

## CHAPTER 2

### THEORETICAL CONSIDERATION

#### 2.1 Function of viscosity modifier

One very important property of lubricant that needs to be taken into account is viscosity which is related to the lubricating effectiveness of an oil under various conditions. Lubricants containing viscosity modifier combine the good starting and friction properties at low temperatures and prevent oil thinning out at high temperatures. Viscosity modifier makes the oil possible to cover several viscosity grades with only one oil.

#### 2.2 Solution property of multigrade oil

Huggins and Kraemer equations (equations 1 and 2) from dilute solution theory have been useful in describing the behaviour of viscosity modifier polymer present in multigrade oil<sup>5</sup>. General relationship between viscosity of oil solution and the concentration of polymer is derived as follows:

$$\frac{\eta_{sp}}{c} = +k'[\eta]^2c + \dots \quad (\text{equation 1})$$

$$\frac{\ln \eta_r}{c} = [\eta] - k'' [\eta]^2c + \dots \quad (\text{equation 2})$$

where  $\eta$             viscosity on oil solution

$c$                 concentration of polymer

$k', k''$  constants

Several relationships have been derived by incorporating with Mark-Houwink relation to form equation 3 below<sup>5</sup>:

$$\ln \eta = K M_v^a c - k'' (M_v^a)^2 c^2 + k'' [\eta]^2 c + \ln \eta_0 \dots \quad (\text{equation 3})$$

Equation 3 indicates that the viscosity of an oil solution should increase logarithmically with polymer concentration and also with the average viscosity molecular weight to the power of **a**. The intercept of the equation will give the log value of base oil viscosity.

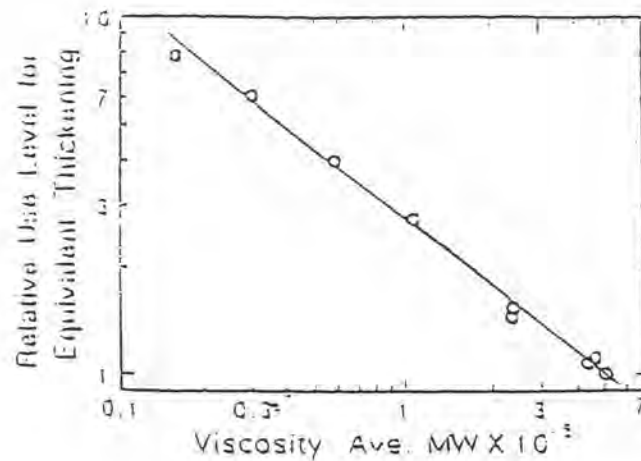
Relationship between the viscosity and the concentration of a specific polymer from a single blend can be derived from above equation. However, more experimental blends will give the second order of polymer-oil solvent interaction to form a more completed relationship. Chemically similar oil solution would give a very similar constant **K** and **a** values with the same base oil viscosity and a better solvent would give a higher value of 'a' constant.

Combining Huggins and Kraemer equations and substituting  $K M_v^a$  for  $[\eta]$ , the relationship for thickening effect of a specific base oil to a specific blend target is shown in equation 4:

