

Solution polymerization of an α,ω -diethynyl diimide to a diacetylene-containing polyimide via oxidative coupling

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Received 1 December 1999; received in revised form 16 June 2000; accepted 31 July 2000

Abstract

The room-temperature solution polymerization of *N,N'*-dipropargyl(4,4'-hexafluoroisopropylidene)bisphthalimide via oxidative coupling was monitored as a function of time by ¹H NMR spectroscopy and gel permeation chromatography. Following formation of the diacetylene-containing polyimide, the reaction proceeded with hydrolysis of the imide rings, made possible by the presence of the base needed for catalyst formation and water released in the oxidative coupling chain-growth steps. The imide groups could be regenerated either thermally or chemically. Prior to hydrolysis of the imide rings, the polymerization was first-order with respect to both catalyst and functional group concentration, with an intrinsic rate constant of 0.14 l/mol h. For sufficiently long polymerization times, chain scission and molecular weight reduction occurred via hydrolysis of the amide linkages. Thermogravimetric analyses were conducted on the solid products as a function of reaction time. All products could be thermally crosslinked; the thermal stability of the crosslinked monomer was greater than that of the crosslinked polymer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oxidative coupling; Diacetylene; Polyimide

1. Introduction

Crosslinkable diacetylene-containing polyimides can be prepared from the oxidative coupling polymerization of α,ω -diethynyl diimide monomers [1]. Owing to their attractive permselectivity characteristics, these materials have been examined as potential components of gas-separation membranes that can be stabilized via a post-membrane-formation crosslinking step [2]. Used as the minor component in a blend with a structurally similar polyimide, the crosslinkable imide can be thermally activated to stabilize the polymeric film against dissolution in the same solvents from which it was formed. Perhaps more importantly, the crosslinking occurs without a reduction in gas permeability [3].

The utility of this crosslinkable imide material as either the major or minor component in a blend, and its ability to stabilize without reducing gas permeability, is dependent on the molecular weight, chain architecture, and chain structure. High molecular weight is desired if the crosslinkable polyimide is to be used alone or as the major component in a blend, while lower molecular weight may be desirable to enhance miscibility for minor components in blends. For

solution polymerizations, molecular weight can be limited if the growing chains reach their solubility limits in the polymerization solvent before high conversions are reached. Thus, the polymerization can be conducted in dilute solution; if dilute enough, cyclic architectures can be formed in addition to the typical linear chains. For these oxidative coupling polymerizations of α,ω -diethynyl diimide monomers, water is a byproduct. The potential thus exists for hydrolysis of the imide rings to amic acid linkages, and even chain scission as polymerization proceeds. If the chain structure consists of some amic acid linkages, the post-membrane-formation thermal crosslinking step is accompanied by re-imidization and loss of water. This is undesirable since volatile evolution can leave a porous network not suitable for gas separations. In fact, one advantage of using diacetylenes is that crosslinking occurs without volatile formation.

The molecular weight, chain architecture, and chain structure are governed by the experimental conditions of the solution polymerization. Some aspects of this polymerization have been examined for the oxidative coupling polymerization of *N,N'*-dipropargyl(4,4'-hexafluoroisopropylidene)bisphthalimide. This diimide monomer is shown in Fig. 1 and will be referred to as “1,1-6FDA”, signifying

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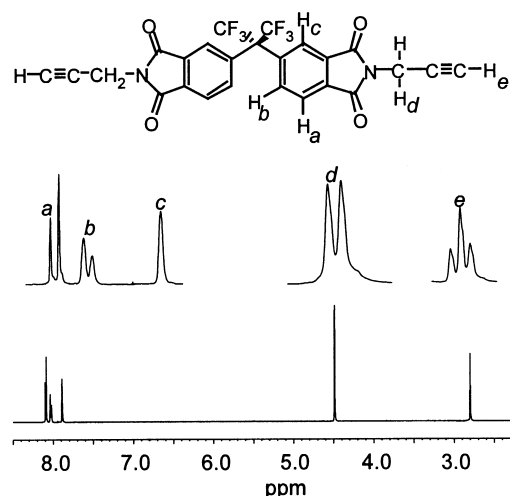


