

Synthesis of Poly(amide-ester)s by Microwave Methods

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ABSTRACT: The polycondensation of sebacic acids and ω -amino alcohols by microwave irradiation was studied. The results were compared to those obtained from conventional melt polycondensation of poly(amide-ester)s. It was found that the reaction proceeded at a much higher rate upon microwave irradiation. A high yield of thermally stable poly(amide-ester)s was obtained. The microwave-synthesized compounds were fully characterized by FTIR and ¹H-NMR spectroscopy, gel permeation chromatography,

and a solubility test. The thermal properties of the poly(amide-ester)s also were investigated. The results showed that the chemical-physical properties of the polymers were in good agreement with those of polymers obtained by conventional synthesis. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1952–1958, 2007

Key words: irradiation; polycondensation; melt; microwave; poly(amide-ester)s; thermal properties

INTRODUCTION

The applications of microwave energy in organic chemistry from 1969, its first recorded use, to 1991 were reviewed by Abramovich.¹ As an alternative to conventional heating techniques, microwave irradiation is an effective, selective, and fast synthetic method to heat molecules directly through the interaction between microwave energy and molecular dipole moments of the starting materials. This internal heating is believed to produce an efficient reaction because the reactive sites, which have strong dipole moments, are the primary source of activation in the microwave electromagnetic field. In the last decade, considerable effort has been devoted to investigating the advantages of microwave irradiation over conventional thermal processing in the heating and synthesis of organic and polymer materials.^{2–5}

In the field of synthetic polymer chemistry, microwave energy has been used for polymerization of vinyl monomers,^{6–8} ring opening polymerization of caprolactam and caprolactone,^{9,10} condensation polymerization of polyesters,^{11,12} polyamides,^{13–15} and polyimides,^{14,16–18} as well as the curing of epoxy^{19,20} and polyurethane resins.²¹

Poly(amide-ester)s^{22–24} synthesized by conventional melt polycondensation have received increasing interest in recent years. These polymers offer an interesting combination of properties: high flexibility of the ester linkages, providing toughness and degradability, and

good mechanical properties resulting from the hydrogen bonds between amide groups. In general, they show susceptibility to degradation with proteolytic enzymes and biodegradability.^{25,26}

In a previous article,²² we reported the synthesis, structure, and properties of a set of poly(amide-ester)s prepared from dicarboxylic acids and amino alcohols. A simple method of synthesis based on condensation in melt was used. In this article we report the polycondensation of sebacic acid and ω -amino alcohols by microwave irradiation compared to by conventional melt polycondensation and the properties of the resulting poly(amide-ester)s.

EXPERIMENTAL

Materials and techniques

All chemicals were commercially obtained from Aldrich (Milwaukee, WI). They were analytical grade or higher and used without further purification. The solvents to be used under anhydrous conditions were dried by standard methods.

Gel permeation chromatography was performed on a Waters model 150°C ALC (Waters Associates, Milford, MA) using *N,N*-dimethylacetamide (DMAc) with 5% 1,1,1,3,3,3-hexafluoro-2-propanol as the solvent. Monodisperse polystyrene standards were used to create a calibration curve.

Infrared absorption spectra were recorded from potassium bromide pellets with a Nicolet model 60SX FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–500 cm⁻¹ range.

¹H-NMR spectra were recorded using Bruker DMX-500MHz solution NMR instrumentation (Bruker,

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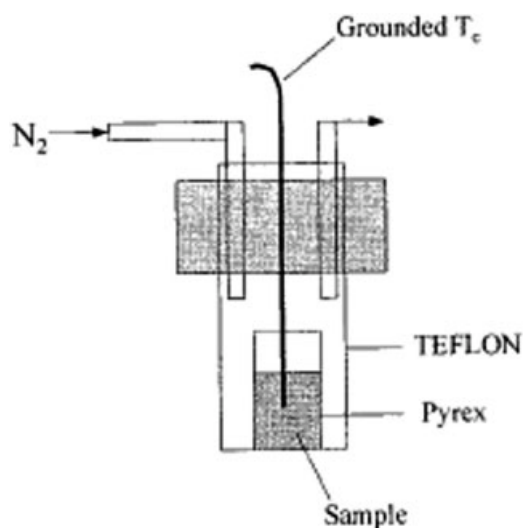


Figure 1 Teflon reactor.

