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ORIGINAL PAPER

Controlled grafting of MMA onto cellulose and cellulose acetate

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Abstract Homogeneous graft copolymerization of methyl methacrylate onto cellulose and cellulose acetate was carried out in various solvents and solvent systems taking ceric ammonium nitrate, tin (II) 2-ethyl hexanoate [$Sn(Oct)_2$] and benzoyl peroxide as initiators. The effect of solvents, initiators, initiator and monomer concentration, on graft yield, grafting efficiency and total conversion of monomer to polymer were studied. Formation of Ce^{3+} ion during grafting in presence of CAN enhances the grafting efficiency. Methylene blue was used as a homopolymer inhibitor and controlled the molecular weight of the grafted polymer and its effect on grafting was also studied. In presence of MB, amount of PMMA homopolymer formation reduced and consequently grafting efficiency increased. The number average molecular weights and polydispersity indices of the grafted PMMA were found out by gel permeation chromatography. The products were characterized by FTIR and ^{1}H-NMR analyses and possible reaction mechanisms were deduced. Finally, thermal degradation of the grafted products was also studied by thermo-gravimetric and differential thermo-gravimetric analyses.

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Keywords Cellulose · Cellulose acetate · Homogeneous medium · Grafting efficiency · Homopolymer inhibitor · Mechanism of grafting

Introduction

Cellulose is the most abundant natural polymer which is used as such or its derivatives in a number of applications, for instance in paper, packaging or lacquer technologies. Moreover, cellulose is biodegradable and obtainable from renewable sources, and, thus acceptable from the environmental point of view. However to reach the required application properties, cellulose has to be modified, mostly by a reaction of hydroxyl groups leading to cellulose esters and ethers (Edgar et al. 2001; Heinze and Liebert 2001). In addition, cellulose backbone can be grafted with synthetic polymers via 'grafting from' or 'grafting—onto' ways, using various polymerization techniques. Thus, various materials were obtained by grafting, with different properties such as elasticity, ion exchange ability, thermal stability and mechanical properties. The grafting is mostly realized via free radical polymerization initiated with redox systems, based prevailingly on ceric or ferrous salts or sodium hydrogen sulfite systems in combination with peroxides (McDowal et al. 1984; Bhattacharya and Misra 2004; Casinos 1992). Also, depending on the reaction medium, the grafting reaction may be divided into two types viz. heterogeneous and homogeneous grafting.

Heterogeneous graft copolymerization of synthetic polymers onto cellulose and cellulose acetate has been studied extensively over the past decades (Gupta and Khandekar 2003; Gupta et al. 2002; Gupta and Sahoo 2001; Princi et al. 2005a, b; Sabba and Moktar 2002; Lomberg et al. 2006; Carlmark and Malmstrom 2003; Halab-kessira and Ricard 1999; Saikia and Ali 1999; Hamburger 1969; Mazzei et al. 2002; Sarbu et al. 2006). Grafting of cellulose fiber by atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization after reacting the hydroxyl groups with suitable RAFT chain transfer agents has also been carried out (Liu et al. 2008; Chen et al. 2009; Liu et al. 2010). Using these methods, a wide spectrum of cellulose and cellulose acetate graft copolymers with acrylamide, methyl methacrylate, vinyl acetate and acrylonitrile etc. have been prepared; however, in heterogeneous medium the number, density, length and molecular weight distribution of the grafts are virtually impossible to control. The derivatization and/or grafting reactions in homogeneous conditions assures important advantages over heterogeneous system like, a better control of the degree of substitution (Tosh et al. 2000), a more uniform distribution of substituents along the polymer and a higher conversion yield (Bianchi et al. 1998; Das and Saikia 2003).

CAN in presence of nitric acid is an efficient initiator for graft copolymerization of vinyl monomers onto cellulose (Gupta and Khandekar 2003; Gupta and Sahoo 2001; Gupta et al. 2002) in heterogeneous medium but in homogeneous conditions this will produce gel confirming the regeneration of cellulose and also CA from the solution. It is only reported that CAN in presence of dimethyl sulfoxide (DMSO) can produce Ce^{+4} ion (Bianchi et al. 1998) and can be a suitable redox system to initiate graft copolymerization process, but no work has been carried out on this system. A few work on grafting reactions involving BPO (Sarbu et al. 2006) and $Sn(Oct)_2$ (Videki et al. 2005) as initiator has been carried out in homogeneous conditions. In our earlier study, we have described the homogeneous graft copolymerization of MMA onto cellulose in *N*,*N*-dimethyl acetamide/lithium chloride (DMAc/LiCl) solvent system using CAN in presence of dimethyl sulfoxide (DMSO) as initiator (Tosh and Routray 2011). It has also been reported that, presence of methylene blue in the reaction system reduces the formation of homopolymers in the graft copolymerization process (Molenberg 2007; Bass et al. 2007). Therefore, in the present study, homogeneous graft copolymerization of MMA onto cellulose and cellulose acetate was carried out by dissolving cellulose in DMAc/LiCl and dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system and cellulose acetate (CA) in various solvents like DMSO, DMAc, 1,4-dioxane and acetone using CAN, BPO and $Sn(Oct)_2$ as initiators. Three initiators have been chosen as they follow different reaction mechanisms during grafting. CAN forms free radical in the cellulose ring by homolytic cleavage of the C–C bond and also the presence a metal ion in the reaction medium reduces homopolymer formation and thus enhances grafting efficiency (Bhattacharya and Misra 2004). BPO follows free radical mechanism by homolytic cleavage of O–H bond of the hydroxyl group where as $Sn(Oct)_2$ follows heterolytic cleavage of the O–H bond. No work has also been reported on the grafting of MMA onto cellulose or CA by taking $Sn(Oct)_2$ as the initiator. Therefore, in the present study, the homogeneous grafting of MMA onto cellulose and CA by taking $Sn(Oct)_2$ as the initiator and a comparative study on the effect of solvents and other two initiators on the graft yield and grafting efficiency has been carried out. The effect of varying in reaction time, temperature, concentration of initiator and monomer were studied to optimize the conditions under which grafting would occur more effectively. The effect of methylene blue on the control of homopolymer formation in presence of CAN in all of the solvents was also studied. The grafted products obtained were characterized by Fourier transformation infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and possible reaction mechanisms for different initiators were deduced. The degree of crystallinity of cellulose, CA and the grafted products were found out by X-ray diffraction studies. Finally, thermal degradation of the grafted products was studied by TG and DTG analyses.

Experimental

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 (Saikia et al. 1996) and was found to be 33,500. Cellulose acetate (Sigma Aldrich, 37.9 % acetyl and $M_n \sim 50{,}000$ by GPC) was purified by dissolution in tetrahydrofuran (THF), precipitation in diethyl ether, followed by Soxhlet extraction to remove any trace of low molecular weight alcohols and water. Thereafter it was thoroughly dried under vacuum. Methyl methacrylate (MMA) (Sigma Aldrich) was purified from the polymerization inhibitor (hydroquinone monomethylether) by extraction with 5 % aqueous NaOH, water and dried over Na_2SO_4 and then under CaH_2 at reduced pressure. The stabilizer free monomer was vacuum distilled and stored below 5 °C. DMSO was kept over $CaSO_4$ for overnight. Then it was filtered and distilled over CaH_2 under reduced pressure and stored over 4Å molecular sieves. *N*,*N*-Dimethyl acetamide was fractionally distilled under reduced pressure and stored over molecular sieves. 1,4-Dioxane was pre-dried over sodium wire. Then it was refluxed over Na (1 % w/v) and benzophenone (0.2 % w/v) under nitrogen atmosphere until the blue colour of the benzophenone ketyl radical anion persists. Then it was distilled and stored over 4Å molecular sieves in the dark. Acetone was dried over $CaSO_4$ and distilled and kept over molecular sieves. CAN, BPO, $Sn(Oct)_2$, methylene blue (0.05 wt% solution in water) (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 (Tosh et al. 2000; Das and Saikia 2003). 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 (Saikia et al. 1996; Tosh and Saikia 1997).

Graft copolymerization

125 mL of 1 % cellulose solution (7.25 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 (0.91 to 1.28 mmol) dissolved in 10 mL DMSO was added separately followed by addition of 1.25–2.0 mL (11.7–18.7 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 (0.91–1.28 mmol) followed by addition of 1.25–2.0 mL (11.7–18.7 mmol) of MMA.

1.25 g CA (7.0 mmol of the corresponding anhydroglucose unit by considering 37.9 % acetyl content of CA) was dissolved in 125 mL DMSO, DMAc, 1,4-dioxane and acetone taken separately to make 1 % solution. To this differing amounts of CAN ranging from 0.5 to 0.7 g (0.91–1.28 mmol) was added followed by addition of 1.25–2.0 mL (11.7–18.7 mmol) of MMA. When DMAc, 1,4-dioxane and acetone were taken as solvents, 0.5 g of CAN was dissolved in 12.5 mL of DMSO and added to the reaction system followed by addition of MMA. Reactions having BPO and $Sn(Oct)_2$ as catalyst, 1.1 mmol of respective catalyst were taken followed by 18.7 mmol of MMA. All the reactions were carried out in a dry nitrogen atmosphere. The reactions were carried out for 2–6 h at varying temperature range of 30–80 °C and for acetone the temperature was restricted to 55 °C. The reaction was terminated by addition of hydroquinone (Nishioka and Kosai 1981). 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 24 h to remove any adherent homopolymer and then dried at 50 °C and stored over P_2O_5.

Analysis of the polymers

The graft yield (GY), total conversion of monomer to polymer (TC), grafting efficiency (GE) and number of

grafts per cellulose or CA chain were calculated on the basis of oven-dried weight of the cellulose or CA from the increase in weight after grafting by using the following relations (Tosh and Routray 2011).

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

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

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

$$\text{No.of grafts per cellulose (or CA) chain} = \frac{\text{Molecular weight of cellulose (or CA)}}{\text{Molecular weight of grafted PMMA}} \times \frac{\text{GY}}{100}$$

where A is the weight in grams of the original cellulose or CA taken for the reaction; B is the weight in grams of the grafted cellulose or CA 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

The graft copolymer was dipped in 72 % H_2SO_4 for 24 h for complete hydrolysis. The residual acid was neutralized by Na_2HCO_3 and then extracted with chloroform to isolate PMMA. The complete hydrolysis of the grafted product was ensured by analyzing the isolated PMMA by FTIR spectrophotometer. The intrinsic viscosities (η) (in cm^3g^{-1}) of isolated graft polymers were measured at 25 °C, taking acetone as a solvent to estimate the viscosity average molecular weight (Mη)by using the following Mark-Houwink-Sakurada equation (Saikia and Ali 1999).

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

GPC analysis

The number average molecular weight (M_n) and polydispersity indices (PDI) of the grafted PMMA extracted from the graft copolymer of some selected samples were measured by GPC on an Agilent 1100 instrument equipped with 3 PSS GPC 8 300 mm, 5 µm, 10^6, 10^5, 10^3 A column using THF as the eluent at a flow rate 0.8 mL/min at 20 °C. The system was calibrated with polystyrene standards having molecular weights of 200–10^6 g/mol.

FT-IR analysis

IR spectra of the grafted samples were recorded on a PerkinElmer spectrometer (Spectrum RX1, PerkinElmer, Singapore) using chloroform as a solvent for cellulose grafted products and using KBr palette technique for CA grafted products, in the range 4,000–400 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 cellulose grafted products and DMSO-d_6 for CA grafted samples.

XRD analysis

XRD analysis of cellulose, CA and the grafted products were performed with a Shimadzu diffractometer (XRD 6100, Shimadzu, Japan) with a Cu Kα target at 40 kV and 30 mA. The diffraction angle ranged from 5 to 40° with a scanning speed 5 deg/min. The crystallinities of the samples were calculated by Xc (%) = (Fc/(Fc + Fa)) × 100, where Fc and Fa were the areas of the crystalline and amorphous regions respectively.

