

Effect of Stoichiometric Imbalances on the Melt Condensation Polymerization of Poly(dodecamethylene terephthalamide) Studied by Intrinsic Viscosity and ^{13}C -NMR

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ABSTRACT: Poly(dodecamethylene terephthalamide) (PA-12,T) was synthesized by melt condensation polymerization of 12,T salt with 0, 1, 3, 5, or 10% molar excess of 1,12-diaminododecane (DA), terephthalic acid (TA), or benzoic acid (BA). Intrinsic viscosities (IV) (0.5 g/dL in 96% H_2SO_4 at 25°C) were measured to determine relative molecular weight differences. IV was highest for reactions containing 1 and 3 mol % excess DA (1.36 and 1.31 dL/g, respectively), followed by the product of pure 1 : 1 salt (1.25 dL/g). For all concentrations of excess TA and BA, IV was decreased. ^{13}C -

NMR chemical shifts for DA, TA, and BA end groups were identified and their concentrations determined by comparison with the intensity of main chain polymer peaks. A log-log plot of IV versus number average molecular weight calculated from ^{13}C -NMR data shows a linear trend with Mark-Houwink constants of $K = 55.8 \times 10^{-5}$ dL/g and $\alpha = 0.81$. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3388–3395, 2010

Key words: polyamides; step-growth polymerization; NMR; solution properties

INTRODUCTION

Semi-aromatic polyterephthalamides (SAPT) are reaction products of aliphatic diamines and terephthalic diacids. SAPT's have been demonstrated to possess improved thermal and mechanical properties relative to purely aliphatic polyamides, while being easier to process than wholly aromatic polyamides.¹ Symmetrical aromaticity in the polymer backbone results in higher melting and glass transition temperatures, rendering them useful for high temperature automotive applications. For example, poly(-hexamethylene terephthalamide) (PA-6T) has a melting temperature of 370°C and a glass transition temperature of 125°C compared to 265°C and 60°C for PA-6,6. However, high melt viscosities and melting temperatures that approach the degradation temperature cause difficulty in conventional melt processing of SAPT's. Overcoming these obstacles has been the focus of much patent literature.^{2–13} Melting temperatures of SAPT's can be tuned to suitable ranges by changing the chemical composition of monomers. For example, increasing the length of diamine from 6

to 12 carbon atoms decreases the polymer melting temperature from 370°C to 295°C.

Controlling molecular weight during melt condensation polymerizations of SAPT's is crucial for obtaining desired mechanical properties and processability. For instance, below a critical molecular weight, mechanical properties are poor, resulting in brittle materials. Increasing molecular weight above the critical value results in high melt viscosities and complicates processing. Control of molecular weight is attained by adjusting the stoichiometry of reactants for the A-A B-B system. Although perfect stoichiometric balance is theoretically most favorable for obtaining high molecular weight condensation polymers, there exists a practical discrepancy between relative concentrations of starting materials and finished products. Industrial practices and patents indicate that excess diamine⁴ or terephthalic acid⁶ are required to be added to the diacid/diamine salt to generate suitable products. In doing this, the stoichiometry is purposefully imbalanced to achieve a product of desired molecular weight. Additionally, end capping is also a technique used to limit the molecular weight during melt condensation polymerizations.¹⁴ In SAPT literature, end cappers are referred to as terminal blocking agents,⁹ viscosity stabilizers,² and molecular weight stabilizers.⁶ Commonly used end capping agents for SAPT's are benzoic acid (BA) and acetic acid.

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Although adjusting stoichiometry is common practice in SAPT patent literature, there is a need for a fundamental study that uses a systematic approach to quantify effects on molecular weight and end group functionality. Typically, single-point intrinsic viscosity (IV) measurements are used to determine relative molecular weight changes, but no Mark-Houwink constants are available for SAPT's. Therefore, the magnitude of the impact on molecular weight of the products is unknown.

Our group has developed ^{13}C -NMR spectroscopy as a tool for examining end groups, *cis* amide content, and number average molecular weights of various aliphatic polyamides.^{15,16} The present study uses ^{13}C -NMR spectroscopy to determine end group concentrations and number average molecular weights of poly(dodecamethylene terephthalamide) (PA-12,T). Molecular weights were varied by adjusting the reaction stoichiometry of the melt condensation polymerization.

EXPERIMENTAL

Materials

Terephthalic acid, 1,12-diaminododecane, BA, hexafluoroisopropanol (HFIP), concentrated sulfuric acid (96%) and chloroform-d (CDCl_3) were purchased from Aldrich Chemical Company. BA and 1,12-diaminododecane were sublimed at 70°C and dried at room temperature under vacuum before use. HFIP and CDCl_3 were dried with molecular sieves before use.