Billerica, MA) with deuterated dimethyl sulfoxide (DMSO) as the solvent of choice.

Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) with a Perkin-Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) in order to determine the melting (T_m), crystallization (T_c), and glass-transition (T_g) temperatures of the samples. Unless otherwise noted, the heating and cooling rates were 10 °C/min. All experiments were done under a flow of dry nitrogen through the calorimeter. Indium metal was used for calibration purposes.

Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 at a heating rate of 10 °C min⁻¹ in air and under a stream of nitrogen.

The X-ray powder diffraction spectra were obtained with nickel-filtered Cu K α radiation with an automatic Philips diffractometer (Eindhoven, The Netherlands).

Microwave Equipment and Reaction Setup

A variable frequency microwave furnace (VFMF) model LT 502 Xb (Lambda Technologies, Inc.) with a

frequency range of 2.4–7.0 GHz was used to synthesize the poly(amide-ester)s.

A Teflon container was selected as a synthetic reactor because of its transparency to microwave energy. A Teflon tube was connected to the Teflon reactor to provide a nitrogen blanket during the reactions (Fig. 1). The polymerization temperature was measured and controlled by a grounded Omega K-type thermocouple, which was calibrated beforehand with a Luxtron optical fiber temperature probe. A low microwave input power, 50–70 W, was applied in these processes because of the high absorption of microwaves by the starting materials. Temperature control was achieved by changes in the applied electric field, which was programmed to maintain a set temperature by a pulse power on-off cycle.

Synthesis procedures

Polycondensation of poly(amide-ester)s under microwave irradiation

The general procedure for polycondensation was as follows: equimolecular quantities of sebacic acid and ω -amino alcohol were mixed with stannous 2-ethyl hexanoate as the catalyst [Sn(Oct)₂ ~ 0.2 mol % of total reactants]. The ω -amino alcohols used in this study included 3-aminopropanol, ethanolamine, and 6-aminohexanol. The reaction mixtures were heated to 180 °C, 200 °C, and 220 °C, respectively, for the periods shown in Tables I and II. Because of the high absorption of microwaves by the starting materials, a low microwave forward power (50–70 W) was applied during these processes. Temperature control was achieved by changing the applied electric field, which was programmed to maintain a set temperature by pulsing the power on-off. The resulting material, a hard solid, was purified by washing with methanol and then dried under vacuum at 80 °C to give a white or slightly yellow powdery polymer. The resulting poly(amide-ester)s were: poly(sebacic acid-co-2-aminoethanol) (mwPSE), poly(sebacic acid-co-3-aminopro-

TABLE I
Comparison of Microwave and Thermal Results of Poly(sebacic acid-co-3-aminopropanol)

Polymer	Reaction conditions		Yield (%)	$M_w \times 10^3$	Polydispersity (M_w/M_n)
	Temp. (°C)	Time (h)			
PSP ^a	~220	3	70	38	1.5
mwPSP ^b	220	1	75	45	1.5
mwPSP ^b	220	0.5	68	36	1.6
mwPSP ^b	200	2	73	35	1.5
mwPSP ^b	200	1	64	23	1.4
mwPSP ^b	200	0.5	55	18	1.3
mwPSP ^b	180	2	73	33	1.5

^a Melt polycondensation of poly(sebacic acid-co-3-aminopropanol).

^b Microwave-synthesized poly(sebacic acid-co-3-aminopropanol).

TABLE II
Comparison of Microwave and Conventional Melt Polycondensation
Results of Poly(amide-ester)s

Polymer	Synthesis time (h)	Yield (%)	$M_w \times 10^3$	Polydispersity (M_w/M_n)
PSE ^a	3	70	42	1.6
mwPSE ^b	1	70	43	1.6
PSP ^c	3	70	38	1.5
mwPSP ^d	1	75	45	1.5
PSH ^e	3	73	15	1.2
mwPSH ^f	1	80	37	1.6

^a Melt polycondensation of poly(sebacic acid-*co*-2-aminoethanol).

^b Microwave-synthesized poly(sebacic acid-*co*-2-aminoethanol).

^c Melt polycondensation of poly(sebacic acid-*co*-3-aminopropanol).

^d Microwave-synthesized poly(sebacic acid-*co*-3-aminopropanol).

^e Melt polycondensation of poly(sebacic acid-*co*-6-aminohexanol).

