diamine [17]. The literature extensively documents the rapid formation of polyamic acids at low temperatures, contrasting with the high-temperature requirement for imidization to occur. Copolymers containing maleic anhydride (MA) have been instrumental in crafting functional polymers, primarily attributed to the ring-opening reaction of the anhydride unit [18–20]. The 1-octadecene-alt-maleic anhydride (OC-MA) copolymer used in this paper has been synthesized in the authors' previous work [21–23]. The OC-MA copolymer underwent reactions with aniline (An), methylamine (MeA), ammonia (Am), and hexamethylenediamine (HMDA), yielding maleamic acid and maleimide derivatives of OC-MA, as depicted in Fig. 1. These derivatives of the OC-MA copolymer were called as amidic acid-1-octadecene, bismaleamic acid, maleimide and bismaleimide 1-octadecene copolymers. The polymers were characterized using Fourier transform infrared spectroscopy (FTIR), followed by comparison of their thermal degradation curves using TGA. Maleic anhydride-alt-1-octadecene (OC-MA) copolymer were sequentially modified by methylamine (MeA), ammonia (Am), aniline (An) and hexamethylenediamine (HMDA) to obtain copolymers of poly(amidic acid-1-octadecene) and poly(Bisamidic acid-1-octadecene) (BisAA-OC) by opening the maleic anhydride ring in the OC-MA copolymer.

In terms of novelty achieved, the main purpose of the present study is to obtain modified copolymers with higher thermal stability compared to the original copolymer and to expand their areas of use by synthesizing materials that are more robust and durable, especially against cracking.

Experimental

Materials

Monomers Maleic anhydride (MA, MW: 98,06) and 1-octadecene (OC, MW: 252,49) were obtained from Merck made in Germany, aniline (An, MW: 93,13), methylamine (MeA, MW: 31,06) ammonia (Am, MW: 17,03). Hexamethylenediamine (HMDA, MW: 116,21) were obtained from Aldrich Chemical Company, UK. *N,N*-dimethylformamide (DMF, MW: 73,09) was obtained from Merck Chemical Company, Germany.

Maleic anhydride- alt- 1-octadecene copolymer: OC-MA

Amidic acids:

Amidic acid-1-octadecene: AA-OC

Methylamidic acid-1-octadecene: MeAA-OC

Phenyl amidic acid-1-octadecene: PhAA-OC

Bis amidic acid-1-octadecene: BisAA-OC

Imides:

Maleimide 1-octadecene: MI-OC

Methylmaleimide 1-octadecene: MeMI-OC

Phenylmaleimide 1-octadecene: PhMI-OC

Bismaleimide 1-octadecene: BisMI-OC

Synthesis of Maleic anhydride-alt-1-octadecene copolymers

19.6 g of maleic anhydride was placed in a large dried test tube and dissolved in 30 mL of ethyl acetate. 21.6 mL 1-octadecene (1:1) and 0.8 g 2,2'-Azobis(2-methylpropionitrile) (AIBN) were added on it. It was heated from room temperature in a 70 °C water bath for two hours. Then, the mixture was placed in a beaker and precipitated by adding propanol. Following the precipitation of the maleic anhydride-alt-1-octadecene copolymer, it was filtered through a Buchner funnel under vacuum assistance. The copolymer was left in hexane solution for 24 hours, then filtered and dried again

Synthesis of Amidic acid, Bisamidic acid, Maleimide and Bismaleimide Derivatives

The poly(amidic acid-1-octadecene) copolymers were synthesized by reacting the OC-MA copolymer with An, Me, Am, and HMDA in DMF using a mixer in a large tube at room temperature. For the synthesizing amidic acid copolymers, the required amount of OC-MA copolymer is 10.0 g, one of An, MeA, Am and HMDA are 8.0 cm³ and one of DMF used as solvent are 30 cm³. While the reactions between OC-MA copolymer with Me, Am and HMDA rapidly are occurred when they are mixed at room temperature, those of OC-MA copolymer with An is obtained by mixing at 60 °C for 2 h. While the precipitates of amidic acid and BisAA-OC copolymers are white colored, PhAA-OC precipitate is red colored. This precipitates were dried under the vacuum at 60 °C. For the obtained maleimide-1-octadecene and BisMI-ST copolymers, 5.0 g of this precipitate are added to 50.0 cm³ DMF and thus, they obtained a solution of amidic acid copolymers. The solutions were heated to 150°C for 5 hours and subsequently cooled to room temperature. The solid samples in the solution were filtered and dried under vacuum.

