

## Grafting onto Natural Rubber: Part I—Graft Copolymerization of Methyl Acrylate Using Radical Initiators

B N MISRA\* & JYOTI KAUL

Department of Chemistry, Himachal Pradesh University, Simla  
171 005

Received 7 January 1982; revised 18 May 1982; accepted 26 May 1982

Graft copolymerization of methyl acrylate (MA) onto natural rubber (NR) has been studied using benzoyl peroxide (BPO) azobisisobutyronitrile (AIBN) and potassium persulphate (KPS) as radical initiators in benzene-water medium at 60, 65 and 70 °C. While BPO produces significant grafting of poly(methyl acrylate) (PMA) onto NR, AIBN and KPS under similar conditions give only homopolymer.

Natural rubber (NR), though used extensively till the discovery of synthetic materials, suffers from certain drawbacks which can be improved by suitably modifying it with vinyl monomers. Among various methods available for effecting modification of natural polymers, grafting appears attractive. Graft copolymerization of vinyl monomers onto NR can be carried out by a number of methods which include: chemical<sup>1</sup>, mechanical<sup>2</sup> and irradiation<sup>3</sup>. Of these the chemical method finds extensive applications. Graft copolymerization of vinyl monomers onto NR in the presence of benzoyl peroxide (BPO) has been reported<sup>4,5</sup>. However, evaluation of relative reactivities of different radical initiators towards graft copolymerization of a variety of acceptor and donor monomers onto NR is lacking. We report in this note studies on graft copolymerization of methyl acrylate (MA) onto NR using BPO, azobisisobutyronitrile (AIBN) and potassium persulphate (KPS) as radical initiators in water-benzene medium, and evaluation of relative reactivities of these initiators.

Creppe natural rubber (NR) with ash content = 0.6% and acetone extract = 2.2% was obtained as a gift from Dr S K De of IIT Kharagpur. BPO (BDH) was recrystallised from CHCl<sub>3</sub> and AIBN (BDH) from MeOH. KPS (BDH) was used as such.

Graft copolymerization of MA was carried out in benzene-water medium under nitrogen atmosphere using BPO, AIBN and KPS as radical initiators at 60, 65° and 70° for various reaction periods.

Extraction of the crude product with benzene was carried out in order to remove completely the homopolymer. Percentage of grafting (%G) and per cent efficiency (%E) were calculated using the relations

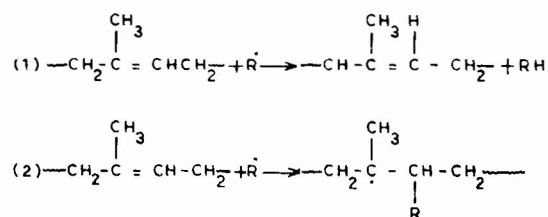
$$\%G = \frac{W_1 - W_0}{W_0} \times 100; \%E = \frac{W_1 - W_0}{W_2} \times 100$$

where W<sub>0</sub>, W<sub>1</sub> and W<sub>2</sub> denote respectively the weight of natural rubber, weight of grafted rubber and the weight of vinyl monomer. That the grafting of MA onto NR has occurred is revealed by the following facts:

(i) The νC=C of NR appearing at 1666 cm<sup>-1</sup> disappeared in the grafted sample which also exhibited in its IR spectrum a strong absorption at 1731 cm<sup>-1</sup> attributable to νC=O.

(ii) Comparison of scanning electron micrographs of NR and grafted rubber indicated that considerable amount of PMA is deposited onto NR.

It is well known that free radical species can abstract hydrogen atom from a polymer backbone to generate active sites where vinyl monomer could be grafted. When the polymeric backbone contains unsaturations, the radical fragment (R) arising from the decomposition of initiator molecule or the growing homopolymeric chain can generate active sites on polymeric backbone by addition process also. Natural rubber has a 1, 4-*cis*-polyisoprene structure. The mechanism shown in Scheme 1 for initiation of grafting of MA onto NR appears reasonable:



Scheme 1

It is observed from Table 1 that only BPO brought about significant grafting while both KPS and AIBN produced only homopolymers. The failure of KPS and AIBN to produce graft copolymer has been attributed to the resonance stabilization of  $\dot{\text{R}}$  arising from the decomposition of AIBN and KPS which show 'initiator effects'.

