This chapter includes two sections, viz., materials and experimental. The description and specifications of the various materials used for the synthesis of the block copolymers are given in the first section. The experimental section deals with the various synthetic and analytical procedures. This also includes a description of the various equipments and devices used for the study.

2.1. Materials

Natural crumb rubber (ISNR-5), weight average molecular weight = 8,20,000, Intrinsic viscosity in benzene at 30°C = 4.45 dL/g, Wallace plasticity, $P_0 = 39.0$ was supplied by Rubber Research Institute of India, Kottayam, Kerala.

Hydrogen peroxide (30% w/v) supplied by E. Merck, India was used without further purification. Toluene supplied by E. Merck, India was used as solvent without any further purification. Methanol supplied by BDH, India was used without further purification. Toluene diisocyanate (TDI) (80/20 mixture of 2,4- and 2,6-isomers) supplied by Fluka, Switzerland was used as received.

Polyethylene oxide (PEO) of four different molecular weights ($\bar{M}_n$) PEO-4000, PEO-6000, PEO-8000 and PEO-10000 supplied by Aldrich was used as received. Polypropylene oxide (PPO) of four different molecular weights ($\bar{M}_n$),
PPO-1000, PPO-2000, PPO-3000 and PPO-4000 supplied by Aldrich was used as received. Polytetramethylene oxide (PTMO) of three different molecular weights ($M_n$) PTMO-1000, PTMO-2000, PTMO-2900 supplied by Aldrich was used as received.

Dibutyl tin dilaurate (DBTDL) supplied by Fluka, Switzerland was used as catalyst without further purification. Chloroform supplied by BDH, India was used after distillation.

2.2. Experimental

2.2.1 Preparation of hydroxyl terminated liquid natural rubber (HTNR) by photodepolymerisation of natural rubber (NR)

Natural crumb rubber was cut into small pieces and a 5% solution of NR in toluene was taken in a flat-bottomed flask of 15 L capacity. To the NR solution was added 30% (w/v) hydrogen peroxide solution and thoroughly mixed with the rubber solution. The mixture was then homogenised by the addition of methanol. NR solution, hydrogen peroxide and methanol were taken in the volume ratio 20:1:3 respectively. The flask was fitted with a water condenser and a mechanical stirrer and the whole assembly was placed in sunlight.

HTNR of desired molecular weight can be produced by adjusting the exposure time. The extent of depolymerisation was reported to increase with decreasing concentration of NR solution, increasing amount of hydrogen peroxide and by longer exposure time. Methyl alcohol being a nonsolvent for NR has the advantage that the viscosity of the reaction mixture will be slightly reduced by its addition.

After about 60 h of irradiation, a layer of water separated at the bottom along with white deposits as by-product. This was removed and the liquid rubber was recovered from the top toluene layer by distilling off the solvent under low pressure. The liquid NR recovered from the solution was almost clear and
colourless. On keeping, its viscosity increases gradually. Therefore, after depolymerisation, about 0.02% (w/v) of hydroquinone was dispersed in the solution for the removal of radical species that may be present in the solution. The recovered material was further purified by adding 0.5% (w/v) of Santowhite, a nonstaining antioxidant HTNR becomes slightly coloured after these modifications but it increases shelf life without any significant change in viscosity. Phenyl-β-naphthylamine can also be used as antioxidant for HTNR but the material becomes profusely coloured.

### 2.2.2 Determination of the molecular weight ($\bar{M}_v$) of HTNR

The molecular weight of HTNR was determined using Ubbelohde viscometer. The viscosity of a high polymer solution is related to the molecular weight of the polymer by Mark-Houwink equation

$$[\eta] = KM^a$$

where $\eta$ is the intrinsic viscosity, $M$, the molecular weight; $K$ and $a$ are constants.

