

**Preparation of Bromodeoxycellulose and Derivatives from
Shambat Cotton Lint Using Dimethyl Acetamide / Lithium
Bromide Solvent System**

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ABSTRACT

This study was designed to prepare cellulose derivatives with different functional groups from Sudanese Shambat cotton lint using a homogenous solubilisation medium. The raw cotton lint was mercerized in (15%) NaOH solution to weaken the aggregation of the bundles of cellulose fibers; and was subsequently dissolved in N,N-dimethylacetamide/lithium bromide (DMA/LiBr) as a homogenous solvent system. Bromodeoxycellulose was synthesized by treatment, of the

solubilised cotton cellulose with N-bromosuccinimide (NBS) in the presence of triphenylphosphine (Ph_3P) to convert the hydroxyl groups into the bromodeoxy derivative of cellulose. The chemical structure this derivative was investigated using infrared spectroscopy, elemental analysis which confirmed the presence of C-Br bonds. Thermal analysis (TGA, DSC) has shown that unlike chlorordeoxycellulose and unmodified mercerized cotton, bromodeoxycellulose was relatively thermally stable. Azido and amino deoxycellulose were easily prepared from bromodeoxycellulose since bromide is a good leaving. Solubility in some organic solvents was tested to explore possible new uses and applications.

Keywords: Bromodeoxycelluiose, Shambat, Cotton Lint

INTRODUCTION

Cellulose and cellulose derivatives are of growing importance in the development and application of renewable polymeric materials (Gandini, 2008). This has triggered a distinct renaissance of cellulose research and application all over the world. However, a major challenge in cellulose chemistry is dissolving it in aqueous or organic media to perform

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint Using Dimethyl Acetamide / Lithium Bromide Solvent System homogenous effective reactions, instead of the heterogenous reactions commonly employed. This difficulty has been overcome by using novel cellulose solvents (Heinze and Liebert, 2001). One of these is the N,N-dimethylacetamide/lithium chloride (DMA/LiCl) solvent system (McCormick and Callias, (1987). Deoxycellulose is a cellulose derivative with functional groups partially or completely replacing the hydroxyl groups in the glucosyl (anhydroglucose) units, which are the repeat units of cellulose polymer chain (Figure (1)).

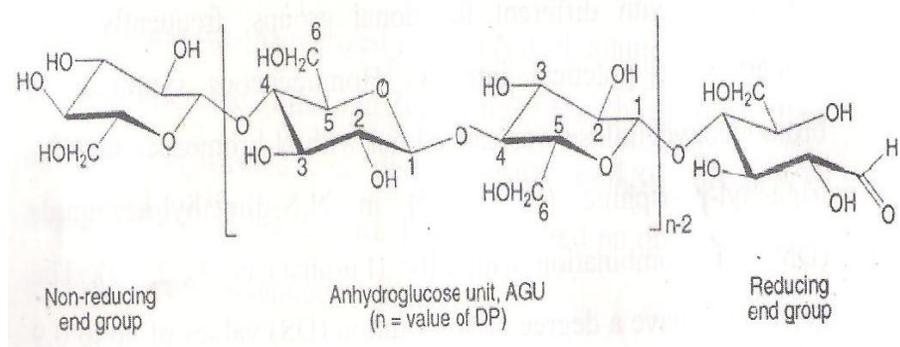


Figure (1): Molecular structure of cellulose with the reducing and non-reducing end groups.

Halodeoxycelluloses has recently assumed importance since the halogen groups serve as good leaving groups to facilitate the preparation of unconventional cellulose derivatives (Nada,2010). There has been considerable interest in the halogenated derivatives of natural compounds, since these structures often have interesting chemical and biological properties. Halogenodeoxy derivatives of cellulose are examined in terms of a wide range of their characteristics: synthesis, structure, reactions, and properties. The halogenodeoxy derivatives of cellulose are used for the synthesis of a wide variety of cellulose derivatives with different functional groups, frequently with properties of practical interest. Homogeneous synthesis of bromodeoxycellulose was carried out with N-bromosuccinimide-triphenyl-phosphine (NBS-Ph₃P) in N,N-dimethyl-acetamide (DMA) in combination with LiBr (Furuhata et al., 1992). The derivatives have a degree of substitution (DS) values of up to 0.9 and are selectively functionalized at C-6 (Kryalova et al., 1978). Bromine is well known as a better leaving group than chlorine; and the C-Br bond is more stable than the C-I bond (Morrison and Boyd, 1992). Bromodeoxycelluloses should therefore be a more useful intermediates than chlorodeoxycelluloses or iododeoxycelluloses for the preparation of cellulose derivatives

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System
(Tseng et al., 1994; Kryalova et al., 1978).

