Polymer Chemistry

β-Methyl-δ-valerolactone-containing Thermoplastic Poly(ester-amide)s: Synthesis, Mechanical Properties, and Degradation Behavior

Journal:	*Polymer Chemistry*
Manuscript ID	PY-ART-01-2021-000040.R1
Article Type:	Paper
Date Submitted by the Author:	14-Feb-2021
Complete List of Authors:	Guptill, David; University of Minnesota, Chemistry Chinta, Bhavani Shankar; University of Minnesota, Chemistry Kaicharla, Trinadh; University of Minnesota, Chemistry Xu, Shu; University of Minnesota, Chemistry Hoye, T.; University of Minnesota, Chemistry

ARTICLE

β-Methyl-δ-valerolactone-containing Thermoplastic Poly(ester-amide)s: Synthesis, Mechanical Properties, and Degradation Behavior

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

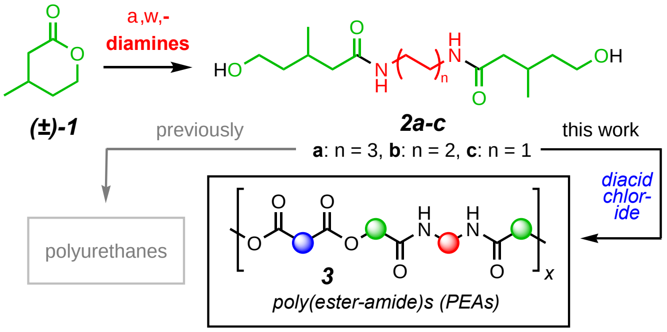
David M. Guptill,[a] Bhavani Shankar Chinta,[a] Trinadh Kaicharla,[a] Shu Xu,[a] Thomas R. Hoye[a*]

Poly(ester-amide)s (PEAs) have been prepared from (glucose-derived) β-methyl-δ-valerolactone (MVL) by reaction of MVL-derived diamidodiols with diacid chlorides in solution to form poly(ester-amide)s having alternating diester-diamide subunits. The PEAs formed by this method exhibit plastic properties and are of sufficiently high molecular weight to be tough, ductile materials (stress at break: 41–53 MPa, strain at break: 530–640%). The length of the methylene linker unit (n = 1,2,3) between amide groups of the diamidodiols affects the Young's modulus; longer linkers reduce the stiffness of the materials. This allows tuning of the properties by judicious choice of precursors. MVL was also converted to a diacid chloride that was then used to prepare a PEA that is 76 wt% MVL-derived. The degradation rates of suspensions of these new PEAs in basic aqueous media were benchmarked and their instability in aqueous acid was also observed. NMR studies were used to detect the hydrolytic degradation products of both these PEAs as well as a structurally simpler analog.

Introduction

As the rate of worldwide production of plastics grows, the impact of these materials on the environment is of growing concern.[1] The source of the raw materials themselves as well as the degradability of the polymers after use (end-of-life issues) are two important concerns.[2] Currently, the most prominent class of degradable polymers comprises aliphatic polyesters,[3,4,5] prepared by condensation polymerization or by ring-opening trans-esterification polymerization of lactones.[6,7] The susceptibility of aliphatic polyesters to hydrolytic degradation enables rapid breakdown. This characteristic is also of considerable significance in the biomedical field.[8,9,10] Aliphatic polyesters have been incorporated into block copolymers[11,12,13,14,15] as well as polyurethanes,[16,17,18] which has expanded their range of potential applications. Despite some notable advances, bio-based, degradable polymers constitute only a small fraction of the market for plastics. The most successful example to date is poly(lactic acid) (PLA).[19] Though PLA has been commercialized for applications such as packaging and beverage cups, it is somewhat brittle, and the glass transition temperature (T_g) is relatively low (ca. 55 °C).[20] These properties limit, somewhat, the applications for PLA.

Many aliphatic polyesters are limited by having non-ideal melting temperatures and poor mechanical properties. The incorporation of nitrogen functionality into the polymer backbone in the form of ureas [poly(ester-urea)s][21] or amides [poly(ester-amide)s (PEA)s][22,23,24,25,26,27] has been used to improve the tunability of polyester properties. Such poly(ester-urea)s[28,29,30] and PEAs[31,32,33] have also been exploited for biomedical applications.



Scheme 1. Synthesis of diamidodiols **2** from (±)-β-methyl-δ-valerolactone (MVL, **1**) and their use in the preparation of poly(ester-amides)s (PEA)s **3**.

Recently, (±)-β-methyl-δ-valerolactone (**1**, MVL, Scheme 1) has emerged as an attractive monomer,[13,15,18] available on scale by fermentation of glucose to mevalonate followed by straightforward chemical processing.[13] We have described[34] the synthesis of diamidodiols **2** by the straightforward reaction of racemic MVL[35] with various α,ω-diamines (Scheme 1) and the subsequent use of **2** as chain extenders in the synthesis of polyurethanes. We also envisioned using these diamidodiols as monomers for preparing alternating PEAs such as **3**. Diamidodiols derived from petroleum-based lactones have been used to prepare PEAs,[36,37,38,39,40,41,42] but examples of

---

[a] Department of Chemistry University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455 USA

Electronic Supplementary Information (ESI) available: PDF of procedures for preparation and characterization data for all new compounds and polymers, including copies of ^{1}H and ^{13}C NMR spectra]. See DOI: 10.1039/x0xx00000x