$$\log c = -a \log M_v + K_s \quad (\text{equation 4})$$

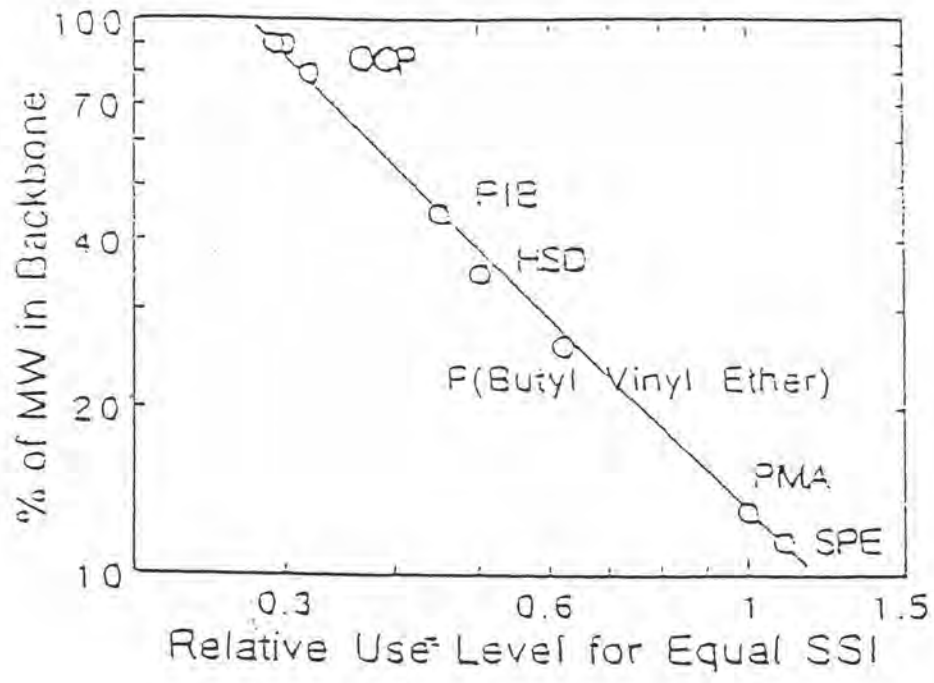
$K_s$  is a very complex constant containing the constants for polymer interaction  $k'$  and  $k''$  from both the Huggins and Kraemer equations, **K** from the Mark-Houwink equation, as well as both the base oil and blend viscosities.

Intrinsic viscosity or some other molecular dimension in the solution, is an important driving force in the thickening efficiency<sup>6</sup>. However, chemically different polymers of the same molecular weight may not give the same thickening behaviour in oil solution. Consequently, polymers with different chemical structures would not give the same thickening characteristic.



**Figure 2.1** Relationship of polymethacrylate between thickening efficiency and viscosity modifier molecular weight<sup>5</sup>.

For high molecular weight polymers, the unperturbed mean square end-to-end distance in solution is a function of only the degree of polymerisation and is dependent of the presence or absence of side chains. The addition of long alkyl side chain makes the polymer more soluble in the oil solution but will not effect on thickening efficiency of the polymer. Relative thickening efficiency across polymer chemistry is a function of the percentage of the mass of that molecule which is in the backbone (Figure 2.2)