Thermal analysis

Thermo gravimetric (TG) analysis of the grafted products was carried out using a PerkinElmer simultaneous thermal analyzer (STA 6000), in the temperature ranges from 50 to 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 copolymerization of MMA onto cellulose dissolved in DMAc/LiCl solvent system using

1.1 mmol of BPO, 1.1 mmol of $Sn(Oct)_2$ and 0.91 mmol of CAN (dissolved in 10 mL DMSO) as initiators is carried out respectively at 50–80, 50–70 and 60–80 °C with reaction times ranging from 2 to 6 h with 1 h interval. The molecular weight of the grafted polymer versus reaction time at different reaction temperatures are shown in Figs. 1, 2 and 3. Grafting of MMA onto CA in presence of 1.1 mmol of BPO, 1.1 mmol of $Sn(Oct)_2$ and 0.91 mmol of CAN (dissolved in 10 mL DMSO) as initiators in DMSO, DMAc and 1,4-dioxane is carried out at 30, 40, 50, 60, 70 and 80 °C and in acetone the reaction is carried out at 30, 40, 50 and 55 °C with reaction time ranging from 2 to 6 h with 1 h interval. The molecular weight of the grafted PMMA versus reaction time at different reaction temperatures are shown in Figs. 4, 5, 6, 7, 8, 9, 10, 11 and 12. It is observed that the molecular weight of the grafted PMMA increases with increase in reaction time in all the cases. The data on weight gain with respect to reaction time for the grafting reactions of cellulose carried out in DMAc/LiCl and DMSO/PF solvent system and CA in DMSO at 70 °C using different initiators are shown in Table 1. It is also evidenced from the table that, the GY and TC increases with increase in reaction time for all the cases.

From the Figs. 1, 2 and 3, where graft copolymerization of MMA onto cellulose dissolved in DMAc/LiCl solvent system is carried out using BPO, $Sn(Oct)_2$ and CAN as the initiators, it is observed that, at a particular reaction time the molecular weight of grafted PMMA increases with increase in temperature up to 70 °C and then decreases. Grafting reaction is also carried out in DMSO/PF solvent system using CAN as the initiator at a reaction time of 3 h and temperature ranging from 30 to 80 °C (Fig. 13). It is observed that for this solvent system, the molecular weight of the grafted polymer increases up to 70 °C and then decreases.

Graft copolymerization of CA carried out in DMSO taking BPO as the initiator, the data show (Fig. 4) a regular decrease in molecular weight of the grafted PMMA with increase in reaction temperature at a particular reaction time. But for the reactions in DMAc at a temperature of 70 °C, it gives the maximum value and then decreases with increase in temperature for a particular reaction time (Fig. 5). In 1,4-dioxane (Fig. 6) and acetone (Fig. 7), when the reaction is carried out taking BPO as initiator, the

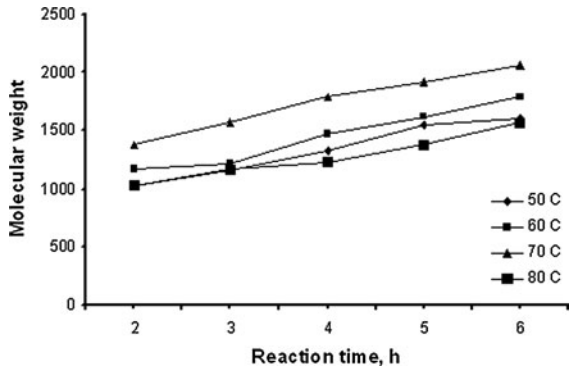


Fig. 1 Effect of reaction time on molecular weight of grafted PMMA onto cellulose in DMAc/LiCl solvent system in presence of BPO at various temperatures: cellulose, 1 % (7.25 mmol); MMA, 11.7 mmol; BPO, 1.1 mmol

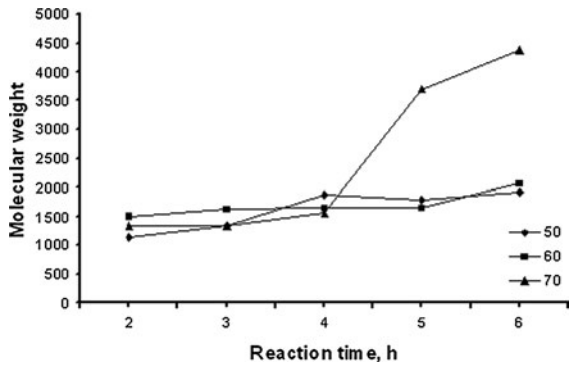


Fig. 2 Effect of reaction time on molecular weight of grafted PMMA onto cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ at various temperatures: cellulose, 1 % (7.25 mmol); MMA, 11.7 mmol; $Sn(Oct)_2$, 1.1 mmol

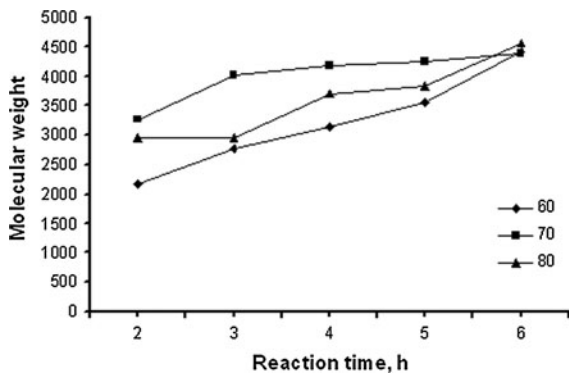


Fig. 3 Effect of reaction time on molecular weight of grafted PMMA onto cellulose in DMAc/LiCl solvent system in presence of CAN at various temperatures: cellulose, 1 % (7.25 mmol); MMA, 11.7 mmol; CAN, 0.91 mmol

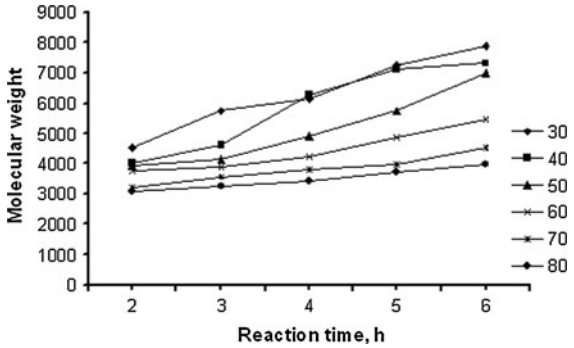


Fig. 4 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of BPO at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; BPO, 1.1 mmol

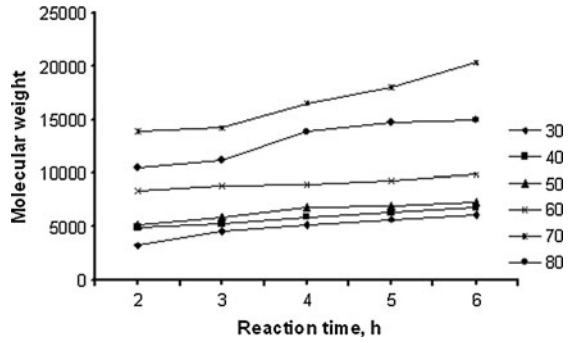


Fig. 5 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMAc in presence of BPO at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; BPO, 1.1 mmol

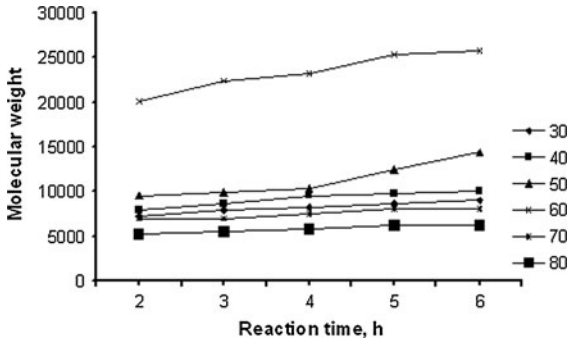


Fig. 6 Effect of reaction time on molecular weight of grafted PMMA onto CA in 1,4-dioxane in presence of BPO at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; BPO, 1.1 mmol

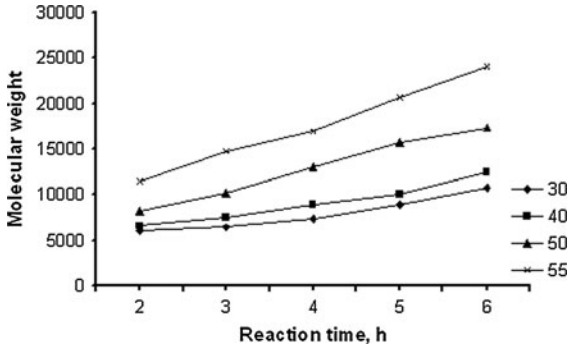


Fig. 7 Effect of reaction time on molecular weight of grafted PMMA onto CA in acetone in presence of BPO at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; BPO, 1.1 mmol

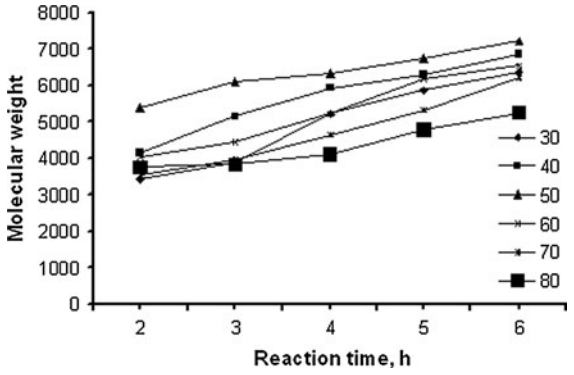


Fig. 8 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of $Sn(Oct)_2$ at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; $Sn(Oct)_2$, 1.1 mmol

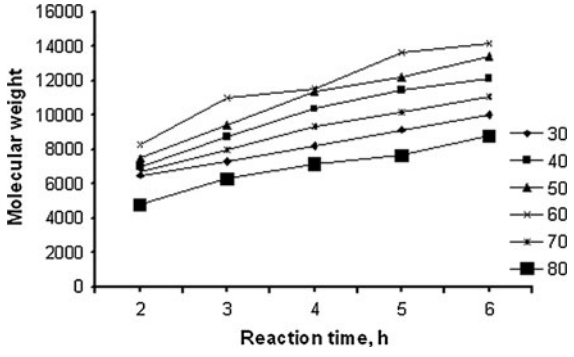


Fig. 9 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMAc in presence of $Sn(Oct)_2$ at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; $Sn(Oct)_2$, 1.1 mmol

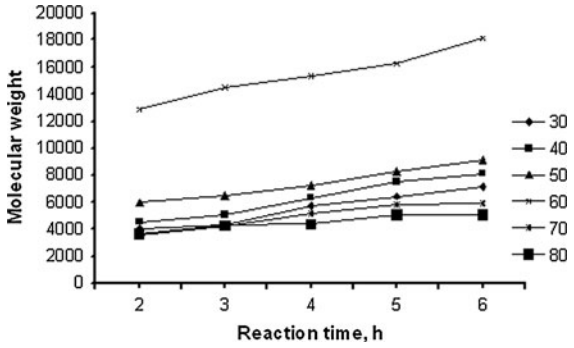


Fig. 10 Effect of reaction time on molecular weight of grafted PMMA onto CA in 1,4-dioxane in presence of $Sn(Oct)_2$ at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; $Sn(Oct)_2$, 1.1 mmol

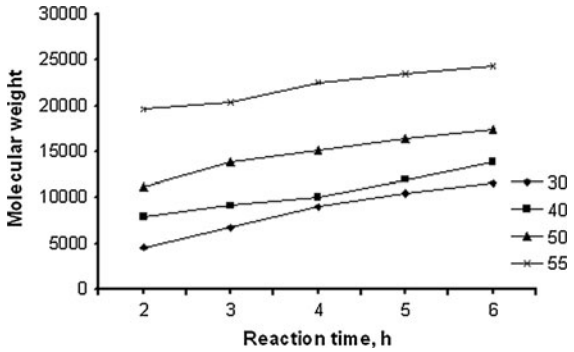


Fig. 11 Effect of reaction time on molecular weight of grafted PMMA onto CA in acetone in presence of $Sn(Oct)_2$ at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; $Sn(Oct)_2$, 1.1 mmol

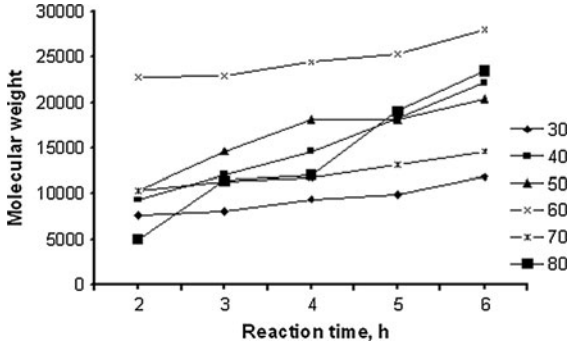


Fig. 12 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of CAN at various temperatures: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; CAN, 0.91 mmol

molecular weight of the grafted PMMA is maximum at 60 and 55 °C respectively for a particular reaction time.