PEAs with a regular, alternating structure incorporating such diamidodiols are less common.[36,41,42] In most cases, additional aliphatic diols[39,40] or oligomeric telechelic ester diols[37,38] have also been incorporated. Our own attempts to work with ε-caprolactone- and δ-valerolactone-derived diamidodiols have been thwarted by their limited solubility in any convenient solvents.[41] In contrast, each of the diamidodiol monomers **2a-c** contains a pair of methyl substituents that introduce disorder. Because the samples of MVL monomers are racemic, there are diastereomeric relationships within the backbone that further reduce organization. Our experience with incorporating **2a-c** into polyurethanes[34] suggested that those monomers also might be better suited for the synthesis of the alternating PEAs **3** compared to their unbranched ε-caprolactone- and δ-valerolactone-derived counterparts. This was a primary motivation behind the studies described here. Learning about the impact of the degree of methyl substitution within the PEA backbone on fundamental thermal and mechanical properties was also a goal. Finally, further demonstration of the versatility of the bio-based MVL monomer in the preparation of novel polymers is of inherent value. We describe here the preparation and characterization of a set of such materials in the form of new PEAs.

Experimental

Materials

Solvents: All solvents were used as received from the manufacturer. Acetone (Certified ACS) for recrystallizations was purchased from Fisher. Absolute ethanol was purchased from Pharmco-AAPR; for use with sodium ethoxide and diethyl malonate, the ethanol was treated with sodium and distilled directly into the flask used for the reaction. Chloroform was purchased from Fisher. Chloroform used for polymerization reactions was washed several times with H_2O, dried over $MgSO_4$ and filtered, and further dried by distillation from CaH_2 (chloroform purified in this manner was stored under a N_2 atmosphere in a glovebox). Pyridine used for polymerization reactions was dried by distillation from CaH_2 (pyridine purified in this manner was stored in a Schlenk flask over 4Å sieves.

Reagents for monomer synthesis: β-Methyl-δ-valerolactone (MVL) was prepared according to a previously reported procedure.[13] Ethylenediamine, 1,4-diaminobutane, and 1,6-diaminohexane were purchased from Sigma-Aldrich and used as received. Aliphatic acid chlorides were prepared from the corresponding acids by heating with 3 equivalents of thionyl chloride (Aldrich); the crude acid chlorides were purified by two sequential distillations and stored in a Schlenk flask under N_2. HBr in acetic acid (33% w/w) was purchase from Aldrich and used as received. Sulfuric acid was purchased from Macron Chemicals and used as received. Diethyl malonate (99%) was purchased from Lancaster and used as received. Sodium (in kerosene) was purchased from Aldrich and cut into appropriately sized pieces before use. Hydrochloric acid (37%) was purchased from Aldrich and used as received.

Reagents for polymer synthesis: *N*,*N*-Dimethylaminopyridine (DMAP) was purchased from Aldrich and used as received.

Instrumental Methods

Nuclear magnetic resonance spectroscopy (NMR): Spectra were collected on a Bruker Avance III or Avance II 500 (500 MHz) or a Bruker Avance III 400 (400 MHz) spectrometer. Chemical shifts for ^1H NMR in $CDCl_3$ and d_6-DMSO are referenced to $CHCl_3$ (7.27 ppm) and $CHD_2(S{=}O)CD_3$ (2.50 ppm), respectively. Chemical shifts for ^{13}C NMR in $CDCl_3$ and d_6-DMSO are referenced to $\mathit{C}DCl_3$ (77.00 ppm) and $\mathit{C}D_3(S{=}O)\mathit{C}D_3$ (39.52 ppm), respectively. Resonances are reported in the following format: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^1H NMR assignments are indicated by the environment in which the proton resides (e.g., CH_aH_b).

The poly(ester-amide)s were soluble in DMSO upon warming. The samples were dissolved and allowed to cool before then collecting the NMR spectra.

IR spectroscopy (IR): IR spectra were recorded with a Bruker Alpha Platinum ATR-FTIR instrument that uses a diamond single bounce crystal. The data are reported as the average of 32 scans.

Thermogravimetric analysis (TGA): Performed on a TA instruments Q-500, under an atmosphere of nitrogen, using a heating rate of 10 °C/min. Sample sizes were between 8 and 15 mg.

Differential scanning calorimetry (DSC): Differential scanning calorimetry data were collected on a TA instruments Q-1000 under nitrogen. Samples were prepared in hermetically sealed, aluminum pans. Data were collected from two heating cycles from –70 to 200 °C at a heating rate of 10 °C /min and cooling at a rate of 5 °C/min in between. The reported T_gs and T_ms were those observed during a second heating cycle.

Size exclusion chromatography (SEC): $CHCl_3$ SEC data were obtained by passing the sample (50 μL, ca. 2 mg/mL) through three successive PLgel Mixed C columns (7.5 mm id, 25 cm length) at a rate of 1 mL/min. The eluant was detected using a refractive index detector (HP1047A). The values are reported relative to poly(styrene) standards.