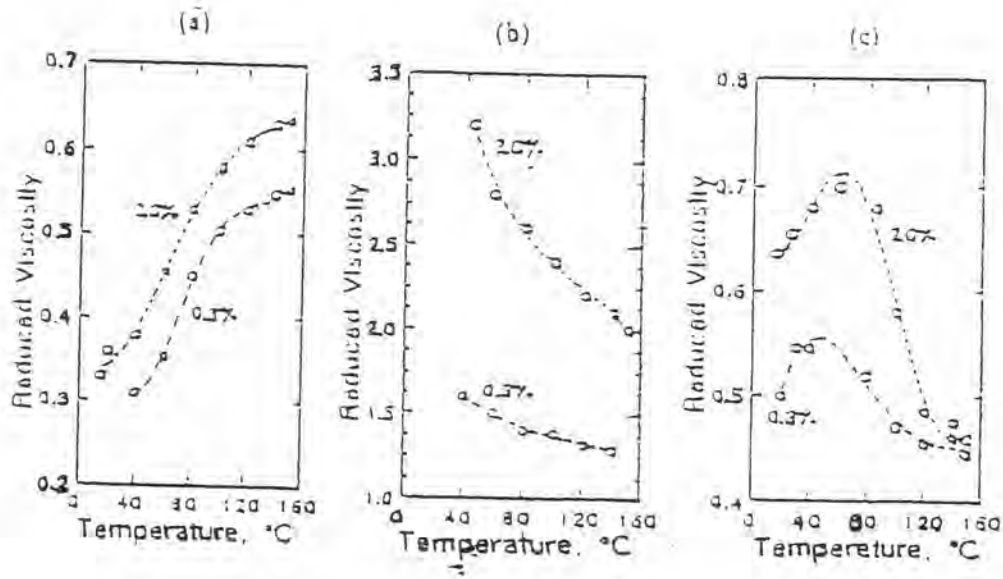


**Figure 2.2** Relative thickening efficiencies of various chemically type viscosity modifiers. (OCP: Ethylene propylene copolymer; PIB: Polyisobutene; HSD: Hydrogenated styrene butadiene copolymer; P (Butyl Vinyl Ether): Poly *n*-butyl vinyl ether; PMA: Polymethacrylate; SPE: Styrene polyester).

### 2.3 Thickening property

Viscosity modifier treat level plays an important role on the oil viscosity at high temperature and consequently formulation economic. The thickening property can be described from temperature dependence factors from Solution Theory: Constants  $k'$ ,  $k''$  in the Huggins Kraemer equations and  $K$  and  $a$  in the Mark-Houwink equation. These constants are related in complex fashion and also influenced by physical properties of other components in multigrade oil. Selby hypothesised that the mode of action focused on the hydrodynamic volume of the molecule as a function of temperature<sup>7</sup>. The molecular size on the solution was highly contracted at low temperature and thus contributed little to viscosity. Increase in temperature caused expansion of molecular size and would give a larger contribution of polymer molecule to viscosity of oil.

Muller reported that three major chemistry commercialise use types, only polymethacrylate (PMA) exhibits an intrinsic viscosity which increases uniformly with increasing temperature<sup>8</sup>. Hydrocarbon type viscosity modifiers tend to exhibit a uniformly decreasing intrinsic viscosity with temperature or in some cases can exceed the maximum at some temperature ranges (Figure 2.3)



**Figure 2.3** Temperature dependence of polymer coil dimensions for major viscosity modifier chemistry: (a) Polymethacrylate (PMA), (b) Olefin copolymer (OCP), (c) Hydrogenated styrene isoprene copolymer (HSD)<sup>8</sup>

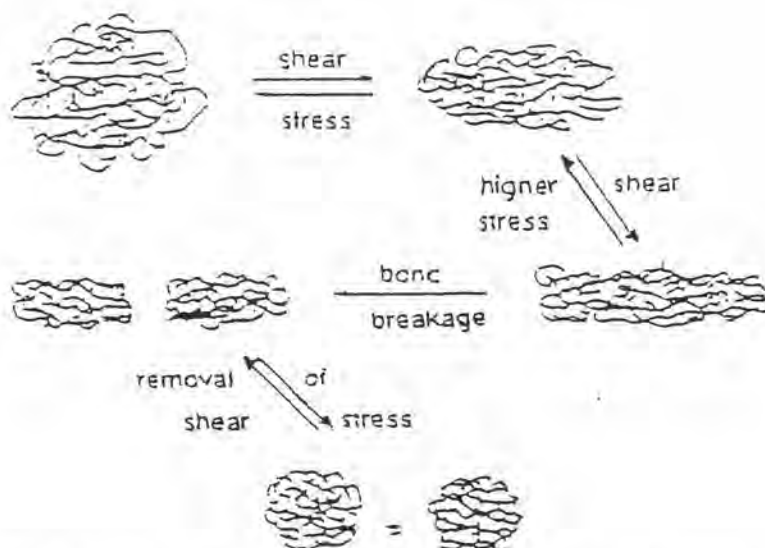
Jordan *et al* suggested the effect of temperature on the flow behaviour of polymer in mineral oil was controlled by the entropy of activation for viscous flow<sup>9</sup>. Tamai also found similar observation as Jordan *et al.* for polymethacrylate type in both light paraffinic and naphthenic base oils<sup>11</sup>. This result also was a good agreement with results obtained by Jordan *et al*<sup>9</sup>. for heavy base oils of high viscosity index.

