Synthesis and Solution Processing of Nylon-5 Ferroelectric Thin Films: The Renaissance of Odd-Nylons?

Philipp vonTiedemann, Saleem Anwar, Ulrike Kemmer-Jonas, Kamal Asadi,* and Holger Frey*

Among odd-nylons, nylon-5 exhibits the highest remanent polarization and is thus a desirable material for many applications of ferroelectric polymers. However, nylon-5 has never been used as a ferroelectric material, because the synthesis of nylon-5 and its processing into thin films are challenging. This work revisits the synthesis of nylon-5 via anionic ring opening polymerization (AROP) and studies the effect of reaction time and scale-up on (i) molecular weight (M_n), (ii) melting point (T_m), (iii) yield, and (iv) ferroelectric properties. For the first time, the molecular weight of nylon-5 is characterized via size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, as well as matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI ToF-MS), showing M_n values of up to 12 500 g mol^{-1}. Extended reaction times and the synthesis on a larger scale increase the molecular weight and yield. Nylon-5 thin films are fabricated from a TFA:acetone (60:40 mol%) solvent mixture. Nylon-5 thin-film capacitors are ferroelectric and show a remanent polarization as high as 12.5 ± 0.5 µC cm^{-2}, which is stable in time. The high remanent polarization values, combined with the facile solution processing, render nylon-5 a promising candidate for future microelectronic and multi-ferroic applications.

P. von Tiedemann, U. Kemmer-Jonas, Prof. H. Frey
Institute of Organic Chemistry
Johannes Gutenberg University
Duesbergweg 10-14, 55128 Mainz, Germany
E-mail: hfrey@uni-mainz.de
P. von Tiedemann
Graduate School Materials Science in Mainz
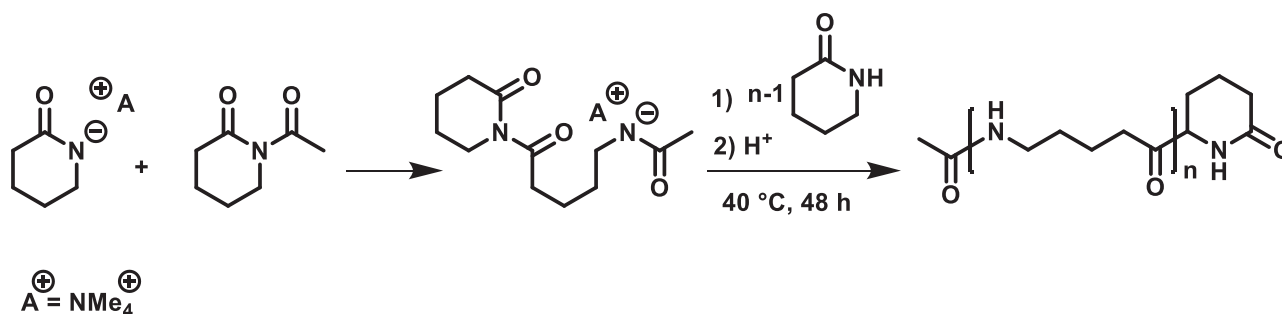Staudinger Weg 9, 55128 Mainz, Germany
S. Anwar, Dr. K. Asadi
Max-Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz, Germany
E-mail: asadi@mpip-mainz.mpg.de
S. Anwar
School of Chemical & Materials Engineering
National University of Sciences and Technology
Sector H-12, 44000 Islamabad, Pakistan

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/macp.201900468.

1. Introduction

Ferroelectric polymers are key materials for applications in sensors, actuators, memory devices and energy harvesting.[1] Polymers can be processed from solution to form thin films at low cost. This feature can be used to create functional devices, such as capacitors, transistors and diodes.[2] Despite the availability of a variety of known ferroelectric polymers such as odd-numbered nylons and fluoropolymers, the work on solution-processable ferroelectric polymers is almost exclusively centered around fluoropolymers like polyvinylidene difluoride (PVDF) and its random copolymer with trifluoroethylene, P(VDF-TrFE).[3] This is mainly due to the difficulties related to solution-processing of odd-numbered nylons in their ferroelectric crystalline phase. Recently, we have demonstrated that solution quenching allows to fabricate ferroelectric thin films of odd-numbered nylons.[4] Advances in the chemistry of nylons and the versatility in their design compared to fluoropolymers, combined with the recent realization of solution-processing motivates revisiting the synthesis and especially the molecular characterization of odd-numbered nylons.

