*Applied Chemical Engineering (2026) Volume 9 Issue 4* ISSN: 2578-2010 (O)
doi: 10.59429/ace.v9i4.6102

ORIGINAL RESEARCH ARTICLE

# Synthesis and characterization of azo polymers based on chitosan and acrylamide derivatives

**Nawar Jamal Abdulrada[1,*], Mohammed Ali Mutar[2]**

[1] *Department of Chemistry, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad 10071, Iraq*

[2] *Department of Chemistry, College of Science, University of Al-Qadisiyah, Al-Diwaniyah 58002, Iraq*

***Corresponding authors:** Nawar Jamal Abdulrada, nawar.j.ar@ihcoedu.uobaghdad.edu.iq

## ABSTRACT

Two azo-containing materials, an acrylamide-derived azo compound (AZO 1) and a chitosan-derived azo material (AZO-chitosan 2), were prepared by diazo coupling with o-cresol under alkaline conditions at 0–5 °C. The acrylamide-derived monomer was subsequently converted to an azo polymer by free-radical photopolymerization under nitrogen using 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) as the photoinitiator. The products were characterized by FTIR, $^{1}$H NMR, and $^{13}$C NMR spectroscopy, and their thermal behavior was evaluated by TGA and DSC. The acrylamide-derived azo compound was obtained in 78% yield, whereas the AZO-chitosan product was obtained in 70% yield. The spectral changes support formation of the azo-containing products and consumption of the polymerizable double bond. The two polymer samples showed TGA onset temperatures of 110 and 100 °C, 50% mass-loss temperatures of 260 and 270 °C, and residues of 92% and 90% at 600 °C, respectively. DSC gave glass-transition temperatures of 180 and 250 °C. These results establish the structural and preliminary thermal characteristics of the prepared materials. Molecular-weight distribution and photoisomerization were not measured and therefore remain subjects for further study.

***Keywords:*** azo polymers; chitosan; acrylamide; photopolymerization; thermal analysis

**ARTICLE INFO**

Received: 30 June 2026
Accepted: 3 August 2026
Available online: 04 November 2026

**COPYRIGHT**

Copyright © 2026 by author(s).
*Applied Chemical Engineering* is published by Arts and Science Press Pte. Ltd. This work is licensed under the Creative Commons Attribution-NonCommercial 4.0 International License (CC BY 4.0).
https://creativecommons.org/licenses/by/4.0/

## 1. Introduction

Azo-containing polymers incorporate –N=N– chromophores in the main chain or as pendant groups. Their optical response, thermal behavior, and mechanical performance depend on the chromophore structure, polymer backbone, and mode of attachment. Such materials have been investigated for optical storage, liquid-crystal systems, nonlinear optics, and light-responsive devices[1–12].

Reversible trans–cis isomerization is a defining property of azobenzene derivatives and can alter molecular geometry, dipole moment, and chromophore orientation[9–11]. Chitosan offers hydroxyl and amino functionalities, film-forming ability, and a renewable polysaccharide backbone, whereas acrylamide provides a polymerizable vinyl group and a polar amide functionality. Studying both substrates therefore permits comparison between a vinyl monomer route and functionalization of a biopolymer backbone.

Free-radical photopolymerization can proceed at lower bulk temperature and offers rapid initiation and temporal control. In the present work, it was selected to prepare the acrylamide-based azo polymer in the presence of 1-hydroxycyclohexyl phenyl ketone. The

objective was to synthesize and characterize two azo-containing products, designated AZO 1 and AZO-chitosan 2, and to evaluate the structure and preliminary thermal behavior of the resulting materials by FTIR, $^{1}H$ NMR, $^{13}C$ NMR, TGA, and DSC. The study does not claim molecular-weight control because GPC/SEC data were not obtained.

# 2. Materials and Instruments

## 2.1. Materials

Acrylamide, chitosan, o-cresol, HCl, $NaNO_2$, and NaOH were obtained from Thomas Baker, India. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184) was obtained from BDH, USA.

## 2.2. Instruments

FTIR spectra were recorded with an FTIR-8400S spectrometer. $^{1}H$ NMR and $^{13}C$ NMR spectra were acquired on a Bruker 400 MHz instrument using DMSO-$d_6$. Melting points were measured with a Stuart SMP30 apparatus. TGA and DSC measurements were performed with a PerkinElmer thermal analyzer over 30–800 °C at a heating rate of 10 °C $min^{-1}$ under an inert gas atmosphere. A K-VO27 vacuum drying oven was used for drying the products. Spectral assignments followed established spectrometric references[14,15], while interpretation of the thermal measurements considered prior thermal-analysis and polymer studies[16–18].

## 2.3. Synthesis of AZO (1)

Acrylamide (1.53 g, 10 mmol) was placed in a 500 mL conical flask and treated with concentrated HCl (10 mL), water (25 mL), and ice (25 g). The mixture was stirred and cooled to 0 °C. A solution of $NaNO_2$ (3.45 g, 50 mmol) in water (7.5 mL) was added dropwise over 10 min, and stirring continued for 20 min at 0–5 °C. A solution of o-cresol (1.38 g, 10 mmol) in 10% NaOH (3 g NaOH in 25 mL water) was then added dropwise, and the mixture was stirred for 1 h at 0–5 °C. The precipitated product was collected by filtration, washed with water, and dried under vacuum overnight at room temperature. The color, isolated mass, yield, and melting point of AZO 1 are summarized in **Table 1**.