For isoprene toluene system $K = 50.2 \times 10^{-3}$ and $a = 0.667$.

$$[\eta] = \left(\frac{\eta_{sp}}{c}\right)_{c \to 0} = \left(\frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent} \times c}\right)_{c \to 0} = \frac{t - t_0}{t_0 \times c}$$

where $\eta_{sp}$ = specific viscosity; $t$ = time of flow for solution; $t_0$ = time of flow for solvent; $c$ = concentration of the solution.

$$\left(\frac{\eta_{sp}}{c}\right)$$ is plotted against $c$ and $$\left(\frac{\eta_{sp}}{c}\right)_{c \to 0}$$ is obtained by the extrapolation of the plot to zero concentration. This gives the value of $\eta$ which is substituted in the Mark-Houwink equation to get $\bar{M}_v$. 

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The molecular weights ($\bar{M}_v$) of the depolymerised NR is listed in the Table below along with the hydroxyl value and epoxy value.

**Table 2.1.**

<table>
<thead>
<tr>
<th>HTNR molecular weight ($\bar{M}_v$)</th>
<th>Hydroxyl value (mgs of KOH/g)</th>
<th>Epoxy value (mgs of KOH/g)</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>32</td>
<td>2.74</td>
<td>1.96</td>
</tr>
<tr>
<td>8800</td>
<td>26</td>
<td>2.71</td>
<td>1.96</td>
</tr>
<tr>
<td>10000</td>
<td>22</td>
<td>2.4</td>
<td>1.94</td>
</tr>
<tr>
<td>17000</td>
<td>18</td>
<td>2.71</td>
<td>1.90</td>
</tr>
</tbody>
</table>

2.2.3 *Estimation of hydroxyl value*³

Estimation of the hydroxyl groups was carried out by acetylation method. The hydroxyl groups in the sample were acetylated using acetylating mixture (acetic anhydride in pyridine)

$$R(OH)_n + n(CH_3 CO_2)O \rightarrow R(OOCOCH_3)_n + nCH_3 COOH$$

The excess acetic anhydride was converted to acetic acid which was estimated using a standard alkali.

HTNR ca 3 g was weighed out into an RB flask and 20 ml of acetylating mixture (1 volume of acetic acid + 3 volumes of pyridine) was added. The flask was fitted with a water condenser and refluxed for 30 min. A blank was also carried out. The mixture was cooled to room temperature and 50 ml of distilled water was added through the condenser. The free acid was determined by titration with standard KOH using phenolphthalein.
Hydroxyl value is defined as the number of milligrams of KOH (equivalent to the amount of acetic acid) that react by acetylation with one gram of a hydroxyl containing material. The acid value of the sample must also be considered.

Hydroxyl value = 56.1 (B–A) N/W + acid value

where

A = Volume of KOH required for reaction with sample
B = Volume of KOH required to titrate the blank
N = Normality of alcoholic KOH
W = Number of grams of the sample

### 2.2.4 Estimation of epoxy value

HTNR ca 2-3 g was weighed out into a conical flask and 20 ml of HCl-dioxane solution (0.2 N) was added. The sample was dissolved completely in the solution by heating at 40°C. To this solution, 25 ml neutralised cresol red-ethanol solution was added. The excess HCl was determined by back titration with 0.5 N NaOH. The end point was the first appearance of a violet colour. A blank was also done.

Note: (a) Preparation of 0.2 N HCl-dioxane solution: About 1.6 ml HCl (Specific gravity 1.9) was pipetted out into 100 ml dioxane in an amber coloured bottle and shaken well. The solution was used immediately after preparation.

(b) Preparation of neutralised cresol red-ethanol solution: About 1 g of cresol red sodium salt was dissolved in 100 ml of 50% ethanol. One ml of this solution was added to 100 ml 95% ethanol and neutralised with 0.1 N methanolic NaOH.
2.3. Synthesis of block copolymers

2.3.1 Synthesis of block copolymers based on HTNR and PEO by solution polymerisation

2.3.1.1 Two-shot method

HTNR was dissolved in chloroform to get a 35% solution and taken in a flat-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, water condenser and a dropping funnel. Dibutyl tin dilaurate (DBTDL) catalyst (0.3% by weight of HTNR) was added and the solution brought to reflux with vigorous stirring. The stoichiometric amount of TDI (1:2.01:1 of HTNR, TDI and PEO respectively) was added in drops in 30 min followed by 2 h of the reaction to complete HTNR. This was accompanied by the addition of the required amount of PEO as a solution in chloroform (35% w/v) dropwise during 1.5 h followed by 2 h of the reaction.

The excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone release agent. The sheet was removed from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent present and then cured at 70°C for 24 h followed by one week ageing at room temperature in a moisture-free atmosphere.

2.3.1.2 One-shot method

HTNR in chloroform (35% w/v) along with DBTDL catalyst (0.3% by weight of HTNR) was taken in a flat-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet and a reflux condenser and a dropping funnel. A solution of PEO in chloroform (35% w/v) was prepared and added into the flask. The solution was stirred vigorously and was brought to reflux. TDI was added dropwise with constant stirring over a period of 30 min followed by 1.5 h of the reaction. HTNR, TDI and PEO were taken in the ratio of 1:2.01:1 for the synthesis.
The excess chloroform distilled off and the viscous polymer was cast in trays treated with silicone release agent. The sheet was removed from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent present and then cured at 70°C for 24 h followed by ageing at room temperature for one week in a moisture-free atmosphere.

2.3.2 Synthesis of block copolymers based on HTNR and PPO by solution polymerisation

The synthesis of block copolymers from HTNR and PPO by solution polymerisation was carried out in chloroform at the reflux temperature but the procedure for one-shot and two-shot synthesis was modified by (1) increasing the amount of the catalyst to 1% and (2) increasing the reaction time. The end of the reaction was followed by IR spectroscopy and the disappearance of the signal due to NCO group at 2260 cm\(^{-1}\) indicated the end of the action.

The above modifications in the synthesis involving PPO arise due to the following reason. PPO glycols contain secondary hydroxyl groups which are less reactive than primary hydroxyl groups.\(^5\) This entails longer reaction time and higher amount of catalyst.

2.3.2.1 Two-shot method

HTNR in chloroform (35% w/v) along with DBTDL catalyst (1% by weight of HTNR) was taken in a flat-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet, a reflux water condenser and a dropping funnel. The solution was stirred vigorously and brought to reflux. The stoichiometric amount of TDI (1: 201:1 of HTNR, TDI and PPO respectively) was added in drops in 30 min followed by 2 h of the reaction to endcap HTNR. This was accompanied by the addition of the required amount of PPO as a solution in chloroform (35% w/v) dropwise during 1.5 h followed by 3 h of the reaction.
The excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone release agent. The sheet was removed from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent present and then cured at 70°C for 24 h followed by one week ageing at room temperature in a moisture-free atmosphere.

2.3.2.2 One-shot method

HTNR in chloroform (35% w/v) was taken along with DBTDL catalyst (1% by weight of HTNR) in a flat-bottomed flask provided with a magnetic stirrer, nitrogen inlet and outlet and a reflux water condenser and a dropping funnel. A solution of PPO in chloroform (35% w/v) was prepared and added into the flask dropwise and the solution was stirred vigorously and brought to reflux. The stoichiometric amount of TDI (1.2.01:1 ratio of HTNR, TDI and PPO respectively) was added dropwise with constant stirring over a period of 30 min followed by 2.5-3 h of the reaction.

The excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone release agent. The sheet was removed from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent present and then cured at 70°C for 24 h followed by ageing at room temperature for one week in a moisture-free atmosphere.

2.3.3 Synthesis of block copolymers based on HTNR and PTMO by solution polymerisation

2.3.3.1 Two-shot method

HTNR dissolved in chloroform (35% w/v) along with DBTDL (0.3% by weight of HTNR) was taken in a flat-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and outlet and a reflux water condenser. The stoichiometric
amount of TDI (1: 2.01:1 of HTNR, TDI and PTMO respectively) was added dropwise over a period of 30 min followed by 2 h of the reaction to endcap HTNR with constant stirring at reflux temperature. The required amount of PTMO as a solution in chloroform (35% w/v) was added in drops during 1.5 h. The reaction was allowed to continue for another 2 h. At the end of the reaction the solution became viscous.

The excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone release agent. The sheet is peeled off from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent present and then cured at 70°C for 24 h followed by one week ageing at room temperature in a moisture-free atmosphere.

2.3.3.2 One-shot method

HTNR was dissolved in chloroform to get a (35% w/v) solution in a flat-bottomed flask filled with a magnetic stirrer, nitrogen inlet and outlet and a reflux water condenser and a dropping funnel. A solution of PTMO in chloroform (35% w/v) was added into the flask in drops. The solution was brought to reflux with vigorous stirring. The stoichiometric amount of TDI (1: 2.01:1 ratio of HTNR, TDI and PTMO respectively) was added dropwise over a period of 30 min. The reaction was then allowed to continue for 1.5 h.

The excess chloroform was distilled off. The viscous polymer was cast in trays treated with silicone release agent. The sheet was removed from the tray after 24 h, kept in a vacuum oven at 60°C to remove the traces of solvent. It was cured at 70°C for 24 h followed by ageing at room temperature for one week in a moisture-free atmosphere.
2.4. **Hydrogels: swelling studies on block copolymers from HTNR and PEO**

The block copolymers based on PEO and HTNR are capable of forming hydrogels due to the highly hydrophilic nature of PEO.

2.5. **Measurements**

2.5.1 **Infrared spectral analysis**

The block copolymers were characterised by IR spectroscopy on a Shimadzu IR470 infrared spectrometer using chloroform as the solvent.

2.5.2 **NMR spectral analysis**

$^1$H-NMR spectra of the block copolymers were recorded from a solution in CDCl$_3$ using a JEOL-JNM spectrometer. $^{13}$C-NMR spectrum was recorded under ambient condition from a solution in CDCl$_3$ using a JEOL-FX 90Q FT NMR spectrometer operating at 22-49 MHz.

2.5.3 **Differential scanning calorimetric (DSC) analysis**

The thermal properties of the samples were studied using a Perkin Elmer Delta series DSC 7 calorimeter. The sample mass was approximately 10 mg. All DSC scans were first scans. A heating rate of 10°C min$^{-1}$ was used.

2.5.4 **Thermogravimetric analysis (TGA)**

The TGA studies were carried out using Perkin Elmer TGA 7 analyser at a scan rate of 10°/min.
2.5.5 Scanning electron microscopic (SEM) analysis

The fracture surfaces of the samples from tensile tests were sputter coated with 300 Å of gold and examined on a Hitachi S-415 A scanning electron microscope to study the tensile fracture surface of the samples.

2.5.6 Optical microscopy

Very thin films of the samples were examined with a Leitz Orthoplan optical microscope using a magnification of 100 X.

2.5.7 Stress-strain behaviour

Dumbbell shaped test specimen from the cast sheets were tested on a Zwick 1474 universal testing machine (UTM) as per ASTM D 412-80 test method at room temperature at a constant crosshead speed of 500 mm/min.

2.5.8 Tear strength

Tear strength of the samples were tested on a Zwick 1474 UTM as per ASTM D 624-81 test method using nicked 90° angle specimen.

2.5.9 Shore A hardness

The shore A hardness of the samples were measured at room temperature using 60 13805 type A Durometer as per ASTM D 2240-75 test method. The values were taken as the arithmetic mean of five measurements at different positions on the specimen. The readings were taken within 15 sec after the presser foot was in firm contact with the specimen.
2.5.10 Polymer designation

The block copolymers studied in this work are designated as follows. NR/PEO(3000/4000)-1 indicates the sample containing HTNR and PEO where HTNR molecular weight is 3000 and PEO molecular weight is 4000. The number 1 shown at the end of the designation indicates that the sample was synthesised by the one-shot method. The number 2 in the place of 1 in the designation indicates that the synthesis was by the two-shot method, i.e., NR/PPO(3000/4000)-2.

In the above designation, PEO is replaced by PPO for samples based on PPO, i.e., NR/PPO(3000/4000)-1. In the PTMO series, PEO is replaced by PTMO, i.e., NR/PTMO(3000/1000)-1.

2.6. References