MATERIALS AND METHODS

Cotton sample:

The cotton lint sample of Shambat variety was obtained from the Cotton Breeding Section, Agricultural Research Corp., Wad Medani, Sudan. It was treated first with the Shirley analyzer machine for removal of trash content, and further treatments of the sample was carried out according to practical requirements.

Cotton mercerization

Cotton was mercerized in 15% NaOH solution at 0 °c for one hour (Buschle-Diller and Zeronian, 1992). The alkali swollen material was washed with distilled water until the pH of the filtrates remained unchanged. The mercerized product was dried at 60⁰C, then stored under vacuum.

Bromination of cotton cellulose:

0.25 g of dried mercerized cotton was placed in a flask containing 25 ml of DMA, and the mixture was heated for 2 h at 160⁰C with stirring. The temperature was lowered to 90⁰C and 5.5 g of LiBr were added. The mixture was kept for a further 1 h at this temperature with stirring. The temperature was then lowered to 60⁰C and the mixture was kept at this temperature

with stirring. A clear solution was obtained within 12 h. The cellulose solution was then stirred under cooling with ice-water, and 1.25 g of NBS and Ph₃P (each in 12.5 ml DMA solvent) were added in this order. The final volume of DMA was 50 ml. The solution was kept at 70°C for 2 h with stirring. After the reaction, the solution was poured into 400 ml of acetone and the separated material was washed several times with acetone, dialyzed against tap water and then distilled water. The coloured samples were treated with a solution of Na₂CO₃ (pH 10) at room temperature for 24 h. The sample was dried and weighed.

The bromine contents of the products were determined by an oxygen flask combustion method (WHO Pharmacopeia 2011). The DS by bromine was calculated from the bromine content.

Determination of the bromine content:

Using the oxygen flask method (WHO Pharmacopeia 2011); a specified quantity of bromodeoxycellulose was burned. The absorbing liquid consists of 17 ml of hydrogen peroxide (60 g/l) and 3 ml of water. When the process is complete, the stopper and side of the flask were rinsed with 40 ml of water. 5 drops of bromophenol blue in ethanol were added, then sodium hydroxide (0.1 N) was added dropwise until the colour changed from

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / Lithium Bromide Solvent System
yellow to blue. Then 1 ml of nitric acid was added followed by 5

drops of diphenylcarbazone in ethanol as an indicator. The mixture was titrated with mercuric nitrate (0.01 M) until the solution turned light violet. Bromide ions were precipitated according to following equation:



Each ml of 0.01M mercuric nitrate is equivalent to 1.598 mg of bromine.

Determination of the nitrogen content:

Elemental analysis was performed on dry finely ground samples using elemental analyzer flash EAI 112 series instrument. The samples were analyzed in the Central Petroleum Laboratories (CPL) in Khartoum, Sudan. DS values for azido and amino deoxy cellulose were calculated on the basis of nitrogen percent using the following equation (Mischnic and Momclovic, 2010):

$$\text{DS} = \frac{162 \text{ subst } \%}{M_{\text{subst}} - \{(M_{\text{subst}} - 1) \text{ subst} \%\}}$$

Where:

162 = molecular weight of the anhydroglucose unit of cellulose

M_{subst} = mass of the substituent

Nucleophilic displacement of bromodeoxycellulose by sodium azide:

Bromodeoxycellulose (0.2 g) was suspended in DMSO (20 ml). After addition of sodium azide (NaN_3) (0.58 g) and tetrabutylammonium iodide ($\text{n-Bu}_4\text{NI}$) (0.033 g), the mixture was stirred at 70°C for 5 h, and poured into distilled water. The precipitate was filtered off and washed with distilled water. The residue was further stirred in distilled water for 2 h, filtered off, washed with distilled water and CH_3OH , and dried to give a product as a slightly brown powder.

