Jl. Rubb. Res. Inst. Sri Lanka (1994) 74, 57–78

KINETIC STUDY OF THE GRAFT POLYMERIZATION OF UNSATURATED MONOMERS WITH NATURAL RUBBER LATEX AND WITH DEPROTEINIZED NATURAL RUBBER LATEX

K G Karnika De Silva, A E Hamielec[1]

(Accepted 24 September 1994)

ABSTRACT

The non – rubber substances present in natural rubber (NR) latex seem to have an influence on the rate of polymerization reaction, degree of grafting and grafting efficiency of the graft copolymerization reaction of Methyl Methacrylate on to natural rubber. The released amino acids on enzymatic destruction of phospholipid/protein barrier in natural rubber latex may probably by the cause for the improvement of the reaction kinetics; such that reaction under redox conditions could be conducted without purification of the monomer with inhibitors.

Presence of emulsifier, type of enzyme, monomer diffusion time in rubber particle, size of the particle are shown to have an influence on the physical properties of the final product. ^{1}H NMR has been used to study the composition of the final product.

INTRODUCTION

The backbone unsaturation in natural rubber, cis–1,4 polyisoprene, facilitates certain types of chemical modifications to yield a range of modified natural rubber based materials. As such chemical grafting of different polymer side chains on to natural rubber could result in graft copolymers with novel properties, there by

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[1] MIPPT, Chem. Eng. Dept., McMaster University, Hamilton, Ont. L8S 4L7, Canada

enhancing the possibilities of using natural rubber based materials in a wider range of industrial applications.

The polymer grafted rubber may have low density, improved toughness and gloss when compared to rubber and improved elongation and impact strength when compared to plastics. The grafted polymer side chains on the backbone polymer may exist as coils inside the rubber particles, simulating the function of particulate fillers, (eg- carbon black, lignin, cyclized rubber *etc*) giving a self-reinforcing effect to natural rubber. Also, being polymeric in character the side chains might be expected to improve properties which are characteristic to those polymers, without a loss in elastic properties of natural rubber. Hence, there is a possibility of controlling the elastic properties of the product by varying the polarity, flexibility and chemical reactivity of the attached side chains. Further, some of these materials may have a particular combination of physical properties which are available from directly moulded products without the need for chemical crosslinking and its associated complex, cumbersome mixing and curing cycles. (eg. as in SBS block copolymers)

However, the graft copolymer of natural rubber and polymethylmethacrylate which has been in commercial production for many years, is a tough material that will soften on heating, and cannot be directly processed by injection moulding, or even compression moulding, because of its very high viscosity and gel content.

Conventional mastication will confer a degree of processability but the product will not have high strength or toughness unless it is subsequently vulcanized.

Several authors (Pendle, 1973, 1974; Campbell, 1973; Burfield and Nu, 1975) have demonstrated that the graft copolymers have a small number of very long hard polymer chains and also significant proportion of backbone chains which carry no graft chain at all whereas the block copolymers have a fairly large number of short hard polymer chains attached to each rubbery backbone and this difference in chemical nature of the hard polymer is responsible for the property differences. As, such although we would expect the copolymers of diene rubbers with polymethylmethacrylate and polystyrene (glass polymers with similar glass transition temperatures) to show similar properties but they show different properties. The two major differences between the well known styrene-diene block copolymers and graft copolymers of polyisoprene rubber and polymethylmethacrylate are the chemical nature of the hard polymer and the molecular architecture of the resultant graft copolymer. In the graft copolymer of polyisoprene rubber and polymethylmethacrylate, the hard polymer (polymethylmethacrylate) is in a graft structure whereas styrene-diene block copolymers have polystyrene hard polymer in a block structure.

The preparation of comb graft copolymers by carbanionic polymerization techniques has been studied (Falk and Schlott, 1973). The method is applicable to the preparation of comb grafts from synthetic polyisoprene and polystyrene but cannot be extended to natural rubber because of the detrimental effects of the non–rubber substances on living polymer systems and the dispersed aqueous medium of natural rubber latex. Chemical reactions directly on natural rubber latex or dry rubber can be influenced by the presence of non–rubber contaminants such as proteins. About 25% of proteins out of 1.5% non–rubbers that are adsorbed on the rubber particles will have a major effect on the grafting reactions. These contaminants can for example act as catalyst inhibitors and can influence the course of free radical reactions (De Silva and Fernando, 1985). We have therefore had to adopt an alternative approach to the synthesis of graft copolymers with natural rubber. Since the grafting reactions of natural rubber while still in the latex form is clearly more challenging and economical than in the dry state we have paid much attention on the grafting reactions in natural rubber latex.

One way by which the chemical reactions with natural rubber latex can be carried out effectively is to remove the non–rubber substances. The conventional methods used for concentration of field latex, can remove non–rubbers to a considerable extent. However in the presence of monomers, the graft copolymers obtained do not show an increase in the efficiency of graft copolymerization in concentrated latex, but only show high reactivity compared to field latex, indicating an inhibiting action of graft copolymerization reaction in the presence of non–rubber substances *eg* proteins. Also, it should be mentioned here that when field latex is used as the natural rubber substrate in the grafting reactions, with a monomer concentration higher than 10%, the latex tends to coagulate even in the presence of different amounts of various stabilizers.

Hence we have attempted to remove this polymeric protein–phospholipid barrier present on the rubber particles in latex prior to the graft copolymerization reaction of monomers by free radical methods. An effective technique by which this layer can be destroyed is by enzymatic hydrolysis of the protein segments. However this process can result in destabilization of latex resulting in coagulation of natural rubber.

In our work a proteolytic enzyme is used to hydrolyse the protein component of this membrane thereby effectively releasing (freeing) the natural rubber hydrocarbon. In order to prevent destabilization of latex a non–ionic emulsifier is used to keep the released hydrocarbon in suspension. The low nitrogen content of the dry rubber isolated by coagulating this treated (deprotenized natural rubber, DPNR) latex indicates that the proteolytic enzyme effectively hydrolyses the protein in natural rubber latex.

The grafting reactions with DPNR and natural rubber latex were carried out by using various free radical initiators at different temperatures. Free radical

polymerizations are the simplest and most widely used for the synthesis of graft copolymers. Although the products of free radical grafting reactions are somewhat ill-defined, this method offers certain advantageous, some of which are listed below.

1) As a result of the variety of monomers which can be polymerized *via* radical methods a more varied range of chemical structures is possible compared to those from anionic and cationic methods.

2) Free radicals can be generated by a diverse range of process. eg– high energy radiation, photochemical initiation, classical chemical initiation and others.

3) Polymerization can be conducted with in the polymer particles in a latex thus producing grafted copolymer in aqueous suspension which can be recovered as solid polymer for various end uses.

