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Solvothermal Polymerization of Diaminomaleonitrile Reveals Optimal Green Solvents for the Production of C≡N-Based Polymers

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ABSTRACT: Solvothermal polymerization (STP) of diaminomaleonitrile (DAMN) was evaluated using a wide variety of solvents and in the temperature range from 80 to 170 °C. The highest yields, almost quantitative, were achieved with protic n-alcohols such as n-pentanol or n-hexanol at 130 and 150 °C, respectively. The kinetic behavior was studied by gravimetry and the DAMN consumption was monitored by UV−vis spectroscopy and HPLC. GC−MS identified byproducts of the DAMN hydrolysis and oxidation reactions, which were significantly reduced when n-pentanol or n-hexanol were used with respect to hydrothermal conditions. This led to an exploration of compositional changes and microstructural variations by FTIR and NMR spectroscopy and simultaneous thermal analysis. n-Hexanol appears to be an ideal eco-friendly solvent for the DAMN self-STP. The results presented here are not only of interest for the design of polymeric materials based on C≡N structures but also show remarkable implications for prebiotic chemistry.

Protic solvents
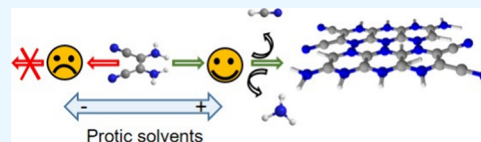
1. INTRODUCTION

Diaminomaleonitrile (DAMN or 2,3-diamino-cis-2-butenedinitrile) is a diamine of relatively small molecular size with weak Lewis base behavior that can be synthesized from HCN oligomerization, by the hydrogenation of diiminosuccinonitrile (DISN)[1,2] or from acetone cyanohydrin through organosulfur catalysis.[3] DAMN is of great interest within organic chemistry due to its inherent symmetric structure with amine and nitrile groups and conjugated systems between them. For these characteristics, it is broadly used as synthon for the production of a wide selection of N-heterocycles and Schiff's bases [see, e.g., refs 4 and 5] and for the design of chemosensors [see, e.g., refs 6−8].

Beyond the use of DAMN in fine, medical, or analytical chemistry, it can self-polymerize when it is thermally activated. Thus, it can undergo bulk thermal polymerization in the solid state[9,10] and from the melt,[11] as well as under several hydrothermal conditions.[12−14] These DAMN polymers present suitable properties for the development of capacitors, semiconductors, biosensors, and catalysts.[13−16] On the other hand, the DAMN molecule, as the formal tetramer of HCN, is of considerable interest in astrochemistry and prebiotic chemistry.[2,17−24] However, several aspects related to DAMN polymerization pathways remain elusive.

Thus, due to the relevance that the synthesis of polymers derived from DAMN has been acquiring in the field of materials science and the importance of the HCN chemistry in the field of prebiotic chemistry and in the hypotheses about the origins of life,[25−29] the present work tries to establish some criteria that will help improve the understanding of certain mechanistic aspects related to the polymerization of DAMN and the modulation of the properties of DAMN polymers based on the following main goals: (i) The effects of

temperature and solvent on DAMN polymerization are studied by exploring solvents of different polarities and properties to establish the maximum degree of conversion that can be achieved, taking hydrothermal polymerization at 80 °C as a reference, and (ii) whether there are microstructural differences in the DAMN polymers obtained by varying the synthesis conditions is analyzed.

These two aspects are interesting because DAMN polymerization has scarcely been studied. The bulk thermal polymerization of DAMN is simple, fast, and highly efficient, but little control over the morphological properties of these promising functional materials has been achieved, which can be an alternative to well-known polymeric carbon nitrides (g-CNs), as has been recently described.[30] However, polymerization in the absence of solvent allowed us to obtain abundant information about the kinetics, thermodynamics, and mechanistic details of these processes. Thus, during the polycondensation of DAMN, HCN and NH_3 are released,[30] and at least a three-stage autocatalytic kinetic mechanism has been proposed for bulk polymerization.[31] In the case of aqueous DAMN polymerization, the yields of DAMN polymers decrease due to secondary hydrolysis and oxidation processes, which occur during these precipitation polymerization reactions, as unequivocally is demonstrated in the following pages. These collateral processes raise new questions about

Table 1. Physical Properties of the Solvents Used in the DAMN STP Reactions and the Corresponding Conversion Values of These Polymerizations (α)

Solvent	ε	Polarity[a]	bp (°C)	DAMN Solubility (g/L)	DAMN Solubility (%)[d]	T_p (°C)	t_p (h)	α (%)
Water	82	1	100	5[b]	19	80	24	60
						80	168	75
DMSO	47	0.444	189	>125[c]	100	110	24	
MeCN	37	0.460	82	70[b]	100	80	168	5
ButOH	18	0.586	118	0.07[c]	0.26	80	168	10
						110	24	8
PentOH	14.8	0.568	138	0.12[c]	0.44	130	24	46
HexOH	13		157	0.27[c]	1	150	24	67
Aniline	7.0	0.420	184	>125[c]	100	110	24	7
						170	24	40
Toluene	2.4	0.099	111	<0.01		110	24	

[a]Empirical parameter of solvent polarity from ref 38. [b]DAMN solubility from ref 39 at 25 °C. [c]DAMN solubility from the experiments present in this work at 25 °C. [d]Percentage in weight of DAMN (135 mg) dissolved in 5 mL of the corresponding solvent. ε = dielectric constant; bp = boiling point of the solvents; T_p = DAMN polymerization temperatures used in this study; t_p = polymerization time for each reaction performed.

how they can affect the intricate DAMN polymerization mechanism.

Therefore, the effects of solvent and temperature on the solvothermal polymerization (STP) of DAMN must be studied to better understand the complex chemistry of HCN and to determine accurate synthetic conditions to improve the properties of DAMN-based polymers. To our knowledge, this is the first time that DAMN polymerization has been evaluated in the presence of organic solvents. Hence, we have attempted to develop new synthetic routes that, on the one hand, can provide materials with better qualities and, on the other hand, can discern the fundamental prominence of water in the increase in the molecular complexity in prebiotic environments. Therefore, we explored these precipitation reactions using several solvents (water and organics) with temperatures ranging from 80 to 170 °C and reaction times ranging from 1 day to 1 week. The kinetics of all the experimental series were evaluated by a gravimetric methodology, and the consumption of DAMN was monitored by UV−vis spectroscopy and high-performance liquid chromatography (HPLC). Moreover, a comparative study of the DAMN polymeric microstructures was carried out using FTIR and NMR spectroscopies and thermal analysis, revealing the key role of the solvent in the characteristics of these C=N-conjugated systems.

2. MATERIALS AND METHODS

2.1. DAMN STP. For each DAMN polymerization reaction described in this work, 0.25 M dispersions/solutions of DAMN (98%, purchased from Sigma-Aldrich, St. Louis, MO, USA, and used as received) in different organic solvents or water were prepared by adding 135 mg of DAMN to 5 mL of the chosen solvent in 20 mL vials that were sealed with Teflon/silicone caps. The vials were placed in a heating block at ≈10 °C below the boiling point of the chosen solvents for the detailed kinetic study discussed in Section 3.2 [90 °C for water, 110 °C for n-butanol (ButOH), 130 °C for n-pentanol (PentOH), and 150 °C for n-hexanol (HexOH)]. Please see Table 1 to consult the boiling point of each solvent used in this work. For the completed polymerization series, the reaction time was increased by 24 h (i.e., from 24 to 168 h) for each series of these four solvents. After the reaction time had elapsed, the final suspensions were filtered under vacuum. After filtration,

the brown/orange solutions were collected, and the precipitated black solids were washed with acetonitrile (MeCN) to remove any trace of unreacted DAMN. In reactions using n-alcohol as the solvent, DAMN polymers were oven-dried for 2 days at 20 °C below the boiling point of the solvent after vacuum filtration. This approach aimed to eliminate solvent residues, which are challenging to remove due to their solid matrix retention, as explained below. On the other hand, to remove the water from the solids, the solids were freeze-dried after vacuum filtration until a constant weight was achieved. The methodology described herein for the synthesis of the DAMN polymers was completely analogous to that previously described in ref 13 using hydrothermal conditions at 80 °C. Thus, this hydrothermal series at 80 °C was used for comparative purposes throughout the main text of this paper in order to properly check the new data from the 90 °C hydrothermal series and the other DAMN STP series with the previously reported data.

The polymeric conversions were calculated as follows: α (%) = [(final weight of the insoluble dark solid/initial weight of DAMN)·100]. At least three independent syntheses were considered to calculate the average value of α. As a rule, throughout the full text, the conversion is equal to the calculated values of α.

Other polymerizations of DAMN were carried out with the same methodology explained above using different solvents (Section 3.1), such as MeCN, dimethyl sulfoxide (DMSO), toluene, and aniline, at the temperatures and polymerization times indicated in Table 1.

DAMN was handled carefully following the specifications indicated in the safety data sheet provided by the supplier. All the reactions were carried out using an extractor hood and with a good general ventilation of the laboratory to prevent occasional intoxications by HCN or NH₃. DAMN polymers to the best of our knowledge do not present toxicity by inhalation or skin contact.