Structural Characterization and Thermal analysis of Copolymers

The copolymers were spectrophotometrically characterized using a Unicam Mark Mattson 1000 model FTIR spectrophotometer with KBr pellets. The TGA and DSC experiments were conducted utilizing a Shimadzu TA50i model, employing a heating rate of 10°C min⁻¹ under a flowing nitrogen atmosphere. The temperature range spanned from 25 to 600°C. Polymer samples weighing 10 mg each were employed for the examination. The nitrogen gas flow rate was maintained at 25 cm³ min⁻¹.

Results and Discussion

Structural Characterization

The OC-MA copolymer (Fig. 1) exhibited anhydride units with characteristic peaks at 1804 and 1855 cm⁻¹, attributed to the symmetric and asymmetric C=O stretching vibrations, respectively [24]. The absence of these bands in the modified copolymer spectra indicates that the ring has opened and transformed into the amidic acid structure.

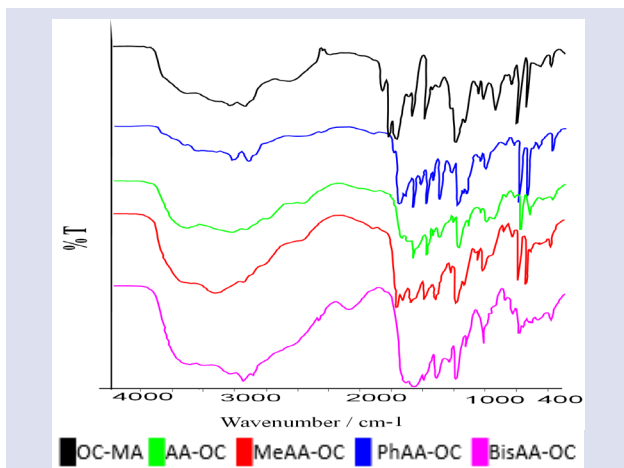


Figure 1. FTIR spectra of its amidic acid and bisamidic acid derivatives and OC-MA copolymer.

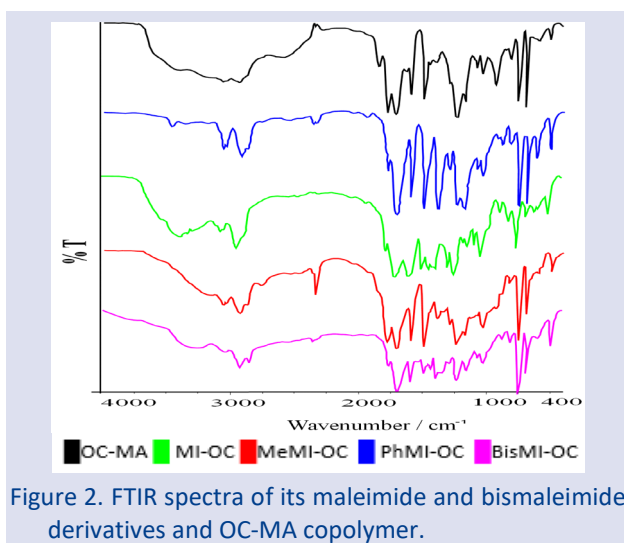


Figure 2. FTIR spectra of its maleimide and bismaleimide derivatives and OC-MA copolymer.

The C–O–C stretching vibrations stemming from the maleic anhydride (MA) ring were detected at 1025 and 935 cm^{-1} . Conversely, new peaks appeared within the range of 1778–1640 cm^{-1} , exhibiting characteristic peaks at 1640 and 1736 cm^{-1} , as well as 1727 and 1778 cm^{-1} , (Fig. 2) likely corresponding to the maleimide and maleimide groups [25].