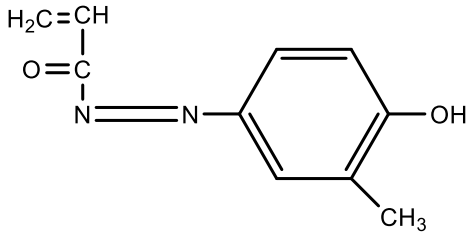



**Figure 1.** Chemical structure of AZO 1.

**Table 1.** Color, yield, and melting point of AZO 1.

| Compound | Formula | Substances | Color | m.p /°C | Weight (gm) | Yield (%) |
|---|---|---|---|---|---|---|
| AZO 1 | $C_{10}H_{10}N_2O_2$ | Acrylamide, o-cresol | Brown | 117-119 | 1.13 | 78 |

## 2.4. Synthesis of AZO Polymer

AZO 1 (5.0 g) was dissolved in DMSO and stirred for 30 min. The solution was purged with nitrogen and irradiated in the presence of 1-hydroxycyclohexyl phenyl ketone (0.10 g) as the photoinitiator. After photopolymerization, DMSO was removed under reduced pressure and the product was dried under vacuum. Residual monomer and initiator were not quantified, and molecular-weight parameters ($M_n$, $M_v$, and dispersity)

were not measured; these limitations are considered when interpreting the material as a preliminary polymer product.

### 2.5. Synthesis of AZO-Chitosan (2)

Chitosan (1.53 g, reported as 10 mmol), concentrated HCl (10 mL), water (25 mL), and ice (25 g) were combined in a 500 mL conical flask and cooled to 0 °C. $NaNO_2$ (3.45 g, 50 mmol) in water (7.5 mL) was added dropwise over 10 min, followed by stirring for 20 min at 0–5 °C. The mixture was then added gradually to o-cresol (1.38 g, 10 mmol) in 10% NaOH (3 g NaOH in 25 mL water), and stirring continued for 1 h in the ice bath. The product was filtered, washed with water, and dried under vacuum overnight at room temperature. The proposed attachment shown in **Figure 2** should be regarded as a representative azo-functionalized chitosan repeat unit because the substitution position and degree of substitution were not independently determined. The color, isolated mass, and yield of AZO-chitosan 2 are summarized in **Table 2**.

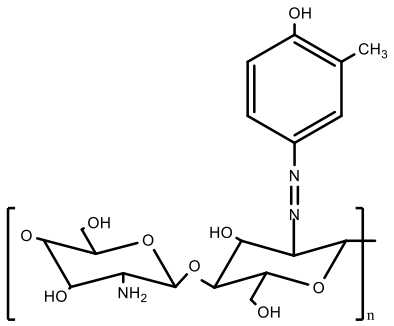



**Figure 2.** Proposed repeat-unit representation of AZO-chitosan 2.

**Table 2.** Color and isolated yield of AZO-chitosan 2.

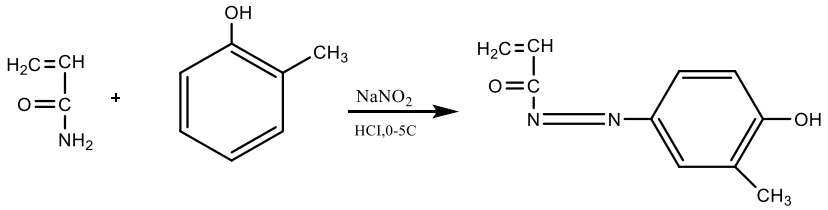
| Polymer | Formula | Substances | Color | Weight (gm) | Yield (%) |
|---|---|---|---|---|---|
| AZO Chitosan 1 | AZO-chitosan 2 | Chitosan, o-cresol | brown | Brown | 70 |

## 3. Results and Discussion

### 3.1. Synthesis of AZO compounds

#### 3.1.1. Synthesis of AZO (1)

AZO 1 was prepared by diazo coupling of acrylamide with o-cresol, as summarized in Scheme 1.