Fig. 1. ^1H NMR spectrum of N,N' -dipropargyl(4,4'-hexafluoroisopropylidene) bisphthalimide monomer (1,1-6FDA) in acetone- d_6 . Above the spectrum are expanded insets displaying the splittings for each group of peaks.

the anhydride from which the monomer was synthesized, and the number of methylenes separating the terminal ethynyl groups from the imide nitrogens. Nuclear magnetic resonance spectroscopy, gel permeation chromatography (GPC), and thermal analyses were conducted as a function of polymerization time.

2. Experimental section

All solvents and reagents were purchased from Aldrich and used without further purification. ^1H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 MHz. Recycle delays of 20 s and 90° pulse lengths were used for quantitative analysis. Infrared spectroscopy was conducted with a Bruker Vector 22 using a Pike diffuse reflectance sampling accessory. GPC was conducted in tetrahydrofuran using a Waters 510 HPLC pump, a Waters 410 differential refractometer, and Phenomenex Phenolgel columns ($300 \times 78 \text{ mm}^2$; 5×10^3 , 5×10^4 , and 5×10^5). Molecular weights are reported based on polystyrene standards. Thermogravimetric (TG) and differential thermal analyses (DTA) were conducted on a Seiko TG/DTA 320 thermobalance operating at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere.

Preparation of the 1,1-6FDA monomer and its polymerization via oxidative coupling has been reported [1]. The procedure used for this study is similar.

2.1. Poly[N,N' -dipropargyl(4,4'-hexafluoroisopropylidene)bisphthalimide] (1,1-6FDA polyimide)

A solution of 1,1-6FDA monomer (5.18 g, 0.01 mol) in 40 ml of anhydrous DMSO was charged to a three-necked round-bottomed flask equipped with a condenser, a

magnetic stir bar, a thermometer, air inlet bubbler and air outlet. The solution was stirred and bubbled with air for at least 10 min. A solution of copper(I) chloride and N,N,N',N' -tetramethylethylenediamine (TMEDA) in 20 ml of DMSO was added to initiate the reaction, which proceeded under continuous stirring and air bubbling for 300 min. Aliquots (5 ml) were taken at 30-min intervals and poured into 15 ml of an acidified methanol/water mixture (by volume: 1% conc. HCl, 24% MeOH, 75% H_2O). The precipitate was filtered, washed several times with acidified methanol, soxhlet-extracted with methanol for 48 h, and dried under high vacuum at 60°C for 48 h. The solid products were white to beige, with depth of shade increasing with increasing polymerization times.

This polymerization was conducted four times with the following CuCl amounts: 0.25 g (0.042 M), 0.75 g (0.13 M), 1.0 g (0.17 M), and 1.5 g (0.25 M). In each case, TMEDA was added to maintain a N/Cu ratio of 2.6. For example, for 1.0 g (0.01 mol) of CuCl, 2.0 ml (0.013 mol) of TMEDA was used. The initial monomer concentration was 0.17 M for each polymerization.

3. Results and discussion

The 1,1-6FDA monomer was prepared in high yield and purity from propargyl amine and 4,4'-hexafluoroisopropylidene)diphthalic anhydride via a solution imidization [1]. The structure is shown in Fig. 1 along with its ^1H NMR spectrum [4] in acetone- d_6 . The expanded insets above the spectrum reveal a mutually coupled triplet ($\equiv\text{CH}$) and doublet ($-\text{CH}_2-$) for the propargyl residue. Either one of these peaks could be used to monitor the ethynyl functional group concentration during the oxidative coupling polymerization.

