Arabian Journal of Chemical and Environmental Research

Vol. 03 Issue 2 (2016) 64–74

Polymers based on succinic acid and chain mobility: the melting point study by introducing a high number of methylene

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Received 30 Dec 2015, Revised 14 Jun 2016, Accepted 16 Jun 2016

Abstract

Biodegradable polyesters were synthetized based on succinic acid. The diols used are ethylene glycol, propylene glycol, butylene glycol and polyethylene glycol, and this to see the impact of the increase in the number of methylene from diols on the mobility of the polymer chain. The follow-up will be carried out by DSC. The intra-group comparison made it possible to conclude with certainty that the polycondensation of the diols with succinic does not make it possible to predict the melting point by introducing a high number of methylene into the polymer chain.

Keywords: Hydrolytic degradation; Biodegradation; Crystalline morphology; NMR studies

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1. Introduction

Polyesters have attracted attention through their hydrolytic or enzymatic degradation. The method of polycondensation of diacids and diols from renewable resources is simple but effective for synthesizing polyesters with large molecular masses, for example polybutylene succinate (PBS) [1-6]. Polyesters have found their place in various sensitive fields, such as the medical field [7-9]. Several studies have been carried out to improve their mechanical and thermal properties and in particular their biodegradability [10-11]. Enzymes like lipases show a specific behavior when breaking up ester ponds with different chemical compositions. For polyesters the same question arises: why some polyesters can be degraded by lipases and others are resistant. Several factors such as the hydrophobicity of the surface, the molar mass of the polymer or its chemical composition have been investigated to determine if they can control the biodegradability of polyesters. Experience has shown that none of the above factors could really explain the degradation behavior of polyesters [12-15]. Despite the theoretical aspect of the hydrolytic / enzymatic degradation of esters, it appears that aliphatic polyesters are easily attacked by enzymes while their aromatic counterparts are more resistant to attack. In the case of a mixed polyester, the trend shows that the biodegradation decreases with the level of aromatic constituents [16]. This result could be interpreted by the steric hindrance which prevents the access of enzymes to the ydrolysable site. However, other studies have shown that low molecular weight polyesters with aromatic rings are accessible to enzymatic attack [17]. From its results, we can conclude that the steric hindrance around the ester bridge is not the major factor determining the biodegradability of aromatic polyesters, but an amount related to the nature of the material. Polyesters with short aliphatic chains are used for their controlled degradation time in most medical applications [18]. In the same way in these work we will synthesis biodegradable polyesters based on succinic acid. The diols used are ethylene glycol, propylene glycol, butylene glycol and polyethylene glycol, and this to see the impact of the increase in the number of methylene from diols on the mobility of the polymer chain.

2. Materials and methods

2.3. Polymers synthesis

The diacids (n_1), the molar quantities of diols (n_2) and paratoluenesulphonic acid (APTS 0.1% of the total mass of the reactants) are introduced into a 500 ml pyrnex glass reactor, fitted with a magnetic stirring and topped with a Dean-Stark / refrigerant system. The solvent used in its syntheses is toluene and the entire system is immersed in a bath of silicone oil. The heating is maintained at reflux for 48 hours during the first reaction step, oligomers of low masses are formed. The Dean-Stark / condenser assembly is removed, the solvent is removed by rotary steamer, a drop of titanium butoxide is added by Pasteur micropipette to the reaction mixture is placed under vacuum, during the second reaction step (P = 1 torr). This operation is maintained for 7 hours. The crusts are dissolved in dichloromethane and precipitated by adding a suitable cosolvent. The results resume in Fig.1.

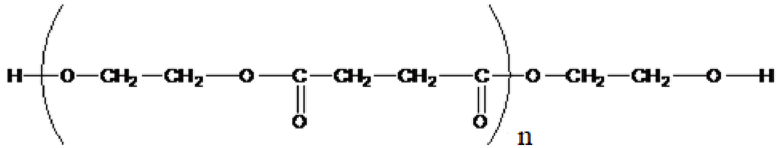
2.4. Nuclear magnetic resonance (^{1}H NMR)

The ^{1}H NMR spectra of the synthesized copolymer was recorded in UATARS – CRNST – Rabat-

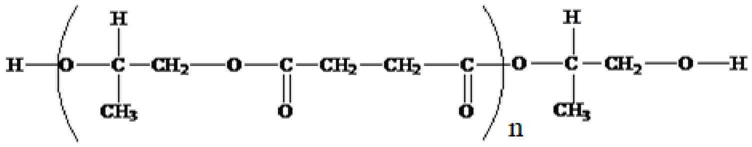
Morocco, using spectrometer BRUKER the solvent used $CDCl_3$ with trifluoracetic acid and TMS as internal reference.