**Scheme 1.** Synthesis of AZO 1.

FTIR analysis of AZO 1

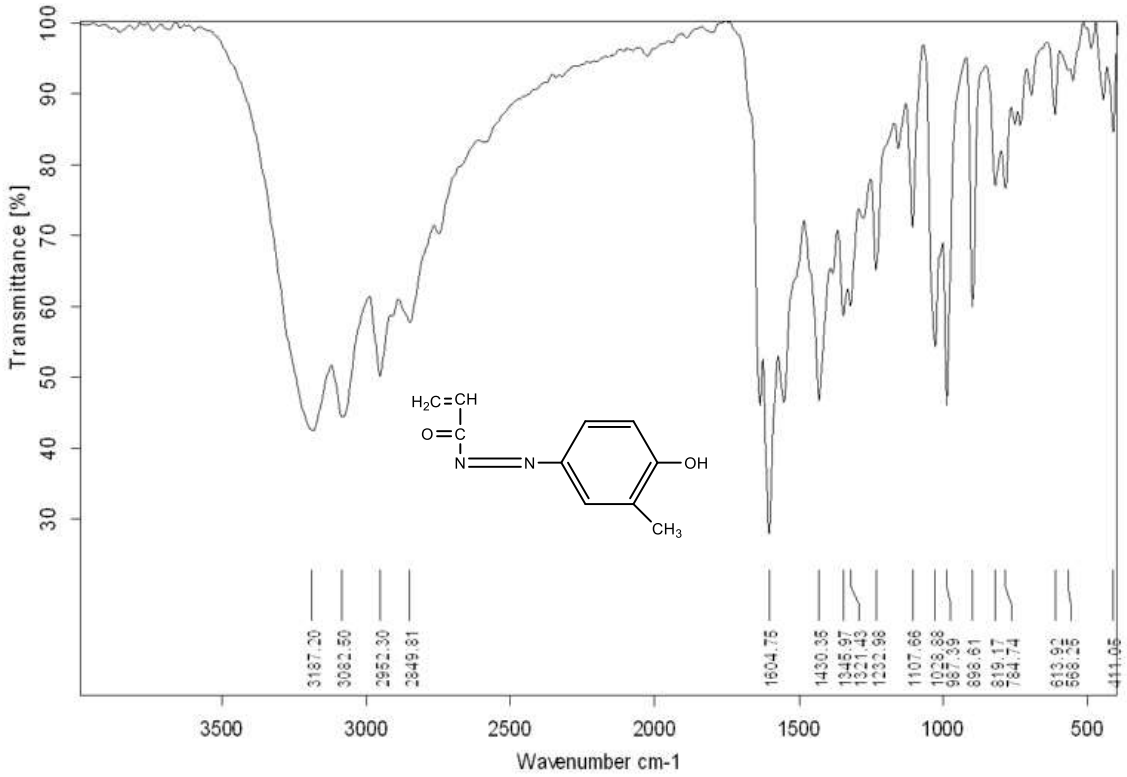



**Figure 3.** FTIR spectrum of AZO 1.

The FTIR spectrum of AZO 1 (**Figure 3**) shows a broad band at 3187 $cm^{-1}$ assigned to overlapping O–H and N–H stretching vibrations. Bands at 1604 and 1232 $cm^{-1}$ are assigned to amide C=O and C–N vibrations, respectively. The aromatic C=C and C–H stretching bands occur at 1430 and 3082 $cm^{-1}$, and an aliphatic C–H band appears at 2952 $cm^{-1}$. The band at 1345 $cm^{-1}$ is retained as an observed feature but is not assigned unequivocally to N=N because azo stretching is commonly observed at higher wavenumber; confirmation would require complementary analysis.

$^{1}$H NMR analysis of AZO 1

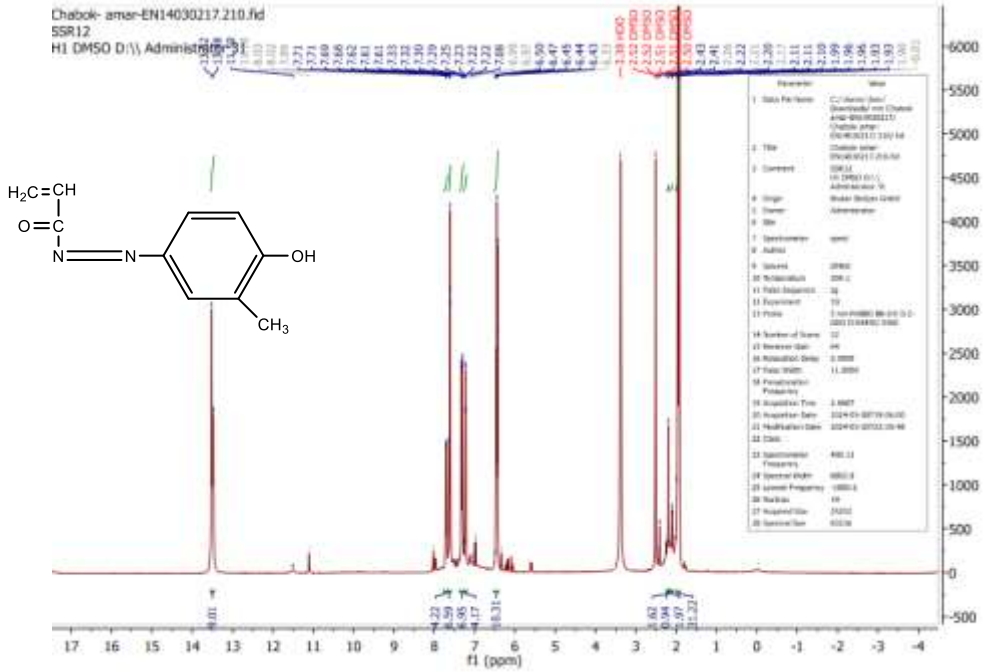
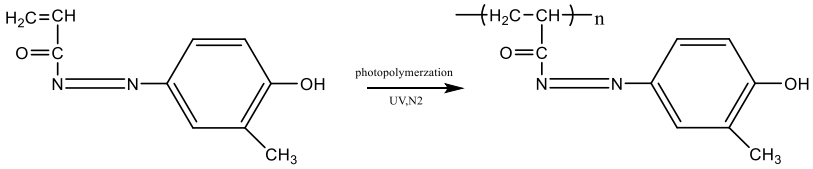



**Figure 4.** $^{1}$H NMR spectrum of AZO 1.

The $^1$H NMR spectrum of AZO 1 (**Figure 4**) contains signals at δ 2.0–2.3 ppm assigned to aliphatic protons, δ 6.5–7.7 ppm assigned to four aromatic protons, δ 13.5 ppm assigned to a strongly hydrogen-bonded phenolic OH proton, and δ 3.5 ppm assigned to exchangeable NH protons. Because individual resonances were not confirmed by two-dimensional NMR, these assignments are provisional and are limited to functional-group environments.

## 3.2. Synthesis of AZO polymer

AZO 1 was subjected to nitrogen-purged free-radical photopolymerization with 1-hydroxycyclohexyl phenyl ketone as the photoinitiator. Scheme 2 distinguishes this polymerization step from the monomer-forming diazo-coupling reaction shown in Scheme 1.