The ferroelectric properties of the odd-numbered nylons, particularly with low number of carbon atoms in the repeating unit, called "low order nylons," are comparable to those of PVDF and P(VDF-TrFE).[5] The large dipole moment of the amide groups combined with a high dipole density results in high remanent polarization (P_r) values. Nylon-5 for instance, shows a ferroelectric P_r value that exceeds that of PVDF and approaches 12.5 µC cm^{-2}. Furthermore, nylon-5 has a melting point that is above 250 °C, far above that of PVDF and its copolymers.[6] The ease of synthesis at low cost due to polymerization in bulk and the possibility to tune the polymer structures renders low order nylons, such as nylon-5, an attractive class of materials. However, to date, there are only few and dated reports on the synthesis and especially the molecular structure characterization of the resulting polymers.

To date, nylon-5 is only accessible via the anionic ring opening polymerization (AROP) of 2-piperidone, which can in principle be polymerized using basic catalysts and the activated

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Scheme 1. Polymerization mechanism (AROP) of 2-piperidone.

monomer (AM) mechanism (**Scheme 1**). Several alkali metals and acyl compounds have been studied for their effectiveness in the AROP. The effect of catalyst loading and initiator (N-acetyl piperidone) concentration as well as the effect of polymerization temperature on the monomer conversion has been studied.[7] It was shown that polymerization temperatures below 50 °C are generally required to control the equilibrium of the AROP of lactams. The characterization of the resulting nylon-5 is strongly limited due to the poor solubility of the material. To the best of our knowledge, to date no thorough molecular weight characterization and end group analysis has been reported.

As suitable catalysts quaternary ammonium salts[8,9] are known to be more effective in the polymerization of 2-piperidone compared to the early use of alkali metals,[7] resulting in high monomer conversion as well as reasonable yields. The AROP of 2-piperidone is challenging due to the low ring strain of the monomer, the very low solubility of the resulting polymer (due to H-bonding and very high polarity) as well as the tremendous sensitivity of the polymerization procedure toward side reactions (especially condensation reactions)[10] and unintentional termination resulting from impurities. Long ago Yoda et al. showed that the presence of only 1% of water drastically reduces the monomer conversion to 3%.[7] Although various aspects concerning the polymerization of 2-piperidone have been studied,[11,7,8] further research is crucial in view of the promising ferroelectric properties of this polymer. Due to the prospect for application in solution-processable ferroelectric thin films, and to further improve the performance of nylon-5 in thin-film ferroelectric devices, there is a need to reassess the synthesis and to achieve comprehensive characterization of the resulting polyamides.

2. Experimental Section

Instrumentation and reagent details are given in Supporting Information.

2.1. General Synthesis Procedure for the Polymerization of Nylon-5

Nylon-5 was synthesized according to a considerably altered procedure compared to the one reported by Sekigushi and co-workers.[8] Four samples of nylon-5 were prepared via AROP of 2-piperidone in bulk at 40 °C, using N-acyl-2-piperidone as an initiator and tetramethyl-ammonium 2-oxopiperidin-1-ide as a catalyst. All polymerizations were carried out in all glass 100 or 250 mL Schlenk flasks, equipped with a magnetic stir bar and Teflon stopper at 40 °C under argon. 2-Piperidone (30 g, 0.3 mol) was dried by stirring over CaH$_2$ at 40 °C under vacuum overnight, degassed by four freeze-pump-thaw cycles prior to use and then distilled into the polymerization flask. The polymerization was initiated by adding N-acetyl-2-piperidone (0.42 mL, 3.0 mmol) via 1 mL syringe after the rapid addition of tetramethyl-ammonium 2-oxopiperidin-1-ide (4.17 g, 24.2 mmol) as a solid at once. The solution was stirred overnight to ensure a high monomer conversion. After 12 h, the polymer was dissolved in a small amount of formic acid and precipitated in 300 mL of water. The mixture was left to stir overnight. Then the white solid polymer was separated by centrifugation and dried at 40 °C under reduced pressure for three days. For yields, see **Table 1**.

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 4.46 (s, 30H, b), 2.79 (t, J = 6.8 Hz, 36H, c), 1.79 (t, J = 7.5 Hz, 34H, f), 1.53 (s, 3H, a), 1.27–0.95 (m, 74H, d+e).

^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = 176.24 (b), 174.44 (g), 38.56 (c), 34.77 (f), 27.05 (d), 21.82 (e), 20.32 (a).

2.2. N-acetyl-2-piperidone

A solution of 2-piperidone (4.9 g, 49.4 mmol) and acetic anhydride (5.1 g, 50 mmol) was heated under reflux for 2 h. Subsequently acetic acid was evaporated, and the residue distilled (70 °C at 5 mm Hg) to give N-Acetyl-2-piperidone as a colorless liquid. Yield: 79%

Table 1. Synthesis results of nylon-5 polymers.