Note that solvothermal synthesis typically occurs in a solvent at temperatures exceeding its boiling point and at high pressures. Traditional STP experiments use autoclaves. However, our first STP approach involved adjusting the polymerization temperature below the solvent boiling point. Moreover, conducting STP under atmospheric conditions
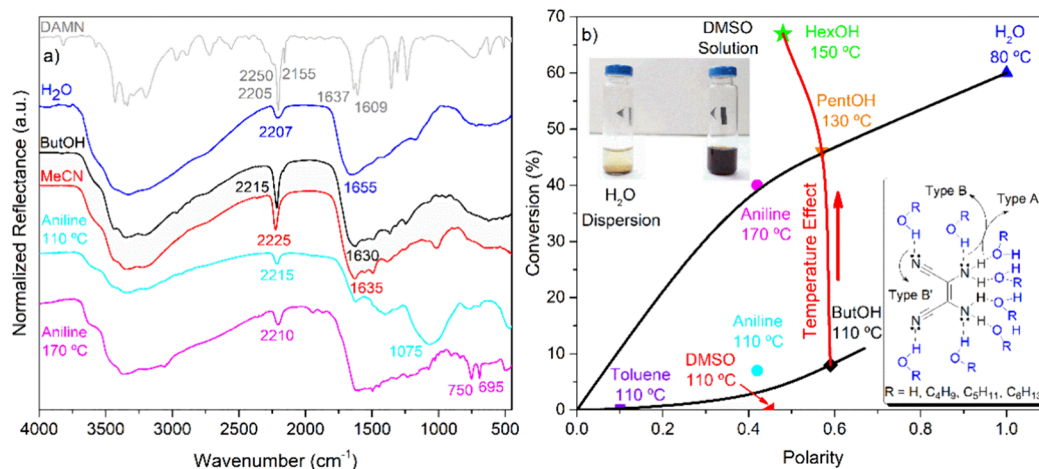
Figure 1. (a) Normalized FTIR spectra of DAMN and the corresponding polymers obtained by STP in water,[13] ButOH, and MeCN at 80 °C for a reaction time of 168 h and in aniline at 110 and 170 °C for a reaction time of 24 h. Note that the bands centered at approximately 3300, 2200, and 1640 cm^{-1} are characteristic of DAMN polymers and, in general, of HCN-derived polymers.[36] (b) Conversion vs polarity of the solvents used in the DAMN STP for a reaction time of 24 h (data from Table 1). The trend lines have been plotted only to guide the eye. The black line, 110 °C series (toluene, DMSO, aniline, and ButOH), shows the increase in conversion due to the increase in solvent polarity. The red line indicates the increase in the conversion value with increasing temperature for the *n*-alcohol series (ButOH, PentOH, and HexOH, from 110 to 150 °C). In the case of using different solvents other than water, it seems that highest conversion values for DAMN polymerization reactions require solvents with available −OH groups and moderately high temperatures. In addition, the inset plot shows the possible types of different hydrogen bonds between DAMN and the solvent molecules, and the inset photo shows the look of a water suspension and a DMSO solution of DAMN (photo taken and edited by A.L.-G. and J.L.F.).

simplified DAMN polymerization, benefiting from the known air tolerance of these processes.[14,30]

2.2. Detection of DAMN Consumption via UV−Vis Spectroscopy. The UV−vis spectra were recorded with an Agilent 8453 instrument, whose working interval was within the range of 190 to 850 nm with a resolution of 2 nm. To record the spectra, 0.5 μL of the raw sol fractions was taken, and the same solvent in which polymerization was carried out was added until a final volume of 3 mL was obtained. These yellowish-orange solutions were measured (Figure S1).

2.3. Quantification of DAMN by HPLC. For quantification of the unreacted DAMN in the sol fractions collected, the following procedure was carried out: HPLC analysis of DAMN was achieved with an Agilent Technologies 1260 Infinity II quaternary system capable of working at a maximum pressure of 600 bar and a maximum flow of 5 mL/min and equipped with a photodiode array (PDA) detector. A C18 3 × 150 mm, 2.7 μm Poroshell 120 EC-18 column, which was maintained at 30 °C, was used. An isocratic method was performed using MeCN:water as the mobile phase at a ratio of 20:80, with a flow of 0.55 mL/min and an injection volume of 3 μL. Chromatograms were recorded at 296 nm, the maximum absorption wavelength of DAMN (Figure S1). The total analysis time for this method was 11 min. The sol fractions were injected at a 50:50 ratio in MeCN; that is, 500 μL of the raw sol fractions (independent of the solvent used in the different DAMN polymerization reactions) was added to 500 μL of MeCN, and these solutions were analyzed by HPLC after centrifugation.

DAMN eluted cleanly and with no appreciable tailing using the analytical method developed. We ran a calibration curve that demonstrated the linearity of this method with a linear range that extended from 1 to 100 ppm (Figure S2). In this way, multiple-point external standardization was used to quantify the amount of unreacted DAMN. Using this HPLC methodology, diaminofumaronitrile (DAFN), *trans*-isomer of

DAMN (95%, purchased from SIA Enamine, Riga, Latvia), and DISN (95%, purchased from Riga, Latvia) were also analyzed.

2.4. Gas Chromatography−Mass Spectrometry (GC− MS) Analysis of the Hydrolysis/Oxidation Products Obtained during the DAMN Polymerization Reactions. GC−MS analyses were performed in "full-scan" mode on a 6850 GC chromatograph coupled to a 5975 VL MSD triple-axis detector operating in electron impact (EI) mode at 70 eV (Agilent) using an HP-5 MS column (30 m × 0.25 mm × 0.25 μm thick) and helium (He) as the carrier gas. To identify the polar organic compounds in the sol fractions, the following protocol was used: (1) The sol fractions were dried; in the case of the reactions carried out in water, these phases were freeze-dried, and those carried out in *n*-alcohols were dried in a rotary evaporator. (2) Approximately 5 mg of each dried sample was derivatized using 100 μL of BSTFA with 1% TMCS (N,O bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane, from Thermo Scientific), with the resulting suspensions being heated at 80 °C for 3 h to finally obtain the respective TMS derivatives. (3) The derivatized samples were analyzed by GC−MS using the following GC temperature ramp: 60 °C (the initial temperature) was maintained for 1.5 min, and then samples were heated to 130 °C at 5 °C/min, which was maintained for 11 min, heated to 180 °C at 10 °C/min with a holding time of 10 min, and finally heated to 220 °C at 20 °C/ min with a final holding time of 15 min. A total of 1 μL of each derivatized sample was injected. The injector temperature was 275 °C, and the injections were carried out in split mode for the samples made in aqueous solution and in splitless mode for those made in *n*-alcohols. The detector temperature was 300 °C. The carrier gas flow rate was 1.1 mL/min. Compound identification was performed in full-scan mode with a range of 50 to 650 amu. The identification of glycine, urea, oxalic acid, and formamide was confirmed against the retention times and mass spectra of commercial standards.

2.5. Characterization of the DAMN Polymers. The DAMN polymers obtained were characterized by elemental analysis, FTIR and NMR spectroscopy, and thermal analysis. The equipment and details about these measurements are reported in ref 13. The extent of the reactions (EOR) was calculated from the normalized and baseline-corrected FTIR spectra. The EORs were calculated as follows: EOR (%) = $[I_{1630}/(I_{2200} + I_{1630})] \cdot 100$. I_{1630} and I_{2200} are the intensity of the bands centered around 1630 and 2200 cm^{-1} from normalized FTIR spectra. The assignment of these spectroscopic features is described in Section 3.4.3. EOR is a semiquantitative parameter that describes the reach of DAMN polymerization, and it is considered useful for comparative purposes in nitrile polymer chemistry.[32] At least three independent FTIR spectra were considered to calculate the average EOR.

3. RESULTS AND DISCUSSION

3.1. Identifying Optimal Solvent and Temperature for Effective DAMN STP. As a starting point, the hydrothermal reaction of DAMN is a heterogeneous polymerization process, specifically categorized as nonconventional precipitation polymerization (because DAMN is only partially soluble in water). It lacks an initiator, catalyst, or cross-linker, and the growing polymer chains phase separate due to the low solubility of the DAMN polymers. Precipitation polymerization, known for its ease of operation and the absence of any surfactant or stabilizer,[33,34] is applied to all the STP reactions discussed here. However, as mentioned in Section 1, to our knowledge, no study has explored DAMN polymerization in solution outside of the aqueous environment, which is inspired by prebiotic chemistry.

Therefore, first, DAMN polymerization in MeCN was analyzed. DAMN is soluble in this common solvent,[35] and the reaction temperature was set to 80 °C because, in a previous study under hydrothermal conditions at this temperature, high conversion values were achieved (~75%).[13] FTIR spectroscopy confirmed the effectiveness of this polymerization in MeCN: the spectrum of the precipitated black solid was compared to that of commercial DAMN and other DAMN polymers from a previous study.[13] Using this methodology, the spectroscopic features of the DAMN polymer, obtained as a black insoluble solid from the MeCN solution, agreed with those recorded for the samples synthesized by aqueous polymerization (Figure 1a, where the IR spectra of the different solvothermally produced samples are shown). However, DAMN hardly polymerized in MeCN at this moderate temperature, even when a long reaction time of 168 h was used (Table 1). This result was revealing because it differed from a process where the monomer is poorly soluble, such as the hydrothermal polymerization of DAMN, unlike a process where the monomer is completely solubilized in an organic reaction medium. Therefore, despite the complete solubility of DAMN in a medium-polarity solvent such as MeCN (Table 1), low polymerization yields discourage the use of this solvent under mild thermal conditions. Thus, ButOH was explored as a protic solvent, and new reactions were conducted again at 80 °C. DAMN is less soluble in ButOH than in MeCN (Table 1). Nevertheless, higher conversion rates were achieved than those achieved with MeCN, albeit they were still lower than those achieved with water (Table 1).

This preliminary analysis with unexpected and inconclusive results led to a new series of polymerization reactions that used organic solvents, had reaction temperatures increased by 30 °C

(110 °C), and had the same reaction time (24 h). In this way, toluene, a nonpolar solvent; DMSO, a polar solvent; and aniline, a protic solvent, were tested together with ButOH. Notably, in DMSO and aniline, DAMN completely dissolved at the start of the reaction, similar to MeCN (Table 1 and Figure 1b). No polymerization was observed in either DMSO or toluene, but in the case of ButOH and aniline, similar conversions were found (Table 1). However, the solution polymerization of DAMN in the presence of aniline led to the generation of DAMN polymers with marked spectroscopic differences in relation to the FTIR data (Figure 1a). This may be due to secondary reactions between the amine group of the aniline and the nitriles of DAMN (acting as electrophiles), as discussed below. In any case, considering only the conversion values, initially, effective DAMN polymerization requires a protic solvent and a strong thermal impulse, independent of the DAMN solubility, as is qualitatively and clearly shown in Figure 1b (series 110 °C, black line), where the conversion limits achieved for all the STPs are represented as a function of solvent polarity, which is a parameter well known to influence reactivity under strong vibrational coupling, as has been recently reported.[37] In this regard, alcohols emerge as possible preferential solvents for DAMN polymer formation via STP. Considering that a higher energy requirement is also mandatory, new reactions using PentOH and HexOH at 130 and 150 °C, respectively, were developed. In addition, the singular behavior of aniline, which has different acid−base characteristics, was studied at a higher polymerization temperature, 170 °C. Promising monomer conversion values for DAMN polymers were achieved using these alcohols, even higher than those achieved using aniline at higher temperatures (Table 1). The results of this current set of STPs at higher temperatures are also plotted in Figure 1b. The overall effect of the protic solvents aniline, PenOH, and H$_2$O can be observed through the trend line drawn, with HexOH clearly above it. In addition, the effect of temperature on the three n-alcohols is also indicated in the same figure (red line). However, independent of the thermal influence, this observed trend agrees with the recent study by Piejko et al., who demonstrated significant changes in reactivity in reactions performed using alcohols as solvents as a consequence of strong vibrational coupling via intra- and intermolecular interactions, which demonstrates the key role of the dispersion forces considered above.[37]