**Scheme 2.** Photopolymerization of AZO 1 to the acrylamide-based azo polymer (polymer 1).

FTIR analysis of acrylamide-based azo polymer 1

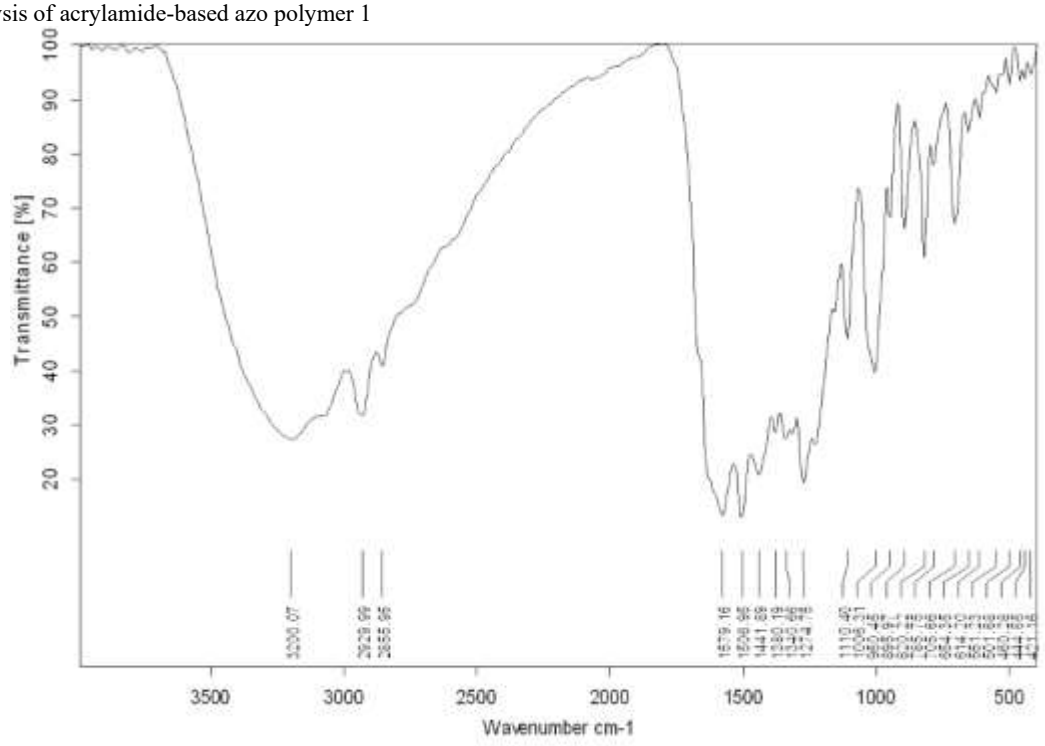



**Figure 5.** FTIR spectrum of acrylamide-based azo polymer 1.

The FTIR spectrum of acrylamide-based azo polymer 1 (**Figure 5**) shows an O–H/N–H band at 3200 cm$^{-1}$, aliphatic C–H at 2929 cm$^{-1}$, aromatic C–H at 3082 cm$^{-1}$, C–N at 1274 cm$^{-1}$, N=N at 1441 cm$^{-1}$, amide C=O at 1579 cm$^{-1}$, and aromatic C=C at 1506 cm$^{-1}$. Changes in the vinyl-region signals relative to AZO 1 are consistent with consumption of the polymerizable double bond. The carbonyl shift can reflect the altered conjugation and local electronic environment after polymerization.

$^1$H NMR analysis of acrylamide-based azo polymer 1

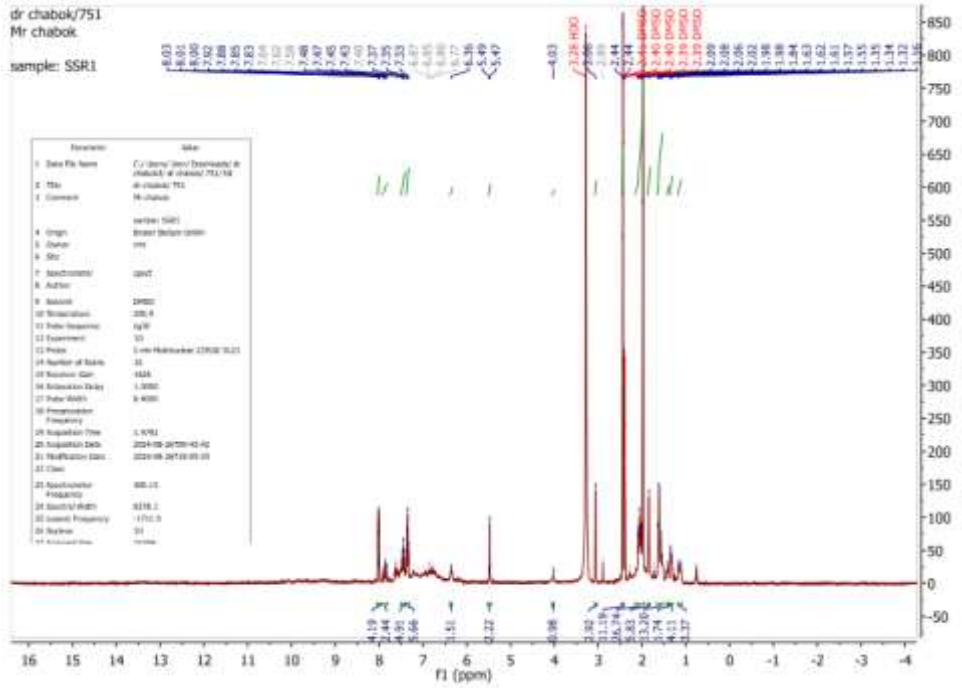
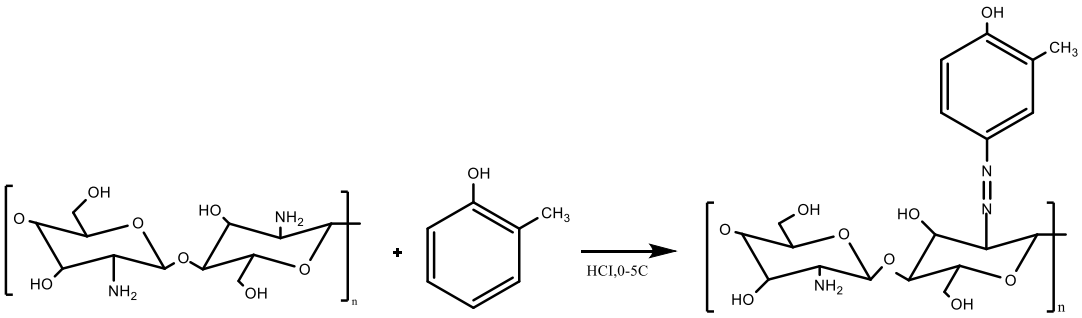



