Poly(amide-ester)s Derived from Dicarboxylic Acid and Aminoalcohol

Anna Borriello,[1] Luigi Nicolais,[1] Samuel J. Huang[2]

[1]*Dipartimento di Ingegneria dei Materiali e della Produzione, P.le Tecchio 80, 80125 Naples, Italy*
[2]*Institute of Materials Science—Polymer Program, University of Connecticut, Storrs, Connecticut 06269-3136*

ABSTRACT: A series of alternating aliphatic poly(amide-ester)s, derived from dicarboxylic acid and aminoalcohols, were obtained by polycondensation in melt. All poly(amide-ester)s were characterized by FTIR and ^{1}H/^{13}C-NMR spectroscopies. The synthesized polymers showed an inherent viscosity ranging from 0.4 to 1.0 dL g^{-1}. Thermal analysis showed melting points within the range 100–115°C and glass transition within the range 30–60°C. Decomposition temperatures were more than 200°C higher than the corresponding melting temperatures. The polymers can thus be processed from the melt. The processed polymers were partially crystalline with good thermal stability. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 362–368, 2005

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

INTRODUCTION

Poly(amide-ester)s[1–3] have received increasing interest in recent years. These polymers offer an interesting combination of properties: a 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.[4,5]

Poly(amide-ester)s can be synthesized as random copolymers,[6] alternating copolymers,[7] or segmented copolymers.[8] Each type has its own characteristics.

Regular poly(amide-ester)s are usually prepared in a two-step synthesis. First, well-defined monomers are prepared that react in a second step to give alternating poly(amide-ester)s.[9] They usually show intermediate properties between those of polyesters and polyamides.

An one-step synthesis, in which all the monomers are reacted in the some time, usually, yield a polymer of low order.[10] The irregular structure hinders the ordering and packing in a crystalline structure.[11,12] As a result, the modulus above the glass-transition temperature (T_g) is lowered.

We report here the synthesis, structure, and properties of a set of alternating poly(amide-ester)s, of various methylene/amide ratios, prepared from dicarboxylic acids and aminoalcohols. A simple method of synthesis, based on condensation in the melt, was used. The melt polymerization method is particularly advantageous for industrial production because no posttreatment is necessary after polymerization. Among our intentions was to obtain the samples by an easy procedure for subsequent commercial production, which until now has not been possible because of scaling-up difficulties.[13] Poly(amide-ester)s thus prepared were fully characterized and their basic properties relevant to their potential applications were explored.

EXPERIMENTAL

Materials and techniques

All chemicals were commercially obtained from Aldrich (Milwaukee, WI). They were analytical grade or higher and used without further purification. Solvents to be used under anhydrous conditions were dried by standard methods. The intrinsic viscosity of the polymers was measured with a Cannon–Ubbelohde (State College, PA) microviscometer in chloroform (CHCl$_3$) at 47.0 ± 0.1°C. Gel permeation chromatography was performed on a Waters Model 150-C ALC (Waters Associates, Milford, MA) using dimethyl acetamide (DMA) with 5% 1,1,1,3,3,3-hexafloro-2-propanol as solvent and monodisperse polystyrene standards were used to create a calibration curve.

Infrared absorption spectra were recorded from potassium bromide pellets with a Nicolet model 60SX FT-IR spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–500 cm^{-1} range. ^{1}H-NMR spectra were recorded using a Bruker DMX-500MHz

solution NMR instrumentation (Bruker, Billerica, MA) with deuterated dimethyl sulfoxide (DMSO) as a solvent of choice; ^{13}C-NMR spectra were recorded using a Bruker AMX-300MHz spectrometer with deuterated trifluoroacetic acid (TFA) as a solvent. Tetramethylsilane (TMS) was used as internal reference.

