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Polyurethane Incorporating Oxidatively Degradable Diacylhydrazine Moiety: Synthesis, Characterization, and Thermal Analysis

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Abstract

Oxidatively degradable and thermally stable polyurethanes incorporating diacylhydrazine moieties were synthesized via solution polymerization of 4-hydroxy-*N*'-(4-hydroxybenzoyl)benzohydrazide with hexamethylene diisocyanate and toluene-2,4-diisocyanate. Structural characterization by NMR and IR confirmed the successful incorporation of diacylhydrazine and carbamate groups. TGA-DTA analysis revealed multi step thermal degradation with high stability. The polymers exhibited rapid oxidative degradation in 10% aqueous sodium hypochlorite (NaClO) solution, yielding carboxylic acids. Strong intermolecular hydrogen bonding rendered them insoluble in most organic solvents but soluble in highly polar media such as NMP and concentrated H_2SO_4. This study presents a versatile strategy for designing polyurethanes with both thermal robustness and controlled oxidative degradability.

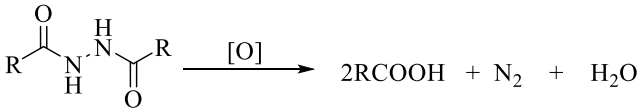
Keywords: Oxidative degradation, Diacylhydrazine, Polyurethane, TGA-DTA, Diisocyanates

I. Introduction

Polyurethanes (PUs) represent an important class of thermoplastic and thermoset polymers as their mechanical, thermal, and chemical properties can be tailored by the reaction of various diols and diisocyanates. PUs are polymers characterized by the presence of a substantial number of urethane linkages (–HN–COO–), irrespective of the remaining molecular structure [1-2]. Polyurethanes are one of the most versatile materials in the world, have become the integral part of modern life [3-4]. They are integrated into nearly every part of our daily lives—embedded in the shoes we wear, the cushions we sit on, the carpets and underlays beneath our feet, the fibers in our clothing, and the insulation within our homes. They are found in household appliances such as refrigerators and water heaters, as well as in automobiles—ranging from seating and structural foams to paints and coatings. Even our furniture and mattresses rely on them. Quite simply, their presence is widespread and indispensable [5-6].

Polymeric waste pollution has become a serious concern in recent times, leading to growing interest in the development of degradable polymers. Among the degradable polymers, biodegradable and photodegradable are most common. Biodegradable polymers offer several advantages, but we cannot control the degradation of biodegradable and photodegradable polymers. An oxidatively degradable polymer that remains thermally stable during use but decomposes upon exposure to an oxidative trigger could provide an excellent solution to this problem.

Recently, poly(diacylhydrazine) (PDAH), a polyamide in which hydrazine serves as the diamine component, has emerged as a promising oxidatively degradable polymer. It undergoes rapid decomposition in the presence of oxidizing agents such as sodium hypochlorite solution, while maintaining stability under exposure to oxygen and hydrogen peroxide, even in the presence of transition metal ions. The degradability is attributed to the oxidative degradation of the dicyclohexylhydrazine group. This process yields carboxylic acid and nitrogen gas as the primary degradation products. Both by-products are environmentally benign, with nitrogen gas being inert and non-toxic, while the resulting carboxylic acid can be recovered and potentially reused in the synthesis of the original monomer (**Scheme 1**)[7-9].



Scheme 1 Oxidative degradation of diacylhydrazine group

PDAH also exhibits high thermal stability in air, along with a high glass transition temperature (T_g); notably, no T_g is observed below its decomposition temperature (T_d). In addition, epoxy resins derived from bisphenols functionalized with diacylhydrazine moieties have demonstrated similar oxidative degradability. These resins serve as strong and durable adhesives for metal and glass, yet can be easily and cleanly removed upon treatment with sodium hypochlorite, leaving no residue[10]. K. Wongwailikhit et al. further reported that L-leucine-based poly(diacylhydrazine) exhibits high thermal and chemical stability during use, while undergoing oxidative degradation in the presence of sodium hypochlorite as an oxidative trigger[11]. Moreover, the incorporation of diacylhydrazine moieties into the main chain of polyesters has also been shown to impart oxidative degradability to the resulting materials[12].

