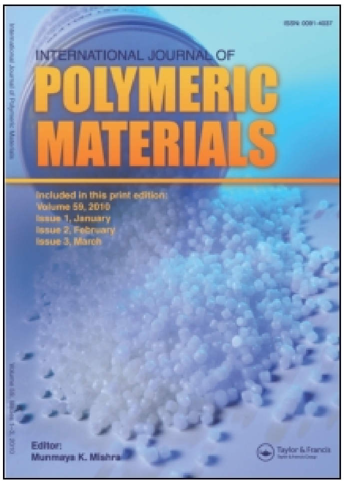

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Synthesis and Characterization of Coumarin – Trioxane – Thiourea Copolymers

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4-Methyl-7-hydroxy coumarin-trioxane-thiourea (MHCTTU) copolymers were prepared by copolycondensation of 4-methyl-7-hydroxy coumarin (MHC), trioxane (T) and thiourea (TU) in the presence of 2M HCl/H_2SO_4 as a catalyst with different molar ratios of reacting monomers. The copolymers were characterized by elemental analysis, IR spectral and TGA studies. Number average molecular weight ($\overline{Mn}$) of all the copolymers were determined by non-aqueous conductometry titration. The electrical conductivity of all copolymers was measured at various temperatures.

Keywords: 4-Methyl-7-hydroxy coumarin; trioxane; thiourea; TGA; electrical conductivity

INTRODUCTION

Coumarins (2H-1-benzopyran-2-ones) are important oxygen containing heterocycles and possess variety of functions including various physiological activities. A survey of the literature reveals that although a huge amount of work has been carried out on monomeric coumarin derivatives, a little attention has been given to coumarin polymers. Though the reports related to coumarin polymers are few, they are of very much interest. Yen *et al.*, have reported coumarin polymers with anticlotting and antihaemorrhagic properties [1]. Copolymers derived

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from coumarin and *N*-vinylpyrrolidine have been reported to decrease blood pressure in cats [2]. Coumarin–acrylonitrile copolymers are used in synthetic fibres [3]. Coumarin-*N*-vinylindole copolymer is reported to have photoconducting properties [4]. Patel and Patel have reported some poly(3-phenoxycoumarin methylene)s possessing anti-fungal activities [5]. Coumarin–formaldehyde polymers are reported to have good thermal stability [6].

Looking to these interesting properties [1–6] of coumarin polymers and with a view to exploring the field of coumarin polymers we here by report the synthesis of some novel coumarin–trioxane–thiourea copolymers. The copolymers (MHCTTUs) were prepared by the condensation of 4-methyl-7-hydroxy coumarin (MHC) with trioxane (T) and thiourea (TU) in the presence of 2M HCl/H_2SO_4 as a catalyst with different molar ratios of the reacting monomers. The resultant copolymers were duly characterized.

RESULTS AND DISCUSSION

The produced copolymers are based on the phenol-formaldehyde and thiourea-formaldehyde condensation type reaction. For the removal of the homopolymers formed during the copolymer synthesis, separate polymerization of coumarin–formaldehyde and thiourea-formaldehyde were carried out under the similar experimental conditions and solubility of the polymers was checked. As these homo polymers were soluble in THF, the product was repeatedly washed with hot THF to remove homopolymers. The resultant copolymers were pale yellow powders and were obtained in 60–80% yield. The elemental analysis C, H, N and S are furnished in Table I.

Typical IR spectra of copolymers are shown in Figure 1. All the copolymers give rise to essentially similar IR spectra. IR spectra of all copolymers comprise a broad band at 3500–3300 cm^{-1} with a maximum at around 3400 cm^{-1} due to —OH and —NH stretching vibrations. A weak absorption band around 2950–2850 cm^{-1} appeared in the spectra of all copolymers was attributed to C—H stretching of the $—CH_2—$ linkage. The copolymers also show strong band at 1730 cm^{-1} due to the coumarin lactone carbonyl. This indicates that the coumarin ring has remained intact throughout the copolymer formation. In addition, a band corresponding to the

TABLE I Characterization of coumarin–trioxane–thiourea copolymers (MHCTTUs)

