Research Article

Study of the Effect of Solvent and Initiator on Grafting Parameters during Homogeneous Grafting of Methyl Methacrylate onto Cellulose

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Abstract

Homogeneous graft copolymerization of methyl methacrylate (MMA) onto cellulose was carried out in N, N – dimethyl acetamide/LiCl (DMAc/LiCl) and dimethyl sulfoxide/ paraformaldehyde (DMSO/PF) solvent system taking ceric ammonium nitrate (CAN), benzoyl peroxide (BPO) and tin (II)-2-ethyl hexanoate [$Sn(Oct)_2$] as initiators. Different grafting parameters like graft yield (GY), grafting efficiency (GE) and total conversion of monomer to polymer (TC) were evaluated at different reaction conditions of temperature, time, and variation of the amount of monomer and initiator. The viscosity average molecular weight of grafted PMMA and number of grafts per cellulose chain were also calculated. The products were characterized by FT-IR and ^{1}H-NMR analyses and possible reaction mechanisms were deduced. Thermal degradation of the grafted products was also studied by thermo-gravimetric analysis (TG) and differential thermo-gravimetry (DTG).

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Introduction

Cellulose and cellulose derivatives have potential applications as functional polymers in fiber, paper, and paint industries. The polymeric material with desired properties is a current need of the society. To control the properties such as hydrophobicity, adhesivity, selectivity in drug delivery, wettability and thermo-sensitivity, graft copolymerization of suitable monomer is the versatile technique for cellulose modification [1]. Although cellulose has good properties, it has some undesirable ones such as low tensile strength, high moisture regain, and low strength against microbial attack. Grafting of synthetic polymers onto cellulose eliminates these drawbacks and allows the acquisition of additional properties of grafted polymers without destroying its own properties [2].

Heterogeneous grafting of synthetic polymers onto cellulose back bone has been carried out by many researchers [1-10]. The derivatization and/or grafting reactions in homogeneous conditions assures important advantages over heterogeneous system like, a better control of the degree of substitution [11], a more uniform distribution of substituents along the polymer and a higher conversion yield [12,13]. During past few years a number of cellulose derivatives have already been synthesized under homogeneous conditions [11-21], but so far a comparative study on homogeneous graft copolymerization of cellulose dissolved in N,N-dimethyl acetamide/lithium chloride (DMAc/LiCl) and dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system using ceric ammonium nitrate(CAN), benzoyl peroxide (BPO) and tin(II) 2-ethyl hexanoate [$Sn(Oct)_2$] has not been investigated.

CAN in presence of nitric acid is an efficient initiator for graft copolymerization of vinyl monomers onto cellulose [1-3] in heterogeneous medium but in homogeneous conditions this will produce gel confirming the regeneration of cellulose from the solvent system. It is only reported that CAN in presence of dimethyl sulfoxide (DMSO) can produce Ce^{+4} ion [12] and can be a suitable redox system to initiate graft copolymerization process, but no work has been carried out on this system. Grafting reactions involving BPO [22] and $Sn(Oct)_2$ [23] as initiators has also been reported. In our earlier study we have described the homogeneous graft copolymerization of methyl methacrylate (MMA) onto cellulose in DMAc/LiCl solvent system taking CAN in presence of DMSO as initiator [24]. Therefore in the present paper we have carried out a comparative study of graft copolymerization of MMA on to cellulose by dissolving cellulose in DMAc/LiCl and DMSO/PF solvent system and taking CAN, BPO and $Sn(Oct)_2$ as initiators. The

effect of varying in reaction time, temperature, amount of initiators and monomer are studied to optimize the conditions under which grafting would occur most effectively. The effect of solvents and initiators on the graft yield and grafting efficiency has also been studied. The grafted products obtained are characterized by Fourier transformation infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The viscosity average molecular weight of the grafted PMMA and number of grafts per cellulose backbone are determined. Finally thermal degradation of the grafted products is studied by thermo gravimetric (TG) and differential thermo-gravimetric (DTG) analyses.

Materials and Methods

Materials

Cellulose powder from cotton linters, having viscosity 50 – 150 cp (Brookfield RTV, Spindle # 1, 20 rpm) was obtained from Sigma Aldrich Chemicals Pvt. Ltd. It was purified by washing with methanol, acetone, and de-ionized water and finally dried in an oven at 50 °C for 7 days. The viscosity average molecular weight was calculated by nitrating the sample and using Mark-Houwink-Sakurada equation [25] and was found to be 33,500. Methyl methacrylate purchased from Sigma Aldrich was purified from polymerization inhibitor (hydroquinone monomethyl ether) by extracting with aqueous sodium chloride – sodium hydroxide solution and dried over sodium sulfate. The stabilizer free monomer was vacuum distilled and stored below 5 °C. DMAc (sd-fine chemicals) was distilled under reduced pressure and stored on molecular sieve (4Å) under nitrogen atmosphere. DMSO (E-Merck) was kept over $CaSO_4$ for overnight. Then it was filtered and distilled over CaH_2 under reduced pressure and stored over molecular sieves (4Å). CAN, BPO and $Sn(Oct)_2$ (All E-Merck chemicals) were of reagent grade and used without further purification. N_2 gas was passed through alkaline pyrogallol, sulfuric acid and potassium hydroxide solution before it was passed into the reaction mixture.

Preparation of cellulose solution

A 2% solution of cellulose was prepared by taking 8 g cellulose in 400 mL of DMAc, heated at 150 °C for 26 min in a round bottom flask equipped with a short path condenser. Then 40 g LiCl was added and heated up to 165 °C for 8 min. It was stirred overnight to get a clear solution [11,13]. The solution was made 1% during grafting. In DMSO/PF solvent system, 5 g cellulose and 6 g PF in the ratio 1:1.2 were dispersed in 200 mL of DMSO at room temperature taken in a three necked round bottom flask. Then it was heated to 100 °C with occasional stirring for about 5 h to get a clear solution. After complete dissolution the solution was diluted to 1% concentration [16, 25].

Grafting

25 mL of 1% cellulose solution (1.45 mmol of the corresponding anhydroglucose unit) in DMAc/LiCl solvent system was taken in three necked round bottom flasks, equipped with magnetic stirrer and temperature controlled oil bath. To this 0.25 g (1.1 mmol) BPO, 0.7 mL (1.1 mmol) $Sn(Oct)_2$ and different amount of CAN ranging from 0.5 to 0.7 g (0.91to 1.28 mmol) dissolved in 10 mL DMSO was added separately followed by addition of 1.25 – 2.0 mL (11.7 to 18.7 mmol) of MMA. When cellulose solution in DMSO/PF solvent system was taken, the reaction was carried out by direct addition of different amount of CAN ranging from 0.5 to 0.7 g (0.91to 1.28 mmol) followed by addition of 1.25 – 2.0 mL (11.7 to 18.7 mmol) of MMA. All the reactions were carried out in a dry nitrogen atmosphere. The reaction was carried out at different temperatures between 30 and 80 °C for 2-6h. The reaction was terminated by addition of hydroquinone [14]. The polymerization mixture was poured into cold distilled water with vigorous stirring and kept overnight at 5 °C and then filtered, washed thoroughly in cold distilled water and dried at 50 °C and weighed. Then the products were soxhlet extracted with acetone for 24h to remove any adherent homopolymer. The extracted cellulose-grafted products were then dried at 50 °C and stored over P_2O_5.