^f Microwave-synthesized poly(sebacic acid-*co*-6-aminohexanol).

panol) (mwPSP), and poly(sebacic acid-*co*-6-aminohexanol) (mwPSH).

Polycondensation of poly(amide-ester)s under conventional conditions

The same reactant ratios and catalyst used in the microwave procedure were utilized in the melt polycondensation. The reaction mixture was placed in a 250 mL two-necked flask equipped with a stir bar.

The polymerization was carried out in the bulk under an inert nitrogen atmosphere. The reactants was charged in the presence of a catalytic amount of Sn(Oct)₂ (≈ 0.2 mol %). With sufficient stirring, the vessel was immersed for 3 h in an oil bath maintained at about 220°C, followed by slow cooling to room temperature. During the polycondensation reaction the water formed was distilled off continuously. The resulting material, a hard solid, was purified by washing with methanol and then was dried under vacuum at 80°C to give a white or slightly yellow powdery polymer. The resulting poly(amide-ester)s were: poly(sebacic acid-*co*-2-aminoethanol) (PSE), poly(sebacic acid-*co*-3-aminopropanol) (PSP), and poly(sebacic acid-*co*-6-aminohexanol) (PSH).

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

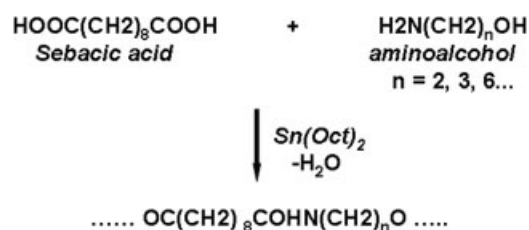
Compared to conventional thermal heating, microwave irradiation provides a fast, volumetric, and possibly selective synthetic method for heating molecules directly through the interaction of microwave electromagnetic energy with the molecular dipole moments of monomers. The polar functional groups in sebacic acid and ω-amino alcohols with their strong permanent dipole moments are the primary source of activation in the microwave electromagnetic field. Effective microwave absorption creates internal heating on a

molecular level, causing an efficient chemical reaction of these functional groups. Therefore, the sebacic acid and ω-amino alcohols monomers used in this study were inherently amenable to microwave copolymerization studies.

All polymers were synthesized according to the methodology described in the Experimental section and outlined in Scheme 1.

The polymerization technique used is simple and rendered polymers of higher molecular weight in very good yields. The reaction conditions, yields, and molecular weight data for thermal and microwave cures of the poly(amide-ester)s, after purification in methanol to remove catalyst and residual monomers, are summarized in Tables I and II. For poly(sebacic acid-*co*-3-aminopropanol) (Table I), the thermal process required a temperature of approximately 220°C for 3 h, yielding a product with a 70% yield, a molecular weight of 38,000, and a polydispersity of 1.5.

PSP synthesized in 1 h by the microwave method, giving a higher-molecular weight product with a higher yield than that by the thermal process at the same temperature for 3 h. In fact, the microwave process produced PSP in a 75% yield after 1 h, with a molecular weight of 45,000 and a polydispersity of 1.5. In half an hour the microwave process produced PSP in a 68% yield with properties almost equivalent to those in the thermal process.



Scheme 1 Synthesis of poly(amide-ester)s by melt polymerization.