Thermal analysis of the polymers was performed by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 (Perkin Elmer Cetus Instruments, Norwalk, CT) to determine the melting (T_m) and the glass-transition temperatures (T_g) of the samples. Unless otherwise noted, heating and cooling rates were 10°C min^{-1}. All experiments were done under a flow of dry nitrogen through the calorimeter. Indium metal was used for calibration purposes. Thermogravimetic 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.

Optical micrographs were recorded on a polarizing optical microscope (Reichert-Jung Mod. Polyvar, Arnsberg, Germany). X-ray powder diffraction spectra were obtained with nickel-filtered Cu–K$_\alpha$ radiation with an automatic Philips diffractometer (Eindhoven, The Netherlands).

Synthesis

Dicarboxylic acids with 4 and 8 carbon atoms and *n*-amino-1-alcohols with 2, 3, and 6 carbon atoms were purchased from Aldrich. The general procedure for the polycondensation was as follows: equimolecular quantities of dicarboxylic acid and amino alcohol were placed in a two-neck 250-mL flask, equipped with a Dean–Stark trap.

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)$_2$ ($\approx$ 0.20% mol).

With sufficient stirring provided, the vessel was immersed in an oil bath maintained at 200°C for 3 h, followed by slow cooling to room temperature. The resulting material, a hard solid, was purified by washing with methanol and then dried under vacuum at

HOOC-(CH$_2$)$_m$- COOH   +   H$_2$N- (CH$_2$)$_n$-OH

dicarboxylic acid   *aminoalcohol*
m = 4,8   *n = 2, 3, 6*

Sn(Oct)$_2$
-H$_2$O

⋯⋯ OC(CH$_2$)$_m$COHN(CH$_2$)$_n$O ⋯⋯
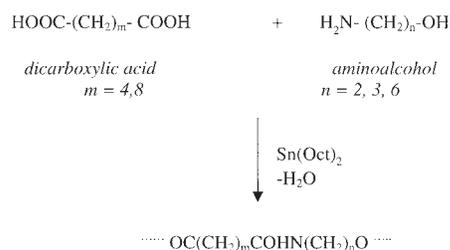
Scheme 1 Synthesis of poly(amide-ester)s by melt polymerization.

TABLE I
Synthesis Results of the Poly(amide-ester)s

Polymer	Yield (%)	$[\eta]^a$ (dL/g)	$M_w{}^b$	M_w/M_n
PSE	65	0.97	40,800	1.7
PSP	68	0.62	36,100	1.5
PSH	70	0.47	10,700	1.3
PAH	60	0.45	10,200	1.2

^{a} Measured in chloroform at 45 $\pm$ 0.1°C.
^{b} Measured by GPC.

80°C to give a white or slightly yellow, powdery polymer.

The resulting poly(amide-ester)s are: poly(sebacicacid-*co*-2-aminoethanol) (**PSE**), poly(sebacicacid-*co*-3-aminopropanol) (**PSP**), poly(sebacicacid-*co*-6-aminohexanol) (**PSH**), and poly(adipicacid-*co*-6-aminohexanol) (**PAH**).

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

All polymers were synthesized according to the methodology previously reported in the experimental part and outlined in Scheme 1.

Melt polycondensation of dicarboxylic acid with aminoalcohol in a one-step reaction has been demonstrated to be an efficient and versatile procedure to obtain regular poly(amide-ester)s. The polymerization technique is simple and rendered polymers with higher molecular weight in quite good yields. Data and results in polymerization reaction, after purification in methanol to remove catalyst and residual monomers, are shown in Table I. Intrinsic viscosities measured in chloroform ranged from 0.45 to 1 dL g^{-1}, corresponding to weight-average molecular weights between 10,000 and 40,000 and polydispersities between 1.2 and 1.7.