Synthesis

PA-12,T salt—Into a 2 L beaker, 1200 mL of deionized water, 40.1 grams (0.20 mol) of 1,12-diaminododecane and 32.9 grams (0.198 mol) of terephthalic acid were added and the slurry was heated to a boil. Additional water was added and brought to boil to give a supersaturated clear salt solution (6.3 wt %). The hot salt solution was then added to a 2 L beaker containing 800 mL of reagent alcohol and cooled to room temperature, followed by overnight cooling in a freezer at 0.5°C . The precipitate was then filtered and washed with reagent alcohol, producing 68 g of PA-12,T salt with a 95% yield. The salt was recrystallized using a water/ethanol mixture and dried overnight at 80°C under vacuum (mp: 271.9°C , $\Delta H_{\text{melting}}$ 428 J/g).

Melt condensation polymerization of polyamide (12,T)

PA-12,T was synthesized using 0, 1, 3, 5, and 10 mol % excess 1,12-diaminododecane (DA), terephthalic

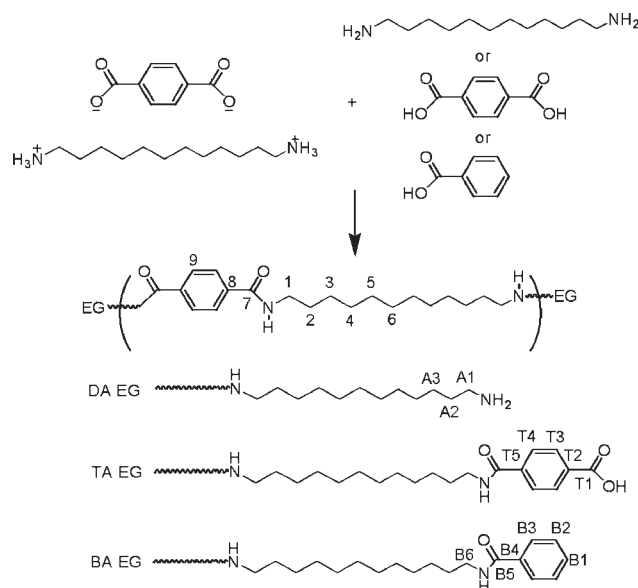


Figure 1 Synthesis of PA-12,T showing end group (EG) assignments for ^{13}C -NMR spectra.

acid (TA), or BA. The synthesis scheme of PA-12,T is depicted in Figure 1. PA-12,T salt, excess reactant (DA, TA, or BA), and antioxidant (0.5 wt %) were weighed and mixed with a mortar and pestle. The solid mixture was added to a test tube with ~ 50 wt % water and mixed to create a slurry. Thirteen test tubes (with different stoichiometric imbalances) were loaded into a Parr reactor, which was then sealed and purged with nitrogen.

Temperature in the Parr reactor was monitored with a thermocouple located in one of the test tubes. Heater set points were programmed into the reactor controller. The reactor was surrounded by insulation for more precise heating control. Pressure was controlled manually with nitrogen and measured by a gauge on the reactor head. Temperature and pressure profiles of the melt condensation polymerization are plotted versus time in Figure 2. The reaction can be divided into three stages according to the pressure profile. In the first stage, pressure was maintained at 125 kPa and the heater was set to 180°C . The temperature ramped up to a plateau at 126°C as the water boiled. At ~ 110 min, the temperature increased indicating that all the water had evaporated. In the second stage of the reaction, the pressure was increased to 1724 kPa and the heater was set at 290°C . The high pressure was intended to minimize volatilization of monomer. At 145 min, the temperature had increased to 275°C , at which point the pressure valve was opened. At 180 min the reactor had reached atmospheric pressure and the temperature was 315°C . This marks the beginning of the third stage of the reaction where nitrogen gas purged through the reactor at zero gauge pressure and the maximum reaction temperature of 315°C

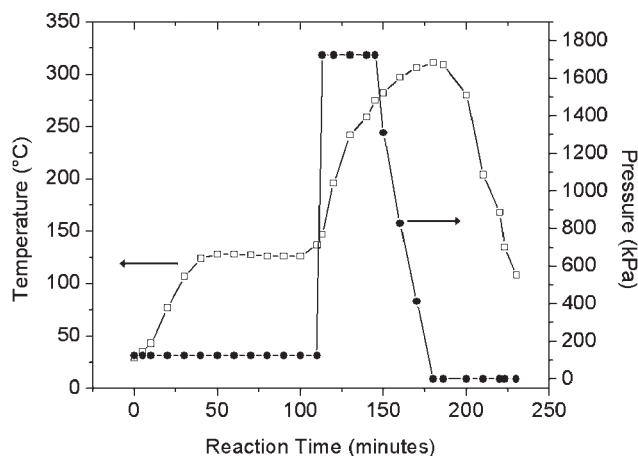


Figure 2 Temperature (\square) and pressure (\bullet) profiles of PA-12,T melt condensation polymerization.

was held for 15 min. Following this hold time, the heaters were turned off, insulation was removed, and the reactor was allowed to cool to 80°C before opening. Differential scanning calorimetry thermographs of the resulting product showed a melting temperature of 295°C, confirming that the polymer was molten during polymerization.

Sample preparation

Material plugs were immersed in liquid nitrogen for ~ 10 min, then ground using a Waring blender with stainless steel mixing jar. Resulting pellets were dried at 80°C under vacuum for 24 h, and placed in a desiccator before characterization.