Oxidative coupling of α,ω -ethynyl compounds can be used to yield high-molecular-weight polymers [5–9]. The catalyst is copper ligated with a diamine and activated by bubbling oxygen (or air) into the reaction mixture. The diamine was N,N,N',N' -tetramethylethylenediamine (TMEDA), which has been shown to be one of the most effective ligands in these oxidative coupling polymerizations. The solvent was dimethyl sulfoxide (DMSO), which was chosen primarily because it was the best solvent for the diacetylene-containing polyimide product. This dipolar aprotic solvent interacts with the monomer via hydrogen bonding with the terminal ethynyl protons. This is based on a ^1H NMR chemical shift of 3.27 ppm for the ethynyl proton in DMSO- d_6 , which is deshielded compared to the 2.80-ppm value in acetone- d_6 shown in Fig. 1. These ethynyl ^1H chemical shifts correlate precisely with published hydrogen bond acceptance values for these and other solvents [10]. The methylene and other protons do not display such a large solvent dependence for their NMR resonances. Solvent effects on reaction rates and equilibria

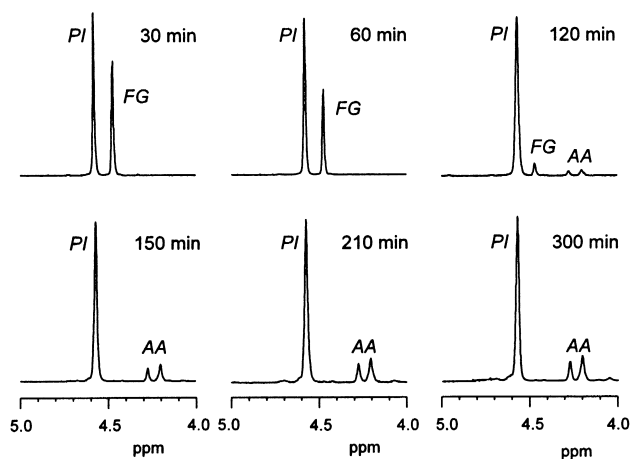


Fig. 2. ^1H NMR spectra as a function of polymerization time for the oxidative coupling of 1,1-6FDA using 0.17 M CuCl. Only the methylene portions of the spectra are shown here. Methylenes next to unreacted ethynyl functional groups resonate at 4.48 ppm and are marked "FG", methylenes between imide and diacetylene groups appear at 4.59 ppm and are marked "PI", and methylenes between amide and diacetylene groups are marked "AA" and appear at 4.28 ppm (meta to the 6F group) and 4.20 ppm (para to the 6F group).

are well known [10], but have not been quantitatively described for oxidative coupling reactions.

The ethynyl protons disappear during the oxidative coupling polymerization as the polyimide is formed. Evolution of the primary structure can be followed by ^1H NMR. In addition to the disappearance of the signal at 3.27 ppm (in DMSO- d_6), the methylene resonance at 4.48 ppm also decreases, and a new methylene resonance appears at 4.59 ppm for the methylenes between imide nitrogens and diacetylene groups. This can be observed in Fig. 2, the methylene portion of the ^1H NMR spectrum as a function of polymerization time. The peak at 4.48 ppm (methylene next to ethynyl groups) is labeled "FG" because it provides a measure of the ethynyl functional group concentration. The methylene signal at 4.59 ppm is labeled "PI" for polyimide. By 120 min, nearly all of the functional groups have disappeared, and two other peaks, labeled "AA" appear in the methylene region at 4.20 and 4.28 ppm. These peaks are attributed to methylenes next to amic acid linkages. Evolution of these AA structural linkages is illustrated in Fig. 3, and is made possible by the release of water in the oxidative coupling and the presence of the organic base, TMEDA. Two AA peaks are present because the imide ring can open in two different positions to give the amide linkage either meta (AA_{meta}) or para (AA_{para}) to the hexafluoroisopropylidene group. The nonequivalent AA NMR peak intensities reflect the different susceptibilities of the imide ring carbonyl groups toward nucleophilic attack. Such differences have been examined for a series of bridged dianhydrides [11]. A linear relationship was found between the electron affinity of the bridging group and the percentage of para isomer produced. For the hexafluoroisopropylidene

dianhydride, methanolysis resulted in a para to meta product ratio of 0.52 to 0.48. Thus, the formation of the para isomer was slightly preferred. Based on these findings, the peak at 4.20 ppm, which at all times had higher intensity than the peak at 4.28 ppm, is assigned to the methylene protons of the para isomer [12].¹ From the NMR spectra, no evidence of methylenes between amide linkages and ethynyl groups is seen. Thus, the hydrolysis takes place in the polymer, and not in the monomer or at the chain termini.

