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Synthesis, optimization and characterization of graft copolymers from *Leucaena glauca* seed gum and methylmethacrylate*

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The effects of respective concentrations of hydrogen peroxide (H_2O_2), methylmethacrylate (MMA) and *Leucaena glauca* seed gum (LGG) on the graft copolymerization of LGG–MMA have been studied by evaluating the rates of total polymerization (k_{tp}), homopolymerization (k_h) and graft copolymerization (k_g) at different reaction times. The study shows that the grafting depends greatly upon the rate influencing factors. The grafted products have been characterized by infra-red sepctroscopy and thermogravimetry along with the usual methods based on grafting parameters. The optimum grafting conditions derived from the investigation at 85 °C are: H_2O_2 concentration 10 mM litre^{-1}, a backbone to monomer concentration ratio of 0·20 for 120 min, which yielded nearly 48% of grafting.

INTRODUCTION

To alter the physico-chemical properties of the substrate, especially the surface characteristics, the proved technique is grafting of polymeric side chains on to the substrate. The process involves the formation of a covalent bond between the substrate and the new incoming polymer. One interesting change is the provision of thermodynamic stability to the copolymer in heterogeneous solutions. Upon dissolving the copolymers in heterogeneous fluid blends, they migrate to the fluid interphases with the backbone in one medium and the branches dangling into the other. This provides better interphase stability and leads to stable emulsions. Thus graft copolymers in solution can be regarded as a composite species whose inner core is lypophobic and the outer is lypophylic in character.

Some of the authors' research work (Raval *et al.*, 1988*a*, *b*) describes modification of guar gum by graft copolymerization. The current publication deals with grafting of MMA onto LGG. LGG is a polysaccharide, found in the seeds of *Leucaena glauca* trees, and structurally related to guar gum. The seeds contain 25% of the polygalactomannan which consists of 43% galactose and 57% mannose. These structural units are chiefly arranged as the main chain of 1,4-linked polymannan with 1,6-linked single galactose at about every seventh or eighth mannose unit, along with some unusual linkages of galactose residues occupying interchain positions (Unrau, A. M., 1961).

The aim of the present investigation is to synthesize the graft copolymers of LGG–MMA by varying the rate influencing parameters and to understand the nature of the reaction in detail. Concentration variations range respectively for H_2O_2, MMA and LGG from 5–25 mM litre^{-1}, 0·05–0·25 M litre^{-1} and 0·006 17–0·0309 M AGU. The grafting period is varied from 30 min to 120 min. The usual grafting parameters such as per cent grafting, grafting efficiency, etc., are calculated by applying standard equations to characterize the products. Further support to the characterization of products is gained from the infra-red spectral and thermogravimetric results.

EXPERIMENTAL

LGG was extracted as reported earlier (Raval *et al.*, 1988*c*). The dried powder was slurried in water to a 1% concentration. Oxidation of LGG was allowed at 60 °C

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*Dedicated to H. S. D. H. Pramukh Swami on Yogiji Maharaj Birth Centenary Celebrations.

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by desired concentration of hydrogen peroxide for 30 min. The required amount of freshly distilled MMA was charged and the copolymerization was performed at 85°C in a thermostatically-controlled water bath with constant stirring for different time intervals. The reaction slurry was then cooled to room temperature and precipitated by methanol. The product was filtered, washed and dried in a vacuum oven at 40°C for 24 h. Soxhlet apparatus was used to separate homopolymer by benzene extraction until no precipitates were found by adding methanol to the extracted solvent. The grafting parameters like total monomer conversion (TMC), per cent add-on (PA), grafting efficiency (GE), grafting frequency (GF), and the rates k_{tp}, k_h and k_g were evaluated by applying their standard definitions (Hecker de Carvalho & Rudin, 1984; Vijaykumar *et al.*, 1985; Raval *et al.*, 1988*a,b*).

Grafted polymethylmethacrylate (PMMA) was freed from polysaccharide by the perchloric acid method (Dennenberg & Abbot, 1976). PMMA remains as a white insoluble mass on the water. The polymer so obtained was purified by solvent extraction method and dried in a vacuum oven at 40°C. The number average molecular weights of these separated PMMA samples were calculated from the intrinsic viscosity values determined in benzene at 30°C by using the Ubbelohde suspension level viscometer (Otey *et al.*, 1976).