The graft yield (GY), total conversion of monomer to polymer (TC), grafting efficiency (GE) and number of graft per cellulose chain were calculated on the basis of oven-dried weight of the cellulose from the increase in weight after grafting by using the following relations [26].

$$GY\ (\%) = \frac{C-A}{A} \times 100$$

$$GE\ (\%) = \frac{C-A}{B-A} \times 100$$

$$TC\ (\%) = \frac{B-A}{D} \times 100$$

Number of grafts per cellulose chain =

$$\frac{\text{Molecular weight of cellulose}}{\text{Molecular weight of grafted PMMA}} \times \frac{GY}{100}$$

Where A is the weight in grams of the original cellulose taken for the reaction; B is the weight in grams of the grafted cellulose before extraction; C is the weight in grams of the grafted product after extraction; and D is the weight in grams of monomer charged.

Molecular weight

Cellulose grafted with PMMA was hydrolyzed with 72 % H_2SO_4 to isolate PMMA [14]. The intrinsic viscosities [η] (in cm^3g^{-1}) of isolated graft polymers were measured at 25 °C, taking acetone as solvent to estimate the viscosity average molecular weight by using the following Mark-Houwink-Sakurada equation [14].

$$[\eta]_{Acetone} = 5.3 \times 10^{-3} M^{0.73}$$

FT-IR analysis

IR spectra of the grafted and ungrafted cellulose samples were recorded on PerkinElmer spectrometer (Spectrum RX1, PerkinElmer, Singapore) using chloroform as a solvent, in the range 4000-400 cm^{-1}, with a resolution of 2 cm^{-1}, using 4 scans per sample.

NMR analysis

The ^{1}H-NMR spectra of the grafted products were collected on a Bruker WM–400 spectrometer operating at 300 MHz for proton. All the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent for the samples.

Thermal analysis

Thermo gravimetric (TG) analysis of the grafted products was carried out using a PerkinElmer simultaneous thermal analyzer (STA 6000), in the temperature range from 50 – 600 °C at a heating rate 10 °C.min^{-1}, in nitrogen atmosphere. Indium was used as reference material for the study. 7 – 17 mg of the samples were taken for analysis.

Results and Discussion

Effect of reaction time and temperature

The graft co-polymerization of MMA onto cellulose dissolved in DMAc/LiCl solvent system using BPO, $Sn(Oct)_2$ and CAN (dissolved in DMSO) as initiators are carried out respectively at 50 – 80, 50 – 70 and 60 – 80 °C with reaction time ranging from 2 – 6 h with 1 h interval. The data on weight gain with respect to reaction time at different temperatures are shown in **Tables 1, 2 and 3**. The reaction is also carried out by changing the MMA and CAN concentration at 80 °C and the data are given in **Table 4**. Graft copolymerization of MMA onto cellulose dissolved in DMSO/PF solvent system is carried out at 30 – 80 °C with 10 °C interval for a reaction time of 3 and 6 h. The data on weight gain with respect to reaction time are given in **Table 5** and the data for variation of MMA and CAN concentration are given in Tables 6. It is observed that the GY and TC are increased with increase in reaction time in all the cases. When the reaction is carried out in DMAc/LiCl solvent system taking BPO as the initiator, it is observed that (Table 1), at a particular reaction time the GY and TG go on increasing with increase in temperature up to 70 °C and then decreases. When $Sn(Oct)_2$ is used as an initiator (Table 2), the GY and TC decrease with increase in temperature. The data for the reactions carried out taking CAN as the initiator is reflected in Table 3 and it is observed that at a particular reaction time the GY of the MMA grafted product increases with increase in temperature. Grafting reaction is also carried out in DMSO/PF solvent system using CAN as the initiator at a reaction time of 3 and 6 h and temperature ranging from 30 – 80 °C (**Table 5**). It is observed that for this solvent system, at a particular reaction time the GY goes on decreasing with increase in temperature.

Effect of MMA concentration

At a reaction temperature of 80 °C in DMAc/LiCl solvent system , keeping the CAN concentration at 5% (0.91 mmol) the concentration of MMA is changed from 5% (11.7 mmol) (Samples; Cell-*g*-PMMA-46 to Cell-*g*-PMMA-50; Table 3) to 6% (14.0 mmol) (Samples; Cell-*g*-PMMA-51 to Cell-*g*-PMMA-55; **Table 4**) and 8% (18.7 mmol) (Samples; Cell-*g*-PMMA-56 to Cell-*g*-PMMA-60; **Table 4**). It is observed that the GY and TC increase with increase in reaction time and monomer concentration.

The grafting reaction in DMSO/PF solvent system is carried out at 70 °C, keeping the initiator concentration at 5% (0.91 mmol), the MMA concentration is changed from 5% (11.7 mmol) (Sample; Cell-*g*-PMMA-79 and 80; **Table 5**) to 6% (14.0 mmol)(Samples; Cell-*g*-PMMA-83 and 84; Table 6) and 8% (18.7 mmol) (Samples; Cell-*g*-PMMA-85 and 86; Table 6). It is observed that, the GY, GE and TC do not show any regular trend. It is more or less the same with variation of monomer concentration.

Effect of CAN concentration

Grafting reactions in DMAc/LiCl are carried out at 80 °C at MMA concentration 8 % (18.7 mmol) and CAN concentration is changed from 5 % (0.91 mmol) (Samples; Cell-*g*-PMMA-56 to Cell-*g*-PMMA-60; Table 4) to 6% (1.1 mmol) (Samples; Cell-*g*-PMMA-61 to Cell-*g*-PMMA-65; **Table 4**) and 7% (1.28 mmol) (Samples; Cell-*g*-PMMA-66 to Cell-*g*-PMMA-70; Table 4). As evident from the tables, the GY and TC increases with increase in the initiator concentration at a particular reaction time.

The reaction is also carried out in DMSO/PF solvent system at 70 °C and now keeping the MMA concentration at 8% (18.7 mmol), CAN concentration is changed from 5% (0.91 mmol) (Samples; Cell-*g*-PMMA-85 and 86; Table 6) to 6% (1.1 mmol) (Samples; Cell-*g*-PMMA-87 and 88; **Table 6**) and 7% (1.28 mmol) (Samples; Cell-*g*-PMMA-89 and 90;Table 6).