Reduction of the azido group of azidodeoxycellulose to the amino group:

Azidodeoxycellulose (0.2 g) was added to DMSO (40 ml). The mixture was stirred at 60°C , and became a clear solution within 1 h. After the addition of NaBH_4 (0.9 g), the mixture was stirred at 60°C for 6 h. HCl (1 M) was slowly added to the mixture at 0°C until generation of gas ceased, the mixture was neutralized by saturated NaHCO_3 and then centrifuged for 10 min, washed with distilled water 10 times and dried to give a powdery product.

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System

FTIR spectroscopy:

To study the chemical structure of cellulose sample and their derivatives, vibration spectroscopy was applied according to Abbott, et al. (1988). Fourier transform infrared (FTIR) spectra for cellulose and derivatives were acquired on a Shimadzu FTIR 8400 S.CE instrument using potassium bromide (KBr) discs prepared from the sample mixed with dry KBr in the ratio 1: 100. The spectra were performed in the Central Research Laboratories at the University of Khartoum, Sudan.

Thermogravimetric analysis:

Thermogravimetric analysis (TGA) is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA studies were carried out using a powdered form of the samples on a Shimadzu – 50 instrument at a heating rate of min - under nitrogen flow (20 ml min^{-1}) over a temperature range from room temperature up to 500°C . Thermogravimetric analyses were carried out in the laboratories of the Faculty of Science, University of Cairo, Egypt.

Solubility:

The solubility of all derivatives was determined at the concentration 0.01 g /ml in various organic solvents (DMA, .DMF, DMSO, THF, dioxane, acetone, chloroform and formic acid).

RESULTS AND DISCUSSIONS

Cotton dissolution:

Strong intermolecular hydrogen bonding is the major cause of the insolubility of cotton cellulose in common solvents; therefore, the breakage of hydrogen bonds is necessary for the dissolution of cellulose. The use of a high concentration of NaOH (15%) for cotton mercerization would weaken the aggregation of the bundles of cotton cellulose fibres; and subsequently facilitates the dissolution in DMA/LiBr. During mercerization, the alkali penetrates the cellulose fibres and causes a rearrangement of the crystal packing of the chains. This change is irreversible and is normally accompanied by a decrease in crystallinity. It should be stressed that untreated raw cotton cellulose, remains insoluble in DMA/LiBr under the same conditions. Table (1) shows that higher salt concentration was necessary for dissolution of cotton cellulose in DMA/LiBr as

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System
compared with DMA/LiCl. This may be explained on the basis of

weaker interaction of non-solvated bromine ions with hydroxyl
hydrogen atoms as compared with that of non solvated chloride
ions.

**Table (1): Dissolution of cotton lint cellulose in lithium
halide /DMA solvent system for 2 h in 25 ml of DMA**

Temp. (^o C)	Cotton (g)	LiBr/DMA			LiCl/DMA		
		LiBr. (g)	LiBr: cotton	Solubility	LiCl (g)	LiCl: cotton	Solubility
90	0.25	5.5	22:1	Soluble	2.5	10:1	Soluble
90	0.25	2.5	10:1	Insoluble	2.0	8:1	Insoluble
70	0.25	5.5	22:1	Insoluble	2.5	10:1	Insoluble
70	0.25	7.5	30:1	Soluble	5.0	20:1	Soluble

Pretreatment of mercerized cellulose in DMA at 160^oC

before the addition of lithium bromide was necessary for smooth
dissolution. If pretreatment was omitted, dissolution was slow.