The reaction is also carried out in DMSO, DMAc, 1,4-dioxane and acetone taking $Sn(Oct)_2$ as initiator and the data are reflected in Figs. 8, 9, 10 and 11 respectively. As observed from the figures molecular weight of the grafted polymer has its maximum value at 50, 60, 60 and 55 °C for DMSO, DMAc, 1,4-dioxane and acetone respectively. It is observed that the reactions carried out in DMSO taking CAN as initiator (Fig 12), at a particular reaction time the molecular weight of the grafted PMMA increases with increase in reaction temperature up to 60 °C and then decreases. The reaction taking CAN (dissolved in DMSO) as the initiator, in DMAc, 1,4-dioxane and acetone is carried out for 6 h at different temperatures and the data on the molecular weight of the grafted PMMA with respect to reaction temperature is given in Fig. 14. As evidenced from the figure, the molecular weight of PMMA has its maximum value at 80, 80 and 50 °C for DMAc, 1,4-dioxane and acetone respectively.

Effect of MMA concentration

At a reaction temperature of 70 °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) (Fig. 3) to 6 % (14.0 mmol) and 8 % (18.7 mmol) (Fig. 15). It is observed that the increase in MMA concentration in the reaction system increases the molecular weight of the grafted product. The grafting reaction in DMSO/PF solvent system is carried out for 6 h 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-17; Table 1) to 8 % (18.7 mmol) (Sample; Cell-g-PMMA-18; Table 2). It is observed that, the $M\eta$ of the grafted PMMA and GY do not change appreciably with increase in monomer concentration; but there is an increase in the PDI and decrease in the M_n of the grafted PMMA with increase in monomer concentration.

For the graft copolymerization of MMA onto CA in DMSO solvent, at a reaction temperature of 70 °C keeping CAN concentration at 0.91 mmol the concentration of MMA is changed from 11.7 mmol (Fig. 12) to 14.0 mmol and 18.7 mmol (Fig. 16). The data show that the molecular weight of the grafted products increases with increase in reaction time but decreases with increase in monomer concentration to 14 mmol and then increases a little with increase in

Table 1 Graft copolymerization of MMA onto cellulose and CA in different solvent systems at 70 °C using 1.1 mmol of BPO, 1.1 mmol of $Sn(Oct)_2$ and 0.91 mmol of CAN

Sample code	Solvent—initiator	Reaction time (h)	GY (%)	GE (%)	TC (%)	$M\eta$ of PMMA	M_n of PMMA	PDI	No of grafts/ polymer chain
Cell-g-PMMA-01	DMAc/LiCl—BPO	2	20	30.0	10.1	1,380	1,030	1.76	4.9
Cell-g-PMMA-02		3	28	29.3	11.4	1,570	1,190	1.82	6.0
Cell-g-PMMA-03		4	40	28.7	16.9	1,790	1,450	1.81	7.5
Cell-g-PMMA-04		5	48	27.9	17.2	1,920	1,620	1.95	8.4
Cell-g-PMMA-05		6	52	28.8	17.8	2,070	1,770	1.99	8.4
Cell-g-PMMA-06	DMAc/LiCl—$Sn(Oct)_2$	2	4	25.0	7.9	1,340	1,250	1.10	1.0
Cell-g-PMMA-07		3	8	21.3	11.7	1,340	1,300	1.22	2.0
Cell-g-PMMA-08		4	18	19.5	12.3	1,560	1,390	1.19	3.8
Cell-g-PMMA-09		5	16	15.7	13.2	4,360	3,230	1.12	1.2
Cell-g-PMMA-10		6	18	18.8	16.0	3,690	3,450	1.15	1.6
Cell-g-PMMA-11	DMAc/LiCl—CAN	2	12	60.0	4.2	3,270	2,920	2.21	1.2
Cell-g-PMMA-12		3	16	57.1	6.0	4,010	3,460	2.18	1.3
Cell-g-PMMA-13		4	20	62.5	6.8	4,190	3,600	2.15	1.6
Cell-g-PMMA-14		5	28	77.8	7.7	4,260	3,650	2.11	2.2
Cell-g-PMMA-15		6	36	47.4	16.2	4,390	3,720	2.19	2.8
Cell-g-PMMA-16	DMSO/PF—CAN	3	28	14.6	34.2	7,150	5,260	2.13	1.3
Cell-g-PMMA-17		6	48	22.6	37.7	5,600	4,990	2.01	2.9
CA-g-PMMA-01	DMSO—CAN	2	16	40.0	8.5	10,330	7,890	2.18	1.0
CA-g-PMMA-02		3	24	54.5	9.4	11,210	8,350	2.17	1.4
CA-g-PMMA-03		4	28	46.6	12.8	11,710	9,500	2.11	1.5
CA-g-PMMA-04		5	36	60.0	12.9	13,160	10,620	2.12	1.7
CA-g-PMMA-05		6	44	68.7	13.6	14,660	10,760	2.12	2.0
CA-g-PMMA-06	DMSO—BPO	2	16	44.4	7.9	3,200	2,570	1.88	3.1
CA-g-PMMA-07		3	20	41.7	10.4	3,570	2,730	1.89	3.7
CA-g-PMMA-08		4	24	42.9	11.9	3,800	3,000	1.88	4.0
CA-g-PMMA-09		5	28	41.1	14.6	3,990	3,120	1.91	4.5
CA-g-PMMA-10		6	32	40.0	17.1	4,540	3,530	1.90	4.5
CA-g-PMMA-11	DMSO—$Sn(Oct)_2$	2	8	13.3	12.8	3,520	3,270	1.11	1.2
CA-g-PMMA-12		3	12	15.8	16.2	3,980	3,710	1.10	1.6
CA-g-PMMA-13		4	16	14.2	23.8	4,630	4,520	1.12	1.8
CA-g-PMMA-14		5	20	14.7	29.9	5,320	4,960	1.13	2.0
CA-g-PMMA-15		6	24	16.2	31.6	6,230	5,790	1.15	2.1

monomer concentration to 18.7 mmol. As the molecular weight of the grafted PMMA decreases in DMSO by increasing the amount of MMA from 11.7 mmol in both the cases of cellulose and CA, it may be inferred that, 11.7 mmol is the optimum amount of monomer to get effective grafting. It may also be noted that, the grafting efficiency (GE) of cellulose decreases with increase in monomer concentration (Sample; Cell-g-PMMA-17; Table 1 and Cell-g-PMMA-18; Table 2). The same thing is also observed in the case of CA, where the GE of the product prepared by using 11.7 mmol of MMA is found to be 68.7 %, which decreases to 50.0 % for the product prepared by using 14.0 mmol of MMA and 48.1 % for the product prepared by using 18.7 mmol of MMA.

Effect of CAN concentration

Grafting reactions of cellulose in DMAc/LiCl are carried out at 70 °C at MMA concentration 8 %

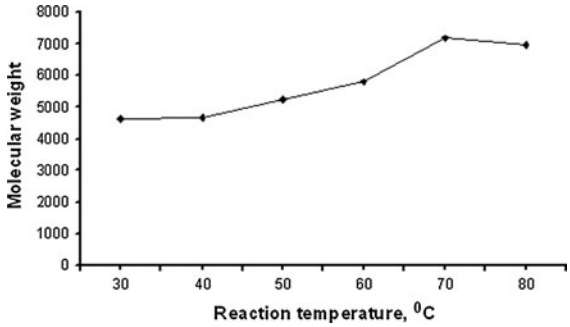


Fig. 13 Effect of reaction temperature on molecular weight of grafted PMMA onto cellulose in DMSO/PF solvent system in presence of CAN at 3 h: cellulose, 1 % (7.25 mmol); MMA, 11.7 mmol; CAN, 0.91 mmol

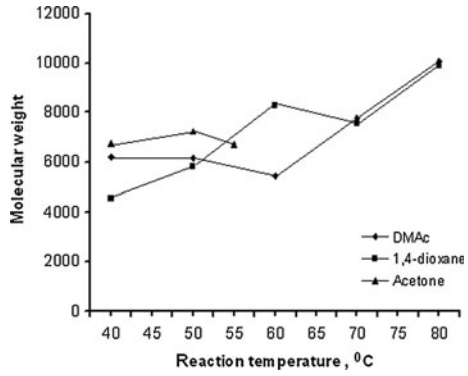


Fig. 14 Effect of reaction solvents on molecular weight of grafted PMMA onto CA in presence of CAN at 6 h: CA, 1 % (7.00 mmol); MMA, 11.7 mmol; CAN, 0.91 mmol

(18.7 mmol) and CAN concentration is changed from 5 % (0.91 mmol) (Fig. 15) to 6 % (1.1 mmol) and 7 % (1.28 mmol) (Fig. 17). As evident from the figure, there is not much variation in molecular weight of the grafted PMMA with respect to initiator concentration at a particular reaction time. The reaction is also carried out in DMSO/PF solvent system for 6 h, at 70 °C and now keeping the MMA concentration at 8 % (18.7 mmol), CAN concentration is changed from 5 % (0.91 mmol) (Sample; Cell-g-PMMA-18; Table 2) to 7 % (1.28 mmol) (Sample; Cell-g-PMMA-19; Table 2). As evident from the tables, the GY decreases with increase in initiator concentration but the molecular weight of the grafted PMMA increases noticeably and the PDI decreases. 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

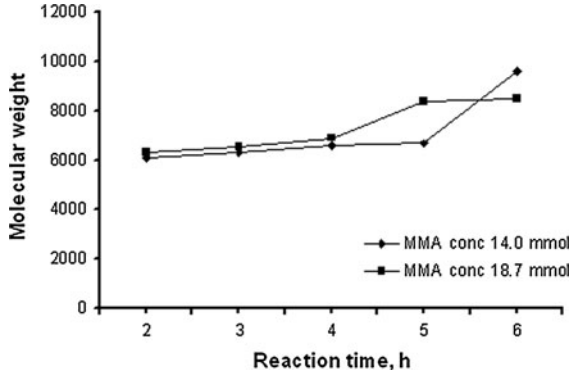


Fig. 15 Effect of reaction time on molecular weight of grafted PMMA onto cellulose in DMAc/LiCl solvent system in presence of CAN at 70 °C: cellulose, 1 % (7.25 mmol); MMA, 14.0 and 18.7 mmol; CAN, 0.91 mmol

products increases and number of grafts per cellulose chain decreases at higher initiator concentration.

Grafting reactions of CA in DMSO solvent are carried out at 70 °C at MMA concentration 18.7 mmol and CAN concentration is changed from 0.91 mmol (Fig. 16) to 1.1 mmol and 1.28 mmol (Fig. 18). As evident from the figure, molecular weight of the grafted PMMA decreases with increase in the initiator concentration at a particular reaction time except at 3 h.