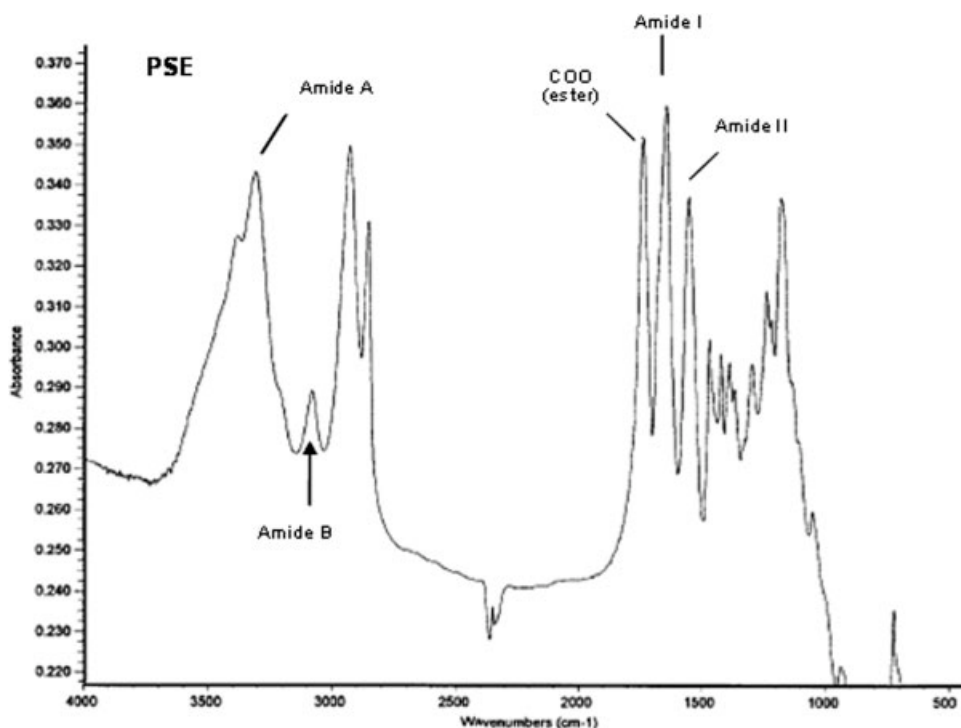


Figure 2 IR spectrum of mwPSE.

Variation in the ω -amino alcohol to produce various poly(amide-ester)s was investigated by thermal and microwave processes. Table II clearly demonstrates that the microwave process produced product with higher molecular weight and equivalent or higher yield in one third the time than did the thermal process.

Both IR and $^1\text{H-NMR}$ spectra displayed all the characteristic bands and signals anticipated for the constitution of the poly(amide-ester)s, with clear identification of amide and ester groups.

The infrared spectra showed the characteristic absorption bands of methylene, ester, and amide groups (Fig. 2). It was possible to observe bands in the $3600\text{--}3000\text{ cm}^{-1}$ region, which corresponded to the stretching vibrations of the N—H group. The relatively sharp band around 3350 cm^{-1} was split into two distinct, overlaying maxima at 3309 and 3380 cm^{-1} of a slightly lower intensity. This indicated that more types of hydrogen bonds with different bond distances for the N—H groups were formed. The absorption bands in the region from 1800 to 1500 cm^{-1} were associated with amide I and amide II bands. Amide I at 1639 cm^{-1} (C=O stretching, C—N stretching, and C—C—N deformation vibrations) and amide II at 1552 cm^{-1} (N—H bending, C—N stretching, and C—C stretching vibrations) were sharp and appeared in the region characteristic of hydrogen bonding. Table III shows the characteristic infrared bands of the poly(amide-ester)s studied.

A representative $^1\text{H-NMR}$ spectrum recorded from mwPSE is shown in Figure 3 for illustration. Copolymerization was confirmed by the presence of a peak at 8 ppm for the hydrogen of the amide group. The integration of each component matched the polymer structure. All the other polymers, obtained by thermal and microwave methods, showed essentially similar features to those obtained by $^1\text{H-NMR}$, with only minor changes corresponding to the different number of methylene carbons inside the chain.

Properties

The behavior patterns of poly(amide-ester)s obtained from the microwave process regarding solubility are described in Table IV. The general behavior of the polyamides showed they were soluble in strong hydrogen-bond-breaking solvents such as formic acid or tri-

TABLE III
Characteristic Infrared Bands (cm^{-1}) of
Poly(amide-ester)s Studied

Polymer	Amide A	Amide B	C=O ester	Amide I	Amide II
mwPSE	3270	2900	1738	1660	1547
mwPSP	3309	2920	1737	1630	1549
mwPSH	3300	2870	1726	1653	1543
PSE	3268	2905	1740	1657	1548
PSP	3310	2920	1735	1628	1550
PSH	3305	2870	1729	1655	1545