As a result, in agreement with the data shown in Figure 1b, efficient STP processes using DAMN as a monomer require protic polar solvents with available hydroxyl groups. DAMN is a compound with a donor−acceptor character (electron donor parts, −NH$_2$ groups, and acceptor parts, −CN). As shown in the inset plot of Figure 1b, these molecules can form hydrogen bonds with the proton donor molecules of these protic solvents through the electronegative nitrogen atom of the amine and nitrile groups (hydrogen bond types B and B', respectively) and with proton acceptor molecules of solvents through the hydrogen atoms from the amine groups (hydrogen bond type A). This leads to the formation of monomer−solvent intermolecular complexes, and the polarity and polarizability of the solvent also affect the chemical and physicochemical properties of DAMN. In this regard, the STP of DAMN could be related to the indispensable formation of these hydrogen bonds among the solvent and the DAMN functional groups, as was observed in the growing chains of other nitrile polymers, such as polyacrylonitrile, during aqueous polymerization.[40]
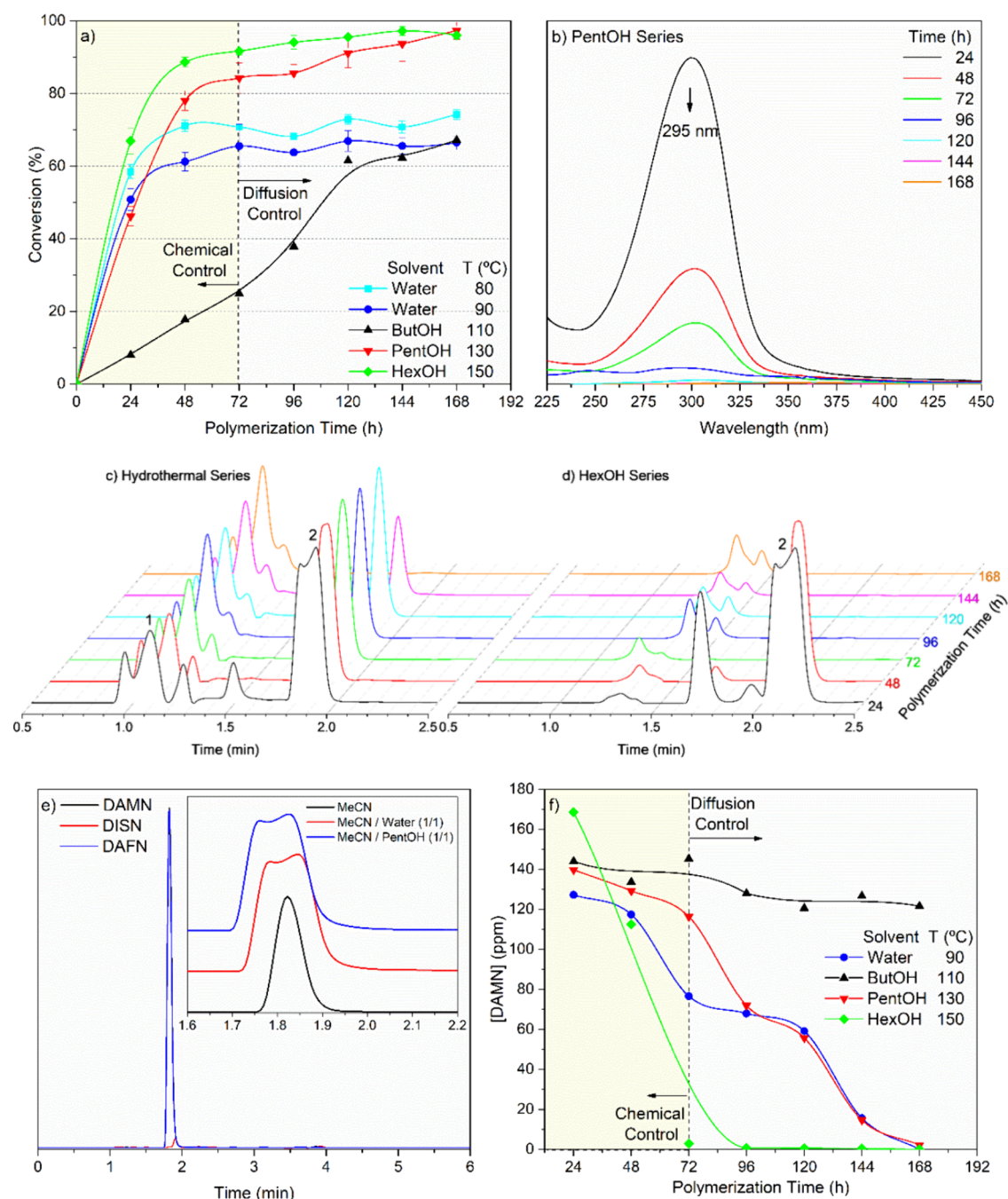
Figure 2. (a) Gravimetric conversion vs reaction time for the STP of DAMN; (b) representative UV−vis spectra of the sol fractions (after filtration and centrifugation of the reaction crude) for STP in PentOH at 130 °C. Note that no additional absorptions were identified upon detailed inspection of these spectra over a wide range of wavelengths (from 210 to 700 nm). HPLC chromatograms of the sol fractions from the STP of DAMN in (c) water at 90 °C and (d) HexOH at 150 °C, where 1 = oxalic acid and 2 = DAMN. (e) HPLC chromatograms for DAMN, DISN, and DAFN in MeCN (100 ppm). HPLC chromatograms of DAMN in different solvents (100 ppm for each case) are shown in the inset. (f) Quantification by HPLC of the unreacted DAMN concentration in the sol fractions vs reaction time for the STP of DAMN.

3.2. Determining the Polymerization Time and Probing the Kinetics. Based on the above background, we extended the STP strategy to a wide range of reaction times. Thus, from this approach, detailed monitoring of the DAMN polymerization reactions was carried out using water, ButOH, PentOH, and HexOH as solvents at 90, 110, 130, and 150 °C, respectively. A gravimetric methodology was used to weigh the DAMN polymers obtained and collected from the corresponding polymerization (gel fraction) performed for different times, from 24 to 168 h.[13,41] Figure 2a shows that the highest yields

are reached for HexOH (150 °C), although for the longest reaction times, equal results are obtained for the PentOH series (130 °C), which are almost quantitative. In fact, even though no kinetic model was applied, as that was not the aim here, both solvents show similar kinetic profiles, as shown by the lines drawn to guide the eye. At lower temperatures, 80 and 90 °C, both hydrothermal series also exhibit conversion limits after 48−72 h, although the yields are lower than those of the two previous series. In contrast, the ButOH series at 110 °C shows continuous conversion growth throughout the time

Scheme 1. Summary of the Main Chemical Network of DAMN According to Several Previous Works[46,49,55]
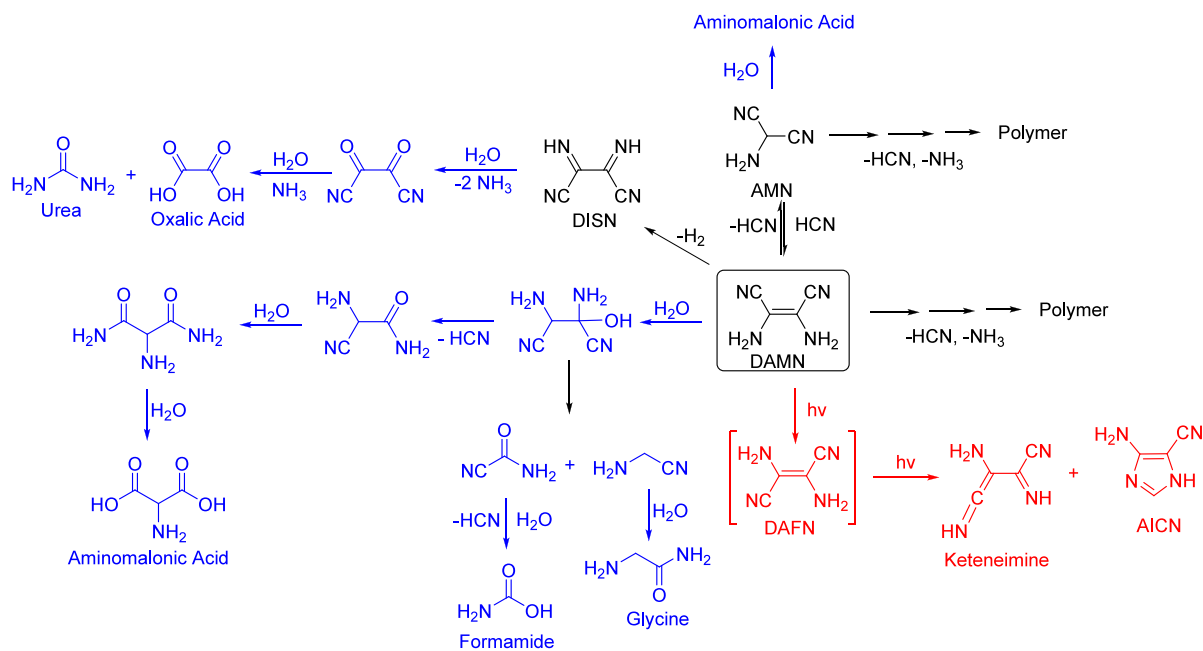
interval, reaching a maximum yield similar to that achieved with DAMN hydrothermal polymerization at 90 °C. Moreover, in Figure 2a, two zones may be differentiated: a kinetically controlled region at the beginning of the reaction, where the reaction is chemically controlled, and a diffusion control zone as the polymerization progresses (termination processes of the growing chain as well as cross-linking reactions), reaching a conversion limit. This same behavior has been well documented in the literature for aqueous HCN polymerization.[42]