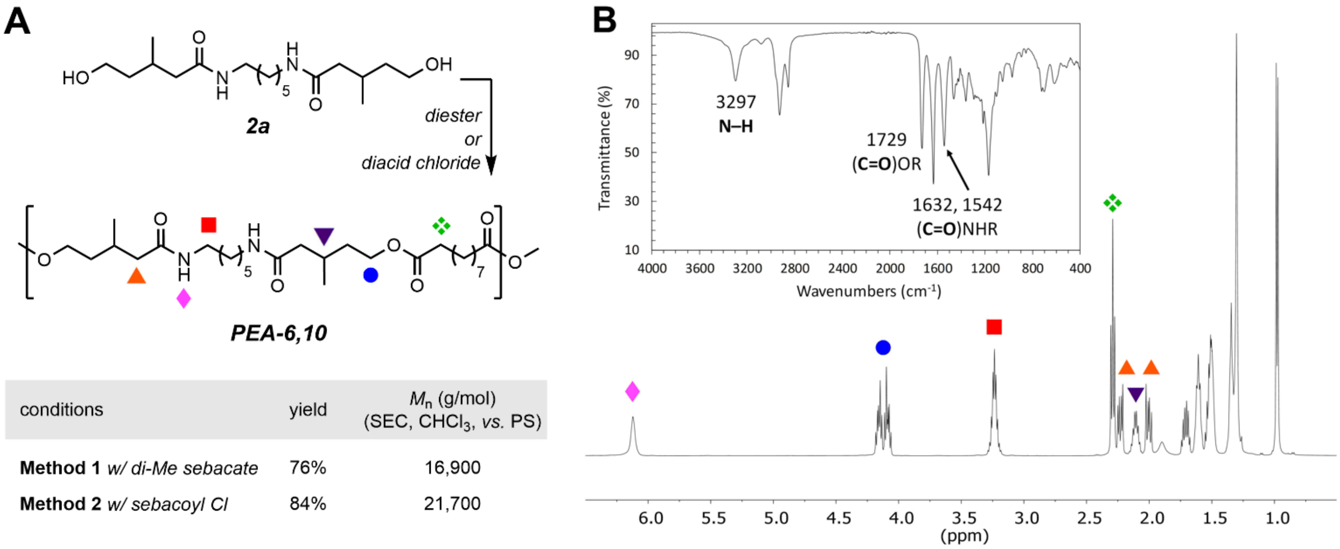
The relative molecular weights of the PEAs were estimated using size exclusion chromatography with a DMF mobile phase (doped with 0.1 M LiBr). A flow rate of 1 mL/min and sample concentrations of ca. 2 mg/mL was used. These samples (20 μL injection volume) were passed through a pair of Styragel HT4 columns (7.8 mm id, 30 cm length). Again, the values are reported relative to poly(styrene) standards.

HFIP SEC data were collected at 0.35 mL/ min at 40 °C using an eluant containing potassium trifluoroacetate (0.025 M). Two Tosoh TSKgel SuperAWM–H columns were used. Molecular masses were determined by calibration vs. polymethyl methacrylate (PMMA) standards. Prior to analysis, samples were filtered through a 0.2 µm filter (Whatman).

Tensile testing: A Shimadzu Autograph AGS-X Series tensile tester (Columbia, MD) was used to collect uniaxial extension data. Samples were observed at a constant crosshead velocity of 10 mm min^{-1} until failure. Data from these experiments are reported as the average from 5–7 separate specimens prepared from the same batch of polymer film.

Films for all PEAs were prepared by compression moulding. The precipitated polymer samples were first heated above their melting point in a PTFE dish and compressed by hand with another slightly smaller PTFE dish. The films so produced (> 1 mm thickness) were then pressed into films (0.3 to 0.5 mm) by compression moulding between two PTFE sheets at 150 °C. The films were allowed to cool to room temperature and aged for at least 24 hours before the tensile testing.

Tensile bars were cut from each of the above films using a dogbone-shaped dye. The final dogbone bars were ca. 3.0 mm wide and had a gauge length of ca. 11.5 mm.



conditions	yield	M_n (g/mol) (SEC, $CHCl_3$, *vs.* PS)
Method 1 *w/ di-Me sebacate*	76%	16,900
Method 2 *w/ sebacoyl Cl*	84%	21,700

Figure 1. (A) Reaction of amidodiols **2a** with sebacic acid derivatives to give poly(ester-amide) **PEA-6,10** via bulk or solution polymerization. Method 1: $Ti(O^iPr)_4$, 180 °C, neat; Method 2: DMAP (cat.), pyridine:$CHCl_3$ 2:3, ambient T. (B) ^{1}H NMR spectrum ($CDCl_3$) and FTIR spectrum (inset) of the **PEA-6,10** prepared by solution polymerization.

Results and discussion

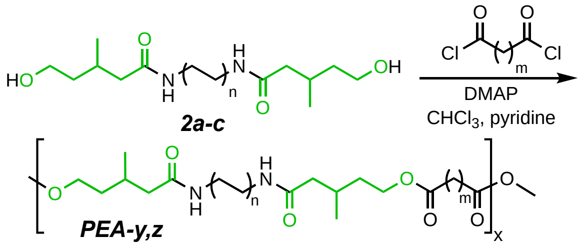
We initiated our studies by investigating the bulk step-growth polymerization of **2a** with dimethyl sebacate in the presence of Ti(i-OPr)$_4$ (Figure 1A) at 180 °C (Method 1). The polymer **PEA-6,10** was produced in 76% yield (after precipitation) with a number average molecular weight (M_n) of ~16 kg mol^{-1}. Attempts to obtain higher molar mass polymer by increasing the temperature or applying a vacuum to assist in the removal of methanol were unsuccessful. On larger scales (> 1 mmol), MVL (**1**) distilled from the reaction mixture, suggesting that an amide bond in monomer **2a** (and/or in oligomeric **PEA-6,10**) was being cleaved, likely by back-biting by a terminal hydroxy group, under these forcing conditions (180 °C).