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 effect of reaction time on Mη at different temperature are shown in Figs. 1, 2 and 3. The data on weight gain along with M_n and PDI when the reaction is carried out at 70 °C by using the above initiators are reflected in Table 1. For BPO (Fig. 1), the maximum value of Mη of the grafted PMMA is found to be 2,070 at 70 °C for a reaction time of 6 h. When $Sn(Oct)_2$ is used as an initiator (Fig. 2), this value is 4,360 at the above mentioned temperature and reaction time. In case of CAN (Fig. 3), the value is 4,390 at 70 °C and the reaction time of 6 h. It can be seen from Table 1, that when CAN is used as the initiator; the molecular weight of the grafted PMMA is higher and more uniform in comparison to the other two initiators. Also, the grafting efficiency for the samples prepared using CAN as the initiator in DMAc/LiCl solvent system (Samples; Cell-g-PMMA-11 to 15) is higher in comparison to those prepared by using

Table 2 Graft copolymerization of MMA onto cellulose in DMSO/PF and DMAc/LiCl solvent systems for 6 h at 70 °C with different amount of monomer and initiator and in present and absence of methylene blue 0.7 mL (1.09 ppm)

Sample code	Solvent	Monomer/initiator conc. (mmol)	Inhibitor (MB)	GY (%)	GE (%)	TC (%)	$M\eta$ of PMMA	M_n of PMMA	PDI	No of grafts/ cell. chain
Cell-g-PMMA-18	DMSO/PF	18.7/0.91	Absent	48	19.1	26.9	5,650	4,330	2.19	2.85
Cell-g-PMMA-19	DMSO/PF	18.7/1.28	Absent	36	8.3	46.6	6,200	5,470	2.11	1.94
Cell-g-PMMA-20	DMAc/LiCl	18.7/1.28	Absent	48	45.8	12.8	9,670	7,990	2.07	1.66
Cell-g-PMMA-21	DMSO/PF	18.7/0.91	Present	44	20.4	38.5	10,320	6,230	1.88	1.42
Cell-g-PMMA-22	DMSO/PF	18.7/1.28	Present	72	27.7	46.3	5,800	5,150	1.81	4.16
Cell-g-PMMA-23	DMAc/LiCl	18.7/1.28	Present	60	62.5	13.4	3,140	2,120	1.83	6.10

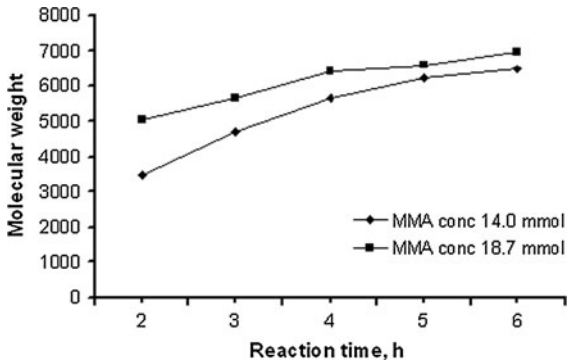


Fig. 16 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of CAN at 70 °C: CA, 1 % (7.00 mmol); MMA, 14.0 and 18.7 mmol; CAN, 0.91 mmol

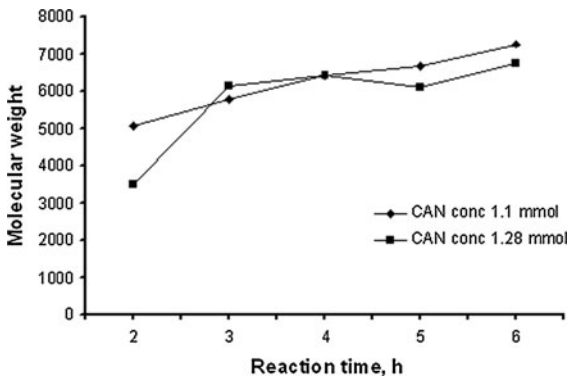


Fig. 18 Effect of reaction time on molecular weight of grafted PMMA onto CA in DMSO in presence of CAN at 70 °C: CA, 1 % (7.00 mmol); MMA, 18.7 mmol; CAN, 1.1 and 1.28 mmol

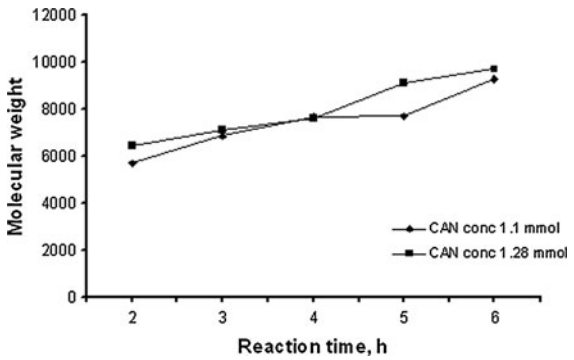
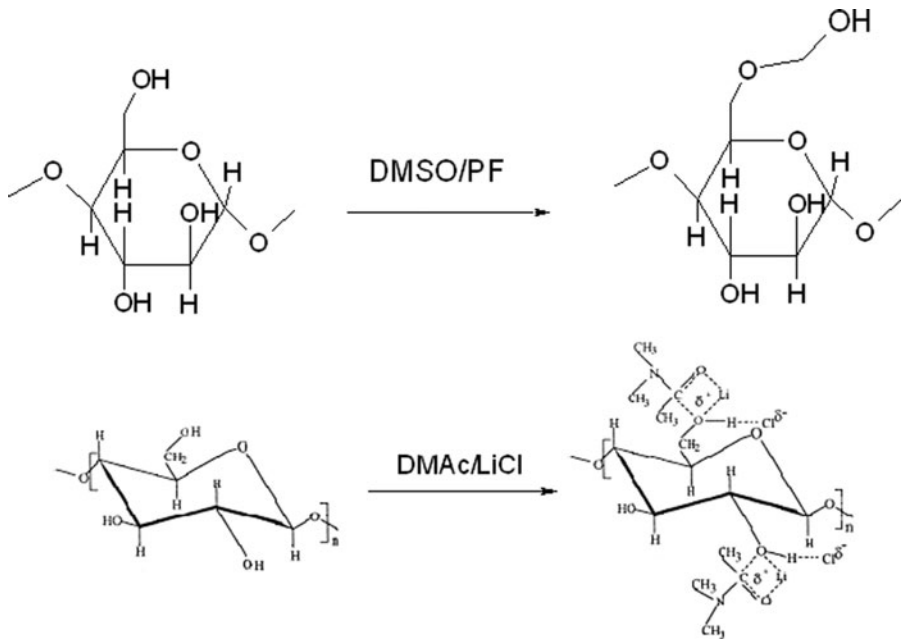


Fig. 17 Effect of reaction time on molecular weight of grafted PMMA onto cellulose in DMAc/LiCl solvent system in presence of CAN at 70 °C: cellulose, 1 % (7.25 mmol); MMA, 18.7 mmol; CAN, 1.1 and 1.28 mmol

BPO (Samples; Cell-g-PMMA-01 to 05) and $Sn(Oct)_2$ (Samples; Cell-g-PMMA-06 to 10) as initiators. 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 Fig. 13. As seen from the figure, the molecular weight of the grafted PMMA is found to be 7,150 at 70 °C at a reaction time of 3 h with CAN 0.91 mmol and MMA 11.7 mmol. As the molecular weight and GY are higher in this solvent system (Table 1), it may be inferred that DMSO/PF serves as a better solvent in comparison to DMAc/LiCl for graft copolymerization of MMA onto cellulose. Dissolution of cellulose in DMSO/PF solvent system forms methylol cellulose where as in DMAc/LiCl it forms a complex the structure of which are shown in Scheme 1 (Tosh et al. 2000; Tosh 1999). The formation of the complex hinders the reaction

Scheme 1 Structure of cellulose in DMSO/PF and DMAc/LiCl solvent system



sites for the formation of free radicals for grafting and thereby decreases the GY.

Grafting of MMA onto CA is carried out in DMSO, DMAc, 1,4-dioxane and acetone taking BPO as the initiator and the data are shown in Figs. 4, 5, 6 and 7 respectively. The molecular weight of the grafted polymer is found to be highest (25,750) when the reaction is carried out in 1,4-dioxane at 60 °C in 6 h. For DMSO it had the lowest value. Hence it may be inferred that for the grafting reactions using BPO as the initiator 1,4-dioxane serve as a good solvent.

Grafting reactions of CA in the above mentioned solvents using $Sn(Oct)_2$ as the initiator is carried out and the data on the molecular weight of the grafted PMMA versus reaction time are given in Figs. 8, 9, 10 and 11. For this initiator, the molecular weight is found to be the highest (24,230) when the reaction is carried out in acetone at 55 °C for 6 h and hence can be treated as a better solvent. For CAN the molecular weight is found to be the maximum (28,030) (Fig. 12) in DMSO solvent system in comparison to other three solvents (Fig. 14). As seen from Table 1, the GY and GE is more for the grafting reactions of CA carried out in DMSO taking CAN as the initiator (Sample; CA-g-PMMA-01 to 05) in comparison to that in case of BPO (Samples; CA-g-PMMA-06 to 10) and $Sn(Oct)_2$ (Samples; CA-g-PMMA-11 to 15). The TC is also less for the former case. As CAN forms Ce^{3+} ion during grafting, the metal ion reduces homopolymer formation and increases the grafting efficiency.

Effect of inhibitor

It is already discussed that, CAN serves as a better initiator for grafting of cellulose or CA in different solvent systems or solvents. Hence, to study the effect of methylene blue as the inhibitor for the formation of homopolymer, the grafting reactions of cellulose are carried out in DMSO/PF solvent system at 70 °C for 6 h with MMA 18.7 mmol, CAN 0.91 and 1.28 mmol and methylene blue 0.7 mL (1.09 ppm). In DMAc/LiCl solvent system the amount of MMA, CAN and methylene blue is kept at 18.7 mmol, 0.91 mmol and 1.09 ppm respectively. The data on weight gain, molecular weight of the grafted PMMA and number of grafts per cellulose chain are given in Table 2. As evidenced from the Table, the GY and number of grafts per cellulose chain increases in presence of MB in DMSO/PF solvent system having initiator 1.28 mmol (Samples; Cell-g-PMMA-19 and 22). At lower amount of CAN (0.91 mmol) (Samples; Cell-g-PMMA-18 and 21) the GY and number of grafts per cellulose chain decreases in presence of MB. This indicates lower concentration of the initiator is not suitable for the inhibitor to act effectively. The molecular weight (both $M\eta$ and M_n) of the grafted PMMA decreases by

Table 3 Graft copolymerization of MMA onto CA in various solvents for 6 h at different temperature with MMA 11.7 mmol and CAN 0.91 mmol and methylene blue 0.7 mL (1.09 ppm)

Sample code	Solvent	Temp. (°C)	Inhibitor (MB)	GY (%)	GE (%)	TC (%)	Mη of PMMA	M_n of PMMA	PDI	No of grafts/ cell. chain
CA-g-PMMA-16	DMSO	70	Present	20	50	8.0	4,290	3,110	1.79	3.2
CA-g-PMMA-17	DMAc	70	Absent	44	32	6.8	7,790	3,930	2.01	5.6
CA-g-PMMA-18	DMAc	70	Present	36	60	12.8	2,460	1,560	1.86	11.5
CA-g-PMMA-19	1,4-dioxane	70	Absent	56	32	6.8	7,570	4,390	1.96	6.4
CA-g-PMMA-20	1,4-dioxane	70	Present	76	86	18.8	2,980	2,150	1.75	17.7
CA-g-PMMA-21	Acetone	40	Absent	28	12	2.56	6,760	3,850	2.08	3.6
CA-g-PMMA-22	Acetone	40	Present	24	55	9.4	1,500	1,120	1.71	10.7

addition of MB both in DMSO/PF (Samples; Cell-g-PMMA-19 and 22) and DMAc/LiCl (Samples; Cell-g-PMMA-20 and 23) solvent system.

For CA the graft copolymerization reaction is carried out at 70 °C with MMA 11.7 mmol, CAN 0.91 mmol and methylene blue 0.7 mL (1.09 ppm) using DMSO, DMAc and 1,4-dioxane as the solvents. When acetone is used as the solvent, the above conditions are maintained except the temperature, which is restricted to 40 °C. The data on weight gain along with Mη, M_n and PDI are presented in Table 3. When the reaction is carried out using DMSO as the solvent, in the presence of MB, the GY and GE found to be decreased (Sample; CA-g-PMMA-16) in comparison to that prepared in the absence of inhibitor (Sample; CA-g-PMMA-05; Table 1). In case of all the four solvents, the Mη, M_n and PDI decreases and number of grafts per CA chain increases in the presence of inhibitor. This indicates MB acts as an inhibitor for homopolymer formation and controls the molecular weight of the grafted PMMA by increasing the reaction sites in the cellulose or CA chain.

FTIR studies

FTIR spectra of the grafted cellulose in DMAc/LiCl solvent system using BPO (Sample; Cell-g-PMMA-A), $Sn(Oct)_2$ (Sample; Cell-g-PMMA-B) and CAN (Sample; Cell-g-PMMA-C) as initiator and the grafted product in DMSO/PF solvent system using CAN as the initiator (Sample; Cell-g-PMMA-D) are shown in Fig. 19a–d. All the products show identical peaks at 3,432 cm^{-1} (OH str of cellulose), 2,948 cm^{-1} (–CH_2– of PMMA), 1,728 cm^{-1} (>C=O str. of PMMA), 1,632 cm^{-1} (C–C str of PMMA), 1,484 cm^{-1} (OH bending of cellulose), 1,447 cm^{-1} (CH bending of cellulose), 1,397 cm-1 (CH deformation of cellulose), 1,261 cm^{-1} (–C–O–C– str of PMMA), 1,190 and 1,147 cm^{-1} (C–C str of cellulose and PMMA), 1,014 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 (3,432 cm^{-1}) absorption for samples prepared by taking BPO and $Sn(Oct)_2$ (Fig. 19 a, b) as the initiators in comparison to that prepared by taking CAN (Fig. 19 c, d).

