STUDIES ON POLYURETHANE ELASTOMERS BASED ON LIQUID NATURAL RUBBER

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DECLARATION.

I hereby declare that the work presented in this thesis is based on the original work done by me under the supervision of Dr.D.Joseph Francis, Professor & Head, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, in the Department of Polymer Science and Rubber Technology. No part of this thesis has been presented for any other degree from any other institution.

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CERTIFICATE

This is to certify that this thesis is a report of original work carried out by Mr. T.Ravindran, under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other university.

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PREFACE

Degradation of Natural Rubber (NR) into shorter chain segments with reactive end groups is a prerequisite for the production of new materials such as segmented polyurethanes and block copolymers based on natural rubber. Segmented polyurethanes belong to a class of thermoplastic elastomers having great commercial importance. For the polyurethane synthesis, as well as for the production of block copolymers based on NR, hydroxyl end groups are most suitable for chain extension reactions.

Many methods are reported in literature for the depolymerisation of NR. But many of these suffer from the disadvantage that the end products are not suitable for chain extension. There are some reports on the production of NR oligomers with different functional groups; the only one describing the production of hydroxyl terminated natural rubber (HTNR), use drastic conditions, which is an obvious disadvantage.

In the present work a method has been developed for the depolymerisation of NR. The photodepolymerisation of NR in the presence of hydrogen peroxide in a homogenising solvent is described together with the experimental procedures. The production of HTNR with $\overline{Mn}$ 3000 - 3300 is described.

Methods of preparation of segmented polyurethanes based on HTNR are presented. A series of HTNR containing polyurethanes are synthesised by different synthetic routes with varying hard segment content (TDI/BDO). Syntheses are done in one step and two step processes by bulk and solution polymerisations.

Characterisation of these polyurethanes showed that there existed a complete or very nearly complete phase segregation indicated by the independence of the soft segment Tg value with the content of hard segments. Evaluation of mechanical and thermal properties of polyurethanes are also described. Dynamic mechanical analysis results of these material are also presented. Effect of catalysts on polyurethane synthesis and effect of HTNR molecular weight on mechanical properties of polyurethanes are studied and results presented.

The experimental procedures for the preparation of block copolymers based on HTNR and preformed poly(ethylene oxide) with different molecular weights with TDI as coupling agent are described. Different procedures followed for the preparation of block copolymer are also presented. Tensile properties and water absorption capabilities of these polymers are determined and hydrogels upto 80% water content are obtained. Results of the characterization of these block copolymers by IR spectroscopy, differential scanning calorimetry, thermogravimetry and optical microscopy are also presented.

To conclude, an efficient and economical method for the preparation of HTNR by the photodegradation of NR has been developed. Utility of HTNR produced by these methods in the synthesis of segmented polyurethanes and block copolymers are demonstrated.

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CHAPTER-I

INTRODUCTION

Part I : Depolymerisation of Rubbers.

Depolymerisation of Natural Rubber (NR) into shorter chain segments with reactive end groups is a pre-requisite for the production of new materials like thermoplastic elastomers, adhesives, binders for rocket propellants, polyurethanes etc. Depolymerisation of NR was performed for the first time by K.V.Hardman in the year 1923. Liquid Elastomer first appeared in the market in 1923 and was obtained by the degradation of solid NR by mechanical/chemical peptisation.[1] Several methods were reported for the depolymerisation based on thermal, chemical, mechanical[2] and photochemical effects.

Mechanical degradation by mastication is a non-random process, where scission occurs only in those molecules possessing greater than a critical chain length[2-5] which tends to limit the extent of degradation. Much work has been published on the mastication behaviour of high polymers, in particular of natural and synthetic rubbers. Most of this has been concerned with the mechanism of the breakdown process[6] and the chemical consequences, both in the absence and presence of various species, such as oxygen[7], carbon black[8] and polymerisable monomers[9]. It was reported that rubber masticated at low temperatures is likely to have significantly better properties than that masticated at high temperatures.[10] The minimum rate of breakdown occurs at about 115°C and at temperatures of 45°C above and below this, the rate is increased fivefold.[11]

1.1 Mechanical breakdown

The energy of mechanical action is on the deformation of valence angles and the scission of polymer chains. In the process of scission of macromolecular chains, the energy necessary for scission of macromolecules includes the energy consumption in the deformation of valence angles and the breaking of the valence bonds. Hence the products formed in mechanical scission of the polymer chains should possess a large chemical potential and easily enter into various chemical conversions.

