Electrochemical initiation in methyl methacrylate–natural rubber latex systems

Investigations of electrochemical initiation of monomers both in aqueous and non-aqueous systems have progressed steadily in recent times[1–4]. However, few attempts at preparation of graft and block copolymers by electrochemical methods have been reported[5,6]. We felt that the preparation of Heveaplus type, natural rubber (NR)-*g*-methyl methacrylate (MMA) copolymer deserved investigation especially since so much other information on preparation by chemical methods of initiation is available[7]. Some preliminary results of research in progress are reported.

The experimental procedure consisted of electrochemical initiation of MMA monomer in the presence of NR latex. Addition of MMA monomer causes destabilization of NR latex, which was prevented by following Bloomfield's procedure[8]; MMA monomer containing oleic acid was added with stirring to stabilized* NR latex. The resulting NR–MMA emulsion was subjected to electrolysis following the method used by Palit[3] for electrochemical initiation of MMA monomer in an aqueous medium. The electrodes consisted of platinum foil, electrolyte was 0.3 M sodium acetate and no attempt was made to separate the anode from the cathode compartment. A stable d.c. source was used to adjust the current density. After electrolysis for a specified period, power was switched off and polymerization allowed to proceed i.e. post-polymerization[3].

In a typical experiment 500 ml of NR–MMA emulsion was electrolysed in a glass beaker at a current density of about 100 mA/cm^2. After 4 h of electrolysis, power was switched off and contents kept undisturbed at room temperature (27°–30°C) for one day. Gross products formed (any graft copolymer and free polymer) were coagulated, filtered, dried and weighed. Free NR and PMMA were removed by Soxhlet extraction using petroleum ether and acetone, respectively[9]. The material not extracted was assumed to be the graft copolymer and composition obtained by weighing. Independent confirmation of composition was obtained by quantitative i.r. spectroscopy. *Table 1* gives results obtained for two sets of experiments using NR latex of 2% (sample A) and 5% (sample B) dry rubber content, initially containing quantities of monomer equal to the amount of dry rubber present in each sample. It is seen that graft copolymer formation is minimal although polymerization of monomer appears to be satisfactory when compared with other published data for electrochemical polymerization of MMA in aqueous systems[3]. A parallel could be drawn to the case when an azonitrile type initiator is used for chemical initiation of MMA monomer in the presence of NR, which results in satisfactory polymerization but little or no graft copolymer formation[7].

Table 1 Analysis of gross products (NR latex and monomer present together from start of electrolysis)

Sample	MMA poly-merized (%)	Free PMMA	Free NR	Graft
A	37	29	65	6
B	32	19	77	4

Figures in the last three columns refer to percentages of total amount of gross product formed

In a second series of experiments, stabilized NR latex together with sodium acetate electrolyte (without any MMA monomer) was subjected to electrolysis for 4 h as in the earlier experiments, power switched off and immediately afterwards monomer added (note that in the earlier experiemnts, NR latex and monomer were present together from the commencement of electrolysis). Contents were kept undisturbed at room temperature as before and it was observed that polymerization had taken place. Analysis of gross products was performed as previously. *Table 2* gives results for samples C and D containing 2 and 5% dry rubber respectively, amounts of monomer equal to amounts of rubber present in each case being subsequently added. It is seen that yields of homopolymer and graft copolymer are somewhat improved compared with the earlier cases. The gross products also exhibited 'hard' and 'soft' forms characteristic of Heveaplus type graft copolymers[10] (gross products were dissolved in benzene and 'collapsed' with methanol yielding the 'hard' form or with petroleum ether yielding the 'soft' form). The gross products obtained in the earlier experiments failed to exhibit this phenomenon.

In a third series of experiments, the stabilized NR latex with sodium acetate was subjected to electrolysis as in the previous case, followed by addition of MMA monomer and a ferrous sulphate, tetraethylenepentamine (TEP) activator system as described by Sekhar[9]. Polymerization at room temperature was allowed to proceed as before. *Table 3* gives results of analysis of gross products for samples E and F containing 2 and 5% dry rubber, amounts of monomer equal to the weight of dry rubber added in each case. It is seen that yields of monomer polymerized are greater than in the earlier instances and graft copolymer formation is also correspondingly improved. The gross products also exhibited 'hard' and 'soft' forms.

Blank experiments conclusively showed that electrolysis of NR latex (with sodium acetate electrolyte) yielded an initiator for MMA polymerization. This could happen by hydroperoxide formation on NR through electrolytic oxygen. The improved grafting efficiencies in *Tables 2* and *3* suggest that the initiator is polymeric in nature since it is generally accepted that Heveaplus graft formation is a consequence of

Table 2 Analysis of gross products (monomer added to electrolysed NR latex)

Sample	MMA poly-merized (%)	Free PMMA	Free NR	Graft
C	56	62	25	13
D	45	52	33	15

Figures in the last three columns refer to percentages of total amount of gross product formed

Table 3 Analysis of gross products (monomer, $FeSO_4$ and TEP added to electrolysed NR latex)

Sample	MMA poly-merized (%)	Free PMMA	Free NR	Graft
E	80	40	35	25
F	83	42	29	29

Figures in the last three columns refer to percentages of total amount of gross product formed

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* With a non-ionic–cationic system.

polymerization brought about by polyisoprenyl radicals. When NR and MMA monomer together is subjected to electrolysis, initiation of MMA probably via oligomeric radicals[3] appear to be favoured independent of NR as shown by poor yields of graft copolymer (*Table 1*). However, when monomer is added after subjecting NR latex alone to a period of electrolysis, any polyisoprenyl radicals generated could initiate polymerization giving improved yields of graft copolymer. The highest yields of graft copolymer obtained when the $FeSO_4$/TEP activator system was used (*Table 3*) appear to confirm the hydroperoxide formation theory since similar results were obtained in NR latex systems known to form hydroperoxides by aeration[9].

Our experiments appear to show that electrolysis of NR latex could yield polymeric initiators probably via hydroperoxide formation. Confirmation of this novel phenomenon using separated electrolytic compartments, changing electrode material and other electrochemical diagnostic techniques recently published[4,11] is being investigated and will be reported in detail.

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