

Poly(hepten-1-alt-maleic anhydride)-hexamethylenediamine conjugate: synthesis and characterization of the thermal behaviour

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Nowadays, metals and polymeric materials are widely used in modern industry. In high technological applications, polymeric materials can be used instead of metals. Use of polymers have advantages over metals since their low density, low heat capacity, electrical conductivity high mechanical resistance elasticity and low cost of production etc. From this point of view, they have an important technological properties. Maleic anhydrides and acids are important classes of carbonyl compounds. Maleic anhydrides are useful intermediates in organic synthesis, and have found application both in the preparation of biologically active molecules and as monomers for polymerization [1]. In a molecule of maleic anhydride (MA), there is a conjugated-bond and electron-withdrawing carboxyl group. Therefore, it is difficult to polymerize, even with heating. However, MA can be copolymerized easily with electron-donor monomers such as styrene and vinyl acetate [2–4]. The anhydride groups, which are present in the polymer chain, cause this copolymer to be very reactive and has applications in various fields. The copolymers of MA are often used as compatibilizers in polymer blends [5–9].

Polyimides are important high temperature materials. They are made by the imidization of polyamic acids, which have been formed by the reaction of dianhydride with diamine. It is well known that the formation of polyamic acids proceeds quickly at low temperatures, but the imidization requires high temperatures. Furthermore, the imidization is reported to proceed by fast and slow first-order processes when FTIR spectroscopy was used to monitor the imide ring formation [10].

The copolymers of MA has been used in preparing functional polymers since active agents can be linked to it via ring opening reaction of anhydride unit [11–13]. In this study, HPMA was reacted with Hexamethylenediamine(HMDA) for the obtained the amide and imide derivatives of HPMA as shown in the Scheme 1. These derivatives were called as maleamide-hepten-1 and maleimide-hepten-1 copolymer. The curves of DSC and TGA of the polymers were compared which were characterized by FTIR.

Maleic anhydride was obtained from Aldrich Chemical Company, UK, was used after sublimation. Hexamethylenediamine was obtained from Aldrich Chemical Company, UK. Hepten-1 and dimethylformamide (DMF) were obtained Merck Chemical Company, Germany. Tetrahydrofuran (THF) was obtained from Pro-labo Company, France, analytical grade and was purified just before use. THF, bp: 67 °C, was purified by distillation.

A solution of the previously prepared copolymer of HPMA was added to a solution of HMDA in dimethylformamide (DMF). The calculated molar ratio of the MA unit and HMDA was approximately 1:2. The mixture was heated 150 °C at about for 2 h, cooled to room temperature, and finally precipitated into tetrahydrofuran (THF). The precipitate was redissolved in DMF, and precipitated again into THF to obtain HPMA-HMDA.

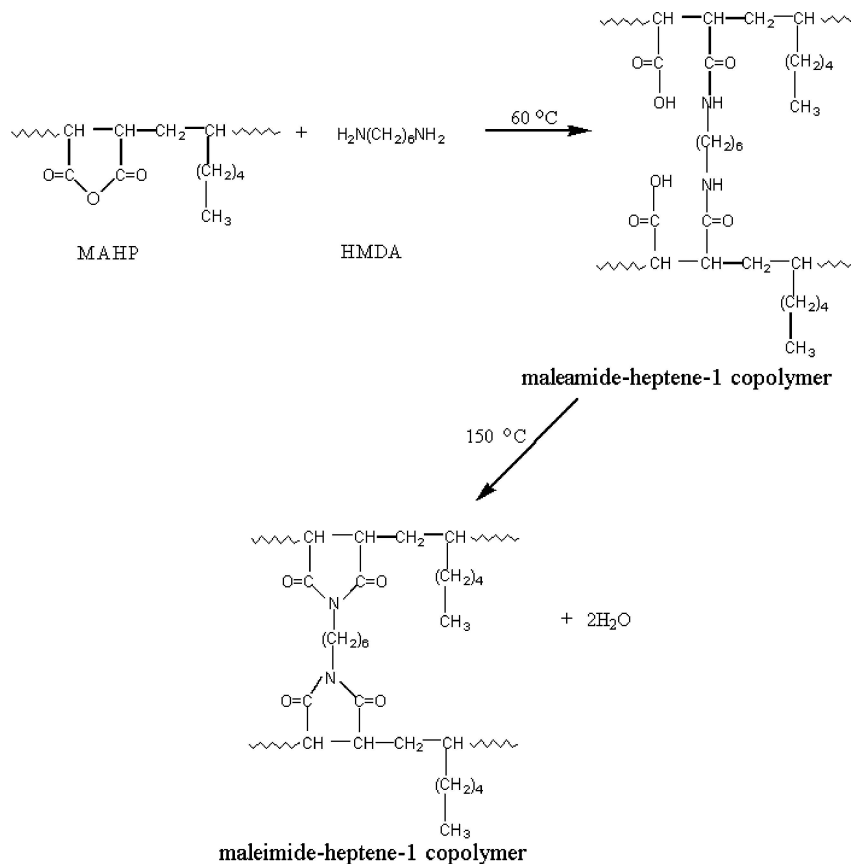
Unicam mark Mattson 1000 model FTIR (Fourier Transform Infrared Spectroscopy) was used for the spectrophotometric characterization of the copolymers prepared with KBr.

