

## NATURAL RUBBER GRAFT COPOLYMER SYNTHESIS - A REVIEW

BY  
WAN AIZAN WAN ABDUL RAHMAN  
POLYMER ENGINEERING DEPARTMENT

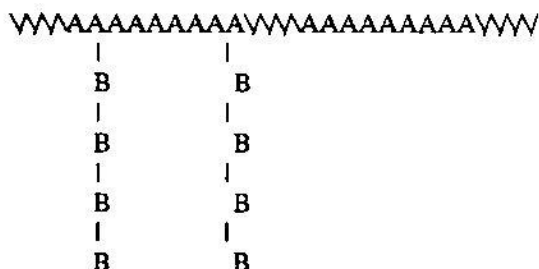
## ABSTRACT

Interest in modifying natural rubber has dampened after the emergence and development of the plastics and synthetic rubber industries and the bottom fell out of the natural rubber market. The current modification is being epoxide and thermoplastic natural rubber (TPNR).

In synthesising TPNR several routes can be adopted, but with natural rubber grafting is one of the distinguished route. Practically all methods that have been adopted for the general synthesis of graft copolymers can be used for the synthesis of graft copolymers of natural rubber. This paper is intended to give a general idea on methods which can be utilised specifically for the synthesis of well defined and well characterised graft copolymers of natural rubber.

## Introduction.

A graft copolymer contains one or more different homopolymer i.e.,



The sequence, of A units, is referred to as the backbone chain and the branches, of B units, are the grafts. Since A and B are two different monomer types, therefore the side chains have constitutional or configurational features different from those comprising the main chain, exclusive of branch point. The main chains and the branch chains are generally thermodynamically incompatible, therefore most graft copolymers are multiphase materials.

Practically all the methods that have been adopted for the general synthesis of graft copolymers can be used for the synthesis of graft copolymers of natural rubber. Rempp and Franta in his reviews discussed the techniques for the synthesis of well defined and well characterised block and graft copolymers. An excellent article was published by Quirk recently, also on the same subject.

## Methods of synthesis.

### (i) Free radical polymerisation.

Free radical polymerisation methods are the simplest, oldest and most widely used procedures for the synthesis of graft copolymers. Unfortunately, this methods generally lead to materials which are difficult to characterise and contain varying amounts of the corresponding homopolymers and gel fractions. However, this method offers certain advantages:

- a) a more varied range of chemical structures is possible,
- b) generate more complex product,
- c) free radicals can be generated by a diverse range of processes, such as mechanico-chemical methods, high- energy radiation, photochemical initiation and classical chemical initiation methods.

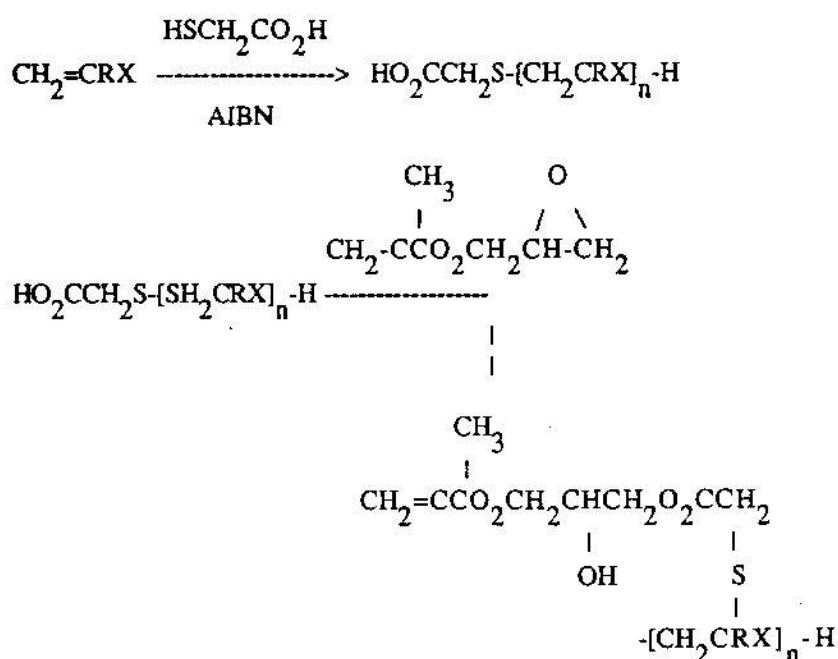
Several advances have been made in using free-radical polymerisation methods to prepare graft polymers with structures which are more predictable and more amenable to structural characterisation such as:

- a) selective generation of backbone initiation sites.

-An approach championed by Eastmond which utilised a backbone polymer having reactive groups, which can be used to efficiently generate radical initiation sites singly e.g using redox reactions. This procedure also known as "grafting from". In order to have controlled synthesis, reaction conditions must be homogeneous, kinetics of polymerisation of the grafting monomer controllable and random bimolecular termination of growing graft chain.