Effect of reaction conditions on the degree of substitution:

In cellulose chemistry the degree of substitution (DS)
denotes the average number of substituted OH groups per
anhydroglucose (AGU) unit (Heinze and Liebert, 2001). The
results of the bromination of mercerized cotton cellulose with N-

bromosuccinimide (NBS) in the presence of triphenylphosphine (Ph₃P) in DMA/LiBr are summarized in Table (2). The DS of the bromination products obtained at different values of reagent ratios for reactions. for 2 h at 70⁰C are given. At lower reagent ratios the DS was very low whereas a sample of high DS was obtained at reagent ratio 5:1 and levelled off at reagent ratio 6:1 (Figure(2)). This result shows that the bromination system (DMA/LiBr) is useful for the preparation of high molecular Weight bromodeoxycellulose samples with a reagent ratio 5:1

Table (2): Bromination of mercerized cotton cellulose in homogeneous system (DMA/LiBr) at 70⁰C for 2 h at different reagent ratios

NO	Cotton (g)	NBS,Ph3P:AGU	Br%	DS
1	0.25	3:1	9.11	0.40
2	0.25	4:1	12.99	0.57
3	0.25	5:1	20.74	0.91
4	0.25	6:1	20.73	0.91

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System

Preparation of azidodeoxycellulose and aminodeoxycellulose:

Bromodeoxycellulose was treated with NaN_3 in the presence of n-tetra butylammonium iodide in DMSO at 70°C for 5 h. The reaction mixture became a clear solution after 24 h, although the bromodeoxycellulose initially did not dissolve completely in DMSO. Azidodeoxycellulose of DS 0.8 was obtained. Reduction of the azido group to amino with NaBH_4 has been used to prepare aminodeoxycellulose, as shown in Figure (3). The DS of aminodeoxycellulose was found to be 0.5 as shown in Table (3). Bromodeoxycellulose can therefore be easily substituted since the bromide ion is known to be a good leaving group in nucleophilic substitution (Morrison and Boyd, 1992).

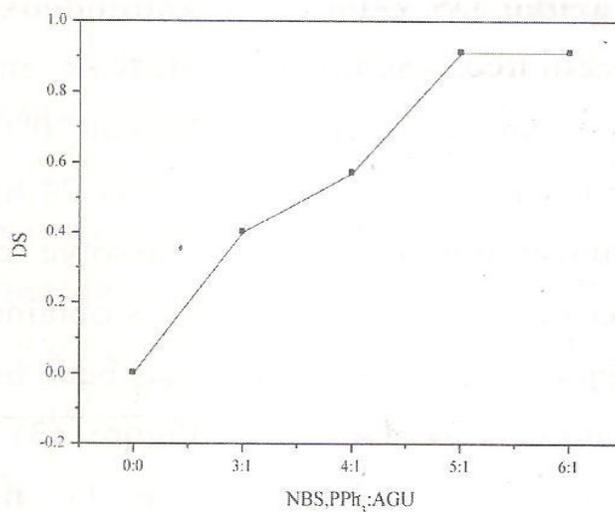


Figure (2): Effect on DS by using different reagent ratios on the bromination of mercerized cotton cellulose in homogeneous system (DMA/LiBr) at 70⁰C for 2 h.

