GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE (MMA) ONTO CELLULOSE ACETATE IN HOMOGENEOUS MEDIUM: EFFECT OF SOLVENT, INITIATOR AND HOMOPOLYMER INHIBITOR

CHITTARANJAN ROUTRAY and BIRANCHINARAYAN TOSH

Department of Chemistry, Orissa Engineering College, Bhubaneswar 751 007, India

Received June 29, 2012

Cellulose acetate-g-polymethyl methacrylate (CA-g-PMMA) copolymer was synthesized in homogeneous medium, taking dimethyl sulfoxide (DMSO), 1,4-dioxane, N,N-dimethyl acetamide (DMAc) and acetone as solvents and ceric ammonium nitrate (CAN), benzoyl peroxide (BPO) and tin(II) 2-ethyl hexanoate [$Sn(Oct)_2$] as initiator. The effects of solvents and initiators on graft yield (GY) and grafting efficiency (GE) were studied. The viscosity average molecular weight of grafted PMMA was calculated. The role of methylene blue (MB) as a homopolymer inhibitor and its effect on grafting was also studied. In the presence of MB the molecular weight of the grafted PMMA reduced and consequently grafting efficiency and the number of grafts per polymer chain increased. The products were characterized by FTIR and ^{1}H-NMR analyses and possible reaction mechanisms for different initiators were deduced. The thermal degradation of the grafted products was also studied by thermogravimetric analysis (TG) and differential thermogravimetry (DTG).

Keywords: homogeneous grafting, methyl methacrylate (MMA), grafting efficiency, methylene blue, thermal analysis,mechanism of grafting

INTRODUCTION

Cellulose acetate (CA) is one of the many important, commercially available cellulose derivatives. It is a tough material with excellent optical clarity. Major applications are found in films, textile fibers, and cigarette tow. It is well known that cellulose acetate has a dimensional stability problem under high humidity and at elevated temperature. Other shortcomings are its high cost, very limited compatibility with other synthetic polymers and high processing temperature.[1] Grafting of synthetic vinyl monomers onto cellulose acetate offers the potential of preparing a new class of engineering materials. The properties of the derived graft copolymers may be tailored to meet certain specifications by controlling parameters, such as the molecular weight of the grafted side chain, the number of the grafted side chains and the type of the grafted side chains.[2] The production of the graft copolymers can be classified by two reaction schemes: (a) graft polymerization of monomers initiated by the active sites on the polymer backbone; (b) coupling of two reactive polymers.[3] Graft polymerization proceeds by different mechanisms (free radical, anionic, cationic, ring opening etc.), depending on the nature of the active sites on the backbone and the type of monomer. Again depending on the reaction medium, grafting reactions may be divided into two types, viz. heterogeneous and homogeneous. Heterogeneous graft polymerization of synthetic polymers onto cellulose and cellulose acetate has been studied extensively over the past decades.[4-16] The derivatization and/or grafting reactions under homogeneous conditions assures important advantages over the heterogeneous system, like a better control of the degree of substitution,[17] a more uniform distribution of substituents along the polymer and a higher conversion yield.[18-20]

During the past few years, a number of cellulose derivatives have been synthesized under homogeneous conditions[17,21-23] and homogeneous grafting of vinyl monomers onto cellulose and some cellulose derivatives in non-degradable solvent systems, such as DMSO/PF,[21,22,24,25] DMSO/PhMe[26] and DMAc/LiCl,[18,19,27,28] has been

tried using different initiators, like ammonium persulfate (APS), azobisisobutyronitrile (AIBN), and benzoyl peroxide, but so far the effect of solvent, initiator and homopolymer inhibitor on homogeneous graft copolymerization of cellulose acetate has not been reported.

CAN in the presence of nitric acid is an efficient initiator for graft copolymerization of vinyl monomers onto cellulose[4-6] in heterogeneous medium, but under homogeneous conditions it will produce gel, confirming the regeneration of cellulose and CA from the solution. It has been reported that CAN in the presence of dimethyl sulfoxide (DMSO) can produce Ce^{+4} ion[18] and can be a suitable redox system to initiate graft copolymerization process, but no work has been carried out on this system. It is also reported that presence of methylene blue in the reaction system reduces the formation of homopolymers in the graft copolymerization process.[29] A few works on grafting reactions involving BPO[16] and $Sn(Oct)_2$[30] as initiator have been carried out under homogeneous conditions. In our earlier study, we described the homogeneous graft copolymerization of methylmethacrylate (MMA) onto cellulose in DMAc/LiCl solvent system taking CAN in the presence of DMSO as initiator.[20] Therefore, in the present study we have applied the same principle to cellulose acetate and a comparative study between CAN, BPO and $Sn(Oct)_2$ as initiators and their effect on graft yield (GY) and grafting efficiency (GE) has been carried out. Cellulose acetate has been dissolved in DMSO, DMAc, 1,4-dioxane and acetone and the grafting reaction has been carried out using CAN in DMSO, BPO and $Sn(Oct)_2$ as initiators. DMSO acts as a solvent for CA and also produces Ce^{+4}ion for initiation of the reaction. The effect of varying reaction time, temperature, concentration of initiators and monomer are studied to optimize the conditions under which grafting would occur most effectively. The effect of methylene blue on homopolymer formation is also studied. A comparative study on the effect of solvents and initiators on the graft yield and grafting efficiency has also been carried out. The grafted products obtained are characterized by Fourier transformation infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopies and their molecular weight and number of grafts per cellulose backbone was determined. Finally, thermal degradation of the grafted products has been studied by thermogravimetric (TG) analysisand differential thermogravimetry (DTG).

EXPERIMENTAL

Materials

Cellulose acetate (Sigma Aldrich, 37.9% acetyl and M_n ~50,000 by GPC) was purified by dissolution in tetrahydrofuran (THF), precipitation in diethyl ether,followed by Soxhlet extraction with the same solvent to remove any trace of low molecular weight alcohols and water. Thereafter it was thoroughly dried under vacuum. Methylmethacrylate (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_2at 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 4A 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 sodium (1% w/v) and benzophenone (0.2% w/v) under nitrogen atmosphere until the blue colour of the benzophenoneketyl radical anion persisted. Then it was distilled and stored over 4A 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 (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.

Grafting

1.25 g CA (7.0 mmol of the corresponding anhydroglucose unit by considering 37.9% acetyl content of CA) was dissolved in125 mL DMSO, DMAc, 1,4-dioxane and acetonetaken separately in three-necked round bottom flasks, equipped with a magnetic stirrer and temperature controlled oil bath to make 1% solution. To this, differing amounts of CAN ranging from 0.3-0.5 g (0.55-0.916 mmol) were added, followed by the 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 the addition of MMA. Reactions having BPO and $Sn(Oct)_2$ as catalyst, 1.0 mmol of the respective catalysts 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 a varying temperature, ranging between 30-80 °C, while for acetone the temperature was restricted to 55 °C. The reaction was terminated by the addition of hydroquinone.[21]

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. The extracted CA-grafted products were then dried at 50 °C and stored over P_2O_5.

A comparative study was also carried out to observe the effect of methylene blue in the formation of homopolymer by adding 0.7 mL (1.09 ppm) of methylene blue to the reaction at 80 °C having monomer concentration of 11.7 mmol and initiator concentration of 0.55 mmol in DMSO. For DMAc, 1,4-dioxane and acetone, the reaction was carried out at 70, 70 and 40 °C, respectively.

The graft yield (GY), total conversion of monomer to polymer (TC), grafting efficiency (GE) and number of graft per cellulose acetate chain were calculated on the basis of oven-dried weight of the CA from the increase in weight after grafting by using the following relations:[31]

$$GY(\%) = 100 \times (C-A)/A$$

$$GE(\%) = 100 \times (C-A)/(B-A)$$

$$TC(\%) = 100 \times (B-A)/D$$

Number of grafts per CA chain = (molecular weight of CA/molecular weight of grafted PMMA) x GY/100,

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

CA grafted with PMMA was hydrolyzed with 72% H_2SO_4 to isolate the 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 by using the following Mark-Houwink-Sakurada equation:[21]

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

GPC analysis

The number average molecular weight (Mn) 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 an eluent at a flow rate of 0.8 mL/min at 20°C. The system was calibrated with polystyrene standards having molecular weights of 200-10^6 g/mol.

FTIR analysis

IR spectra of the grafted and ungrafted CA samples were recorded on a PerkinElmer spectrometer (Spectrum RX1, PerkinElmer, Singapore) using chloroform as a solvent for CA and the KBr pellet technique for the grafted products, in the range of 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 internal standard and DMSO-d_6 as solvent for the samples.

Thermal analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses of the grafted products were carried out using a PerkinElmer simultaneous thermal analyzer (STA 6000), in the temperature ranges of 50-600 °C at a heating rate of 10 °C.min^{-1}, in nitrogen atmosphere. Indium was used as reference material for the study. 6-19 mg of the samples was taken for analysis.

RESULTS AND DISCUSSION

Effect of reaction time and temperature

Graft copolymerization of MMA onto CA in DMSO, DMAc and 1,4-dioxane has been carried out at 30, 40, 50, 60, 70 and 80 °C, and in acetone the reaction has been carried out at 30, 40, 50 and 55 °C, with reaction times ranging between 2-6 h with 1 h interval. The data on weight gain with respect to reaction time at different temperatures are shown in Tables 1-10. It is observed from the tables that theGY and TC increase with an increase in reaction time.