**Figure 6.** $^1$H NMR spectrum of acrylamide-based azo polymer 1.

The $^1$H NMR spectrum of acrylamide-based azo polymer 1 (**Figure 6**) shows broad aliphatic backbone signals at δ 1.0–2.4 ppm, aromatic signals at δ 6.3–7.8 ppm, an exchangeable OH signal near δ 8.0 ppm, and an NH-region signal near δ 3.4 ppm. Broadening of the aliphatic and aromatic resonances relative to the monomer is consistent with reduced segmental mobility in the polymer. The assignments remain provisional because molecular weight and two-dimensional NMR data were unavailable.

## 3.3. Synthesis and characterization of AZO-chitosan 2

AZO-chitosan 2 was obtained by diazo coupling involving chitosan and o-cresol, as summarized in Scheme 3. This material is distinct from acrylamide-based azo polymer 1.




**Scheme 3.** Preparation of AZO-chitosan 2.

FTIR analysis of AZO-chitosan 2

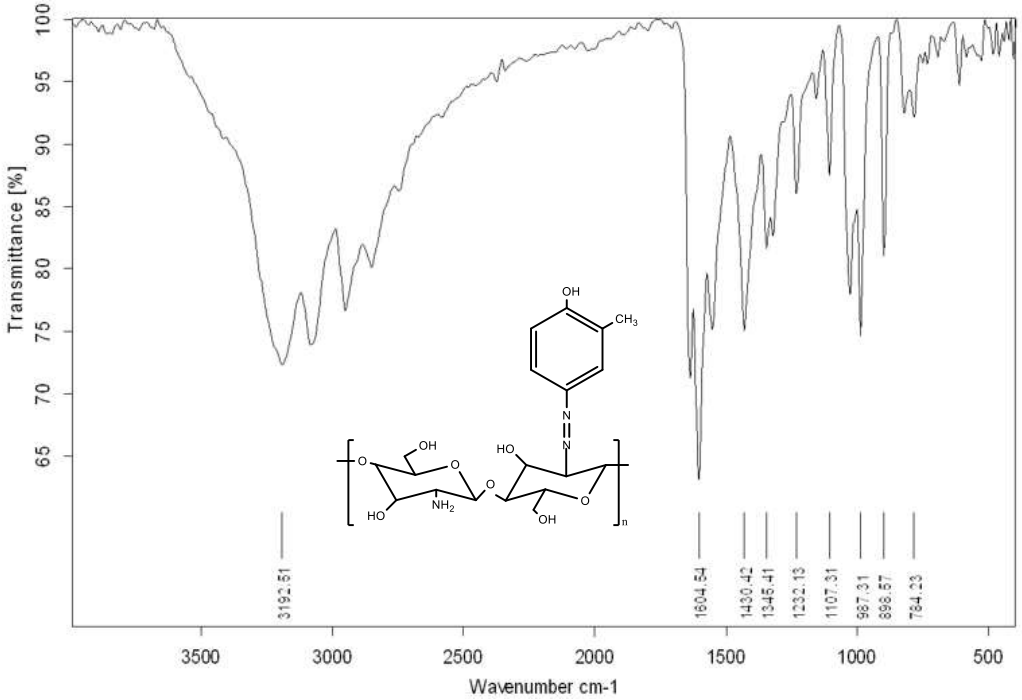



**Figure 7.** FTIR spectrum of AZO-chitosan 2.

The FTIR spectrum of AZO-chitosan 2 (**Figure 7**) shows bands at 3188 $cm^{-1}$ (O–H), 3067 $cm^{-1}$ (N–H), 2951 $cm^{-1}$ (aliphatic C–H), 1635 $cm^{-1}$ (amide I/NH–CO region), 1157 $cm^{-1}$ (C–O–C), 1107 $cm^{-1}$ (C–O), 1431 $cm^{-1}$ (azo-region vibration), and 1604 $cm^{-1}$ (aromatic C=C). The reported 163 $cm^{-1}$ value was a typographical error and has been corrected to 1635 $cm^{-1}$. The combined bands support retention of the polysaccharide framework and incorporation of aromatic azo functionality.