2.5. Calorimetric investigation

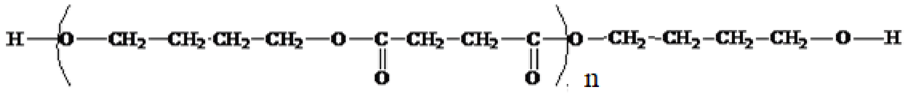
Test calorimetric analysis DSC differential scanning unit are formed by a TA DSC Q20 (United State). We placed about 10 mg of sample in sealed capsules made of aluminum, and subjected to two scans from – 40 to 200 ° C with a rate of 10 °C/min



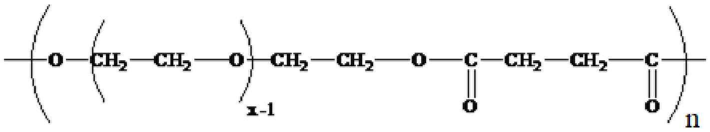
Poly(ethylene succinate)



Poly(propylene succinate)



Poly(butylene succinate)



Poly(PEG2000) succinate

Fig.1. Structure of the Polymers based on succinic acid studied

3. Results and discussion

The figure 2 below shows the results of the ^{1} H NMR analyses of polymers based on succinic acid. Polyethylene succinate is intensively investigated, commercial polymer of the chemical industry of aliphatic polymers (BIONOLLE), widely used for its properties, the rate of biodegradation which can be controlled [19]. ^{1}H-NMR analysis has identified the microstructure of the synthesized polyethylene succinate. The polycondensation of two monomers generated new peaks (Fig. 2), we can clearly indicate the peak at $\delta = 2.55 – 2.67$ ppm characteristic of the methylene proton of succinic acid and the peak at $\delta = 4.18 – 4.3$ ppm characteristic of the proton methylene of ethylene glycol, the same result was found by the team K. Chrissafis et al. [19]. However, the signal of the aliphatic proton $-CH_2-$ end of the polymer chain appears between $\delta = 3.6 – 3.65$ ppm.