Both IR and ^{1}H- and ^{13}C-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 show the characteristic absorption bands of methylene, ester, and amide groups. It is possible to observe the bands in the 3600–3000 cm^{-1} region, which correspond to the stretching vibrations of the N—H group. The relatively sharp band around 3350 cm^{-1} (Fig. 1) is split into two distinct, overlaying maxima at 3309 and 3380 cm^{-1}, of a slightly lower intensity, indicating that more types of hydrogen bond with different bond distances for the N—H group are formed. The shoulder at approximately 3440 cm^{-1} is also weakly visible; it can be interpreted as being responsible for the vibrations of the "free" N—H groups, and in this case only a small amount is
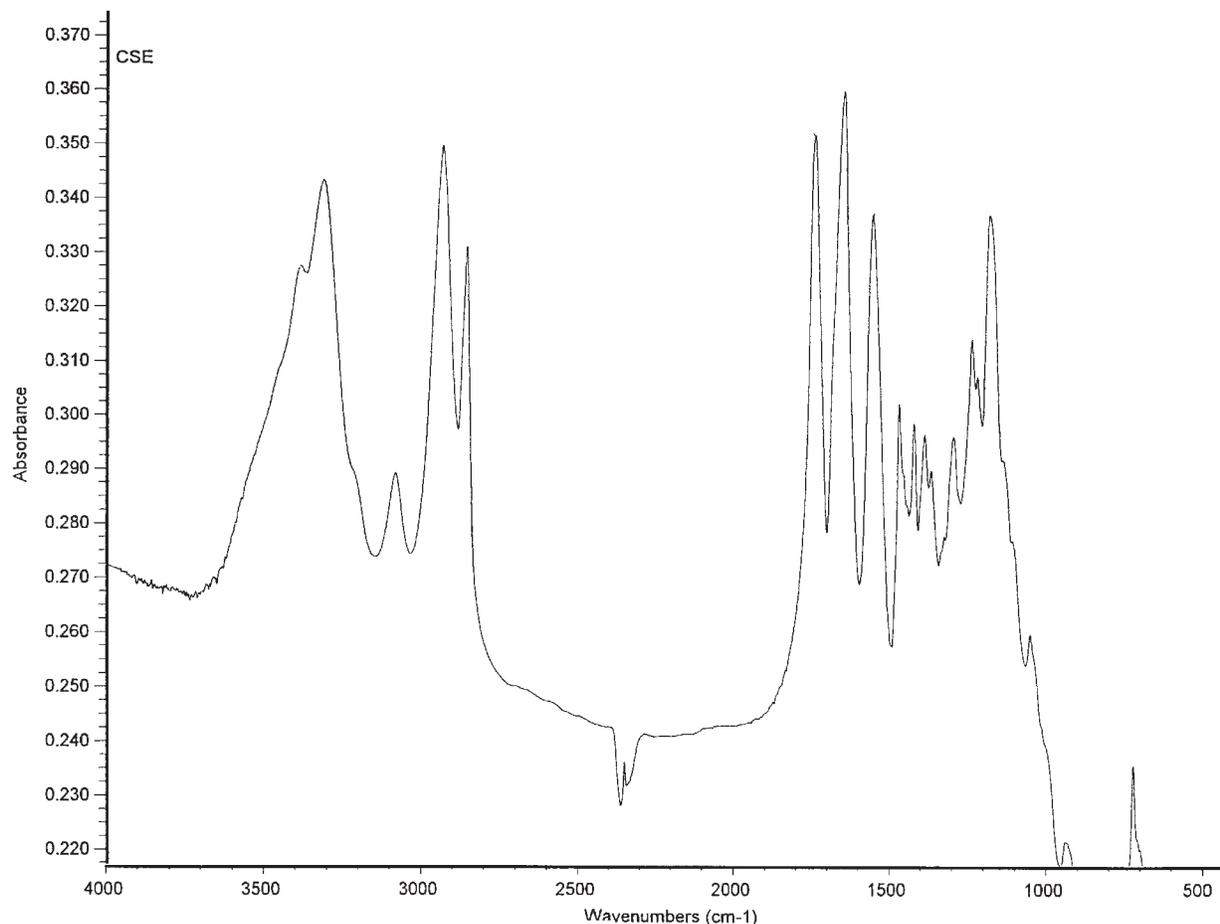
Figure 1 IR spectra of PSE.

present.[14] The absorption bands in the region from 1800 to 1500 cm^{-1} are associated with the 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) are sharp and appear in the region characteristic of hydrogen bonding. Table II shows the characteristic infrared bands for the poly(amide-ester)s studied in this work.