^1H NMR spectra such as those shown in Fig. 2 were measured at 30-min intervals for 300 min. The integrated peak intensities were translated into concentration values and plotted versus time in Fig. 4 for 0.25 M CuCl. At 120 min, no trace of ethynyl functional groups remained, the polyimide methylene concentration peaked, and the amic acid methylene concentration began to level off. After 120 min, a slight gradual reduction in the PI methylene concentration is mirrored by a slight gradual increase in the AA methylene concentration. In addition to the data shown in Fig. 4 for 0.25 M CuCl, concentration evolution curves were also constructed for three other CuCl concentrations: 0.042, 0.13, and 0.17 M. No measurable reaction was observed in the absence of catalyst.

The conversion was calculated from the NMR data as $([\text{FG}]_0 - [\text{FG}]_t)/[\text{FG}]_0$, where $[\text{FG}]_0$ is the initial functional group concentration and $[\text{FG}]_t$ represents the functional group concentration at time t . Percent conversion versus time curves are shown in Fig. 5 for three CuCl catalyst concentrations. The initial reaction rate is proportional to the catalyst concentration. For the two higher CuCl concentrations (0.17 and 0.25 M), complete conversion was reached. Complete conversion was reached earliest (at 120 min) for the reaction containing the highest CuCl concentration (0.25 M). For the reaction with the lowest CuCl concentration (0.042 M), the conversion did not exceed 86% even after 300 min. It is postulated that the conversion is limited by the binding of the copper by the acid functionalities formed by hydrolysis of the imide linkages, and the effective deactivation of the catalyst. Catalyst contamination by evolved acid is known to occur in copper-catalyzed oxidative coupling polymerizations of 4-halo-2,6-disubstituted phenols [13,14].

The concentration evolution curves of Fig. 4 were also used to determine the degree of hydrolysis as $[\text{AA}]_t/([\text{PI}]_t + [\text{AA}]_t)$, where $[\text{AA}]_t$ is the sum of AA_{para} and AA_{meta} and $[\text{PI}]_t$ is a measure of the imide concentration in the polymer. At 120 min, when all functional groups have been consumed, the degree of hydrolysis is already 20%. This rises slowly to plateau around 30% at 180 min.

The rate of the oxidative coupling polymerization of 1,1-6FDA was determined by monitoring the disappearance of

¹ The appearance of the AA linkages was also accompanied by new resonances for the aromatic protons. The new resonances appeared just upfield and with the same general splitting patterns as the peaks shown between 7.8 and 8.2 ppm in Fig. 1.