Characterization

Nuclear magnetic resonance (NMR)

NMR samples containing 10 wt % polymer in a 3 : 1 volume ratio of HFIP to CDCl_3 were prepared by dissolving pellets in HFIP, followed by addition of CDCl_3 . Solution ^{13}C spectra were collected on a Varian $^{\text{UNITY}}$ INOVA NMR spectrometer operating at a frequency of 125.7 MHz. Routine acquisitions were obtained using a 1.3 second acquisition time, a 45° pulse width of 2.9 μs , and a 1 second recycle delay. The number of accumulate transients ranged from 15,000 to 30,000, involving 12–24 hour collection times. Spectra were recorded at 25°C. Data was zero-filled up to 256 k points and filtered with 1 Hz of line broadening before application of Fourier transformation. Baselines were corrected using a 10th order polynomial.

Viscometry

Solutions containing 0.5 g/dL of polymer in concentrated sulfuric acid were made to obtain a single

point IV. The solutions were prepared by adding 0.25 grams of polymer and 25 mL of concentrated sulfuric acid into a 50 mL flask. After 12 h of mixing using magnetic stirring, the solutions were diluted with an additional 25 mL of sulfuric acid, and stirring continued for another 12 h. If visible gelled material was present, it was removed by passing the samples through a funnel packed with glass wool. Measurements were obtained using a Cannon viscometer in a 25°C controlled water bath. The viscometer was washed with sulfuric acid and a portion of the next sample to be tested before measurements were recorded. Flow times were an average of three measurements that agree within ± 0.2 seconds. Flow times of concentrated sulfuric acid and polymer solution were used to calculate the specific and relative viscosities. Single point IV's were then calculated using the Solomon and Ciuta relationship; $[\eta] = [(2 \times (\eta_{\text{sp}} - \ln(\eta_{\text{rel}}))^{1/2})]/C$ where, η_{sp} is specific viscosity, η_{rel} is relative viscosity, and C is sample concentration.¹⁷

RESULTS AND DISCUSSION

Intrinsic viscosity

Single-point IV measurements are shown in Figure 3. The melt condensation polymerization of pure salt yields PA-12,T polymer with an IV of 1.25 dL/g. Adding 1 and 3 mol % excess DA to the reaction increases IV to 1.36 and 1.31 dL/g, respectively. However, adding excess DA beyond 3 mol % results in products with lower IVs of 1.08 and 0.70 dL/g for 5 and 10 mol % excess DA, respectively. The PA-12,T salt is stoichiometrically balanced before the polymerization and should yield the highest IV. However, PA-12,T synthesized using 1 and 3% excess DA have higher IV's. Since, 1,12-diaminododecane

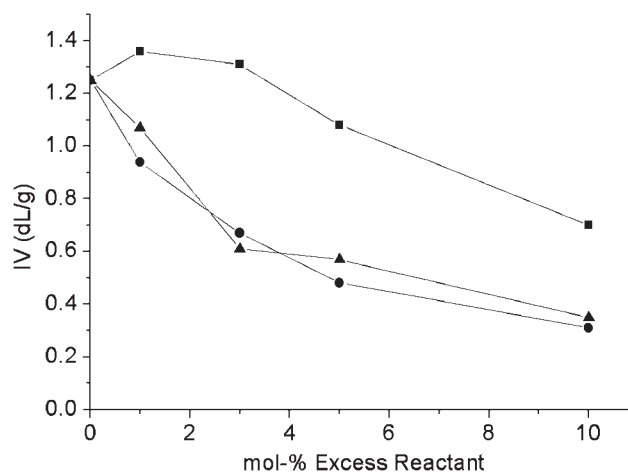


Figure 3 Single point intrinsic viscosities of PA-12,T salt polymerized with 1,12-diaminododecane (\blacksquare), terephthalic acid (\bullet), and benzoic acid (\blacktriangle).