Nuclear Molecular Resonance spectroscopy (NMR) technique has been used in study by Dare-edwards *et al.* to show the effect of viscosity modifier on the translational mobility of solvent molecules<sup>11</sup>. They found that there was a reduction in translational mobility with increasing polymer concentration in *t*-butylbenzene and *t*-butylcyclohexane.

## 2.4 Shear stability

### 2.4.1 Permanent viscosity shear loss

When polymers are subjected to high shear stress in equipment, the random coil is severely distorted. In extreme cases for many areas in equipment eg. between the piston rings and cylinder wall or in the valve train of an engine, between the gear teeth of an axle, bond energies can be exceeded and the polymer bond will break. Schematic of mechanical degradation is shown in Figure 2.4



**Figure 2.4** Schematic of mechanical polymer degradation.

The shearing process itself is a simple homolytic scission of a carbon-carbon bond, producing two polymeric radicals. There is no evidence that these radicals are involved in other aspects of lubricant chemistry as they are rapidly terminated by other species in the oil. The bond strengths of backbone carbon-carbon of different viscosity modifiers are much the same and thus none is inherently more shear stable than others. The shearing is suggested to take place at some point of weak bond links resulting from severe steric hindrance.



When the polymer is stretched, it is predicted that the maximum energy is concentrated in the middle of the molecule, or some distance away from the ends. When the polymer is subjected under mechanical shear, two fragments are obtained and molecular weight will be about half of the unsheared polymer<sup>12</sup>. The higher molecular weight is the more likely polymer to break. However, the mechanical shear degradation is self-limiting. At some points, a molecular weight is reached where the energy concentration during coil distortion is sufficient to break further bonds. Viscosity loss occurs during in service is thus characterised by a rapid decrease in viscosity as the larger molecules break, followed by a slower loss and finally a terminal molecular weight is reached.

Study done by Hillman *et al.* using gel permeation chromatography technique is consistent with theory<sup>13</sup>. Gel permeation chromatogram (Figure 2.5) shows that high molecular weight polymers are degraded and intermediate molecular weight polymers are produced.

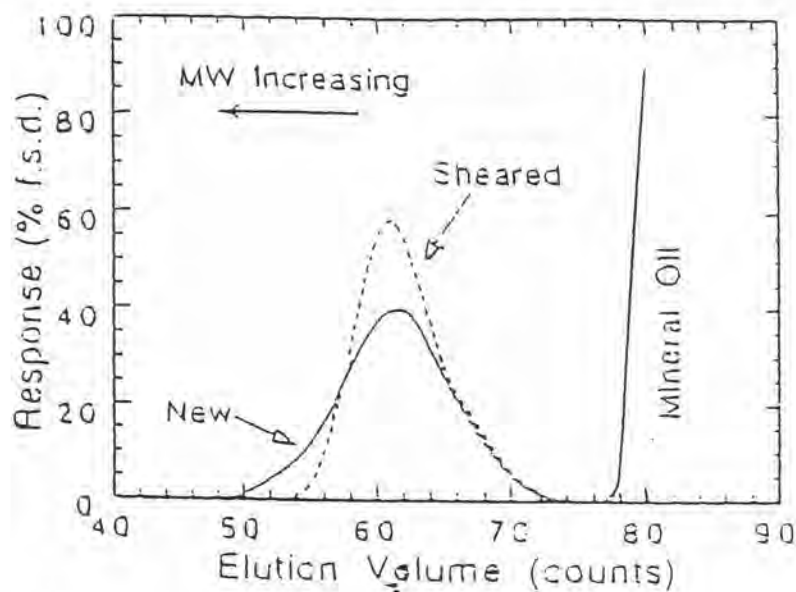


Figure 2.5 Effect of mechanical shear on molecular weight distribution.



The kinetics of the degradation process have been studied by many workers but most of them tend to take the general form of that described by Ovenall *et al.* studied using ultrasonic waves (see equation 4)<sup>14</sup>

$$\frac{dB_i}{dt} = k(P_i - P_e)n_i \quad (\text{equation 4})$$

where  $\frac{dB_i}{dt}$  is rate of bond breakage

$P_i$  is degree of polymerisation

$P_e$  is limiting degree of polymerisation for bond breakage

$n_i$  Is number of molecular size  $P_i$

$K$  is a rate constant

The total rate of bond breakage is therefore summed over all molecular weight species that are degraded by mechanical shear.