The most important commercially available graft copolymers by free radical synthesis are the impact resistant plastics such as HIPS, ABS and MBS. The common feature of these product is that the main chain is polybutadiene. The polymerization processes can be carried out in latex with conventional redox initiators. Though grafted polybutadiene latex is not directly used in practical applications, cast films can be obtained by evaporation at room temperature. The cast films are void of cracks or with a very few large cracks depending on the percentage of polymer grafted on to polybutadiene, indicating a considerable grafting efficiency and hence compatibility.

The common monomers available in liquid form at room temperature are more polar than isoprene. Their homopolymers are also more polar than polyisoprene in natural rubber. The compatibility of these polymers are low and phase separation can occur in dry films unless a higher percentage of homopolymer is converted to side chain polymer.

As with homopolymerization, copolymerization too can be used to vary the physical properties of rubber.

Synthetic polyisoprene latex has been used (Blackley et al, 1985) as a model to study certain aspects of the behaviour of natural rubber latex it has simpler chemical compositions than natural rubber latex and can be characterized more comprehensively due to the absence of non rubber substances. Since synthetic polymer is not a stereospecific linear cis-1, 4-polyisoprene but a branched polyisoprene of mixed microstructure it might be a disadvantage especially when interpreting chemical reaction involving the polymer.

Accordingly, the probable causes for the difference in the reactivity of natural rubber and synthetic lattices eg-polyisoprene, polybutadiene towards the monomers may be two fold. Firstly, the existence of adsorbed protein-phospholipid layer around the rubber hydrocarbon in natural rubber latex. The protein-phospholipids barrier is a continuous chemically inter-linked membrane covering the natural rubber hydrocarbon, effectively suspending the rubber particles with the aid of its negative charge. The adsorbed proteins unlike the emulsifier additives in polybutadiene, could inhibit the penetration of monomers resulting in lesser number of growing polymeric radicals. Secondly, the structure of the synthetic latex may not be stereospecifically similar to that of natural rubber. In natural rubber all cis, alkyl substituted double bonds are electron - rich via both hypocongugative and inductive effects but are also somewhat sterically hindered.

EXPERIMENTAL

The reagents used in this work are as follows.

Styrene and Methylmethacrylate: Inhibited styrene and methyl methacrylate were obtained from BDH Ltd. The inhibitor was removed in the standard way, by first shaking the monomer with aqueous sodium hydroxide solution in a separating funnel and separating off the organic fraction, drying it with anhydrous Na_2SO_4 and then distilling the predistillate (contaning some water).

Rubber: The natural rubber latex used in this study was obtained from Goodyear of USA and from Rubber Research Institute of Sri Lanka. Natural rubber latex free of non-rubber materials which is generally known as deproteinized natural rubber or DPNR latex was prepared by treating natural rubber latex diluted with water in 1:1.15 ratio, with a proteolytic enzyme, papain in the presence of a non-ionic stabilizer for six days. The resultant latex was used to study the effect of non-rubber substances on the grafting reactions. DPNR latex was coagulated with methanol and washed well to obtain DPNR used in dry rubber studies.

Non - ionic Stabilizer - Proprietary

Methyl Ethyl Ketone, Benzene and methanol - Fisher, certified

Tert-butylhydroperoxide (Florochem), the tetraethylene pentamine (Fluka AG) and oleic acid (BDH Ltd) were also used as received.

The reactions were carried out in the presence of carefully selected non-ionic stabilizers to avoid any destabilization that may occur during the polymerization. It has been experienced that the careful control of the level and the type of stabilizer are vital in these systems.

The apparatus used for all polymerization reactions is shown in figure 1. The reactor used was a three necked round bottom 1000ml pyrex flask fitted with a mechanical stirrer. The system was purged with nitrogen gas and a vapor trap was used to condense any styrene vapor leaving the reactor. The flask was immersed in a water bath at 60^0C for reaction in liquid phase. At 30 minutes intervals samples of reaction mixture were sucked out of the reactor with a pipette.

The experimental runs with a natural rubber latex (containing 52.01% dry rubber) samples were conducted as follows.

250g of natural rubber latex and 125ml of water were charged to a weighed resin flask (Figure 1). In the experimental runs with DPNR latex, 250g of natural rubber latex was diluted with 75g of water and was treated, with 0.97g of papain (0.75% on dry rubber content) in 25ml of water in the presence of 1.3g of a non ionic stabilizer (0.1% on dry rubber content) in 25ml of water, for six days before the reactions were performed.

To the latex mixture in the resin flask was added 35g of 4% ammonia solution and the mixture was de-oxygenated by bubbling nitrogen gas for about 45 minutes. The pH of the mixture was kept above 8.5 by adding excess 4% ammonia solution. 2g of oleic acid was then added while stirring to form ammonium oleate *in situ* which acts as a stabilizer for natural rubber latex. The flask with the contents was weighed accurately (w_1).

The nitrogen flow was then reduced to a low level and the temperature was increased to 50^0C before the addition, drop wise over 15 minutes, of various proportions of styrene or methyl methacrylate monomer (Table 1) and t-butylhydroperoxide at 0.4 phr.