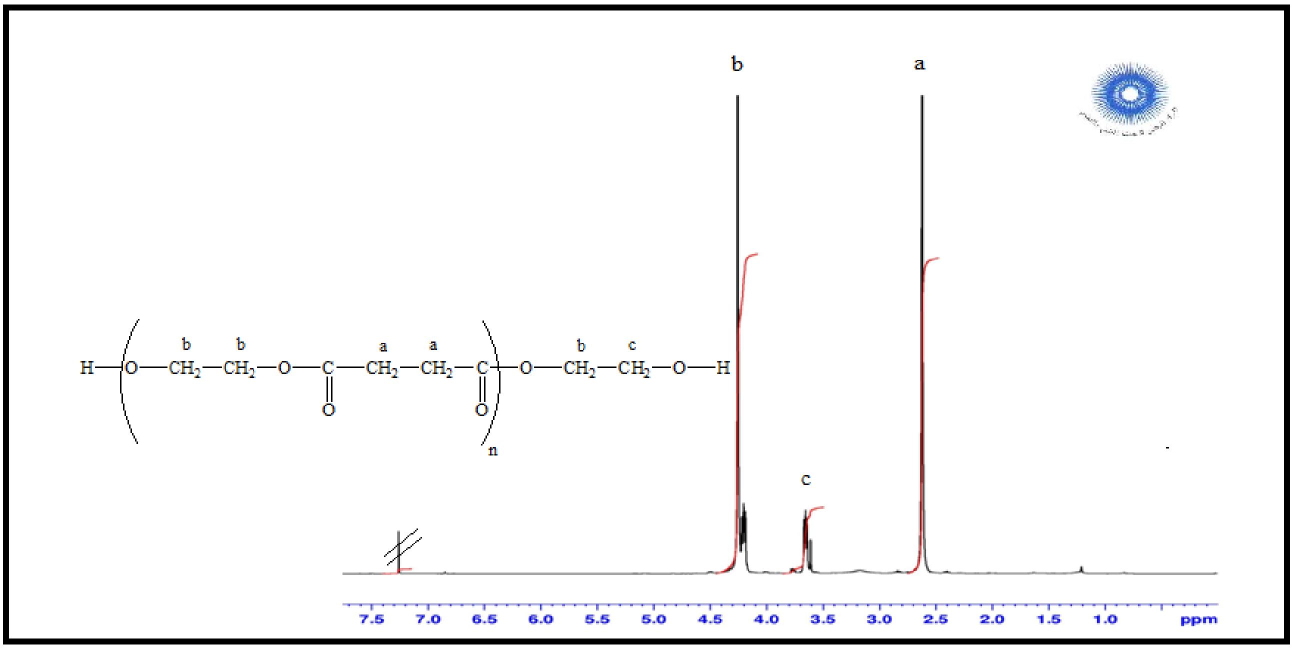


Fig. 2: Analysis by^{1}H NMR spectrum of polyethylene succinate

The ^{1}H NMR spectrum of polypropylene succinate (Fig. 3) made it possible to find peaks similar to polyethylene succinate at δ = 2.5 - 2.55 ppm and at δ = 4.1 - 4.3 ppm which corresponds to the methylene proton of succinic acid and to the methylene of 1-2 propanediol respectively and it is obvious that the reaction took place between the diol and the acid, we note a small peak at δ = 3.62 - 3.65 ppm which corresponds to the aliphatic proton -CH_2- located in position α of the alcohol function.

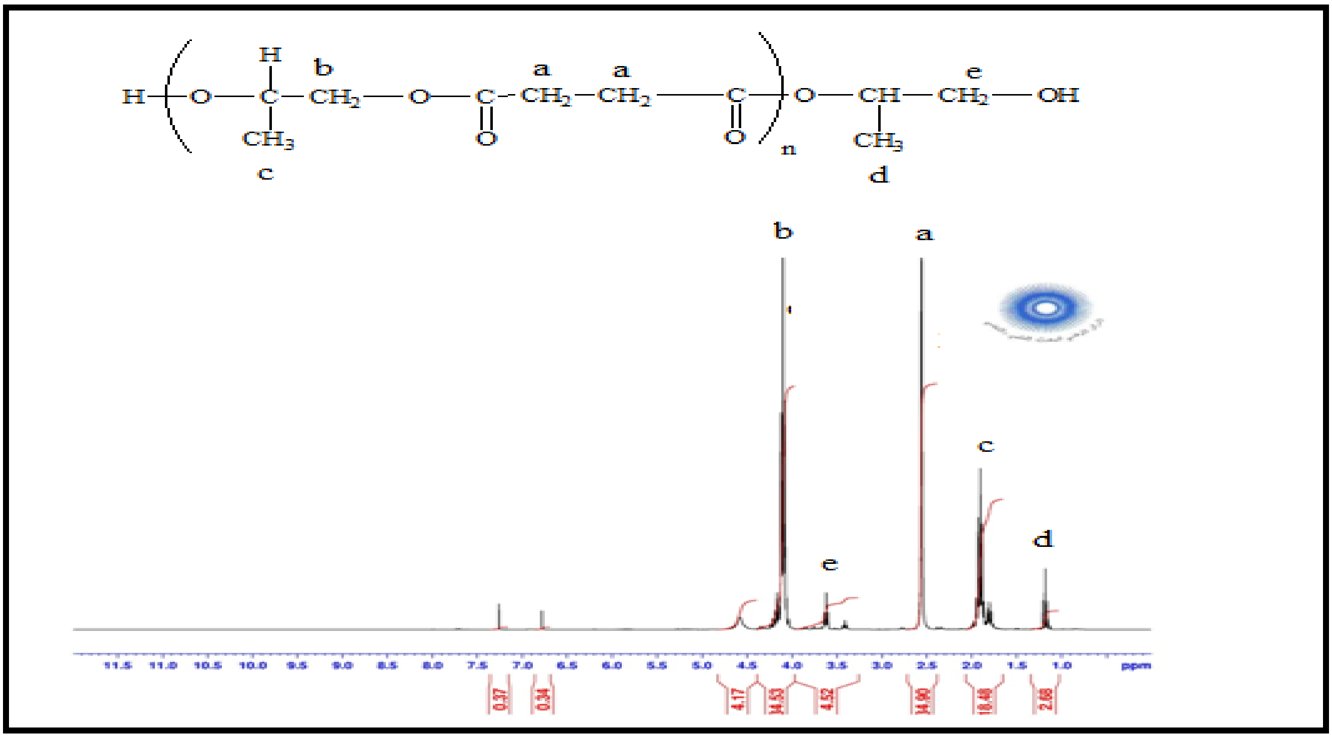


Fig. 3: Analysis by ^{1} H NMR of polypropylene succinate.