For the reactions carried out in DMSO taking CAN as initiator (Table 1), at a particular reaction time, the GY of the MMA grafted products decreases with an increase in reaction time, except at 60 °C. The total conversion of monomer to polymer (TC) reduces drastically and grafting efficiency (GE) increases comparatively at 60 °C. This may be due the higher tendency of homopolymer formation in comparison with graft copolymer, which can be verified by considering the molecular weight of PMMA.

For the reactions carried out in DMSO taking BPO as initiator, the data show (Table 2) a regular decrease in GY and TC with an increase in reaction temperature at a particular reaction time. The GE is also high at low temperature. But for

the reactions in DMAc at a temperature of 70 °C, GY and TC gives the maximum value and then decreases with an increase in temperature for a particular reaction time (Table 3). In 1,4-dioxane (Table 4) and acetone (Table 5), when the reaction is carried out taking BPO as initiator, the GY and TC give their maximum value at 60 °C and 55 °C, respectively, for a particular reaction time.

The reaction has been also carried out in DMSO, DMAc, 1,4-dioxane and acetone, taking $Sn(Oct)_2$, as initiator and the data are reflected in Tables 6-9, respectively. As observed from the tables, the GY and TC give their maximum value at 50, 60, 60 and 55 °C for DMSO, DMAc, 1,4-dioxane and acetone, respectively.

As discussed earlier, the GY and TC increase with the increase in reaction time. Graft copolymerization reaction of MMA onto CA has been carried in DMAc at for 6 h by taking 0.73 mmol of CAN dissolved in 12.5 mL of DMSO and 11.7 mmol of MMA, the data are shown in Table 10. It is observed that the GY and TC increase with an increase in temperature up to 70 °C and then decrease. This may be due to the fact that the rate of homopolymer formation increases at a higher temperature as the molecular weight of the extracted PMMA is higher at a higher temperature (Sample CA-g-PMMA-255). The same trend is also observed in 1,4-dioxane solvent (Table 10), while in acetone the maximum value is observed at a lower temperature (Sample CA-g-PMMA-261).

Table 1
Graft copolymerization of PMMA onto CA in DMSO at different temperatures with 11.7 mmol MMA and 0.55 mmol CAN

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-01	2	32	14.2	47.8	9434	1.70
	CA-g-PMMA-02	3	36	15.0	51.2	11991	1.50
	CA-g-PMMA-03	4	44	18.3	52.1	14662	1.50
	CA-g-PMMA-04	5	48	16.2	61.5	18273	1.31
	CA-g-PMMA-05	6	52	16.3	66.6	22059	1.18
40	CA-g-PMMA-06	2	32	11.2	29.8	9434	1.70
	CA-g-PMMA-07	3	32	22.3	29.9	7608	2.10
	CA-g-PMMA-08	4	36	20.4	34.2	8046	2.24
	CA-g-PMMA-09	5	48	16.9	35.7	9894	2.43
	CA-g-PMMA-10	6	52	27.3	41.8	11803	2.20
50	CA-g-PMMA-11	2	28	20.1	29.9	18029	0.78
	CA-g-PMMA-12	3	32	21.8	32.7	20338	0.79
	CA-g-PMMA-13	4	36	18.4	32.4	18030	1.00
	CA-g-PMMA-14	5	40	29.2	35.7	14662	1.36
	CA-g-PMMA-15	6	48	25.2	34.9	10291	2.33
70	CA-g-PMMA-21	2	16	40.0	8.52	13161	0.61
	CA-g-PMMA-22	3	24	54.5	9.40	11207	1.07
	CA-g-PMMA-23	4	28	46.6	12.8	14662	0.95
	CA-g-PMMA-24	5	36	60.0	12.9	10330	1.74
	CA-g-PMMA-25	6	44	68.7	13.6	11710	1.88
80	CA-g-PMMA-26	2	08	40.0	4.27	4891	0.82
	CA-g-PMMA-27	3	12	42.8	5.98	11446	0.52
	CA-g-PMMA-28	4	16	40.0	8.54	12105	0.66
	CA-g-PMMA-29	5	16	66.6	5.12	19023	0.42
	CA-g-PMMA-30	6	20	50.0	8.77	23423	0.43

Table 2
Graft copolymerization of PMMA onto CA in DMSO at different temperatures with 18.7 mmol MMA and 1.0 mmol BPO

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-31	2	32	66.66	10.25	4525	3.54
	CA-g-PMMA-32	3	36	64.28	11.94	5752	3.13
	CA-g-PMMA-33	4	38	62.5	13.65	6142	3.09
	CA-g-PMMA-34	5	42	61.11	15.35	7232	2.90
	CA-g-PMMA-35	6	44	57.71	17.91	7856	2.80
40	CA-g-PMMA-36	2	28	63.36	9.38	4010	3.49
	CA-g-PMMA-37	3	32	61.53	11.09	4626	3.46
	CA-g-PMMA-38	4	36	60.00	12.79	6252	2.88
	CA-g-PMMA-39	5	38	58.82	14.50	7112	2.67
	CA-g-PMMA-40	6	40	57.89	16.21	7324	2.73
50	CA-g-PMMA-41	2	24	54.54	9.47	3927	3.06
	CA-g-PMMA-42	3	28	53.84	11.09	4121	3.40
	CA-g-PMMA-43	4	32	53.33	12.79	4901	3.26
	CA-g-PMMA-44	5	36	52.94	14.50	5757	3.13
	CA-g-PMMA-45	6	38	52.63	16.21	6989	2.72
60	CA-g-PMMA-46	2	20	55.55	7.67	3787	2.64
	CA-g-PMMA-47	3	24	50.00	10.23	3892	3.08
	CA-g-PMMA-48	4	28	46.66	12.79	4201	3.33
	CA-g-PMMA-49	5	32	43.05	15.35	4875	3.28
	CA-g-PMMA-50	6	36	40.07	17.06	5457	3.30
70	CA-g-PMMA-51	2	16	44.44	7.90	3195	2.50
	CA-g-PMMA-52	3	20	41.66	10.41	3572	2.80
	CA-g-PMMA-53	4	24	42.85	11.94	3801	3.16
	CA-g-PMMA-54	5	28	41.11	14.57	3992	3.51
	CA-g-PMMA-55	6	32	40.00	17.12	4539	3.53
80	CA-g-PMMA-56	2	12	33.33	7.25	3078	1.95
	CA-g-PMMA-57	3	16	36.36	9.35	3264	2.45
	CA-g-PMMA-58	4	20	38.46	11.10	3434	2.91
	CA-g-PMMA-59	5	24	40.00	12.80	3727	3.22
	CA-g-PMMA-60	6	28	41.17	14.50	3984	3.51

Table 3
Graft copolymerization of PMMA onto CA in DMAc at different temperatures with 18.7 mmol MMA and 1.0 mmol BPO

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-61	2	8	40.00	4.26	3224	1.24
	CA-g-PMMA-62	3	12	30.00	10.23	4550	1.32
	CA-g-PMMA-63	4	16	26.66	12.79	5110	1.57
	CA-g-PMMA-64	5	20	23.80	17.91	5740	1.74
	CA-g-PMMA-65	6	24	20.68	24.74	6170	1.94
40	CA-g-PMMA-66	2	12	20.00	12.79	4920	1.22

	CA-g-PMMA-67	3	16	21.06	16.21	5235	1.53
	CA-g-PMMA-68	4	20	20.83	20.47	5892	1.70
	CA-g-PMMA-69	5	24	21.42	23.89	6375	1.88
	CA-g-PMMA-70	6	28	21.87	27.30	6789	2.06
50	CA-g-PMMA-71	2	16	11.42	29.86	5134	1.56
	CA-g-PMMA-72	3	20	11.36	37.54	5904	1.69
	CA-g-PMMA-73	4	24	12.5	40.95	6782	1.77
	CA-g-PMMA-74	5	28	13.46	44.36	6905	2.03
	CA-g-PMMA-75	6	32	14.54	46.92	7251	2.21
60	CA-g-PMMA-76	2	36	21.05	32.42	8317	2.16
	CA-g-PMMA-77	3	40	20.00	38.39	8795	2.27
	CA-g-PMMA-78	4	44	20.40	41.80	8947	2.46
	CA-g-PMMA-79	5	48	24.07	46.07	9213	2.61
	CA-g-PMMA-80	6	52	23.72	50.34	9818	2.65
70	CA-g-PMMA-81	2	72	45.00	34.12	13815	2.61
	CA-g-PMMA-82	3	80	42.55	40.00	14220	2.81
	CA-g-PMMA-83	4	84	39.62	43.53	16522	2.54
	CA-g-PMMA-84	5	92	40.35	48.63	17988	2.56
	CA-g-PMMA-85	6	96	40.00	51.19	20332	2.36
80	CA-g-PMMA-86	2	56	38.88	30.71	10524	2.66
	CA-g-PMMA-87	3	60	38.46	33.27	11210	2.68
	CA-g-PMMA-88	4	68	39.53	36.68	13824	2.46
	CA-g-PMMA-89	5	72	40.42	40.10	14777	2.44
	CA-g-PMMA-90	6	76	40.00	42.66	14981	2.54