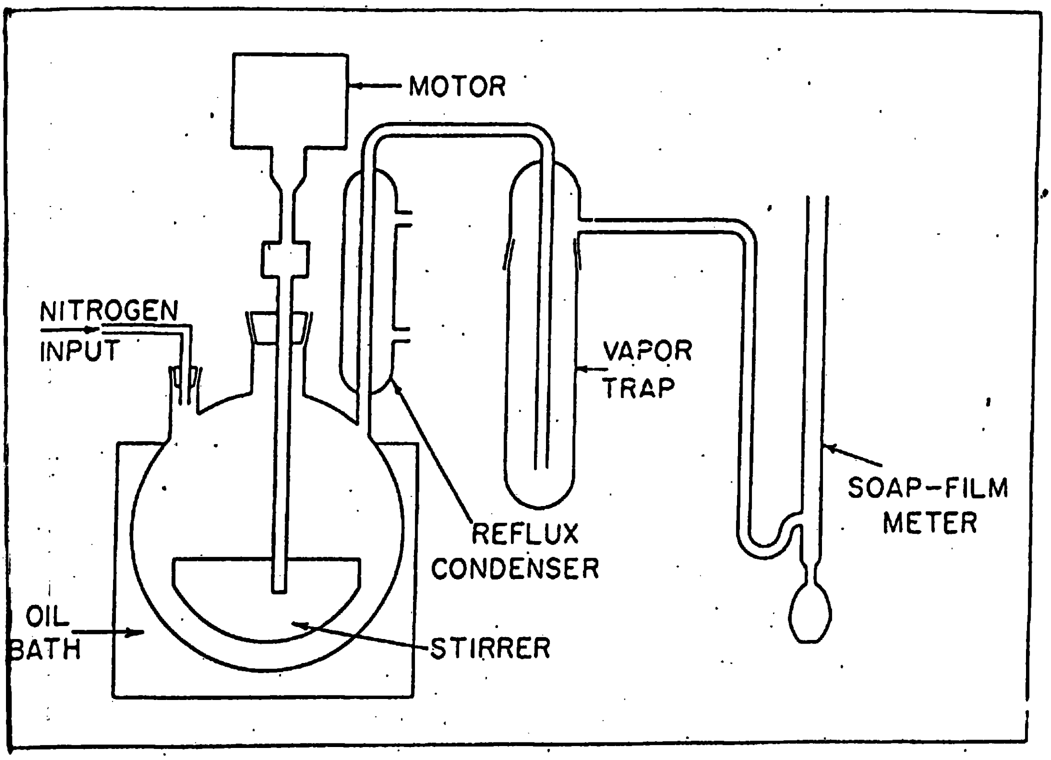


Fig. 1 Schematic of reactor used for kinetic study

Table 1. *Weights of styrene/methyl methacrylate and the reaction mixture used in the grafting reactions with 250 g of natural rubber latex of with 52.01% dry content*

		Weight of the reaction mixture		
Rubber: monomer ratio	styrene/MMA g	DPNR/styrene	NR/styrene	DPNR/MMA
90:10	14.44	382.43	-	-
80:20	32.50	400.02	-	-
70:30	55.72	423.09	422.86	418.11
60:40	86.68	453.67	-	-
50:50	130.02	496.85	-	-

After about 15 minutes the amine activator, tetraethylenepentamine (1.8g from a 10% w/v solution) was added. At 30 minutes intervals two samples were drawn out of the reactor with syringe (10ml).

To establish, gravimetrically, the degree of conversion. one sample was emptied into a weighed 25ml sample bottle and reweighed. The contents were then poured into a glass beaker and coagulated with methanol (care was taken in transferring all the contents into the beaker). The methanol precipitates all the polymer dissolving unreacted monomer. The precipitated polymer was then leached in four different batches of de-ionized water for 24 hrs to remove any water soluble impurities present in rubber.

The second sample was cast in horizontal glass trays of 1mm height to give a final opaque sheet. Cracking of these cast sheets was observed in DPNR/ polymethylmethacrylate grafts when the polymer composition is greater than 40% and in natural rubber/polymethylmethacrylate grafts at a lower monomer composition of 30%. Hairline cracks were observed in DPNR/ polystyrene grafts when the monomer composition was 30%. Once dry, the sheets were removed from the tray and transferred to a vacuum oven at 40^{0}C to remove any traces of monomer. The dried sheet was then leached in six different batches of de-ionized water for two days to remove any water soluble impurities present in rubber.

The polymer obtained as coagulum or sheet was then washed with methanol and left over night in 150ml of methanol to ensure that all the unreacted monomer is extracted. The polymer was cut into pieces, washed well with methanoland vacuum dried at 1mm Hg at 40^{0}C and weighed accurately (W_2).

The percentage conversion of monomer can be calculated as follows with suitable modifications.

$$\% \text{ conversion} = \frac{W_2 - \dfrac{RS_1}{W_1}}{\dfrac{SS_1}{W_1}} \times 100$$

Where W_2 = weight of monomer free dry residue from S_1
R = weight of the rubber in the initial reaction mixture
S = weight of monomer in the initial reaction mixture
S_1 = weight of the sample drawn out of the reaction
W_1 = initial weight of the reaction mixture

Due to the excessive times required soxhlet extractions were performed only on the dry residues (W_2), obtained from the reaction mixtures of DPNR latex/styrene, natural rubber latex/styrene and DPNR latex/MMA. These extractions were useful for further analysis to obtain grafting efficiency and degree of grafting. Acetone and petroleum ether were used to extract the homopolystyrene or homopolymethylmethacrylate and ungrafted rubber respectively. These extractions were performed for 24 hrs under nitrogen gas to avoid any degradation of natural rubber during extractions. The samples were dried in a vacuum drying chamber (1mm Hg at 40°C) to remove any traces of solvents. The samples were dried to a constant weight W_4, after extraction with acetone and W_5, after extraction of the same sample with petroleum ether to remove ungrafted rubber. The extracts were evaporated separately in a fume hood under nitrogen, dried in a vacuum oven and weighed to check the amount of homopolystyrene or homopolymethylmethacrylate and ungrafted rubber present in the grafts at different intervals.

The grafting efficiency and degree of grafting for the reactions involving styrene and rubber were calculated by the method given in Appendix 1. Same method is applied to the reactions involving methylmethacrylate and rubber.

RESULTS AND DISCUSSION

The particle size analysis (Table 2) has been also helpful in providing a positive proof of the removal of non–rubber layers around the rubber particles by showing reduced particle sizes, after the treatment of natural rubber latex with enzymes. An increase in latex particle size was observed immediately after the grafting reaction is initiated. This observation is reasonably straight forward increase being due to swelling of latex particles in the presence of added styrene, and this increase seems to be significant with the DPNR latex. The particles shrink after the grafting reaction is completed and reach a constant size, which is in between the value of the initial and swollen latex particles.

Table 2. *Data obtained for natural rubber latex, treated latex (DPNR latex), styrene monomer swollen DPNR latex and DPNR/Polystyrene latex (grafted latex), using the Nicom particle size analyzer*

% concentration of styrene	diameter (microns) 15 minutes after mixing	 after 3hr of reaction time
10	1.2175	0.9981
20	1.2925	1.0156
30	1.3110	1.0298
40	1.3243	1.0143
50	1.3423	1.0158

The different degrees of grafting efficiency and the incompatibilities of the polymers and the natural rubber are reflected in the appearance of the films produced when the grafted lattices are dried. It was also noted that methylmethacrylate could form crack free films with a higher amount of polymer concentration when compared with styrene indicating that methyl methacrylate is structurally similar and hence more compatible with natural rubber than styrene. The colour of the films from the grafted latex change from amber to white when the monomer concentration is increased from 10% to 50%, based on the dry rubber content in the natural rubber latex.

The presence of emulsifiers, type of enzyme, monomer diffusion time in rubber particles, size of the original particles *etc* may have an influence on the physical properties of the final product. Furthermore, certain initiators (eg- t-butylhydroperoxide in the presence of polyamine) seem to promote grafting while others (eg- azobisisobutyronitrile), which form radicals with weak hydrogen-abstracting properties do not.