Infra-red spectra of the graft copolymer were recorded in KBr pellets between 600 and 4000 cm^{-1} on a Perkin-Elmer IR 983 spectrophotometer. The IR spectra of a representative sample of the graft copolymer has been compared with that of LGG (see Fig. 1).

Thermogravimetric analysis (TGA) of the powdered samples was performed on Du Pont-951 thermogravimetric analyzer under static air atmosphere. The dynamic heating rate of 10°C min^{-1} was employed.

RESULTS AND DISCUSSION

Infra-red spectral evidence for grafting

Figure 1 depicts the comparative study of the infra-red spectra of LGG (See Fig. 1(a)) and LGG-g-PMMA (see Fig. 1(b)). The additional absorption peaks at 2960 cm^{-1} and 1740 cm^{-1} in Fig. 1(b) strongly suggest the presence of PMMA chemically attached to the LGG molecules. These peaks may be respectively assigned to the asymmetric stretching of methyl groups and the carbonyl stretching frequencies due to PMMA. Thus infra-red studies yielded sound evidence for grafting.

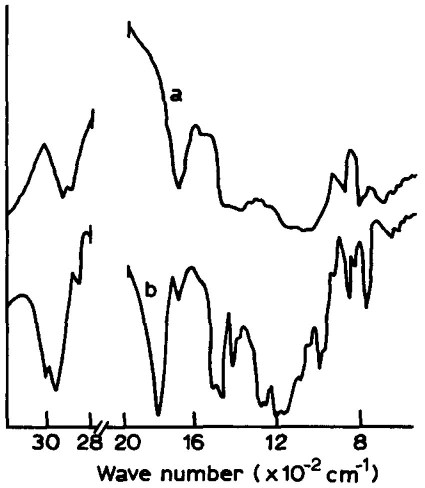


Fig. 1. Infra-red spectra of (a) LGG (b) LGG-g-PMMA.

Thermogravimetric analysis

The TG-thermograms of LGG, its grafted product (PA, 47·9) and homopolymer are produced in Fig. 2. By using the Broido relation (eqn (1)) the activation energy (*E*) was calculated.

$$\ln\ln\left(\frac{1}{Y}\right) = -\frac{E}{R}\left(\frac{1}{T}\right) + \text{constant} \qquad (1)$$

The significance of the above equation is customarily the same as described by Broido (1969); where *Y* represents the unreacted weight fraction of the copolymer under study, R denotes the gas constant and T is absolute temperature. It is observed that a single step mechanism is followed for the thermal degradation of polymers studied. The participation of first order kinetics in the thermal reactions is confirmed by the successful application of the Broido method. The grafted sample shows a remarkable decrease in the activation energy value (Table 1). The substitution of synthetic polymeric chains on the parent backbone molecule may be considered responsible for the above decrease. T_{50} and T_{max}, the respective temperatures at half decomposition and maximum decomposition, for homopolymer and grafted copolymer have higher values than that of LGG (Table 1). The superior thermal stability is evident with increase in these values. Thus enhancement in T_{50} and T_{max} not only suggests the higher thermal stability of grafted copolymer but also corroborates the chemical attachment of PMMA onto LGG. Integral procedural decomposition temperature (IPDT) values were calculated using Doyle's method (1961). The copolymer has an intermediate temperature value of 646·1 K as compared to LGG (603·3 K) and PMMA (678·1 K) in Table 1. These values also support the presence of PMMA on LGG.

Kinetic study and its interpretation

All the copolymerization reactions were performed under identical conditions. The following paragraphs describe the observed fact as revealed from the kinetic approach.