Representative ^{1}H- and ^{13}C-NMR spectra recorded from PSE and PSP, respectively, are shown in Figure 2 and 3 for illustration. In the proton spectrum (Fig. 2),

TABLE II
Characteristic Infrared Bands (cm^{-1}) for the Poly(amide-ester)s Studied

Polymer	Amide A	Amide B	C=O ester	Amide I	Amide II
PSE	3270	2900	1738	1660	1547
PSP	3309	2920	1737	1630	1549
PSH	3300	2870	1726	1653	1543
PAH	3264	2937	1730	1670	1550

the polymerization 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. Carbon spectra (Fig. 3) are fully consistent with the chemical constitution expected for these poly(amide-ester)s and no additional signals were detected; it may be concluded that the polymers are characterized by a structural regularity. A reliable complete assignment of peaks could be done with the help of two-dimensional techniques, which revealed that, contrary to the expectations, the resonance attributed to the amide carbons are those appearing downfield from ester carbons.

All of the other poly(amide-ester)s showed essentially similar features by NMR spectra, with only minor changes corresponding to the different number of methylene carbons inside of the chain.

Properties

The behavior patterns of poly(amide-ester)s with respect to solubility are described in Table III. In general it can be stated that, according to the general behavior of polyamides, they are soluble in strong hydrogen