We studied the thermal behavior of our copolymers by differential scanning calorimetry (DSC) and thermal gravimetry (TG). Thermogravimetry (TG) and DSC measurements were performed on a Shimadzu TG-50 and DSC-50 in nitrogen atmosphere at a heating rate of 10 °C min⁻¹ and a heating range from room temperature to 600 °C. The gas flow rate was 25 cm³ min⁻¹.

Maleic anhydride and hepten-1 form copolymer by charge transfer complex (CTC) formation reaction, according to Schema 1. HPMA was reacted with HMDA. The ring-opening reaction resulted in the formation of carboxyl and amide groups. The FTIR spectra clearly indicated that the absorption peaks of anhydride carbonyl groups (1804 and 1855 cm⁻¹ in Fig. 1a) disappeared completely, as shown in Fig. 1b. Instead, new peaks emerged in the range of 1778 and 1727 cm⁻¹, which probably correspond to the carboxyl and amide groups. This result indicates that the maleic anhydride rings in the HPMA backbone were almost completely opened by the reaction with HMDA.

The thermal transition of HPMA-HMDA was measured with differential scanning calorimetry (DSC; a

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Scheme 1 Formation of amide and imide derivatives.

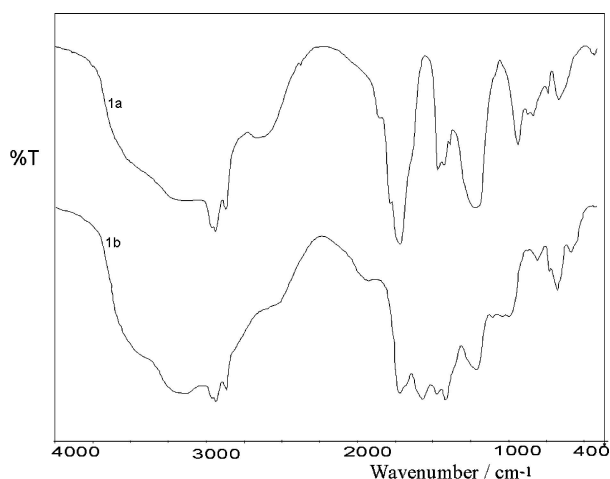


Figure 1 FTIR spectra of HPMA (a) and HPMA-HMDA (b) (KBr).

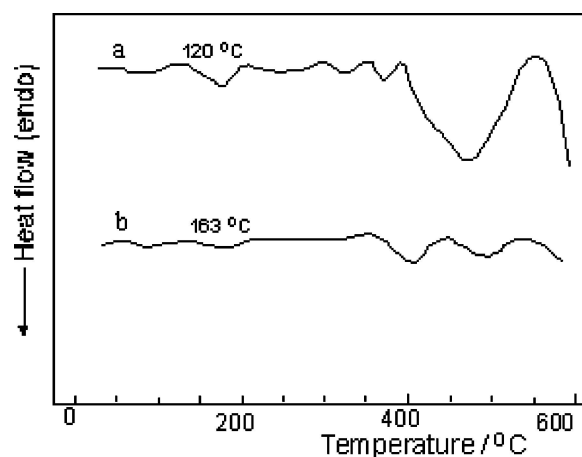


Figure 2 DSC thermograms of HPMA (a) and HPMA-HMDA (b).