Table 1 Graft co-polymerization of MMA onto cellulose in DMAc/LiCl solvent system at different temperatures with MMA 11.7 mmol and BPO 1.1 mmol

Reaction temp. (^{0}C)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
	Cell-*g*-PMMA-01	2	8	39.2	7.1	1028	2.6
	Cell-*g*-PMMA-02	3	12	37.8	8.4	1152	3.5
50	Cell-*g*-PMMA-03	4	20	36.5	10.3	1320	5.1
	Cell-*g*-PMMA-04	5	28	31.3	12.9	1550	6.1
	Cell-*g*-PMMA-05	6	32	30.3	15.8	1610	6.6
	Cell-*g*-PMMA-06	2	12	38.6	8.8	1172	3.4
	Cell-*g*-PMMA-07	3	16	36.4	9.4	1224	4.4
60	Cell-*g*-PMMA-08	4	24	35.1	10.9	1470	5.5
	Cell-*g*-PMMA-09	5	32	37.3	12.2	1615	6.6
	Cell-*g*-PMMA-10	6	40	36.6	16.9	1785	7.5
	Cell-*g*-PMMA-11	2	20	30.2	10.1	1378	4.9
	Cell-*g*-PMMA-12	3	28	29.3	11.4	1570	6.0
70	Cell-*g*-PMMA-13	4	40	28.7	16.9	1790	7.5
	Cell-*g*-PMMA-14	5	48	27.9	17.2	1922	8.4
	Cell-*g*-PMMA-15	6	52	28.8	17.8	2071	8.4
	Cell-*g*-PMMA-16	2	8	26.7	7.3	1030	2.6
	Cell-*g*-PMMA-17	3	12	27.4	8.6	1157	3.5
80	Cell-*g*-PMMA-18	4	16	26.5	9.3	1230	4.4
	Cell-*g*-PMMA-19	5	20	25.3	10.5	1375	4.9
	Cell-*g*-PMMA-20	6	28	24.9	11.6	1567	6.0

Table 2 Graft co-polymerization of MMA onto cellulose in DMAc/LiCl solvent system at different temperatures with MMA 11.7 mmol and $Sn(Oct)_2$ 1.1 mmol

Reaction temp. (^{0}C)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
	Cell-*g*-PMMA-11	2	8	29.4	9.8	1142	2.3
	Cell-*g*-PMMA-22	3	12	28.1	10.1	1340	3.0
50	Cell-*g*-PMMA-23	4	28	25.3	15.8	1877	5.0
	Cell-*g*-PMMA-24	5	32	24.7	16.3	1787	6.0
	Cell-*g*-PMMA-25	6	40	24.0	17.9	1915	7.0
	Cell-*g*-PMMA-26	2	5	20.3	8.4	1498	1.1
	Cell-*g*-PMMA-27	3	14	17.2	11.9	1611	2.9
60	Cell-*g*-PMMA-28	4	19	16.0	13.3	1625	3.9
	Cell-*g*-PMMA-29	5	24	13.2	14.4	1633	4.9
	Cell-*g*-PMMA-30	6	37	12.0	16.0	2058	6.0
	Cell-*g*-PMMA-31	2	4	25.0	7.9	1341	1.0
	Cell-*g*-PMMA-32	3	8	21.3	11.7	1340	2.0
70	Cell-*g*-PMMA-33	4	18	19.5	12.3	1564	3.8
	Cell-*g*-PMMA-34	5	16	15.7	13.2	4358	1.2
	Cell-*g*-PMMA-35	6	18	18.8	16.0	3687	1.6

Table 3 Graft co-polymerization of MMA onto cellulose in DMAc/LiCl solvent system at different temperatures with MMA 11.7 mmol and CAN 0.91 mmol dissolved in 10 mL DMSO

Reaction temp. (^{0}C)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
	Cell-*g*-PMMA-36	2	8	28.6	5.6	2172	1.23
	Cell-*g*-PMMA-37	3	12	30.0	8.0	2760	1.45
60	Cell-*g*-PMMA-38	4	16	23.5	12.8	3135	1.71
	Cell-*g*-PMMA-39	5	20	26.3	15.2	3564	1.88
	Cell-*g*-PMMA-40	6	28	29.2	19.2	4404	2.13
	Cell-*g*-PMMA-41	2	12	60.0	4.2	3268	1.23
	Cell-*g*-PMMA-42	3	16	57.1	6.0	4014	1.34
70	Cell-*g*-PMMA-43	4	20	62.5	6.8	4189	1.60
	Cell-*g*-PMMA-44	5	28	77.8	7.7	4258	2.21
	Cell-*g*-PMMA-45	6	36	47.4	16.2	4385	2.75
	Cell-*g*-PMMA-46	2	20	57.1	6.0	2974	1.80
	Cell-*g*-PMMA-47	3	24	55.6	7.7	2956	2.27
80	Cell-*g*-PMMA-48	4	28	50.0	10.2	3695	2.60
	Cell-*g*-PMMA-49	5	32	57.2	12.0	3829	2.80
	Cell-*g*-PMMA-50	6	40	58.8	14.5	4573	2.93

Table 4 Graft co-polymerization of MMA onto cellulose in DMAc/LiCl solvent system with different amount of monomer and CAN dissolved in 10 mL DMSO at 80 ^{0}C

MMA/ CAN (mmol)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
	Cell-*g*-PMMA-51	2	20	62.5	5.7	6280	1.06
	Cell-*g*-PMMA-52	3	24	50.0	5.7	6664	1.20
14.0 / 0.91	Cell-*g*-PMMA-53	4	28	70.0	7.1	9553	0.98
	Cell-*g*-PMMA-54	5	36	60.0	10.7	6546	1.84
	Cell-*g*-PMMA-55	6	44	61.1	12.8	6065	2.43
	Cell-*g*-PMMA-56	2	36	69.2	7.5	6305	1.45
	Cell-*g*-PMMA-57	3	40	62.5	8.5	8441	1.58
18.7 / 0.91	Cell-*g*-PMMA-58	4	44	61.1	9.6	8340	1.76
	Cell-*g*-PMMA-59	5	52	46.4	14.9	6888	2.53
	Cell-*g*-PMMA-60	6	56	40.0	18.7	6496	2.89
	Cell-*g*-PMMA-61	2	40	58.8	9.1	6826	1.96
	Cell-*g*-PMMA-62	3	44	50.0	11.8	9246	1.88
18.7 / 1.1	Cell-*g*-PMMA-63	4	48	48.0	13.4	7703	1.91
	Cell-*g*-PMMA-64	5	52	39.4	17.6	7653	2.10
	Cell-*g*-PMMA-65	6	60	40.5	19.8	5685	2.35
	Cell-*g*-PMMA-66	2	44	55.0	10.7	7566	1.94
	Cell-*g*-PMMA-67	3	48	45.8	12.8	9665	1.66
18.7 / 1.28	Cell-*g*-PMMA-68	4	52	7.1	18.6	9128	1.90
	Cell-*g*-PMMA-69	5	56	28.0	26.7	7096	2.83
	Cell-*g*-PMMA-70	6	60	29.4	27.2	6406	2.93