Thermal Analysis

The thermal transitions of amidic acid, BisAA-OC, MI-OC and BisMI-OC were measured by TG technique and compared with that of OC-MA copolymers. The thermal curves are illustrated in Fig. 3 and Fig. 4, while the corresponding thermal parameters extracted from these figures are tabulated in Table 1. The thermal decomposition peaks observed at these temperatures are also reflected in the TGA thermograms, which can be observed in Fig. 3 and Fig. 4 for all the polymers. In the blue, green, red and pink colored thermograms In Figure 3, mass loss has been seen at 150 °C. This mass loss is due to loss of water arisen from the heating of amidic acid structures. Most water loss is seen in the pink colored thermogram. While 1 mol H_2O in the blue, green and red colored thermogram is removed, 2 mol H_2O in the pink colored thermogram has been removed. This structure is an indicator of bismaleimid formation.

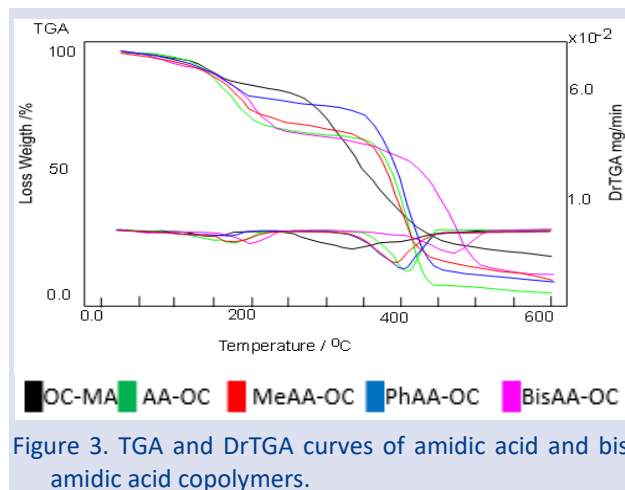


Figure 3. TGA and DrTGA curves of amidic acid and bis amidic acid copolymers.

Figure 4 by heating at 150°C for 2 hours in solution media amidic acids were heated for their imidization. their thermograms were taken and then comparatively presented. As can be shown in Figure 4, according to Figure 3 the mass loss was less than those of 150 oC. The cause of this situation may be still continuing of imidization reaction.

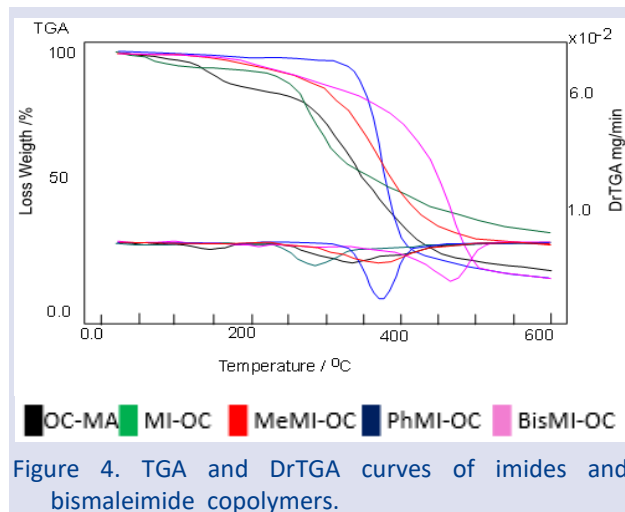


Figure 4. TGA and DrTGA curves of imides and bismaleimide copolymers.

The modification samples synthesized in Figure 4 were imitated in DMF medium at 150 °C for 5 hours. The thermograms of these modified samples were taken, which were imitated at room temperature up to 600 °C. The samples, which were both imitated outside and subjected to chemical transformation by heating the device, showed better stability against heat from the first steps compared to the starting material in this thermogram. As we mentioned in Fig. 4 and Fig. 3, there is also a regularity in thermal stability depending on the molecule size. The thermal parameters extracted from Fig. 3 and Fig. 4 indicate that the initial and final temperatures signify higher thermal stabilities for the amidic acid and MI-OC copolymers compared to the OC-MA copolymer, as depicted in Fig. 4. Based on these elucidations, the thermal stability of MI-OC surpasses that of the other copolymers due to the formation of cross-linkages via imidization, coupled with the elimination of 2 moles of water, as illustrated in Fig. 3.

