

Articals

Grafting onto Natural Rubber: Part II— Benzoyl Peroxide Initiated Graft Copolymerization of Ethyl Acrylate & Butyl Acrylate & Comparison of Monomer Reactivities

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Maximum percentage of grafting in the title investigation occurs within 180 min at 65°C. Evidence for grafting has been obtained from comparison of infrared spectra and scanning electron micrographs of natural rubber with those of grafted rubber. Thermogravimetric analyses of natural rubber and grafted rubber also indicate the formation of the graft. The reactivities of different monomers towards grafting onto natural rubber follow the order: EA > BA > MA.

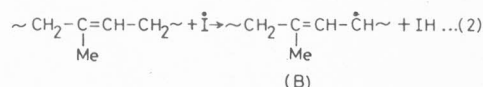
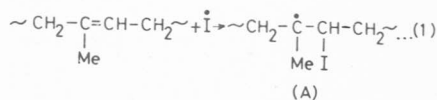
Recently we have reported that grafting of methyl acrylate (MA) onto natural rubber is considerably enhanced¹ when grafting is carried out in water-benzene medium using benzoyl peroxide (BPO) as an initiator. No attempts seem to have been made to compare relative reactivities of different donor and acceptor monomers towards BPO initiated grafting onto natural rubber. The title investigation is an attempt in this direction.

The natural creppe rubber had ash content = 0.6% and acetone extractive = 2.2%. Ethyl acrylate (EA) and butyl acrylate (BA) were washed with 5% aqueous sodium hydroxide followed by water, dried over anhydrous sodium sulphate and distilled; the middle fractions were used. Graft copolymerization of EA and BA onto natural rubber was carried out in benzene-water medium in the presence of BPO as radical initiator following the method reported earlier¹.

Evidence of grafting was obtained from IR spectroscopic and scanning electron microscopic studies of grafted and ungrafted samples. Thermogravimetric studies indicate the formation of the graft. Solubility behaviour of the grafted samples in benzene was different from that of ungrafted samples.

In the previous paper¹ we have proposed a mechanism for grafting of MA onto natural rubber involving direct initiator attack, in agreement with the mechanism proposed by other workers^{2,3}. Direct initiator attack to generate active sites onto rubber

would involve two modes of initiation and these are: (a) addition of initiator radical (I) to the polyisoprenes double bond (reaction 1); and (b) abstraction of methylenic hydrogen atom from the polyisoprene by initiator radical (I) (reaction 2)



Although these two initiation steps are reasonable, the present results agree well with the mechanism of initiation by reaction (2). The polymeric radical (B) because of allylic resonance stabilization is more likely to be formed than the *tert*-alkyl radical (A). Independent evidence exists³ that polyisoprenyl radicals structurally related to (B) are capable of vinyl polymerization. That the mechanism of initiation of grafting involved polyisoprenyl radical (B) is evident from the fact that the IR spectrum of grafted rubber showed C=C (*cis*) absorption in the region 830-900 cm⁻¹, thus ruling out the possibility of polyisoprene radical (A) involved in grafting.

In agreement with the proposed mechanism for grafting, percentage of grafting increased with increase in the concentration of BPO upto a certain limit, beyond which grafting decreased with all the monomers studied. At higher concentration of BPO, termination of the growing grafted chains leads to a decrease in per cent grafting. Further in the presence of mixed solvent (benzene-water) grafting occurs selectively with minimum of homopolymerization which is preferred in the presence of pure benzene. Maximum grafting of EA and BA occurs at 65°C within 180 min at [EA] = 76.6 M and [BA] = 58.6 M with [BPO] = 0.86 M in both the cases. Further increase in temperature leads to decrease in grafting. This may indicate that at higher temperature various chain transfer reactions having higher activation energy are accelerated leading to decrease in grafting. It is concluded that the reactivity of different vinyl monomers towards BPO initiated grafting onto natural rubber differs and follows the order: BA > EA > MA¹.

A comparison of the primary thermograms of natural rubber and grafted rubber indicates that the initial decomposition temperature of grafted rubber is

lowered upon grafting of acrylate polymers. Decrease in the thermal stability of graft copolymer is expected since polyacrylates are known to depolymerize upon pyrolysis⁴. Initial decomposition temperature of natural rubber (NR) is 400°C and those of NR-g-PBA and NR-g-PEA are 375° and 380°C respectively.

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