Table 4
Graft copolymerization of PMMA onto CA in 1,4-dioxane at different temperatures with 18.7 mmol MMA and 1.0 mmol BPO

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-91	2	30	38.17	11.96	7212	2.08
	CA-g-PMMA-92	3	36	36.21	12.56	7911	2.28
	CA-g-PMMA-93	4	40	35.11	14.21	8120	2.46
	CA-g-PMMA-94	5	44	34.28	17.32	8540	2.58
	CA-g-PMMA-95	6	48	32.28	20.17	8997	2.67
40	CA-g-PMMA-96	2	40	40.27	15.88	7942	2.52
	CA-g-PMMA-97	3	48	38.91	19.46	8622	2.78
	CA-g-PMMA-98	4	54	36.21	22.89	9456	2.86
	CA-g-PMMA-99	5	62	33.13	26.47	9842	3.15
	CA-g-PMMA-100	6	70	29.75	27.13	10021	3.49
50	CA-g-PMMA-101	2	56	68.63	47.13	9547	2.93
	CA-g-PMMA-102	3	68	65.44	49.52	9920	3.43
	CA-g-PMMA-103	4	76	60.72	51.72	10322	3.68
	CA-g-PMMA-104	5	84	59.13	53.97	12441	3.38
	CA-g-PMMA-105	6	92	57.29	54.16	14321	3.21
60	CA-g-PMMA-106	2	132	86.16	28.79	20101	3.28
	CA-g-PMMA-107	3	140	85.36	29.2	22311	3.14
	CA-g-PMMA-108	4	144	83.92	30.4	23156	3.11

	CA-g-PMMA-109	5	148	82.75	30.92	25317	2.92
	CA-g-PMMA-110	6	152	80.03	31.22	25752	2.95
70	CA-g-PMMA-111	2	36	39.55	62.44	6972	2.58
	CA-g-PMMA-112	3	40	38.05	68.25	7033	2.84
	CA-g-PMMA-113	4	48	36.71	70.41	7551	3.18
	CA-g-PMMA-114	5	52	34.12	73.23	7981	3.26
	CA-g-PMMA-115	6	60	32.95	74.15	8022	3.74
80	CA-g-PMMA-116	2	28	29.76	70.13	5224	2.68
	CA-g-PMMA-117	3	36	28.19	72.13	5512	3.27
	CA-g-PMMA-118	4	40	27.54	74.97	5817	3.44
	CA-g-PMMA-119	5	44	25.22	75.53	6122	3.59
	CA-g-PMMA-120	6	48	23.71	76.24	6224	3.86

Table 5
Graft copolymerization of PMMA onto CA in acetone at different temperatures with 18.7 mmol MMA and 1.0 mmol BPO

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-121	2	24	20.68	24.74	5981	2.01
	CA-g-PMMA-122	3	32	22.22	30.71	6424	2.49
	CA-g-PMMA-123	4	44	26.19	35.83	7333	3.00
	CA-g-PMMA-124	5	56	29.78	40.10	8812	3.18
	CA-g-PMMA-125	6	68	31.48	46.07	10720	3.17
40	CA-g-PMMA-126	2	36	30.00	25.59	6522	2.76
	CA-g-PMMA-127	3	44	32.35	29.01	7511	2.93
	CA-g-PMMA-128	4	56	35.00	34.12	8799	3.18
	CA-g-PMMA-129	5	64	34.78	39.24	10031	3.19
	CA-g-PMMA-130	6	72	36.00	42.66	12445	2.89
50	CA-g-PMMA-131	2	48	40.00	25.59	8112	2.96
	CA-g-PMMA-132	3	64	48.48	28.15	10224	3.13
	CA-g-PMMA-133	4	76	50.00	32.42	13031	2.92
	CA-g-PMMA-134	5	88	48.88	38.39	15626	2.82
	CA-g-PMMA-135	6	104	54.16	40.95	17231	3.02
55	CA-g-PMMA-136	2	64	57.14	23.89	11346	2.82
	CA-g-PMMA-137	3	80	62.50	27.30	14772	2.71
	CA-g-PMMA-138	4	100	69.44	30.71	16852	2.97
	CA-g-PMMA-139	5	132	82.50	34.12	20581	3.21
	CA-g-PMMA-140	6	156	86.66	38.39	24011	3.25

Effect of amount of MMA and CAN

At a reaction temperature of 30 °C, keeping CAN concentration at 0.55 mmol, the amount of MMA is changed from 11.7 mmol (Samples CA-g-PMMA-01 to CA-g-PMMA-05; Table 1) to 14.04 mmol (Samples CA-g-PMMA-264 to CA-g-PMMA-268; Table 11) and 18.72 mmol (Samples CA-g-PMMA-269 to CA-g-PMMA-273; Table 11). The data show that the GY and TC of the grafted products increase with the increase in reaction time and amount of monomer.

Grafting reactions are carried out at 30 °C at 18.72 mmol MMA and by increasing the amount of CAN from 0.55 mmol (Samples CA-g-PMMA-269 to CA-g-PMMA-273; Table 11) to 0.73 mmol (Samples CA-g-PMMA-274 to CA-g-PMMA-278; Table 11) and 0.916 mmol (Samples CA-g-PMMA-279 to CA-g-PMMA-283; Table

11). As evident from the tables, the GY and TC increase with the increase in the amount of initiator at a particular reaction time.

Table 6
Graft copolymerization of PMMA onto CA in DMSO at different temperatures with 18.7 mmol MMA and 1.0 mmol $Sn(Oct)_2$

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-141	2	8	33.33	5.11	3424	1.17
	CA-g-PMMA-142	3	12	30.00	8.53	3907	1.54
	CA-g-PMMA-143	4	20	33.33	12.79	5215	1.92
	CA-g-PMMA-144	5	24	33.33	15.35	5872	2.04
	CA-g-PMMA-145	6	28	31.81	18.77	6342	2.21
40	CA-g-PMMA-146	2	16	33.33	10.23	4141	1.93
	CA-g-PMMA-147	3	20	29.41	14.50	5125	1.95
	CA-g-PMMA-148	4	24	30.00	17.06	5919	2.03
	CA-g-PMMA-149	5	28	29.16	20.47	6292	2.23
	CA-g-PMMA-150	6	32	27.58	24.74	6835	2.34
50	CA-g-PMMA-151	2	20	25.00	17.06	5413	1.85
	CA-g-PMMA-152	3	24	23.07	22.18	6122	1.96
	CA-g-PMMA-153	4	28	21.87	27.30	6312	2.22
	CA-g-PMMA-154	5	32	21.05	32.42	6755	2.37
	CA-g-PMMA-155	6	36	21.42	35.83	7220	2.49
60	CA-g-PMMA-156	2	12	60.00	4.26	4020	1.49
	CA-g-PMMA-157	3	16	40.00	8.53	4434	1.80
	CA-g-PMMA-158	4	20	29.41	14.50	5227	1.91
	CA-g-PMMA-159	5	24	25.00	20.47	6171	1.94
	CA-g-PMMA-160	6	28	24.13	24.74	6543	2.14
70	CA-g-PMMA-161	2	8	13.33	12.79	3515	1.14
	CA-g-PMMA-162	3	12	15.78	16.21	3981	1.51
	CA-g-PMMA-163	4	16	14.21	23.84	4626	1.73
	CA-g-PMMA-164	5	20	14.70	29.9	5322	1.88
	CA-g-PMMA-165	6	24	16.21	31.56	6225	1.93
80	CA-g-PMMA-166	2	8	7.40	23.03	3741	1.07
	CA-g-PMMA-167	3	8	5.58	29.01	3811	1.05
	CA-g-PMMA-168	4	12	7.69	33.27	4123	1.46
	CA-g-PMMA-169	5	16	8.69	39.24	4772	1.68
	CA-g-PMMA-170	6	24	10.63	43.51	5246	2.29

Table 7
Graft copolymerization of PMMA onto CA inDMAc at different temperatures with 18.7 mmol MMA and 1.0 mmol $Sn(Oct)_2$

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-171	2	24	37.5	13.65	6515	1.84
	CA-g-PMMA-172	3	32	33.33	20.47	7324	2.18
	CA-g-PMMA-173	4	36	28.12	27.30	8241	2.18
	CA-g-PMMA-174	5	40	25.00	34.12	9113	2.19
	CA-g-PMMA-175	6	44	25.00	37.54	10004	2.20

40	CA-g-PMMA-176	2	28	42.10	16.21	6995	2.00
	CA-g-PMMA-177	3	36	34.61	22.18	8724	2.06
	CA-g-PMMA-178	4	44	37.93	29.01	10352	2.13
	CA-g-PMMA-179	5	48	28.57	35.83	11436	2.10
	CA-g-PMMA-180	6	52	27.08	40.95	12156	2.14
50	CA-g-PMMA-181	2	32	36.36	18.77	7520	2.13
	CA-g-PMMA-182	3	40	34.48	24.74	9418	2.12
	CA-g-PMMA-183	4	48	32.43	31.56	11338	2.12
	CA-g-PMMA-184	5	52	30.23	36.68	12225	2.13
	CA-g-PMMA-185	6	56	28.07	42.66	13452	2.08
60	CA-g-PMMA-186	2	36	34.61	22.18	8311	2.17
	CA-g-PMMA-187	3	44	32.35	29.01	10992	2.00
	CA-g-PMMA-188	4	48	30.00	34.12	11501	2.09
	CA-g-PMMA-189	5	56	29.78	40.10	13620	2.06
	CA-g-PMMA-190	6	60	28.84	44.36	14110	2.13
70	CA-g-PMMA-191	2	24	21.42	23.89	6732	1.78
	CA-g-PMMA-192	3	36	27.27	28.15	7987	2.25
	CA-g-PMMA-193	4	40	25.64	33.27	9356	2.14
	CA-g-PMMA-194	5	44	22.00	42.66	10120	2.17
	CA-g-PMMA-195	6	48	22.22	46.07	11039	2.17
80	CA-g-PMMA-196	2	16	15.38	22.18	4778	1.67
	CA-g-PMMA-197	3	24	17.64	28.15	6312	1.90
	CA-g-PMMA-198	4	28	28.57	35.83	7125	1.96
	CA-g-PMMA-199	5	32	27.08	40.95	7618	2.10
	CA-g-PMMA-200	6	38	26.36	46.92	8813	2.16