Shimadzu 150 differential scanning calorimeter) and compared with that HPMA, and results are shown in Fig. 2. A slight weight loss was observed in the temperature range 100–150 °C. This may be attributed to the loss of absorbed water from these polymer samples [14]. The glass transition temperature (T_g) of HPMA-HMDA was measured to be about 163 °C while the T_g of HPMA was 160 °C. The increased T_g of HPMA-HMDA probably resulted from the enhanced molecular interactions due to hydrogen bonding. According to the DSC experiment, the polymer is amorphous since any melting transition of the polymers was not observed in the temperature range. The observed endothermic peak about temperature of 390 to 550 °C is belong to the temperatures of degradation of copolymers. At the

same time, these peaks were observed in TGA thermograms, too.

Thermogravimetric analysis (TGA) indicates that HPMA-HMDA decomposed with two steps at about temperatures 120 and 325 °C, while HPMA began to decompose in one step at 350 °C. The FTIR spectrum of HPMA-HMDA heated at 150 °C for 2 h showed clearly one of two characteristic peaks of acid anhydride group at 1778 cm^{-1} , as shown in Fig. 4. Thus the initial weight loss at a temperature near 120 °C was attributed to the formation of acid anhydride from the carboxyl groups with loss of water. The TGA curves of HPMA-HMDA copolymers heated at 150 °C for 2 h and HPMA were also given in the Fig. 3. According to these curves, the thermal stability of the heated

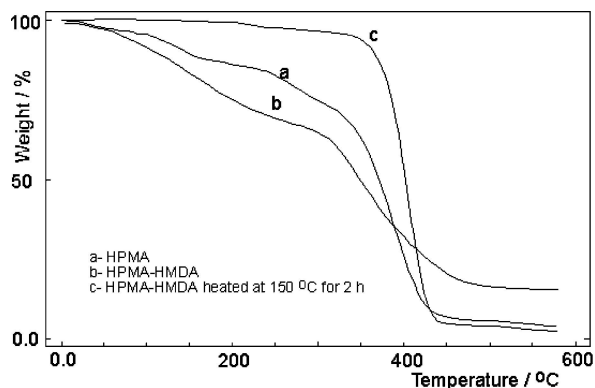


Figure 3 TGA curves of polymers.

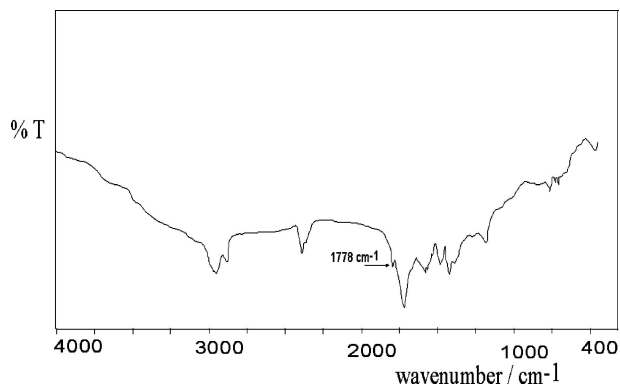


Figure 4 FTIR spectrum of HPMA-HMDA heated at 150 °C for 2 h (KBr).

HPMA-HMDA is higher than that the others copolymers because of the formation of the crosslinking, the imidization and removed of two mole water, as shown in Scheme 1.

HPMA-HMDA was successfully synthesized by reacting HPMA and HMDA. The thermal stability and the T_g of HPMA-HMDA was higher than that HPMA

because of intermolecular hydrogen bonding and the crosslinking. The carboxyl groups in HPMA-HMDA formed anhydride bonds with loss of water at a temperature near 120 °C.

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