The free homopolymer and free rubber occluded in the grafting product were removed by extraction with acetone and petroleum ether respectively. This method is relatively simple and hence the most widely used, though time consuming. It is known that to obtain pure graft copolymer, free of homopolymers, both homopolymers have to be subjected to repeated, alternate extractions. It was thought that in these experiments the coagulation of graft copolymers with methanol may entrap some free rubber and free homopolymer and hence the extractability of the homopolymers with solvents may be somewhat hindered. As a simple solution cast films were prepared from the grafted latex and a few trials were carried out to extract the free polymer with acetone. The free homo polymer extracted from graft films shows slightly higher values or a negligible difference.

The grafting efficiency, degree of grafting and conversion information for 70:30 rubber : monomer grafts are graphically illustrated in figures 2–5. These figures illustrate the data of the grafting reaction of DPNR latex and natural rubber latex respectively with styrene. These figures clearly show that the % grafting efficiency and % degree of grafting for the reactions with natural rubber in all occasions are lower than that with DPNR latex.

It is also clear that when the cis–polyisoprene backbone in natural rubber is chemically clean *ie* with DPNR the grafting efficiency is as high as 66% after 4 hrs of reaction time (figure 3) when compared to the grafts with natural rubber with grafting efficiency of 53% for same reaction time, giving evidence for the interference of the non–rubbers towards the efficiency of graft copolymerization.

Figure 5 illustrates the variation of % graft polystyrene with % total polystyrene present in the grafts with DPNR latex/polystyrene and natural rubber latex/polystyrene. The curves extrapolate through to give a measured 20.8%, % grafted polystyrene (hence 69.5% grafting efficiency) with DPNR latex and 18.8%, % grafted polystyrene with NR latex (hence 62.6% grafting efficiency) with NR latex, at a hypothetical maximum polystyrene content of 30%. The difference is again ascribed to the interference of non–rubber substances in the natural rubber latex.

^{1}H NMR data has been used to study the composition of the final products. Figures 6 and 7 show the ^{1}H NMR spectra for natural rubber and standard polystyrene whereas figures 8 – 11 show the ^{1}H NMR spectra for the grafts, natural rubber/polystyrene, natural rubber/polymethylmethacrylate, natural rubber/polstyrene/polymethylmethacrylate and natural rubber/polystyrene/polyacrylonitrile respectively after 4 hrs of reaction time. In all these cases DPNR latex have been used as he natural rubber substrate in order to get higher monomer compositions in the final products and the products have been extracted with acetone and petroleum ether respectively to remove any ungrafted polymer and ungrafted rubber that are present in the final product. The results obtained from these spectra are shown in appendix 2.

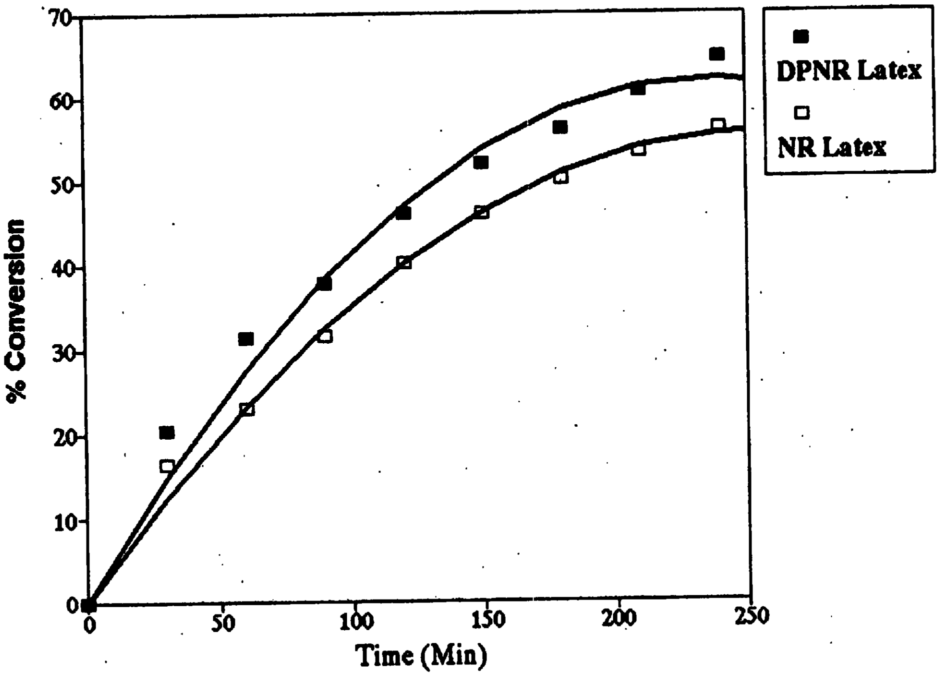


Fig. 2 % Conversion vs time graph (initial rubber : styrene = 70:30)

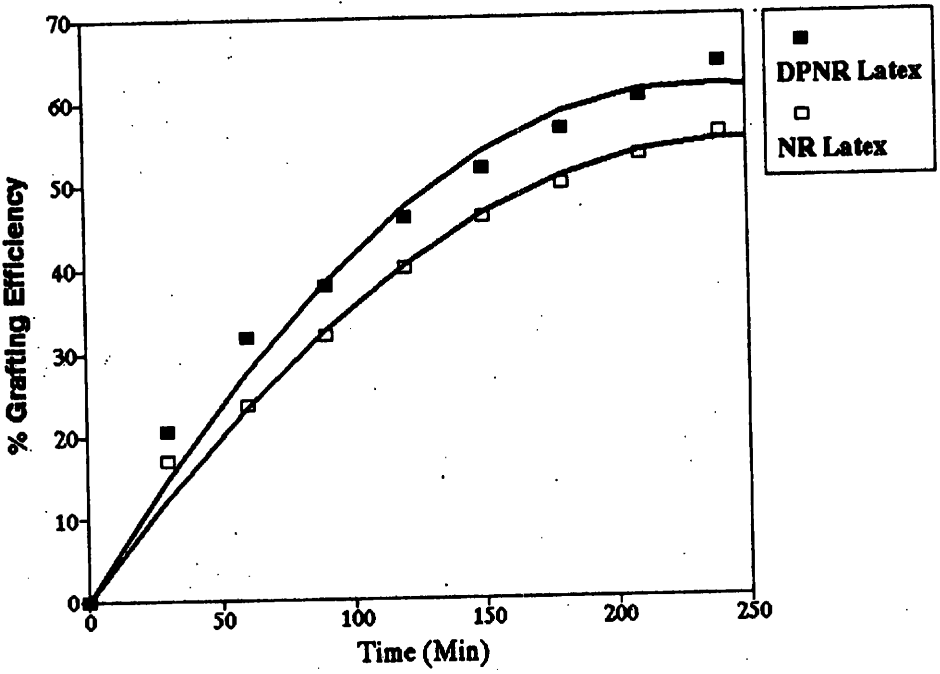


Fig. 3 % Grafting efficiency vs time (initial rubber : styrene = 70:30)