OC-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CO-NH-CH$_2$-CH$_2$-O....
d e$_2$ g$_4$ g$_2$ g$_1$ g$_3$ e$_1$ c b a
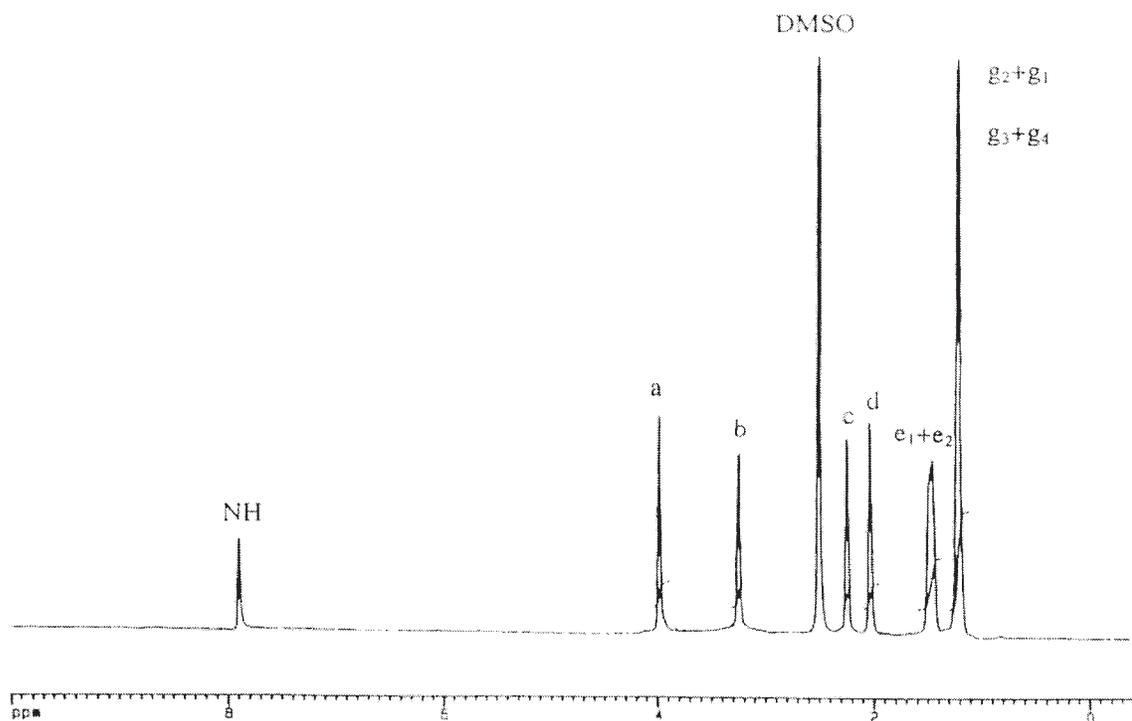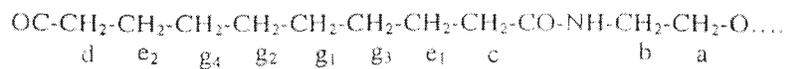
Figure 2 ^{1}H-NMR spectrum of PSE and relative assignments.
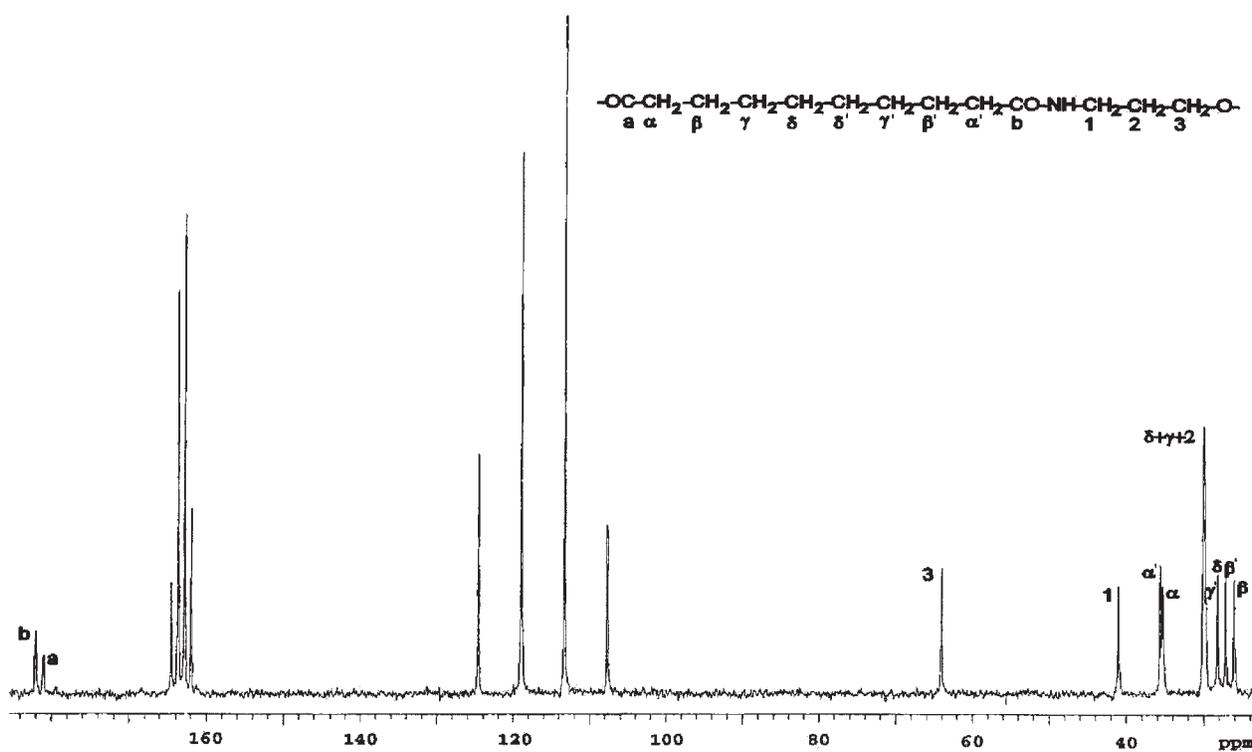
Figure 3 ^{13}C-NMR spectrum of PSP and relative assignments.