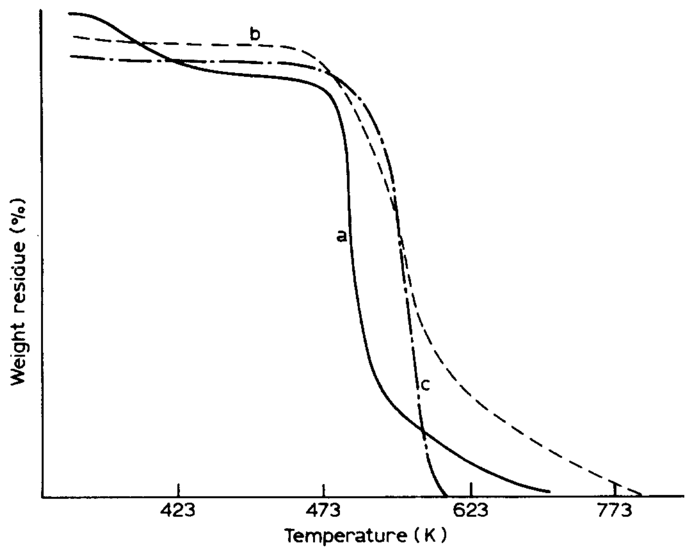


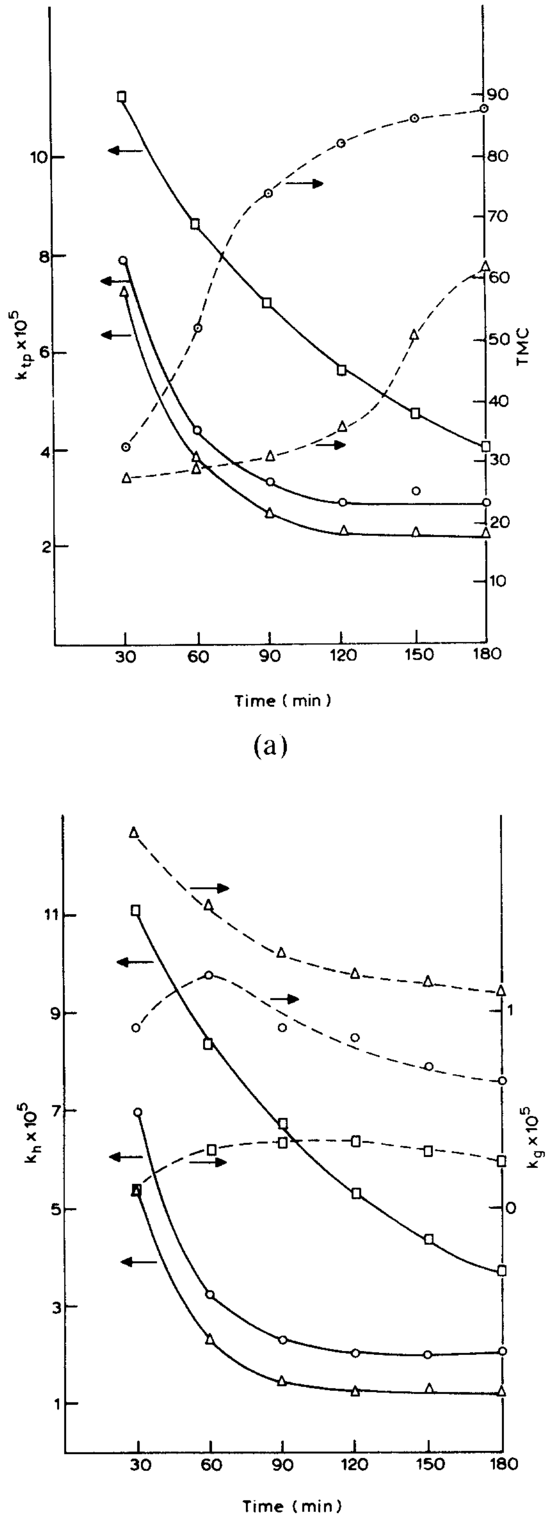
Fig. 2. TGA curves of (a) LGG (——), (b) LGG-g-PMMA (- - - -) and (c) PMMA (-·-·-·-).

Table 1. Thermal parameters of Leucaena glauca seed gum, polymethylmethacrylate and its copolymer

Sample	T_{50} (K)	T_{max} (K)	IPDT (K)	E ± 2 (kJ mol^{-1})
LGG	578	583	603·3	178·2
PMMA	652	658	678·1	221·3
LGG-g-PMMA (PA: 47·9)	637	650	646·1	92·4

Figure 3(a) and (b) respectively describe the time dependency of TMC, k_{tp} and k_h, k_g at various initiator concentrations. All the reactions are found to decrease with an increase in reaction time pertaining to every set of H_2O_2. Such a decrease may be encountered at fewer reactive sites as the reaction proceeds. The hydroxyl free radicals generated by thermal decomposition of initiator are available more in the initial stages than in the later stages. Moreover, the chances of synthetic polymer chain termination by either recombination or disproportionation also increase at higher reaction times. Thus in the earlier stages the abundance of reactive sites favourably promotes initiation and propogation causing enhancement in the k_{tp}, k_h and k_g. The same reason suits to justify the diminution in k_{tp} at lower H_2O_2. The homopolymerization is largely favoured at higher H_2O_2 as reflected by lowering in rates of grafting. The greater availability of free radicals may be considered responsible for enhancing the homopolymerization rather than graft copolymerization at higher H_2O_2. Thus an increase in k_h alone is responsible for higher k_{tp}, yielding poor grafting. Hence grafting is only favoured at lower H_2O_2, as also observed earlier by George & Radhakrishnan (1985).