We therefore turned to a solution polymerization method that could be conducted under milder conditions. Following preliminary screening of several solvents and amine bases, **2a** was treated with sebacoyl chloride in a pyridine/chloroform (ethanol free) cosolvent that contained a catalytic amount of *N*,*N*-dimethyl-4-aminopyridine (DMAP) (Figure 1A, Method 2). **PEA-6,10** was formed in 84% yield with a M_n of ~22 kg mol^{-1}. We found these conditions to be more reproducible and to provide polymers whose films seemed, qualitatively, to be stronger and more ductile.

The ^{1}H NMR and IR spectra of this polymer (Figure 1B) supported the structure of **PEA-6,10**. The IR spectrum showed absorptions for both ester and amide carbonyls as well as the secondary amide N–H. The ^{1}H NMR spectrum also showed the presence of an NH proton (6.1 ppm, $CDCl_3$ and 7.7 ppm, DMSO-d_6) as well as equal intensity resonances for methylene protons bound to ester *O*- and amide *N*-atoms. In addition, the ^{13}C NMR spectrum [see electronic supplementary information (ESI)] contained (sharp) resonances for both ester and amide carbonyl carbon atoms as well as the requisite number of C_{sp3}-carbons, features that are consistent with an alternating backbone. It is notable that the resonances in the NMR spectra of these samples were quite sharp even though the diamidodiol precursors **2** were diastereomeric mixtures; the stereocenters are sufficiently remote that the atacticity is not reflected in the NMR spectroscopic behavior.

We then prepared a series of PEAs by using aliphatic diacid chlorides (Method 2) in which the chain lengths of the central, diamine-derived portion of the diol and/or diacid chloride precursors were varied (Table 1). All of the PEAs were obtained in good yields. The *relative* molar mass and dispersity of the polymers were analyzed by SEC. Across this series, DMF was found to be a universal solvent (see Figure S12). We note that the M_n of **PEA-6,10**, the polymer having the greatest nominal distance of the amide bonds between repeat units, shows a considerably different molar mass when measured by SEC (polystyrene (PS) calibration) in $CHCl_3$ (Figure 1A) vs. DMF (Table 1). Hydrophobic collapse of the PS calibrant in DMF, leading to the substantial overestimation of molecular weight, is a well-recognized phenomenon.[43] Differential scanning calorimetry was then used to measure the thermal properties of the PEAs, which are also given in Table 1.

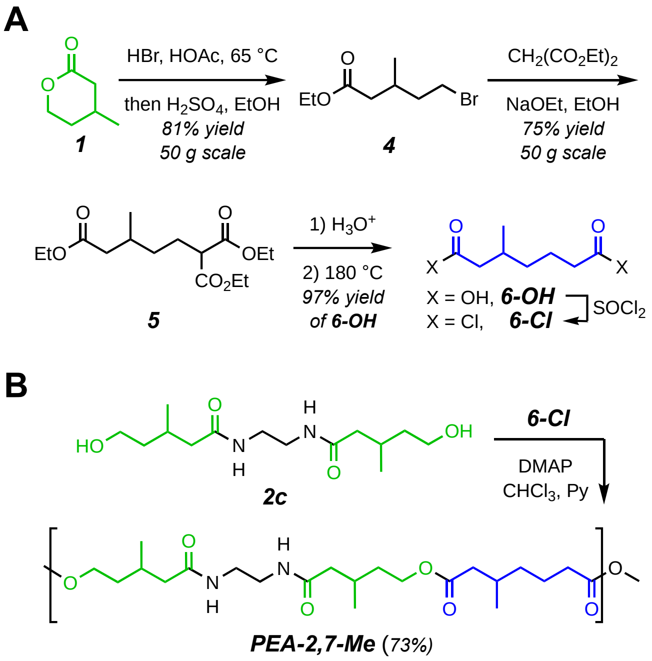
Table 1. Synthesis of MVL-derived poly(ester-amide)s



PEA-y,z[a]	n	m	diol	yield (%)[b]	M_n (Da)[c]	Đ[c]	T_g (°C)[d]	T_m (°C)[d]
PEA-6,10	3	8	**2a**	84	142,000	1.35	–13	106
PEA-6,8	3	6	**2a**	88	121,000	1.43	–11	95
PEA-6,7	3	5	**2a**	85	204,000	1.36	–10	99
PEA-4,10	2	8	**2b**	88	122,000	1.42	–10	120
PEA-4,8	2	6	**2b**	87	165,000	1.46	–8	119
PEA-4,7	2	5	**2b**	68	108,000	1.52	–7	115
PEA-2,10	1	8	**2c**	89	152,000	1.51	–2	119
PEA-2,8	1	6	**2c**	81	128,000	1.43	–3	113
PEA-2,7	1	5	**2c**	70	126,000	1.37	–2	116
PEA-2,7-Me	see Scheme 2B				129,000	1.28	–2	98