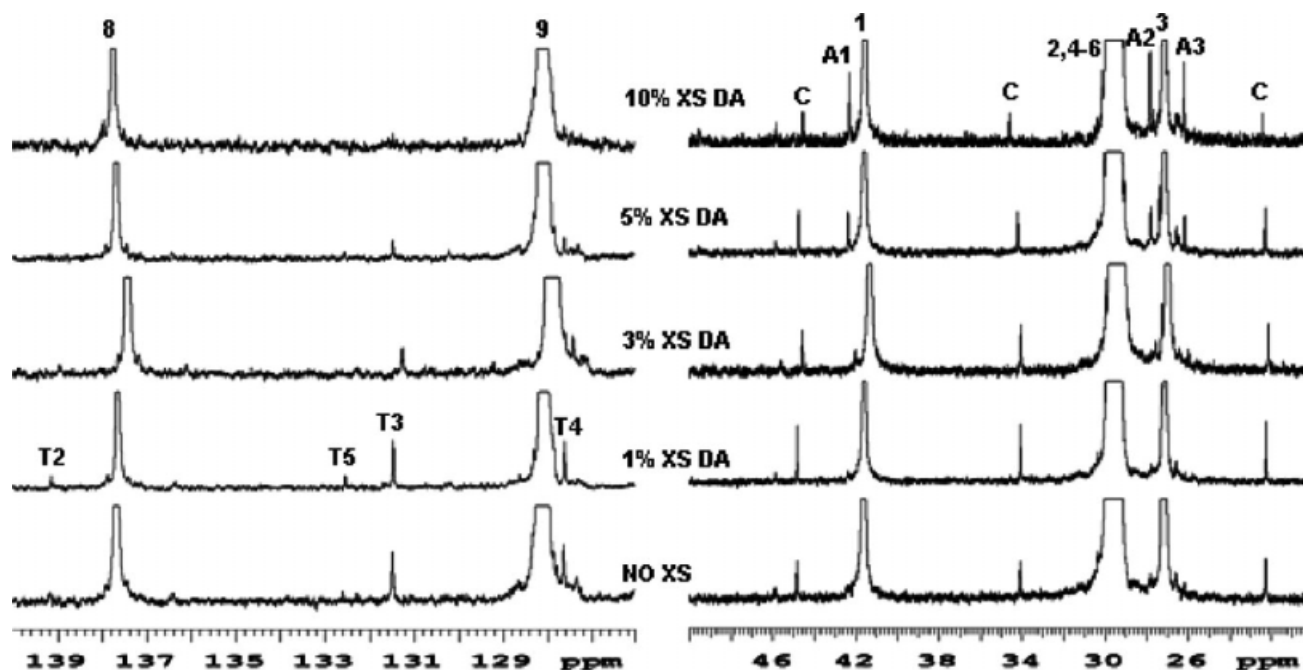


Figure 4 Solution ^{13}C -NMR spectra of polymers synthesized from starting materials containing 0, 1, 3, 5, and 10 mol % excess diaminododecane (XS DA). Left spectra are of aromatic region with peak intensities normalized with respect to backbone carbon 9. Right spectra are of aliphatic region with peak intensities normalized with respect to backbone carbon 1.

boils at a lower temperature than terephthalic acid, an imbalance is imposed by nature of the polymerization. Adding between 1 and 3 mol % DA compensates for this imbalance. Addition of 1 and 3 mol % TA, however, decreases IV to 0.94 and 0.67 dL/g, respectively. Excess TA at any concentration contributes to the imbalance imposed by volatilization of DA resulting in further decreases in IV. Despite their differences in functionality, BA and TA appear to reduce IV to a similar extent at all concentrations.

High resolution ^{13}C -NMR spectroscopy

Peak assignments for polymer repeat units and anticipated end groups are shown in Figure 1. Figures 4, 5, and 6 show the aliphatic and aromatic regions of NMR spectra for polymers synthesized with excess DA, TA, and BA respectively. Vertical scales have been increased to emphasize end groups and other less populous peaks. Peak intensities within each figure have been normalized with respect to a backbone carbon atom to expose trends in the lesser peaks. Aliphatic regions for each figure are normalized with respect to main chain carbon 1, while aromatic regions are normalized with respect to main chain carbon 9. Main chain peaks appear at expected chemical shifts as relatively broad, truncated peaks in each spectrum.

The aliphatic region of Figure 4 contains three peaks at 42.3 (A1), 27.8 (A2), and 26.2 (A3) ppm

with intensities directly proportional to the concentration of excess DA present in starting materials. As excess DA increases from 0 to 10 mol %, the relative intensity of these peaks (measured as peak heights) compared to main chain peak 1 increases from 0 to 5.3%. For all concentrations of excess TA, these peaks are not observed (Fig. 5). This behavior confirms their identities as amine end groups A1, A2, and A3. Specific assignments are based on previous work for PA-6,6 and PA-12.¹⁷

The aromatic region of Figure 5 contains four peaks at 127.6 (T4), 131.5 (T3), 132.6 (T5), and 139.3 (T2) ppm with intensities directly proportional to the concentration of excess TA present in starting materials. As excess TA increases from 0 to 10 mol %, the intensity of these peaks relative to main chain peak 9 increases from 1.5 to 10.7%. The same peaks in Figure 4 are shown to be inversely proportional to molar excess DA. This behavior confirms their assignments as acid end groups. Chemical shifts for peaks T2 and T4 are within 1 ppm of those reported by Hall and coworkers¹⁸ using HFIP as an NMR solvent to observe end groups of other terephthalic acid containing polyamides. However, T3 and T5 are different from those reported by Hall and coworkers by 1–3 ppm for two possible reasons: (1) spectra for the present study were acquired in a mixed solvent system, and (2) end group chemical shifts have been demonstrated to be sensitive to pH