No such "initiator effect" is shown by BPO and this is why  $\dot{\text{R}}$  resulting from decomposition of BPO is reactive enough to generate active sites on the natural

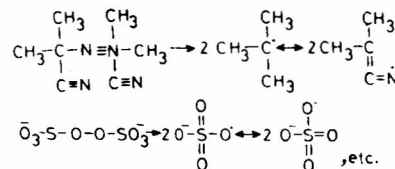


Table 1—Per cent Grafting and Per cent Efficiency of Grafting of MA onto Natural Rubber

MA $\times 10^2$ , M	Time, hr	% Grafting	% Efficiency
KPS ( $0.6 \times 10^{-2}$ M) as initiator			
92.05	3	0	0
128.8	3	0	0
AIBN ( $1.0 \times 10^{-2}$ M) as initiator			
92.05	3	0	0
128.8	3	0	0
BPO ( $0.86 \times 10^{-2}$ M) as initiator			
92.05 <sup>a</sup>	3	78	8.21
92.05	3	505	53.1
92.05 <sup>b</sup>	3	280	20.47
92.05	3	96	10.1
92.05	3	372	39.15
92.05	2½	113	11.8
92.05	3½	393	41.3
92.05	2	46	4.8
55.23	3	256	27.0
128.8	3	770	81.05
165.0	3	78	4.56

Rubber = 500 mg; Water = 60 ml; Bz = 40 ml; Temp = 65°C.

a, [BPO] =  $0.68 \times 10^{-2}$  M

b, [BPO] =  $1.03 \times 10^{-2}$  M

rubber where grafting can occur. Maximum grafting (776%) of PMA onto natural rubber occurred within 3 hr at 65°C. Further increase in temperature led to decrease in per cent grafting. At higher temperature homopolymerization occurred preferentially. It is evident from the data in Table 1 that with increase in the monomer concentration per cent grafting increases and reaches maximum value at [MA] =  $128.8 \times 10^{-2}$  M. With further increase in [MA] per cent grafting decreases because at higher [MA] homopolymerization becomes the preferred process. At a higher percentage of grafting, the grafted material assumed gel like structure. This may indicate that besides grafting, NR and MA undergo cross linking reaction to give a product which is insoluble in benzene. NR is known to undergo cross linking reaction<sup>6</sup> in the presence of BPO

and polyacrylates are known to assume gel like structures.

It has been observed that grafting proceeds smoothly in aqueous medium, when NR is pre-swollen in benzene. Prior swelling of NR in benzene facilitates accessibility of the growing polymeric chains onto active sites. When the grafting is carried out in benzene alone, considerable amount of homopolymer is formed at the expense of the graft. In benzene, NR, MA and PMA are highly soluble and in the homogeneous medium homopolymerization is favoured over graft copolymerization. In the heterogeneous water-benzene (60:40) medium, homopolymerization of MA is slowed down and as a consequence per cent grafting increases. Both water and benzene have very low chain transfer constants but water has practically zero chain transfer constant<sup>7</sup> and therefore, in water medium, various chain transfer processes that lead to wastage of monomer are minimum. It has been observed in our laboratory that grafting of a number of vinyl monomers onto starch<sup>8</sup>, cellulose<sup>9</sup> and wool<sup>10</sup> proceeds smoothly in aqueous medium.

One of the authors (J K) is grateful to Himachal Pradesh University, Simla for the award of a junior research fellowship.

## References

- 1 Allen P W, Ayrey G, Moore C G & Scanlan J, *J polym Sci*, **36** (1959) 55.
- 2 Pike Ma & Watson W F, *J polym Sci*, **9** (1952) 229.
- 3 Turner D T, *J polym Sci*, **35** (1959) 17.
- 4 Bloomfield G F & Swift P McL, *J appl Chem*, **5**, (1955) 609.
- 5 Bevilacqua E M, *J polym Sci*, **24** (1957) 292.
- 6 Morton M, Agarwal N K & Cizmecioglu M, Preprints, (Division of organic coatings & plastics chemistry), 182nd National Meeting of American Chemical Society, **45** (1981) 158.
- 7 Dainton F S, *J chem Soc*, (1952) 1533.
- 8 Misra B N & Dogra R, *J macromol Sci (Chem)*, **A14(5)** (1980) 763.
- 9 Misra B N, Jassal J K & Pande C S, *J polym Sci, Polym Chem Edn*, **16** (1978) 295.
- 10 Misra B N & Chandel P S, *J polym Sci, polym Chem Edn*, **15** (1977) 1545.