Table 8
Graft copolymerization of PMMA onto CA in 1,4-dioxane at different temperatures with 18.7 mmol MMA and 1.0 mmol $Sn(Oct)_2$

Reaction temp (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-201	2	8	20.00	8.53	3981	1.00
	CA-g-PMMA-202	3	12	21.42	16.21	4330	1.39
	CA-g-PMMA-203	4	20	25.00	17.06	5743	1.74
	CA-g-PMMA-204	5	24	25.00	20.47	6420	1.87
	CA-g-PMMA-205	6	28	25.00	23.89	7101	1.97
40	CA-g-PMMA-206	2	12	25.00	10.23	4522	1.33
	CA-g-PMMA-207	3	16	23.52	14.50	5121	1.56
	CA-g-PMMA-208	4	24	28.57	17.91	6324	1.90
	CA-g-PMMA-209	5	32	30.76	22.18	7542	2.12
	CA-g-PMMA-210	6	36	33.33	23.03	8136	2.21
50	CA-g-PMMA-211	2	20	33.33	12.79	5979	1.67
	CA-g-PMMA-212	3	24	27.27	18.77	6522	1.84
	CA-g-PMMA-213	4	28	23.33	25.59	7205	1.94
	CA-g-PMMA-214	5	36	24.32	31.56	8321	2.16
	CA-g-PMMA-215	6	40	23.52	36.68	9142	2.19

60	CA-g-PMMA-216	2	52	37.14	29.86	12856	2.02
	CA-g-PMMA-217	3	60	35.71	35.83	14432	2.08
	CA-g-PMMA-218	4	64	33.33	40.95	15381	2.08
	CA-g-PMMA-219	5	68	31.48	46.07	16261	2.09
	CA-g-PMMA-220	6	72	30.00	51.19	18112	1.99
70	CA-g-PMMA-221	2	8	6.5	27.30	3535	1.13
	CA-g-PMMA-222	3	12	7.50	34.12	4231	1.42
	CA-g-PMMA-223	4	16	8.69	39.24	5156	1.55
	CA-g-PMMA-224	5	20	9.61	44.36	5822	1.72
	CA-g-PMMA-225	6	20	8.47	50.34	5881	1.70
80	CA-g-PMMA-226	2	8	5.40	31.56	3627	1.10
	CA-g-PMMA-227	3	12	7.01	35.83	4321	1.39
	CA-g-PMMA-228	4	12	6.66	37.54	4379	1.37
	CA-g-PMMA-229	5	16	8.33	40.95	5089	1.57
	CA-g-PMMA-230	6	16	6.66	51.19	5102	1.57

Table 9
Graft copolymerization of PMMA onto CA in acetone at different temperatures with 18.7 mmol MMA and 1.0 mmol $Sn(Oct)_2$

Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
30	CA-g-PMMA-231	2	8	37.44	8.15	4521	0.88
	CA-g-PMMA-232	3	16	35.24	10.25	6742	1.19
	CA-g-PMMA-233	4	24	34.78	12.17	8932	1.34
	CA-g-PMMA-234	5	36	32.13	14.09	10441	1.72
	CA-g-PMMA-235	6	40	30.55	15.91	11517	1.74
40	CA-g-PMMA-236	2	20	54.21	9.75	7902	1.27
	CA-g-PMMA-237	3	28	50.00	11.94	9132	1.53
	CA-g-PMMA-238	4	32	47.22	12.22	9997	1.60
	CA-g-PMMA-239	5	40	46.28	14.81	11981	1.67
	CA-g-PMMA-240	6	48	44.13	15.12	13752	1.75
50	CA-g-PMMA-241	2	32	62.13	13.12	11101	1.44
	CA-g-PMMA-242	3	44	60.29	15.27	13771	1.60
	CA-g-PMMA-243	4	52	58.45	16.18	15141	1.72
	CA-g-PMMA-244	5	56	57.32	17.05	16320	1.72
	CA-g-PMMA-245	6	60	56.78	17.89	17421	1.72
55	CA-g-PMMA-246	2	68	84.50	16.09	19572	1.74
	CA-g-PMMA-247	3	72	82.66	16.38	20322	1.77
	CA-g-PMMA-248	4	76	81.71	17.21	22512	1.69
	CA-g-PMMA-249	5	80	78.21	18.35	23403	1.71
	CA-g-PMMA-250	6	84	76.34	19.11	24227	1.73

Effect of solvent and initiators

Grafting of MMA onto CA has been carried out in DMSO, DMAc, 1,4-dioxane and acetone, taking CAN as initiator, the data are shown in Table 1, 10 and 11, respectively. The graft yield (GY) has been found to be the maximum (68%) for the reaction in DMSO medium at 60 °C and for a reaction time of 6 h (Table 1, Sample CA-g-PMMA-20). As the GY increases with the increase in reaction time, so for the other solvents the reaction is carried out for 6 h and the temperature is varied. In DMAc solvent (Table 10), the GY increases with the increase in temperature up to 70 °C and then decreases. The

maximum GY is found to be 44% at 70 °C (Sample CA-g-PMMA-254). When the reaction is carried out in 1,4-dioxane, the same trend is observed as in the case of DMAc, but the maximum GY is found to be of 56% at 70 °C (Table 11; Sample CA-g-PMMA-259). In acetone (Table 12), the GY decreases with the increase in reaction temperature and the maximum GY is found to be of only 28% (Sample CA-g-PMMA-261). Hence it may be inferred that for the grafting reactions taking CAN as initiator, acetone may not serve as a good solvent, which may be due to its non-polar nature, whereas the other three are polar aprotic solvents.

The effect of different initiators on the GY, GE and TC has been also studied in the aforesaid solvents. The grafting reaction has been carried out in DMSO solvent taking CAN, BPO and $Sn(Oct)_2$ – the data are reflected in Tables 1, 2 and 6, respectively. For BPO (Table 2), the GY and TC go on decreasing with the increase in reaction temperature at a particular reaction time. They show the maximum value for the reaction at 30 °C and the reaction time of 6 h (Sample CA-g-PMMA-35). When $Sn(Oct)_2$ is used as initiator in DMSO solvent (Table 6), at a particular reaction time, the GY and TC go on increasing with the increase in reaction temperature up to 50 °C and then decrease. The maximum value of GY and TC (36 and 35.83%, respectively) is obtained at 50 °C and reaction time of 6 h (Sample CA-g-PMMA-155). Hence, CAN is a better initiator in comparison with the other two in DMSO solvent medium.

In DMAc solvent, the grafting of MMA onto CA has been carried out, taking CAN dissolved in DMSO, BPO and $Sn(Oct)_2$ as initiator, the data are given in Tables 10, 3 and 7, respectively. By comparing the tables, it may be inferred that BPO serves as a better catalyst for the graft copolymerization reaction in DMAc solvent and gives the maximum value of GY and TC (96 and 51.19%, respectively) for a reaction time of 6 h at 70 °C (Table 3, Sample CA-g-PMMA-85). The same is the case for 1,4-dioxane solvent using CAN dissolved in DMSO, BPO and $Sn(Oct)_2$ as initiators (Tables 11, 4 and 8) and for this the maximum value of GY is obtained for a reaction time of 6 h at 60 °C, when BPO is used as initiator (Table 4, Sample CA-g-PMMA-110). A similar trend is also observed for acetone (Tables 10, 5 and 9). Hence, BPO is a better initiator in comparison with the other two in DMAc, 1,4-dioxane and acetone solvent media.