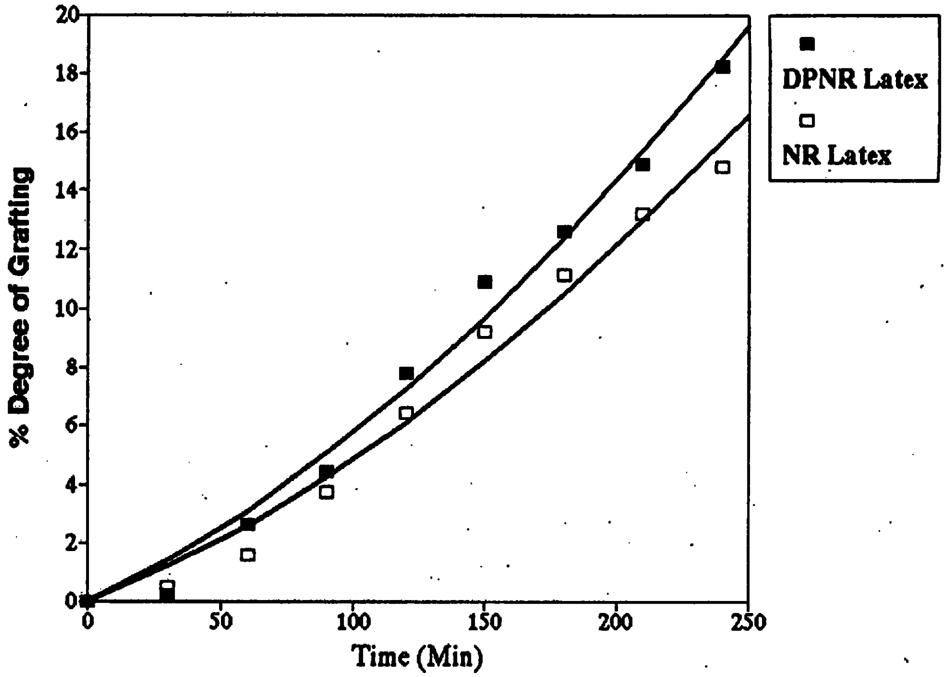


Fig. 4 % Degree of grafting vs time (initial rubber : styrene = 70:30)

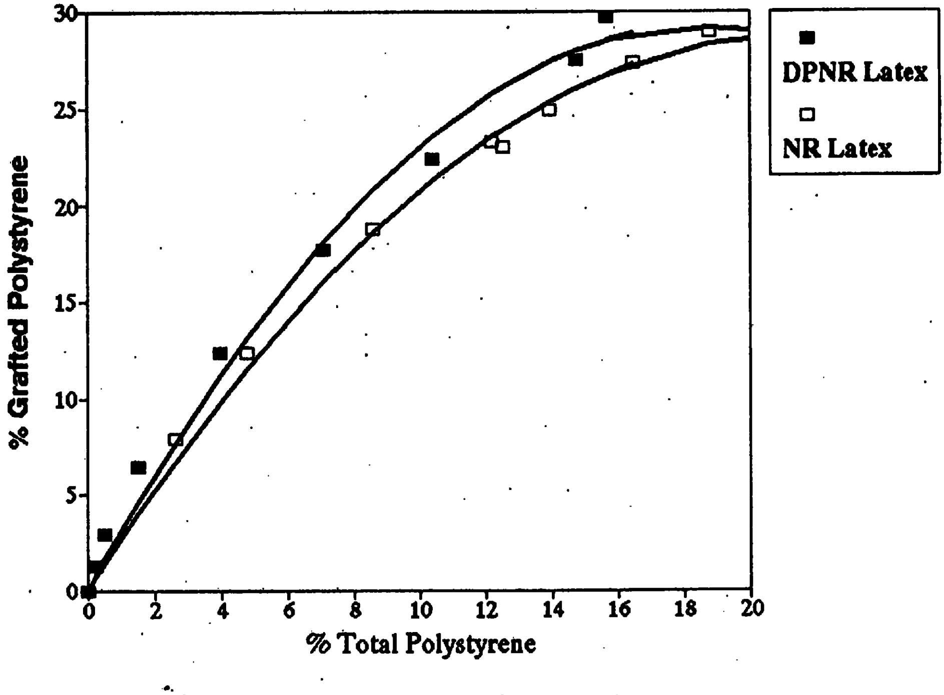
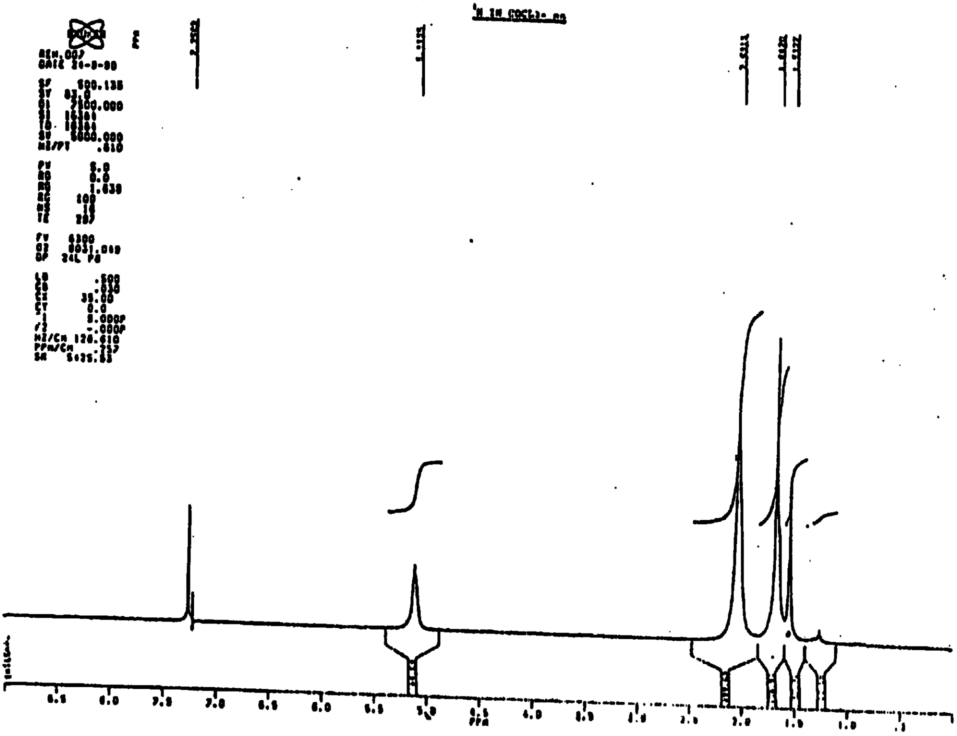