T_i initial degradation temperature, T_f final degradation temperature T_h half time temperature, T_m maximum rate temperature, T_g glass transition, R_m maximum rate and remained substance amount at maximum rate C_m given in

Table 1. The molar masses of the ammonia, methylamine, aniline and hexamethylenediamine substances added as modifications to the OC-MA copolymer are respectively

(17, 31.06, 93.13 and 262.35 gmol^{-1}). Thermal parameters values plotted against molar masses Fig. 5 and Fig. 6 showed linear or parabolic increases.

Table 1. Thermal analysis parameters of copolymers

Copolymers	$T_i / ^\circ\text{C}$	$T_f / ^\circ\text{C}$	$T_h / ^\circ\text{C}$	$T_m / ^\circ\text{C}$	$T_g / ^\circ\text{C}$	R_m / mgdk^{-1}	$C_m / \%$
OC-MA	279	434	348	328	108	0.0081	62
AA-OC	358	426	378	391	133	0.0142	41
MeAA-OC	362	428	384	403	135	0.0186	32
PhAA-OC	374	430	386	398	149	0.0172	42
BisAA-OC	420	495	426	465	160	0.0101	31
Mi-OC	246	355	369	287	129	0.0084	63
MeMi-OC	315	406	380	364	150	0.0096	76
PhMi-OC	348	431	387	372	158	0.0239	61
BisMi-OC	404	495	450	467	169	0.0169	40

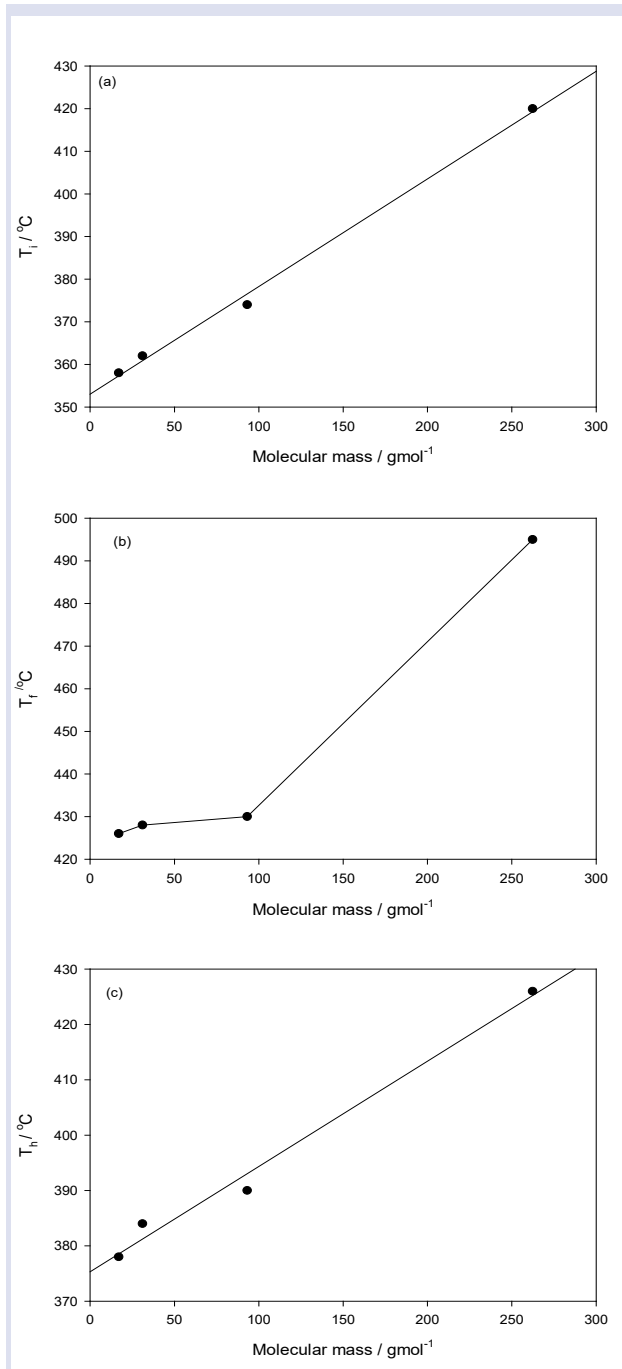


Figure 5. Variation of modified molar masses with thermal parameters (a) T_i , (b) T_f and (c) T_h of amidic OC-MA copolymers