Batch no.	M_n [kg mol^{-1}][a]	M_n [kg mol^{-1}][b]	Đ[b]	T_m [°C][c]	T [h]	Yield [%]
1	0.7	1.7	1.24	236	3	4
2	1.9	2.4	1.54	253	48	10
3	3.4	3.5	1.67	258	16	6
4	3.9	12.5	1.90	269	48	30

[a]Obtained from ^{1}H NMR spectroscopy; [b]Determined by SEC in HFIP (UV signal, PMMA standards); [c]Determined by differential scanning calorimetry (DSC).

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^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 3.77–3.58 (m, 2H, b), 2.62–2.41 (m, 2H, e), 2.49 (s, 3H, a), 1.99–1.68 (m, 4H, c+d).

2.3. Tetramethyl-Ammonium 2-Oxopiperidin-1-ide

Tetramethyl-ammonium 2-oxopiperidin-1-ide was synthesized according to a report of Sekigushi and co-workers.[8,12] In a 100 mL flask equipped with a drying tube (loaded with calcium chloride) and a stir bar sodium (2.3 g, 0.1 mol) was dissolved in dry ethanol (50 mL, 1.09 mol). The resulting solution of sodium ethoxide was poured into a solution of tetramethyl-ammonium chloride (11 g, 0.1 mol) in dry ethanol (75 mL, 1.63 mol). After 1 h dry diethyl ether (75 mL, 0.72 mol) was added. The white precipitate was filtered under argon and the solvent removed under reduced pressure. To the resulting viscous liquid 2-piperidone (12 g, 0.12 mol) was added in diethyl ether (100 mL, 0.96 mol) immediately. The mixture was transferred into a 2 L beaker and the volume adjusted to 1.5 L. The precipitate was filtered, washed with diethyl ether, and dried under vacuum overnight to give tetramethyl-ammonium 2-oxopiperidin-1-ide as a white solid. Yield: 25%; melting point, T_m: 130 °C

2.4. Thin-Film Preparation and Characterization

A nylon-5 solution was prepared in a TFA acetone mixture (60:40 mol%). Thin films were fabricated by spin-coating the solution onto a glass substrate followed by solvent quenching via applying high vacuum. The final thickness of the films was 350 nm. Atomic force microscopy (AFM) (Nanoscope Dimension 3100 Bruker) was used to analyze the surface morphology of the thin films.

2.5. Ferroelectric Characterization

The electrical characterization of the thin-film capacitors was carried out in a probe station in a vacuum of 10^{-5} mbar. Electrical displacement (D) versus electrical field (E) was measured using a Radiant precision multi-ferroic test system (Radiant Technologies, Inc.). Data retention was measured relying on the same setup, using a write pulse followed by two read pulses of the same amplitude but opposite direction. The delay time between two read pulses increased with a factor of 2. All pulse widths were fixed at 10 ms.

3. Results and Discussion

In this work, we characterize nylon-5 with respect to its molecular weight distribution (MWD) via size exclusion chromatography (SEC) in hexafluoro-2-propanol (HFIP). Molecular weight data have not been reported for nylon-5 to date. Further, we determine the exact polymeric structure employing end-group analysis by NMR spectroscopy and matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-ToF MS). Using the samples prepared, we employed a solution

quenching technique to obtain extremely smooth and transparent nylon-5 thin films that are crystallized in the ferroelectric crystalline phase.[4] The resulting films were studied with respect to their ferroelectric properties in detail.

The polymerization was investigated concerning the effect of reaction time and scale-up on i) molecular weight (M_n), ii) melting points (T_m), iii) yields, and iv) ferroelectric properties. The M_n of the synthesized polymers (Table 1, entries 1–4) ranged from 1.7 to 12.5 kg mol^{-1} by SEC (0.7 to 3.9 kg mol^{-1} by NMR), with dispersities ($Đ$) between 1.24 and 1.90.