Copolymer	Molar ratio	Elemental analysis (%)				TGA Weight loss at various temperatures (°C)					
	*MHC-T-TU**	*C*	*H*	*N*	*S*	100	200	300	400	500	600
$MHCTTU_1$	1:2:1	53.18	3.94	11.00	12.30	3.5	7.0	17.5	25.0	57.5	90.0
$MHCTTU_2$	3:4:1	59.24	4.61	3.46	3.76	3.0	4.5	10.0	28.0	66.0	92.0
$MHCTTU_3$	1:1:1	54.34	4.78	7.14	8.29	3.5	10.5	27.5	35.0	62.5	91.0
$MHCTTU_4$	1:4:3	55.12	4.67	5.54	6.40	4.5	5.5	19.5	37.0	65.5	91.0
$MHCTTU_5$	1:2:1	78.36	4.34	5.04	5.57	4.0	6.5	16.5	32.5	65.0	92.0
$MCHTTU_6$	3:4:1	75.01	5.00	4.64	5.20	3.0	5.0	11.0	26.5	56.0	85.0
$MCHTTU_7$	1:1:1	57.95	5.54	8.79	10.09	3.0	5.0	17.5	34.0	60.0	90.5
$MCHTTU_8$	1:4:3	78.65	5.98	11.77	13.25	4.0	6.0	18.0	38.5	69.5	96.0

* Catalyst: HCl (Sample 1–4); H_2SO_4 (Sample 5–8).

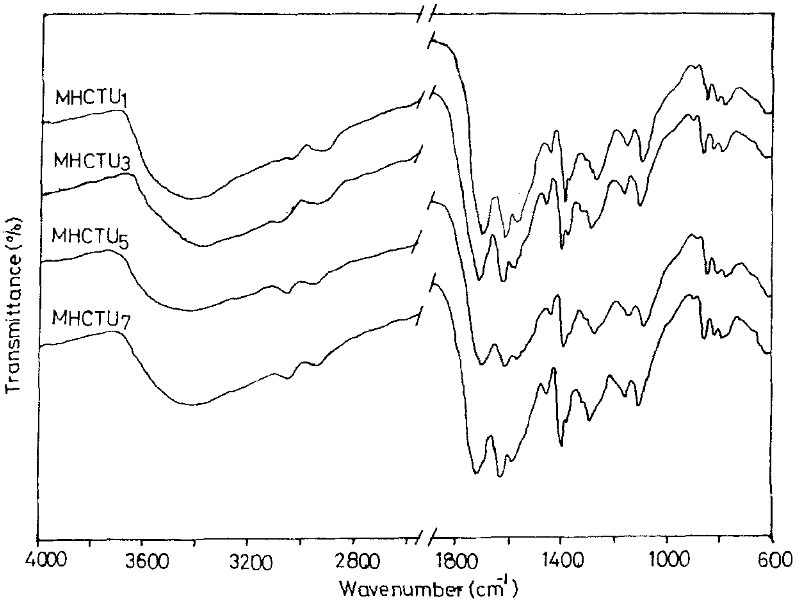
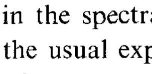
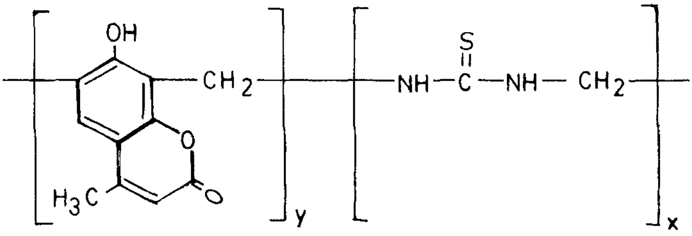


FIGURE 1 IR spectra of MHCTU-1, 3, 5 and 7.



$\overset{S}{\overset{\|}{—C}}—NH—$group of thiourea moiety appeared between 1610 and 1620 cm^{-1}. A band appeared around 1270 cm^{-1} was due to —C=S stretching vibration. The multiple bands observed near 1600–1400 cm^{-1} were attributed to aromatic stretching. The band due to tertiary $—\underset{|}{N}—$ group (*i.e.*, formed through crosslinking) did not appear in the spectra. This indicated that crosslinking did not occur under the usual experimental condition for copolymerization. On the basis of these IR spectral data and the bifunctionality of coumarin (MHC) nucleus, the following structure of all the copolymers can be predicted.