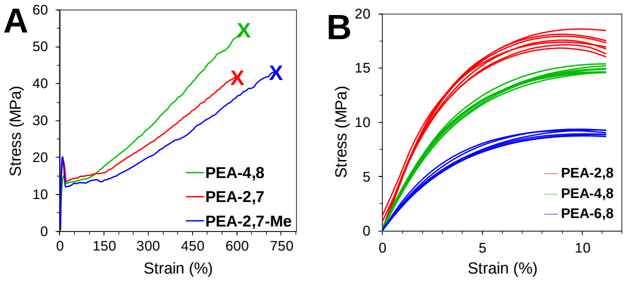
[a] PEAs are named according to the following protocol: PEA-y,z where y = the number of linking carbon atoms between the amide nitrogen atoms (y = 2n) in the diamidodiol monomer and z = the number of carbon atoms in the diacid chloride monomer [z = (m+2)]. [b] Yield of precipitated polymer. [c] M_n and Đ measured by size exclusion chromatography in DMF eluent containing 0.1 M LiBr[44] (vs. PS standards), which reflect relative sizes. [d] Glass transition temperature (T_g) and melting temperature (T_m) determined by DSC; values taken from the second heating ramp.

We also prepared a PEA that incorporated a diacid moiety that was also derived from MVL (**1**, Scheme 2A). Namely, **PEA-2,7-Me** (Scheme 2B) was synthesized using the diamidodiol **2c** and the diacid chloride, **6-Cl**. The precursor diacid, 3-methylpimelic acid (**6-OH**), was prepared (Scheme 2A) by hydrolysis and decarboxylation of the malonic ester derivative **5**. This, in turn, was obtained from the primary bromide **4**, the product of treatment of MVL (**1**) with HBr in acetic acid and Fischer esterification. The composition of the alternating copolymer **PEA-2,7-Me** is 86 wt% bio-derived (green and blue atoms, Scheme 2B). The thermal properties of **PEA-2,7-Me** are also given in Table 1. **PEA-2,7-Me** had a lower melting temperature than the less highly methylated analog **PEA-2,7** (98 vs. 116 °C, respectively), but the T_g values were the same (–2 °C).



Scheme 2. (A) Synthesis of the diacid **6-OH** from MVL (**1**). (B) Reaction of diamidodiol **2c** with the diacid chloride **6-Cl**.

The mechanical properties of the PEAs were studied by uniaxial extension (Figure 2). These materials exhibited high tensile strength and toughness, with stress at break of 41–53 MPa and strain at break of 530–700% (Figure 2A). A trend is seen between the Young's modulus (E) and the structure of the polymer—a greater length of the methylene chain between the amide nitrogen atoms in the PEAs gives rise to a lower modulus and a material with lower stiffness (for example, compare the differences between **PEA-2,8**, **PEA-4,8**, and **PEA-6,8** in Figure 2B). The set of all PEAs prepared from diol **2c** (**PEA-2,z**) have a modulus range of 440–460 MPa, those from **2b (PEA-4,z)**, 300–350 MPa, and those from **2a (PEA-6,z)**, 192–260 MPa (Figure 2C). Comparison of the properties of **PEA-2,7** vs. **PEA-2,7-Me**, shows that the extra methyl substitution in the polymer backbone results in an increase in the modulus (462 vs. 651 MPa) and a material with higher stiffness.



C

PEA-y,z	diol	M_n (kDa)	*E* (MPa)	s_y (MPa)	s_b (MPa)	e_b (%)
PEA-6,10	**2a**	142	255 ± 25	16 ± 2	42 ± 5	600 ± 50
PEA-6,8	**2a**	121	205 ± 11	9 ± 0.2	44 ± 7	612 ± 89
PEA-6,7	**2a**	204	192 ± 15	9 ± 1	47 ± 8	603 ± 40
PEA-4,10	**2b**	122	350 ± 10	16 ± 1	43 ± 5	530 ± 39
PEA-4,8	**2b**	165	323 ± 12	15 ± 0.3	53 ± 6	598 ± 66
PEA-4,7	**2b**	108	304 ± 28	13 ± 0.5	41 ± 6	537 ± 79
PEA-2,8	**2c**	128	436 ± 22	18 ± 1	47 ± 3	642 ± 44
PEA-2,7	**2c**	126	462 ± 38	18 ± 1	41 ± 5	595 ± 73
PEA-2,7-Me	**2c**	129	651 ± 28	21 ± 1	43 ± 2	697 ± 42

Figure 2. Mechanical properties of PEAs: (A) Representative stress-strain curve for **PEA-4,8**, **PEA-2,7**, and **PEA-2,7-Me**; X marks the point of rupture. (B) Expansion showing the elastic region of the stress-strain curves (0–12% strain) for multiple dog-bone samples of three PEAs differing only in the methylene chain length between amide nitrogen atoms. (C) Tabulated properties (including relative molecular weights, M_n, from Table 1), Young's modulus (E), stress at yield (σ_y), stress at break (σ_b), and strain at break (ε_b), determined by uniaxial extension experiments.

Because these PEAs contain hydrolytically cleavable aliphatic ester groups, we examined aspects of their hydrolytic degradability (Figure 3). In acidic aqueous solution (1M HCl), the samples rapidly lost structural integrity, most becoming cracked and fragile within 1-2 days. The fragility of the samples made them difficult to weigh, so mass loss over time was not attempted. When suspended in basic aqueous solution (1M NaOH) at ambient temperature, the PEA samples steadily degraded and the unreacted materials now maintained their integrity. A qualitative correlation between the carbon chain length for either the diacid or the diamine moiety vs. degradation rate was observed: the PEAs with longer carbon chains degraded more slowly. This trend is evident when comparing three sets of results in each of two series of decreasing hydrophobicity: (i) **PEA-4,10** vs **PEA-4,8** vs **PEA-4,7**; and (ii) **PEA-6,8** vs **PEA-4,8** vs **PEA-2,8**. This effect of structure on degradation rate (i.e., reduced hydrophobic character accelerates chain cleavage) provides a platform for tuning hydrolytic stability, which could be advantageous in certain applications. In deionized water (pH ~ 5), the samples were stable (i.e., showed no mass loss) for the entirety of the experiment (*ca*. 90 days).