Under the action of mechanical forces the breaking of macromolecule proceeds not only with covalent bonds but also with ionic ones. The three basic mechanisms of polymer scission are (1) radical, (2) ionic & (3) ionic radical. The formation of polymeric radicals may be expected in the case where the polymer chains contain co-valent bonds[12].

$$-CH_2 \text{——} CH_2- \longrightarrow \dot{C}H_2- + -\dot{C}H_2$$

The formation of macro-radicals in the mechanical breakdown of organic polymers and the possibility of their chemical reactions are reported by Pike and Watson,[13] Berlin[14] et al, Kargin and Slominskii[15] and a number of other research workers.

1.2 Thermal breakdown

Thermal breakdown of NR in presence of air or oxygen causes only softening[16]. According to Voronenkov[17] et al the thermal breakdown of NR proceeds via a cyclic intermediate which is present in small amounts in NR as a result of interaction of the pi-electrons of the $-CH_2$ groups. The interaction increases with increasing temperature, resulting in the formation of unstable methyl cyclobutane, which readily isomerises into isoprene.

1.3 Chemical breakdown

i) Prolonged heating of the solution of NR in chlorobenzene in vacuo at temperatures within the range 25°C to 220°C caused degradation[18].

ii) Hydrogen peroxide under pressure and temperature was used for degradation of masticated NR dissolved in toluene[19].

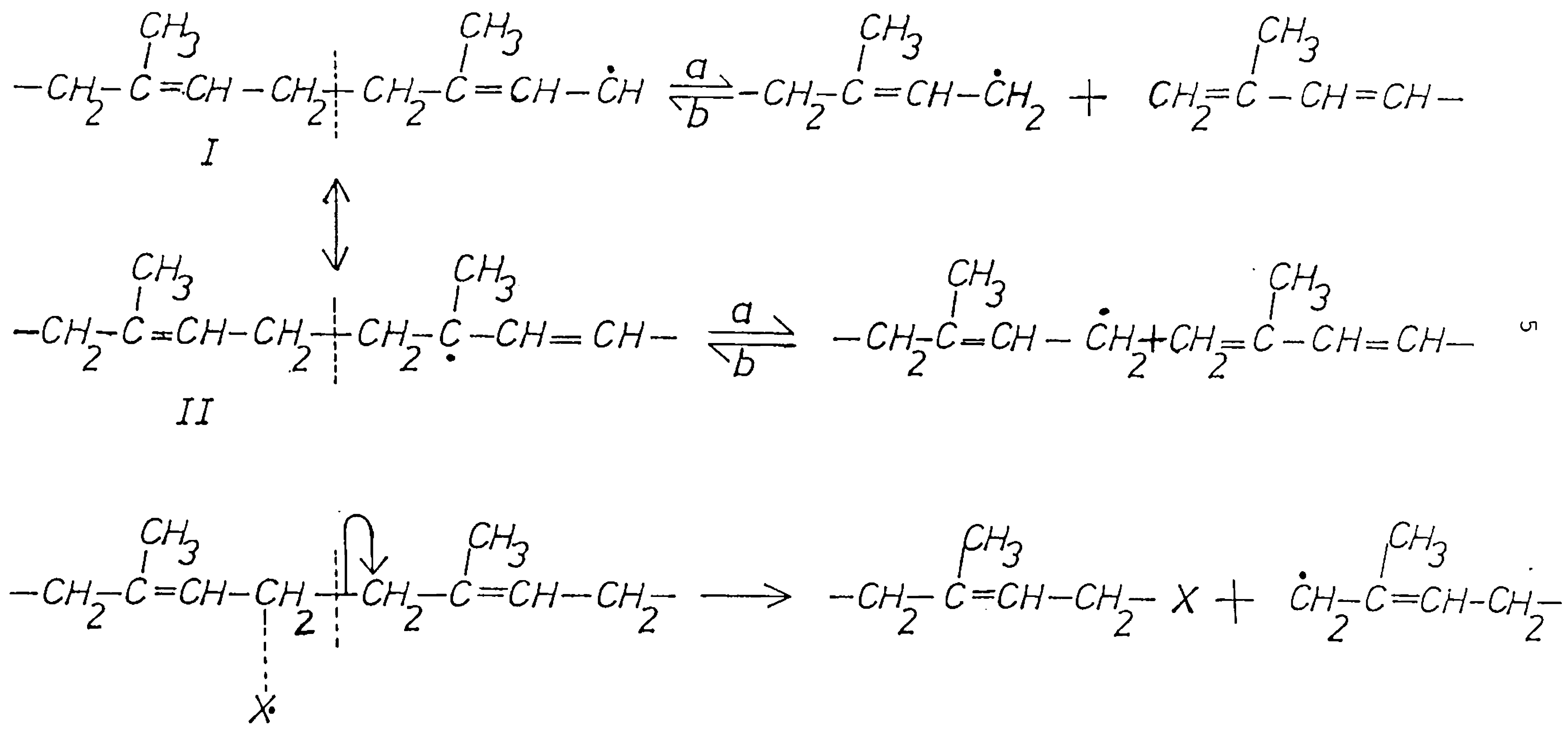
iii) Phenyl hydrazine in presence of ferrous chloride and oxygen[20] was found to degrade a solution of NR in toluene.