Fig. 5 % Grafted polystyrene vs % total polystyrene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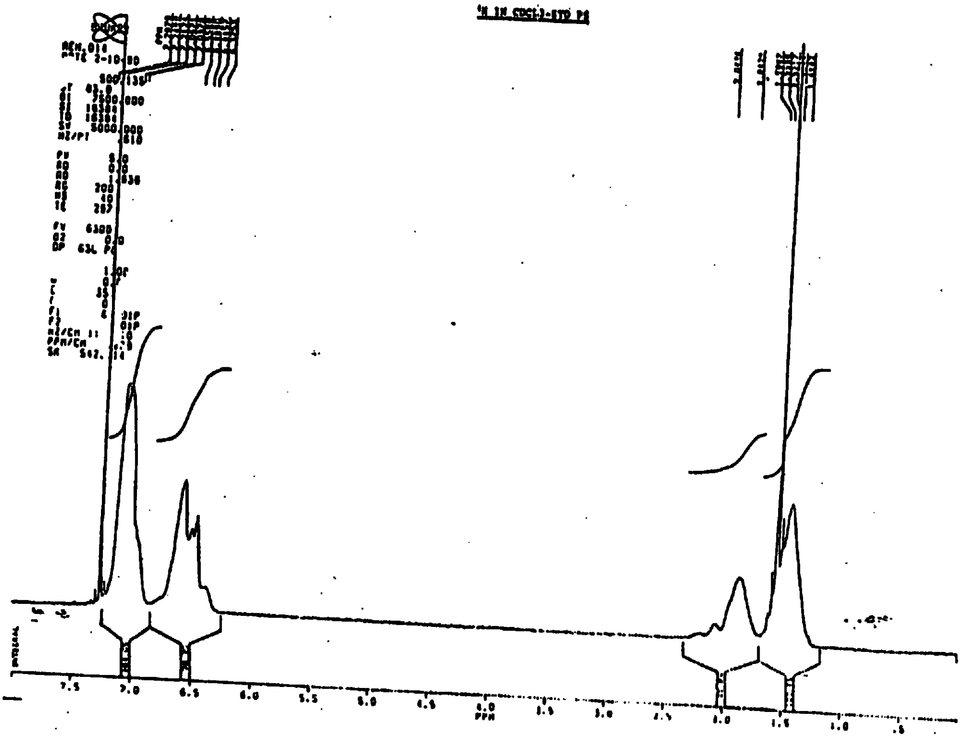
PPM

Fig. 6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PPM

Fig. 7

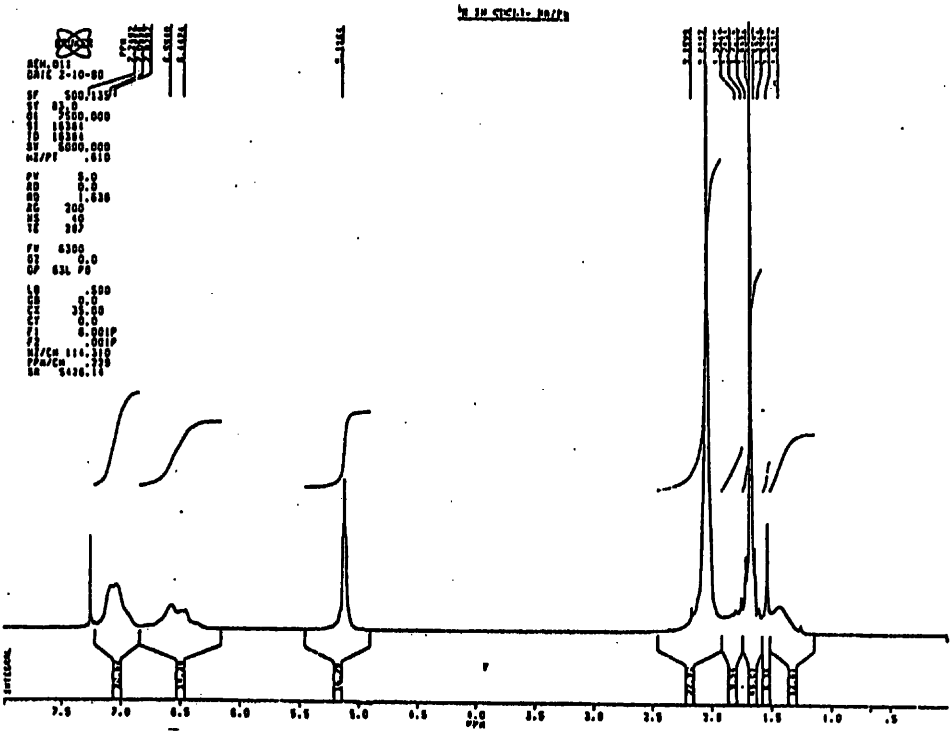
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Fig. 8

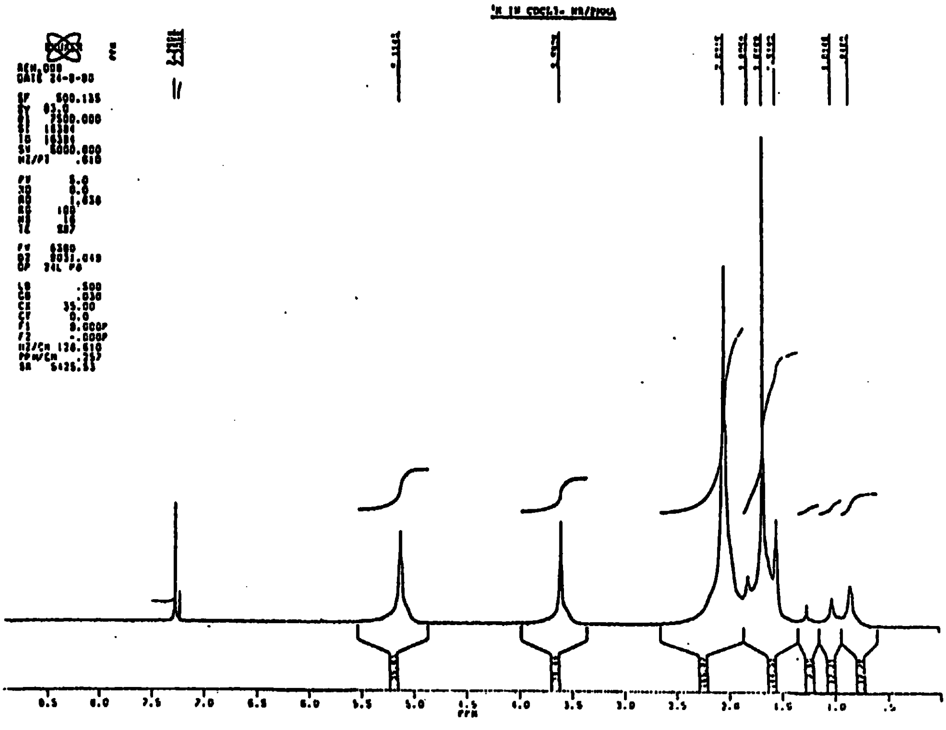
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Fig. 9