Table 10
Graft copolymerization of PMMA onto CA in various solvents at different temperatures with 11.7 mmol MMA and 0.73 mmol CAN dissolved in 12.5 mL of DMSO

Solvents	Reaction temp. (°C)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
DMAc	40	CA-g-PMMA-251	6	4	8	1.7	6222	0.32
	50	CA-g-PMMA-252	6	16	12	2.56	6168	1.30
	60	CA-g-PMMA-253	6	32	20	4.27	5419	2.95
	70	CA-g-PMMA-254	6	44	32	6.83	7788	2.82
	80	CA-g-PMMA-255	6	36	24	5.12	10070	1.79
1,4-dioxane	40	CA-g-PMMA-256	6	12	8	1.7	4571	1.31
	50	CA-g-PMMA-257	6	20	16	3.42	5845	1.71
	60	CA-g-PMMA-258	6	36	24	5.6	8305	2.17
	70	CA-g-PMMA-259	6	56	32	6.8	7568	3.70
	80	CA-g-PMMA-260	6	40	24	5.6	9905	2.02
Acetone	40	CA-g-PMMA-261	6	28	12	2.56	6760	2.07
	50	CA-g-PMMA-262	6	8	8	1.70	7225	0.55
	55	CA-g-PMMA-263	6	4	8	1.70	6737	0.30

Table 11
Graft copolymerization of PMMA onto CA in DMSO at 30 °C with different amounts of MMA and CAN

MMA/CAN (mmol)	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	No of grafts/ CA chain
14.04/0.55	CA-g-PMMA-264	2	36	25.0	25.89	3492	5.15
	CA-g-PMMA-265	3	40	37.03	19.22	4707	4.25
	CA-g-PMMA-266	4	48	46.15	18.51	5642	4.25
	CA-g-PMMA-267	5	52	43.33	21.36	6480	4.01
	CA-g-PMMA-268	6	64	50.00	25.25	6209	5.15
18.72/0.55	CA-g-PMMA-269	2	40	45.40	11.76	5642	3.54
	CA-g-PMMA-270	3	44	47.00	12.55	6575	3.35
	CA-g-PMMA-271	4	48	41.66	15.38	6391	3.76
	CA-g-PMMA-272	5	56	43.80	15.63	6945	4.03
	CA-g-PMMA-273	6	72	48.07	17.77	5042	7.14
18.72/0.73	CA-g-PMMA-274	2	40	25.64	20.83	5745	3.48
	CA-g-PMMA-275	3	48	23.52	27.24	6676	3.59
	CA-g-PMMA-276	4	56	24.13	30.98	6391	4.38
	CA-g-PMMA-277	5	68	29.31	28.31	7240	4.70
	CA-g-PMMA-278	6	80	26.66	40.06	5042	7.93
18.72/0.916	CA-g-PMMA-279	2	36	11.34	42.20	6147	2.93
	CA-g-PMMA-280	3	48	14.63	43.80	6391	3.76
	CA-g-PMMA-281	4	52	15.11	45.94	3492	7.45
	CA-g-PMMA-282	5	60	19.73	40.59	6738	4.45
	CA-g-PMMA-283	6	92	17.16	71.58	6106	7.53

Table 12
Graft copolymerization of PMMA onto CA in various solvents with 11.7 mmol MMA and 0.55 mmol CAN and 0.7 mL methylene blue (1.09 ppm)

Reaction temp. (°C)	Solvents	Sample code	Reaction time (h)	GY (%)	GE (%)	TC (%)	Mw of PMMA	Mn of PMMA	PDI	No of grafts/ CA chain
80	DMSO	CA-g-PMMA-284	2	20	50.0	0.08	14288	-	-	0.70
		CA-g-PMMA-285	3	20	49.15	1.70	26388	-	-	0.38
		CA-g-PMMA-286	4	24	47.27	1.79	29655	-	-	0.40
		CA-g-PMMA-287	5	24	47.08	1.82	31513	21589	1.79	0.38
		CA-g-PMMA-288	6	28	45.19	5.1	27503	19600	2.01	0.51
70	DMAc	CA-g-PMMA-289	6	36	60.00	12.82	2464	1560	1.86	7.31
70	1,4-dioxane	CA-g-PMMA-290	6	76	86.36	18.80	2983	2150	1.75	12.74
40	Acetone	CA-g-PMMA-291	6	24	54.54	09.40	1504	1120	1.71	7.98

Effect of inhibitor

To study the effect of methylene blue as inhibitor for the formation of homopolymer, the reaction has been carried out at 80 °C with 11.7 mmol MMA and 0.55 mmol CAN and 0.7 mL methylene blue (1.09 ppm) in DMSO solvent, the data are shown in Table 12. As the molecular weight of the extracted polymer is not uniform at the reaction temperature of 80 °C (Table 1), the same condition is followed for this comparative study. Table 12 shows that the GY of the grafted products is a little higher, compared to that for a reaction carried out without inhibitor (Table 1). The molecular weight of PMMA is more uniform at a higher reaction time.

The data for the effect of inhibitor on the GY, GE and TC in the other three solvents are shown in Table 16. In DMAc solvent by comparing the

data (Tables 12 and 10), it may be found that the grafting efficiency increases in the presence of inhibitor. The same is true for 1,4-dioxane and acetone (Tables 10 and 12).

Molecular weight of PMMA and number of grafts per CA 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 1, the grafting reactions with 11.7 mmol monomer and 0.55 mmol CAN, under the six temperature conditions give the grafted product, with a good control of the molecular weight of the PMMA and number of grafts per CA chain. At 14.04 and 18.72 mmol of monomer (Table 11), the molecular weight of PMMA goes on increasing with the increase in reaction time up to 5 h and then decreases. The number of grafts per CA chain does not show much variation except at a reaction time of 6 h for sample CA-g-PMMA-273, which has the maximum value of 2.3. The same trend is also observed at 18.72 mmol MMA, with 0.73 and 0.916 mmol of CAN (Table 11), with the maximum value at the reaction time of 6 h (Samples CA-g-PMMA-278 and CA-g-PMMA-283). As the data show, for the reactions with methylene blue (Table 12), there is almost no change in the extracted polymer molecular weight and the number of grafts per CA for the reaction time of 3-6 h. This indicates that methylene blue acts as a good inhibitor for the formation of homopolymer and controls the molecular weight of the graft copolymer, increasing the grafting sites in the CA chain, as evident from Table 12.

Moreover, by observing Tables 1 and 11, the conditions for obtaining sample CA-g-PMMA-273 are considered as the optimum, i.e. grafting at 30 °C for 6 h with 18.72 mmol of monomer, 0.55 mmol of initiator. For this sample, the GY is 72%, GE is 48.07%, the molecular weight of the homopolymer is 5042 and the number of grafts per CA chain is 7.14. The molecular weight of the grafted side chain can be increased by using the inhibitor, as evidenced from Table 12.

As discussed earlier, BPO serves as a better initiator in comparison with CAN and $Sn(Oct)_2$ in DMAc, 1,4-dioxane and acetone, the conditions for getting sample CA-g-PMMA-85 (Table 3) in DMAc, CA-g-PMMA-110 (Table 4) in 1,4-dioxane and CA-g-PMMA-140 (Table 5) in acetone can be considered as the optimum for these solvents.

FTIR studies

FTIR spectra of CA along with PMMA grafted CA in DMSO in the presence of CAN (CA-g-PMMA-273), PMMA grafted CA in DMAc in the presence of BPO (CA-g-PMMA-85), PMMA grafted CA in 1,4-dioxane in the presence of BPO (CA-g-PMMA-110) and PMMA grafted CA in acetone in the presence of $Sn(Oct)_2$ (CA-g-PMMA-250) are shown in Figure 1. All the products show identical peaks at 3439 cm^{-1} (OH str. of CA), 2998 cm^{-1} (-CH_3 and –CH_2- of PMMA and CA), 1725cm^{-1} (>C=O str. of PMMA and CA), 1635 cm^{-1} (C-C str.), 1481 cm^{-1} (OH bending of CA), 1443 cm^{-1} (-CH- bending), 1270 and 1240 cm^{-1} (–C-O-C- bending of PMMA), 1190 and 1144 cm^{-1} (C-C str. of CA and PMMA), 1060 cm^{-1} (–CH_2- wagging of CA), 745 cm^{-1} (CH rocking vibrations of CA and PMMA). The similarity of the spectra of CA (Figure 1a) and the grafted products (Figure 1b-e) 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 1725 cm^{-1} is very intensive, as well as the bands associated with the C-O vibration of the carbonyl group (1240 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 reveals several differences between the two sets of spectra, the most important for us are the decrease of the relative intensity of the –OH (3439 cm^{-1}) (Figure 1c-e) and the increase in the absorbance of the –CH_2- group (2998 cm^{-1}) (Figure 1b-e), thereby indicating the formation of MMA-grafted CA.

NMR studies

^{1}H-NMR spectra of PMMA grafted CA in DMSO in the presence of CAN (CA-g-PMMA-273), PMMA grafted CA in DMAc in the presence of BPO (CA-g-PMMA-85) and PMMA grafted CA in acetone in the presence of $Sn(Oct)_2$ (CA-g-PMMA-250) are shown in Figure 2. 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 peak at 1.18 ppm is for the –CH_3 group.[32] The peak at 5.06 ppm is due to the –OH group of the cellulose chain[33] and the peaks at 4.53 and 2.5 ppm are due to the –**CH_2**-O-CO-CH_3 of CA. The intensity of –OH peak at 5.06 ppm is very low for PMMA grafted CA in DMAc in the presence of BPO (CA-g-PMMA-85) and PMMA grafted CA in acetone in

the presence of $Sn(Oct)_2$ (CA-g-PMMA-250) (Figure 2b and 2c).

Mechanism of polymerization

It is known that metallic cations form complexes with carbon hydrates. After complexation with CA, 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.[11,34,35] Then this free radical initiates the monomer grafting and the polymerization reaction of MMA. The FTIR and ^{1}H-NMR spectra of the grafted products also show 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 shown in Scheme 1.

When BPO is used as initiator, the free radical is formed at the hydroxyl group of CA and grafting takes place by homolytic cleavage of the –O-H bond. The mechanism of polymerization when $Sn(Oct)_2$ is used as initiator is still uncertain.