iv) Para toluene sulfonic acid/ phenyl hydrazine system[21] was used for controlled degradation of NR and synthetic rubbers.

v) Oxidative degradation of 1,4 cis polyisoprene using oxygen in presence of Azo bis isobutyronitrile (AIBN) at 80°C was also reported[22].

Chain scission during the crosslinking of NR with organic peroxides was studied by Moore and Scanlan[23]. Polyisoprenyl radicals were derived from NR by reaction with t-butoxy or methyl radicals formed from peroxides. Unimolecular scission reactions (see Scheme I) whose possible occurence was discussed by Flory[24] and Craig[25], was certainly favoured by the weakness of the $-CH_2-CH_2-$ bond in I and II. Bresler et al[26], in fact had attributed the polymer degradation they observed when dilute benzene solutions of NR were subjected to attack by free radicals.

The chief difficulty encountered in the study of the phenomenon of scission lies in the fact that scission and bridging takes place simultaneously and had opposite effects. Massobian and Tobolsky[27] were able to distinguish the scission phenomenon by studying relaxation under continued tension and then determining the total effect by measurements under intermittent tension. Another possible way to distinguish the scission is to use relatively dilute solution, the effect of dilution is to separate the polymer chains



SCHEME 1

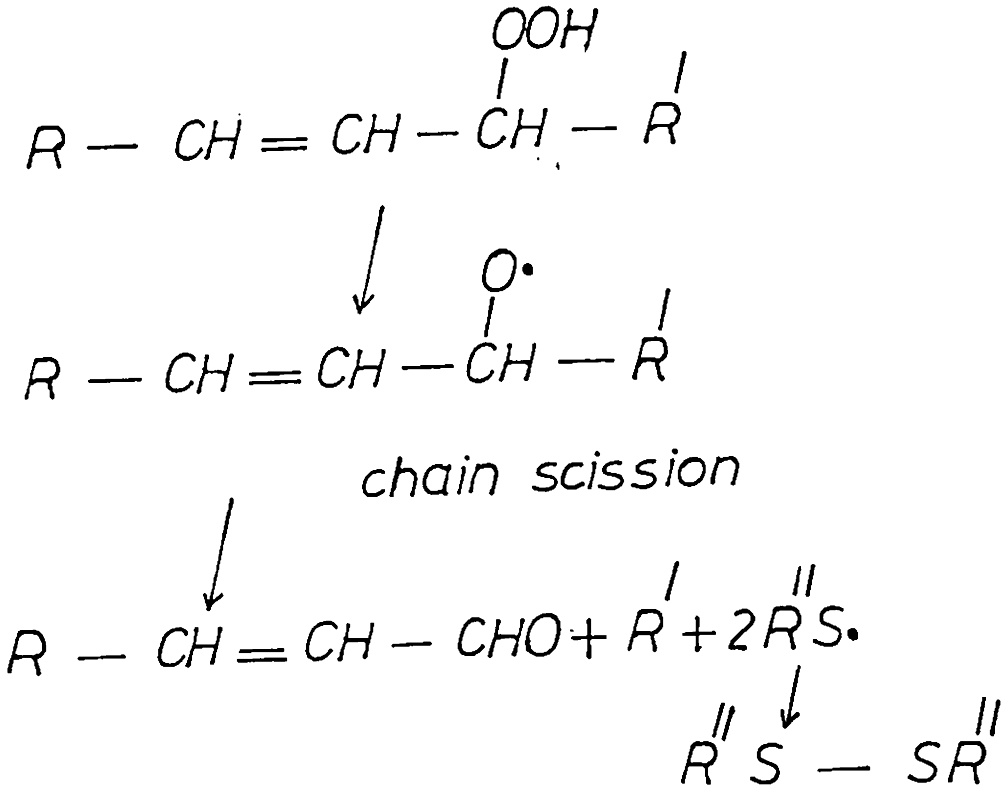
from one another and thereby reduce the probability of bridging[28].