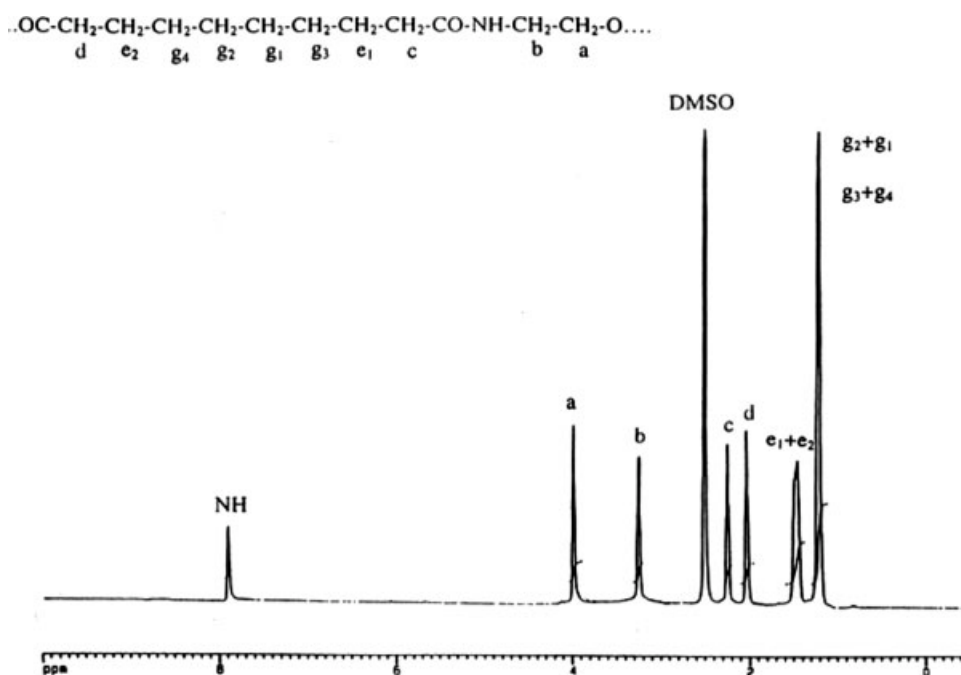


Figure 3 $^1\text{H-NMR}$ spectra of mwPSE and relative assignments.

fluoroacetic acid and insoluble in nonpolar organic solvents such as ethers or ethyl acetate.

The thermal behavior of poly(amide-ester)s at temperatures below decomposition was examined by DSC. The T_g , T_m , T_c , and ΔH_m values recorded from these experiment are listed in Table V. The melting and crystallization transitions were determined using samples of 8–12 mg at a heating and cooling rate of $10^\circ\text{C}/\text{min}$. The peak maxima of the second heating scan and the first cooling scan were taken as the transition temperatures T_m and T_c and the area under the curve as ΔH_m . All poly(amide-ester)s appeared to be crystalline, showing well-defined melting peaks. Furthermore, both the position and the intensity of the peaks were reproduced in the second heating traces, revealing the ability of these polymers to crystallize from the melt.

The mwPSE crude product displayed a profile containing bimodal endotherms arising from melting of a heterogeneous population of crystallites. After annealing at temperatures near the melting point, well-

defined fusion peaks were observed with higher intensity.

The rate of crystallization was defined as the difference between the melting and the crystallization temperatures (ΔT).²⁷ A small undercooling implied a fast crystallization rate. The ΔT values for mwPSE, mwPSP, and mwPSH were 25°C , 23°C , and 31°C , respectively. These small ΔT values suggest very fast crystallization of the polymers, which could be the result of some ordering in the melt of the segments caused by the hydrogen bonds.²⁸ It was obvious that fast crystallization was an advantage in the melt processing of the polymers and indicated a high degree of structural regularity.

The glass-transition temperatures observed from the heating run are reported in Table V. The values were similar to those of the corresponding aliphatic polyamides. This indicates that some of the amide linkages were in the amorphous phase, forming hydrogen bonds and thus restricting the mobility of the amorphous chains.

TABLE IV
Solubility of Poly(amide-ester)s Obtained by Microwave Irradiation^a

Polymer	Ether	Ethyl acetate	CHCl_3	HCOOH	CF_3COOH	DMSO^b	EFP^b
mwPSE	–	–	+	++	++	+	++
mwPSP	–	–	+	++	++	+	++
mwPSH	–	–	+	++	++	+	++

^a ++, Soluble in cold; +, soluble in warm; –, nonsoluble.

^b DMSO, dimethyl sulfoxide; EFP, esafluoropropanol.

TABLE V
Properties of Poly(amide-ester)s Obtained by Microwave Irradiation

Polymer	T_g (°C)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	$T_{d,10}$ (°C) ^a	$T_{d,10}$ (°C) ^b	Crystallinity (%)
mwPSE	58	106	81	72	320	353	25
mwPSP	56	101	78	66	370	375	34
mwPSH	56	103	72	85	400	400	38

^a Decomposition temperature in air.