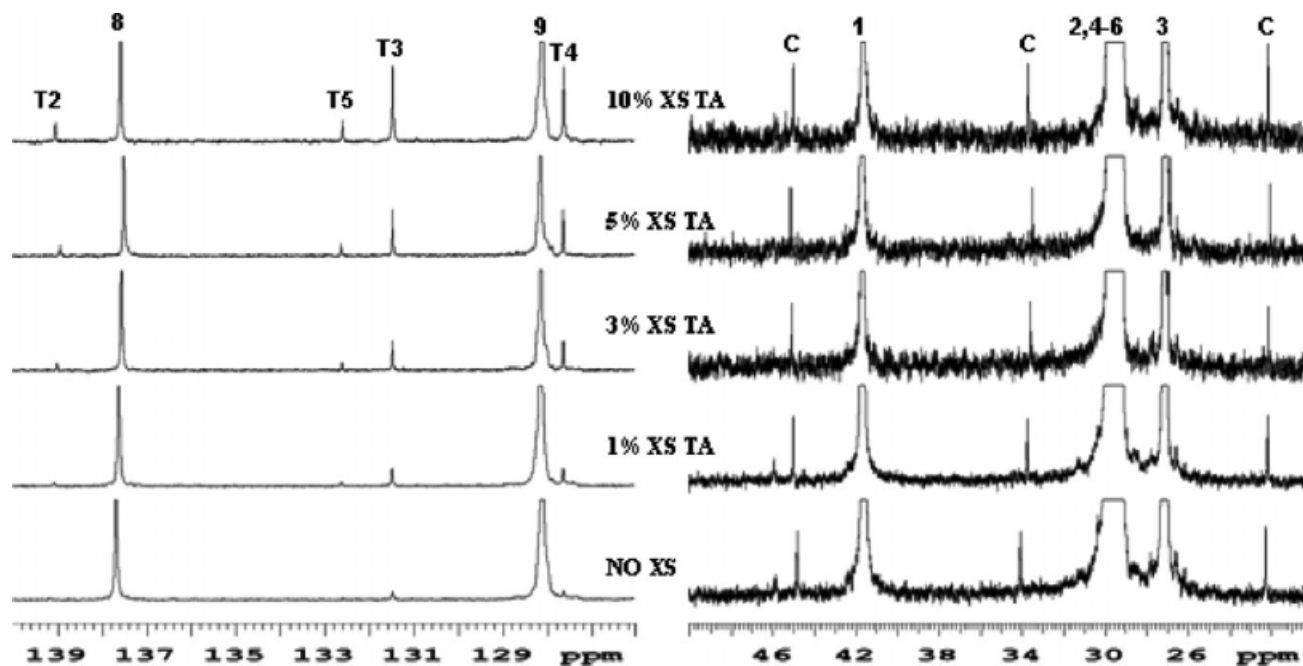


Figure 5 Solution ^{13}C -NMR spectra of polymers synthesized from starting materials containing 0, 1, 3, 5, and 10 mol % excess terephthalic acid (XS TA). Left spectra are of aromatic region with peak intensities normalized with respect to backbone carbon 9. Right spectra are of aliphatic region with peak intensities normalized with respect to backbone carbon 1.

as affected by changes in concentration of acid and amine end groups themselves.^{18,19}

The aromatic region of Figure 6 shows that the intensity of terephthalic acid end group resonance **T3** increases from 1.47 to 5.16% relative to terephthalic main chain peak **9** as excess BA is increased from 0 to 10 mol %. In addition to terephthalic end group peaks, four new peaks appear at 133.6 (**B1**), 132.8 (**B4**), 129.9 (**B3**), and 127.4 (**B2**) ppm in the aromatic region and a single new peak at 42.0 (**B6**) ppm appears in the aliphatic region. The peak at 129.9 ppm increases from 0 to 5.61% as the concentration of BA increases from 0 to 10 mol %. These peaks are assigned to benzamide end groups. Chemical shifts of BA peaks in these systems are within 1 ppm of assignments reported by Hall and coworkers.¹⁹

All NMR spectra shown contain three peaks at 44.9 (C), 33.9 (C), and 22.2 (C) ppm with equal intensities relative to each other. Relative to main chain carbon **1**, their intensities fluctuate between 2.3 and 6.3% with an average of 3.9% for all samples analyzed. Their only apparent trend is that they are more abundant on average for polymers containing excess BA (5.5% average intensity) compared to polymers containing no excess BA (3.2% average intensity). However, the significance of this trend is uncertain. These peaks are not consistent with NMR spectra of monomer, and do not behave like end groups. Remaining possibilities are

that these peaks are cyclic structures or *cis* amide repeat units.

End group concentrations relative to the polymer main chain peaks were calculated using NMR analysis and the equation;

$$[\text{EG}] = I_{\text{EG}} / [(I_1/2 + I_9/4)/2]$$

where $I_{\text{EG}} = I_{\text{A1}}$ or $I_{\text{T3}}/2$ or $I_{\text{B3}}/2$. Figure 7 plots total end group concentration [EG] and IV as a function of excess DA and TA. Note that the positive and negative x-axis values refer to the mol % excess or deficiency of DA. For all samples, end group concentration is inversely proportional to IV. For example, the product synthesized with 10 mol % excess TA has the lowest IV and the highest [EG]. As excess TA decreases from 10 to 0 mol %, [EG] decreases and IV increases progressively. A similar trend is apparent as excess DA decreases from 10 to 3 mol %. However, there is a large difference in IV and [EG] between samples containing 10 mol % excess DA and TA. This deviates from traditional step-growth theory which assumes equivalent imbalances in either A-A or B-B monomer affects molecular weight equally. Further deviation from theory is apparent in the fact that products synthesized with 1 and 3 mol % excess DA had higher IVs than products of pure salt.