In this work, we have synthesized some novel polyurethanes, which are non-biodegradable, but degrade by the action of NaOCl solution. Upon degradation of these

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polymers, environmentally safe products are formed. The degraded products can be reused to synthesize the starting material of the same polymer. In addition to their degradable properties, they show high thermal stability.

II. Experimental

Chemicals and Reagents

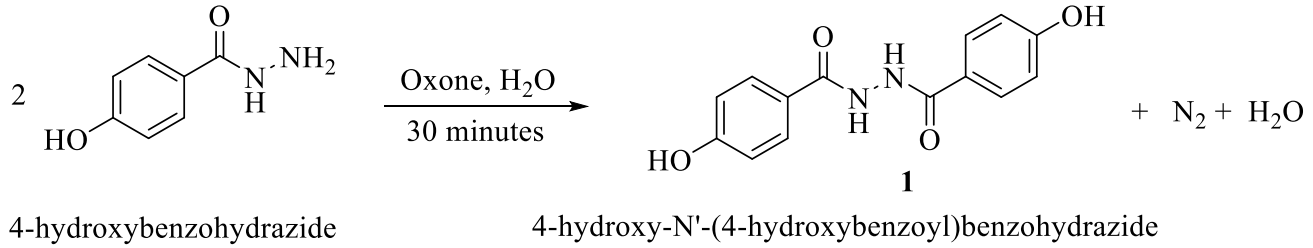
Oxone® ($2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$) (Sigma Aldrich, Germany), 4-Hydroxybenzhydrazide (Alfa Aesar, UK 98.0% purity), Hexamethylene diisocyanate **2a** (TCI, Japan, 98.0 % purity), Toluene-2,4-diisocyanate **2b** (Sigma Aldrich, USA, 80.0 % purity), N-Methyl-2-pyrrolidone (NMP), (Alfa Aesar, UK, 99% purity) were utilized as main chemicals for this research work. All the chemicals were of reagent grade and were utilized without further purification.

Instruments

The ^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. All chemical shifts are reported in δ ppm value using deuterated DMSO solvent. The IR spectra were recorded on Bruker Alpha II spectrometers. TGAs were carried out using a thermogravimetric analyzer (TG/DTA/DTG 6300 Seiko Instrument, Japan).

Synthesis of 4-hydroxy-N'-(4-hydroxybenzoyl) benzohydrazide 1

4-Hydroxy-N′-(4-hydroxybenzoyl)benzohydrazide was synthesized following our previously reported procedure as well as the method described by Kulkarni *et al* [12-13]. Briefly, an aqueous solution of 4-hydroxybenzohydrazide (10 mmol, 1.521 g) in distilled water (250 mL) was treated with Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 1.0 equiv., 3.075 g) at room temperature. The reaction mixture was stirred for 30 min, during which oxidative coupling of two molecules of 4-hydroxybenzohydrazide occurred, leading to the formation of the desired product. As the reaction progressed, the solution gradually deepened in color and a yellow precipitate of 4-hydroxy-N′-(4-hydroxybenzoyl) benzohydrazide **(1)** formed **(Scheme 2)**. The precipitated solid was collected by suction filtration through Whatman filter paper, thoroughly washed with water, and oven-dried to afford the pure product.



Scheme 2 Synthesis of diol 1 by oxidative coupling[12-13]

Yield: 45% (approx.). mp: 261°C. ^{1}H NMR (400MHz, δ ppm, d_6-DMSO): 10.14 (s, 2H, -OH), 10.13 (s, 2H, hydrazide NH proton), 7.78 (d, 2H, J=8.4, Ar-H), 6.84 (d, 2H, J=8.8, Ar-H). ^{13}C NMR (100 MHz, δ ppm, d_6-DMSO): 166.1, 161.0, 129.9, 123.8, 115.5. IR: ν= 3395 cm^{-1} (N-H stretching), 3285 cm^{-1} (broad, O-H stretching), 2970 cm^{-1} (C-H stretching), 1671 cm^{-1} (C=O stretching of diacylhydrazine).