It is well known that a small quantity of an alcohol preferably methanol[29,30] or other polar solvent, which will not cause precipitation, will reduce the viscosity of solutions of NR in benzene or toluene[31-33]. The polar substances reduce the intermolecular attractions due to oxygen containing groups such as carboxyl and hydroxyl formed by oxidation during the processing of latex.[34] It is however, a general principle that the addition of a non solvent to a polymer solution reduces polymer - solvent interaction and the polymer chains tend to coil up instead of being extended, resulting in a decrease in the viscosity of the solution.

Mineral acids such as HCl[35,36] and organic acids like acetic, chloroacetic and benzoic acids[37] also reduce the viscosity of solutions of NR. Sulfinic[38] and sulfonic[39] acids assist the dissolution of NR in toluene and benzene but it had been reported that in presence of O_2 the former class of compounds causes degradation of NR through a free radical mechanism[40]. However chain scission is brought about by the addition of small quantities of substances which causes degradation by free radical mechanism in which O_2 may or may not participate.

It was reported[41] that aliphatic thiols do not reduce the viscosity of rubber solutions. Dodecyl mercaptan causes degradation of SBR in toluene solution when oxygen is present[42]. Of the several aromatic and heterocyclic thiols studied by Montu[41] 2-thio naphthol and xylyl thiol were found to be most active, 2-mercapto benzothiazole was less effective and 2-mercapto benzimidazole was found to be inactive. The zinc salts of 2-thionaphthol and 2-mercapto benzothiazole were also found to be active. It was clear from the above examples that the presence of an -SH group is not the only factor which decides whether a compound will act as a peptizer or not, the structure of the rest of the molecule plays an important part. Kimijima[43] had studied the relationship between the structure and activity of ortho substituted thiophenols and found that the effect of the groups in order of decreasing efficiency as plasticizers to be $CH_3 > OH > OCH_3 > Cl > NO_2 > NH_2$. The effect of an ortho nitro group is greater than that of a meta or para nitro group and 2-thio naphthol is slightly more effective than 1-thionaphthol.

The presence of O_2 is necessary for thiols to be active in lowering the viscosity of rubber solutions,[41,44,45] although there is some evidence of action under nitrogen. Hydroquinone inhibits the action of thiophenol in the presence of air suggesting that plasticisation of rubber is related to the auto-oxidation of thiophenol[44]. Kheraskova and Gamanyova[45], on the basis of kinetic measurements concluded that oxidation of Thiol to disulfide and oxidation of rubber are conjugate reactions. Thiol peroxides are first formed which then attack the rubber chain at the allylic methylene groups with the formation of thiyl radicals and rubber hydroperoxides. The Thiyl radicals will combine to form disulfides whilst the latter decompose as shown in scheme II.