TABLE III
Solubility of the Poly(amide-ester)s[a]

Polymer	Ether	Ethyl acetate	CHCl$_3$	HCOOH	CF$_3$COOH	DMSO[b]	EFP[b]
PSE	−	−	+	++	++	+	++
PSP	−	−	+	++	++	+	++
PSH	−	−	+	++	++	+	++
PAH	−	−	+	+	+	−	+

[a] (++) soluble in cold; (+) soluble in warm; (−) nonsoluble.
[b] DMSO, dimethyl sulfoxide; EFP, esafluoropropanol.

bond breaking solvents such as formic acid or trifluoroacetic acid and insoluble in nonpolar organic solvents such as ethers or ethyl acetate. PAH is less soluble than the other poly(amide-ester)s investigated in this work because it has more specific contents of amide groups.

The thermal behavior of poly(amide-ester)s at temperatures below decomposition was examined by DSC. Representative curves for the polymers are displayed in Figure 4 and T_g and T_m values recorded from these experiment are listed in Table IV. Three runs were performed for each poly(amide-ester). In the initial run, the samples, coming directly from the synthesis, was heated at 10°C/min through fusion and left in the melt for 2–3 min. The cooling was also performed at 10°C/min to observe crystallization from the melt. Finally, a second heating was done to

check the reproducibility of the transitions. This calorimetric analysis indicated thermal stability for the sample of this series. Thus, there are well-behaved melt baselines after the fusion peaks, and the transition observed on heating are reproducible. In general, the samples displayed a profile containing bimodal endotherms arising from melting of 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 is defined as the difference between the melting and the crystallization temperature (ΔT). A small undercooling implies a fast crystallization rate. The ΔT values of PSE, PSP, PSH are small, suggesting a very fast crystallization of the polymers and this could be the result of some ordering in the melt of the segments caused by the hydrogen bonds.[15,16] It is obvious that a fast crystallization is an advantage in the melt processing of the polymers and indicates a high degree of structural regularity.

Glass-transition temperatures, observed from the heating run, are reported in Table IV and Figure 4.

Decomposition (T_d) at heating was evaluated by thermogravimetric analysis. TGA data are collected in Table IV and representative curves are shown in Figure 5 for the case of PSP. The decay of the remaining weight with temperature of a sample that was heated from room temperature to near 700°C show two decomposition steps at the respective temperature ranges of 350–400 and 430–500°C, the second one being of much lesser intensity than that of the former. According to what has been reported in the literature,[17] the first decomposition step must involve imidation and subsequent main-chain scission, whereas
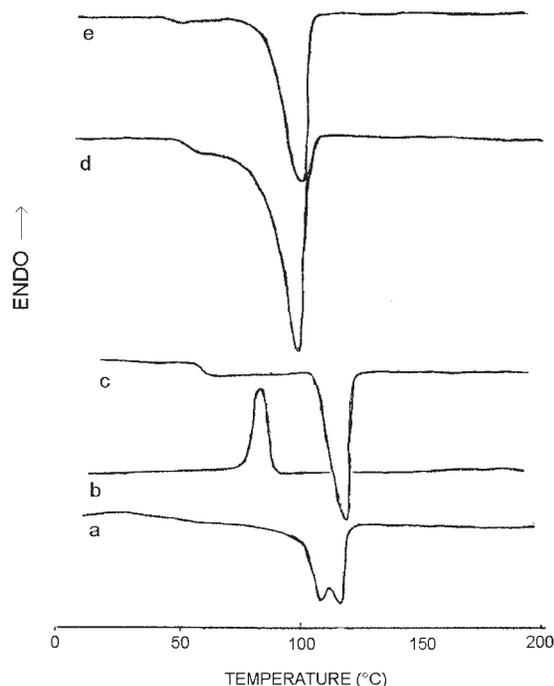
Figure 4   DSC traces of poly(amide-ester)s. Heating traces recorded from a sample of PSE: (a) directly from synthesis, (b) cooling trace after melting, (c) second heating traces, (d) heating traces of PSP after annealing at 90°C, and (e) second heating traces of PSH.