- b) macromonomer procedures

-A versatile methods for the preparation of comb-type graft copolymers. Yamashita and coworkers have prepared a number of macromonomers using the general scheme shown below:-



The macromonomers prepared by free radical techniques can be thoroughly characterised prior to the copolymerisation with another monomer.

*(ii) Cationic syntheses.*

For the synthesis of graft copolymers, the application of cationic polymerisation methods have been an almost explosive growth. Three general methods which can be used are:

a) metalation grafting.

-There is metalation of the backbone chain followed by cationic graft branch growth (grafting from process).

Initiating system used in this procedures examples are  $BCL_2$  which generates chlorine-terminated grafted chains and alkylaluminium catalyst. With well chosen catalyst and experimental conditions, problem of homopolymer formation and gelation can apparently be eliminated in cationic grafting.

b) coupling procedures.

-There is linking of chains which have cationic chain ends with the backbone chain by coupling with functional groups on the backbone chain (grafting onto process).

This methods result in graft copolymers with reasonably well defined structures. Problem inherent in this approach is the possibility of incompatibility if the grafting chain are not compatible with the backbone chain. This can be minimised by lowering the molecular weight of the grafting chains.

c) macromonomer procedures.

-There is copolymerisation of monomers with cationically synthesised macromonomers which have reactive chain-end functionality. A variety of macromonomers have been prepared utilising this method since it can be copolymerised with a backbone-forming monomer using either radical, cationic or anionic method depending on the macromonomer functionality. Chain transfer and chain termination reactions which restrict the scope of cationic polymerisation. However, by proper selection of an initiators and conditions which exclude transfer steps, a well characterised copolymer with high grafting efficiency can be prepared.

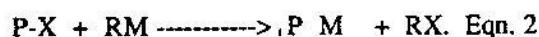
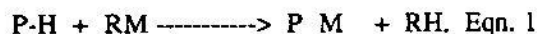
*(iii) Anionic syntheses*

The absence of termination and chain transfer in anionic polymerisation made it suitable for the synthesis of graft copolymers. The anionic non-terminating system have the advantage that branches with uniform length can be prepared providing a graft copolymers with defined structures to delineate the relationships between structure, morphology and properties. Limitations of this method is no control over the generation of the loci for branch formation.

As with the cationic synthesis, three general methods are available:

a) metalation grafting

-This "grafting from" method involves generation of carbanionic initiator sites on the backbone chain either through metalation of carbon-hydrogen bond equation 1, carbon-halogen bond equation 2,



Subsequently, monomer is added and anionic polymerisation takes place to form grafted branches at the sites of metalation. The most studied metalation procedures utilizes an alkyl lithium compound complexed with N,N,N,N-tetraethylenediamine (TMEDA).



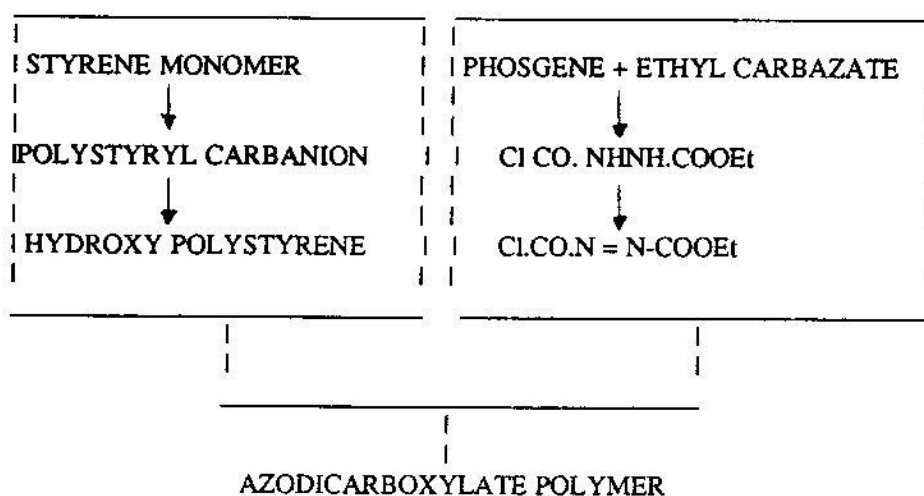
In the prepolymer synthesis the research group from MRPRA first synthesised an azodicarboxylate functional polymer i.e. a hard side chain which then reacted with natural rubber. The sequence involves in the synthesis of terminal azodicarboxylate functionality are:-

- anionic polymerisation of the monomer i.e. styrene react with ethylene oxide and acidification to form hydroxy-functional polystyrene.

- the hydroxy functional polystyrene is converted to polymer chloroformate by reaction with excess phosgene and subsequently to the hydrazine-1,2-dicarboxylate by reaction with ethyl carbazate.

- finally, oxidation of the hydrazine-1,2-dicarboxylate gives the azodicarboxylate functional polymer.