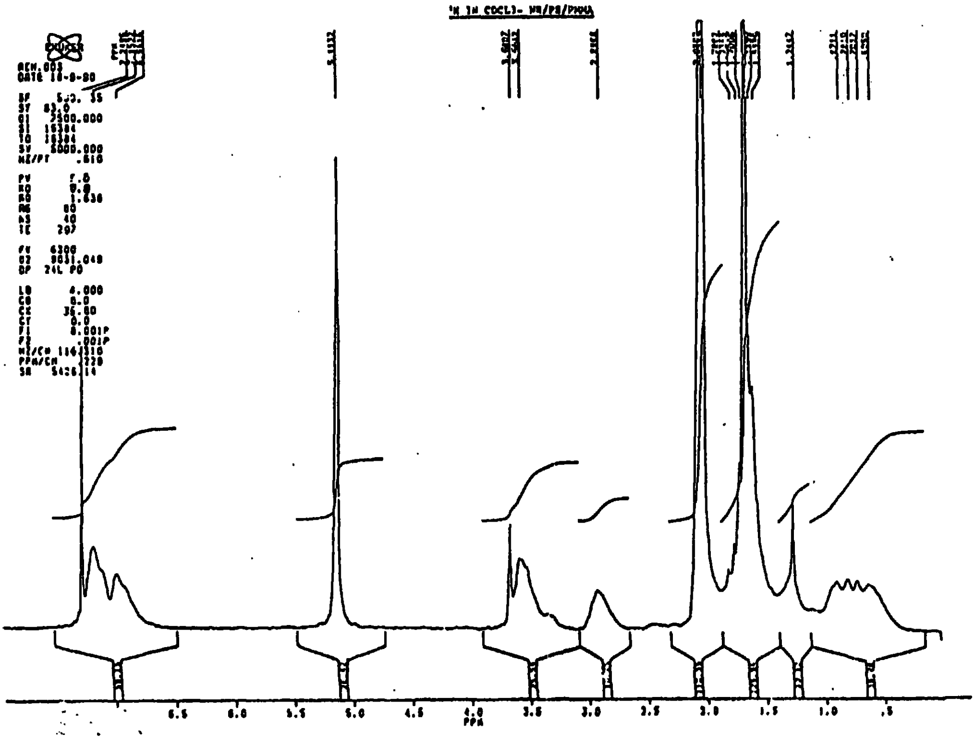
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Fig. 10

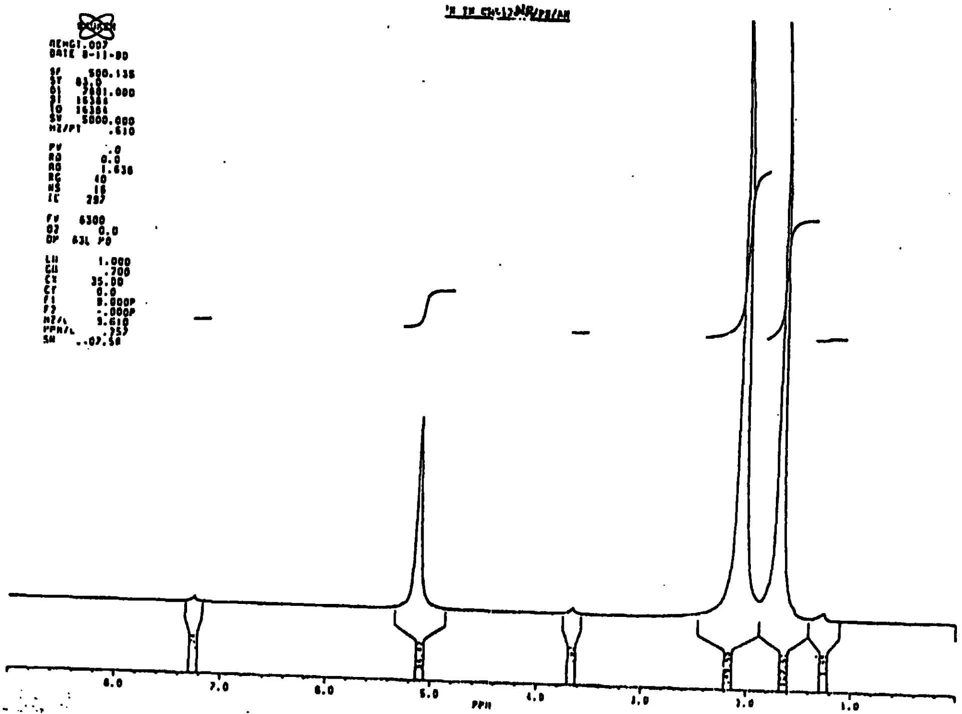
¹H IN CDCL3 NR/PS/AN
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Fig. 11

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial assistance provided by the National Science and Engineering Research Council and Canadian International Development Agency to carry out this research during Sep 91– 31 May 92. One of us, K G Karnika de Silva is thankful to the Rubber Research Institute of Sri Lanka for granting sabbatical leave for this period. The work discussed here is only a part of the research carried out during the period mentioned above.