Table 5 Graft co-polymerization of MMA onto cellulose in DMSO/PF solvent system at different temperatures with MMA 11.7 mmol and CAN 0.91 mmol

Reaction temp. (^{0}C)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
30	Cell-*g*-PMMA-71	3	60	40.5	26.4	4636	4.33
	Cell-*g*-PMMA-72	6	68	31.5	38.5	4095	5.63
40	Cell-*g*-PMMA-73	3	60	53.6	19.9	4680	4.29
	Cell-*g*-PMMA-74	6	68	44.7	27.1	4144	5.50
50	Cell-*g*-PMMA-75	3	28	41.2	12.1	6951	1.35
	Cell-*g*-PMMA-76	6	40	43.5	16.4	6125	2.18
60	Cell-*g*-PMMA-77	3	36	36.0	17.8	5802	2.08
	Cell-*g*-PMMA-78	6	44	39.3	19.9	5875	2.64
70	Cell-*g*-PMMA-79	3	28	14.6	34.2	7150	1.31
	Cell-*g*-PMMA-80	6	48	22.6	37.7	5602	2.87
80	Cell-*g*-PMMA-81	3	16	20.0	14.2	5246	0.47
	Cell-*g*-PMMA-82	6	32	21.1	27.1	6132	1.74

Table 6 Graft co-polymerization of MMA onto cellulose in DMSO/PF solvent system with different amount of monomer and CAN at 70 ^{0}C

MMA / CAN (mmol)	Sample code	Reaction time (h)	% GY	% GE	% TC	Mw of PMMA	No of grafts/ cellulose chain
14.0 / 0.91	Cell-*g*-PMMA-83	3	28	14.3	26.2	7164	1.31
	Cell-*g*-PMMA-84	6	32	14.5	29.4	6259	1.71
18.7 / 0.91	Cell-*g*-PMMA-85	3	32	15.4	22.2	6241	1.71
	Cell-*g*-PMMA-86	6	48	19.1	26.9	5646	2.58
18.7 / 1.1	Cell-*g*-PMMA-87	3	16	7.5	22.7	11500	0.47
	Cell-*g*-PMMA-88	6	32	12.6	27.0	6204	1.72
18.7 / 1.28	Cell-*g*-PMMA-89	3	20	6.9	30.8	10320	0.64
	Cell-*g*-PMMA-90	6	36	8.3	46.6	6204	1.94

As evident from the tables, the GY decreases with increase in initiator concentration up to 1.1 mmol and then increases little. This may be due to increase in the rate of homopolymer formation at higher initiator concentration which is evidenced from the table as the TC of grafted PMMA increases at higher initiator concentration.

Effect of initiator and solvent

Homogeneous graft copolymerization of MMA onto cellulose is carried out in DMAc/LiCl solvent system using BPO, $Sn(Oct)_2$ and CAN (dissolved in DMSO) as initiators and the data are shown in **Tables 1 – 3**. For BPO (Table 1), the GY and TC go on increasing with increase in the reaction temperature up to 70 °C and then decreases. The graft yield at this temperature ranges from 20 – 52% at the reaction time 2 – 6 h respectively. When $Sn(Oct)_2$ is used as an initiator (**Table 2**), the GY

and TC decreases with increase in temperature and is very poor in comparison to BPO. In case of CAN (Table 3), the GY increases with increase in temperature and at 80 °C it ranges from 20 – 40% at the reaction time 2 – 6 h respectively. At this temperature molecular weight of PMMA is also more in comparison to BPO. Hence it may be inferred that CAN in presence of DMSO serves as a better initiator for graft copolymerization of MMA onto cellulose in DMAc/LiCl solvent system. Therefore for the further study to find out the effect of solvent, only CAN is chosen as the initiator.

In DMSO/PF solvent system the graft copolymerization reaction is carried out taking CAN as the initiator and the data are presented in **Table 5**. As seen from the table the GY decreases with increase in temperature at a particular reaction time. The value shows the maximum (68%) at 30 – 40 °C with a reaction time of 6 h (Samples; Cell-*g*-PMMA-72 and 74). As graft yield is more in this solvent system, it may be inferred that DMSO/PF serves as a better solvent in comparison to DMAc/LiCl for graft copolymerization of MMA onto cellulose.

Molecular weight of PMMA and number of grafts per cellulose chain

The molecular weight of PMMA extracted from the grafted samples prepared under different reaction conditions were determined and reported in the respective tables. As seen in Table 3, the grafting reactions with 11.7 mmol of monomer and 0.91 mmol of CAN, in the three temperature conditions give the grafted product having well control on the molecular weight of the PMMA and number of grafts per cellulose chain. At 14.0 and 18.7 mmol of monomer (Table 4) the molecular weight of PMMA goes on increasing up to a reaction time of 3-4 h and then decreases slowly. But the number of grafts per cellulose chain goes on increasing with increase in reaction time. The same trend is also observed at monomer 18.7 mmol with MMA 1.1 and 1.28 mmol (**Table 4**). By observing the tables 3 and 4, the conditions for getting the sample Cell-*g*-PMMA-70 in DMAc/LiCl solvent system is considered as the optimum conditions, which is grafting at 80 ^{0}C for 6 h with a 18.7 mmol of monomer, 1.28 mmol of initiator. For this sample the GE is 60%, GE is 29.4%, molecular weight of the homo polymer is 6406 and number of grafts per cellulose chain is 2.93. For DMSO/PF solvent system lower temperature is more preferred to get a good graft yield. The condition for getting the sample Cell-*g*-PMMA-74 (**Table 5**) may be considered as the optimum which is grafting at 40 °C for 6 h with monomer 11.7 mmol and initiator 0.91 mmol.

FTIR studies

FTIR spectra of the grafted cellulose in DMAc/LiCl solvent system using BPO (Sample; Cell-*g*-PMMA-15), $Sn(Oct)_2$ (Sample; Cell-*g*-PMMA-25) and CAN (Sample; Cell-*g*-PMMA-70) as initiator and the grafted product in DMSO/PF solvent system using CAN as the initiator (Sample; Cell-*g*-PMMA-74) are shown in **Figure 1**(**A – D**).