In addition, considering previous studies,[43−45] the sol fractions were measured by UV−vis spectroscopy to monitor the consumption of DAMN (Figure 2b and Figure S1). Representative spectra of the PentOH series are shown in Figure 2b. The intensity of the DAMN absorbance band at 296 nm decreased with increasing reaction time, as expected. This tendency is found for the rest of the series under study, except for the ButOH series (Figure S1). In addition, spectrophotometry alone is nonspecific and may include absorptions related to other compounds generated during these polymerization reactions, which present very similar or equal UV−vis spectra. This fact motivated us to monitor these STP reactions by using an HPLC instrument coupled with a PDA detector to separate and accurately distinguish DAMN from other products in solution. The HPLC chromatograms of the sol fractions demonstrated that the separation and identification of DAMN can be readily achieved, as observed in Figure 2c,d for the hydrothermal (90 °C) and HexOH series, respectively. For the rest of the series, see Figure S3. However, note that the DAMN peak appears unfolded for the hydrothermal, PentOH, and HexOH series for shorter reaction times and for ButOH for all the times considered herein. This fact led us to think about the possible coelution of DAMN with its isomer DAFN and/or with its oxidation product, DISN (Scheme 1). DAFN has been found during the photoisomerization process of DAMN,[21,46−48] and DISN can form through the oxidation of DAMN during oligomerization, agreeing with Ferry's pioneering studies.[49] Therefore, both DAMN-derived compounds,

DISN and DAFN, were further analyzed by HPLC. DAMN and DAFN present the same retention time and the same absorbance response at 296 nm, i.e., both chromatographic peaks overlap perfectly (Figure 2e). The absorption of DISN at 296 nm is very low and cannot be properly identified with the method used herein (Figure 2e). In conclusion, the unfolding observed for the chromatographic peak of DAMN is not due to a coelution effect. This is due to the mixture of solvents used for sample injection and the high concentration of DAMN, as is clearly indicated in the inset plot of Figure 2e. Indeed, the small differences observed in the retention times for the unconsumed DAMN between the several series are also due to the different polarities of the initial solutions. Therefore, we cannot discard the coelution of DAFN and DISN with DAMN; only the unfolding of the peak is ruled out due the coelution of these analytes, since this unfolding is directly related to concentration and solvent effects, as it was demonstrated experimentally.

Figure 2f shows the HPLC results and the DAMN concentration as a function of polymerization time. Thus, for the HexOH series, a drastic decrease in the DAMN concentration is observed for the initial period of time, where the polymerization reaction is chemically controlled. However, a different tendency is found for the hydrothermal and PentOH series, and in these cases, a decrease in two consecutive steps or stages can be seen, reaching total consumption of DAMN for the longest reaction time. Moreover, the ButOH series presents a singular behavior according to the results extracted from the gravimetric data previously evaluated and agrees with UV−vis spectroscopy results.

From this analysis, it can be concluded that within the *n*-alcohols series, the efficiency of the DAMN STP reactions is strongly influenced by temperature, considering the DAMN conversion achieved as well as the quantification of its consumption. PentOH and, above all, HexOH seem to be ideal green solvents for the STP of DAMN, which is an
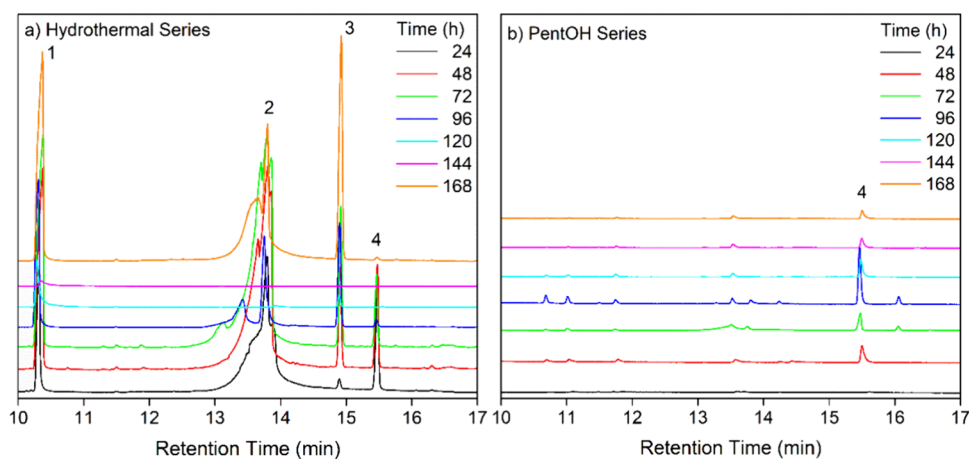
Figure 3. Representative GC−MS chromatograms of the sol fractions from DAMN STP: (a) hydrothermal series at 90 °C; (b) PentOH series at 130 °C. 1 = oxalic acid; 2 = urea; 3 = glycine; 4 = formamide.

alternative to hydrothermal processes where secondary reactions of hydrolysis have a relevant role, as discussed below.

3.3. Some Mechanistic Considerations for Hydrothermal Polymerizations. The chemical network of DAMN is quite complex. According to Ferris's studies[49−51] and a recent work,[46] a large variety of compounds can be produced from the hydrolysis, oxidation, and other multiple reactions of DAMN in aqueous environments (Scheme 1). Through DAMN oligomerization in water, DISN[52] could copolymerize with DAMN or undergoes decomposition into oxalic acid and urea. Furthermore, DAMN can be transformed into formamide, glycine, and aminomalonic acid and can also revert to the HCN trimer aminomalononitrile (AMN). AMN has a very low stability and can immediately react by polymerization[53−55] or can also be hydrolyzed to give aminomalonic acid. Scheme 1 includes the phototransformation of DAMN, where hydrogen-atom transfer was found to be the major process occurring upon UV excitation. As a result, two products were identified, ketenimine and 4-amino-1H-imidazole-5-cabonitrile (AICN), and it appears probable that, in the photochemical generation of both products, DAFN is involved.[46]

Therefore, the hydrolysis reactions proposed in Scheme 1, accompanying DAMN polymerization, could explain the lower yields observed in the hydrothermal series than in the PentOH and HexOH series. To test this hypothesis, the sol fractions from the hydrothermal series and from the PentOH series were analyzed by GC−MS. Thus, in the samples from the hydrothermal series, oxalic acid, glycine, urea, and formamide were identified (Figure 3a), whereas in the PentOH series, only tiny amounts of formamide were observed (Figure 3b). The presence of oxalic acid in the hydrothermal series was also confirmed by HPLC chromatograms (Figure 2c). However, this dicarboxylic acid was absent in the HPLC chromatograms of the alcohol series, in agreement with the GC−MS data. The hydrolysis products observed in the hydrothermal series can also explain the lower yield of DAMN polymers formed under these particular conditions when the temperature increased. High temperatures may improve the yield of the hydrolysis products of DAMN while hindering its polymerization.[14] Consequently, the use of *n*-alcohols at relatively high temperatures leads to more efficient DAMN polymerization than hydrothermal conditions since alcohols prevent the secondary hydrolysis reactions of DAMN. Nevertheless, the

use of water as a solvent is energetically more efficient because significantly lower reaction temperatures are needed.

Considering this important point, relevant questions arise. Is it possible that some of the products that accompany DAMN under hydrothermal conditions could exert a catalytic effect on the polymerization reaction? Could oxalic acid and DISN play a key role in the polymerization chemistry of DAMN? Therefore, further reactions were carried out to answer these questions: DAMN polymerization reactions were conducted using MeCN as the solvent at 80 °C, and 10% oxalic acid or DISN was added. After 48 h of reaction, the precipitated black solids were collected by filtration, washed with MeCN, and dried under reduced pressure using the same method used for all the above-mentioned synthetic series. Considering the weights of these solids, for the reaction with oxalic acid, a conversion of $12 \pm 3\%$ was calculated, and for the reaction in the presence of DISN, the conversion reached $20 \pm 1\%$ against the ~1% observed for the control experiment without additives. For both cases, the FTIR spectra of the isolated solids present wide features centered at approximately 3300, 2200, and 1640 cm^{-1} (Figure 4). These spectra resemble those
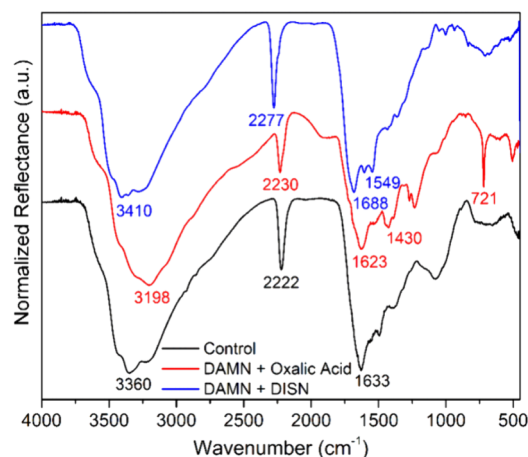

Figure 4. FTIR spectra of DAMN polymers from the reactions of DAMN (135 mg) in MeCN (5 mL) at 80 °C for 48 h in the presence of oxalic acid (red line) or DISN (blue line) at 10% by weight (13 mg). The black line represents the control experiment without additives.