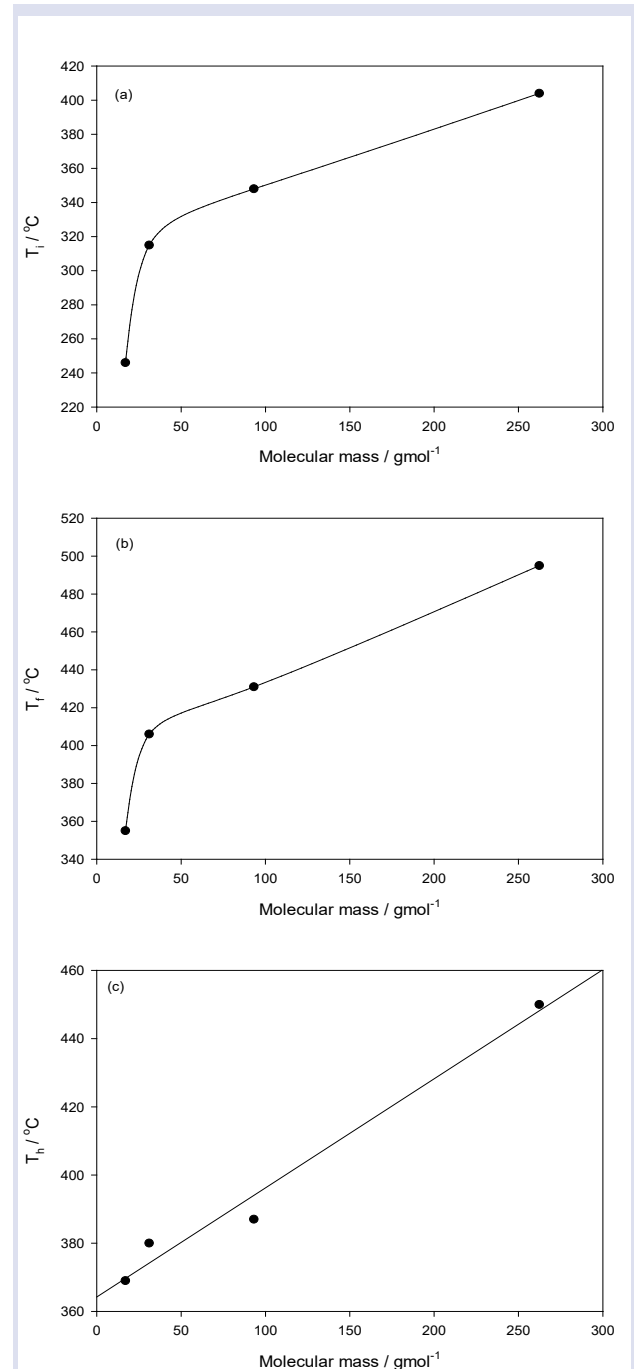


Figure 6. Variation of modified molar masses with thermal parameters (a) T_i , (b) T_f and (c) T_h of imide OC-MA copolymers

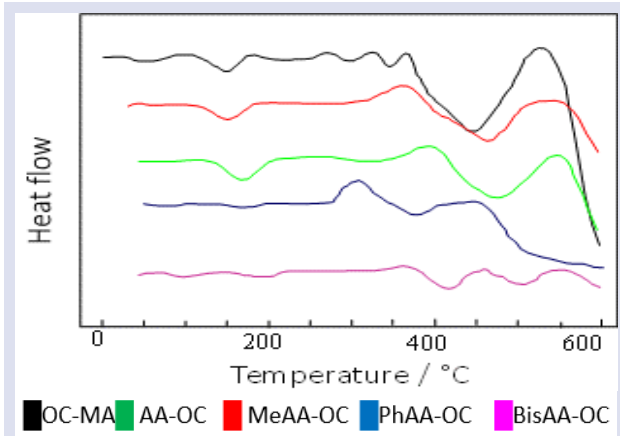


Figure 7. DSC curves of amidic acid and bis amidic acid copolymers.