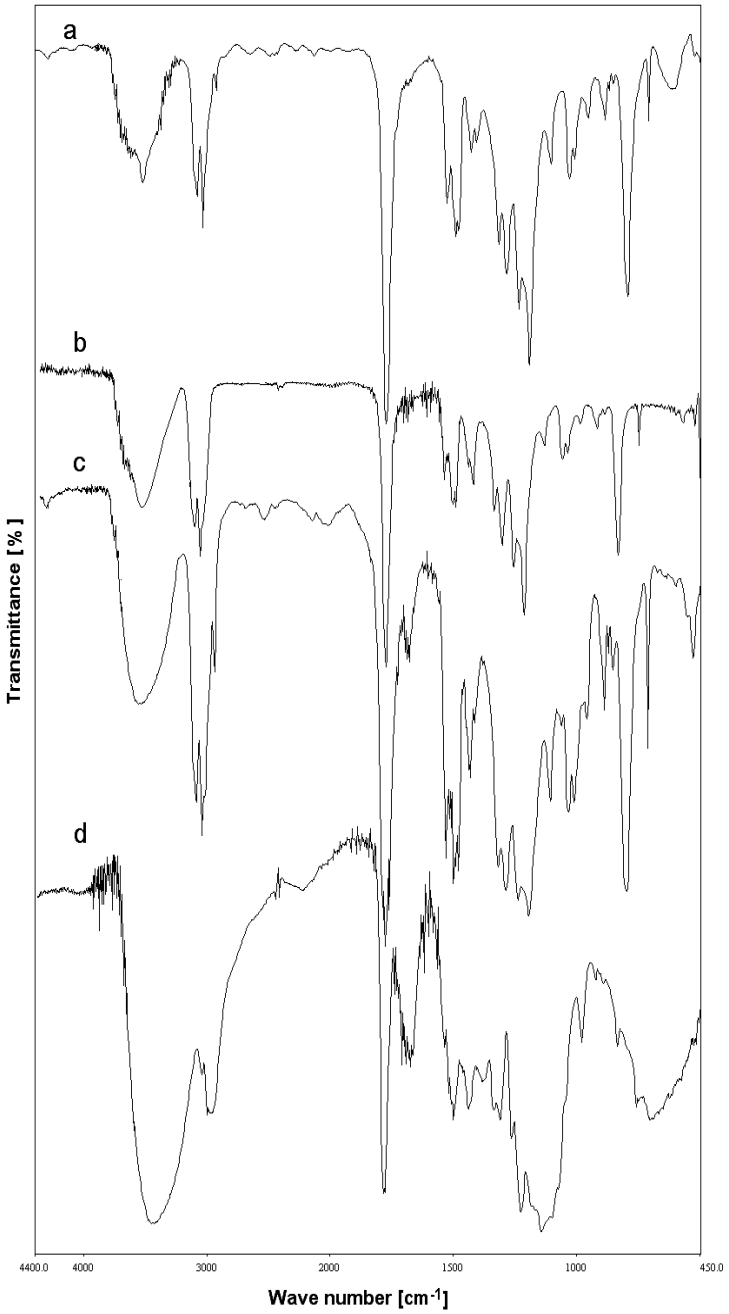


Figure 1 FTIR spectra of PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-*g*-PMMA-15) (A), PMMA grafted cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ (Cell-*g*-PMMA-25) (B), PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-*g*-PMMA-70) (C), PMMA grafted cellulose in DMSO/PF solvent system in presence of CAN (Cell-*g*-PMMA-74) (D).

All the products show identical peaks at 3432 cm^{-1} (OH str of cellulose), 2948 cm^{-1} (–CH_2- of PMMA), 1728cm^{-1} (>C=O str. of PMMA), 1632 cm^{-1} (C-C str of PMMA), 1484 cm^{-1} (OH bending of cellulose), 1447 cm^{-1} (CH bending of cellulose), 1397 cm-1 (CH deformation of cellulose), 1261 cm^{-1} (–C-O-C- str of PMMA), 1190 and 1147 cm^{-1} (C-C str of cellulose and PMMA), 1014 cm^{-1} (–CH_2- wagging of cellulose), 801 and 745 cm^{-1} (CH rocking vibrations of cellulose and PMMA), thereby indicating the formation of MMA-grafted cellulose. A more thorough comparison revels several differences between the two set of spectra, the most important for us is the decrease of the relative intensity of the –OH (3432 cm^{-1}) absorption for samples Cell-*g*-PMMA-15 (**Fig 1A**) and Cell-*g*-PMMA-25 (**Fig 1B**) in comparison to samples Cell-*g*-PMMA-70 (**Fig 1C**) and Cell-*g*-PMMA-74 (**Fig 1D**).

NMR studies

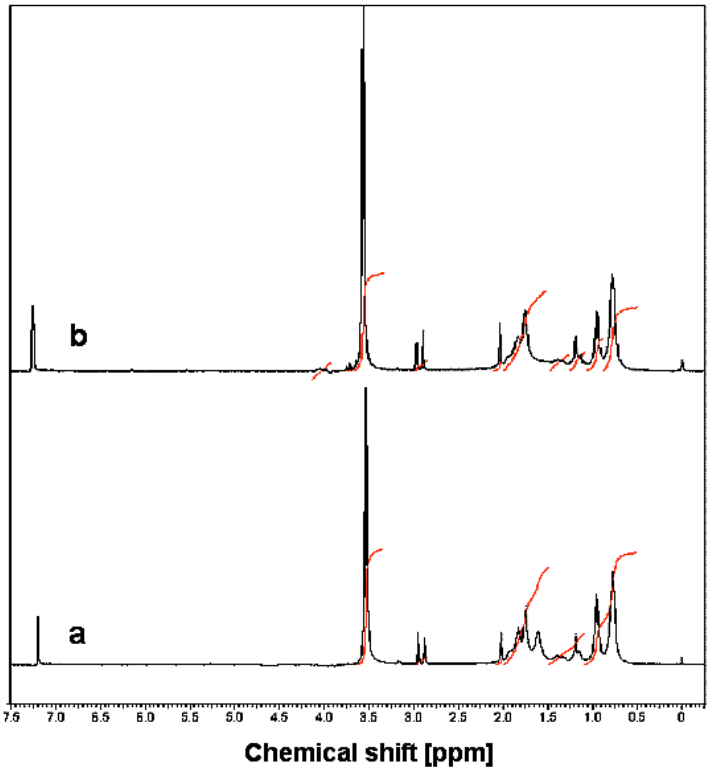


Figure 2 ^{1}H-NMR spectra of PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-*g*-PMMA-15) (A), PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-*g*-PMMA-70) (B)

^{1}H-NMR spectra of the grafted cellulose with PMMA in DMAc/LiCl solvent system using BPO (Sample; Cell-*g*-PMMA-15) and CAN (Sample; Cell-*g*-PMMA-70) as initiator are shown in **Fig 2A** and **2B** respectively. Both the products show identical peaks and the peak at 3.53 ppm is due to the –O–CH_3 group of the grafted polymer. The –CH_2- group shows peaks at 2.02, 1.83 and 1.75 ppm and the peaks at 1.18, 0.95 and 0.78 ppm are for the –CH_3 group [27]. The peak at 4.0 ppm is due to the –OH group of the cellulose chain [28], which is less intense in **Fig 2A**.