Assessing the array of products produced from these PEAs during degradation by NMR spectroscopy was a convoluted undertaking (see ESI for partial assignments of those complex spectra). To gain a more clear understanding of the degradation process, we prepared two simpler analogs having structurally (and spectroscopically) simpler backbones. Specifically, we examined the reactions of the known[41] nor-methylated diamidodiols **2d** and **2e** (from ethylenediamine or 1,6-diaminohexane and valerolactone) with sebacoyl chloride (Scheme 3). It is worth noting that although short-chain oligomers starting from these same diols (M_n ≤1.5 kDa) have been made by condensation polymerization with sebacic acid,[37,38] higher molar mass versions appear to be unknown. The reaction of **2d** with sebacoyl chloride also proved to be problematic because of the very low solubility of this diamidodiol in py/$CHCl_3$. However, the more soluble homolog **2e** effectively gave **norMe-PEA-6,10** under analogous polymerization conditions to those used to prepare the PEAs described earlier [M_n ca. 15 kDa (SEC in HFIP), T_g = 4 °C, T_m = 140 °C]. It is notable that in situ derivatization of a suspension of **norMe-PEA-6,10** in $CDCl_3$ by addition of excess trifluoroacetic anhydride (TFAA) readily acylated the terminal alcohol and carboxylic hydroxyl groups, allowing for NMR quantification of those end groups. Moreover, the backbone amide bonds were exhaustively converted to TFA-derivatized imides, rendering the polymer readily soluble for direct NMR analysis (see ESI for details).

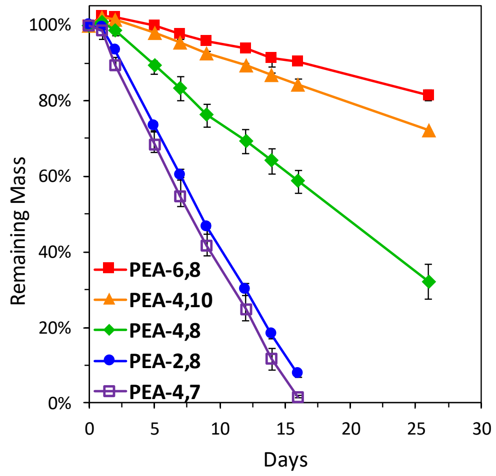
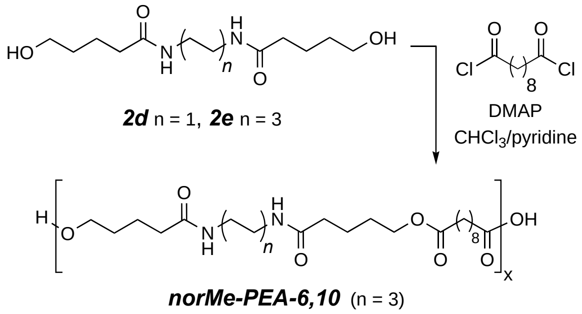


Figure 3. Results of a degradation study conducted at room temperature in basic aqueous solution (1M NaOH): mass loss of solid vs. time.



Scheme 3. Preparation of **norMe-PEA-6,10** from **2e** and sebacoyl chloride.

Spectra of the NMR degradation of **norMe-PEA-6,10** in the presence of aqueous NaOH at several time points is summarized in Figure 4. The analogous behavior of the monomer **2e** (as well as 5-hydroxyvalerate, open orange triangle) is shown in the top panels for comparison. The ester bonds are cleaved more rapidly than the amides, releasing sebacate disodium salt and **2e,** as evident from the t = 2 day spectrum. Over time, resonances for the aminoalkylamido alcohol (open blue square) are observed and these further give rise to 1,6-diaminohexane and correspondingly growing levels of 5-hydroxyvalerate. Again, the unreacted solid polymer film was easily fractured, making study of mass loss over extended times non-trivial.