The TMC curves presented for 10 mM and 20 mM



(a)

(b)

Fig. 3. (a) Effect of H_2O_2 and reaction period on the rate of total polymerization, k_{tp} (——) and total monomer conversion, TMC (- - - -) in grafting of MMA onto LGG. (b) Effect of H_2O_2 and reaction period on the rate of homopolymerization, k_h (——) and rate of grafting, k_g (- - - -) in grafting of MMA onto LGG.
Reaction conditions: LGG = 2·0 g (dry basis); MMA = 10·0 g, H_2O_2 = 10 mM litre^{-1} (△), 15 mM litre^{-1} (○), 20 mM litre^{-1} (⊙), 25 mM litre^{-1} (□).

Table 2. Effect of initiator concentration and reaction time on grafting of methylmethacrylate on to *Leucaena glauca* seed gum

Initiator concentration (mmol/litre)	Reaction time											
	30 min		60 min		90 min		120 min		150 min		180 min	
	GE	GF	GE	GF	GE	GF	GE	GF	GE	GF	GE	GF
5	26·6	9 980	40·7	5 649	48·3	4 233	52·4	3 407	43·9	2 734	40·8	2 330
10	24·7	9 670	40·1	5 022	46·8	3 628	49·0	3 068	47·9	2 568	44·5	1 779
15	12·3	9 175	27·3	3 663	29·2	2 780	30·2	2 064	18·7	1 721	18·5	1 586
20	3·2	9 258	9·1	1 959	9·4	1 252	10·3	985	10·0	861	11·3	642
25	0·9	7 716	3·6	1 234	4·8	649	6·2	427	6·0	396	6·2	308

Reaction conditions: weight of LGG taken, 2·0 g; MMA, 0·1 M/litre, temperature, 85 °C; volume of solvent, 200 ml.

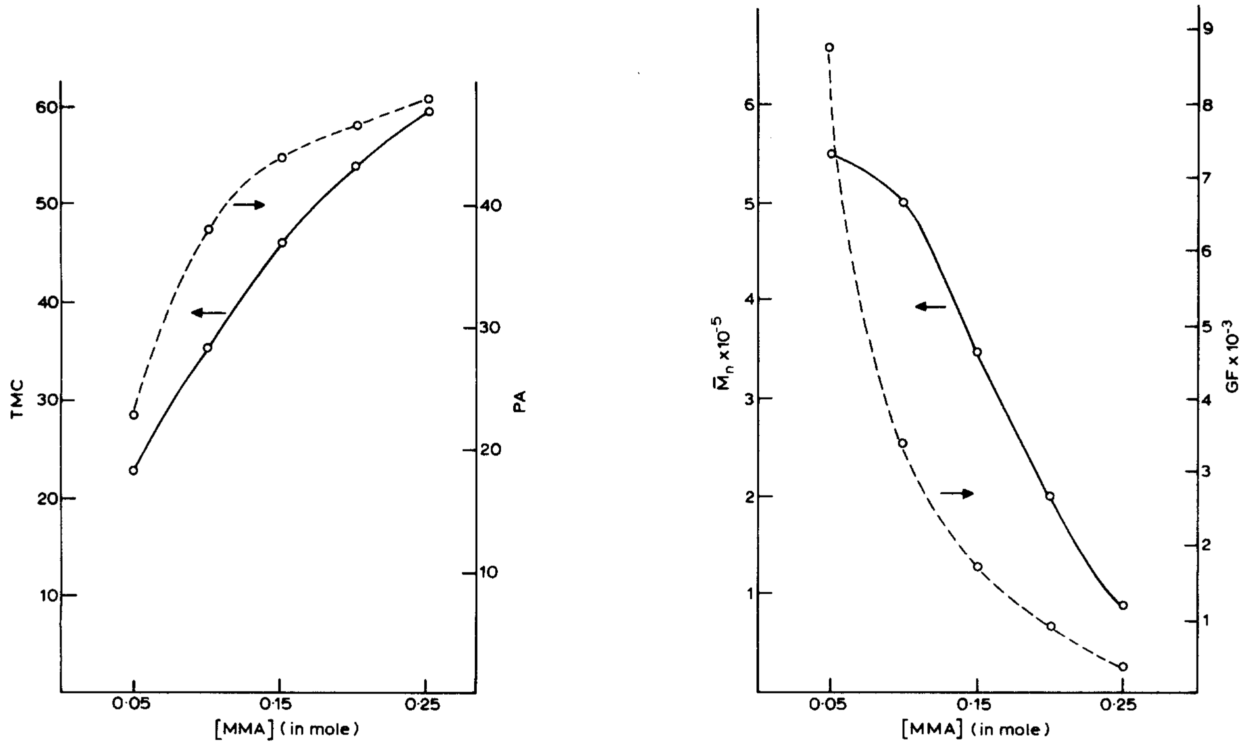
H_2O_2 in Fig. 3(a) also predict higher k_{tp} in the primary stages of grafting reactions. The TMC values achieved are 27·5% and 32·9% respectively for 10 and 20 mM after only 30 min of reaction period. Higher k_{tp} values in the first 30 min of grafting is also evident by prolonging the reaction up to 180 min which adds only 33·6 and 54·7% to the respective TMC values.