The ^{1}H-NMR spectrum records two new peaks, the first at δ = 1.1- 1.2 ppm and the second at δ = 1.8 - 1.9 ppm which corresponds to the methylene proton of 1-2 propanediol and the methylene proton of 1-2 propanediol located at the end of the chain.

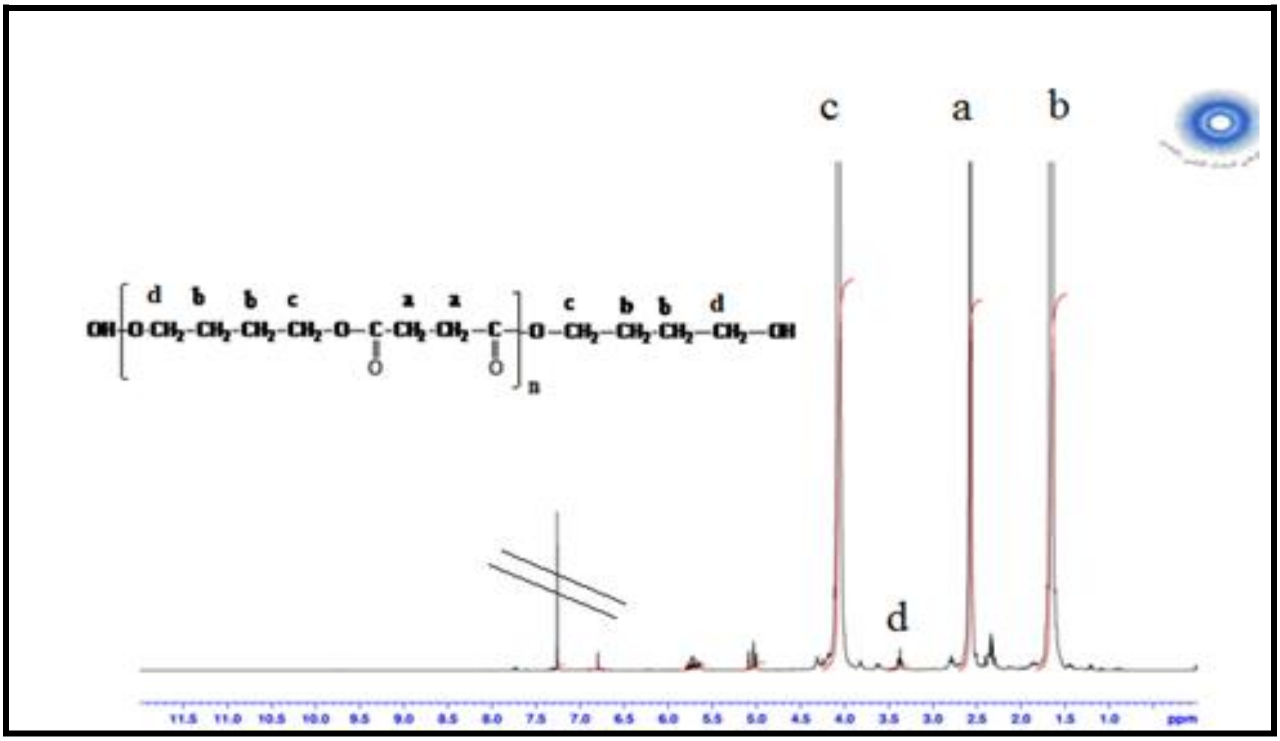


Fig. 4: Analysis by ^{1} H NMR of polybutylene succinate.

Polybutylene succinate and polyethylene succinate are among the most studied polymers in the polyesters category. Polybutylene succinate is a white polymer with good chemical and thermal stability and an elongation strength whose value remains between that of polyethylene succinate and that of polypropylene succinate [20]. Polycondensation of two monomers succinic acid and 1,4-butanediol gave the result of polybutylene succinate. The product analysed by ^{1} H NMR (Fig. 4) shows two peaks similar to polyethylene succinate the peak at δ = 2.65 ppm, the peak at δ = 4.3 ppm and the peak at δ = 3.4 ppm which are attributed to the methylene protons of the succinic acid, to the methylene proton of the CH_2-OCO- group and to the CH_2-O- proton of the end of the polymer chain respectively. The difference between the ^{1}H NMR spectrum of polyethylene succinate and that of polybutylene succinate is the peak at δ = 1.6 ppm which is attributed simply to the methylene proton of the center of 1-4 butanediol. The peak at 4.3 ppm clearly shows that the reaction takes place between the diol and the diacid.