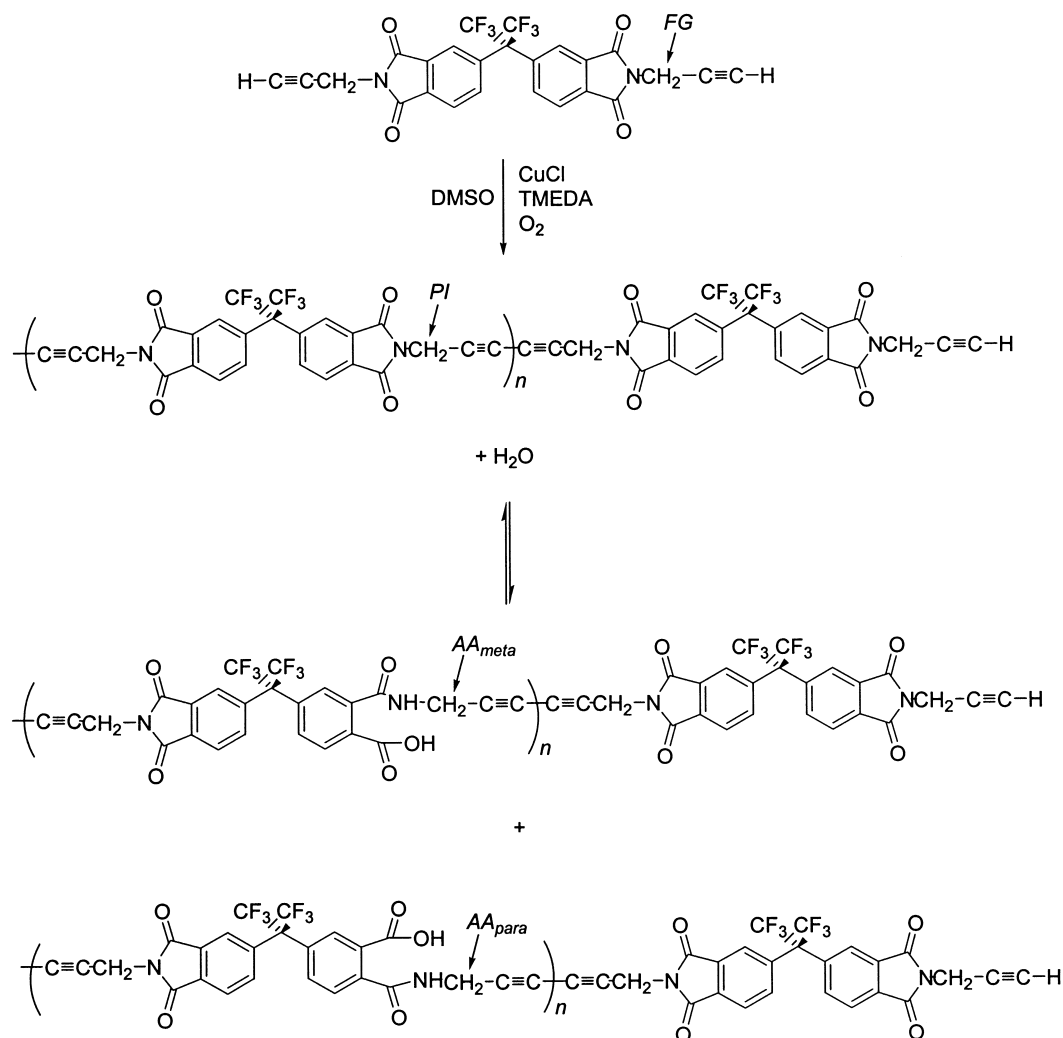


Fig. 3. Complete synthetic scheme for the oxidative coupling polymerization of the ethynyl-terminated 1,1-6FDA diimide monomer to the corresponding diacetylene-containing polyimide. Water is a byproduct of the polymerization, and leads to hydrolysis of the imide ring to the polyamic acids. Note that the ring can open either meta or para to the hexafluoroisopropylidene group to give rise to two different polyamic acids (as evidenced by two different methylene signals in the NMR spectrum).

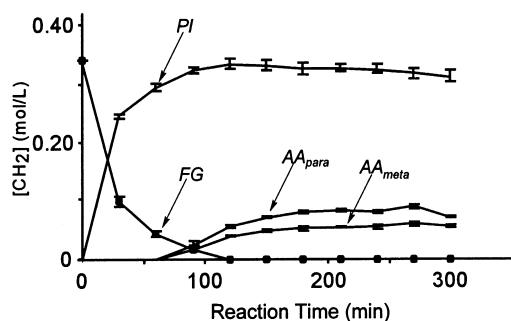


Fig. 4. Concentration evolution curves for the room-temperature, oxidative-coupling, solution polymerization of 1,1-6FDA using 0.25 M CuCl. “FG” are ethynyl functional groups, “PI” means polyimide, and “AA” are amic acid linkages.