Scheme 2. Hypothetical Structures from the Copolymerization of DAMN with Oxalic Acid and DISN
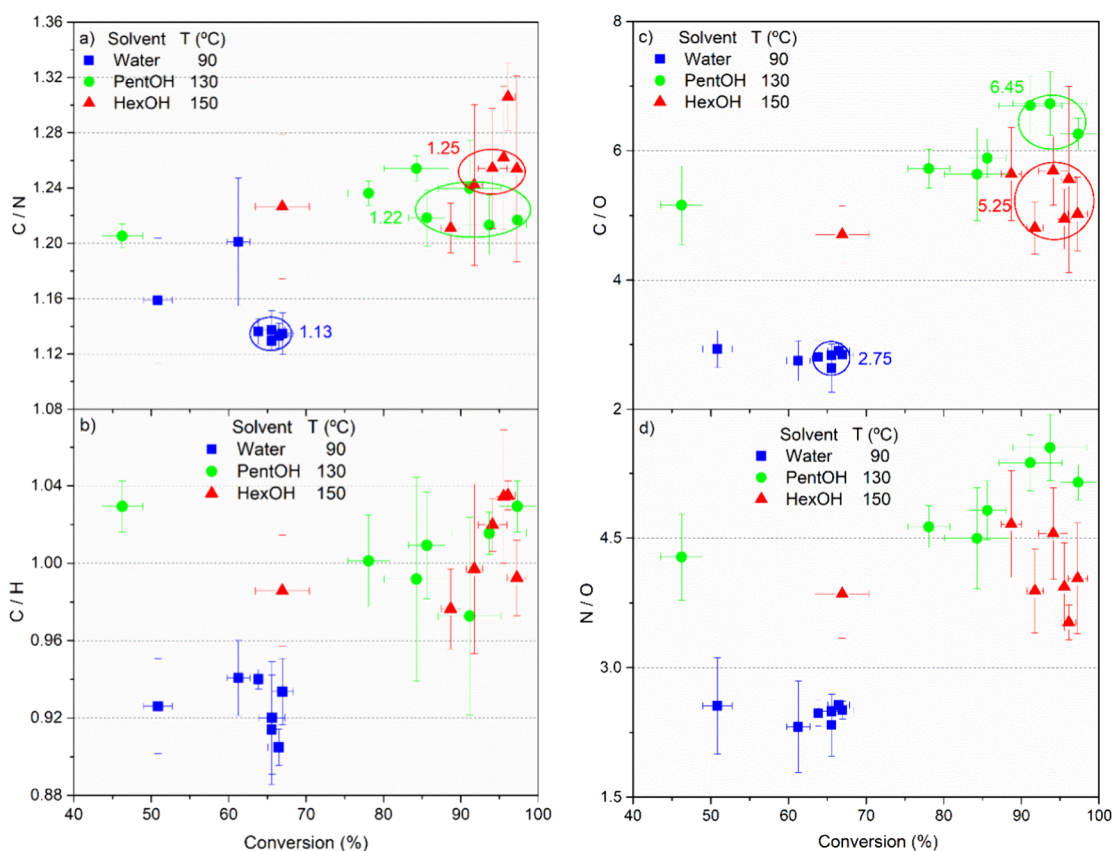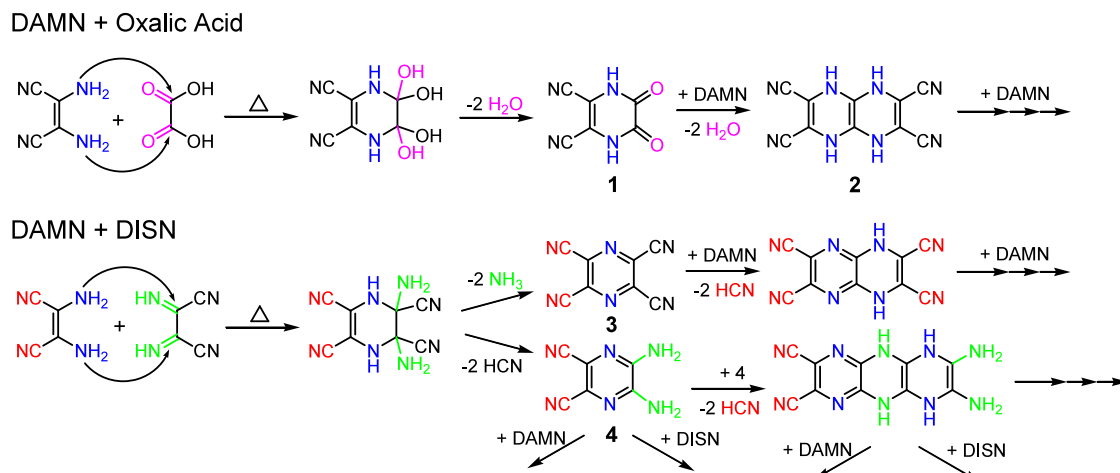

Figure 5. Molar relationships as a function of the conversion, α (%), for several DAMN polymers synthesized using different solvents and reaction temperatures (water, 90 °C; PentOH, 130 °C; HexOH, 150 °C): (a) C/N ratio, (b) C/H ratio, (c) C/O ratio, and (d) N/O ratio. These average values were calculated using the data from at least three independent experiments.

shown in Figure 1a for other DAMN polymers, indicating the success of these reactions. Therefore, the secondary reaction products released during the hydrothermal polymerization of DAMN, such as oxalic acid and DISN, could additionally contribute to the formation of insoluble DAMN-derived polymers through copolymerization processes.

The hypothetical frameworks of these copolymerization reactions are based on double nucleophilic attack by the amine groups of the same DAMN molecule, as illustrated in Scheme 2. After the elimination of water, the reaction of DAMN with oxalic acid might give 5,6-dioxo-1,4,5,6-tetrahydropyrazine-2,3-

dicarbonitrile **1**, which could continue reacting with a new DAMN molecule to yield 1,4,5,8-tetrahydropyrazino[2,3-*b*]pyrazine-2,3,6,7-tetracarbonitrile **2**. This proposal suggests the possibility of synthesizing extended ladder-type pyrazenes using repeated stepwise nucleophilic substitutions through nitrile groups. Similarly, the reaction with DISN involves a bisubstitution reaction, and if it occurs with NH_3 elimination, pyrazine-2,3,5,6-tetracarbonitrile **3** can be obtained, which can evolve in the same way as mentioned above. On the other hand, the addition reaction accompanied by a dehydrocyanation process might lead to the formation of 5,6-diaminopyr-
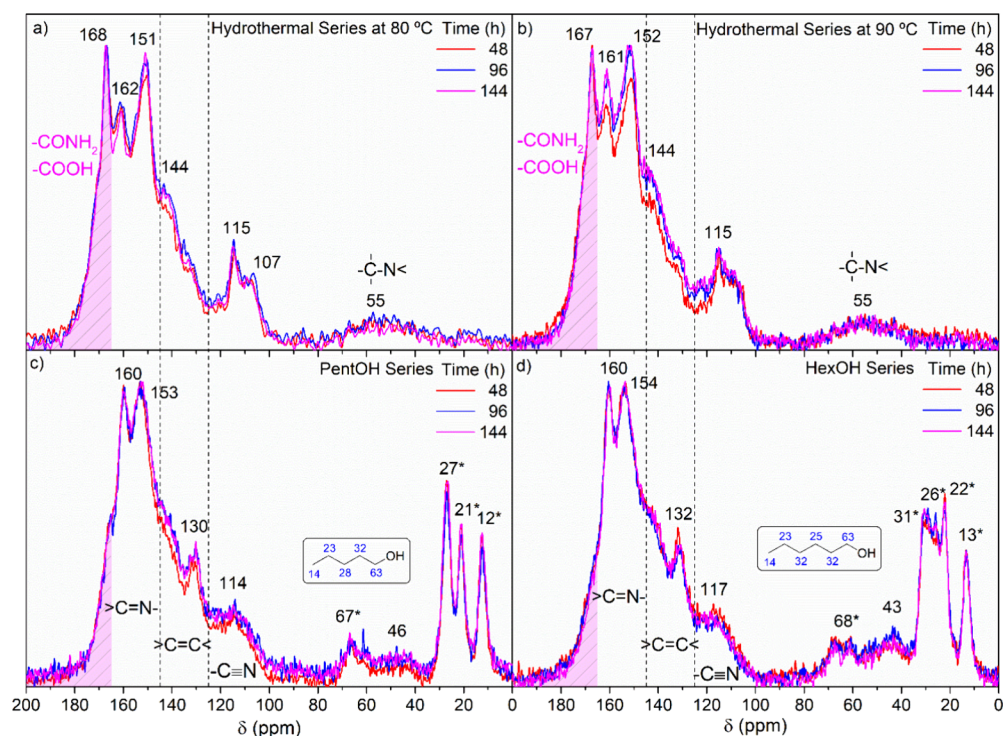
Figure 6. NMR spectra of DAMN polymers from hydrothermal synthesis (a, b) and from solvothermal synthesis in (c) PentOH and (d) HexOH.

azine-2,3-dicarbonitrile **4**. This pyrazine system with amine groups can undergo different condensation reactions, either with itself, as indicated in this scheme, or with another DAMN molecule or even with DISN due to the imine groups having higher electrophilicity than the nitrile groups. This copolymerization of DAMN-DISN reflects greater synthetic versatility than that in the presence of oxalic acid, as suggested in this scheme; therefore, this is in accordance with the higher yields found for this particular reaction.

These DAMN copolymers could in turn act as macromolecular catalysts for the main polymerization reactions of DAMN. This proposal is based on experimental evidence confirming the autocatalytic nature of HCN polymers. This was demonstrated by initiating a toluene solution of HCN with a preexisting dark HCN polymer, resulting in the accelerated formation of new polymers.[9] In this case, DAMN polymerization in water would be improved by, on the one hand, the generation of monomer−solvent intermolecular complexes (as explained above) and, on the other hand, organocatalysis processes.[56] Why, then, does increasing temperature cause a decrease in the yields of DAMN polymers? This is likely because high temperatures favor some reaction kinetics over others in the complex network of DAMN aqueous chemistry, generating more secondary reaction products that cannot lead to the formation of macromolecular structures and/or organocatalysts. Moreover, a behavior similar to oscillatory processes is observed in the diffusion control region of the hydrothermal DAMN polymers (Figure 2a), which could suggest a Lotka−Volterra predator−prey model. The testing of these new mechanistic hypotheses is beyond the scope of the present paper, and they will be addressed in further work but clearly indicate the singular role of water in DAMN polymerization and an extension in HCN chemistry.

At this point, by determining the solvents in which DAMN polymerization is effective and exploring the reaction kinetics,

as well as some mechanistic aspects, in the next sections, we will analyze the evolution of the structural and thermal characteristics of DAMN polymers in relation to the conversion degree of the system.

3.4. Dependence of the Chemical Composition, Microstructure, and Thermal Properties on the Synthetic Polymerization Conditions. A comparative study of the DAMN polymers obtained from the aqueous reactions at 90 °C and through the alcohol-based STP, PentOH, and HexOH series is described. The ButOH series was not considered since no conversion limit for this solvent was observed for the reaction times chosen herein.