$^{1}$H NMR analysis of AZO-chitosan 2

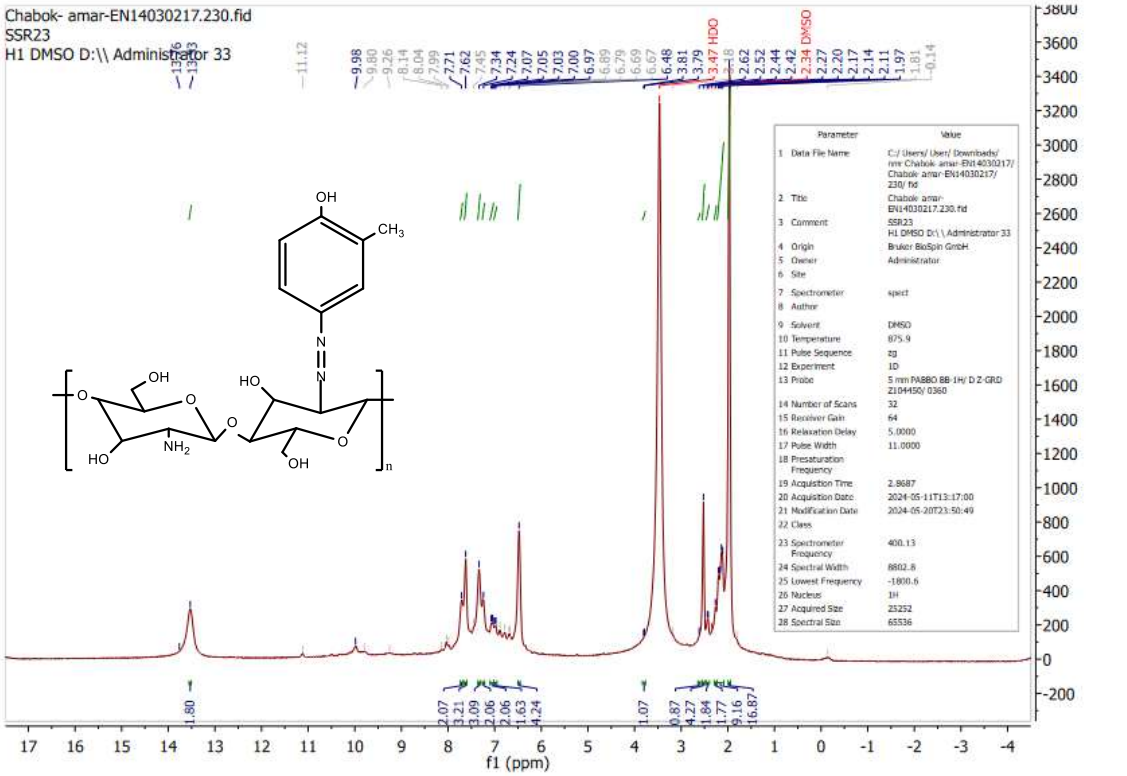



**Figure 8.** [1]H NMR spectrum of AZO-chitosan 2.

The [1]H NMR spectrum of AZO-chitosan 2 (**Figure 8**) shows an aliphatic signal near δ 2.5 ppm, a methyl-region signal near δ 0.9 ppm, aromatic signals at δ 6.5–8.0 ppm, an exchangeable phenolic OH signal near δ 10 ppm, and an NH-region signal near δ 3.5 ppm. Signal overlap from the chitosan backbone prevents unambiguous site-specific assignment; therefore, the spectrum supports azo functionalization but does not establish the exact substitution position.