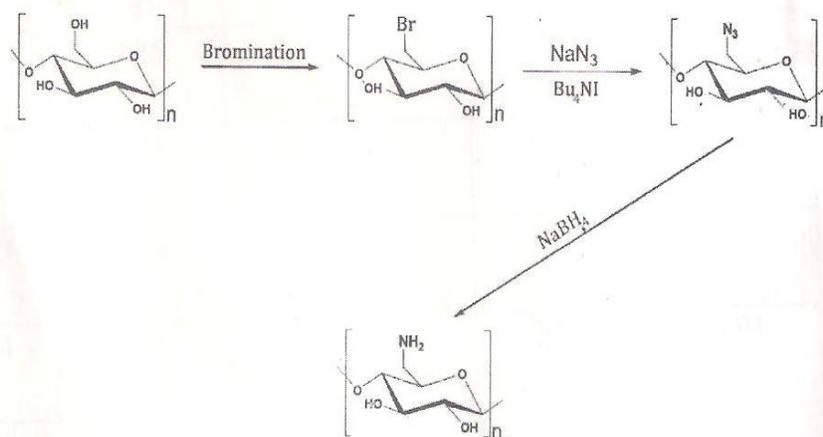


Figure (3):synthesis of 6-amino-6-deoxycellulose

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System

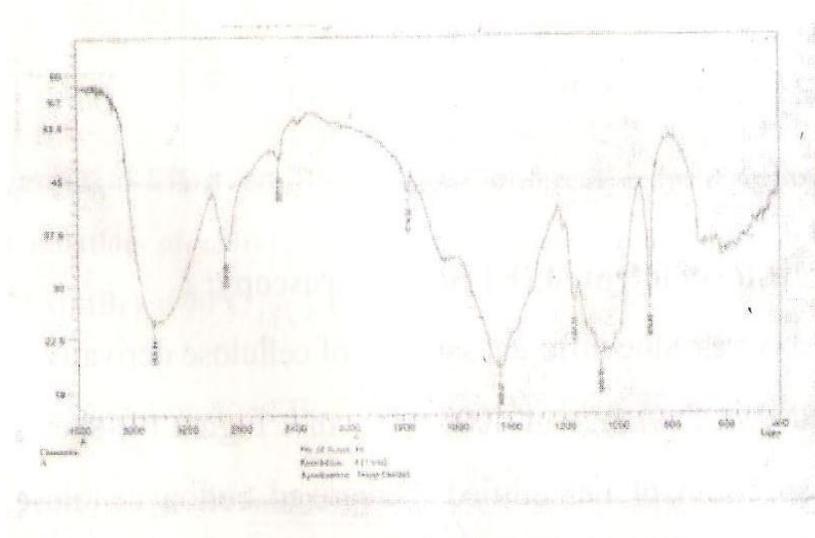
Table (3): Calculated DS values based on elemental analysis of azido and amino dcoxycellulose derivatives prepared from bromodeoxy-cellulose

Sample	Nitrogen(%)from elemental analysis for derivative	Theoretical value of N(%) for DS=3	DS
Azidodeoxy cellulose	14.44	53	0.8
Aminodeoxy cellulose	5.28	30	0.5

Fourier transform infrared (FTIR) spectroscopy:

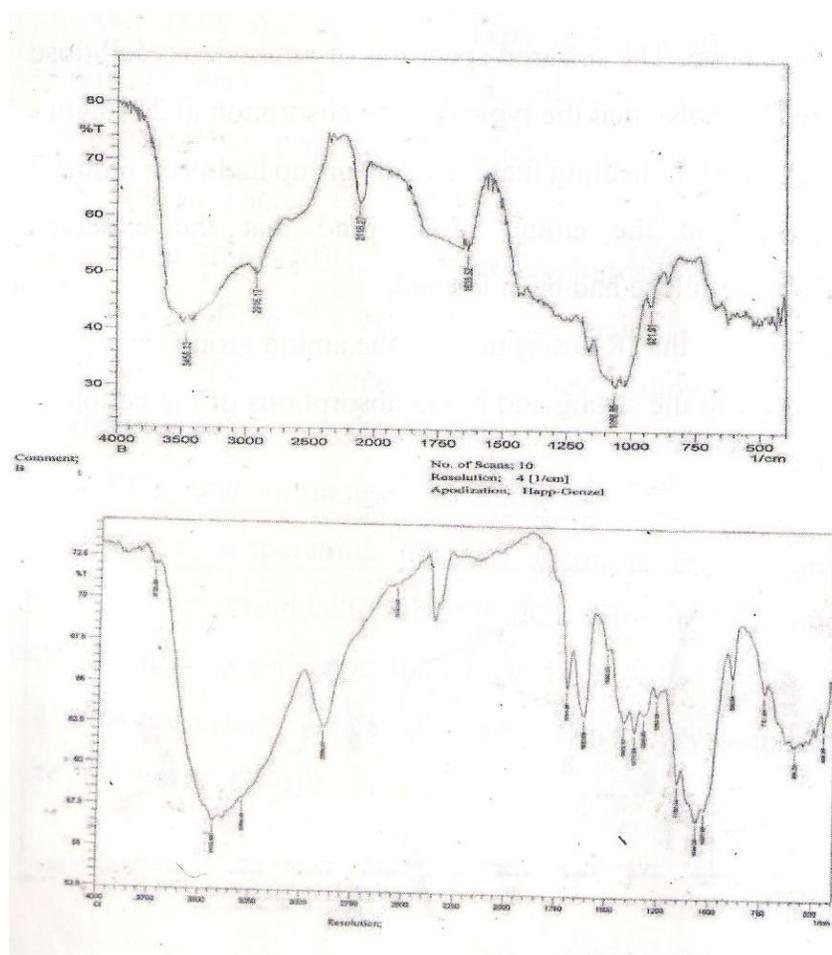
The FTIR spectra of the different samples of cellulose derivatives were recorded in the range of 4000-400 cm^{-1} . Figure (4) shows the FTIR spectrum of unmodified mercerized cotton cellulose which has the typical cellulose absorptions centred at 3439 cm^{-1} (O-H stretch), 2904 cm^{-1} (C-H stretch), 1439 cm^{-1} (C-H bend), and 1001 cm^{-1} (C-O stretch). Figure (5) shows the FTIR spectrum of bromodeoxycelluloses. The typical absorptions of the cellulose backbone are present; and it shows a band with low intensity at 621 cm^{-1} due to the presence of the C-Br bond. The FTIR spectrum of azidodeoxycellulose (Figure (6)) shows