FTIR spectra of CA along with PMMA grafted CA in 1,4-dioxane in presence of BPO (Sample; CA-g-PMMA-A), PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (Sample; CA-g-PMMA-B) and PMMA grafted CA in DMSO in presence of CAN (Sample; CA-g-PMMA-C), are shown in Fig. 20a–d. All the products show identical peaks at 3,439 cm^{-1} (OH str of CA), 2,998 cm^{-1} (–CH_3 and –CH_2- of PMMA and CA), 1,725 cm^{-1} (>C=O str. of PMMA and CA), 1,635 cm^{-1} (C–C str), 1,481 cm^{-1} (OH bending of CA), 1,443 cm^{-1} (–CH– bending), 1,270 and 1,240 cm^{-1} (–C–O–C– bending of PMMA), 1,190 and 1,144 cm^{-1} (C–C str of CA and PMMA), 1,060 cm^{-1} (–CH_2– wagging of CA), 745 cm^{-1} (CH rocking vibrations of CA and PMMA). The similarity of spectra of CA (Fig. 20 a) and the grafted products (Fig. 20b–d) is observed at the first glance, which is not surprising since new groups do not form in the grafting reaction. The vibration of carbonyl group at 1,725 cm^{-1} is very intensive as well as the bands

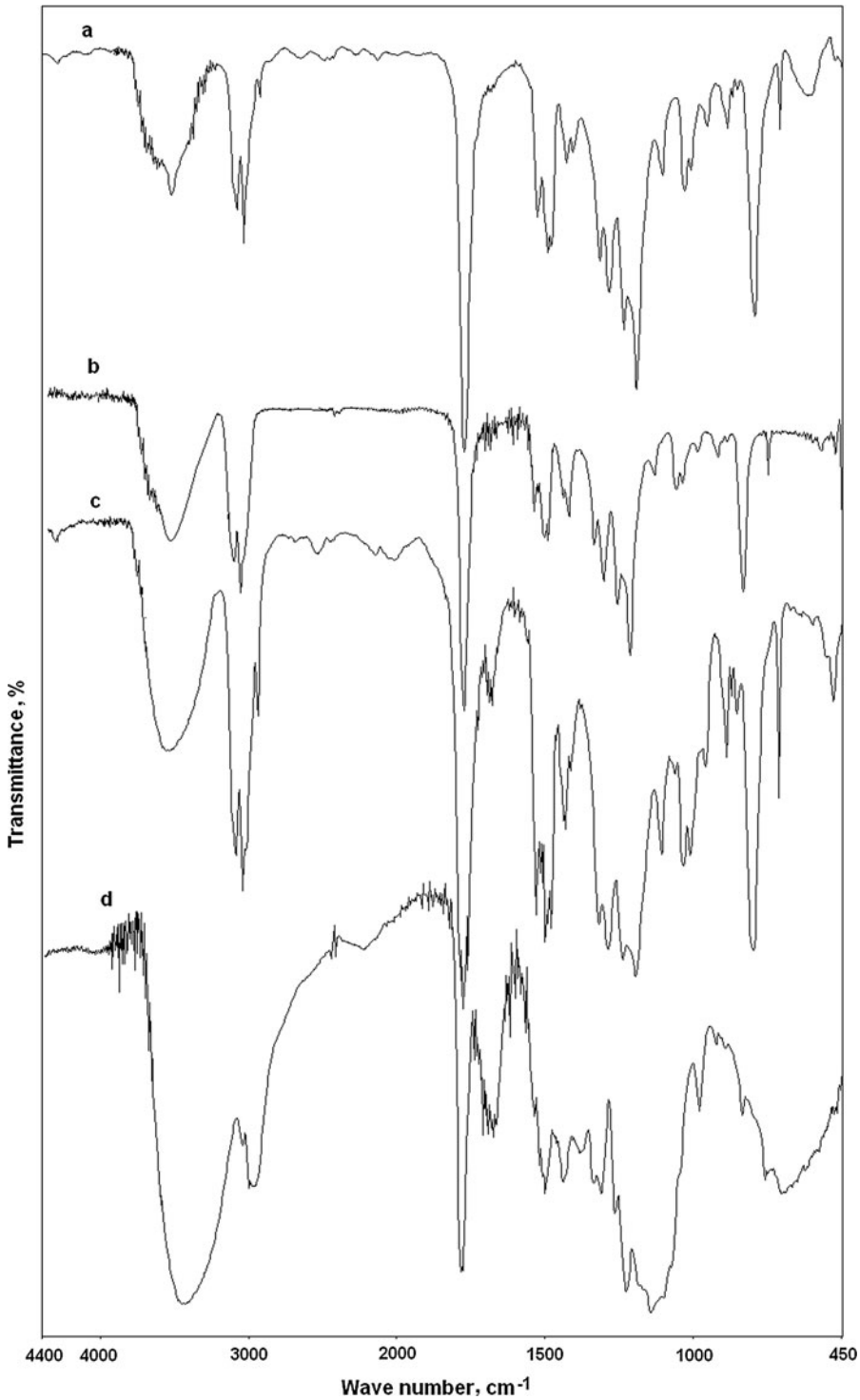


Fig. 19 FTIR spectra of **a** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-g-PMMA-A); **b** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ (Cell-g-PMMA-B); **c** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-g-PMMA-C); **d** PMMA grafted cellulose in DMSO/PF solvent system in presence of CAN (Cell-g-PMMA-D)

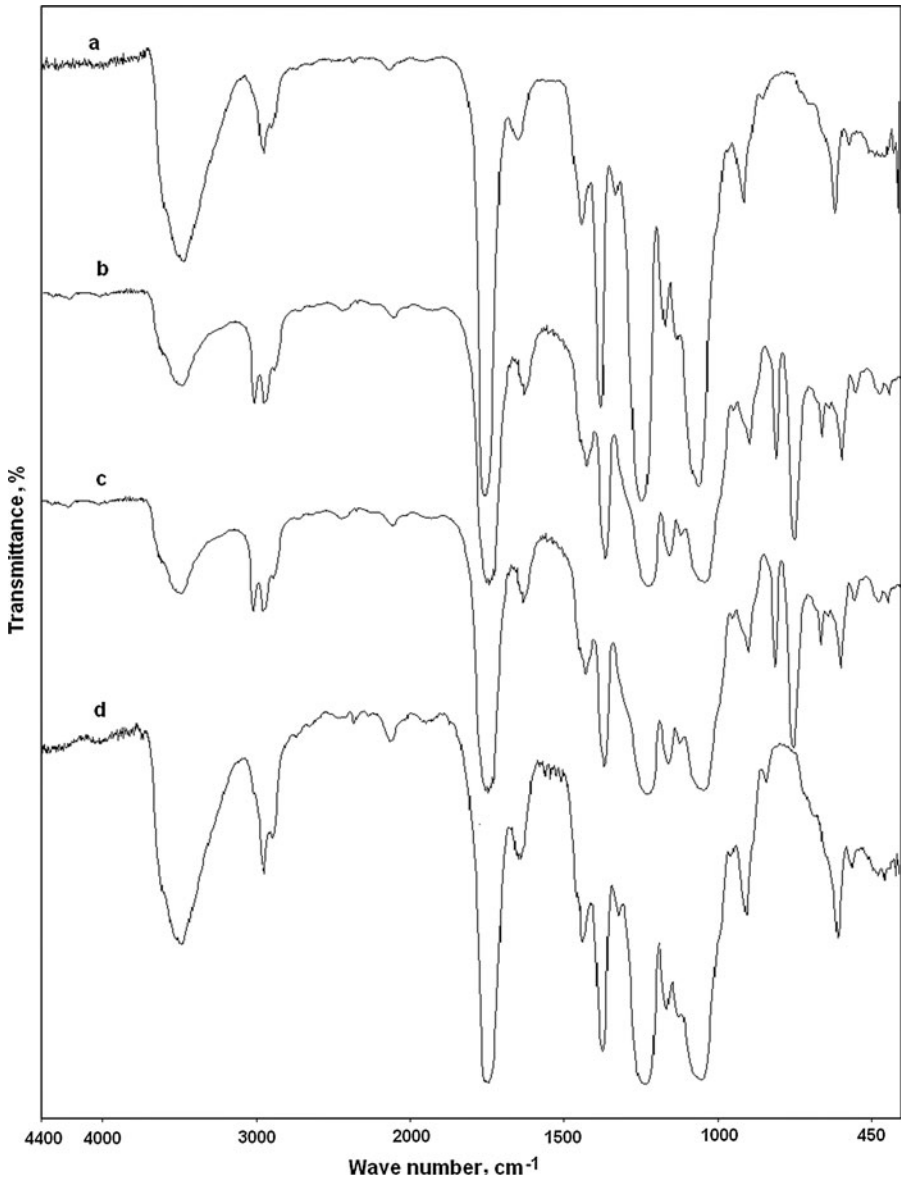


Fig. 20 FTIR spectra of **a** CA; **b** PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-A); **c** PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-B). **d** PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-C)

associated with the C–O vibration of the carbonyl group (1,240 cm^{-1}). Additional vibrations can be assigned to the $–CH_3$ moiety of the acetyl group and to other aliphatic groups included in the chain. A more thorough comparison revels several differences between the two set of spectra, the most important for us are the decrease of the relative intensity of the –OH (3,439 cm^{-1}) (Fig. 20b, c) and the increase in the absorbance of the $–CH_2–$ group (2,998 cm^{-1}) (Fig. 20b–d), thereby indicating the formation of MMA-grafted CA.

NMR studies

^{1}H-NMR spectra of the grafted cellulose with PMMA in DMAc/LiCl solvent system using BPO (Sample; Cell-