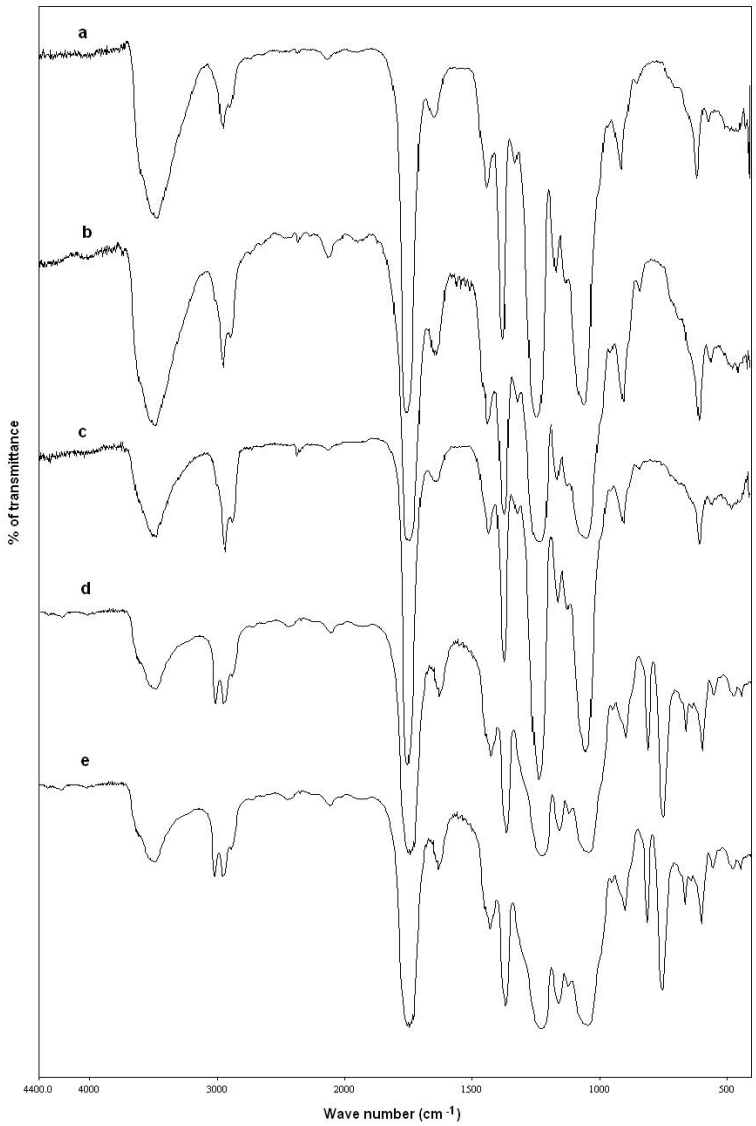


Figure 1: FTIR spectra of (a) CA; (b) PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-273); (c) PMMA grafted CA in DMAc in presence of BPO (CA-g-PMMA-85); (d) PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-110); (e) PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-250)

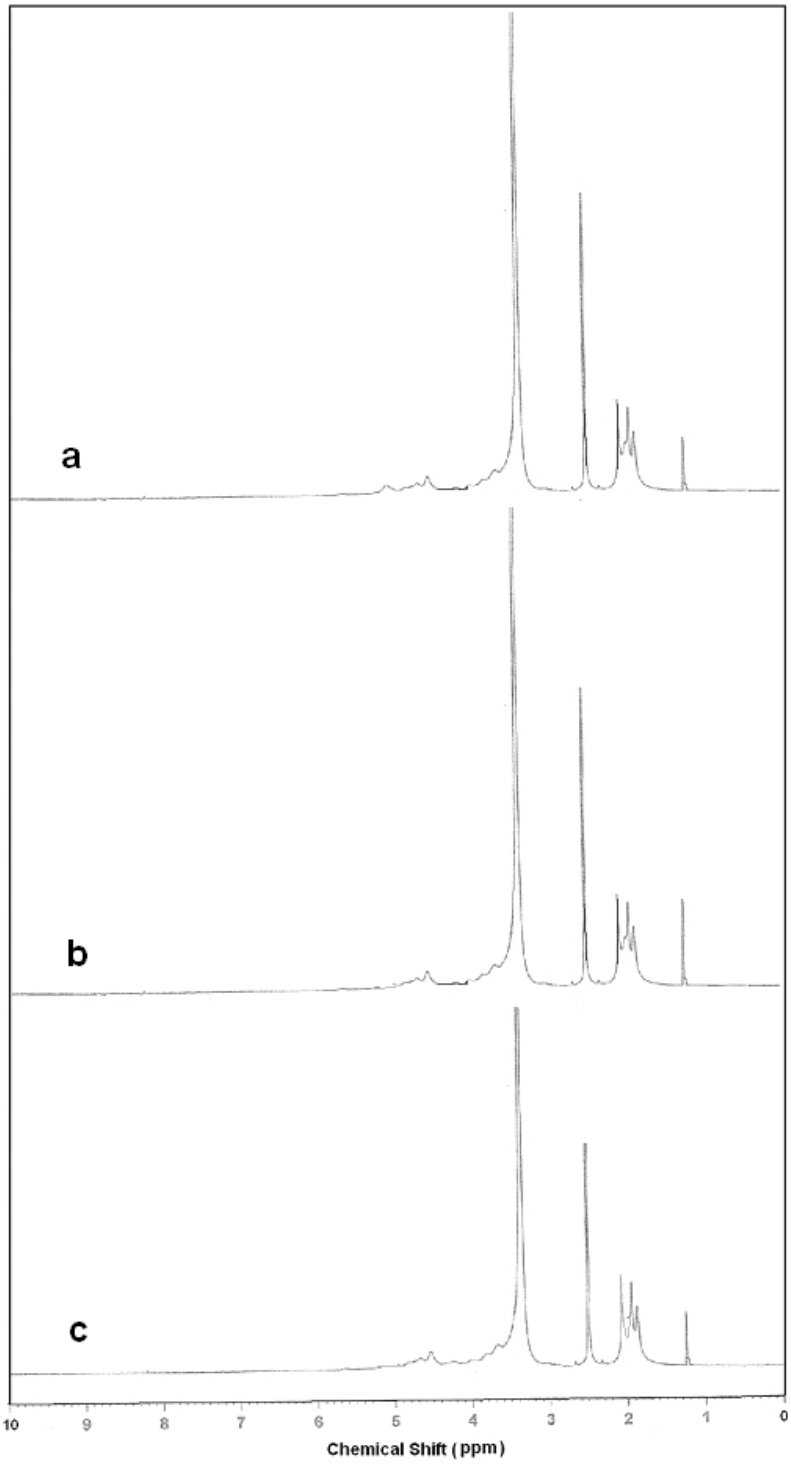
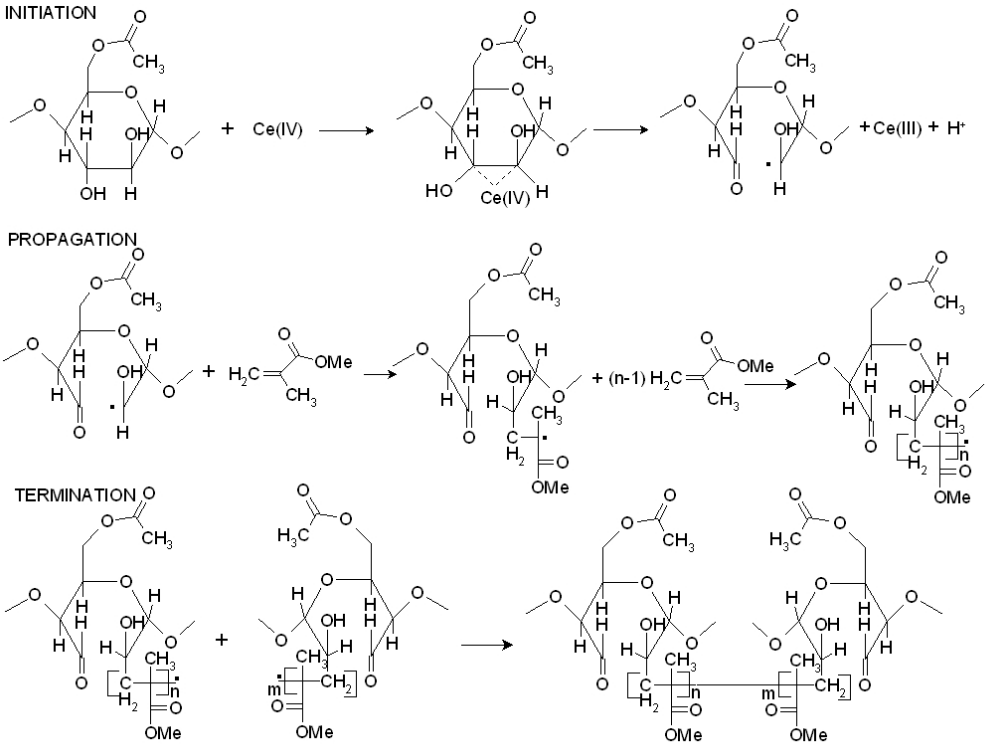