General Synthetic Procedure for Polyurethane Synthesis Containing Diacylhydrazine Moiety

Solution polymerization was performed by reacting equimolar amounts of the synthesized diol **1** with various diisocyanates **2** in NMP **(Scheme 3)**, yielding the desired polyurethane **3**, which remained soluble in NMP. The resulting polymer was purified by precipitating the reaction mixture into water, a nonsolvent, to remove unreacted monomers, oligomers, and residual solvent, affording the polyurethane as an insoluble precipitate.

Synthesis of Polyurethane 3a

A solution of **1** (0.272 g, 1 mmol) in NMP (5 mL) was reacted with 1,6-hexamethylenediisocyanate **2a** (0.168 g, 1 mmol). The mixture was stirred for 24 or 48 h, then precipitated dropwise into water (90 mL), with constant stirring for 30 min. Then, it was filtered, washed with water, and dried in oven to yield an off-white solid polymer **3a**. The yields were 92.5% and 93.2% for the 24 h and 48 h reactions, respectively.

^{1}H-NMR (400MHz, δ ppm, d_6-DMSO): 10.51-10.09 (hydrazide and carbamate proton NH), 6. 85-7.96 (Ar-H), 2.97 (-CH_3), 1.51 (CH_2), 1.33 (CH_2), 1.07 (CH_2), 0.87 (CH_2).

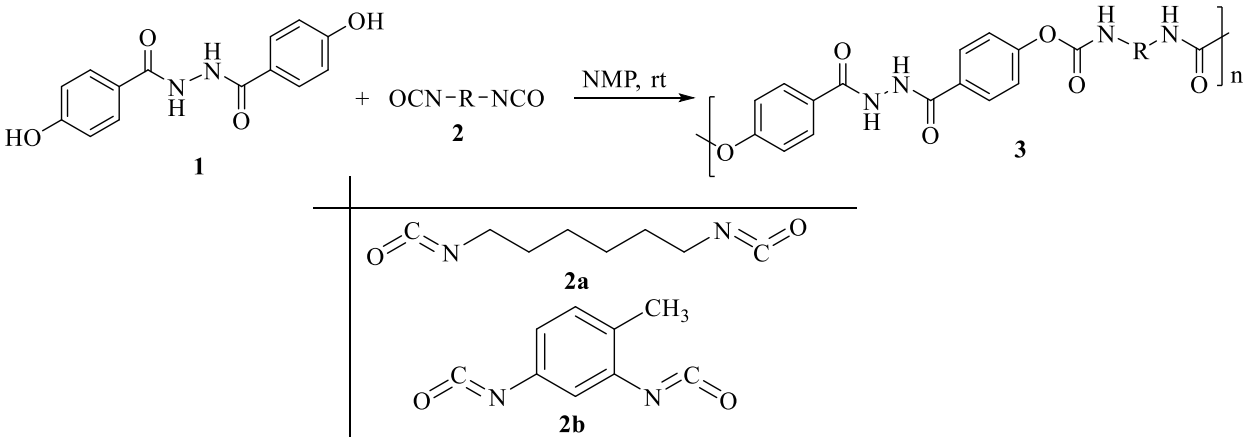
IR: ν= 3400 cm^{-1} (N-H stretching), 2935, 2858 cm^{-1} (C-H stretching), 1721 cm^{-1} (C=O stretching of carbamate), and 1641 cm^{-1} (C=O stretching of diacylhydrazine).

Synthesis of Polyurethane 3b

A solution of **1** (0.272 g, 1 mmol) in NMP (5 mL) was reacted with toluene-2,4-diisocyanate **2b** (0.179 g, 1 mmol) at room temperature. The mixture was stirred for 24 or 48 h, then precipitated dropwise into water (90 mL) with constant stirring for 30 min. Then it was filtered, washed with water, and dried in oven to yield an off-white solid polymer **3b**. The yields were 92.7% and 95.1% for the 24 h and 48 h reactions, respectively.

^{1}H-NMR (400MHz, δ ppm, d_6-DMSO): 10.51-10.10 (hydrazide and carbamate proton NH), 6. 85-7.94 (Ar-H), 2.97 (-CH_3).

IR: ν= 3320 cm^{-1} (N-H stretching), 2932, 2857 cm^{-1} (C-H stretching), 1724 cm^{-1} (C=O stretching of carbamate), and 1643 cm^{-1} (C=O stretching of diacylhydrazine).