The highest molecular weight polymer sample (sample 4) was also found to exhibit the broadest molecular weight distribution ($Đ$ = 1.90). This effect originates from the polymerization in bulk, which is limited by eventual vitrification. The beginning heterogeneity thus broadens the MWD of the resulting material. The molecular weights determined by SEC in HFIP (Table 1, column 2) are found to exceed those determined from ^{1}H NMR spectroscopy 1.3- to 3.2-fold (Table 1, column 1). This can be explained by the difference in hydrodynamic volume of nylon-5 compared with PMMA employed as calibration standard. We have observed that during the bulk polymerization the reaction mixture typically vitrified 10 min after initiator addition. However, for the small-scale syntheses (5 g of 2-piperidone as a starting material) of the polymer, longer reaction times (48 instead of 3 h) facilitate improved yields (up to 10%) compared to the short reaction times as well as higher molecular weights (up to 3.9 kg mol^{-1} by NMR spectroscopy, up to 12.5 kg mol^{-1} by SEC). Unexpectedly, the synthesis on a multi-gram scale (30 g of 2-piperidone as a starting material) (sample 4) gave rise to 3–5 times higher yields as well as 3.2 times higher M_n by SEC. The former effect probably originates from the presence of an increased monomer concentration throughout the polymerization which somewhat delays the polymer precipitation since the monomer acts as a solvent. Moreover, the filtration step is crucial for the effective collection of the precipitated material. This step causes a significant loss in yield, when only a very small amount of material is separated from the liquid compared to a 10 times larger amount. In contrast to other polymer syntheses employing AROP, the observed polymer yields are low. This is not only due to the fact that the polymerization has to be carried out in bulk, but also because the monomer (2-piperidone) exhibits a low thermodynamic driving force toward polymerization. However, at a certain degree of polymerization nylon-5 starts to precipitate and the mixture vitrifies, which also drastically limits further monomer incorporation, resulting in generally low polymer yields. The unreacted monomer was separated and could be reused after distillation. T_m of all synthesized nylon-5 polymers gradually increased from 236 to 269 °C as the molecular weights (by SEC) increased from 1.7 to 12.5 kg mol^{-1} (Figure S5, Supporting Information). **Figure 1** shows the ^{1}H NMR spectrum of nylon-5 (sample 2), measured in HFIP-d_2, as this is one of the few deuterated solvents capable of dissolving the highly polar and crystalline polymer. The ^{1}H NMR spectrum shows the expected four signals (b–f) for the methylene protons, the amide proton of the repeating unit and one signal (b) for the methyl group of the initiator that is used for the determination of molecular weights (M_n) (Table 1, column 2). The ^{1}H NMR spectrum reveals that the amide group is protonated