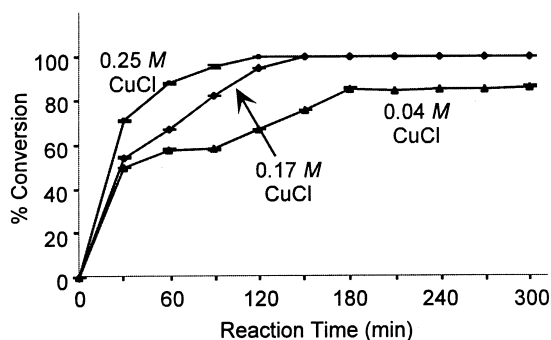


Fig. 5. Conversion versus time curves for the 1,1-6FDA polymerization with different CuCl catalyst concentrations. Conversion is defined as $([\text{FG}]_0 - [\text{FG}]_t)/[\text{FG}]_0$.

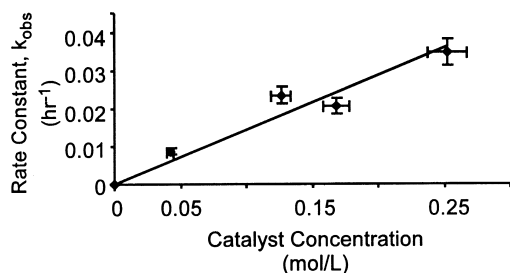


Fig. 6. Observed rate constant, k_{obs} , versus copper catalyst concentration for the oxidative coupling polymerization of 1,1-6FDA in DMSO at room temperature. The slope is used to extract an intrinsic rate constant, $k_{intrinsic}$. The observed rate constants, k_{obs} , were determined from the slopes of functional group consumption curves measured from 1H NMR data for each catalyst concentration.

the ethynyl functional groups ($-d(FG)/dt$). Reaction rates were calculated from the slope of the functional group consumption curve presented in Fig. 4. Functional group concentrations were used in the kinetic analysis only for reaction times prior to the appearance of the amic acid hydrolysis products. The reaction was assumed to be first-order in functional groups and a rate was calculated from Eq. (1):

$$-d[FG]/dt = k_{obs}[FG] \quad (1)$$

The observed rate constant was calculated for each of the four catalyst concentrations. In all cases, the correlation coefficient was greater than 0.95 (R^2 was greater than 0.985 in four of the cases). The possibility for higher-order rates was evaluated. In all cases, first-order kinetics provided the best fit to the experimental data.

The observed rate constant is a product of an intrinsic rate constant and the concentration of the catalyst employed. If the reaction is first-order in catalyst concentration, then this term can be expanded:

$$k_{obs} = k_{intrinsic}[\text{catalyst}] \quad (2)$$

Viersen et al. have shown that the oxidative coupling polymerization of 2,6-dimethylphenol catalyzed by a copper(II)/TMEDA complex followed first-order kinetics with respect to catalyst concentrations [15]. Fig. 6 suggests that the oxidative coupling polymerization of 1,1-6FDA

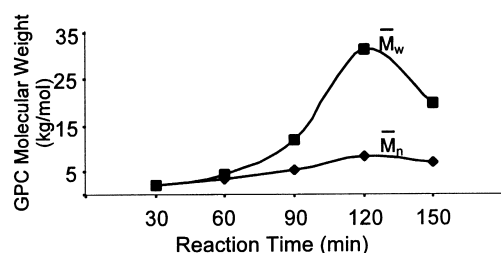


Fig. 7. GPC molecular weight versus polymerization time for the oxidative coupling of 1,1-6FDA using 0.25 M CuCl catalyst. Calculations are based on polystyrene standards. The apparent decrease after 120 min is due to the hydrolysis of amide groups in amic acid linkages.

also follows first-order kinetics in catalyst concentration. Here, the observed rate constant for each catalyst concentration is plotted against that concentration. The slope of the line formed by these data is the intrinsic rate constant for the room-temperature polymerization, 0.14 l/mol h. The data were also analyzed via higher-order reaction kinetics. For the data presented, first-order kinetics are far superior for describing this oxidative coupling polymerization.