the typical strong peak for the azide group at 2116 cm^{-1} . The complete elimination of bromine was confirmed by elemental analysis. These results indicate that the displacement of bromide by azide ion proceeded quantitatively. Thus, azido-deoxycellulose was obtained.



Figure(4): FTIR spectrum of unmodified mercerized cotton cellulose

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System



Figure(5): F TIR spectrum of bromodeoxycellulose cellulose

Figure (6): F TIR spectrum of azidodeoxycellulose

Reduction of the azido group to amino is described in Figure (4) above. The infrared spectrum of aminodeoxycellulose in Figure (7) shows that the typical azide absorption at 2116 cm^{-1} has disappeared, indicating that the azide group had been reduced quantitatively to the amino group, and that the expected aminodeoxycellulose had been formed.

However, the IR absorptions of the amino group can not be observed due to the strong and broad absorptions of the cellulose backbone.

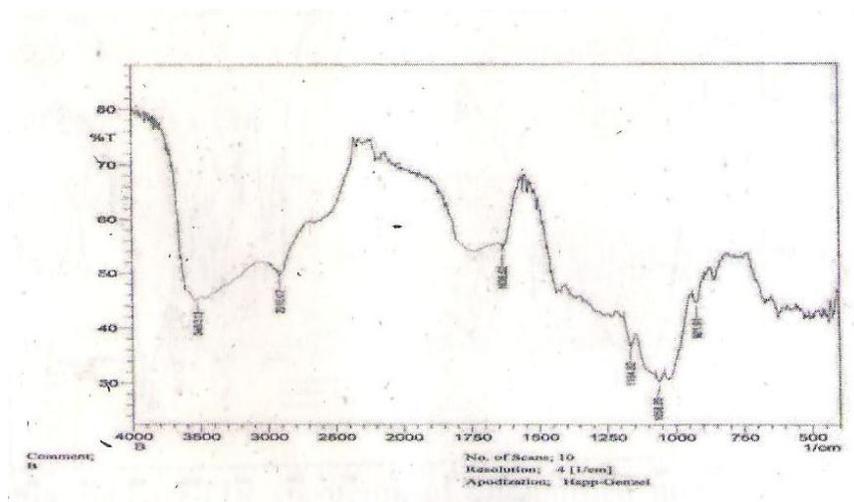


Figure (7): FT-IR spectrum of aminodeoxycellulose

Thermogravimetric Analysis (TGA):

Thermogravimetric analysis (TGA) is one of the thermal analysis techniques used to characterize a wide variety of materials. It provides complimentary and supplementary

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System
characterization information (Monika and Woolfgang, 2008).