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(Received 3 August 1993)

Appendix 1

Let W_2 = weight of dry residue placed in the soxhlet thimble
= weight of (rubber in grafted rubber + ungrafted rubber + polystyrene in grafted rubber + homopolystyrene)
W_3 = weight of ungrafted rubber + grafted rubber in W_2
W_4 = weight of the residue after extraction of W_2 with acetone
= weight of (rubber in grafted rubber + ungrafted rubber + polystyrene in grafted rubber)
W_5 = weight of residue after extraction of W_4 with petroleum ether)
= weight of (rubber in grafted rubber + polystyrene in grafted rubber)

as before,
S_1 = weight of the sample drawn out of the reactor
W_1 = weight of the initial reaction mixture
R = weight of the rubber in the initial reaction mixture

Then if the weight of the rubber in grafted rubber and ungrafted rubber (*ie* total rubber) in $S_1 = W_3$

$$W_3 = \frac{RS_1}{W_1}$$

As defined if, W_4 = weight of the dry sample after extraction with acetone
ie - W_4 = weight of (rubber in grafted rubber + ungrafted rubber + polystyrene in grafted rubber)
Then the weight of the polystyrene in grafted rubber, W_6 is given by

$$W_6 = W_4 - W_3$$

If the weight of the total polystyrene *ie* - polystyrene in grafted rubber + homopolystyrene is W_7

W_7 = (weight of rubber in grafted rubber + ungrafted rubber + polystyrene by grafted rubber + homopolystyrene) - (weight of rubber in grafted rubber + ungrafted rubber)

$$= W_2 - W_3$$

The grafting efficiency is then given by

$$\text{Grafting efficiency} = \frac{\text{weight of polystyrene in grafted rubber}}{\text{weight of total polystyrene}} * 100$$

$$= \frac{W_6}{W_7} * 100$$

The degree of grafting is calculated as the ratio of the polystyrene in grafted rubber and total weights without any ungrafted rubber and free styrene.

$$\text{Degree of Grafting} = \frac{\text{weight of polystyrene in grafted rubber}}{\text{weight of (rubber in grafted rubber + polystyrene in grafted rubber + homopolystyrene)}} *100$$

If the weight of rubber in grafted rubber + polystyrene in grafted rubber + homopolystyrene is given by W_9.

W_9 = weight of (rubber in grafted rubber + polystyrene in grafted rubber + ungrafted rubber + homopolystyrene) – (weight of ungrafted rubber)

And if the weight of ungrafted rubber is W_8,

Then W_8 = weight of (rubber in grafted rubber + ungrafted rubber + polystyrene in grafted rubber) – weight of (rubber in grafted rubber)

$$W_8 = W_4 - W_5$$

(A good check is to weigh the polymeric film left after evaporation of petroleum ether extract)

$$W_9 = W_2 - W_8$$

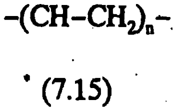
The degree of grafting is calculated as

$$\text{Degree of Grafting} = \frac{W_6}{W_9} * 100$$

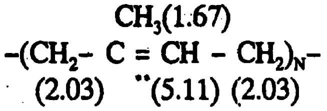
These calculations are based on the assumption that only free polystyrene is extracted with acetone and only ungrafted rubber is extracted with petroleum ether. Diameter of NR particals before the treatments with enzymes ≐ 1.0207 microns

number of days	1 day	5 days	7 days	14 days
diameter in microns	1.0200	0.998	0.904	0.892

Appendix 2 - NMR data



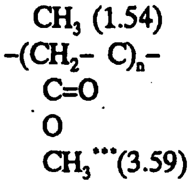
$$\begin{array}{c} -(CH-CH_2)_n- \\ {}^{*}(7.15) \end{array}$$



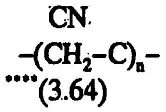
$$\begin{array}{c} CH_3(1.67) \\ -(CH_2-C=CH-CH_2)_N- \\ (2.03)\ \ {}^{**}(5.11)\ (2.03) \end{array}$$

polyisoprene
PS
M.W=104n

cis- 1,4-polyisoprene
(natural rubber)NR
M.W=68n



$$\begin{array}{l} CH_3\ (1.54) \\ -(CH_2-\ C)_n- \\ \ \ C{=}O \\ \ \ O \\ \ \ CH_3{}^{***}(3.59) \end{array}$$



$$\begin{array}{c} CN \\ -(CH_2-C)_n- \\ {}^{****}(3.64) \end{array}$$

polymethylmethacrylate
PMMA
M.W=100n

polyacrylonitrile
PAN
M.W=52n

In figures 8,9,10 and 11

peak at 7.15 resembles intensity of 5H (aromatic) in PS *
peak at 5.11 resembles intensity of 1H in NR **
peak at 3.59 resembles intensity of 3H (methyl) in PMMA ***
peak at 3.64 resembles intensity of 2H (methylene) in PAN ****

Figure 8

^{1}H NMR data for natural rubber and polystyrene grafts (with 30% monomer concentration in the initial reaction mixture) after 4 hrs of reaction time

ratio of intensity of PS:NR = 20.62 : 16.78

total PS $= \frac{20.62}{5} * 104 = 428.89$

total NR $= 16.78 * 68 = 1141.04$

therefore composition of PS : NR
in the graft $= \frac{428.89}{1569.93} : \frac{1141.04}{1569.93}$

$= 27.31 : 72.6$

Figure 9

^{1}H NMR data for natural rubber and polymethylmethacrylate grafts (with 30% monomer concentration in the initial reaction mixture) after 4 hrs of reaction time

ratio of intensity of PMMA:NR = 29.46 : 35.85

total PMMA $= \frac{29.46}{3} * 100 = 982.00$

total NR $= 35.85 * 68 = 2437.80$

therefore composition of PMMA : NR
in the graft $= \frac{982.0}{3419.8} : \frac{2437.8}{3419.8}$

$= 28.71 : 71.28$

Figure 10

^{1}H NMR data for natural rubber, polystyrene and polymethylmethacrylate grafts (with 25% each of styrene and methylmethacrylate in the initial reaction mixture) after 4 hrs of reaction time ratio of intensity of PS : PMMA : NR = 27.25 : 16.31 : 19.18

$$\text{total PS} = \frac{27.25}{5} * 104 = 566.80$$

$$\text{total PMMA} = \frac{16.31}{3} * 100 = 543.66$$

$$\text{total NR} = 19.18 * 68 = 1304.24$$

therefore composition of PS : PMMA : NR

$$\text{in the graft} = \frac{566.80}{2414.7} : \frac{543.66}{2414.7} : \frac{1304.24}{2414.7}$$

$$= 23.47 : 22.51 : 54.01$$

Figure 11

^{1}H NMR data for natural rubber, polystyrene and polyacrylonitrile grafts (with 45% styrene and 5% acrylonitrile in the initial reaction mixture) after 4 hrs of reaction time

ratio of intensity of PS : PAN : NR = 12.01 : 1.83 : 29.79

$$\text{total PS} = \frac{12.01}{5} * 104 = 249.80$$

$$\text{total PAN} = \frac{1.83}{5} * 53 = 48.49$$

$$\text{total NR} = 29.79 * 68 = 2025.72$$

therefore composition of PS : PAN : NR

$$\text{in the graft} = \frac{249.80}{2324.01} : \frac{48.49}{2324.01} : \frac{2025.72}{2324.01}$$

$$= 10.74 : 2.08 : 87.16$$