By using the FG methylene NMR signal as a measure of the number of chain ends, number-average degrees of polymerization (x_n) were determined from the ratios of PI to FG NMR peak areas. For 30, 60, and 90 min, these values were 3.5, 8.3, and 22, respectively, for the oxidative coupling of 1,1-6FDA using 0.25 M CuCl. These values correspond to number-average molecular weights of 1800, 4300, and 11,400 g/mol. At 120 min and greater, the FG methylene signal completely disappears (see Figs. 2 and 4), which means that the concentration of end groups is lower than the noise level in the 1H NMR spectra. For these samples, an apparent minimum molecular weight may be determined from the signal-to-noise ratio. This leads to an x_n value of about 250, corresponding to a molecular weight of 129 kg/mol, which cannot be reconciled with inherent viscosities of 0.4 dl/g [1]. This discrepancy is explained by considering the appearance of new methylene peaks in the NMR spectrum around 3.82–3.87 ppm. These peaks are attributed to methylenes between diacetylenes and chain-end amine groups that result from the hydrolysis of amide linkages.

Hydrolysis of amide linkages for polymerization times of 120 min and greater leads to molecular weight reduction. This is clearly observed in GPC data. The GPC M_n and M_w are shown as a function of reaction time in Fig. 7 for the polymerization conducted with 0.25 M CuCl. Calculations were based on polystyrene standards. A gradual increase in molecular weight is observed up to 120 min. Longer reaction times gave rise to a decrease in the molecular weight. This decrease can be explained by either an actual decrease in average chain length due to hydrolysis of the amide linkages of the amic acids, or simply a reduction in the hydrodynamic volume of the poly(amic acid) compared to the polyimide. Intrinsic viscosity studies have revealed similar hydrodynamic volumes for poly(*p,p'*-oxydiphenylene-pyromellitimide) and its precursor poly(amic acid) [16]. Thus, molecular weight reduction is consistent with amide hydrolysis, signified by the appearance of the 1H NMR signal for methylenes between diacetylenes and chain-end amine groups. Even in the solid state, molecular weight reduction of poly(amic acids) via amide hydrolysis is known to occur during the initial stages ($<125^\circ C$) of cure. At higher temperatures ($>150^\circ C$), the consequent anhydride and amine chain ends react to increase the molecular weight of the ultimate polyimide [17]. No anhydride chain ends were formed during the 1,1-6FDA polymerization since this reaction was carried out in solution at room temperature with water evolution, and not in the solid state at elevated temperature. FTIR studies of the 1,1-6FDA polymerization

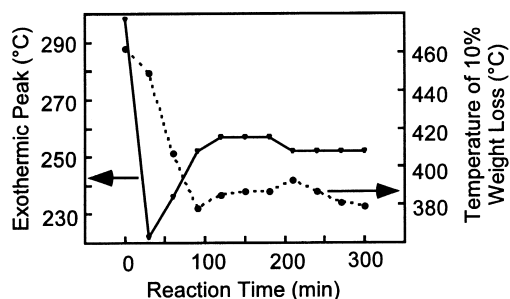


Fig. 8. Thermal data for 1,1-6FDA and its reaction products following oxidative coupling polymerization with 0.25 M CuCl catalyst. The temperature of the most intense exothermic peak was taken from differential thermal analysis (DTA) measurements. The temperature of 10% weight loss was taken from thermogravimetric analysis (TGA) curves and is presented as a measure of thermal stability. The values for the 1,1-6FDA monomer are shown at reaction time = 0. All samples were analyzed under a nitrogen atmosphere using a 10°C/min heating rate.

products revealed no anhydride carbonyl groups due to amide hydrolysis, but did show free acid carbonyl groups.