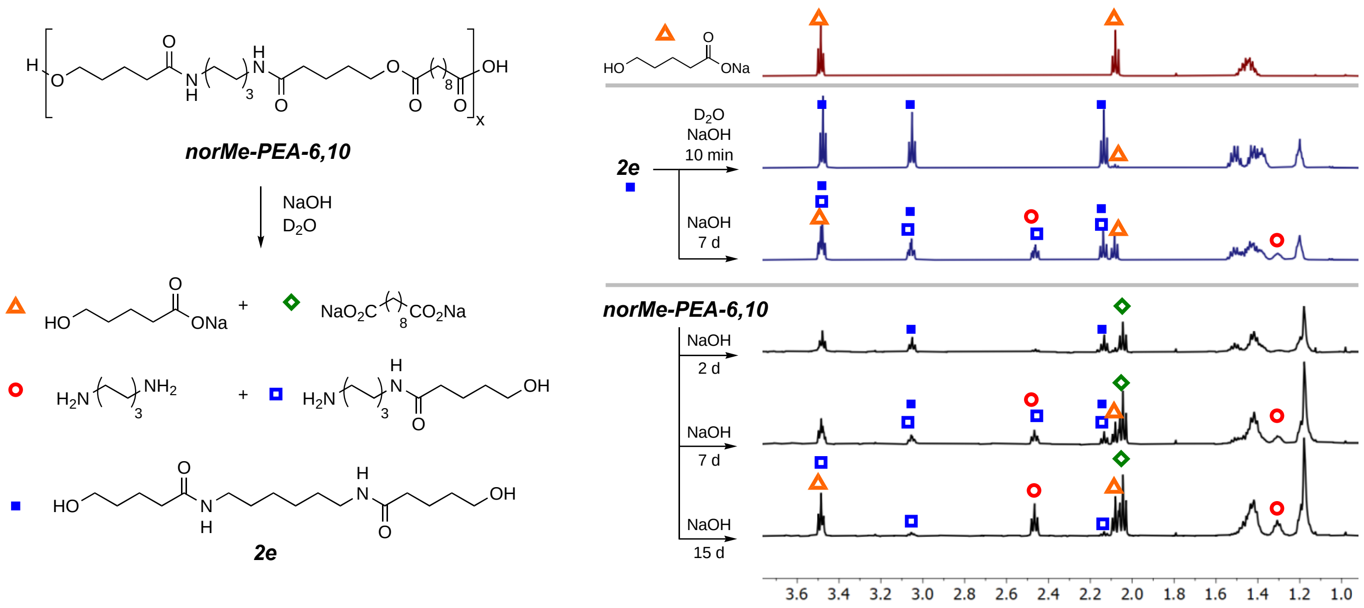


Figure 4. In situ NMR study of the degradation of polymer **norMe-PEA-6,10** in D_2O/NaOH.

Conclusions

In summary, we have prepared new thermoplastic poly(ester-amide)s (PEAs), having backbone repeat units alternating regularly between diamide and diester moieties, from β-methyl-δ-valerolactone. These semi-crystalline polymers are easily synthesized and are characterized by high toughness and ductility. Some of the PEA properties are tunable by the choice of monomers. Furthermore, the materials degrade hydrolytically in basic media at varying rates, which are dependent on the molecular structure, in particular the hydrophobicity of the diamine- and/or diacid-derived chains. Altogether, such properties render these materials an attractive addition to the collection of known PEAs.

Author Contributions

DMG, BSC, TK, and SX performed the experiments and collected and analyzed the data. TRH supervised the research. All authors were involved in writing and reviewing the manuscript.

Conflicts of interest

“There are no conflicts to declare”.

Acknowledgements

We thank Professor Marc A. Hillmyer for providing access to instrumentation. We thank Jacob P. Brutman for helpful discussions and review of the manuscript. Financial support for this research was provided by the Center for Sustainable Polymers at the University of Minnesota, an NSF-supported Center for Chemical Innovation (CHE-1413862). Some of the NMR data were recorded on an instrument purchased with support of the NIH Shared Instrumentation Grant program (S10OD011952).

References

---

1 [1] The New Plastics Economy - Rethinking the future of plastics; World Economic Forum, Ellen MacArthur Foundation, and McKinsey & Company: 2016. [http://www3.weforum.org/docs/WEF_The_New_Plastics_Economy.pdf; accessed 12-26-20]

2 [2] D. E. Fagnani, J. L. Tami, G. Copley, M. N. Clemons, Y. D. Y. L. Getzler and A. J. McNeil, *ACS Macro Letters*, DOI: 10.1021/acsmacrolett.0c00789.

3 [3] M. Okada, *Prog. Polym. Sci.,* 2002, **27**, 87–133.

4 [4] C. K. Williams, *Chem. Soc. Rev.,* 2007, **36**, 1573–1580.

5 [5] J. Rydz, W. Sikorska, M. Kyulavskak and D. Christova, *Int. J. Mol. Sci.,* 2015, **16**, 564–596.

6 [6] C. Jérôme and P. Lecomte, *Adv. Drug Deliv. Rev.,* 2008, **60**, 1056–1076.

7 [7] C. M. Thomas, *Chem. Soc. Rev.,* 2010, **39**, 165–173.

8 [8] M. Vert, *Biomacromolecules*, 2005, **6**, 538–546.

9 [9] H. Seyednejad, A. H. Ghassemi, C. F. van Nostrum, T. Vermonden and W. E. Hennink, *J. Control. Release,* 2011, **152**, 168–176.

10 [10] M. Gigli, M. Fabbri, N. Lotti, R. Gamberini, B. Rimini and A. Munari, *Eur. Polym. J.,* 2016, **75**, 431–460.

11 [11] M. A. Hillmyer and W. B. Tolman, *Acc. Chem. Res.,* 2014, **47**, 2390–2396.

12 [12] M. T. Martello, D. K. Schneiderman and M. A. Hillmyer, *ACS Sustain. Chem. Eng.,* 2014, **2**, 2519–2526.

13 [13] M. Xiong, D. K. Schneiderman, F. S. Bates, M. A. Hillmyer and K. Zhang, *Proc. Natl. Acad. Sci.,* 2014, **111**, 8357–8362.

14 [14] D. K. Schneiderman, E. M. Hill, M. T. Martello and M. A. Hillmyer, *Polym. Chem.,* 2015, **6**, 3641–3651.