Scheme 3 Synthesis of polyurethane[3] bearing diacylhydrzine moiety

Oxidative Degradation

To check the oxidative degradation of the formed polymer, a 10% solution of sodium hypochlorite was prepared and the polymer is treated with the hypochlorite solution. The mixture was stirred well so as to allow the complete degradation of the polymer.

III. Results and Discussion

Thermal Study of Polyurethane 3a and 3b

The TGA-DTA curve of polymer **3a** exhibits multi step thermal degradation. An initial weight loss of ~2.9% below 130 °C, accompanied by an endothermic dip at ~77 °C, corresponds to the removal of absorbed moisture and residual volatiles. Gradual weight reduction up to ~280 °C, with minor endothermic events at 169 °C and 262 °C, indicates the release of low molecular weight species and onset of chain scission. The major decomposition occurs between 280–445 °C, showing a sharp ~35% weight loss, supported by a strong exothermic DTA peak at ~309 °C and the maximum DTG rate, confirming polymer backbone breakdown. Thus, the decomposition temperature (T_d) of polymer 3a is ~280 °C. Further degradation between 445–600 °C, with exothermic peaks at 383 °C and 487 °C, corresponds to char decomposition, leading to an additional ~31% mass loss.

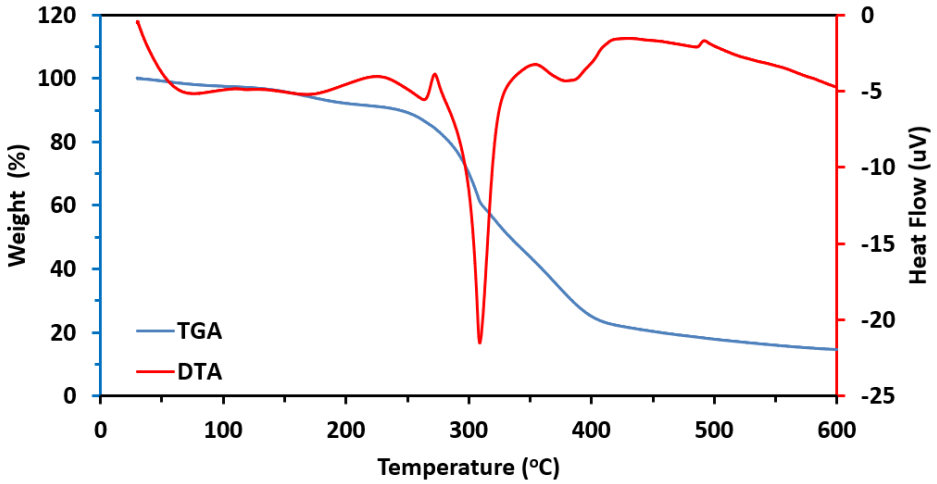


Fig. 1 TGA-DTA profile of polyurethane **3a** (20 ºC/min in air, aluminum reference). Positive heat flow is exothermic in the DTA analysis.

For polymer **3b**, the TGA-DTA thermogram also reveals multi step degradation. The initial ~3.5% weight loss below 100 °C, with an endothermic dip at ~72 °C, is attributed to moisture or residual solvent evaporation. A minor degradation between 200–253 °C (~4% mass loss) suggests low molecular weight volatiles or initial chain cleavage. However, the DTA curve exhibits a heat flow event prior to the onset of degradation, which corresponds to the

evaporation of residual solvent, unreacted monomer, and low molecular weight oligomers. Major decomposition occurs between 253–410 °C, with ~29% weight loss, strong TGA peaks at ~273 °C and ~375 °C, and corresponding exothermic DTA transitions, indicating main chain breakdown. A further degradation stage between 410–514 °C (~19% weight loss), with a DTG peak at 479 °C and exothermic activity at 411 °C, reflects oxidative degradation of charred residues. Therefore, the T_d of polymer **3b** is ~253 °C. Careful observation of both TGA and DTA curves confirms no significant weight loss occurs above the decomposition temperatures.