TABLE IV
Properties of Poly(amide-ester)s

Polymer	T_g (°C)	T_m (°C)	ΔH (J/g)	$T_d{}^a$ (°C)	$T_d{}^b$ (°C)	Crystallinity (%)
PSE	58	107	61	321	333	25
PSP	56	100	54	369	374	30
PSH	56	105	75	400	397	34
PAH	30	114	53	331	320	30

[a] Degradation temperature in air.
[b] Degradation temperature in N$_2$.
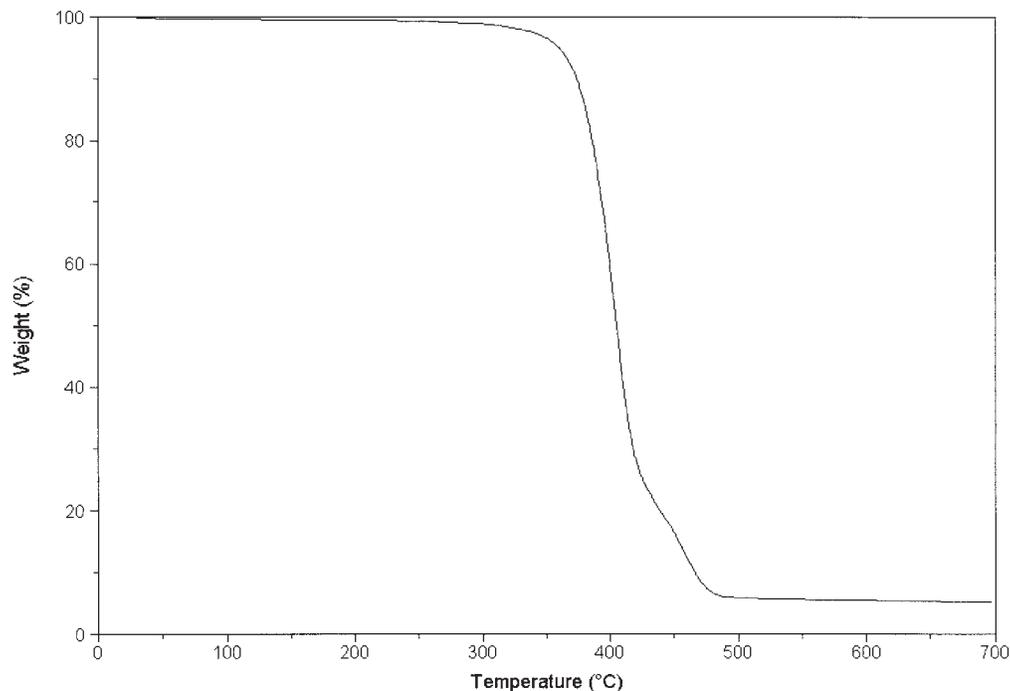
Figure 5 TGA curves of PSP.

an uncontrolled decomposition must take place at the second step. The thermal stability along the poly(amide-ester)s derived from sebacic acid increases with the length of the aminoalcohol. The measured T_d values are always higher than the fusion temperature (>200°C) and thus the polymers can be processed from the melt.

Spherulitic morphologies were observed by crystallization from the melt and by evaporation of solutions in acid formic of poly(amide-ester)s, as shown in Figure 6. Morphological features, sizes, and signs of spherulites were found dependent on both evaporation conditions and polymer constitution. In any case, they prove the crystalline nature of all samples investigated in this work.

The percentage of crystallinity was also calculated and reported in Table IV; the experimental intensities were evaluated by measuring the area of the peaks in the X-ray powder diffraction pattern, after subtraction of the amorphous halo.

All samples were capable of producing films from the melt.