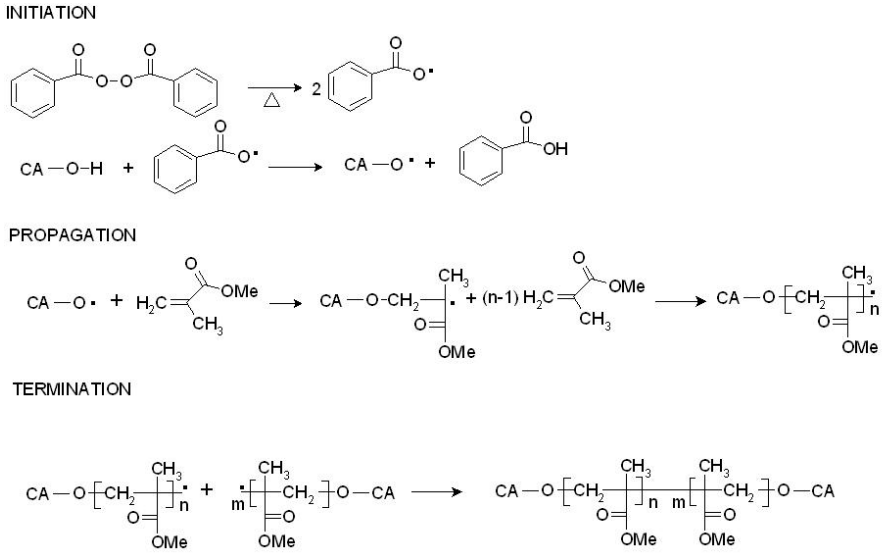
Figure 2: ^{1}H-NMR spectra of (a) PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-273); (b) PMMA grafted CA in DMAc in presence of BPO (CA-g-PMMA-85); (c) PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-250)

The most promising mechanism is a coordination-insertion mechanism, where the hydroxyl group is thought to coordinate to $Sn(Oct)_2$, forming the initiating tin-alkoxide

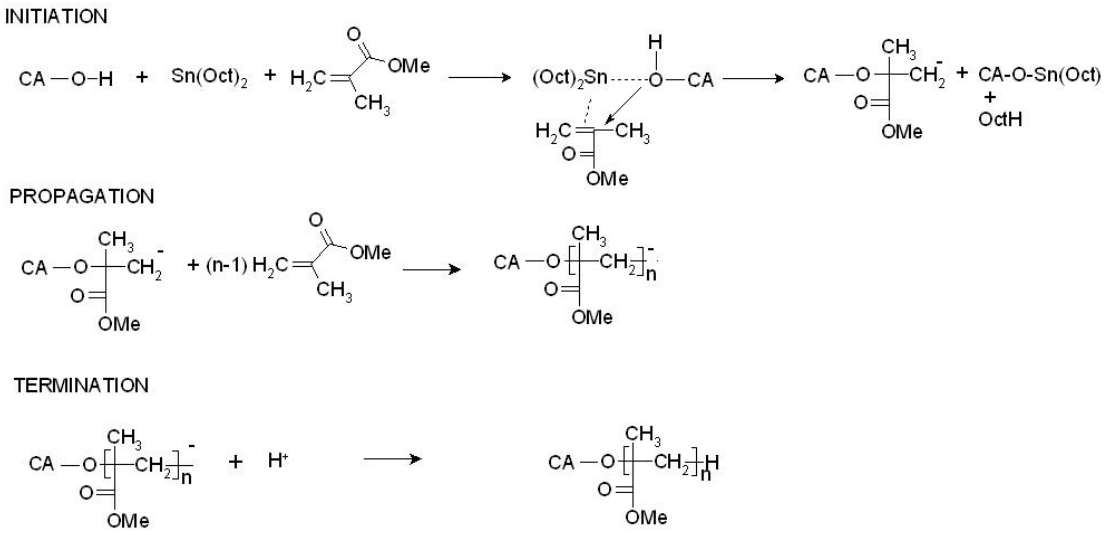
complex.[36] This can be verified by looking into the FTIR (Figure 1c-e) and ^{1}H-NMR (Figure 2b and 2c) spectra of the samples, where the intensity of the –OH peak decreases. Hence the mechanism for graft copolymerization of PMMA onto CA by using BPO and $Sn(Oct)_2$ as tinitiator may be the one presented in Schemes 2 and 3, respectively.



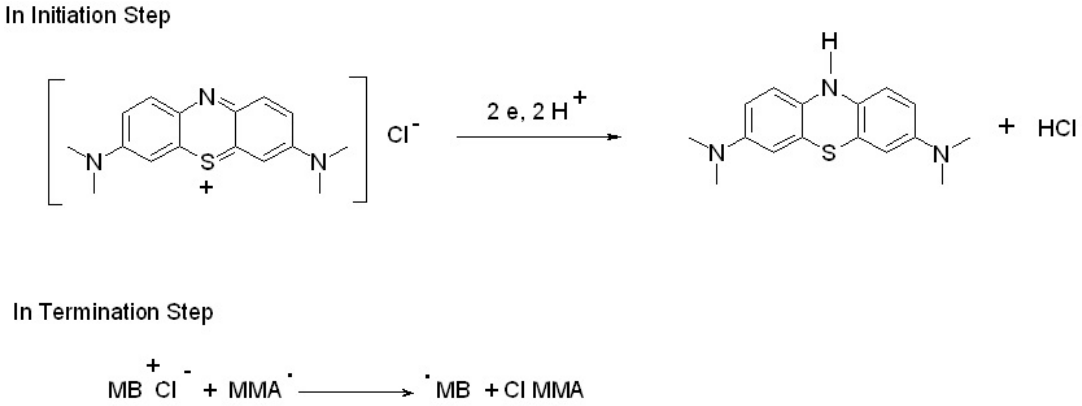
Scheme 1: Mechanism of grafting of PMMA onto CA by Ce^{+4}ion



Scheme 2: Mechanism of grafting of PMMA onto CA by BPO as initiator



Scheme 3: Mechanism of grafting of PMMA onto CA by $Sn(Oct)_2$ as initiator



Scheme 4: Effect of methylene blue (MB) in the initiation and termination step

Methylene blue (tetramethylthionine chloride, $C_{16}H_{18}ClN_3S$) (Scheme 4) is a heterocyclic aromatic dye, a member of the thiazine dyes. The redox properties of MB are provided by the ability to accept or donate hydrogen ions.[37]

Hence, the hydrogen ion generated in the initiation step (Scheme 1) 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, and thereby increases the number of grafts per polymer chain, which can be verified from Tables 10 and 12.

Since the dye affects the termination step,[38] in this step the chloride ion of MB can easily react with the active free radical of the monomer to generate semi-reduced MB radical (Scheme 4), which can readily recombine 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 10 and 12).