Figure 8 shows the concentration of amine and acid end groups as a function of excess DA and TA.

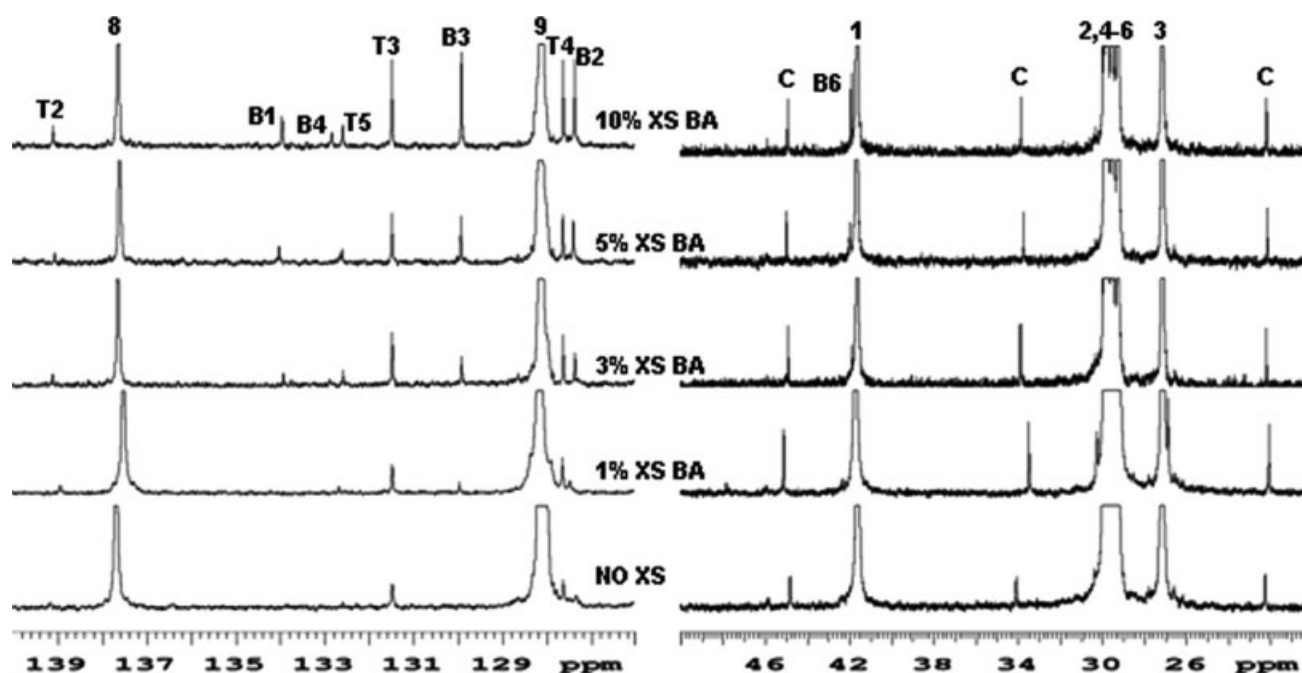


Figure 6 Solution ^{13}C -NMR spectra of polymers synthesized from starting materials containing 0, 1, 3, 5, and 10 mol % excess benzoic acid (XS BA). Left spectra are of aromatic region with peak intensities normalized with respect to backbone carbon 9. Right spectra are of aliphatic region with peak intensities normalized with respect to backbone carbon 1.

No amine end groups were observed at all concentrations of excess TA, therefore, these reactions have reached maximum conversion. With excess TA, molecular weight advances to a point where DA is completely reacted or volatilized resulting polymer with total acid end groups, rendering them nonreactive. Higher molecular weight is obtained by decreasing amount of excess terephthalic acid, thus lowering acid (total) [EG].

Pure PA-12,T salt and excess DA products have both acid and amine end groups. These reactions have not reached full conversion and are still in an

equilibrium state with the given polymerization conditions. The majority of end groups are acid at 1 mol % excess DA, while amine end groups are the majority at 3 mol % DA. Recall that these compositions have the highest IV and the lowest total end group concentration. Interpolation of Figure 8 reveals that end group functionality would be balanced and highest molecular weight would be achieved between these two points at ~ 2.4 mol % excess DA. Without determining the equilibrium constant specifically, qualitative observations show that the highest equilibrium molecular weight would be obtained