In order to examine the thermal properties, the products were analyzed by simultaneous TG and DTA as a function of reaction time. Each product exhibited broad exotherms due to reaction of ethynyl functional groups, reaction of diacetylenes, re-imidization of the amic acid groups, or some combination of these [2]. The temperature of the most intense exothermic peak is shown as a function of reaction time in Fig. 8; even if multiple exothermic peaks are discernible, only the temperature of the most intense peak is shown. The data points at reaction time = 0 are for the pure monomer. For reaction times of 30 min and greater, the data represent the “polymeric” products. The monomer exotherm at 298°C is due to reactions of the ethynyl functional groups. The most intense exotherm for all of the other samples is the diacetylene reaction exotherm. This occurs at 222°C for the 30-min product, and then increases to plateau around 255°C for the 90-min product. The 30-min product is a relatively low-molecular-weight imide oligomer. Its ability to pack and order in the solid state facilitates the diacetylene reaction with only limited thermal energy. It is the only reaction product that turned deep red upon thermal annealing (240°C, 4 h). As the molecular weight increases, the polyimide and mixed imide and amic acid polymers do not pack as readily. Thus, a higher level of thermal energy is required to initiate the reaction, which is reflected in the exotherm maximum increase shown in Fig. 8. Upon thermal annealing at 240°C for 4 h, these higher-molecular-weight products became beige to brown with depth of shade increasing as polymerization time increased. Such a color change indicates the creation of a broad distribution of conjugation lengths, which is expected for diacetylene reactions within amorphous materials. Indeed, the high-molecular-weight 1,1-6FDA polymer was shown to be amorphous by wide-angle X-ray diffraction [18].

Also shown in Fig. 8 is the temperature of 10% weight loss from the TG curves. This is about 462°C for the mono-

mer, and decreases to plateau around 385°C for the 90-min product. While this value is taken as a measure of thermal stability, it is the thermal stability of the crosslinked products that is analyzed here since these temperatures are above the reaction exotherms. Thus, the higher degradation temperature for the monomer is related to the higher stability of the resulting products following thermal crosslinking. As the crosslinking reaction became less facile due to less efficient packing in the higher-molecular-weight products, the thermal stability of the crosslinked products decreased. These results are supported by the char yields at 500°C: 72% for the monomer, decreasing to plateau at 55% for the 90-min product. Since re-imidization of the amic acid linkages began at temperatures near 120°C [2], the structure consisted of imide groups when the crosslinking and degradation temperatures were reached. Thus, hydrolysis and creation of the amic acid linkages had no real effect on the thermal stability of the material, as measured by thermogravimetry with thermal ramping.

The presence of amic acid linkages is undesirable, however, if thermal crosslinking should proceed without evolution of volatiles. This is certainly the case for application of these materials in gas-separation membranes. To prevent the formation of these amic acids, a dehydrating agent could be introduced into the polymerization reactor, as long as it does not interfere with the oxidative coupling reaction. If conversion is not limited by the formation of acid groups (see Fig. 5), the final mixed product may be subjected to a chemical or thermal re-imidization. The chemical re-imidization was successfully accomplished with pyridine and acetic anhydride in a solution procedure. The resulting product exhibited no ^1H NMR signals for the amic acid functionalities.

4. Conclusions

The oxidative coupling polymerization of N,N' -dipropargyl(4,4'-hexafluoroisopropylidene)bispthalimide was analyzed using ^1H NMR spectroscopy, GPC and thermal analysis. High conversions were achieved only for CuCl catalyst concentrations of 0.17 M and higher. As polymerization proceeded, water was given off as a byproduct and alkaline hydrolysis of the imide chain linkages took place. It is postulated that the conversion was limited with lower CuCl catalyst concentrations by the binding of the copper with the acid functionalities created by this hydrolysis. For sufficiently long polymerization times, hydrolysis of the amide linkages occurred resulting in molecular weight reduction. All of the products could be thermally crosslinked. Thermal stability of the crosslinked monomer was higher than that of the crosslinked polymeric products. Thermal treatment proceeded without volatile formation, except for the samples containing amic acid groups; these samples lost water prior to crosslinking. A solution-based

chemical re-imidization was used to regenerate imide linkages in the diacetylene-containing polymer.

Acknowledgements

This work was funded by the Environmental Protection Agency (R824727). The work reported here has not been subjected to the EPA's peer and administrative review and therefore may not necessarily reflect the views of the Agency and no official endorsement should be inferred. NMR instrumentation was made available through a grant from the National Science Foundation (BIR-9306392). We gratefully acknowledge partial support of this work by the Georgia Tech Molecular Design Institute, under prime contract N00014-95-1-1116 from the Office of Naval Research. Special thanks to Birgit Schöberl, Laren Tolbert, Malcolm Polk, and Leslie Gelbaum for their contributions to this work.

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