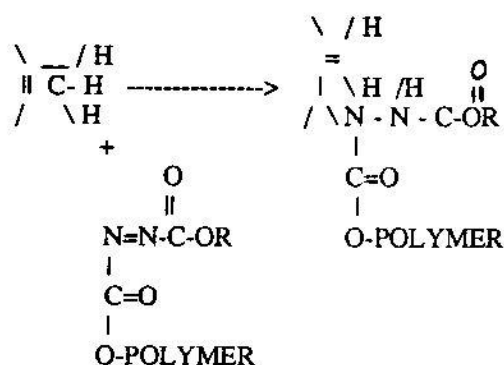
In principle the complete conversion of styrene monomer into azodicarboxylate functional polymer is a one pot process involving successive addition of butyl-lithium initiator, ethylene oxide, acid and reactive azo-acid chloride solution. Reactions are all operated under hydrogen. Initiator used in the reaction is s-butyl-lithium whereby molecular weight distributions obtained are wide. A summary of the above reaction sequence is shown in Scheme 2 below:



Synthesis of terminal azodicarboxylate functionality  
Scheme 2

Chemistry which has been used for the coupling reaction between the prepolymer and the polyisoprene backbone is the "ene" addition of the azodicarboxylate group to an allylic double bond system, Scheme 3.

"Ene" addition of azodicarboxylate group to an allylic double bond system.



Scheme 3

Azodicarboxylate is chosen in dealing with natural rubber because it is the most effective with long term stability at ambient temperature and can withstand exposure to temperature in excess of 100°C. Work with methacrylate group as the hard side chain have been published by Wong Ah Kiew et. al. utilising the terminal azodicarboxylate functionality.

- i) selection of the most appropriate end group chemistry,
- ii) preparation of prepolymer where every chain carries a single group of the chosen type,
- iii) evaluation of conditions under which the natural rubber and the prepolymer can be induced to react.

A macromonomer is an oligomer with a polymerisable end group that can polymerise with various monomers to form comb-type graft copolymers with pendent preformed polymer chains. Variety of methods can be used to prepare macromonomer, but anionic methods provide unique control of average chain length, chain length distribution and chain end functionality. One of the principal advantages of this procedure is that it allows the preparation of well defined graft copolymers with functional groups on the backbone chain which would be unstable (i.e. reactive) towards carbanionic propagating species. Once a macromonomer has been prepared free radical, cationic or anionic polymerisation methods can be used to copolymerise the macromonomer with the backbone forming monomer.

$$\text{PSLi} \xrightarrow{\text{O} \diagup \text{O} \diagdown} \text{PS} - \text{CH}_2 - \text{CH}_2 - \text{OLi}$$

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{COCl} \end{array} \quad \begin{array}{c} | \\ | \\ | \end{array}$$

$$\text{PS} - \text{CH}_2\text{CH}_2 \begin{array}{c} \text{O} \\ || \\ \text{OCC} = \text{CH}_2 \\ || \\ \text{CH}_3 \end{array}$$

PS = Polystyryl

This methacrylate-terminated polystyrene has been copolymerised with various vinyl monomers, using free radical initiators to form graft copolymers. Principally, this method produces polymers with a random distribution of graft with controlled, narrow molecular weight distribution.

### Conclusion

Several methods have been utilised in the preparation of graft copolymer natural rubber, but the most promising method is the conventional coupling method via anionic synthesis. Macromonomer procedure provides a powerful complement to the metalation and the coupling procedures. However, control of the backbone chain length and the chain length distribution is lost if methods other than living anionic or cationic polymerisation are used to form the comb-type graft copolymers.

### Reference

1. P.Rempp and E.Franta, 1979, Polymer Science USSR, vol 21.
2. R.P.Quirk, 1984, Rubber Chemistry and Technology, vol 57.
3. P.Rempp and E.W Merrill, 1986, Polymer Synthesis, Huethig & Wepft Verlag Basel, Heidelberg, New York, Chap. 10.
4. P.Rempp, P. Lutz, P.Mason, E.Franta, 1984, Macromol. Chem Suppl. 8.
5. M.Porter, 1987, The Chemical Modification of NR Methods and Result, MRRDB/USSR Joint Technical Seminar, Moscow.
6. M.Morton, and L.J Fetters, 1975, Rubber Chemistry and Technology, vol. 48.
7. J.C Falk, R.J Schlott, D.F Hoeg and J.F Pendleton, 1973, Rubber Chemical Technology, vol.46.
8. D.S Campbell, D.E Loeber and A.J Tinker, 1978, Polymer, vol.19.
9. D.S Campbell, A.J Tinker and P.G Mente, 1982, European Patent 65366.
10. Wong Ah Kiew, D.S Campbell and A.J Tinker, 1987, Polymer, vol.28.
11. G.O Schulz and R. Milkovich, 1982, Journal of Applied Polymer Science, vol.27.