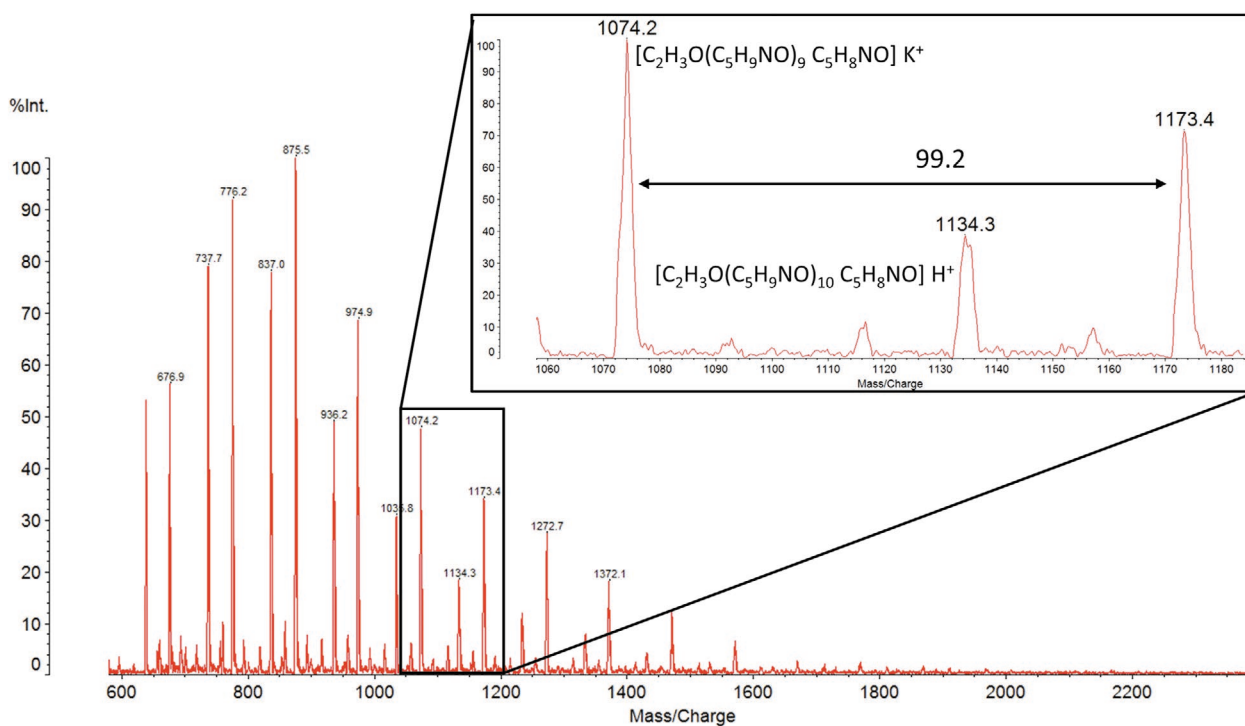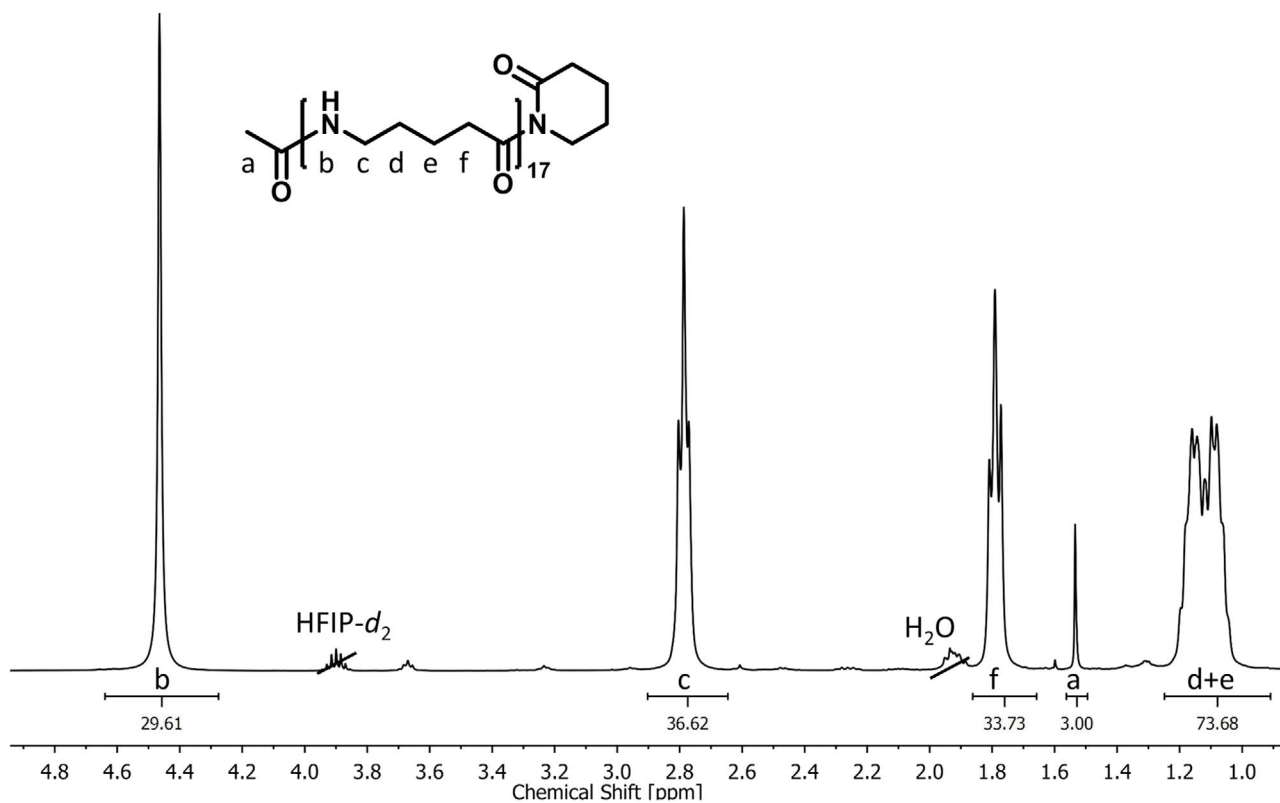**Figure 1.** ^{1}H NMR spectrum of nylon-5 (Table 1, entry 2) (400 MHz, HFIP-d2). (top). MALDI-ToF MS of nylon-5. (bottom).

by the acidic solvent HFIP-d_2. Figure 1 evidences the high purity of the synthesized polymer, revealing that little to no side reactions occurred during polymerization. The ^{13}C NMR spectrum can be found in Figure S3, Supporting Information.

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However, it cannot be excluded that branching still might have happened in very small amounts, but this is below the detectable limit of the employed analytics.