^b Decomposition temperature in N₂.

Decomposition ($T_{d,10}$) at heating, the temperature at which 10% weight loss occurred, was evaluated by thermogravimetric analysis. The TGA data are shown in Table IV, and representative curves for mwPSP are shown in Figure 4. Weight loss was measured as a function of temperature for samples heated at a rate of 10°C/min to a temperature of nearly 700°C. All samples showed two decomposition steps, in the temperature ranges of 350°C–400°C and 430°C–500°C, with the latter much less intense than the former. According to what has been reported in literature,²⁹ the first decomposition step must involve imidation and subsequent main-chain scission whereas an uncontrolled decomposition must take place in the second step. Thermal stability along the poly(amide-ester)s derived from sebacic acid increased with the length of the amino alcohol. The measured decomposition was always higher than the fusion temperature (more than 200°C), and so the polymers could be processed from the melt.

All samples investigated in this work were crystalline in nature. The percentage of crystallinity (X_c) was

calculated (Table V) for each sample from the intensity versus the 2θ curve based on the relative areas of Bragg reflections versus amorphous signal:³⁰

$$X_c = A_{\text{Bragg}} / (A_{\text{Bragg}} + A_{\text{amorph}})$$

Experimental intensities were evaluated by measuring the area of the peaks in the X-ray powder diffraction pattern after subtraction of the amorphous halo.

The results were in good agreement with the chemical-physical properties of some polymers obtained from conventional synthesis.²²

CONCLUSIONS

The polycondensation of sebacic acids and Ω -amino alcohols by microwave irradiation was studied. The results demonstrated that microwave heating is an efficient method (shorter reaction time and high energy efficiency) for polycondensation reactions. Compared

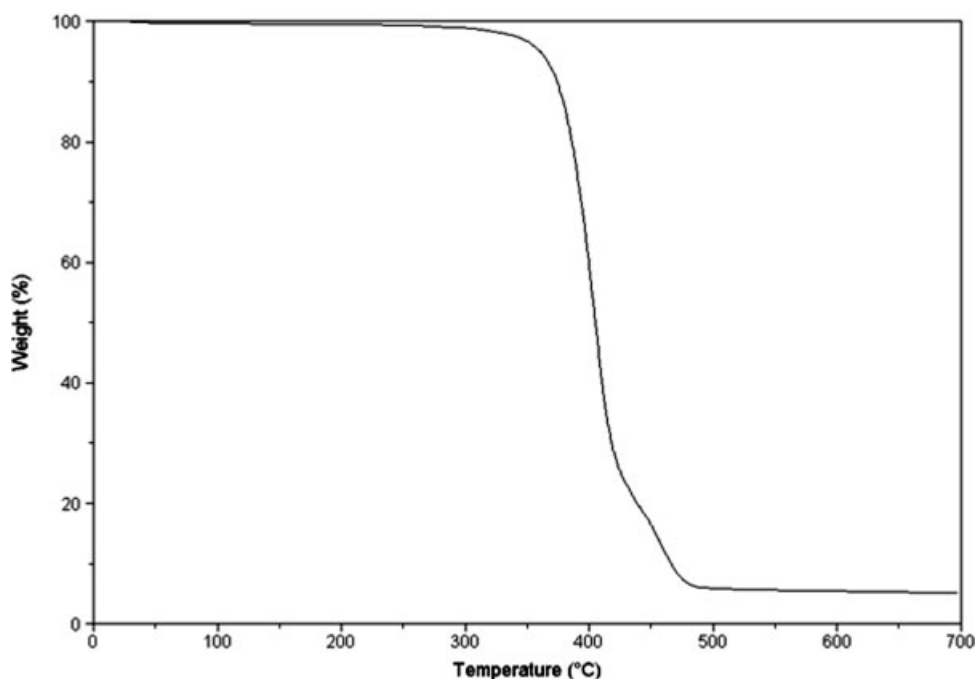


Figure 4 TGA curves of mwPSP.

with the corresponding thermal products, microwave-synthesized copolymers had higher yields and higher molecular weights.

Compared to conventional thermal heating, the higher or equivalent physical and thermal properties generated from microwave-synthesized poly(amide-ester)s in only 1 h demonstrated that the polycondensation of sebacic acid and ω -amino alcohols can be performed efficiently and effectively by microwave irradiation.

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