The spectrum of poly (PEG (2000) succinate)) is simple (Fig. 5) identified the same peaks recorded in the polymers synthesized and this at δ = 2.6 ppm and at δ = 4.30 ppm which corresponds to the protons CH_2-CO and methylene CH_2-O which is at the end of the PEG chain (2000). However, the analysis identified an intense peak a δ = 3.7 ppm which naturally corresponds to the proton -CH_2-O- of the repeated unit. In the DSC comparative study, we will present DSC thermograms. These thermogram will present the melting temperature recorded during the first scan, other phenomena (crystallization….) Exist but will be screened by the software to facilitate the presentation and comparison of the melting temperatures. The melting temperature of semi-crystalline polymers is relative to the fractions of their crystallinities, it is an indirect measure of the capacity of the polymer chain to temporarily leave the strict order in the polymer crystals and temporarily form a kind of able loop enter the active site of the enzyme, which is located on the surface of the material. It should be noted that the measurement of the melting temperature is defined as the indirect measurement of chain mobility of polyesters [21].

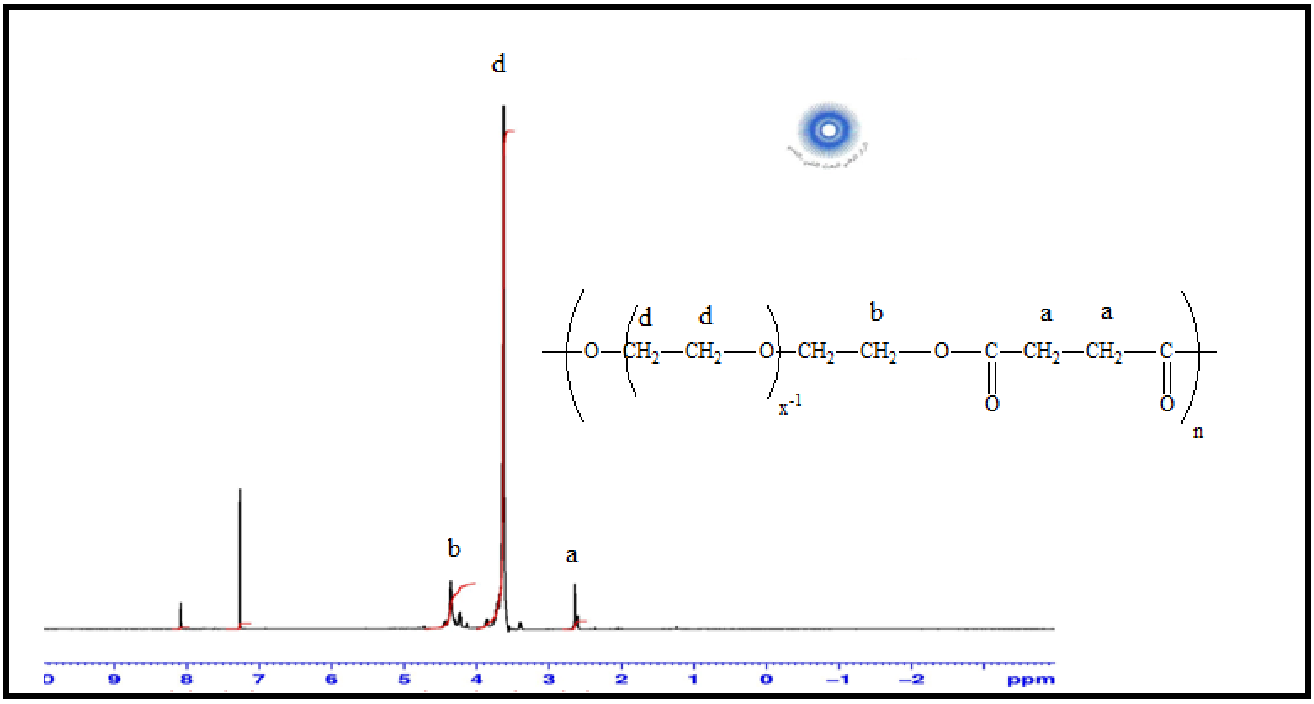


Fig.5: Analysis by ^{1} H NMR of du poly(PEG(2000)) succinate

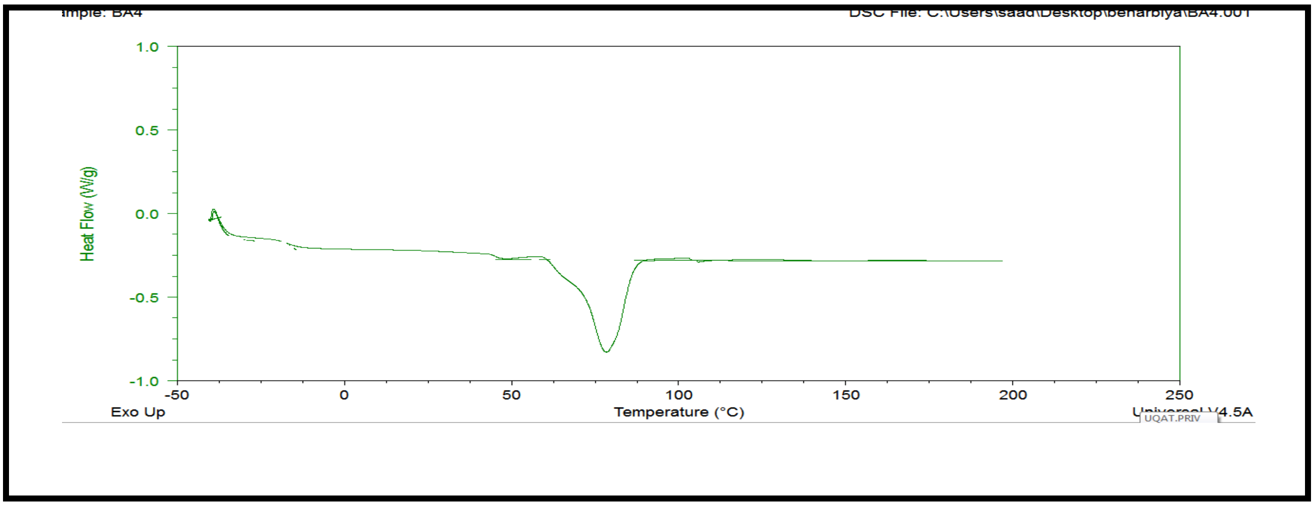


Fig.6 Melting temperature recorded by DSC of polyethylene succinate.

The synthesized polyethylene succinate (Fig. 6) is characterized by a melting point equal to Tm = 77.25 ° C, the authors consider that the melting point of polyethylene succinate is in the temperature range 103-106 ° C which is of course above 77.25 ° C, the authors explain this phenomenon which is known in semi-crystalline polymers by the existence of two types of crystallization mode, crystallization is perfect at high temperature but imperfect crystallization is formed at low temperature [22]. On the other hand, despite the high number of methylene in the aliphatic chain of polybutylene succinate compared to polyethylene succinate, the authors did not suspect the fact that the number of carbons does not have an influence on the melting temperature (Fig. 7).