3.4.1. Elemental Composition of the STP Series. In general, the skeleton for the macrostructures obtained from DAMN proposed in the literature is based on a conjugated C=N system containing diaza heterocyclics, mainly imidazole and pyrazole rings.[9,11,13,14,30] Thus, to observe possible differences in the DAMN polymers from the aqueous series and from the *n*-alcohols, the C/N molar relationships were calculated and evaluated as a function of the degree of conversion (Figure 5a). Notably, there is a difference in the C/N relationships between the hydrothermal series and the *n*-alcohol series. The DAMN polymers from aqueous dispersions, with C/N = 1.13, are richer in nitrogen than those from the alcohol series, with C/N values of approximately 1.22 and 1.25 for PentOH and HexOH, respectively. Similarly, at the C/H molar ratio (Figure 5b), the DAMN polymers from the hydrothermal syntheses present a greater amount of hydrogen than those from the other two series, likely indicating a lower degree of conjugation and/or a greater number of functional groups, such as amine and/or hydroxyl groups.

In agreement with the greater functionalization of the macrostructures, a significant amount of oxygen was present in the DAMN polymers from the hydrothermal series (Figure 5c,d). Thus, for example, C/O is 2.75 for the polymerization
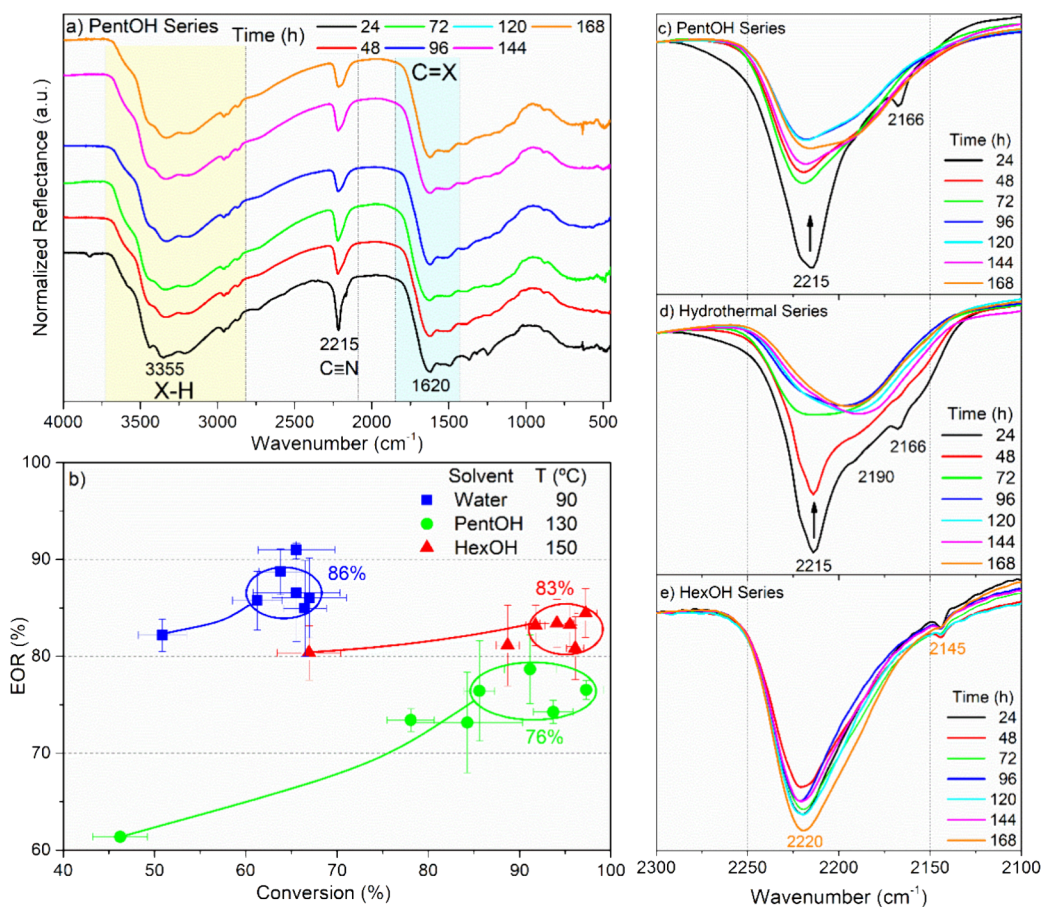
Figure 7. (a) FTIR spectra of the PentOH series; (b) extension of the reaction (EOR) as a function of the degree of conversion; (c−e) FTIR spectra of the nitrile groups in the PentOH, hydrothermal, and HexOH series, respectively.

reactions in the presence of water, 5.25 for HexOH, and 6.45 when PentOH is used as the reaction solvent. These data seem to indicate not only the incorporation of oxygenated functional groups in the polymeric macrostructures from the hydrothermal environment but also the presence of water molecules trapped in the macromolecular networks, as will be shown by thermogravimetric analysis. In the case of the *n*-alcohol series, the presence of oxygen in the DAMN polymers is logically lower, although not absent. As indicated above, HCN-derived polymers are generally highly hydrophilic, so the presence of water, solvent molecules, and other side reaction products (no anhydrous solvents were used) absorbed or occluded inside the polymeric chains cannot be discarded. Moreover, the occlusion of solvent molecules in nitrile polymer chains has been previously reported, and the fault in their elimination despite conscientious drying processes has been related to strong polar interactions between the solvent and these macromolecular systems.[57] The DAMN polymers from the syntheses using PentOH and HexOH are not an exception, and solvent molecules are occluded in their macrostructures despite being carefully dried, as revealed by NMR spectroscopy in the next section.

Therefore, the DAMN polymers from the *n*-alcohol series are clearly less functionalized, more carbonaceous, and conjugated than those from the hydrothermal series, and the presence of oxygen in these polymers can be mainly associated with alcohol molecules trapped in their macrostructures.

Finally, when the conversion limits are reached, the chemical compositions of the DAMN polymers are not significantly

different for any of the STP reactions. In addition, the frameworks of the macrostructures with a highly conjugated C═N system for the PentOH and HexOH series must be practically equal considering the C/N and C/H molar relationships, and only slight differences were found in the oxygen content between these two series. Lower molar C/O and N/O relationships were observed for the STP reactions in the presence of HexOH, indicating more oxygen for these DAMN polymers.

3.4.2. NMR Spectroscopy. Figure 6 shows the solid-state CP MAS ^{13}C NMR spectra of the DAMN polymers from the hydrothermal series at 80 and 90 °C and from the alcohol series with PentOH and HexOH. Taking the spectra of the hydrothermal series at 80 °C as a reference (Figure 6a), no apparent variations are observed when the polymerization temperature is increased to 90 °C (Figure 6b), and only slight differences are found with respect to the rest of the other series. In all the cases studied, the spectra exhibit broad resonances in accordance with the extended complex conjugated structures[58] and with the paramagnetic nature of these types of macromolecular systems.[30,42,59] A detailed discussion of the spectral characteristics of the 80 °C series was provided elsewhere;[13] however, in brief, the observed resonances at low fields up to ~145 ppm can be attributed to imine carbons on a linear segment or block and >C═N− occurring in pyrazines or imidazole rings on the macromolecular chains. Three well-differentiated peaks can be detected under hydrothermal conditions, but for both alcohol series, the peak at ~168 ppm only appears as a minor shoulder.
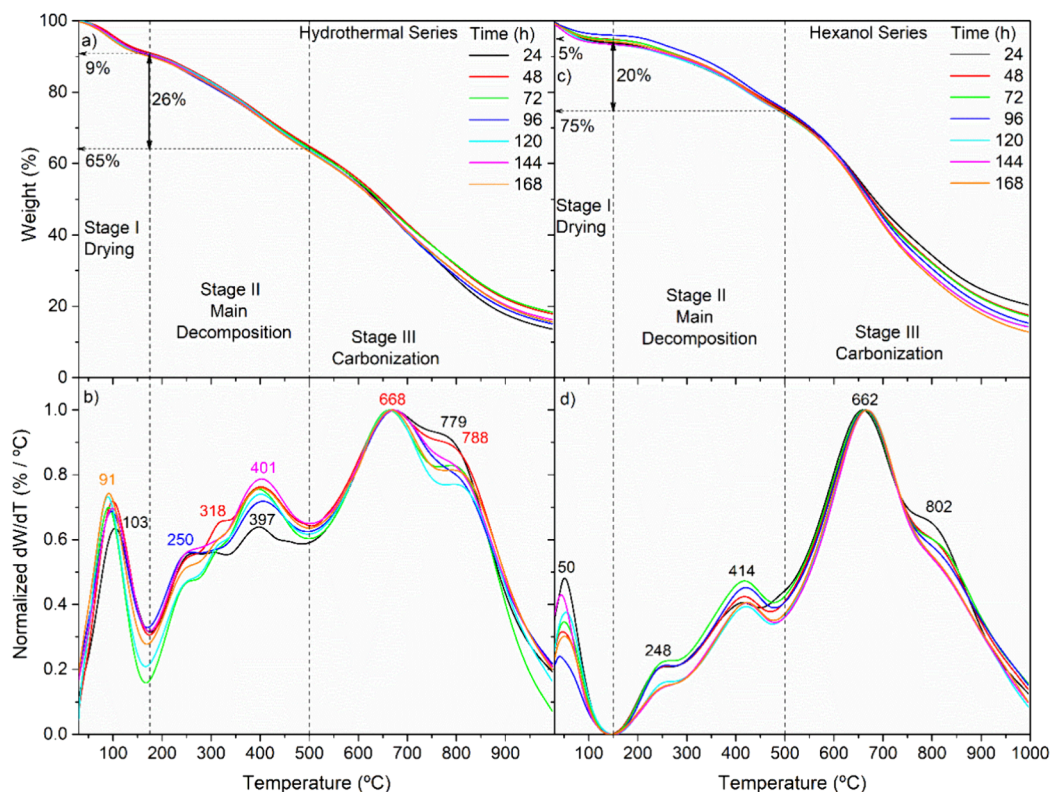
Figure 8. TG and DTG curves at a heating rate of 10 °C/min under an Ar flow of the DAMN polymers from (a, b) hydrothermal and (c, d) HexOH series.

The resonances above 165 ppm could be assigned to carbon atoms associated with nitrogen but also with oxygen, such as amides, likely from the hydrolysis of cyanide groups, since these features are practically not observed in the organic series, as illustrated in this figure.