#### 2.4.2 Non-Newtonian behaviour

All polymer solutions are known to be non-Newtonian i.e. shear stress is not directly proportional to shear rate<sup>5,6</sup>. Viscosity modifier can exhibit pseudo plasticity or shear-thinning behaviour and, as long as the shear stress does not break the molecules and the process is possibly reversible<sup>5,6,15,16,17</sup> (Fig.2.4) i.e. when the shear stress is removed, the viscosity will return to the original value. Some viscosity modifiers also act as associative thickeners, in this process viscosity modifier molecules dissociate to give smaller fragments when entering the shear field but associate again when the shear force is removed.

In the extreme case the bond energies can be exceeded and the bond will break or be totally sheared<sup>7,8</sup>. Polymer degradation or homolytic scission of a carbon-carbon bond is known to cause viscosity loss during service life. The change in viscosity caused by this shearing process is known as 'permanent viscosity loss'.

Many laboratory test methods have been developed to simulate viscosity loss in equipment during service in the field. However, ASTM (American Society for Testing and Materials) has suggested that the best way to measure the shear stability of a lubricant is to use an engine test. This technique is found to be impractical due to the large sample required and the high operational cost. Cold Cranking Simulator (CCS: ASTM D 5293)<sup>18</sup>, High Temperature Low Shear (HTLS: ASTM D 445)<sup>19</sup> and High-Temperature High-Shear-rate (HTHS: ASTM D 4683, ASTM D 4741)<sup>20,21</sup> bench tests are now routinely used to evaluate multigrade engine oil shear stability.

### 2.4.3 Percentage shear viscosity loss

Loss of viscosity after shearing can be expressed by the following equation

$$\% \text{ Overall Viscosity Loss} = \frac{(N_i - N_s)}{N_i} * 100 \quad (\text{equation 5})$$

where:  $N_i$  is initial viscosity and

$N_s$  is the sheared oil viscosity.

Equation 5 is derived based on the assumption that all viscosity degradation comes from shearing of the viscosity modifier only. It is proposed that base oil and other additive components are of sufficiently low molecular weight that they are not affected by mechanical shear.

A more meaningful calculation, which accounts for the effects of other additive components, can be expressed as follows<sup>5,6</sup>.

$$\% \text{ SSI} = \frac{(N_i - N_s)}{(N_i - N_o)} * 100 \quad (\text{equation 6})$$

where: SSI is shear stability index and

$N_o$  is the base oil viscosity including all additives except viscosity modifier improver.

## 2.5 Thermal-oxidative stability

Viscosity modifiers can also undergo thermal and oxidative degradation reactions with the resulting product being different to that formed by mechanical shear processes (Table 2.1). These degradation processes are especially important in regards to automotive engine cleanliness. Rubin found that oxidative degradation led to the production of small fragments which contributed to sludge formation<sup>22</sup>. This chemical degradation pathways lead to low molecular weight fragments present in oil. This effect is important because it influences the amount of viscosity modifier required in the formulation.

Many workers have been studying the thermal and oxidative degradation of various viscosity modifier types. Mark *et al.* examined styrene-containing polymers and suggested that oxidative cleavage caused the formation of formaldehyde and acetaldehyde which can be trapped in the oil phase or in the deposits<sup>22</sup>. Weast studied the carbon-hydrogen bond strength of different viscosity modifiers to determine their tendency to undergo a hydrogen abstraction reaction<sup>23</sup>. Polymethacrylate chemistry type was found to be dominated by thermal effects and other viscosity modifier types are dominated by oxidative effects.