The copolymer composition was calculated on the basis of percentage of N in the respective copolymer (Tab. II). On the basis of percentage of N, the total number of moles of thiourea repeating unit (X) in 100 gm of copolymer is given by,

$$X = \text{Percentage of N}/28.013$$

For example for MHCTTU_1,

$$X = 11.00/28.013 = 0.39\,\text{mole}$$

Hence the weight percentage of thiourea repeating unit in the copolymer is $X \times$ (molecular mass of thiourea repeating unit) *i.e.*, $X \times 88$

$$\therefore\quad 0.39 \times 88 = 34.32 \text{ gm in } 100 \text{ gm of copolymer}$$

and the weight percentage of the comonomer repeating unit in the copolymer is $[100 - (X \times 88)] = 100 - 34.32 = 65.68$ gm in 100 gm of copolymer

From this it follows that

Number of moles of coumarin repeating unit (Y) is

$$Y = \frac{100 - (X - 88)}{\text{molecular mass of coumarin repeating unit}}$$

$$= \frac{65.68}{174} = 0.38 \text{ mole}$$

Therefore, the copolymer composition in 100 gm of copolymer will be given by the molar ratio

thiourea units : coumarin units

$$X : Y$$

Thus in MHCTTU_1 it is,

$$0.39 : 0.38$$

Thus the copolymer composition of sample MHCTTU_1 is 0.39 : 0.38.

So 0.39 mole of thiourea repeating units and 0.38 mole of coumarin repeating units are present in a total of 0.77 mole of copolymer sample. For the consideration of molecular weight of the repeating unit, this composition is extended for two units.

TABLE II Molecular weight determination by conductometric titration

Copolymer	*Copolymer composition* *From %N content in 100 g* *TU : MHC*	*First break (m mol/100 g of copolymer)*	*Final break (m mol/100 g of copolymer)* [a]	$\overline{DP}$	*Copolymer composition for two units*[b] *TU : MHC*	*Mol. wt. of repeating unit* [c] *Z*	*Mol. wt.* $\overline{Mn}$ (±5%) $= Z \times \overline{DP}$
$MHCTTU_1$	0.39:0.38	105	385 (380)	3.67	1.01:0.99	261	958
$MHCTTU_2$	0.12:0.51	40	505 (512)	12.60	0.38:1.62	315	3969
$MHCTTU_3$	0.25:0.44	76	463 (445)	6.10	0.72:1.28	286	1745
$MHCTTU_4$	0.20:0.47	42	471 (478)	11.21	0.60:1.40	296	3318
$MHCTTU_5$	0.18:0.48	37	468 (483)	12.65	0.55:1.45	300	3795
$MHCTTU_6$	0.16:0.49	42	484 (490)	11.50	0.50:1.50	305	3507
$MHCTTU_7$	0.31:0.41	48	400 (416)	8.33	0.86:1.14	274	2282
$MHCTTU_8$	0.42:0.36	76	378 (362)	4.97	1.08:0.92	255	1267

[a] value in brackets are based on %N content.

[c] Calculated from the value mentioned in b.

Hence the copolymer composition for two units of copolymer sample would be

$$\frac{0.39 \times 2}{0.77} : \frac{0.38 \times 2}{0.77}$$

$\therefore$ 1.01 : 0.99.

Therefore the molecular weight of the repeating unit (Z) of

$$\begin{aligned} \mathrm{MHCTTU_1} &= (1.01 \times 88) + (0.99 \times 174) \\ &= 261 \end{aligned}$$

Similarly molecular weights of repeating units (Z) for other copolymers were calculated and are shown in Table II.

The results of non-aqueous conductometry titration in pyridine of all copolymers showed that the neutralization point of the polymer is consistent with the millimoles of —OH group obtained in copolymer composition calculated from the % nitrogen content. Thus, this break in the conductometric titration curve was considered as a final break (*i.e.*, complete neutralization of —OH group) and the $\overline{\mathrm{DP}}$ of all copolymers was calculated. From the copolymer composition the molecular weight of the repeating unit (Z) of each copolymer was obtained and thus the $\overline{\mathrm{Mn}}$ values have been calculated. The results are furnished in Table II. As the value of $\overline{\mathrm{Mn}}$ depends upon the nature of copolymer and copolymerization condition, no further conclusion was made regarding $\overline{\mathrm{Mn}}$. As the copolymer showed poor solubility in *N*, *N*-dimethylformamide and insolubility in other common organic solvents their viscosity studies were not carried out.