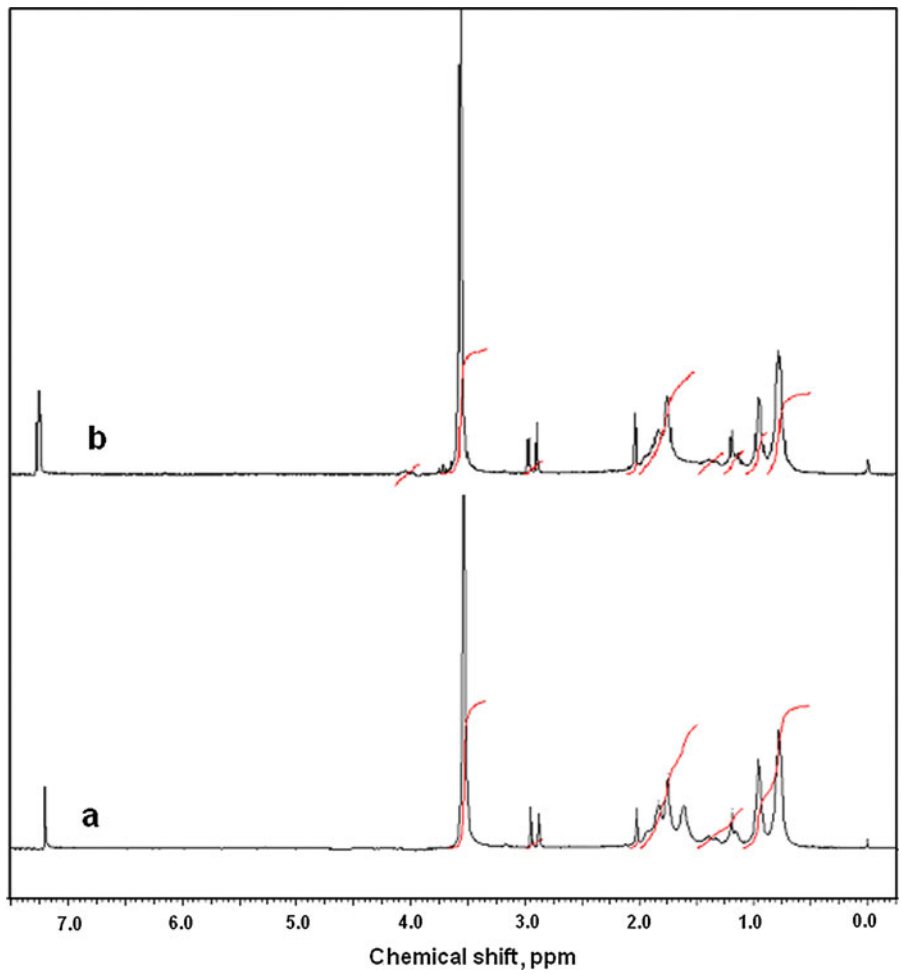


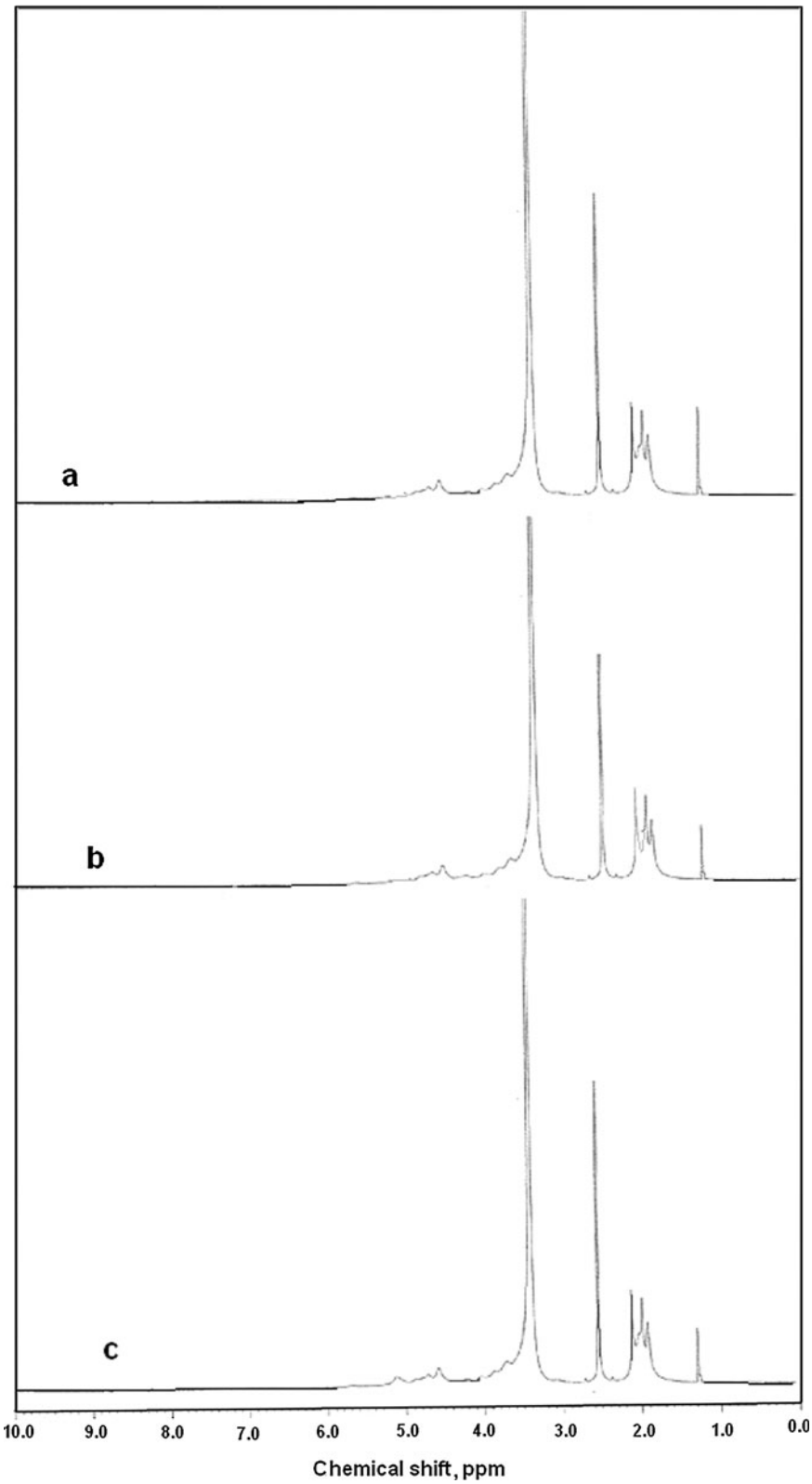
Fig. 21 ^{1}H-NMR spectra of **a** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-g-PMMA-A); **b** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-g-PMMA-C)

g-PMMA-A) and CAN (Sample; Cell-g-PMMA-C) as initiators are shown in Fig. 21a, b. 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 (Kriz et al. 1996). The peak at 4.0 ppm is due to the –OH group of the cellulose chain (Tosh 1999), which is less intense in Fig. 21a.

^{1}H-NMR spectra of PMMA grafted CA in 1,4-dioxane in presence of BPO (Sample; CA-g-PMMA-A), PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (Sample; CA-g-PMMA-B) and PMMA grafted CA in DMSO in presence of CAN (Sample; CA-g-PMMA-C) are shown in Fig. 22a–c. All the products show identical peaks and the peak at 3.36 ppm is due to the –O–CH_3 group of the grafted polymer. The –CH_2– group shows peaks at 2.07, 1.94 and 1.87 ppm and the peaks at 1.18 ppm is for the –CH_3 group. The peak at 5.06 ppm is due to the –OH group of the cellulose chain and the peak at 4.53 and 2.5 ppm are due to the –$\mathbf{CH_2}$–O–CO–CH_3 of CA. The intensity of –OH peak at 5.06 ppm is very less for PMMA grafted CA in 1,4-dioxane in presence of BPO and PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (Fig. 22a, b) in comparison to that in presence of CAN (Fig. 22c).

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

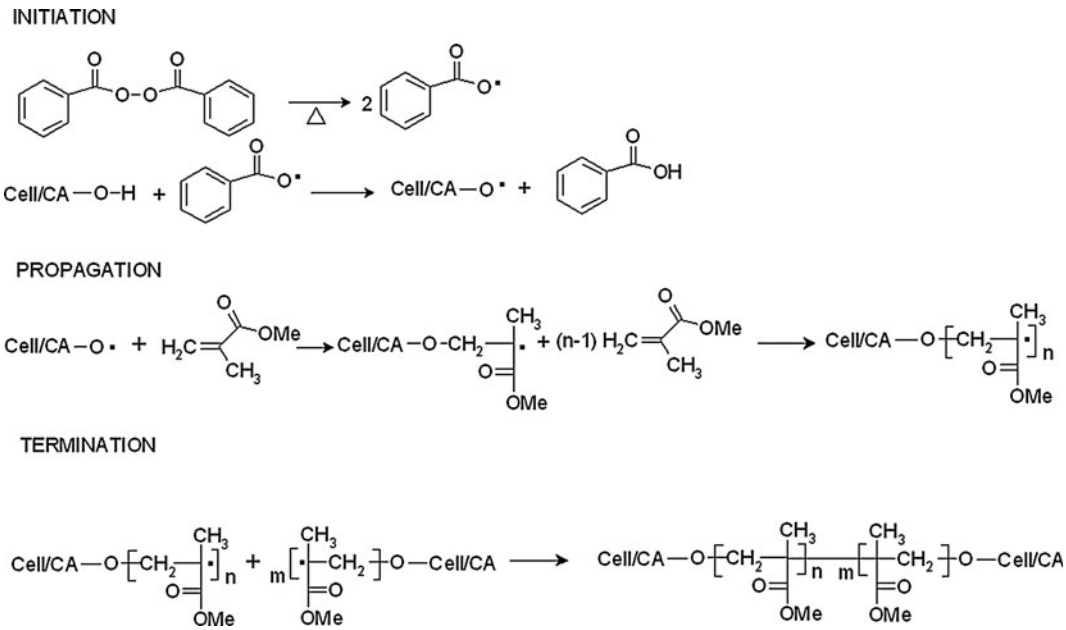

a
b
c
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical shift, ppm

◀ **Fig. 22** ^{1}H-NMR spectra of **a** PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-A); **b** PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-B), **c** PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-C)

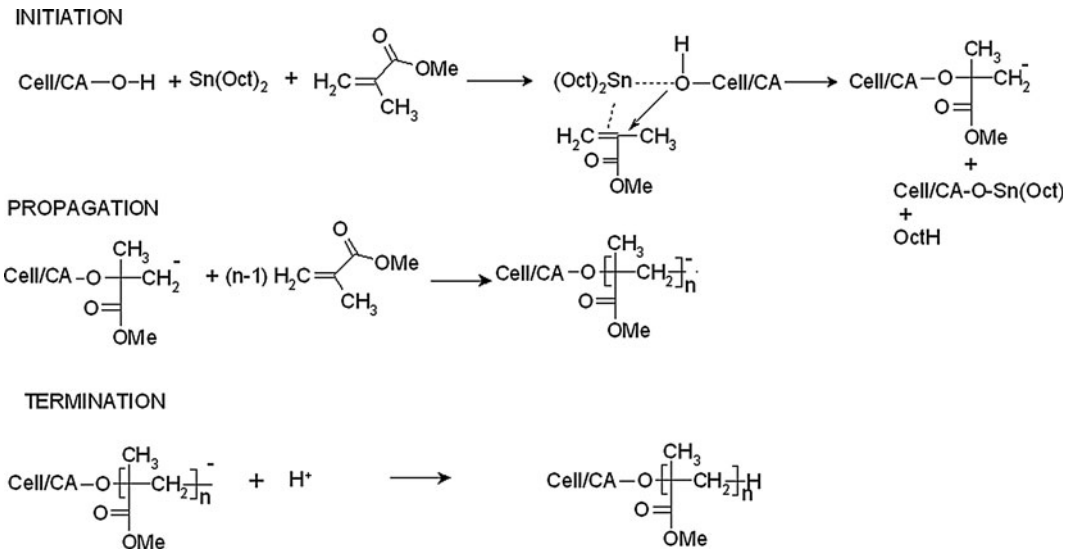
as the initiator is still in dubious. The most promising mechanism is a coordination-insertion mechanism where the hydroxyl group is thought to coordinate to $Sn(Oct)_2$, forming the tin alkoxide complex (Stridsberg et al. 2000). This can be verified by looking into the FTIR (Fig. 19 a, b, 20b, c) and ^{1}H-NMR (Fig. 21 a, 22 a, b) 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 Schemes 2, 3 respectively. It can be seen from Table 1 that, the samples prepared by using $Sn(Oct)_2$ as the initiator show the PDI between 1.1 and 1.2. The low PDI in comparison to other initiators confirms the anionic polymerization mechanism in case of $Sn(Oct)_2$ (Hamaudi et al. 2004).

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 (Halab-kessira and Ricard 1999; Han et al. 2003; Lin et al. 2005). Then this free radical initiates the monomer grafting and the polymerization reaction of MMA. The FT-IR (Fig. 19 c, d, 20d) and ^{1}H-NMR (Fig. 21b, 22c) 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 4. The formation of Ce^{3+} ion reduces the homopolymer formation in the reaction medium and hence controls the molecular weight of the grafted PMMA and increases the grafting efficiency (Bhattacharya and Misra 2004), which can be verified from Table 1 for samples where the reaction is carried out using CAN as the initiator (Samples; Cell-g-PMMA-11 to 15 and CA-g-PMMA-01 to 05).