[13]C NMR analysis of AZO-chitosan 2

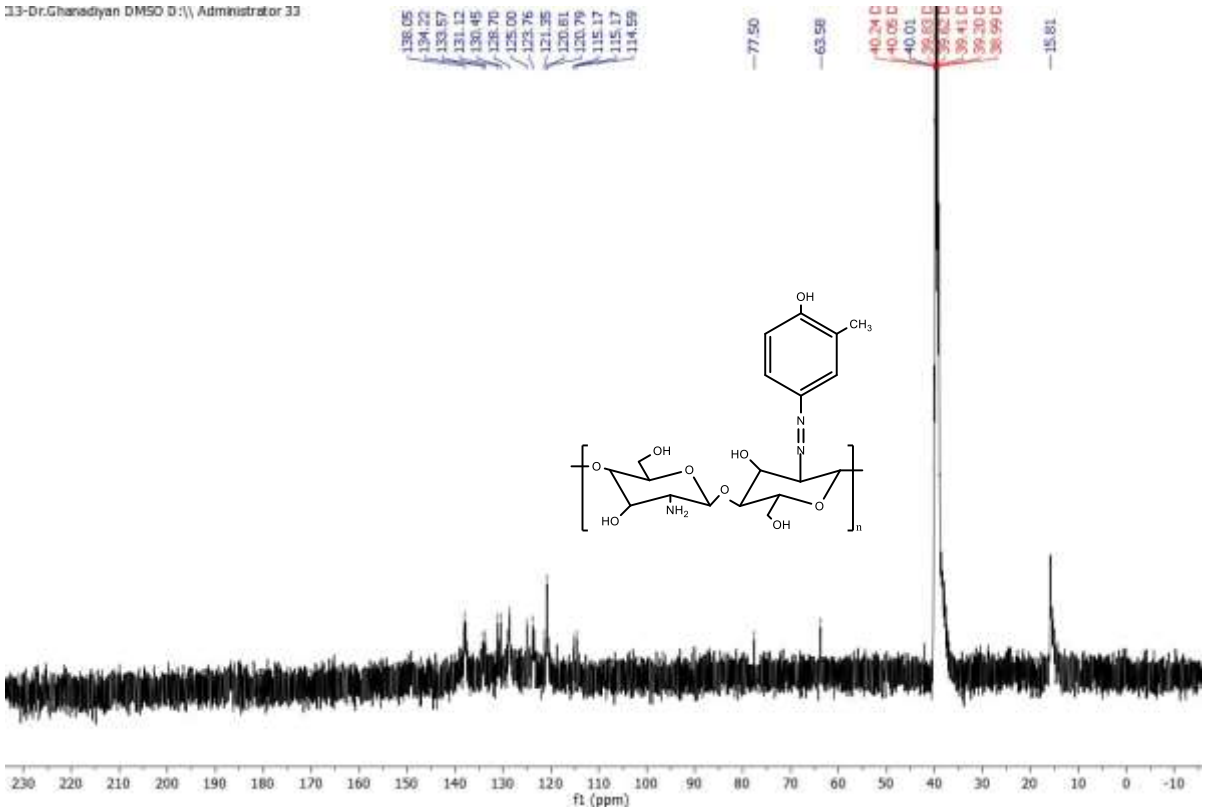



**Figure 9.** $^{13}$C NMR spectrum of AZO-chitosan 2.

The $^{13}$C NMR spectrum of AZO-chitosan 2 (**Figure 9**) contains aromatic signals at δ 115–130 ppm and a signal near δ 62 ppm in the oxygenated/aliphatic carbon region. A downfield signal near δ 185 ppm is reported in the carbonyl region. These data are compatible with the proposed functionalized material, but they do not independently establish the attachment site on the chitosan repeat unit.

## 3.4. Thermo gravimetric analysis (TGA)

TGA was performed from 30 to 800 °C at 10 °C min$^{-1}$ under an inert atmosphere. The initial mass loss near 80 °C is attributed primarily to absorbed moisture and residual low-molar-mass species. The main degradation stage occurs at higher temperature and is associated with cleavage of labile azo and side-chain functionalities, followed by backbone decomposition and carbonization. As summarized in **Table 3**, polymer 1 and AZO-chitosan 2 had onset temperatures of 110 and 100 °C, temperatures of maximum degradation rate of 200 and 230 °C, and 50% mass-loss temperatures of 260 and 270 °C, respectively.

The residues at 600 °C were 92% for polymer 1 and 90% for AZO-chitosan 2, whereas char yields at 400 °C were 82% and 85%, respectively. Within this two-sample dataset, AZO-chitosan 2 shows a slightly higher $T_{50}$ and char yield, while polymer 1 shows a slightly higher onset temperature and final residue. These values indicate substantial char formation under the stated test conditions, but they should not be described as exceptional without direct comparison with composition-matched azo polymers reported in the literature. These interpretations are consistent with reported thermal and interfacial behavior of related materials[13,16–18].

The multistage behavior is consistent with loss of volatile species, cleavage of labile functional groups, and subsequent degradation and carbonization of the organic framework. Differences between the samples may reflect the distinct local bonding environments and the aromatic and polysaccharide contributions. Mechanistic identification of evolved products was not performed, so the proposed degradation sequence remains an interpretation rather than a confirmed pathway.

**Table 3.** Thermal stability parameters obtained from TGA of the azo-containing materials.

| Material | $T_i$ (°C) | $T_{op}$ (°C) | $T^f$ (°C) | $T_{50}$ (°C) | Residue at 600 °C (%) | Char at 400 °C (%) |
|---|---|---|---|---|---|---|
| Polymer 1 | 110 | 200 | 500 | 260 | 92 | 82 |
| AZO-chitosan 2 | 100 | 230 | 400 | 270 | 90 | 85 |

DT: degradation temperature.

$T_i$: onset temperature of degradation.

$T_{op}$: temperature of the maximum degradation rate.

$T^f$: final temperature of the principal degradation stage.

$T_{50}$: temperature at 50% mass loss.

Char: residue at 400 °C.

Residue: residual mass at 600 °C under the stated inert atmosphere.

Differential scanning calorimetry (DSC)

DSC measurements were performed under the same programmed heating conditions used for thermal analysis. The reported transitions were assigned from the recorded thermograms to the glass-transition temperature (Tg), melting/endothermic transition (Tm), and crystallization/exothermic transition (Tc). Because these assignments were not confirmed by repeat heating–cooling cycles, they should be interpreted as preliminary thermal-transition values. The reported transition temperatures are summarized in **Table 4**.

For acrylamide-based azo polymer 1, the reported Tg, Tm, and Tc values were 180, 460, and 410 °C, respectively (**Figure 10**).

For AZO-chitosan 2, the reported Tg, Tm, and Tc values were 250, 410, and 290 °C, respectively (**Figure 11**). The high transition values should be verified in replicate DSC cycles and correlated with mass-loss events before firm structure–property conclusions are drawn.

**Table 4.** Reported glass-transition, melting, and crystallization temperatures of the azo-containing materials.

| Material | Tc (°C) | Tm (°C) | Tg (°C) |
|---|---|---|---|
| Polymer 1 | 410 | 460 | 180 |
| AZO-chitosan 2 | 290 | 410 | 250 |