Thermogravimetric analysis data of all the copolymers are furnished in Table I. Typical thermograms are shown in Figure 2. The TGA shows that the produced copolymer samples exhibited less than 4.5% loss at 100°C, probably corresponding to residual solvent. Degradation began around 200°C depending upon the nature of copolymer. The degradation is about 50% at the temperature of 450°C and the copolymer suffers complete degradation at 600°C. Complete weight loss, *i.e.*, around 85–96% was observed at 600°C. However, in the absence of any other information about the nature of degradation products and the relative proportions thereof, it is not possible to draw any further conclusion about the mechanism of degradation reaction

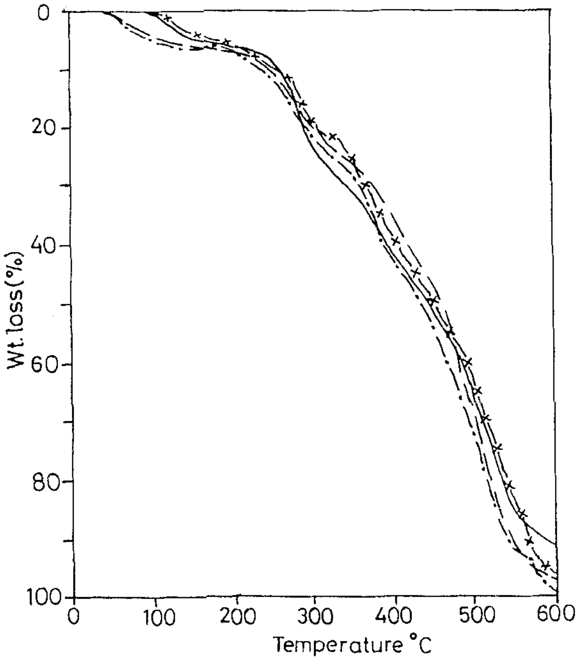


FIGURE 2 TG thermogram of: (1) --- MHCTU$_1$; (2) – – – MHCTU$_3$; (3) –·–·– MHCTU$_5$; (4) –×–×– MHCTU$_7$.

of the copolymers. The electrical conductivites (σ) of all the copolymers were measured at temperature (T) between 303 to 403 K. The plots of log $\sigma \rightarrow 1/T$ were made according to the exponential relation,

$$\sigma = \sigma_0 \, e^{-ERT}$$

Typical plots are shown in Figure 3 and the values of the activation energies (E) are included in Table III. Examination of Figure 3 (plots of log $\sigma \rightarrow 1/T$) for the electrical conductivity reveals that the conductivity increases with increase in the temperature. The values of electrical conductivity of all the copolymers at 303 K varied from 6.91×10^{-12} to $1.65 \times 10^{-11}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$. The energy of activation (E) for the electrical conductivity (σ) of all the copolymers ranged

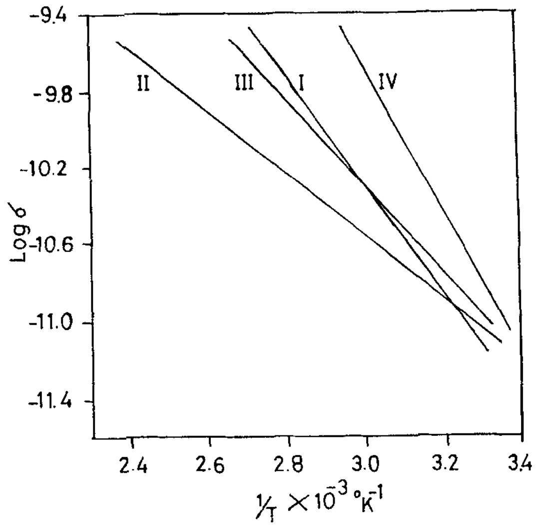


FIGURE 3 I-MHCTTU$_1$; II-MHCTTU$_3$; III-MHCTTU$_5$; IV-MHCTTU$_7$. Plot of log σ 1/T (for electrical conductivity).