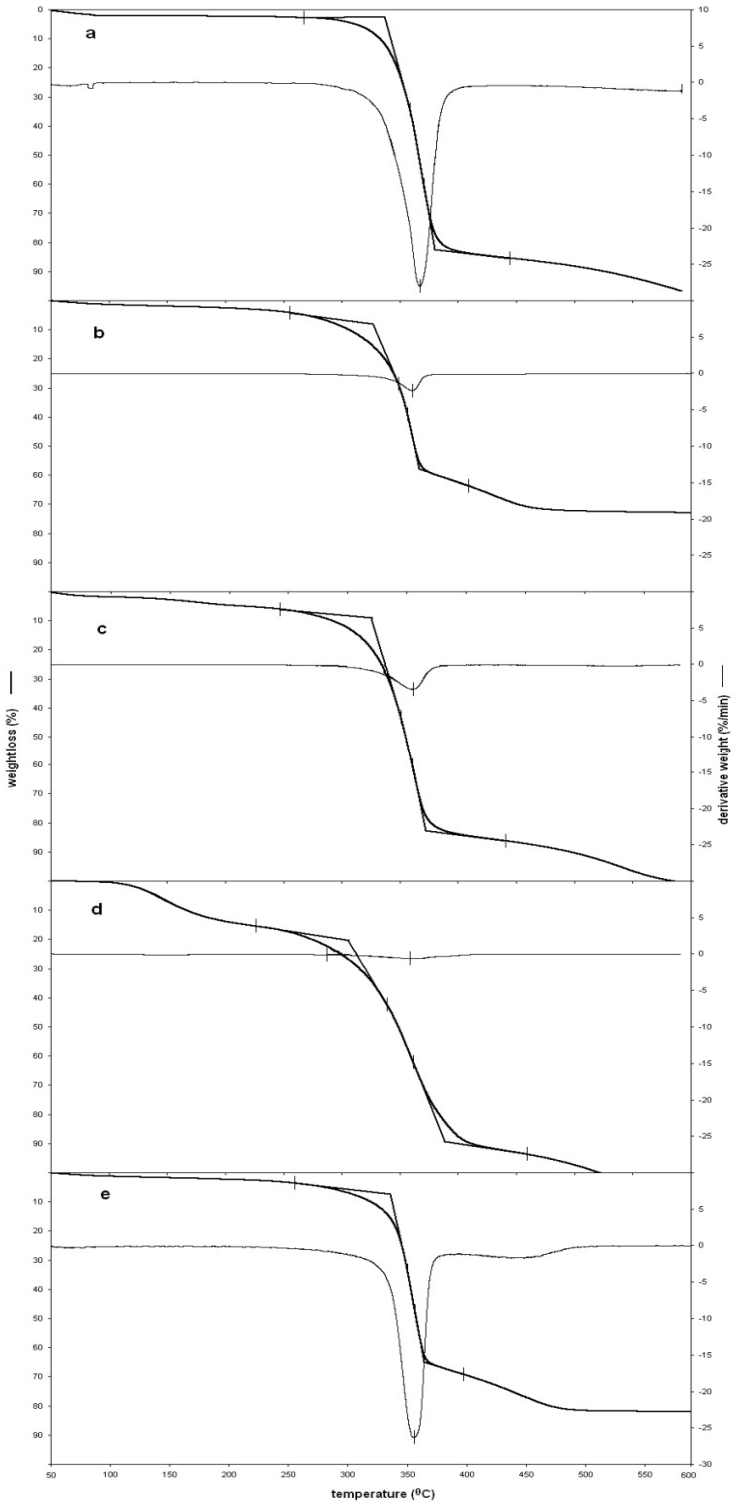


Figure 3: Thermogravimetric analysis (TG and GTD) of (a) CA; (b) PMMA grafted CA in DMSO in presence of CAN (CA-g-PMMA-273); (c) PMMA grafted CA in DMAc in presence of BPO (CA-g-PMMA-85); (d) PMMA grafted CA in 1,4-dioxane in presence of BPO (CA-g-PMMA-110); (e) PMMA grafted CA in acetone in presence of $Sn(Oct)_2$ (CA-g-PMMA-250)

Table 13
Thermal stability of CA and CA grafted products in nitrogen atmosphere at a heating rate of10 °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
CA	337	367	2.3	2.6	3.9	22.4	83.1	85.7	88.2	92.2
CA-g-PMMA-273	321	355	2.6	4.1	10.0	37.2	63.3	70.7	72.4	72.7
CA-g-PMMA-85	316	358	4.6	6.2	11.4	42.0	84.0	86.7	90.4	96.6
CA-g-PMMA-110	305	358	13.9	17.1	25.3	51.2	87.6	93.0	97.4	100.0
CA-g-PMMA-250	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

Thermogravimetric analysis

Dynamic thermogravimetric curves of CA and CA grafted products are given in Figure 3. Each of the curves shows three different zones. An initial zone of slight loss in weight is due to the evaporation of water. Then the break in each thermogram indicates the onset of the decomposition process involving a 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.[39] The percentage weight loss of these samples with temperature are given in Table 13. The initial decomposition for CA-g-PMMA-273 started at 321 °C, for CA-g-PMMA-85 at 316 °C, for CA-g-PMMA-110 at 305 °C and for CA-g-PMMA-250 at 336 °C, which is lower than the initial decomposition temperature of 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-273, 358 °C for CA-g-PMMA-85, 358 °C for CA-g-PMMA-110 and 356 °C for CA-g-PMMA-250. This may be due to the increase in the percentage of grafting and molecular weight of the homopolymer for the grafted products. The results reveal a decrease in the thermal stability with an increase in the percentage of grafting[8] and molecular weight of the grafted polymer.

CONCLUSION

Homogeneous graft copolymerization of MMA onto CA in DMSO solvent system can be carried out by using CAN as initiator. The formation of grafted products has been 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 has been evaluated. Graft copolymerization of CA in the presence of Ce^{4+} proceeds through ring opening of cellulose and formation of free radical in the CA chain, which initiates the polymerization by the free radical mechanism, whereas the reaction in the presence of BPO and $Sn(Oct)_2$ occurs at the hydroxyl group of CA. It is concluded that in the presence of methylene blue as the inhibitor for homopolymer formation, the grafted products show uniform 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. Compared 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 optimum conditions for DMSO grafting reaction are as follows: 30 °C for 6 h with 18.7 mmol of monomer and 0.55 mmol of CAN. As BPO serves as a better initiator in comparison with CAN and $Sn(Oct)_2$ in DMAc, 1,4-dioxane and acetone, the grafting reaction for 6 h with 18.7 mmol of monomer, 1.0 mmol of BPO at 70, 60 and 55 °C in the respective solvent are the optimum conditions. It is also concluded that the increase in the percentage of grafting and molecular weight of the homopolymer decreases the thermal stability of the compound.

ACKNOWLEDGEMENT: The authors are thankful to the Department of Science and Technology, New Delhi, for financial support to carry out the work.

REFERENCES

[1] C. M. Buchanan, S. C. Gedon, B. G. Pearcy, A. W. White and M. D. Wood, *Macromolecules*, **26**, 5704 (1993).
[2] C. J. Biermann, J. B. Chung and R. Narayan, *Macromolecules*, **20**, 954 (1987).
[3] L. Nie and R. Narayan, *J. Appl. Polym. Sci*., **54**, 601 (1994).

[4] K. C. Gupta and K. Khandekar, *Biomacromolecules*, **4**, 758 (2003).
[5] K. C. Gupta, S. Sahoo and K. Khandekar, *Biomacromolecules*, **3**, 1087 (2002).
[6] K. C. Gupta and S. Sahoo, *Biomacromolecules*, **2**, 239 (2001).
[7] E. Princi, S. Vicini, E. Pedemonte, A. Mulas, E. Franceschi *et al*., *Thermochim. Acta*, **425**, 173 (2005).
[8] M. W. Sabba and S. M. Moktar, *Polym. Test*., **21**, 337 (2002).
[9] H. Lomberg, Q. Zhow, H. Brumer, T. T. Teeri, E. Malmstrom and A. Hult, *Biomacromolecules*, **7**, 2178 (2006).
[10] A. Carlmark and E. E. Malmstrom, *Biomacromolecules*, **4**, 1740 (2003).
[11] L. Halab-Kessira and A. Ricard, *Eur. Polym. J*., **35**, 1065 (1999).
[12] C. N. Saikia and F. Ali, *Bioresource Technol*., **68**, 165 (1999).
[13] E. Princi, S. Vicini, N. Proietti and D. Capitani, *Eur. Polym. J*., **41**, 1196 (2005).
[14] C. J. Hamburger, *J. Polym. Sci*., *A-1*, **7**, 1023 (1969).
[15] R. O. Mazzei, E. Smolko, A. Torres, D. Tadey, C. Rocco *et al*., *Radiat. Phys. Chem*., **64**, 149 (2002).
[16] A. Sarbu, M. N. de Pinho, M. R. Freixo, F. Goncalves and I. Udrea, *Enzyme Microb. Technol*., **39**, 125 (2006).
[17] B. Tosh, C. N. Saikia and N. N. Dass, *Carbohyd. Res*., **327**, 345 (2000).
[18] E. Bianchi, E. Marsano, L. Ricco and S. Russo, *Carbohyd. Polym*., **36**, 313 (1998).
[19] P. Das and C. N. Saikia, *J. Appl. Polym. Sci*., **89**, 630 (2003).
[20] B. Tosh and C. R. Routray, *Indian J. Chem. Technol*., **18**, 234 (2011).
[21] N. Nishioka and K. Kosai, *Polym. J*., **13**, 1125 (1981).
[22] N. Nishioka, K. Matsumoto and K. Kosai, *Polym. J*., **15**, 153 (1983).
[23] C. N. Saikia, B. N. Tosh, T. Goswami and A. C. Ghosh, *Indian J. Chem. Technol*., **3**, 333 (1996).
[24] N. Nishioka, K. Minami and K. Kosai, *Polym. J*., **15**, 591 (1983).
[25] N. Nishioka, Y. Matsumoto, T. Yumen, K. Monmae and K. Kosai, *Polym. J*., **18**, 323 (1986).
[26] E. A. Abdel-Razik, *Polymer*, **31**, 1739 (1990).
[27] P. Das, C. N. Saikia and N. N. Dass, *J. Appl. Polym. Sci*., **92**, 3471 (2004).
[28] E. Bianchi, A. Bonazza, E. Marsano and S. Russo, *Carbohyd. Polym*., **41**, 47 (2000).
[29] A. Molenberg, U.S. Patent 7282584 (2007).
[30] B. Videki, S. Klebert and B. Pukanszky, *Eur. Polym. J*., **41**, 1699 (2005).
[31] M. J. Fernandez, I. Casinos and G. M. Guzman, *J. Polym. Sci. A*: *Polym. Chem*., **28**, 2275 (1990).
[32] J. Kriz, B. Masar, H. Pospisil, J. Plestil, Z. Tuzar and M. A. Kiselev, *Macromolecules*, **29**, 7853 (1996).
[33] B. Tosh, Ph.D. Thesis, Dibrugarh University, Assam, 1999.
[34] T. L. Han, R. N. Kumar, H. D. Rozman, M. Azemi and M. Noor, *Carbohyd. Polym*., **54**, 509 (2003).
[35] O. H. Lin, R. N. Kumar, H. D. Rozman, M. Azemi and M. Noor, *Carbohyd. Polym*., **59**, 57 (2005).
[36] K. M. Stridsberg, M. Ryner and A. Albertsson, *Adv. Polym. Sci*., **157**, 41 (2000).
[37] Y. Galagan, W. F. Su, *J. Photochem. Photobiol. A*: *Chem*., **195**, 378 (2008).
[38] A. K. Srivastava, P. K. Misra and G. N. Mathur, *Indian J. Chem*., **21 A**, 303 (1982).
[39] B. Tosh, *Indian J. Chem. Technol*., **18**, 451 (2011).