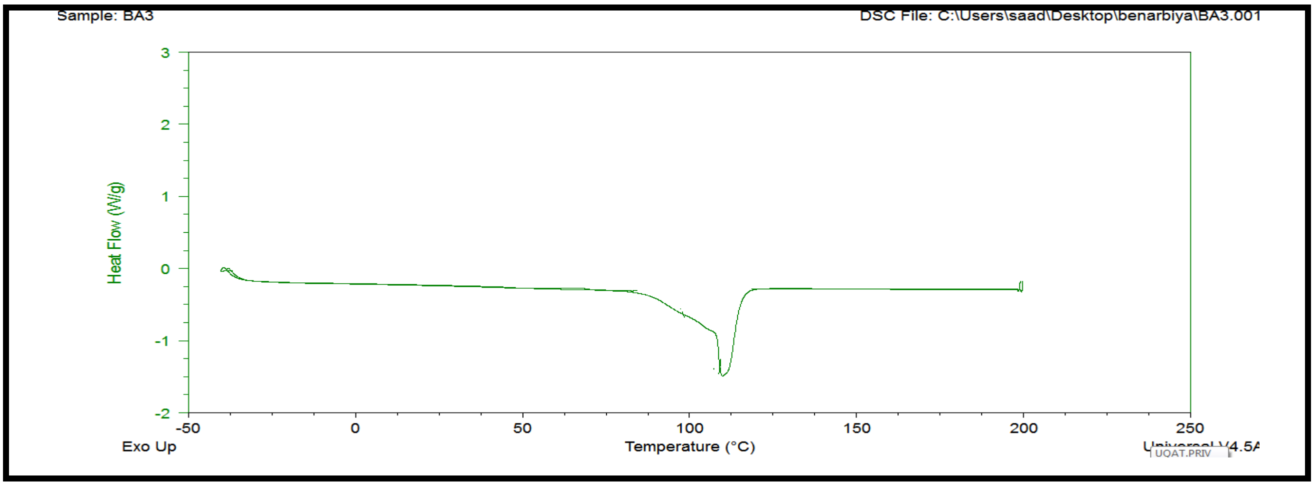


Fig.7: Melting temperature recorded by DSC of polybutylene succinate

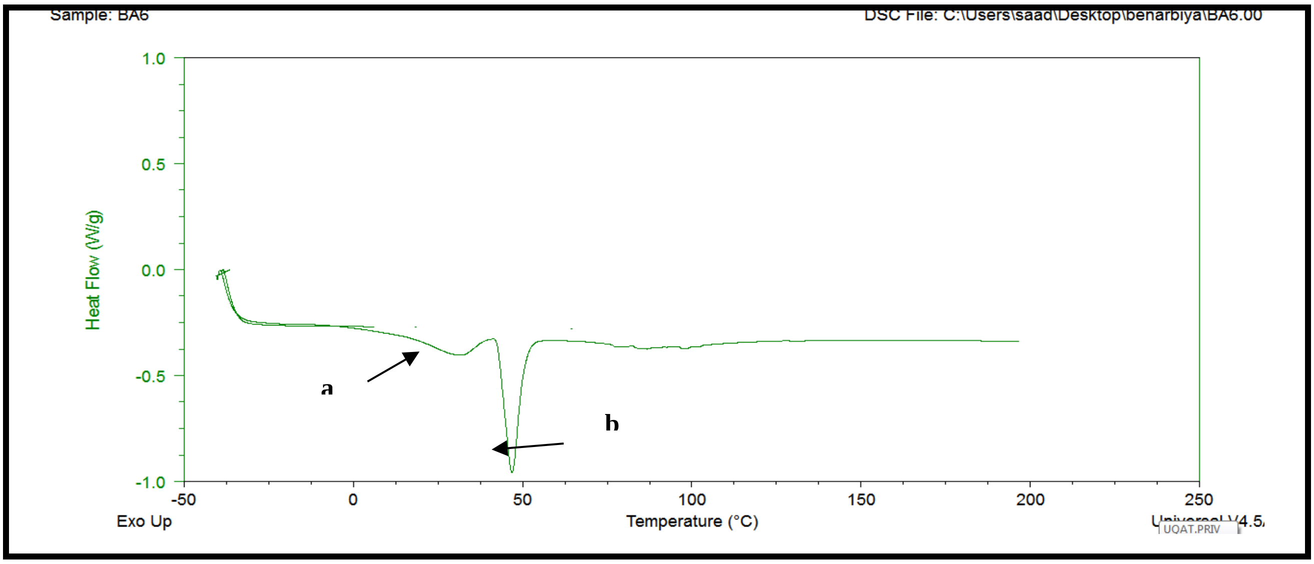


Fig. 8: Melting temperature recorded by DSC of polypropylene succinate

Indeed, experience has always shown that the melting point of polybutylene succinate is Tm = 112 ° C, the same result is presented by Chrissafis et al. [19], the value of the melting point of polybutylene succinate is always higher than that of polyethylene succinate, the mobility parameter of the chain does not seem to be affected by the incorporation of more methylenes from the diols in the aliphatic chain of the polyester. The DSC diagram of polypropylene succinate recorded two melting temperatures during the first scan (Fig. 8), the first barely distinguishable noted (a) at Tf1 = 34.5 ° C, the second noted (b) at Tf2 = 48 ° C. Studies indicate that polypropylene succinate has a low melting point [23-27]. The detection of its two melting temperature is explained by the low crystallinity of the polypropylene succinate, this property gives it the highest rate of degradation compared to all the polyesters used in the medical field this property seems to give it a faster biodegradation rate. Faster than polyethylene succinate. The properties of polypropylene succinate at different molecular weights are recorded by the team Dimitrios et al. [10], in our case for a molar mass of 3201 g / mol, the polypropylene succinate is characterized by a melting point Tm = 48 ° C [28-29].

The melting temperature recorded by DSC during the first sweep of polyPEG (2000) succinate (Fig. 9) is Tf = 53 ° C, this temperature is lower than the melting temperatures of polyethylene succinate Tf = 77.25 ° C and of polybutylene succinate Tf = 112 ° C, but higher than the melting temperature of polypropylene succinate Tm = 48 ° C. It also seems that the polycondensation of a diol monomer with succinic acid does not make it possible to predict with certainty the melting temperature, whatever the number of methylene of the diols, depending on the crystallinity of the polymer as a whole.