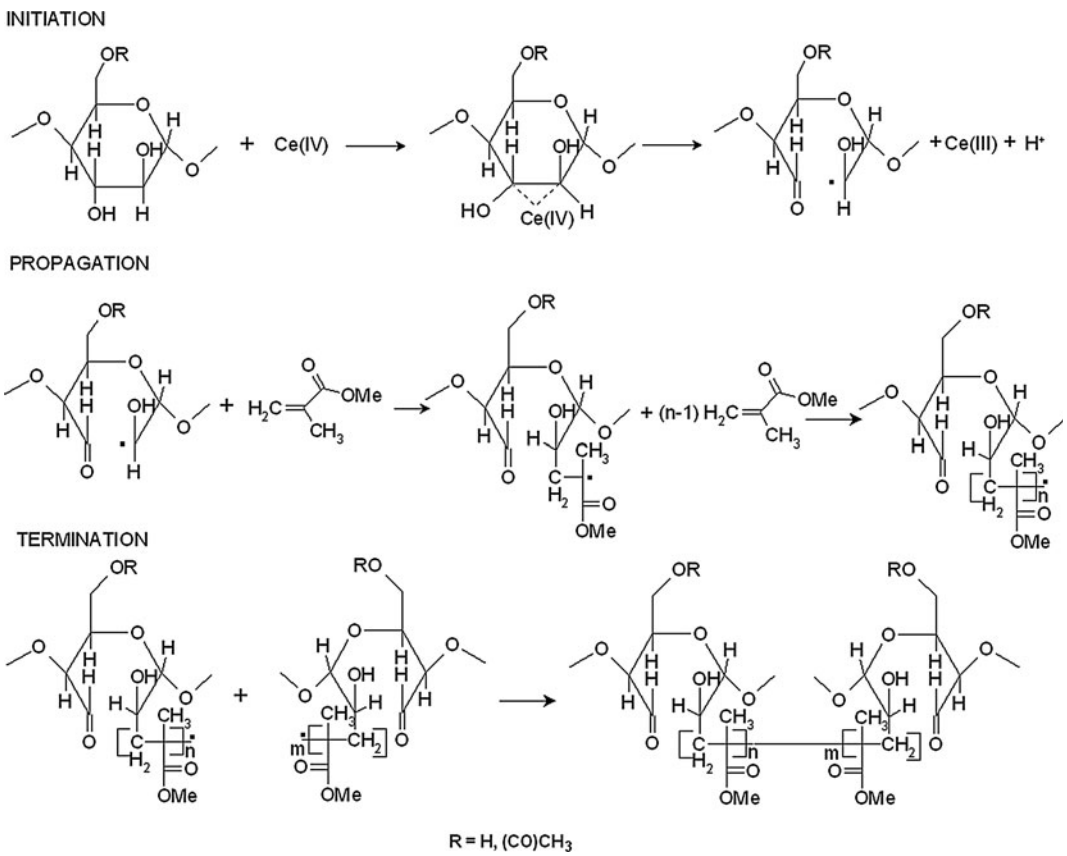
Methylene blue (tetramethyl thionine chloride, $C_{16}H_{18}ClN_3S$) (Scheme 5) is a heterocyclic aromatic dye, a member of thiazine dyes. The redox properties of MB are provided by an ability to accept or donate hydrogen ions (Galagan and Su 2008). Hence the hydrogen ion generated in the initiation step (Scheme 4) reduces MB to leuco methylene blue (LMB) and by this Ce^{3+} is again converted to Ce^{4+}. The Ce^{4+} generated in the reaction medium in the presence of MB, increases the number of reaction sites in the polymer backbone thereby increases the number of grafts per polymer chain which can be verified from Tables 2, 3. In Table 2, the samples prepared at low concentration of



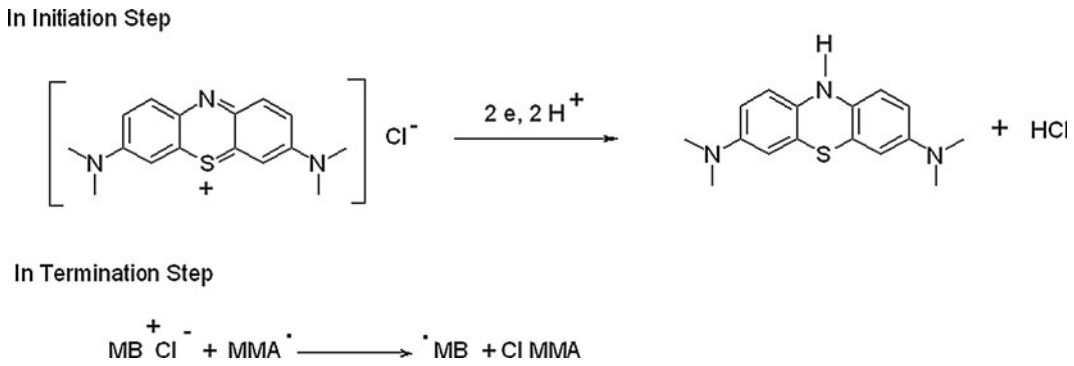
Scheme 2 Mechanism of grafting of PMMA onto cellulose/CA using BPO as the initiator



Scheme 3 Mechanism of grafting of PMMA onto cellulose/CA using $Sn(Oct)_2$ as the initiator



Scheme 4 Mechanism of grafting of PMMA onto cellulose/CA using CAN as the initiator



Scheme 5 Effect of methylene blue (MB) in the initiation and termination step

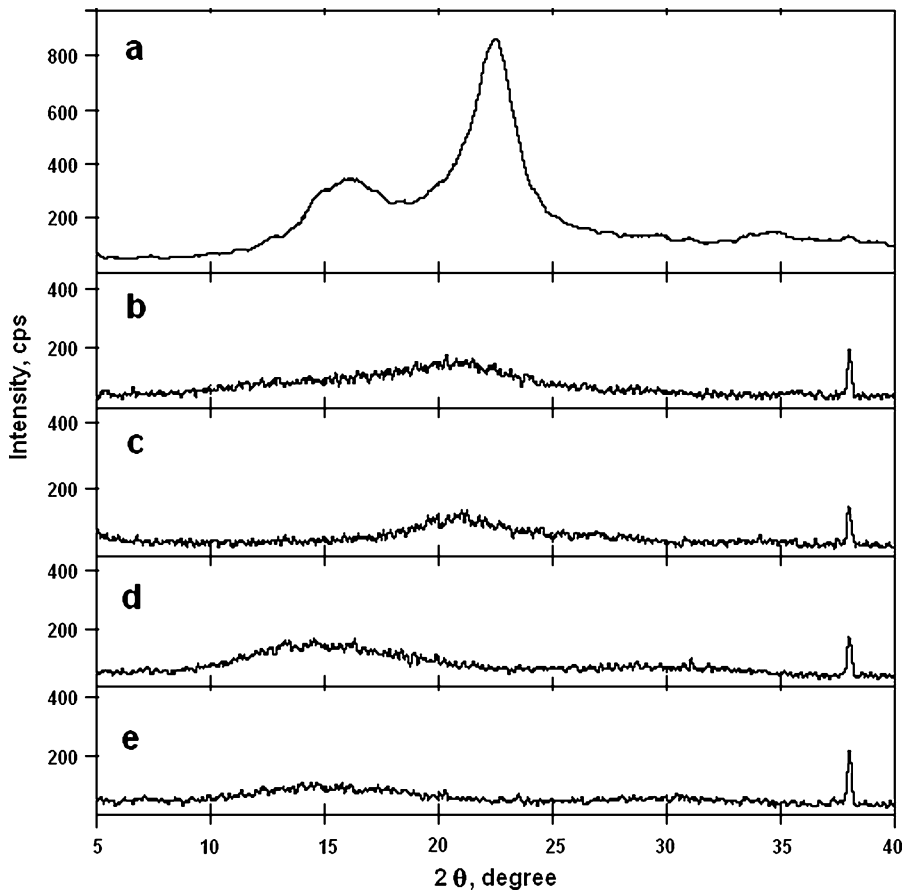


Fig. 23 XRD pattern of **a** Cellulose; **b** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-g-PMMA-A); **c** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ (Cell-g-PMMA-B); **d** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-g-PMMA-C); **e** PMMA grafted cellulose in DMSO/PF solvent system in presence of CAN (Cell-g-PMMA-D)

CAN (Samples; Cell-g-PMMA-18 and 21) are the exception and are explained earlier.

Since the dye affects the termination step (Srivastava et al. 1982), in this step the chloride ion of MB can be easily reacted with active free radical of the monomer to generate semi-reduced MB radical (Scheme 5), which can readily recombined with another radical to terminate the step and for this reason the molecular weight of the grafted PMMA decreases in the presence of MB (Tables 2, 3).

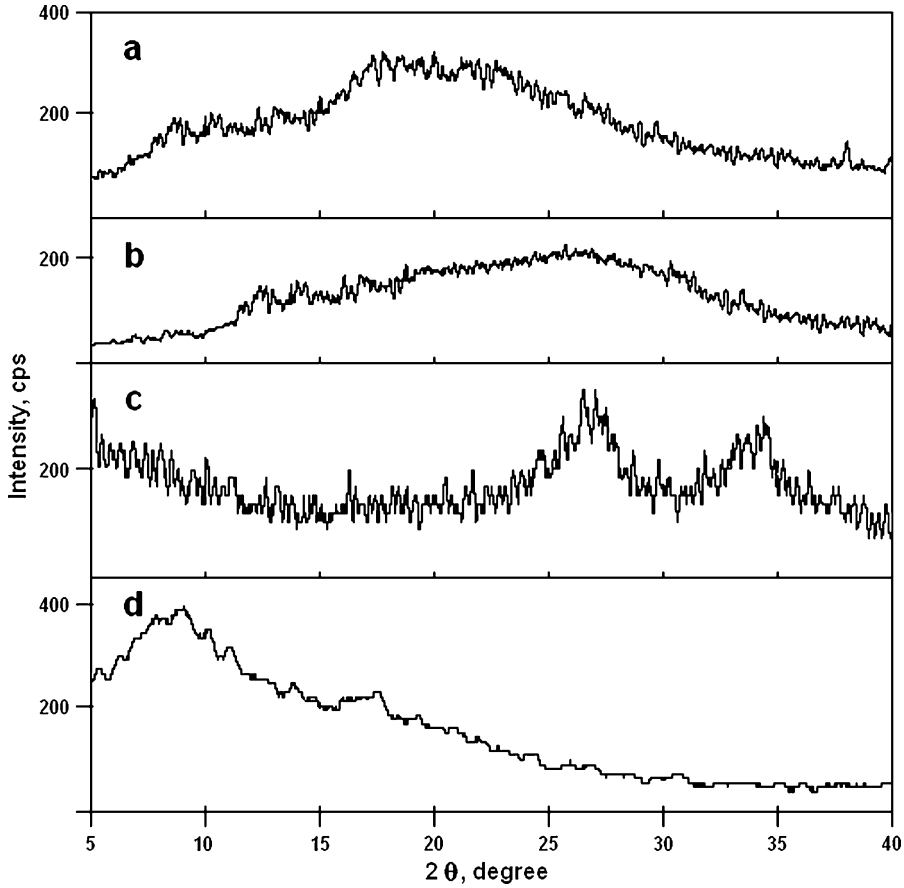


Fig. 24 XRD pattern of **a** CA; **b** PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-A); **c** PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-B). **d** PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-C)

XRD analysis

X-Ray diffractograms of cellulose along with grafted cellulose in DMAc/LiCl solvent system using BPO (Sample; Cell-g-PMMA-A), $Sn(Oct)_2$ (Sample; Cell-g-PMMA-B) and CAN (Sample; Cell-g-PMMA-C) as initiator and the grafted product in DMSO/PF solvent system using CAN as the initiator (Sample; Cell-g-PMMA-D) are shown in Fig. 23 and that of CA along with PMMA grafted CA in 1,4-dioxane in presence of BPO (Sample; CA-g-PMMA-A), PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (Sample; CA-g-PMMA-B) and PMMA grafted CA in DMSO in presence of CAN (Sample; CA-g-PMMA-C) are shown in Fig. 24. The diffraction pattern of pure cellulose (Fig. 23a) shows broad peaks at $2\theta = 15.9°$ and 22.4°. The percentage of crystallinity (Xc) for cellulose is found to be 43.0 %. The XRD patterns of cellulose grafted products (Fig. 23b–e) are broadened indicating the products are to be completely amorphous.

In case of CA the percentage of crystallinity (Xc) is found to be 30.0 % (Fig. 24a) and decreases further on grafting (Fig. 24b–d). It may be explained by the fact that the randomness of the amorphous phase in the graft copolymers was enhanced by the grafting with MMA, which gave rise to a perturbation of long-ranged spacing between the chains (Wan et al. 2011).