15 [15] J. Zhang, T. Li, A. M. Mannion, D. K. Schneiderman, M. A. Hillmyer and F. S. Bates, *ACS Macro Lett.,* 2016, **5**, 407–412.

16 [16] Báez, D. Ramírez, J. L. Valentín and A. Marcos-Fernández, *Macromolecules,* 2012, **45**, 6966–6980.

17 [17] S. A. Gurusamy-Thangavelu, S. J. Emond, A. Kulshrestha, M. A. Hillmyer, C. W. Macosko, W. B. Tolman and T. R. Hoye, *Polym. Chem.,* 2012, **3**, 2941–2948.

18 [18] D. K. Schneiderman, M. E. Vanderlaan, A. M. Mannion, T. R. Panthani, D. C. Batiste, J. Z. Wang, F. S. Bates, C. W. Macosko and M. A. Hillmyer, *ACS Macro Lett.,* 2016, **5**, 515–518.

19 [19] V. Nagarajan, A. K. Mohanty and M. Misra, *ACS Sustain. Chem. Eng.,* 2016, **4**, 2899–2916.

20 [20] A. Södergård and M. Stolt, *Prog. Polym. Sci.,* 2002, **27**, 1123–1163.

21 [21] D. Tang, Z. Chen, F. Correa Netto, C. W. Macosko, M. A. Hillmyer and G. Zhang, *J. Polym. Sci. Part A Polym. Chem.,* 2016, **54**, 3795–3799.

22 [22] A. Díaz, R. Katsarava and J. Puiggalí, *Int. J. Mol. Sci.,* 2014, **15**, 7064–7123.

23 [23] S. K. Murase and J. Puiggalí, Poly(Ester Amide)s: Recent Developments on Synthesis and Application, Chap. 8 In *Natural and Synthetic Biomedical Polymers*; S. G. Kumbar, C. T. Laurencin and M. Deng, Eds.; Elsevier Science: London, 2014; 145–166.

24 [24] M. Winnacker and B. Rieger, *Polym. Chem.,* 2016, **7**, 7039–7046.

25 [25] R. Triki, M. Abid, M. Tessier, S. Abid, R. El Gharbi and A. Fradet, *Eur. Polym. J.,* 2013, **49**, 1852–1860.

26 [26] A. Ali Mohamed, S. Salhi, S. Abid, R. El Gharbi and A. Fradet, *J. Appl. Polym. Sci.,* 2016, **133**, 44220.

27 [27] S. Çakir, M. Eriksson, M. Martinelle and C. E. Koning, *Eur. Polym. J.,* 2016, **79**, 13–22.

28 [28] J. Yu, F. Lin and M. L. Becker, *Macromolecules,* 2015, **48**, 2916–2924.

29 [29] Y. Gao, E. P. Childers and M. L. Becker, *ACS Biomater. Sci. Eng.,* 2015, **1**, 795–804.

30 [30] V. Bhagat, E. O'Brien, J. Zhou and M. L. Becker, *Biomacromolecules,* 2016, **17**, 3016–3024.

31 [31] A. Rodriguez-Galan, L. Franco and J. Puiggalí, *Polymers (Basel),* 2011, **3**, 65–99.

32 [32] K. Ghosal, M. S. Latha and S. Thomas, *Eur. Polym. J.,* 2014, **60**, 58–68.

33 [33] A. C. Fonseca, M. H. Gil and P. N. Simões, *Prog. Polym. Sci.,* 2014, **39**, 1291–1311.

34 [34] D. M. Guptill, J. P. Brutman and T. R. Hoye, *Polymer*, 2017, **111**, 252–257.

35 [35] Enantioenriched MVL, a non-trivially accessible monomer, has been polymerized to PMVL. The thermal properties (T_g and amorphous nature) of that material were very similar to those of the analogous polymer derived from (±)-MVL. C. Zhang, D. K. Schneiderman, T. Cai, Y.-S. Tai, K. Fox and K. Zhang, *ACS Sustainable Chem. Eng.,* 2016, **4**, 4396–4402.

36 [36] S. Katayama, T. Murakami, Y. Takahashi, H. Serita, Y. Obuchi and T. Ito, *J. Appl. Polym. Sci.,* 1976, **20**, 975–994.

37 [37] S. Bera and Z. Jedlinski, *Polymer,* 1992, **33**, 4331–4336.

38 [38] S. Bera and Z. Jedlinski, *J. Polym. Sci. Part A Polym. Chem.,* 1993, **31**, 731–739.

39 [39] H. R. Stapert, P. J. Dijkstra and J. Feijen, *Macromol. Symp.,* 1998, **130**, 91–102.

40 [40] H. R. Stapert, A. M. Bouwens, P. J. Dijkstra and J. Feijen, *Macromol. Chem. Phys.,* 1999, **200**, 1921–1929.

41 [41] J. D. Sudha, *J. Polym. Sci., Part A: Polym. Chem.,* 2010, **38**, 2469–2486.

42 [42] T. Lebarbe, L. Maisonneuve and T. H. N. Nguyen, B. Gadenne, C. Alfos, H. Cramail, *Polym. Chem.,* 2012, **3**, 2842–2851.

43 [43] P. L. Dubin, S. Koontz and K. L. Wright III, *J. Polym. Sci., Polym. Chem. Ed.,* 1977, **15**, 2047–2057.

44 [44] N. D. Hann, *J. Poly. Sci.: Poly. Chem. Ed.,* 1977, **20**, 1331–1339.