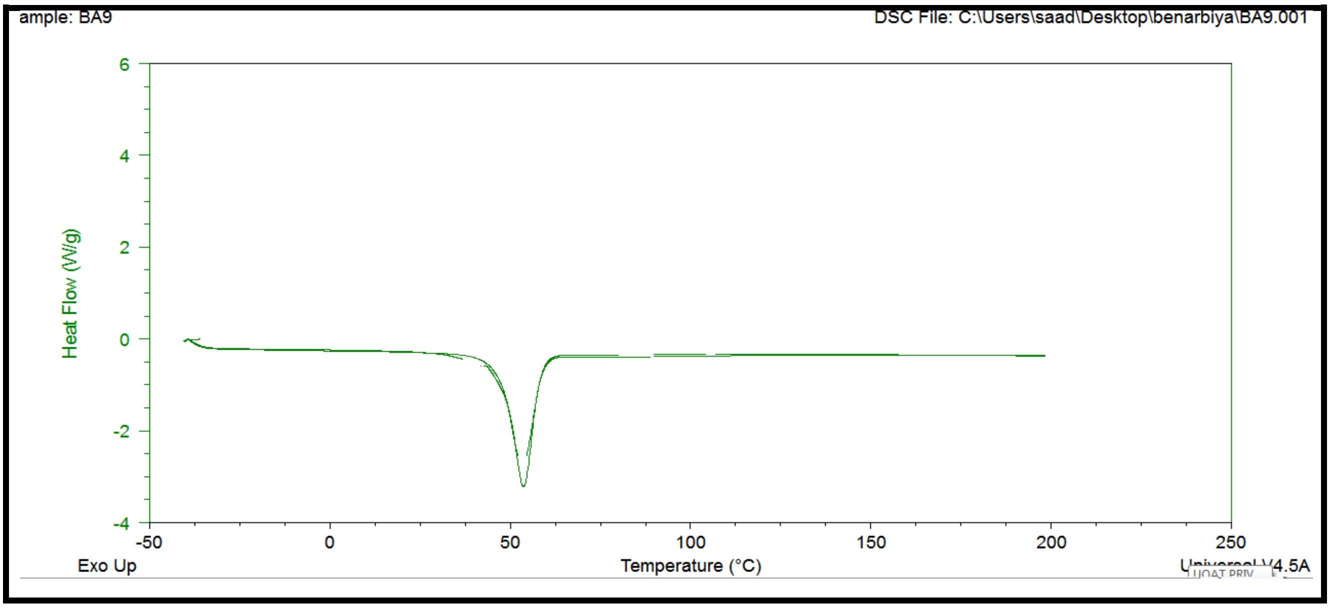


Fig. 9: Melting temperature recorded by DSC of poly **PEG** (2000) succinate.

Indeed, the melting temperature of polymers based on succinic acid record relatively high melting temperatures compared to the polymer based on adipic acid and this whatever the nature of diols incorporated in the polymer chain, the difference values of the melting temperature become more and more noticeable for polymers known for their high crystallinities.

Conclusion

In these work we synthesized an aliphatic polymers based on succinic acid: polyethylene succinate, polypropylene succinate, polybutylene succinate and poly(PEG(2000)) succinate, and this to see the impact of the increase in the number of methylene from diols on the mobility of the polymer chain. The follow-up will be carried out by DSC. The DSC comparative study are presented in DSC thermograms, The melting temperature of semi-crystalline polymers is relative to the fractions of their crystallinities, it is an indirect measure of the capacity of the polymer chain to temporarily leave the strict order in the polymer crystals. It should be noted that the measurement of the melting temperature is defined as the indirect measurement of chain mobility of polyesters. The study follow the melting temperature recorded during the first scan, The melting point of synthesized polyethylene succinate equal to Tm = 77.25 ° C, and for the value of the melting point of polybutylene succinate Tm = 112 ° C, the melting point of polybutylene succinate is always higher than that of polyethylene succinate, the mobility parameter of the chain does not seem to be affected by the incorporation of more methylenes from the diols in the aliphatic chain of the polyester. We also noted that the melting temperature recorded by DSC during the first sweep of polyPEG (2000) succinate is Tf = 53 ° C, this temperature is lower than the melting temperatures of polyethylene succinate Tf = 77.25 ° C and of polybutylene succinate Tf = 112 ° C, but higher than the melting temperature of polypropylene succinate Tm = 48 ° C. It also seems that the polycondensation of a diol monomer with succinic acid does not make it possible to predict with certainty the melting temperature, whatever the number of methylene of the diols, the melting temperature depending on the crystallinity of the polymer as a whole.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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(2016) ; www.mocedes.org/ajcer