The NMR characterization reveals that besides the initiator N-acyl-2-piperidone the end group of the polymer chain is a non-ring-opened monomer 2-piperidone, confirming the mechanism (Scheme 1). The M_n obtained by MALDI-ToF MS was used to estimate the degree of polymerization ($X_n = M_n/M_0$), as described in Equation (1). It should be noted that the molecular weights obtained from MALDI-ToF are underestimated, due to the common mass discrimination effect.[13]

$$M_n = M(\text{Acetyl}) + n \cdot M_0(2-\text{piperidone}) + M(\text{End group}) \quad (1)$$

To study the ferroelectric performance of nylon-5, we prepared solutions of the different nylon-5 polymers in a mixture of trifluoroacetic acid (TFA) and acetone with 60:40 mol% with 5 wt% solution concentration. Thin films were prepared by spin-coating and subsequent solution quenching of the wet films in vacuum. Details of this process are given elsewhere.[4] The process yields optically transparent thin films with a thickness

in the range of 350 ± 10 nm. The resulting morphology of the nylon-5 thin films was investigated by atomic force microscopy (AFM) performed for all nylon-5 samples. The AFM height (**Figure 2**a) and phase images (Figure 2b) show extremely smooth films with an rms roughness of 4 nm. The phase image indicates that the morphology consists of small crystallites. Similar morphologies as the one shown in Figure 2a,b were observed for the other samples of nylon-5, irrespective of the molecular weight of the polymer (Table 1, entries 1–4). The optical transparency and smoothness of nylon-5 thin film is attributed to efficient hindrance of vapor-induced phase separation by the vacuum quenching.[14]

Figure 2c shows a typical $D–E$ ferroelectric hysteresis loop together with the switching current of nylon-5 thin films for sample 2. A linear dielectric displacement response is observed for the field below 300 MV m^{-1}. Increasing the electric field beyond 300 MV m^{-1} opens the hysteresis loop. The polarization saturates at a field of 500 MV m^{-1} with a maximum P_r value of 12.6 μC cm^{-2}, in perfect agreement with the reported value in the literature for thick films.[6] We note full polarization switch has also been obtained at 100 Hz, indicating that the switching
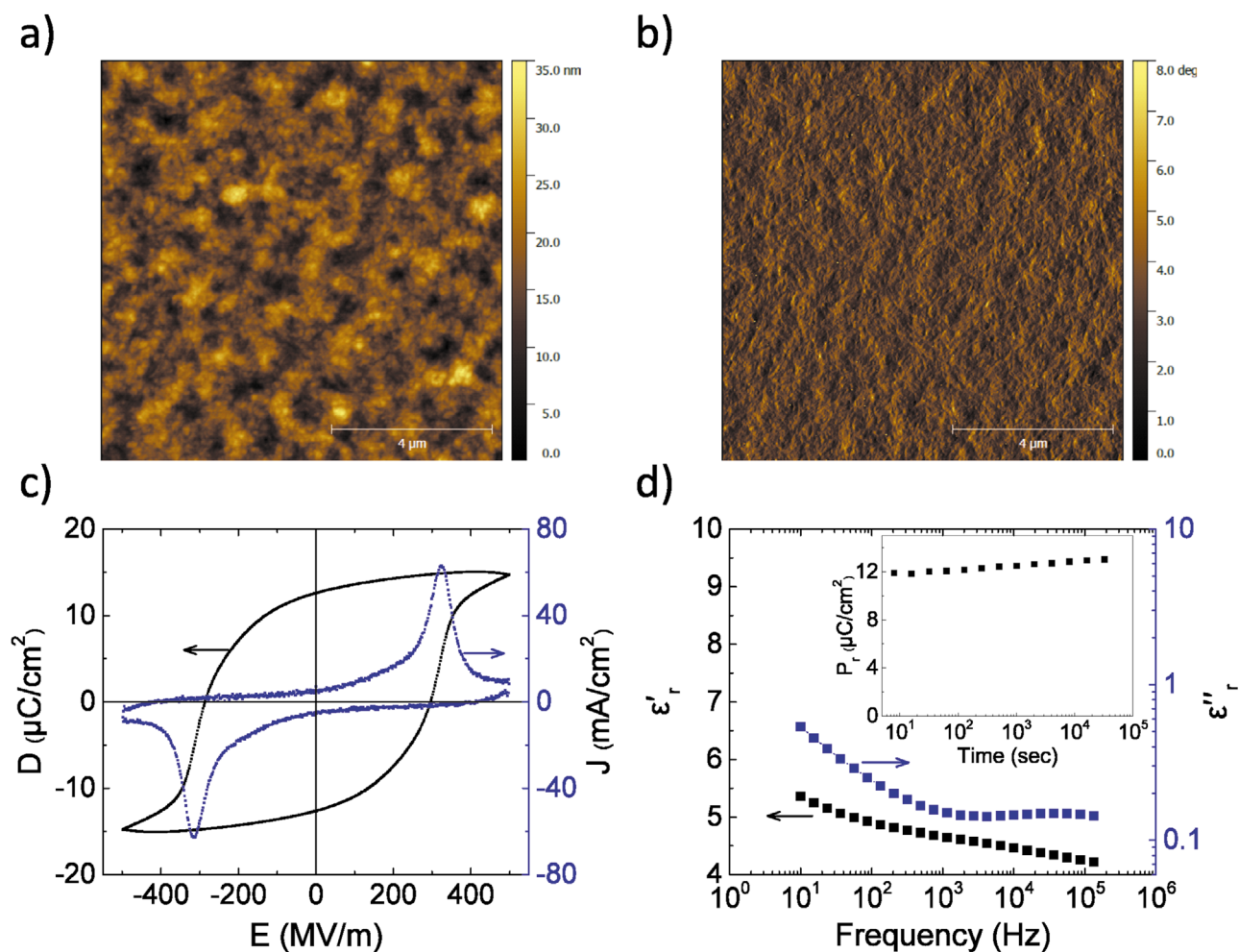
Figure 2. Tapping AFM a) height and b) phase images of nylon-5 thin film. c) $D–E$ hysteresis loop and switching current. d) Frequency dependence of dielectric permittivity (ε') and loss (ε''). The inset shows the data retention as a function of time measured for 11 h.