To ratify the lowering in k_g at higher H_2O_2, GE and GF as the function of H_2O_2 and reaction time are compared in Table 2. The constant decrease in GE values after achieving the maxima at 120 min clearly suggests more homopolymer formation upon extending the reaction period. This may be due to the propagating synthetic polymer chains transfer to the solvent MMA, which may increase the amount of homopolymer rather than grafts. Saroop *et al.* (1988) have also observed the similar trend in grafting of MMA onto another system like polyvinyl chloride. A pronounced decrease is observed in GE values with increases in H_2O_2 for each column differing in reaction time. This again may be attributed to higher k_h at high H_2O_2 due to facile termination of growing polymeric chain at higher concentrations of hydroxyl free radicals. The monomer polymer compatibility may also play its role to increase k_h. Palit *et al.* (1965) has reported that in aqueous polymerization of MMA, growing polymeric chains are more compatible with the monomer. This leads to higher k_h, i.e. lower k_g, as the growing chains can only terminate in the close vicinity of monomer. Moreover, higher degrees of oxidation state of LGG also may be considered responsible for low k_g at increased H_2O_2 as shown in Fig. 3(b).

Grafting frequency (GF) means the average number of anhydroglucose units separating the grafted branches of synthetic polymer. These values are observed to decrease with increasing H_2O_2 as well as the reaction time (Table 2). An almost 32-fold variation in the extreme GF values may be viewed as the enhanced possibility of the free radicals formation of LGG backbone, thereby increasing grafting sites upon extending the reaction period and/or increasing initiator concentration.