The TGA and derivative TGA (DTGA) curves for the unmodified mercerized cotton lint, chlorodeoxycellulose, and bromodeoxycellulose are shown in Figures (8)–(10). The data are summarized in Table (4). In all cases initial loss of moisture takes place at 100–120⁰C; the onset decomposition temperature (T_{onset}) is about 180⁰C. However, the major decomposition temperatures (T_d) increase in the following order: chlorodeoxycellulose (265⁰C), unmodified mercerized cotton lint (273⁰C), and bromodeoxycellulose (286⁰C). The minor decomposition temperatures (T_{dm}) increase in the order: unmodified mercerized cotton lint (390⁰C), chlorodeoxycellulose (394⁰C), and bromodeoxycellulose (444⁰C). Note that T_d and T_{dm} values are clearly indicated by the DTGA curves and data shown in Figures (8)–(10).

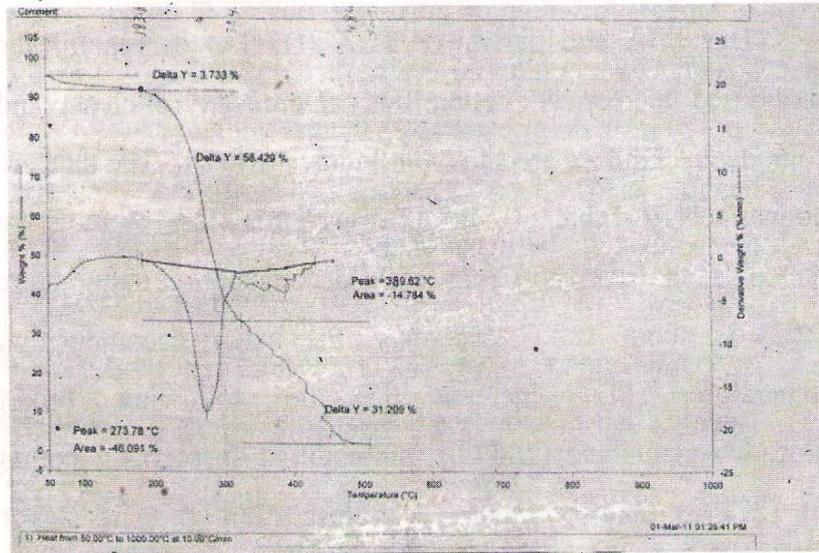


Figure (8): TGA curve of mercerized cotton cellulose

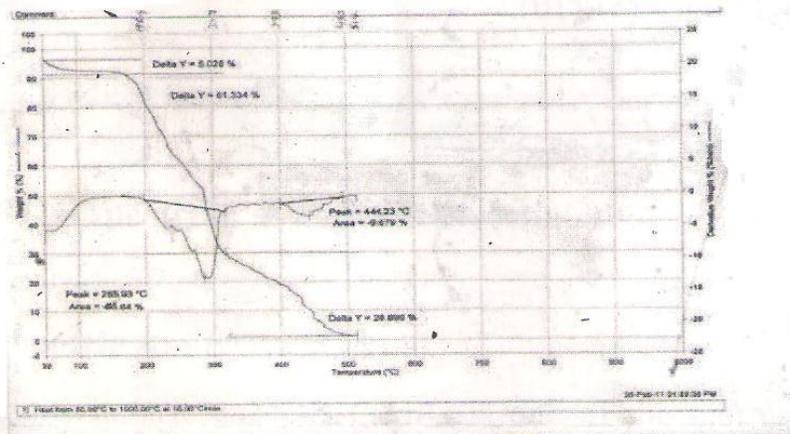


Figure (9): TGA curve of chlorodeoxycellulose

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System

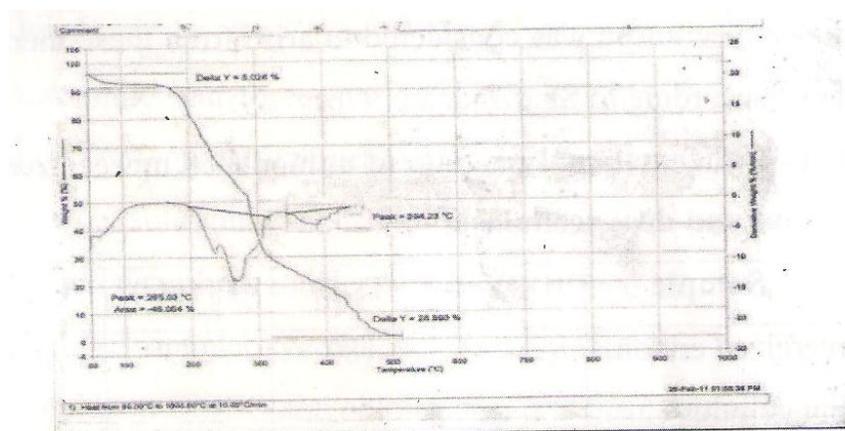


Figure (10): TGA curve of bromodeoxycellulose

The TGA curves in Figures (8)-(10) and the data in Table (4) show that chlorodeoxycellulose has the lowest T_d value; and is therefore thermally less stable than both unmodified mercerised cotton cellulose and bromodeoxycellulose indicating that chlorodeoxycellulose has flame retarding properties (Salim, 2012). This can be attributed to the fact that when chlorodeoxycellulose is heated, it generates hydrogen chloride which catalyses a series of heterolytic reactions including transglycosylation, dehydration, inter- and intramolecular etherification, and condensation. These latter products are ultimately carbonized through free - radical reactions producing

large amounts of char. So the well-known flame retardance of chlorodeoxycellulose was considered to arise from these thermal reactions according to Shafizadeh (1976).

Table (4): Thermal analysis data of unmodified mercerized cotton lint and deoxycelluloses

Sample	DS	T _{onset}	T _d (°C)	T _{dm} (°C)
Mercerized cotton lint cellulose	-	180	273	390
chlorodeoxycellulose	1.5	180	265	394
bromodeoxycellulose	0.9	180	286	444

On the other hand, bromodeoxycellulose has the highest T_d and T_{dm} values; and is therefore more thermally stable than both unmodified mercerized cotton cellulose and chlorodeoxycellulose; and has no flame - retardance properties.

Solubility of cotton cellulose derivatives:

Dissolving a polymer is a process that occurs in two stages. First the solvent molecules slowly diffuse into the polymer to produce a swollen gel. Production of a persistent swollen gel occurs when the polymer intermolecular forces are

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / Lithium Bromide Solvent System
high because of cross - linking, crystallinity, or strong hydrogen

bonding. In the second stage solution takes place if the intermolecular forces are overcome by the introduction of strong polymer-solvent interactions. The gel gradually disintegrates into a true solution. The solution process can be quite slow for materials of high molecular weight (Billmeyer, 1984).

Bromodeoxycellulose is very soluble in formic acid, soluble in DMSO and chloroform. It is insoluble in such common organic solvents such as ethanol and acetone; but it swells in the aprotic solvents dimethylformamide (DMF), DMA, and dioxane.

The increased solubility may be reasonably ascribed to the lowered crystallinity (reduction in hydrogen bonding), possible main-chain scission during halogenation, and/or the change in the chemical structure induced by halogenation. The replacement of hydroxyl groups by halogen will disrupt the hydrogen-bonded structure in which the hydroxyl groups are involved.

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CONCLUSIONS

The general approach of this research was to show the versatility of Sudanese Shambat cotton lint cellulose as a raw material for novel cellulose-based materials. A more specific aim was to prepare deoxybromocellulose by mercerizing the cotton lint first before dissolution in DMA/LiBr as a homogenous solvent system. Bromination was successfully achieved with NBS and Ph_3P . Bromodeoxycellulose was characterized by elemental analysis, FTIR, TGA and solubility tests. It was shown to be more thermally stable than both unmodified mercerized cotton cellulose and chlorodeoxycellulose. Bromodeoxycellulose is also a more useful intermediate than chlorodeoxycelluloses or iododeoxycelluloses for the preparation of cellulose derivatives. Azido and amino derivatives were readily prepared from bromodeoxycellulose. This synthetic method widens and simplifies the existing synthetic methodologies for cellulose modification, to yield novel derivatives.

Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
Using Dimethyl Acetamide / LithiumBromide Solvent System

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Preparation of Bromodeoxycellulose and Derivatives from Shambat Cotton Lint
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