**Table 2.1** Mechanical and thermal-oxidative processes of viscosity modifiers.

<b>Mechanical</b>	<b>Thermal-Oxidative</b>
Molecular weight sensitive	Indiscriminate
Break near middle of molecule	Break at random along chain
Self-limiting	Complete degradation possible
Insensitive to chemistry	Dependent on chemistry

## 2.6 Viscosity modifier chemistry

There are five core technologies currently available for commercial usage including, polymethacrylates (PMA), ethylene propylene copolymer (olefin copolymer or OCP), hydrogenated styrene diene copolymer (HSD) e.g. hydrogenated styrene-isoprene copolymer (SIP), esterified styrene maleicanhydride copolymer (SPE) and a combination of polymethacrylate and olefin copolymers<sup>5</sup>. Simplified chemical structures for the core range of viscosity modifiers are shown in Figure 2.6.

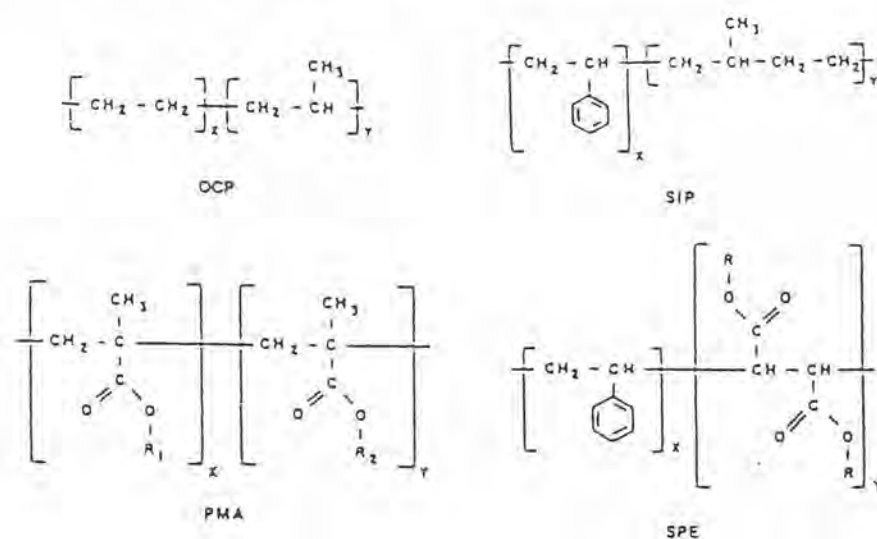


Figure 2.6 General chemical structure of available viscosity modifiers.

### 2.6.1 Olefin copolymer (OCPs)

Olefin copolymers are generally copolymers of ethylene and propylene. The polymerisation is carried out in a dilute solution in hexane at low temperature using a Ziegler-Natta type catalyst (as initiator). These types of initiation/catalysts are based on a combination of transition and group I to III metal compounds, most commonly vanadium-aluminium alkyl halide systems, although many other combinations have been studied<sup>23</sup>.

The ethylene content of an olefin copolymer viscosity modifier is about 40-60 % weight. The actual ratio of ethylene/propylene units used is a compromise between thickening efficiency, low temperature solubility, oxidative stability and wax interaction characteristics. A higher ethylene percentage gives higher thickening efficiency and better oxidative stability but decreases solubility at low temperatures. Blocks of ethylene leads to undesirable low temperature properties due to wax interaction.

The molecular weight ( $M_w$ ) range is from 50,000 to 200,000. The average molecular weight ( $M_w/M_n$ ) is around 2.0-2.5. Olefin copolymers are found to have excellent thickening properties and are used extensively in engine oils. Poor shear stability of this type of viscosity modifier is due to their high molecular weight. It is also difficult to produce this type of polymer with lower molecular weights<sup>5</sup>.

The particular olefin copolymer (OCP1) that will be used in this study is a representative of current technology in a four-stroke motorcycle engine oil formulation. It will be of interest, therefore, to compare the performance of this viscosity modifier with the other types.