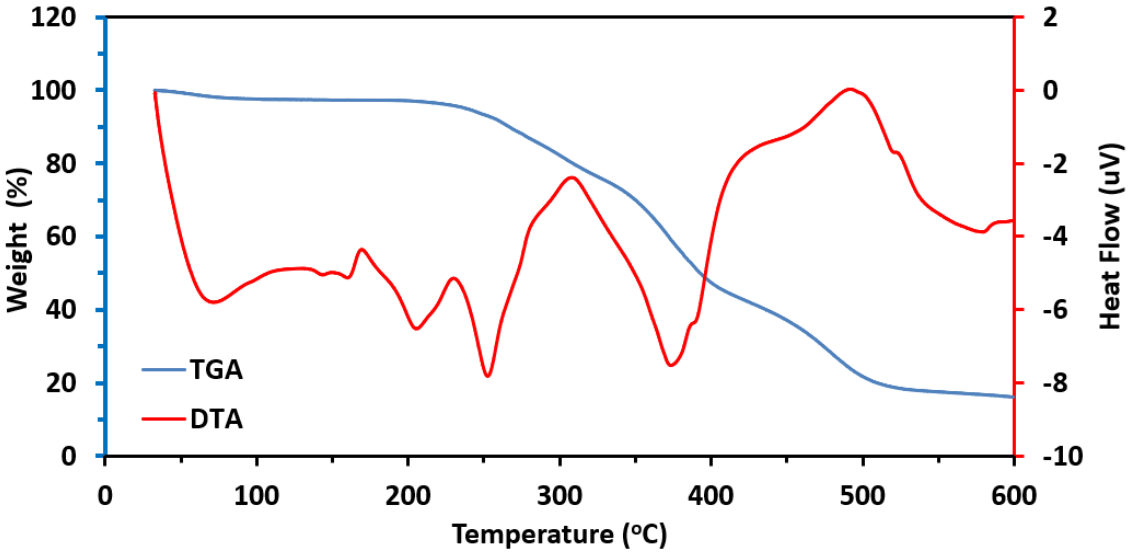
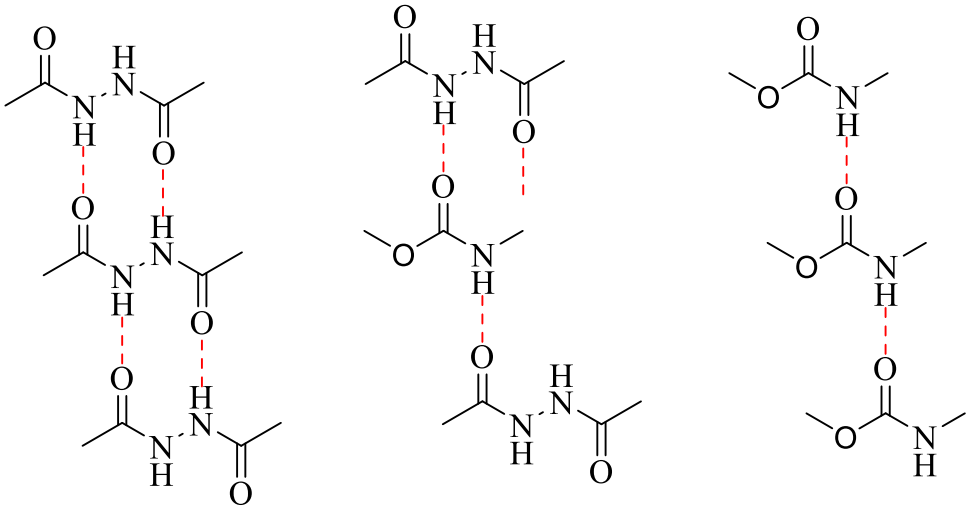


Fig. 2 TGA-DTA profile of polyurethane **3b** (20 ºC/min in air, aluminum reference). Positive heat flow is exothermic in the DTA analysis.

Solubility of the Polyurethane 3

All the synthesized polymers contain both diacylhydrazine and carbamate groups, which are highly polar. The diacylhydrazine groups can form hydrogen bonds not only with the diacylhydrazine groups of adjacent polymer chains but also with the carbonyl groups of carbamates, while carbamate groups of neighboring chains can also hydrogen bond with each other. These strong dipole–dipole interactions and extensive hydrogen bonding generate significant intermolecular forces, making the polymers insoluble in most common nonpolar or low-polarity solvents (**Scheme 4**). However, highly polar solvents such as NMP, and concentrated H_2SO_4, with its very high dielectric constant, can effectively dissolve them (**Table 1**). The limited solubility in low-polarity solvents may adversely affect polymer processability and consequently restrict certain practical applications. Therefore, further structural optimization of the monomer design may be necessary to improve solubility and facilitate easier processing for broader physical and industrial applications.