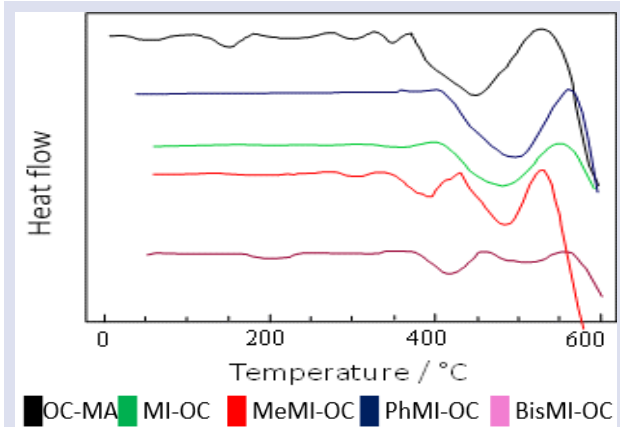


Figure 8. DSC curves of imides and bismaleimide copolymers.

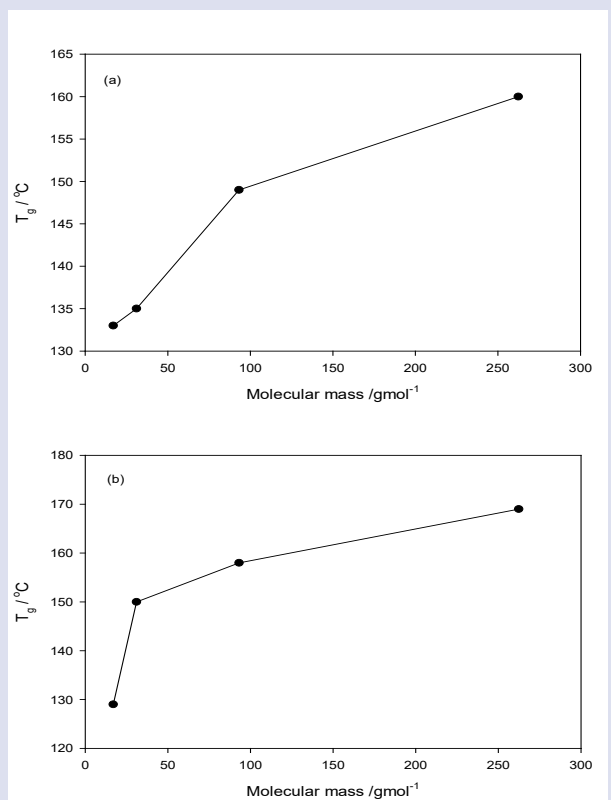
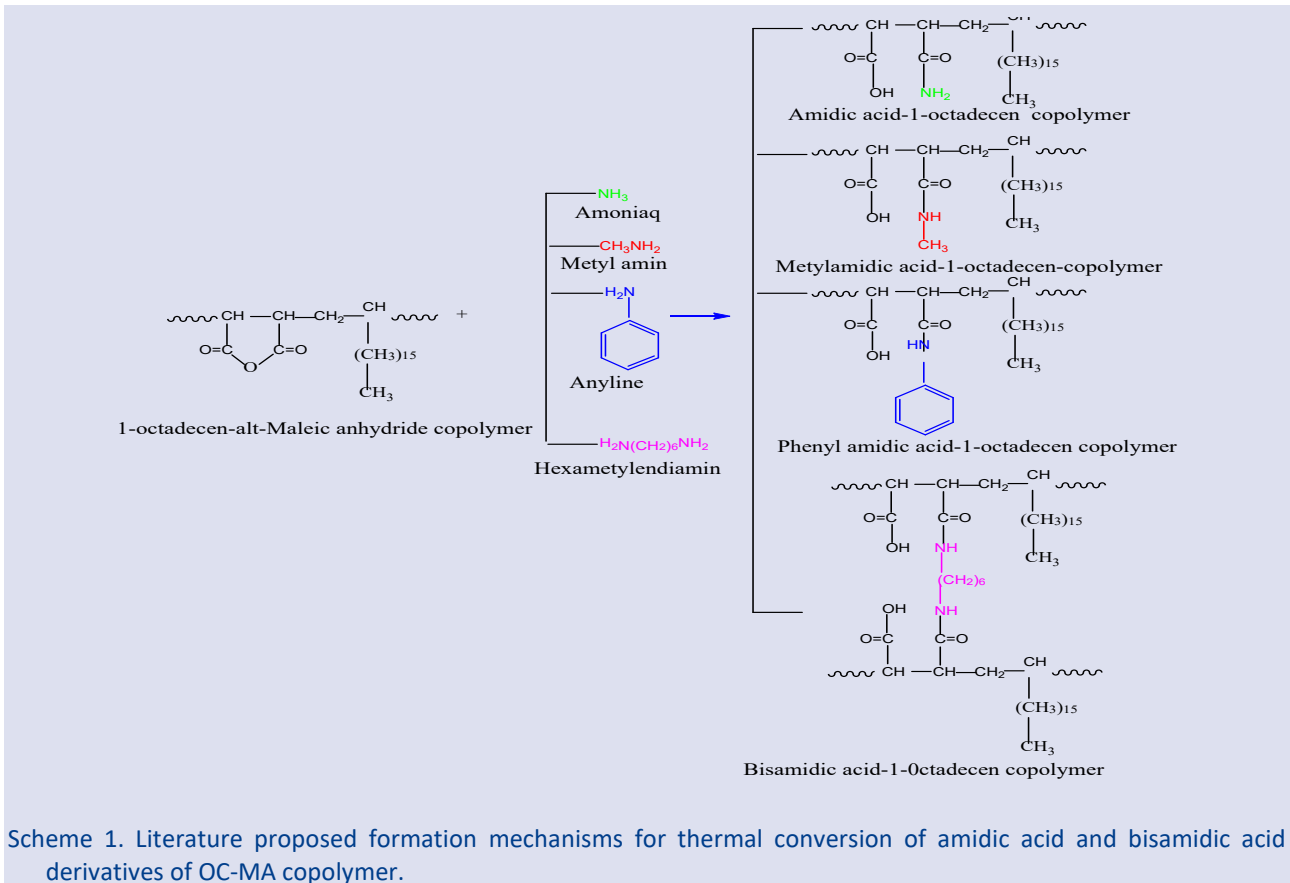
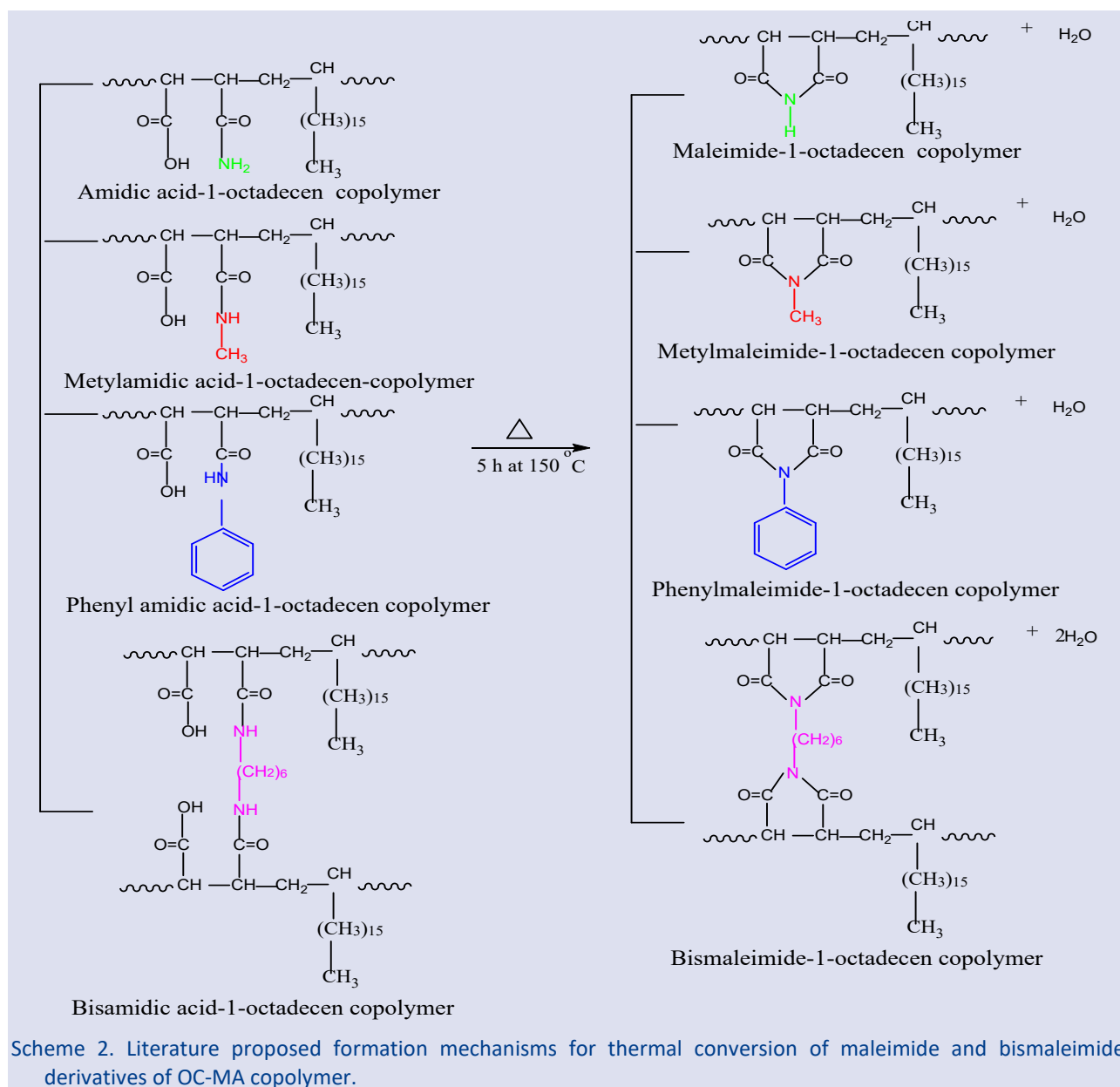