### 2.6.2 Polymethacrylate (PMA)

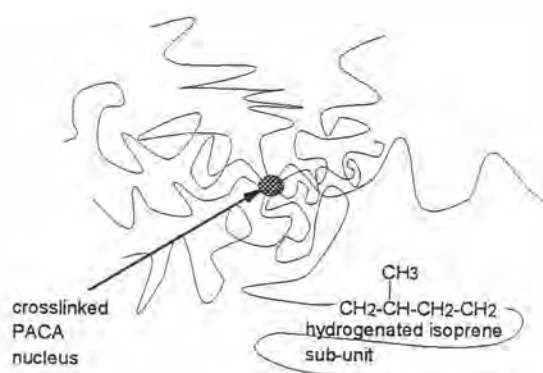
Polymethacrylates have been used in a wide range of engine lubricants. Their versatility is due to the variety of molecular weights and compositions available. This compositional variety comes from the ability to control the free-radical solution chemistry during synthesis<sup>5</sup>. There is an abundance of published material concerning the physical and chemical properties of these viscosity modifiers especially in comparison to olefin copolymers. For this reason polymethacrylate type viscosity modifier's will not be used in this study.

### 2.6.3 Hydrogenated styrene diene copolymer (HSD)

The hydrogenated styrene diene copolymer types are less likely to be satisfactory for four-stroke motorcycle application as they are only generally used where a moderate shear stability is required. A subclass, the star shaped poly-hydrogenated styrene-diene reportedly has relatively greater shear stability characteristics and may therefore have potential for use in this area.

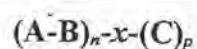
These star polymers are synthesised stepwise by an anionic solution polymerisation of isoprene and/or styrene with an alkyl lithium catalyst (eg. *s*-butyl Li) in an aromatic, allylic or aliphatic hydrocarbon solvent. The 'living' polymer arms are then reacted with a polyalkenyl coupling agent (PACA), such as divinylbenzene, to form the star or comb type structure. The polymerisation is terminated either by the addition of an acidic compound (alcohol, carboxylic acid or water) or, preferably, by the final selective hydrogenation of the isoprene units<sup>23,24,25</sup>.

The anionic polymerisation method allows good control over the molecular weight by varying the concentration of the initiator, and composition of the polymer arms, by varying the amounts, timing and order of addition of the monomer units<sup>26</sup>



**Figure 2.7** General structure of a hydrogenated polyisoprene star polymer.

The general formula of this type of star polymer can be written:



where

**A** = styrene block

**B** = hydrogenated isoprene block

**C** = either hydrogenated isoprene homopolymer or  
styrene/hydrogenated isoprene co-polymer

**x** = crosslinked divinylbenzene nucleus



Variation of  $n, p$  and  $x$  allows a range of star polymers to be produced having tailored chemical and physical properties<sup>26</sup>. These star type viscosity modifiers have greater shear stability than their linear analogues. The reason for this is that even if the polymeric backbone of any one of the arms is severed, due to high shear stresses, the overall shape and structure, and thus any interactions with oil molecules, is largely maintained. A consequence of this compromise between thickening efficiency and shear stability is the high  $M_w$  (300 000 - 700 000 amu), even so, the  $M_w/M_n$  value is 1.5 which is relatively low<sup>5</sup>.

## 2.7 Selection of viscosity modifier

There are five criteria that normally include in selection:

1. Suitable viscometric characteristics to allow the multigrade oil formulation to meet the requirements of modern engine over a wide range and more severe of operating temperatures.
2. Provide satisfactory viscometric stability of multigrade oil in service. This may be influenced by both physical and chemical characteristics i.e. shear stability of the polymer and also by the base oil composition as determined by the blending characteristic of the polymer.
3. Minimisation of detrimental effects in area of engine cleanliness derived from viscosity modifier polymer decomposition or degradation reactions.
4. Flexibility e.g. easy handling and suitable to use for various applications in both gasoline and diesel multigrade oils.
5. Achievement of most critical performance criteria at reasonable cost.

Therefore the choice of viscosity modifier will be made on the basis of economics if no other overriding benefit is evident. The first decision is to determine how the viscosity modifier can contribute to the overall formulation balance.