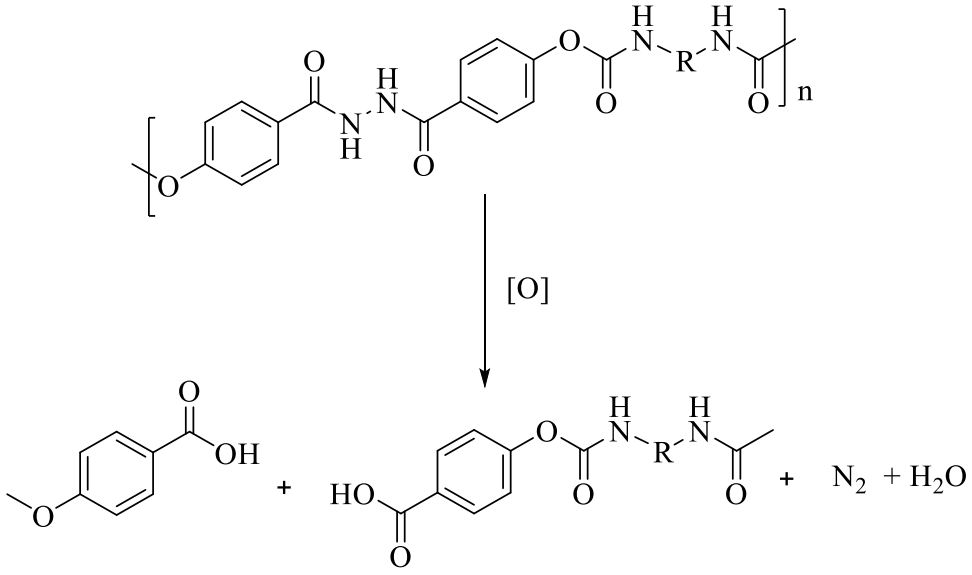


Scheme 4 Intermolecular hydrogen bonding between polymer chains

Table 1. Solubility of Polyurethane 3

Polymer Name	NMP	Ethanol	Acetone	Conc.H_2SO_4	H_2O	Methanol
3a	√	×	×	√	×	×
3b	√	×	×	√	×	×

The oxidative degradability of polyurethane **3a** was evaluated using a 10% sodium hypochlorite (NaOCl) solution. Upon treatment with NaOCl, polyurethane **3a** dissolved completely within five minutes, accompanied by the evolution of nitrogen (N_2) gas bubbles **(Scheme 5)**. This indicates polymer breakdown, as polyurethane **3a** is normally insoluble in water and gradually disappeared when exposed to the hypochlorite solution. Additionally, the pH of the mixture decreased, suggesting the formation of carboxylic acids during the polymer's degradation. After complete degradation, the solution was acidified with concentrated HCl, and the resulting precipitate was collected by filtration and dried under vacuum. IR analysis showed a broad absorption band between 2400–3600 cm^{-1}, along with a characteristic C=O stretching peak at 1700 cm^{-1}, confirming the formation of carboxylic acid groups. Furthermore, the absence of the C=O peak around 1650 cm^{-1}, characteristic of the diacylhydrazine group, verified the oxidative degradation of the hydrazine moiety.



Scheme 5 Oxidative degradation of polyurethane by sodium hypochlorite solution[3]

IV. Conclusions

In this study, oxidatively degradable and thermally stable polymers were synthesized by reacting diol **1** with various diisocyanates **2a/2b**, introducing diacylhydrazine moieties into the main chain. These polymers exhibited high thermal stability and oxidative degradability. Polymer formation was indicated by increased solution viscosity. IR and NMR confirmed the incorporation of diacylhydrazine moieties, with characteristic NH and CO absorptions and new proton signals from carbamate and aromatic groups. The polymers were soluble in NMP and conc. H_2SO_4 but insoluble in most organic solvents and water, attributed to strong intermolecular hydrogen bonding. They also degraded upon treatment with sodium hypochlorite solution.

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