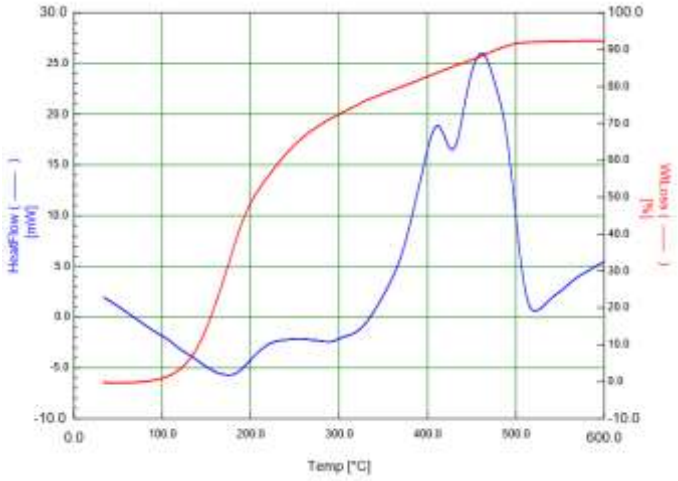



**Figure 10.** TGA and DSC curves of acrylamide-based azo polymer 1.

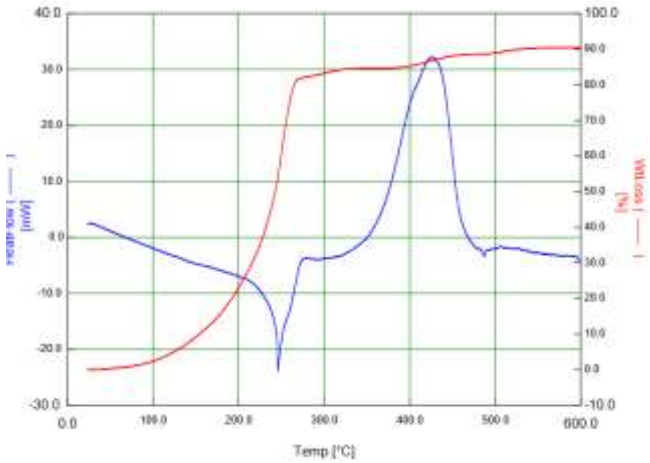



**Figure 11.** TGA and DSC curves of AZO-chitosan 2.

## 4. Conclusion

Two azo-containing products were prepared and characterized: acrylamide-derived AZO 1 and AZO-chitosan 2, with isolated yields of 78% and 70%, respectively. FTIR and NMR results support formation of the azo-containing structures, while spectral changes after irradiation are consistent with polymerization of the acrylamide-derived monomer. TGA showed onset temperatures of 110 and 100 °C, $T_{50}$ values of 260 and 270 °C, residues of 92% and 90% at 600 °C, and char yields of 82% and 85% at 400 °C for polymer 1 and AZO-chitosan 2, respectively. DSC gave reported Tg values of 180 and 250 °C. These findings meet the study objective of establishing preliminary structural and thermal characteristics and show that the two backbones produce different thermal profiles. The conclusions are limited by the absence of GPC/SEC molecular-weight data, quantitative purification checks, substitution-site confirmation for chitosan, replicate thermal cycles, and photoisomerization measurements. Future work should determine $M_n$, $M_v$, and dispersity, measure UV–visible trans–cis switching and cycling stability, and compare the materials directly with composition-matched azo polymers before application claims are made.

## Conflict of interest

The authors declare no conflict of interest.

## References


1. Nuyken O, Weidner R. Advances in Polymer Science. 1986;73–74:145.
2. Nuyken O. In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, editors. Encyclopedia of Polymer Science and Engineering. 2nd ed. Vol. 2. New York: Wiley; 1982. p. 158.
3. Benson R, Guthrie JT, Lartey RB. Polymer 1975;16:903 .
4. Tourasanidis EV, Karayannidis GP. J Macromol Sci Pure Appl Chem A 1999;36(9):1241.
5. Ishihava K, Negishi N, Shinohara I. J Appl Polym Sci 1982;27:1847.
6. Zhang H-Q, Huang W-Q, Li C-X, He B-L. Eur Polym J 1998;34(10):1251.
7. Tian Y, Xie J, Wang C, Zhao Y, Fei H. Polymer 1999;40:3835.
8. Robello DR. J Polym Sci Polym Chem Ed 1990;28:1 .
9. Ding H, Wang Z. Solvothermal synthesis of a new photochromic azo polymer and its self-assembly behavior. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry. 2010;47:1142–1148.
10. Kim S, et al. Synthesis and optical properties of azobenzene side-chain polymers derived from bifunctional fumaric acid and itaconic acid. Polymer. 2014;55:871–877.
11. Natansohn A, et al. Azo polymers for reversible optical storage. 1. Poly[4′-[[2-(acryloyloxy)ethyl]ethylamino]-4-nitroazobenzene]. Macromolecules. 1992;25:2268–2273.
12. Li N, et al. Nonlinear optical properties and memory effects of the azo polymer carrying different substituents. Dyes and Pigments. 2011;88:18–24.
13. Dwivedi R, Maurya A, Verma A, Prasad R, Bartwal KS. Journal of Alloys and Compounds. 2011;509:684.

14. Silverstein RM, Webster FX, Kiemle DJ. Spectrometric Identification of Organic Compounds. 7th ed. John Wiley & Sons; 2005.
15. Pretsch E, Bühlmann P, Badertscher M. Structure Determination of Organic Compounds. 4th ed. Springer-Verlag; 2009.
16. Hamilton I. The Development of Microwave Thermal Analysis (MWTA) and Its Application to the Study of Carbons and Other Materials [PhD thesis]. University of Huddersfield; 2009. pp. 29, 233.
17. Ryan K. Polymer Crystallization as a Reinforcement Mechanism for Polymer–Carbon Nanotube Composites [PhD thesis]. Department of Physics, Trinity College Dublin, University of Dublin; 2005. p. 26.
18. Mittal KL, Lee K-W. Polymer Surfaces and Interfaces: Characterization, Modification and Application. Utrecht, The Netherlands: VSP; 1997.