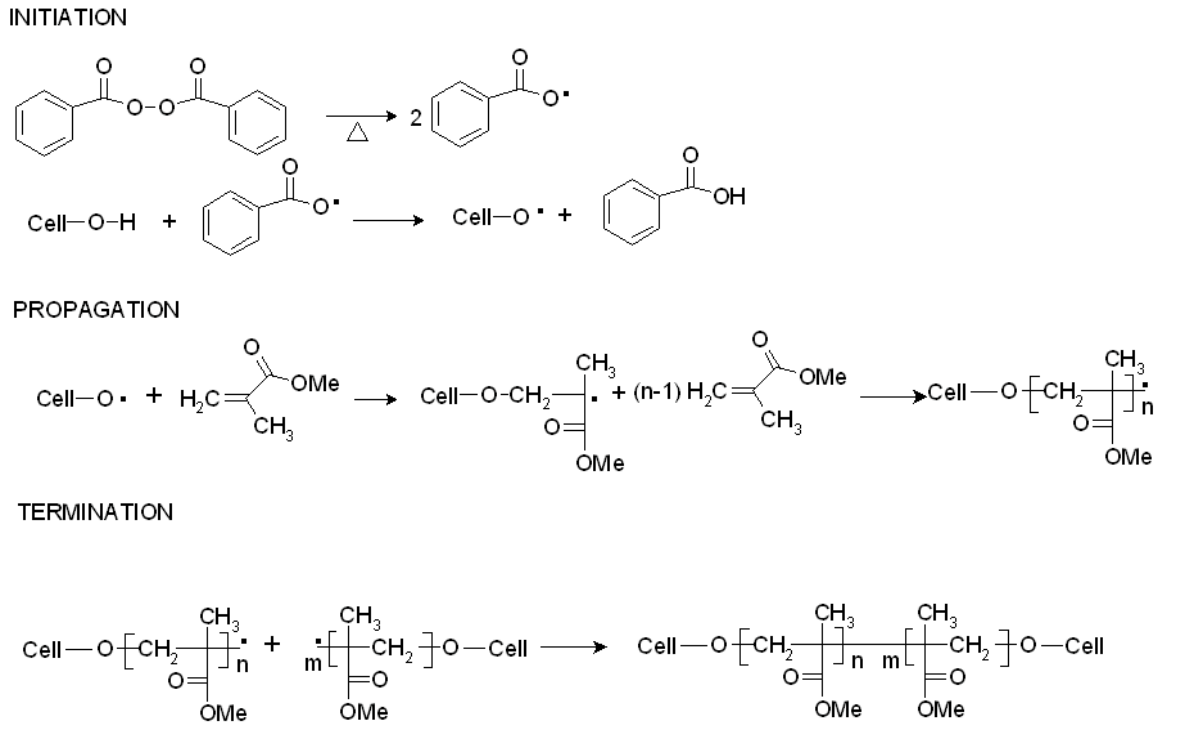
Mechanism of polymerization

When BPO is used as the initiator, the free radical is formed at the hydroxyl group of cellulose and grafting takes place by homolytic cleavage of –O-H bond. The mechanism of polymerization when $Sn(Oct)_2$ is used as the initiator is still in dubious. The most promising mechanism is a coordination-insertion mechanism where thee hydroxyl group is thought to coordinate to $Sn(Oct)_2$, forming the initiating tin alkoxide complex [29]. This can be verified by looking into the FTIR (**Fig 1A** and **1B**) and ^{1}H-NMR (**Fig 2A**) spectra of the samples where the intensity of the –OH peak decreases. Hence the mechanism for graft copolymerization of PMMA onto CA by using BPO and $Sn(Oct)_2$ as the initiator may be one which is shown in **Scheme 1** and **2** respectively

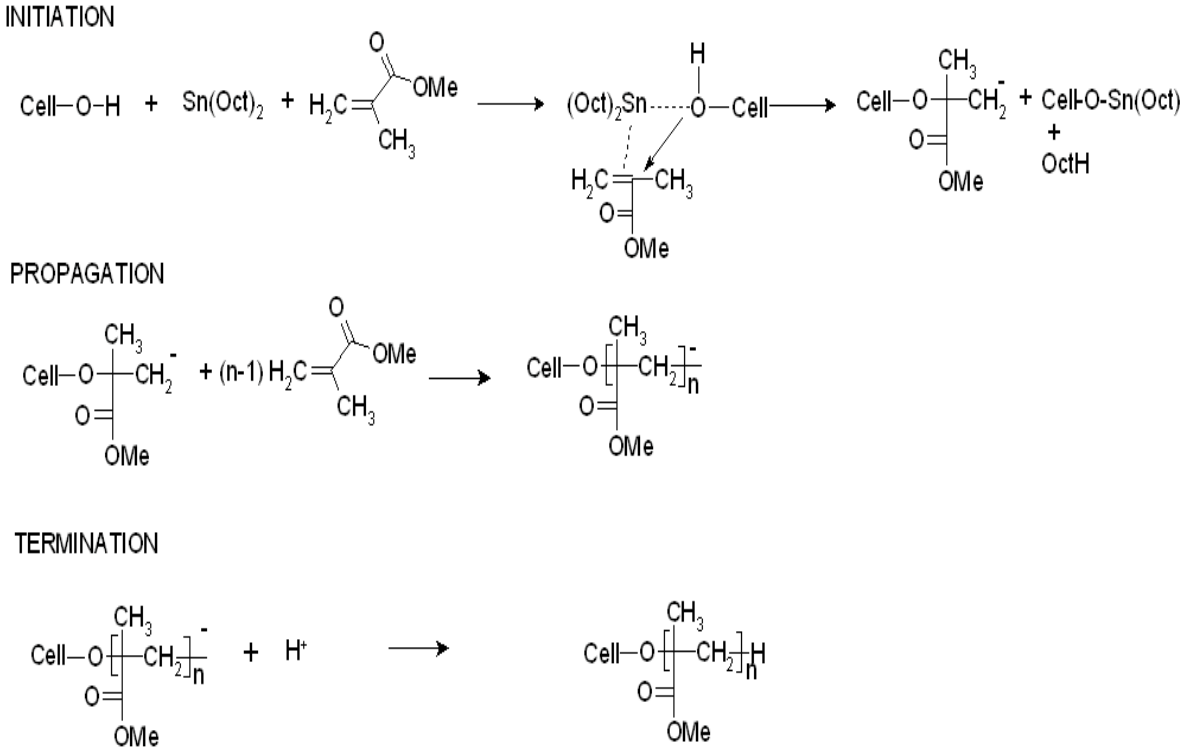
It is known that metallic cations form complexes with carbon hydrates. After complexation with cellulose, ceric ion is reduced to cerous ion, the bond between C_2 and C_3 is broken and a free radical appears on C_2 or C_3 [8]. Then this free radical initiates the monomer grafting and the polymerization reaction of MMA. The FT-IR (**Fig 1C** and **1D**) and ^{1}H-NMR (**Fig 2B**) spectra of the grafted products also shows the peaks for the –OH group which proves that the grafting occurs by breaking of a C-C bond and not at the –OH group. Hence the mechanism is the one which is shown in **Scheme 3**.