CONCLUSIONS

A series of aliphatic poly(amide-ester)s derived from dicarboxylic acid and aminoalcohol were obtained by a simple method of synthesis based on condensation in melt with high yields (65–70%).
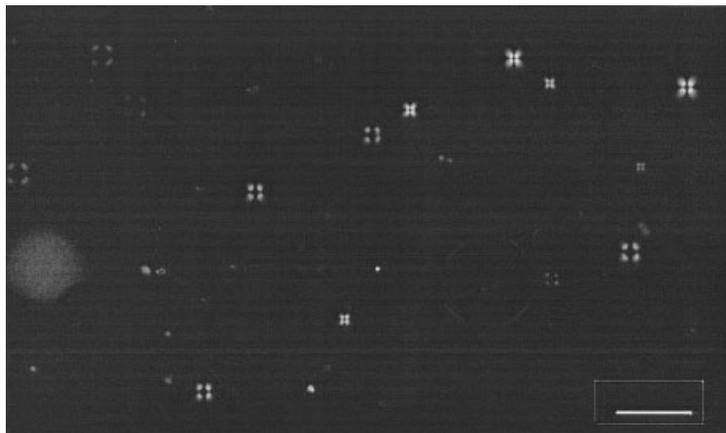
Figure 6 Spherulitic morphologies of poly(amide-ester)s. Scale bar: 200 μm.

^{13}C-NMR spectra are fully consistent with the chemical constitution expected for these poly(amide-ester)s and no additional signals were detected; it may be concluded that the polymers are characterized by a structural regularity.

The polymers show a very fast crystallization. It is an advantage in the melt processing of the polymers, indicating a high degree of structural regularity.

Decomposition temperatures are always more than 200°C higher than the corresponding melting temperatures and thus the polymers can be processed from the melt.

The data indicate that all polymers are crystalline with spherulitic morphologies and with good thermal stability.

Attempts to make films from the polymers synthesized by compression molding were successful.

References

1. Huang, S. J. In: Degradable Polymer, Recycling and Plastics Waste Management; Albertssonn, A.; Huang, S. J., Eds.; Polymer Waste Management—Biodegradation, Incineration, and Recycling; Marcel Dekker: New York, 1995; pp. 1–5.
2. Alla, A.; Rodrýguez-Galan, A.; Martýnez de Ilar-duya, A.; Munoz-Guerra, S. Polymer 1997, 38, 4935.
3. Gaymans, R. J.; de Haan, J. L. Polymer 1993, 34, 4360.
4. Pulapula, S.; Kohn, J. J Biomater Appl 1992, 6, 216.
5. Huang, S. J.; Roby, M. S. J Bioact Compat Polym 1986, 1, 61.
6. Castaldo, L.; De Candia, F.; Maglio, G.; Palombo, R. Strazza, G. J Appl Polym Sci 1982, 27, 1809.
7. De Candia, F.; Maglio, G.; Palumbo, R. Polym Bull 1982, 8, 109.
8. Sorta, E.; Della Fortuna, G. Polymer 1980, 21, 728.
9. Aharoni, S. M. Macromolecules 1998, 21 1941.
10. Carothers, W. H. (to Dupont de Nemours, Inc.) U.S. Pat. 2,071,250, 1931.
11. Goodman, I.; Sheahan, R. J. J Eur Polym 1990, 26, 1081.
12. Goodman, I.; Rodriguez, M. T. Macromol Chem Phys 1994, 195, 1075.
13. Kumar, G. S. Biodegradable Polymers: Prospect and Progress; Marcel Dekker: New York, 1987.
14. Kaczmarczyk, B.; Sek, D. Polymer 1995, 36, 5019.
15. Garcia, D.; Starkweather, H. J Polym Sci Polym Phys Ed 1985, 3, 537.
16. Ramesh, C.; Keller, A.; Eltink, S. J. E. A. Polymer 1994, 35, 5293.
17. Villuendas, I.; Iribarren, J. I.; Munoz-Guerra, S. Macromolecules 1998, 32, 8015.