In contrast, in the >C=C< region indicated in the interval 145−125 ppm, the samples synthesized in the presence of PentOH and HexOH show a well-defined peak at approximately 130 ppm, which is not observed in the hydrothermal series. The region at 120−100 ppm is related to nitrile groups, and the relative decrease in the intensity of these −C≡N signals with respect to the resonances at 161 and 152 ppm (imine region) with reaction time is in good agreement with the variation in the FTIR parameters with reaction time, as indicated in the next section. This fact is especially notable in the sample obtained after 48 h of polymerization in water at 90 °C (Figure 6b). Finally, the broad resonances at 55 ppm may be related to carbon atoms joined by a single bond to a nitrogen atom. In this area, at lower chemical shifts, some additional signals are found in the NMR spectra of the samples obtained when these *n*-alcohols are used as solvents. In Figure 6c,d, the resonances marked with an asterisk correspond to the carbon atoms of the solvent molecules occluded in the macrostructures of the DAMN polymers from the PentOH and HexOH series, respectively, indicating the presence of oxygen in these polymers.

3.4.3. FTIR Spectroscopy. As previously shown (Figure 1a), the FTIR spectra of the DAMN polymers are characterized by their broad and poorly resolved bands in all the spectral regions. The same profiles can also be seen in Figure 7a, where FTIR spectra of the PentOH series were collected for different reaction times. Apparently, no significant differences were found between them or when the spectral characteristics of the other series were inspected (Figure S4). They show similar patterns in all cases, with a broad band between 3600 and 2700 cm^{-1} attributed to the stretching of the N−H band of primary and secondary amines, although their great width also accounts for OH groups and even C−H at approximately 3000 cm^{-1}; therefore, they could be renamed the X-H region. The cyano group manifests itself in all solids isolated through bands centered at ∼2215 cm^{-1}. Finally, the strong absorption close to 1630 cm^{-1} is attributed to C=N stretching, along with C=C (designated as C=X), and other vibrations of different functions because it extends over a wide region of the spectrum almost up to 1000 cm^{-1}, where distinct heterocycles are also present, which has been postulated to be a main part of the chains of DAMN polymers.

To semiquantify some differences between them, the EOR was calculated for each spectrum. The EOR takes values from 0 to 100 as a function of the gradual disappearance of nitrile (C≡N) absorption and the increase in conjugation (C=N and C=C) absorption in this region, and an increase in this value is expected when conversion occurs.[41] The EOR values for each reaction using water, PentOH, or HexOH as solvents are represented against the conversion in Figure 7b. Notably, the EORs for the hydrothermal series are slightly greater than those for the other two *n*-alcohol series, even with lower conversion values. This result might be related to the hydrolysis reactions of the nitrile groups during the formation of the DAMN polymeric macrostructures. On the other hand, the EOR values for the PentOH series are the lowest observed for all the DAMN polymers considered herein, which may indicate a lower reactivity of the cyanide groups under these particular thermal conditions. In addition, in this series, an
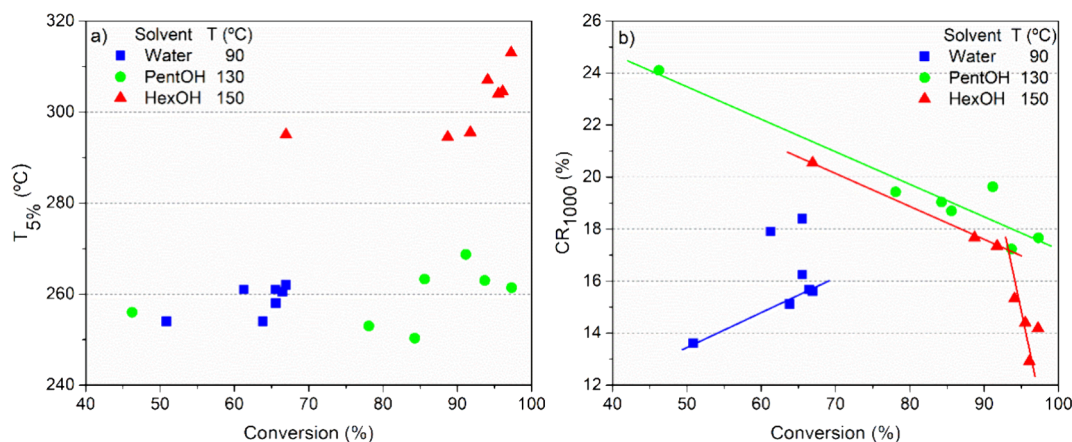
Figure 9. (a) $T_{5\%}$ values; (b) char at 1000 °C as a function of the conversion obtained from TG analysis of the DAMN polymers after heating the samples to 1000 °C at 10 °C/min under an Ar flow.

increase in EOR with the degree of conversion is more clearly observed. Moreover, the three series were compared using the nitrile region at ≈2200 cm^{-1} since it is more representative of HCN-derived polymers[60] (Figure 7c−e). The practical null variation in intensity and shape of this band with respect to the reaction time for the HexOH series (Figure 7e) is significant compared with that for the other two series, in which a clear evolution of this feature is observed more notably for the hydrothermal series (Figure 7c,d). This fact must be related to the collateral reactions that accompany the DAMN polymerization, such as the hydrolysis reaction of the nitrile groups, as previously mentioned and which might occur to a minimum (or null) extent if n-hexanol is present in the reaction medium. Moreover, the final position of this band (corresponding to the reaction times and conversions of the diffusion control region, time > 72 h) for the hydrothermal series is clearly different from that for the other series, again indicating the singularity introduced for the water in the DAMN polymerization reactions, as indicated above and shown by the results of the thermal analysis.

3.4.4. Thermal Profiles. The TG curves for all the samples of the hydrothermal series are shown in Figure 8a, while Figure 8c shows the corresponding thermodegradative profiles for the HexOH series; for the PentOH series, please see Figure S5. The usual three thermal decomposition stages are observed for all the samples, although the first stage is actually a thermal drying process in which solvent molecules or compounds generated during the course of STP are eliminated. This first stage occurs between 25 and 175 °C for the hydrothermal series. Peaks centered at approximately 100 °C are observed in the derivative thermogravimetry (DTG) curves (Figure 8b). These peaks can be assigned to the dehydration process and are related to a weight loss of approximately 9%. This result proves the extraordinary hydrophilicity of the DAMN polymers from this hydrothermal series. In contrast, for the two alcohol series, this first stage occurred from 25 to 150 °C. In this case, DTG peaks are observed at ∼50 °C (Figure 8d), which suggests that the thermal desorption of some compounds likely occurred during the careful drying of the samples and/or absorption from the ambient environment, not due to solvent molecules, and is associated with a lower weight loss, with an average value of 5%. The second degradation stage reached 500 °C. This stage is due to the breaking of the weakest bonds within the macromolecular chains. Again,

significant differences were found between the series. For the hydrothermal series, after the first dehydration step, a weight loss of 26% is observed, while for the HexOH series, this value is only 20%. Finally, in the carbonization stage (from 500 to 1000 °C), the maximum weight loss rate occurs at approximately 670 °C for all the series, which is related to the main endothermic decomposition process, as observed in the corresponding DSC curves (Figure S6). However, in this last stage, the DTG profiles also present differences, especially related to the last peaks close to 800 °C. These peaks are more prominent for the hydrothermal series. These DTG curves seem to indicate that the DAMN polymers from all the series present a main common structure with a higher grade of functionalization and/or more labile thermal secondary structures for the case of the polymers from the hydrothermal series, in agreement with the elemental analysis data reported above. In addition, these differences observed for the hydrothermal series could also be related to potential mixtures of the main structure with the copolymers derived from DAMN, which are likely produced in aqueous environments, as suggested above.

Furthermore, differences in microstructure become apparent when analyzing characteristic decomposition temperatures and other parameters, such as the percentage of ash. Figure 9a,b shows the 5% ($T_{5\%}$) weight loss temperatures and the char residues at 1000 °C (CR_{1000}), respectively, as a function of DAMN conversion. Note that these specific $T_{5\%}$ values were determined after the first drying stage to determine the thermal stability of these samples. Thus, the $T_{5\%}$ values for the DAMN polymers from the hydrothermal series are comparable to those of the PentOH series when the conversion limits are reached (∼230−250 °C), whereas the values for the HexOH series are much greater. Thus, the HexOH series seems to present structures with a minor percentage of thermolabile pendant groups. On the other hand, Figure 9b shows that the DAMN polymers from the PentOH series exhibit higher values of char, and a decreasing linear trend of the amount of ash with respect to the degree of conversion is observed. A similar tendency is observed for the HexOH series, although a sharp reduction in the char values is found at the highest conversions, above 90%. In contrast, for the hydrothermal series, a direct relationship between the char percentages and conversion is not observed, with values comparable to those of the other two series. These results provide structural