Thermogravimetric analysis

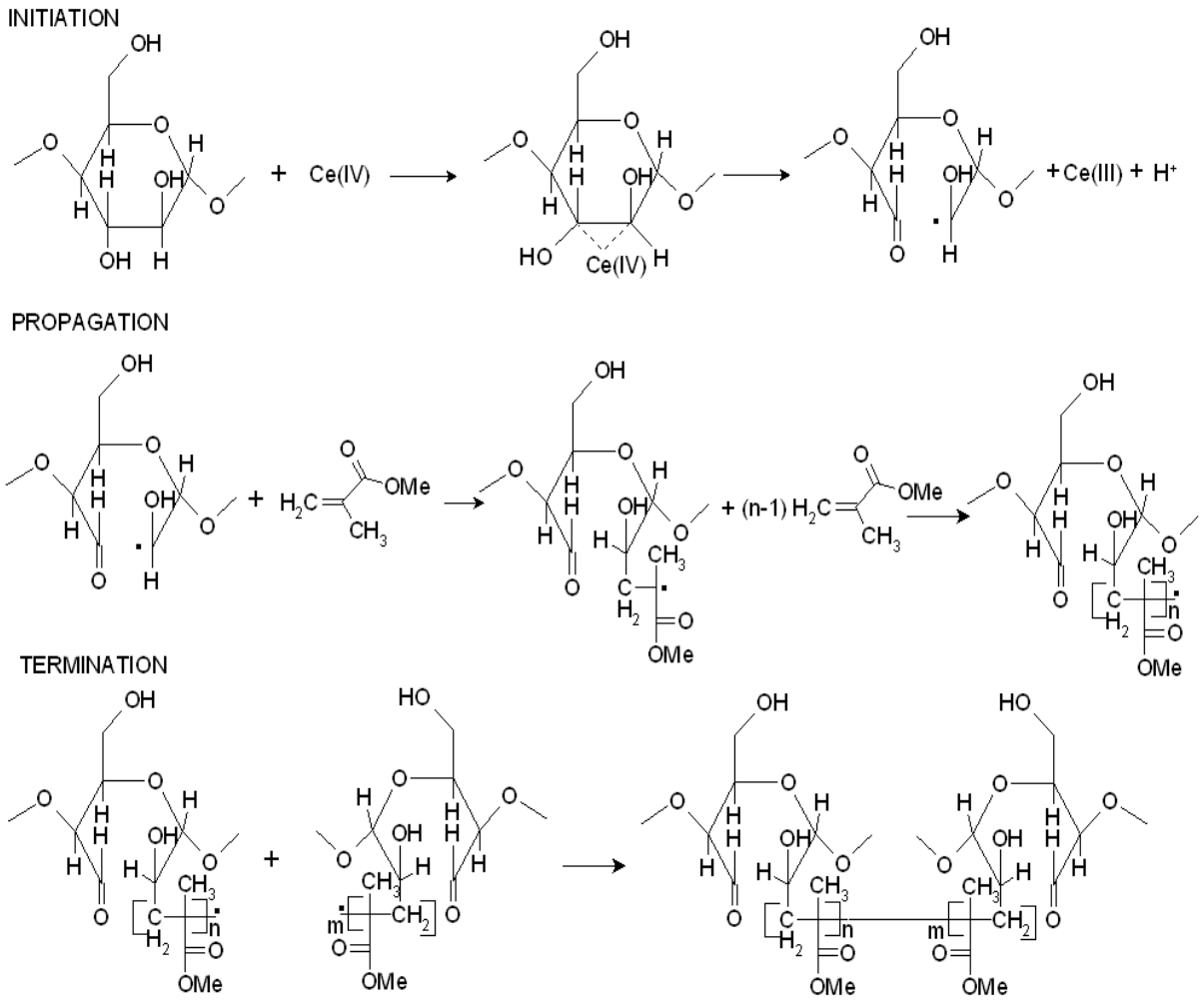
Dynamic thermo-gravimetric curves of the grafted samples Cell-*g*-PMMA-15, Cell-*g*-PMMA-25, Cell-*g*-PMMA-70 and Cell-*g*-PMMA-74 are given in **Fig 3**. Each of the curves shows three different zones. An initial zone of slight loss in weight is due to evaporation of water. Then the break in each thermogram indicates the onset of the decomposition process involving rapid loss in weight. At the end of this break a slight curvature is formed which might be due to the formation and evaporation of some volatile compounds. Finally, the decomposition rate decreases gradually to a constant weight representing carbonization [30]. The percentage weight loss of these samples with temperature is given in **Table 7**. The initial decomposition for Cell-*g*-PMMA-15 starts at 251 °C where as that for Cell-*g*-PMMA-25 it is 240 °C, for Cell-*g*-PMMA-70 it is 221 °C and for Cell-*g*-PMMA-74 it is 205 °C. The DTG curves show the temperature of active decomposition (ADT), which is 274 °C for Cell-*g*-PMMA-15, 264 °C for Cell-*g*-PMMA-25, 255 °C for Cell-*g*-PMMA-70 and 258 °C for Cell-*g*-PMMA-74. There is not much variation of thermal stability between Cell-*g*-PMMA-15 and Cell-*g*-PMMA-25 (only 10 °C);



Scheme 1 Mechanism of grafting of PMMA onto Cellulose using BPO as the initiator.



Scheme 2 Mechanism of grafting of PMMA onto Cellulose using $Sn(Oct)_2$ as the initiator.



Scheme 3 Mechanism of grafting of PMMA onto Cellulose using CAN as the initiator.

Table 7 Thermal stability of cellulose grafted products in Nitrogen at heating rate 10 °C.min^{-1}.