TABLE III Electrical conductivity data of copolymers

Copolymer	*Electrical conductivity (σ) at 303 K (ohm^{-1} cm^{-1})*	*Intrinsic electrical conductivity (σ_0) (ohm^{-1} cm^{-1})*	*Activation energy for electrical conductivity E (KJ mole^{-1})*
MHCTTU$_1$	1.64×10^{-11}	1.26×10^{-8}	46.95
MHCTTU$_2$	6.91×10^{-12}	1.0×10^{-7}	76.57
MHCTTU$_3$	1.16×10^{-11}	1.12×10^{-9}	30.36
MHCTTU$_4$	9.29×10^{-12}	3.39×10^{-10}	26.79
MHCTTU$_5$	9.21×10^{-12}	1.58×10^{-8}	46.20
MHCTTU$_6$	7.33×10^{-12}	4.36×10^{-10}	31.32
MHCTTU$_7$	1.65×10^{11}	5.00×10^{-7}	70.00
MHCTTU$_8$	9.39×10^{-12}	2.51×10^{-11}	66.03

from 26.79 to 76.57 KJ mole^{-1}. This shows that the copolymers have semiconducting properties.

EXPERIMENTAL

Materials

The required 4-methyl-7-hydroxy coumarin was prepared by a reported procedure [7]. The trioxane and thiourea used were of laboratory grade. The acids HCl and H_2SO_4 used were of A. R. grade.

Synthesis of Copolymers (MHCTTUs)

All the copolymers (MHCTTUs) were prepared by condensing 4-methyl-7-hydroxycoumarin with trioxane and thiourea of different molar ratios in the presence of either 2M HCl or 2M H_2SO_4. A typical copolymer synthesis is described as follows:

A mixture of 4-methyl-7-hydroxycoumarin (0.01 mole), trioxane (0.02 mole) and thiourea (0.01 mole) was heated in the presence of 2M HCl (100 ml) at 110°C for four hours. The solution was cooled and the separated solid polymer was filtered out and was washed with hot water and then with ethanol to remove the monomers.

The possibly formed homopolymers of coumarin–formaldehyde and thiourea-formaldehyde were removed by repeated wash of the copolymer with hot tetrahydrofuran. The copolymer was dried and powdered. The copolymer (MHCTTU_{1-8}) produced are listed in Table I.

Measurements

The C, H and N contents of all the polymers were estimated by means of a Heraeus C, H, N, S elemental analyser (West Germany). The sulfur contents were obtained by Carius method [8]. IR spectra were taken in KBr using a Perkin Elmer 983 spectrophotometer. The number average molecular weight ($\overline{\mathrm{Mn}}$) was determined by non-aqueous conductometric titration in pyridine. Metrohm Konductoscope 365 instrument was used for the conductometric titration. The titration was carried out by taking 50 mg sample in 50 ml dry pyridine against standard 0.1 N sodium methanolate in pyridine. The degree of polymerization ($\overline{\mathrm{DP}}$) of copolymer samples were calculated by the formula reported earlier [9].

$$\overline{\mathrm{DP}} = \frac{\begin{array}{c}\text{No. of millimoles at final break of the titration curve}\\ (\textit{i.e.}, \text{ neutralization of all —OH groups})\end{array}}{\begin{array}{c}\text{No. of millimoles at first break of the titration curve}\\ (\textit{i.e.}, \text{ neutralization of first —OH group})\end{array}}$$

Thermogravimetric analysis of all the copolymers were carried out in air at a heating rate of 10°C min^{-1} on Du pont 950 thermogravimetric analyser.

Prior to measurement of the electrical conductivity of the copolymer samples, all the samples were heated twice to 100°C and subsequently cooled to room temperature. This treatment was employed to stabilize the structure of the sample and to remove impurities such as water, organic solvents *etc*. For the electrical conductivity measurement, a pellet (1.3 cm diameter and 0.2 cm thickness) of copolymer under study was prepared by pressing a finely powdered and dried sample under hydrostatic pressure at 20,000 psi for 2 minutes.

A uniform thin layer of silver paste was applied to both the sides of the pellet providing electrical contacts. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed through the pellet holder connections. The entire assembly was placed in a furnace. It was heated at a uniform heating rate. The electrical resistivities of the samples were measured by a Hewlett Packard 4329A high resistance meter.

CONCLUSIONS

1) 4-Methyl-7-hydroxy coumarin, trioxane and thiourea reacts smoothly to give the copolymers in good yields.
2) The copolymers showed thermal stability upto 200°C and degraded almost completely at 600°C.
3) The electrical conductivity data reveals that the copolymers have semiconducting properties.

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