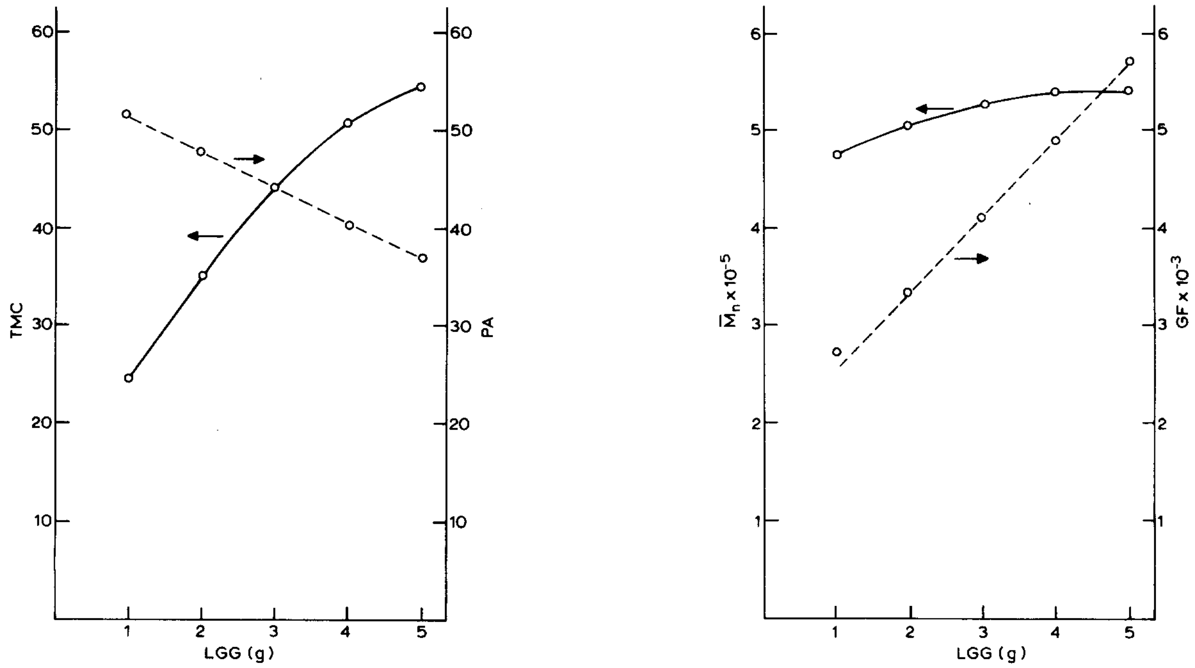
The effects of monomer concentration on the grafting were studied as a set of MMA between 0·05 M to 0·25 M keeping other reaction conditions constant as shown in Fig. 4(a) and 4(b). TMC and PA are found to increase steadily with MMA concentration (see Fig. 4(a)). This enhancement may be interpreted in terms of MMA concentration at very near proximity of the gum back bone which increases with increases in MMA/LGG ratio. The monomer molecules at the immediate vicinity of the reaction sites accept the LGG radicals and initiate the chain which then may act as free radical donor predominantly for the neighbours. Gaylord (1972) and Hebeish *et al.* (1979) have put forward a similar reason for the increase in grafting. Higher PA accompanied by lower GF with increasing monomer concentration suggests the grafting of shorter side chains on the LGG molecules. This is supported by the observed 5-fold decrease in the molecular weight of the separated PMMA from the grafted samples (see Fig. 4(b)).

Figure 5(a) and (b) depict the effects of LGG concentration on the copolymerization. The lack of initiator as compared to LGG, to produce more and more active sites for grafting on to LGG, is revealed by the proportionate increase in GF values (see Fig. 5(b)). GF values are found to be double with increasing LGG by a factor of 5. This may also be explained in terms of parent backbone polymer dispersions resulting in more frequent formation of free radical sites on the LGG chain (i.e. lower GF) than the more concentrated dispersions (Fanta *et al.*, 1969). The molecular weights of the grafted PMMA increase up to a particular value and then level off. The abundance of LGG and integrated surface area of LGG may affect the copolymerization by influencing the interactions of MMA and free radicals. The swelling of gum may be considered responsible for the diffusion of MMA to the growing chains preferentially in the gum matrix. The levelling



(a) (b)

Fig. 4. (a) Effect of MMA on total monomer conversion, TMC (——), percent add on (- - - -) in grafting of MMA onto LGG. (b) Effect of MMA on average molecular weight of grafts, $\bar{M}_n$ (——) and frequency of grafts, GF (- - - -) in grafting of MMA onto LGG. Reaction conditions: LGG = 2·0 g, H_2O_2 = 10 mM litre^{-1}, reaction time = 2 h, temperature = 85°C.



(a) (b)

Fig. 5. (a) Effect of LGG on total monomer conversion (TMC ——), percent add-on (PA, - - - -) in grafting of MMA onto LGG. (b) Effect of LGG on average molecular weight of grafts ($\bar{M}_n$ ——) and frequency of grafts (GF, - - - -) in grafting of MMA onto LGG. Reaction conditions: MMA = 10·0 g, H_2O_2 = 10 mM litre^{-1}, reaction time = 2 h, temperature = 85°C.

off of the $\bar{M}_n$ values suggests the shortage of MMA at higher LGG. Thus PA values are found to decrease with decreasing monomer (see Fig. 4(a)) and increasing LGG (see Fig. 5(a)). This also supports lack of MMA at higher LGG/MMA ratios.

CONCLUSION

The results presented above confirm the grafting of MMA onto LGG. High H_2O_2 favours homopolymerization rather than grafting, MMA and LGG play important roles in controlling PA, the net amount of synthetic polymer grafted on the parent backbone. The instrumental analysis also provides sound evidence for grafting.

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