Table 2. Ferroelectric and dielectric properties of nylon-5 with different molecular weights.

Batch no.	P_r [μC cm^{-2}]	E_c [MV m^{-1}]	ε' [at 100 Hz]	ε'' [at 100 Hz]
1	9.45 ± 0.3	338 ± 18	6.7 ± 0.5	0.75 ± 0.1
2	12.9 ± 0.9	300 ± 14	4.5 ± 0.1	0.38 ± 0.04
3	11.9 ± 0.7	295 ± 10	4.7 ± 0.2	0.22 ± 0.02
4	12.3	263	4.8 ± 0.05	0.16 ± 0.02

time is shorter than 10 ms. The higher P_r value of nylon-5, as compared to other nylons, is related to its high dipole density, that is, 2.94×10^{-2} D Å^{-3} (calculated by dividing the net dipole moment in the unit cell by the unit volume).[15] We note that sample 1 with low molecular weight shows rather low P_r compared to the other samples. Otherwise, there is no significant difference in P_r for different molecular weights and molecular weight distributions, as shown in **Table 2**. One can speculate regarding the origin of lower P_r for sample 1, because the capacitors typically suffer from electrical breakdown as the field is increased beyond 400 MV m^{-1}, which impedes achieving a fully saturated polarization loop. The E_c of the different molecular weights shows a decreasing trend with increasing molecular weight, starting from 338 ± 18 MV m^{-1} for lowest (0.7 kg mol^{-1}) to 263 MV m^{-1} for the highest (3.9 kg mol^{-1}) molecular weight. The reason for the high E_c for solution-processed odd-nylons is a higher degree of hydrogen bonding order, as explained in our previous work.[4] We have also measured the dielectric constant for all nylon-5 samples. Considering the measurement error bars, the dielectric constant can be considered constant and independent of the molecular weight and amounts to 4.7 ± 0.2, except for sample 1. We attribute the higher dielectric constant for sample 1 to higher dielectric loss (conductivity). It is interesting to note that the dielectric loss decreases from 0.75 to 0.16 when increasing the molecular weight of the polymer from 0.7 to 3.9 kg mol^{-1}, respectively. The nylon-5 ferroelectric capacitors show stable polarization in time (up to 11 h, as shown in the inset of Figure 2d), hence exhibiting good polarization retention, which is crucial for data storage applications. A slight increase of the polarization upon successive electrical measurements is attributed to electric field induced polarization or electroforming.[16]

4. Conclusions

In summary, we have both revisited and further developed the synthesis of nylon-5 via AROP. For the first time, detailed characterization of nylon-5 with modern analytical techniques such as NMR spectroscopy, SEC, and MALDI-ToF MS was achieved, permitting to improve and better understand the synthesis of odd-numbered nylons. The exact polymer structure and the molecular weight distributions have been characterized. The molecular weights (M_n) range from 1.7 to 12.5 kg mol^{-1} (SEC) with dispersities between $Đ = 1.24$ and 1.90. We studied the effect of reaction time and scale-up on M_n, T_m, and yield, and have found that extending reaction times (up to 48 h) as well as the synthesis on a larger scale afford higher yields (up to 30%), higher molecular weights (up to 3.9 kg mol^{-1} by NMR and up to