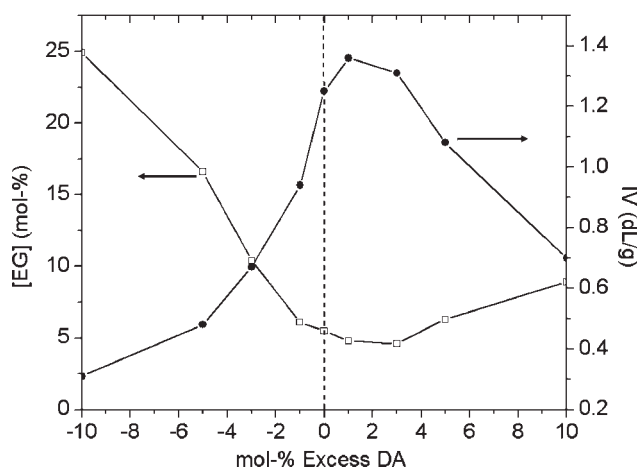


Figure 7 Total end group concentration (□) and IV (●) of PA-12,T synthesized with excess DA (positive values) and excess TA (negative values of DA).

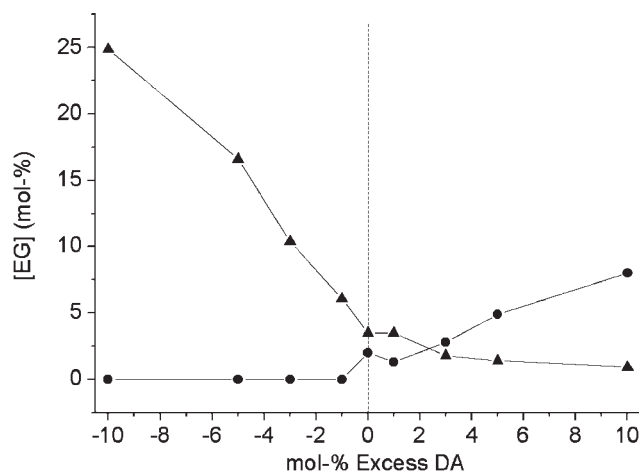


Figure 8 Acid (▲) and amine (●) end group concentrations of PA-12,T synthesized with excess DA (positive values) and TA (negative values).

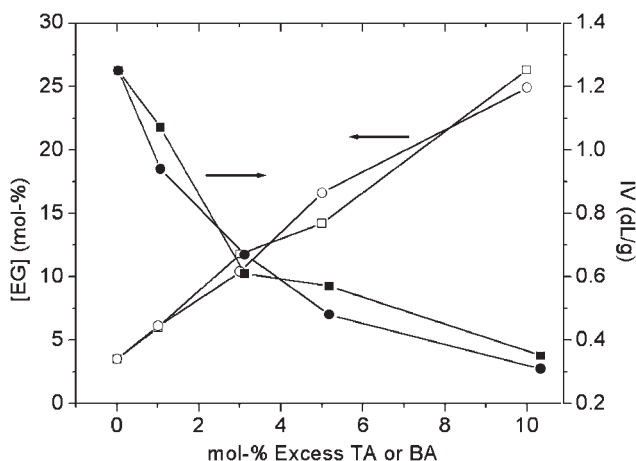


Figure 9 IV (solid) and total end group concentration (hollow) of PA-12,T synthesized with TA (●, ○) and BA (■, □).

at this value of DA. This data suggests that maximum molecular weight is achieved when the stoichiometry of the product is balanced, which is not necessarily the same as balancing the stoichiometry of the initial reactants. This is a result of volatilization of the diamine from the reaction.

Total end group concentrations and IV for PA-12,T synthesized with excess BA and TA are presented in Figure 9. No amine end groups were detected in polymers synthesized with excess BA or TA. Therefore, reactions have reached full conversion and the total end group concentration is the sum of terephthalic acid and benzamide end groups. As the initial concentration of excess BA and TA increased, the total end group concentration increased and IV is decreased. The magnitude of the effects of BA and TA on IV and [EG] were identical on a molar basis despite their different functionality.

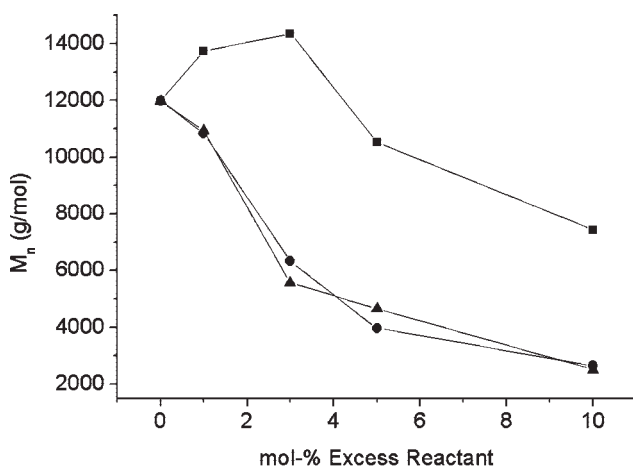


Figure 10 PA-12,T number average molecular weights calculated by NMR analysis plotted as a function of mol % excess 1,12-diaminododecane (■), terephthalic acid (●), or benzoic acid (▲).