Sample code	IDT[a] (°C)	ADT[b] (°C)	Wt loss (%)							
			200^{0}C	250^{0}C	300^{0}C	350^{0}C	400^{0}C	450^{0}C	500^{0}C	550°C
Cell-*g*-PMMA-15	251	274	6.3	9.8	37.7	48.9	57.9	68.5	82.9	98.8
Cell-*g*-PMMA-25	240	264	8.9	19.6	47.7	52.4	56.6	60.1	63.2	65.4
Cell-*g*-PMMA-70	221	255	2.6	4.1	10.0	37.2	63.3	70.7	72.4	72.7
Cell-*g*-PMMA-74	205	258	8.9	12.1	20.3	46.2	82.6	88.0	92.4	100.0

[a] IDT is the initial decomposition temperature.
[b] ADT is the temperature of active decomposition

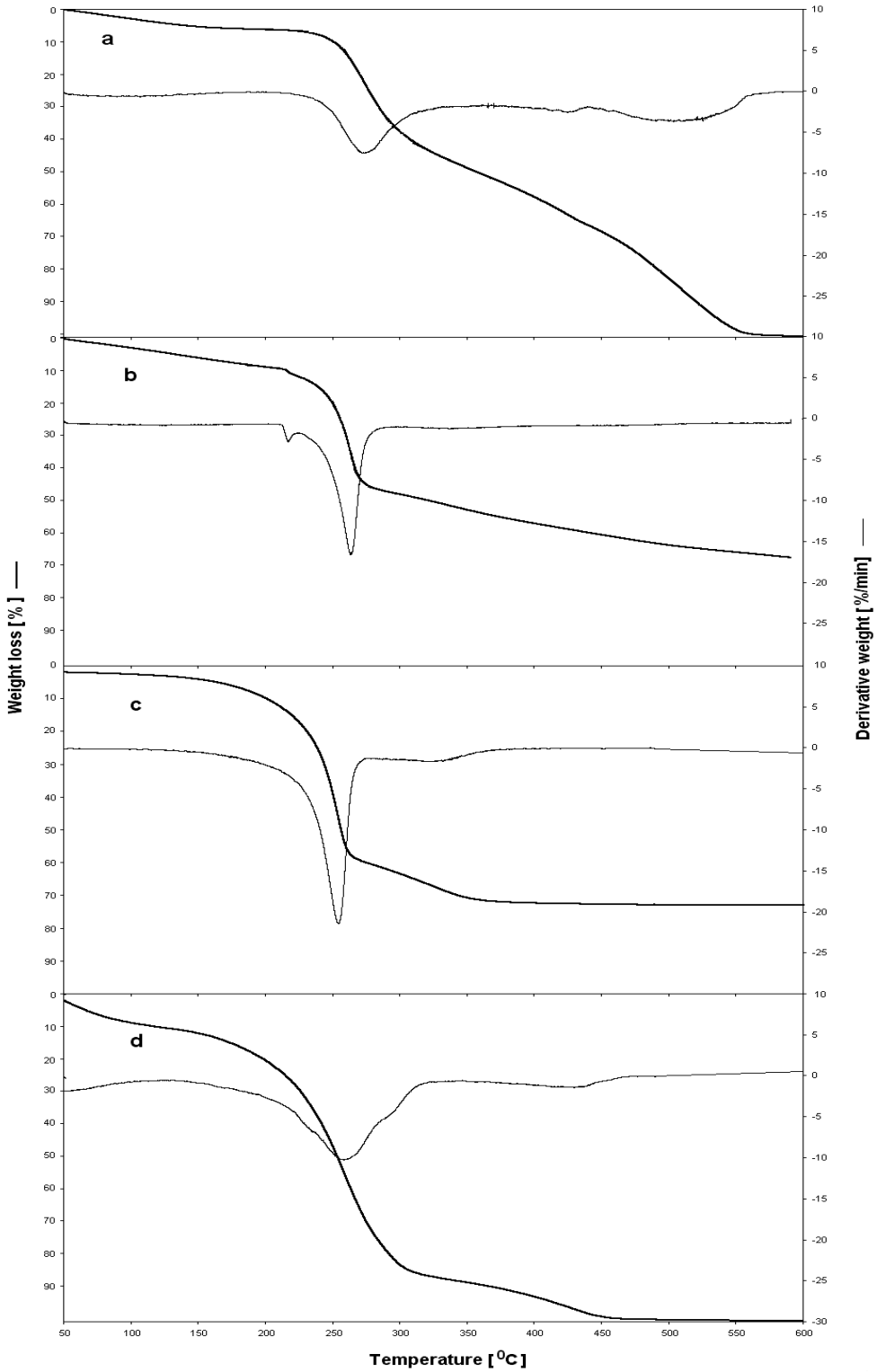


Figure 3 Thermogravimetric analysis (TG and GTD) of PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-*g*-PMMA-15) (A), PMMA grafted cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ (Cell-*g*-PMMA-25) (B), PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-*g*-PMMA-70) (C), PMMA grafted cellulose in DMSO/PF solvent system in presence of CAN (Cell-*g*-PMMA-74)(D).

but thermal stability of Cell-*g*-PMMA-70 is still less than the above two samples. This may be due to the increase in the molecular weight of the grafted homopolymer in Cell-*g*-PMMA-70. When grafting is carried out in DMSO/PF solvent system, the thermal stability of the grafted product (Sample; Cell-*g*-PMMA-74) is still lower, which may be due to the formation of methylol cellulose in the said solvent system. Due to the presence of ether linkage, methylol cellulose is thermally less stable that cellulose [30].

Conclusions

Homogeneous graft copolymerization of MMA onto cellulose in DMAc/LiCl and DMSO/PF solvent systems can be carried out by using BPO, $Sn(Oct)_2$ and CAN as initiator. The formation of grafted products is confirmed by FTIR and ^{1}H-NMR spectroscopy. The effect of reaction time and temperature, monomer and initiator concentration on the GY, GE and TC are evaluated. Graft copolymerization of cellulose in presence of BPO and $Sn(Oct)_2$ proceeds through free radical mechanism by hemolytic cleavage of –O-H bond of cellulose whereas in presence of CAN proceeds through ring opening of cellulose and formation of free radical in the cellulose chain, which initiates the polymerization by free radical mechanism. It is concluded that CAN serves as a better initiator in both of the solvent systems, and DMSO/PF serves as a better solvent for graft copolymerization of MMA onto cellulose. In DMAc/LiCl solvent system, grafting at 80 ^{0}C for 6 h with a 18.7 mmol of monomer, 1.28 mmol of initiator is found to be optimum condition. For DMSO/PF solvent system lower temperature is more preferred to get a good graft yield and the optimum condition is found to be the grafting at 40 °C for 6 h with monomer 11.7 mmol and initiator 0.91 mmol. Cellulose forms methylol cellulose in DMSO/PF solvent system and due to this the thermal stability of the grafted products in this solvent system is less in comparison to the grafted products prepared in DMAc/LiCl solvent system.

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