12.5 kg mol^{-1} by SEC and higher melting points (up to 269 °C). We have solution-processed extremely smooth (4 nm rms roughness) ferroelectric thin films from a nylon-5 solution in TFA:acetone (60:40 vol%) mixture by solution quenching. The measured P_r values of nylon-5 amount to 12.5 ± 0.5 μC cm^{-2} and remain stable in time. The dielectric parameters of nylon-5 namely ε' and P_r do not depend on the molecular weight. However, the polymer shows a strong inverse dependence of E_c and ε'' on molecular weight. The observation of high P_r, E_c values in combination with the high melting temperatures evidence that nylon-5 is an ideal electroactive material for piezoelectric applications. Moreover, the ability to solution-process thin films renders nylon-5 a potential candidate for applications in solution-processable devices, such as non-volatile ferroelectric memories. The present work is therefore a stepping stone toward the renaissance of improved synthesis methods for lower-order nylons with more versatile structures and tailored dielectric as well as ferroelectric properties.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

[1] a) S. Bauer, *Ferroelectrics* **1996**, *80*, 5531; b) E. Fukada, *IEEE Trans. Sonics Ultrason.* **2000**, *47*, 1277; c) T. Sekitani, K. Zaitsu, Y. Noguchi, K. Ishibe, M. Takamiya, T. Sakurai, T. Someya, *IEEE Trans. Electron Devices* **2009**, *56*, 1027.

[2] a) R. C. G. Naber, K. Asadi, P. W. M. Blom, D. M. de Leeuw, B. de Boer, *Adv. Mater.* **2010**, *22*, 933; b) H. Sharifi Dehsari, M. Kumar, A. Saad, M. Hassanpour Amiri, C. Yan, S. Anwar,

G. Glasser, K. Asadi, *ACS Appl. Nano Mater.* **2018**, *1*, 6247; c) M. Kumar, H. Sharifi Dehsari, S. Anwar, K. Asadi, *Appl. Phys. Lett.* **2018**, *112*, 123302; d) J. J. Brondijk, K. Asadi, P. W. M. Blom, D. M. de Leeuw, *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 47.

[3] L. Ruan, X. Yao, Y. Chang, L. Zhou, G. Qin, X. Zhang, *Polymers* **2018**, *10*, 228.

[4] S. Anwar, D. Pinkal, W. Zajaczkowski, P. von Tiedemann, H. Sharifi Dehsari, M. Kumar, T. Lenz, U. Kemmer-Jonas, W. Pisula, M. Wagner, R. Graf, H. Frey, K. Asadi, *Sci. Adv.* **2019**, *5*, eaav3489.

[5] Q. Jing, S. Kar-Narayan, *J. Phys. D: Appl. Phys.* **2018**, *51*, 303001.

[6] B. Z. Mei, J. I. Scheinbeim, B. A. Newman, *Ferroelectrics* **1993**, *144*, 51.

[7] N. Yoda, A. Miyake, *J. Polym. Sci.* **1960**, *43*, 117.

[8] B. Coutin, H. Sekiguchi, *J. Poly. Sci.: Polym. Chem. Ed.* **1977**, *15*, 2539.

[9] H. Sekiguchi, B. Coutin, *J. Polym. Sci.: Polym. Chem. Ed.* **1973**, *11*, 1601.

[10] J. Roda, Z. Votrubcová, J. Králíček, J. Stehlíček, S. Pokorný, *Makromol. Chem.* **1981**, *182*, 2117.

[11] a) H. Tani, T. Konomi, *J. Polym. Sci. Part A-1: Poly. Chem.* **1966**, *4*, 301; b) H. Tani, T. Konomi, *J. Polym. Sci. Part A-1: Poly. Chem.* **1968**, *6*, 2295.

[12] H. Sekigushi, B. Coutin, *Macromol. Synth.* **1977**, *6*, 57.

[13] D. C. Schriemer, L. Li, *Anal. Chem.* **1997**, *69*, 4176.

[14] H. S. Dehsari, J. J. Michels, K. Asadi, *J. Mater. Chem. C* **2017**, *5*, 10490.

[15] S. M. Aharoni, *n-Nylons: Their Synthesis, Structure, and Properties*, Wiley, Chichester, UK **1997**.

[16] D. Zhao, I. Katsouras, M. Li, K. Asadi, J. Tsurumi, G. Glasser, J. Takeya, P. W. M. Blom, D. M. de Leeuw, *Sci. Rep.* **2015**, *4*, 5075.

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