Scheme 3. Proposed Synthetic Routes with an Initiation Stage via Bicondensation between Nitrile and Amine Groups for DAMN Polymerization
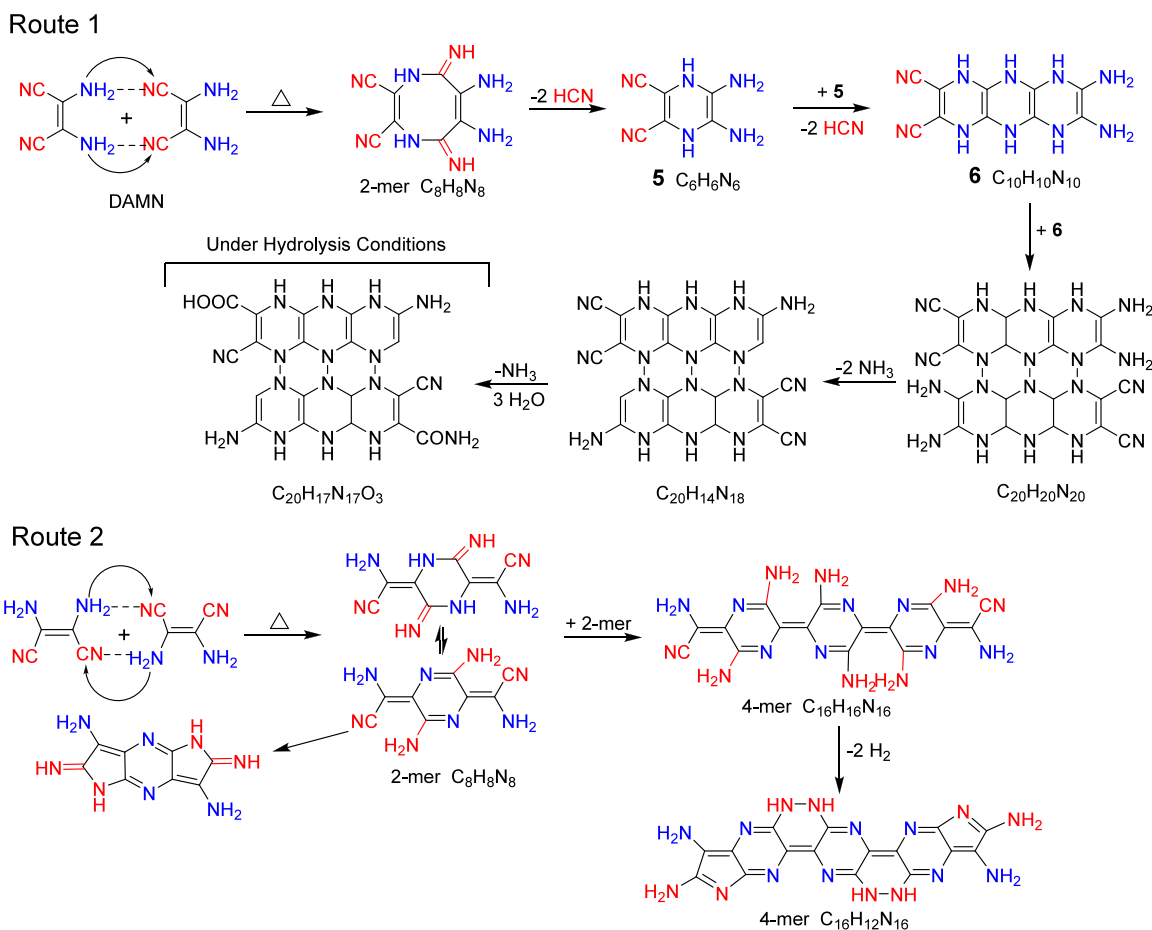
information about the studied polymeric system since cyclic and heterocyclic rings contribute to the char yield. Thus, DAMN polymers with CR_{1000} values above 20% may have greater proportions of heterocyclic systems in their macrostructures. However, it should not be forgotten that these values can also be affected by the degree of cross-linking during the thermal degradation process. At this point, only CR_{1000} can indicate the different behaviors of the hydrothermal series compared to the other series due to the clear structural differences observed by elemental analysis and NMR and FTIR spectroscopy. Moreover, although the PentOH and HexOH series resemble each other, also direct variances are observed between them, likely due to the increase in the synthesis temperature.

As a result of all of the data discussed in this section, for all of the STP series studied, no chemical composition or spectral variations were observed once the conversion limits were reached, and in the case of the DTG curve profiles, no significant changes were found. That is, after 72 h for the hydrothermal series and after 96 and 120 h for the HexOH and PentOH series, respectively, the properties of the DAMN polymers remain unchanged. On the other hand, while there is a clear thermal synthetic effect on the characteristics of the DAMN polymers from the PentOH and HexOH series, the presence of water even more significantly increases the macrostructural differences.

3.5. Intramolecular Hydrogen Bonds as a Key Factor for DAMN Polycyclocondensation. In this last section, two

hypothetical mechanisms are suggested to explain the production of DAMN polymers via self-cyclocondensation (Scheme 3). Both postulated pathways propose the formation of intramolecular hydrogen bonds between the DAMN molecules involved in the initial step of polymerization. This proposal underlines the importance of these types of bonds in DAMN chemistry, as has been shown in this work and as has been recently described elsewhere.[61] Indeed, the crucial role of water and alcohols as solvents in other DAMN condensation reactions has been reported.[62]

In a previous study on bulk DAMN polymerization, we postulated that its oligomerization occurs via different synthetic routes, both through the addition of nitrile groups and through the addition of imine groups, the latter of which is from the tautomeric form of DAMN. However, in both cases, only a single nucleophilic attack by amine groups at these electrophilic centers was considered (see Schemes 1 and 2 in ref 30). However, the results shown above, which indicate certain synthetic analogies with organic molecular materials based on DAMN,[62,63] may lead us to consider the possibility of the formation of extended ladder-type structures using repeated stepwise double nucleophilic substitutions, as indicated in Scheme 3, and in accordance with the synthetic methods proposed in Scheme 2 for the likely copolymerization of DAMN.

Thus, in route 1, the formation of 5,6-diamino-1,4-dihidropyrazine-2,3-dicarbonitrile **5** from the condensation of two DAMN molecules occurs in the first step. This method of

reacting DAMN is the same as that described by Richards et al. for the synthesis of pyrazinacenes composed of fused pyrazine rings.[63] Thus, the formation of a derivative of 1,4-diazocine (2-mer), which is converted to an *N*,*N*′-dihydropyrazine ring after the elimination of two HCN molecules, is proposed. Herein, the identification of formamide by GC−MS in all cases, as a hydrolysis product of HCN, might indicate these decyanation processes. In a consecutive step, this dihydropyrazine could undergo self-condensation to give oligopyrazine **6**, which could lead to a graphitic macrostructure and a deamination reaction. Hydrolysis of the cyano groups has also been included in route 1 to respond to the formation of oxygenated functional groups, especially when the polymerization reactions are carried out by hydrothermal methods.

On the other hand, in route 2, another possible self-bicondensation of DAMN is proposed considering the different orientations of the two DAMN molecules involved in this first step to give the corresponding dimer. This synthetic method is based on the fact that tetracyanoquinodimethane undergoes a similar double nucleophilic substitution of two of its nitrile groups by amines or alcohols.[64,65] In this case, dihydropyrazine is formed without the elimination of HCN molecules, and it can react with another molecule to give the oligomer 4-mer with seven fused rings suggested here after new intramolecular cyclization reactions, some of which have also been indicated on the formulated dimer. Both oligomers present imino and amino end functional groups, which can condense in subsequent stages, although they can also be hydrolyzed or oxidized, as has been contemplated in route 1. Note that some of the polymeric structures proposed in route 2 are free of cyanide groups, which is not in agreement with the FTIR spectroscopic data or with the NMR spectra shown above. However, a final mixture of C=N-based macro-structures cannot be ruled out, some of which have terminal −CN groups and others are free of terminal −CN groups.

These two hypothetical pathways are only reasonable conjectures based on the data available here, despite the poor information provided by spectroscopy techniques due to the high heterogeneity and complexity of HCN-derived polymers. Both the NMR and FTIR spectra correlate with those reported previously for other DAMN polymers; therefore, the pathways discussed here can be considered to complete other reaction mechanisms before being described elsewhere.[9,11,13,14,30]

4. OUTLOOK AND CONCLUDING REMARKS

Most of the literature employing the term STP deals with the radical polymerization of different vinyl monomers;[66] however, polycondensation reactions using this synthetic methodology are scarce. Only recently, high-performance polyheterocyclics, such as polyimides, have been synthesized via STP.[66,67] Thus, interestingly, the results discussed herein have shown one-step STP synthetic processes, which yield clean polymer particles that are free of any surfactants and/or cross-linkers. The separation of the products was simple, and the production method for the DAMN polymers was also eco-friendly, since green solvents were used. These factors might facilitate potential synthetic scaling at the industrial level for these singular polymeric systems.

Although the hydrothermal polymerization of DAMN is prominent among HCN-derived polymer synthesis techniques, this study has introduced new, straightforward, experimentally simple, and environmentally answerable synthetic strategies

based on STP for producing a novel generation of conjugated functional materials, which serve as alternatives to the widely recognized *g*-CNs.[30] From the foundational methodology presented here to the remarkable tunable properties of HCN-derived polymers synthesized via microwave radiation (MWR)-assisted reactions,[14,68] our group is currently advancing research to develop innovative DAMN polymers using this promising approach, since it is extensively accepted that MWR substantially decreases the reaction time polymerizations. In this way, DAMN polymers have successfully synthesized under hydrothermal conditions in as little as 4 min.[14] On the other hand, the highly efficient melt polymerization of this monomer is achieved with a reaction time of only 10 min.[30] These two protocols represent the fastest procedures established to date for the synthesis of DAMN polymers. The MWR-assisted synthetic technique faced the challenge of low yields (around 35%) but produced uniform nanoparticles. In contrast, the bulk approach resulted in DAMN polymers with very high conversion degree (approximately 90%) but produced larger particles with irregular and poorly defined shapes. However, it is expected that the DAMN polymers synthesized using *n*-alcohols present similar macromolecular structures and catalytic and semiconducting properties to those DAMN polymers synthesized in bulk, since the aqueous side reactions are absent. Further comparative works are in progress to test this resemblance and it is projected that MWR-driven polymerizations of DAMN using *n*-alcohols might lead to similar materials to those synthesized in bulk but with improved morphological properties. Therefore, considering the previous findings and the methodology herein described, the MWR-assisted polymerization of DAMN with *n*-alcohols as solvents is predictable to be a valuable, efficient, and quick synthetic strategy to the further development of polymeric multifunctional nanomaterials.

n-Hexanol provides excellent synthetic results with almost quantitative yields in the production of DAMN polymers and the results shown here indicate the beneficial role of water in increasing molecular complexity. At the industrial level, clean processes with the lowest byproducts input are of interest; in prebiotic chemistry, the opposite is stimulating. We have shown that water could lead to the generation of side reactions and likely copolymerization, considerably increasing molecular complexity in possible prebiotic scenarios; i.e., water as a life-related solvent seems to be directly involved in molecular evolution processes. That is, at the industrial level, clean solvents that are as inert as possible and do not interfere with the main synthetic process are needed; however, for studies on the origin of life, understanding the role that water could play in a possible protobiochemistry is imperative.[69,70]

Therefore, as a main conclusion, in this work, we have shown that conjugated materials based on −C=N− structures can be obtained almost quantitatively from DAMN using alcohols as green solvents and that water is not an inert solvent but one that can modulate the properties of prebiotic systems.

■ ASSOCIATED CONTENT

Data Availability Statement

The processed data underlying this study are available in the published article and its Supporting Information. The raw data (replicates) are available from the corresponding author upon request.

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Notes

The authors declare no competing financial interest.

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