Thermo-gravimetric analysis

Dynamic thermo-gravimetric curves of the grafted cellulose in DMAc/LiCl solvent system using BPO (Sample; Cell-g-PMMA-A), $Sn(Oct)_2$ (Sample; Cell-g-PMMA-B) and CAN (Sample; Cell-g-PMMA-C) as initiator and the grafted product in DMSO/PF solvent system using CAN as the initiator (Sample;

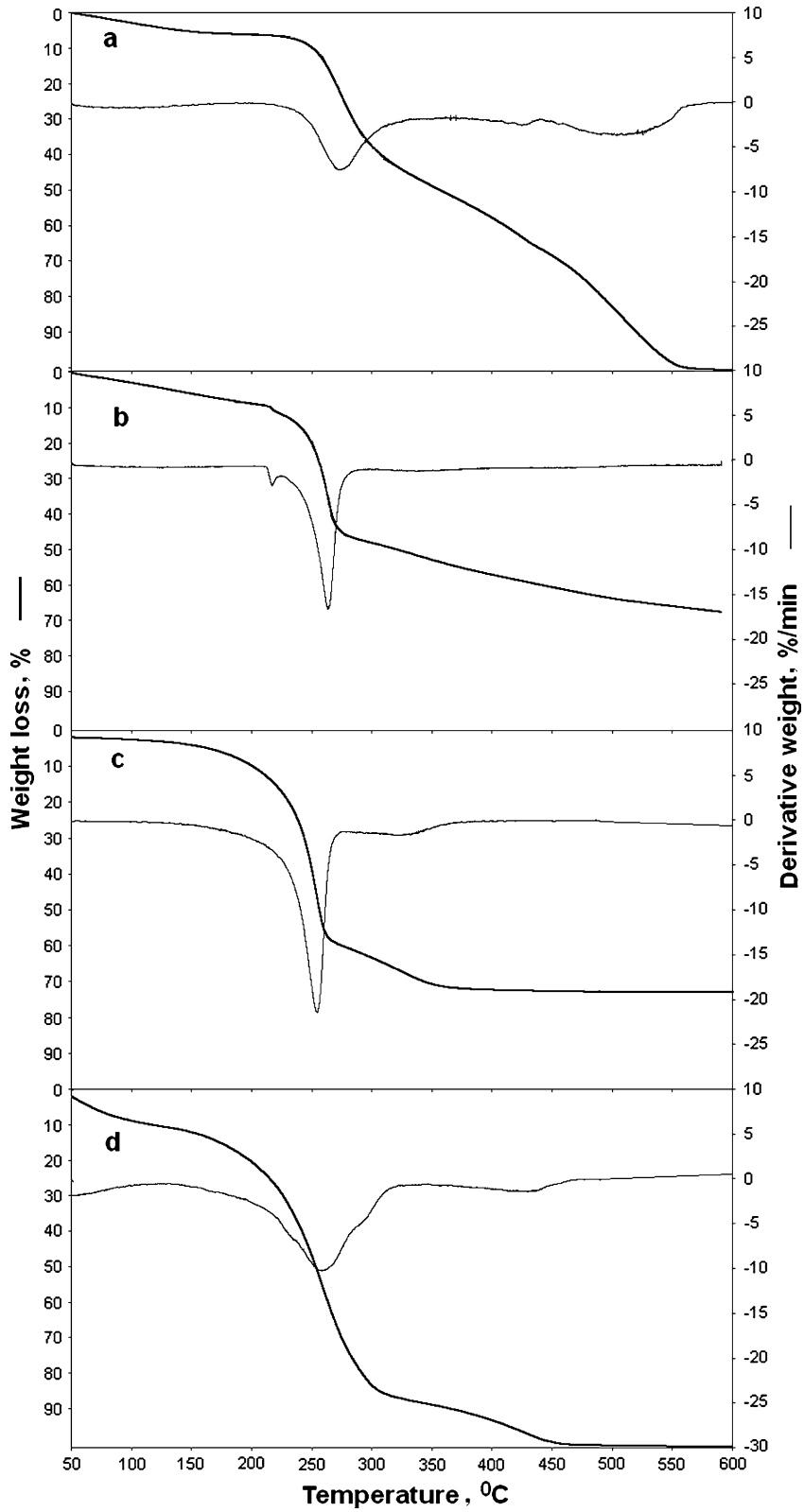


Fig. 25 Thermogravimetric analysis (TG and DTG) of **a** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of BPO (Cell-g-PMMA-A); **b** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of $Sn(Oct)_2$ (Cell-g-PMMA-B); **c** PMMA grafted cellulose in DMAc/LiCl solvent system in presence of CAN (Cell-g-PMMA-C); **d** PMMA grafted cellulose in DMSO/PF solvent system in presence of CAN (Cell-g-PMMA-D)

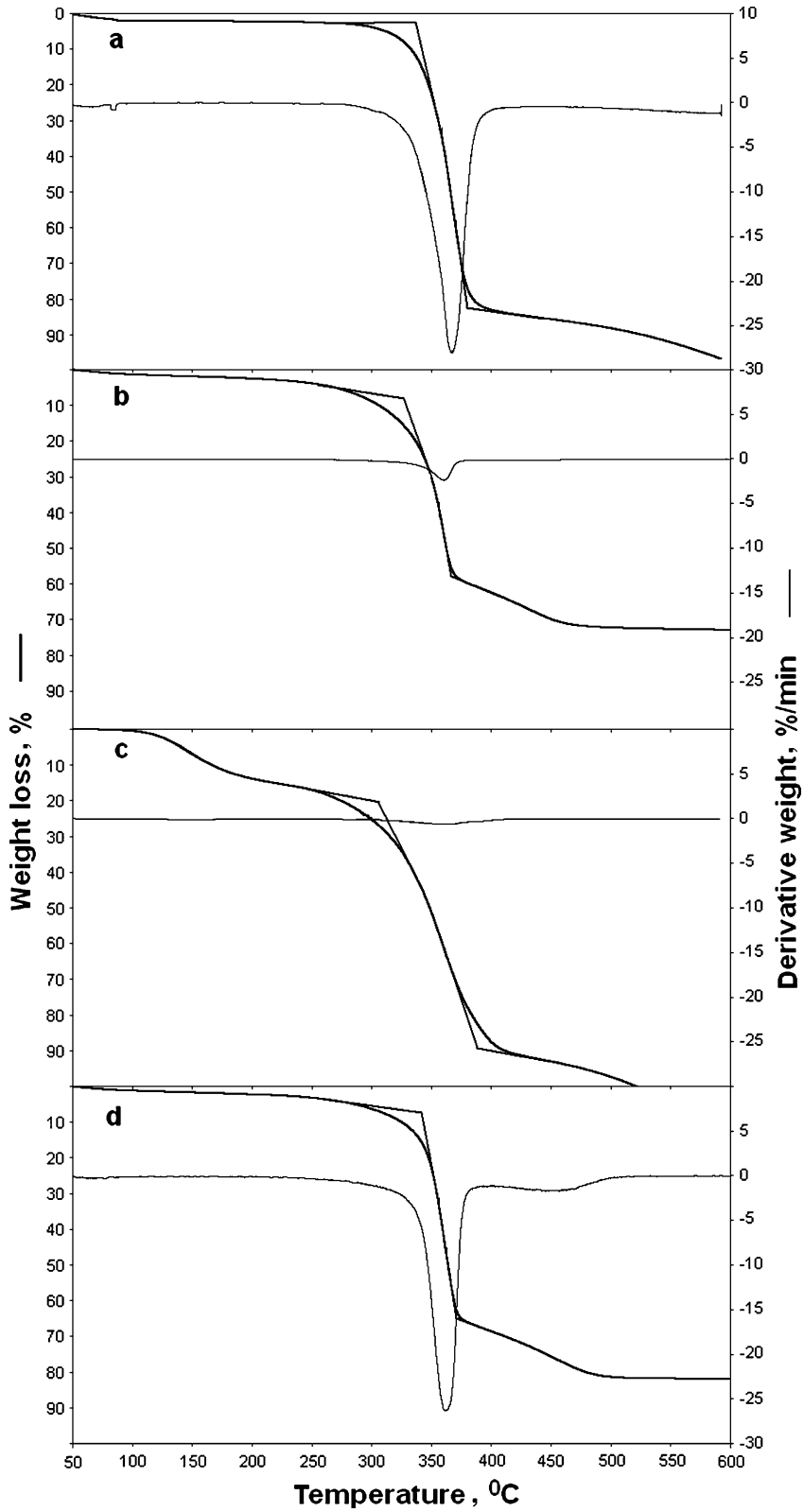


Fig. 26 Thermo-gravimetric analysis (TG and DTG) of **a** CA; **b** PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-A); **c** PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-B). **d** PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-C)

Table 4 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 °C	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C
Cell-g-PMMA-A	251	274	6.3	9.8	37.7	48.9	57.9	68.5	82.9	98.8
Cell-g-PMMA-B	240	264	8.9	19.6	47.7	52.4	56.6	60.1	63.2	65.4
Cell-g-PMMA-C	221	255	2.6	4.1	10.0	37.2	63.3	70.7	72.4	72.7
Cell-g-PMMA-D	205	258	8.9	12.1	20.3	46.2	82.6	88.0	92.4	100.0
CA	337	367	2.3	2.6	3.9	22.4	83.1	85.7	88.2	92.2
CA-g-PMMA-A	321	355	2.6	4.1	10.0	37.2	63.3	70.7	72.4	72.7
CA-g-PMMA-B	305	358	13.9	17.1	25.3	51.2	87.6	93.0	97.4	100.0
CA-g-PMMA-C	336	356	2.3	3.4	6.9	32.5	69.5	77.0	81.6	81.9

[a] IDT is the initial decomposition temperature

[b] ADT is the temperature of active decomposition

Cell-g-PMMA-D) are shown in Fig. 25 and that of CA along with PMMA grafted CA in 1,4-dioxane in presence of BPO (Sample; CA-g-PMMA-A), PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (Sample; CA-g-PMMA-B) and PMMA grafted CA in DMSO in presence of CAN (Sample; CA-g-PMMA-C) are shown in Fig. 26. 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 (Tosh 2011). The percentage weight loss of these samples with temperature is given in Table 4. The initial decomposition for Cell-g-PMMA-A starts at 251 °C where as that for Cell-g-PMMA-B it is 240 °C, for Cell-g-PMMA-C it is 221 °C and for Cell-g-PMMA-D it is 205 °C. The DTG curves show the temperature of active decomposition (ADT), which is 274 °C for Cell-g-PMMA-A, 264 °C for Cell-g-PMMA-B, 255 °C for Cell-g-PMMA-C and 258 °C for Cell-g-PMMA-D. There is not much variation of thermal stability between Cell-g-PMMA-A and Cell-g-PMMA-B (only 10 °C); but thermal stability of Cell-g-PMMA-C 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-C. When grafting is carried out in DMSO/PF solvent system, the thermal stability of the grafted product (Sample; Cell-g-PMMA-D) 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 (Tosh 2011).

The initial decomposition for CA-g-PMMA-A started at 321 °C and that for CA-g-PMMA-B it is 305 °C and for CA-g-PMMA-C it is 336 °C, which is less than CA (337 °C). The DTG curves show the temperature of active decomposition (ADT), which is 367 °C for CA and goes on decreasing to 355 °C for CA-g-PMMA-A, 358 °C for CA-g-PMMA-B and 356 °C for CA-g-PMMA-C. This may be due to the increase in the percentage of grafting and molecular weight of the homo polymer for the grafted products. The results reveal a decrease in the thermal stability with an increase in the percentage of grafting (Sabba and Moktar 2002) and molecular weight of the grafted polymer (Table 1).

Conclusion

Homogeneous graft copolymerization of MMA onto cellulose in DMAc/LiCl and DMSO/PF solvent systems and that of CA in DMSO, DMAc, 1,4-dioxane and acetone as the solvents can be carried out by using BPO, $Sn(Oct)_2$ and CAN as initiator. The formation of grafted products is confirmed by FTIR spectroscopy. The effect of reaction time and temperature, monomer and initiator concentration on the molecular weight of

the grafted PMMA are evaluated. Graft copolymerization of cellulose or CA in presence of BPO and $Sn(Oct)_2$ proceeds through free radical and anionic mechanism respectively by cleavage of –O–H bond of cellulose or CA 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. 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.

It is concluded that in presence of methylene blue as the inhibitor for homopolymer formation, the grafted products shows more number of grafts per polymer backbone and well controlled molecular weight of the grafted chain. For grafting of CA in homogeneous medium, CAN serves as a better initiator in DMSO and BPO is a better initiator in DMAc, 1,4-dioxane and acetone. Compare to DMSO, DMAc and 1,4-dioxane; acetone is not a good solvent for graft copolymerization of PMMA onto CA. It is also concluded that the increase in the percentage of grafting and molecular weight of the homo polymer decreases the thermal stability of the compound.

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