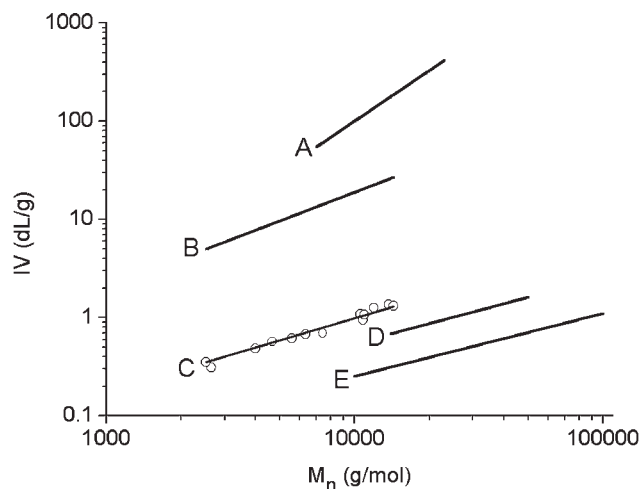


Figure 11 Log-log plot of IV versus M_n for: (A) poly(*p*-benzamide),²¹ (B) PA-6,I,^{22,23} (C) experimental data (○) and best fit curve for PA-12,T, (D) PA-6,6,²³ (E) PA-12.²³ All data recorded at 25°C in concentrated sulfuric acid.

Thus, the only difference observed between PA-12,T synthesized with excess BA and TA was end group functionality. An excess of 1 mol % BA yielded polymer containing 71% acid and 29% benzamide end groups. At 10 mol % excess BA, the resulting polymer had 48% acid and 52% benzamide end groups. Differences in the reactivity and polarity of these end groups can affect post polymerization processes, dyeability⁵ and interactions with fillers in a composite.²⁰

Number average molecular weights (M_n) were calculated by multiplying the molecular weight of the repeat unit for PA-12,T ($M_0 = 330.5$ g/mol) by the average degree of polymerization (DP) using the equation;

$$M_n \text{ (g/mol)} = M_0 [I_1/2 + I_9/4]/2 / [(I_{A1} + I_{T3}/2 + I_{B3}/2)/2]$$

The DP was calculated by NMR analysis as the ratio of average main chain repeat units to the sum of end group units. I_1 and I_9 represent the intensity of amine and acid main chain peaks, respectively, while I_{A1} , I_{T3} , and I_{B3} respectively represent the intensity of amine, terephthalic acid, and BA end group peaks as assigned in Figure 1. M_n versus excess reactant is plotted in Figure 10. Similar trends in Figures 3 and 10 demonstrate strong agreement between IV measurements and M_n calculations based on NMR analysis. Both confirm that 1–3 mol % excess DA yielded polymers with higher M_n and IV than the product of pure 12,T salt. Both M_n and IV decreased progressively above 3 mol % excess DA and for all concentrations of excess BA and TA.

Figure 11 shows a log-log plot of IV versus M_n with a linear trend for these polymers. A best fit line

was used to calculate Mark-Houwink constants of $K = 55.8 \times 10^{-5}$ dL/g and $a = 0.81$. The physical significance of these data is a tendency for the net polymer system to behave more like flexible chains than rigid rods under these conditions.¹⁹ Sulfuric acid is not a theta solvent for these polymers; therefore plots are only shown over the molecular weight range where the Mark-Houwink relationship has been demonstrated to be accurate for each system.²¹⁻²³ IV of PA-12,T is 1–2 orders of magnitude less than poly(*p*-benzamide) and PA-6, I over the range of molecular weights studied. However, PA-12,T shows only a marginal increase in IV over completely aliphatic nylons of comparable molecular weights. For example, at a M_n of 14,300 g/mol, PA-6,6 has an IV of 0.70 g/dL (commercial grade) and PA-12,T has an IV of 1.30 g/dL.

CONCLUSIONS

PA-12,T of varying molecular weight was synthesized by melt condensation polymerization of 12,T salt with 0–10 mol % excess 1,12-diaminododecane, terephthalic acid, or BA. Molecular weight differences as identified by IV were shown to be in agreement with relative end group concentrations determined by ¹³C-NMR. Addition of 1 and 3 mol % excess diamine increased the number average molecular weight of products compared to pure salt. Calculations predict that acid and amine polymer end groups would be at equal concentration with 2.4 mol % excess DA added to the salt. Using these specific processing conditions, maximum molecular weight polymer would be obtained. On a molar basis, excess terephthalic acid and BA both decreased molecular weights to a similar degree. Molecular weights of all polymers calculated using ¹³C-NMR showed a linear trend on a $\log(M_n) - \log(IV)$ plot with Mark-Houwink constants of $K = 55.8 \times 10^{-5}$

dL/g and $\alpha = 0.81$. Since these values are based on single-point IV measurements used to a great extent in semi-aromatic polymer patent literature, they are useful in determining the magnitude of molecular weight changes of similar monomer systems with polymerization processes in both existing literature and future investigations.

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