Figure 9. Variation of molecular mass size with glass transition temperature (a) T_g of amidic acid and (b) T_g imide

The glass transition temperatures obtained from DSC Fig.7 and Fig.8 thermograms showed a non-linear relationship with the size of the molecular masses of the modified amines [26].



Scheme 1. Literature proposed formation mechanisms for thermal conversion of amidic acid and bisamidic acid derivatives of OC-MA copolymer.



Conclusions

The fact that the anhydride ring is active against amine groups enabled the reaction to occur in a short time period. The selection of modified amine groups was based on a simple structure such as ammonia, an aromatic structure such as aniline, and a hexamethylenediamine structure. The size of the molecular masses of the amines in the order of ammonia, methyl amine aniline and hexamethylenediamine (17, 31.06, 93.13 and 262.346 g mol⁻¹). The effect of the molar mass of the modified amines on thermal stability was clearly seen. The thermal stability of the newly modified copolymers obtained after modification of the OC-MA copolymer, shown in black in TGA, is higher than the OC-MA copolymer. The thermal parameters obtained in the TG curves increased linearly or parabolically with the molecular masses of the modified amine groups. This tells us that one way to

increase the thermal stability of a polymer is to modify an active group in that polymer chain. Again, the glass transition temperatures obtained from the DSC curves increased either linearly or parabolically with the molar mass of the amine groups, similar to the thermal parameters in the TGA curves. Graphs were drawn between the molar mass and thermal parameters regarding the interpretation of the values obtained in the Table 1. Increases are generally seen in the graphs.

The bottom line is to modify a polymer to increase its thermal stability depending on where it will be used. The size of the molecular masses of the added modifying reactant groups causes a large effect here.

Conflicts of interest

There are no conflicts of interest in this work.

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