$$R-CH=CH-\overset{OOH}{CH}-R'$$

$$\downarrow$$

$$R-CH=CH-\overset{O\cdot}{CH}-R'$$

chain scission

$$\downarrow$$

$$R-CH=CH-CHO+R'+2R''S\cdot$$

$$\downarrow$$

$$R''S-SR''$$

SCHEMEII

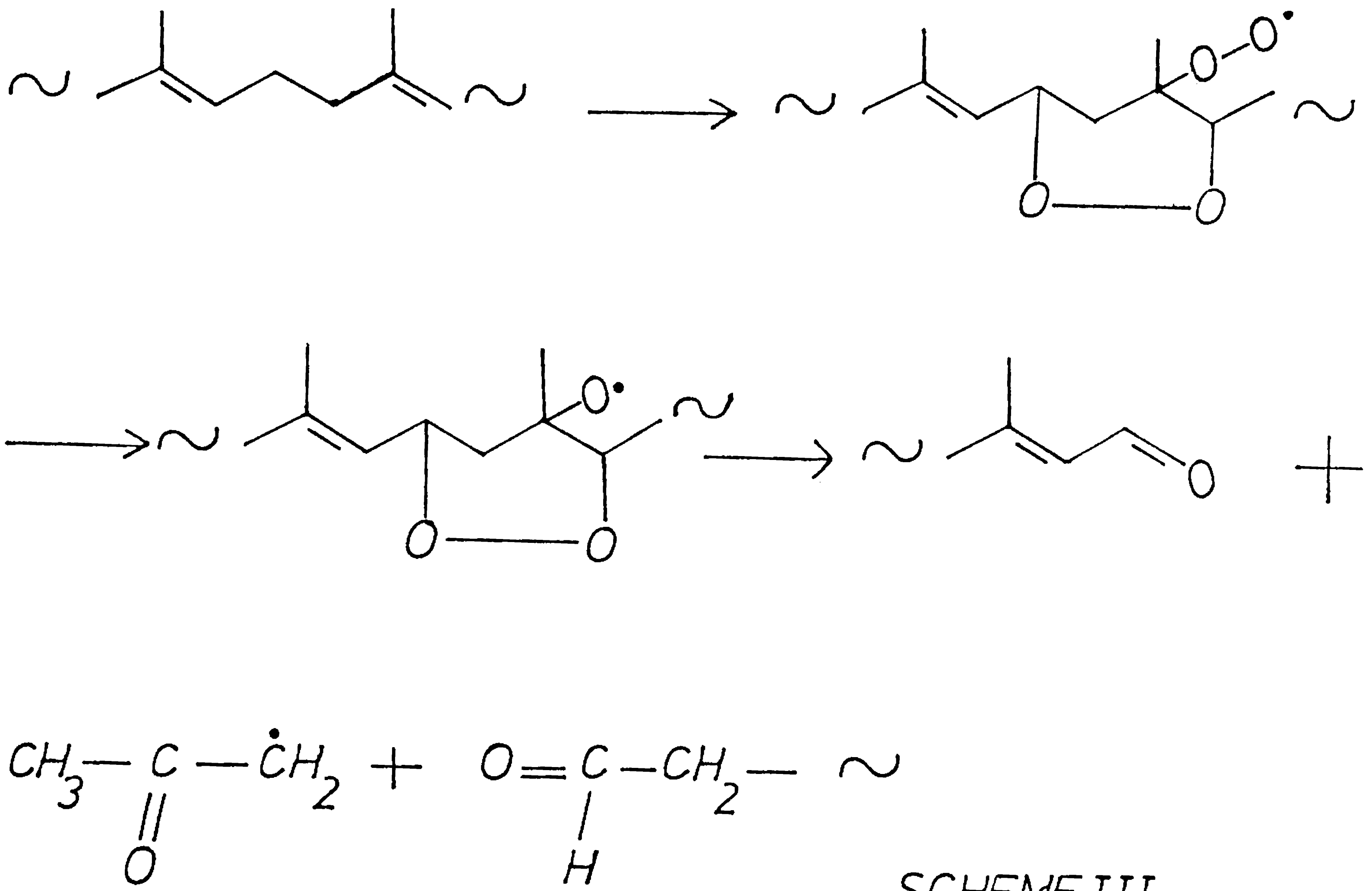
There is still appreciable lowering of the viscosity of rubber solutions by 2 2' dibenzamino diphenyl disulfide in the absence of O_2 which is in agreement with its behaviour as an aid for mastication of NR at low temperatures and that scission of the polymer molecule does not always go via the hydro peroxide; scission by direct attack by free radicals is also possible. The action of tetra methyl thiuram disulfide on poly vinylchloride[46] appears to be an example of this mechanism.

During the degradation of rubbers in solution, the disulfides presumably dissociate to give free radicals which abstract hydrogen from rubber molecule to produce a rubber free radical which then breaks down into smaller chains with or without the intervening step of peroxide formation according to whether O_2 is present or not[47]. Tetramethyl thiuram disulfide accelerates the photochemical depolymerisation of NR[48]. Imoto and Kiriyama[49] have shown that squalene was degraded by benzoate free radicals with the production of isoprene diol benzoate so that scission must have occured at $—CH_2—CH_2—$ links. The degradation of solution of NR by benzoyl peroxide is well known[41,50-52]

Redox systems of hydroperoxide and reducing agents cause structurizing SBR solutions in hydrocarbon solvents. A typical system used composed of benzoyl peroxide, benzoin and ferric naphthenate. Oxygen repress the process and causes degradation of rubber[53] The system H_2O_2/ferric naphthenate/oxygen causes degradation of polybutadiene at room temperature[53] and it was suggested that other redox systems produce H_2O_2 and it is the breakdown of this in the presence of O_2 which initiates degradation. Thiokol and poly isobutylene rubbers are also degraded by redox systems[54] .

It has been shown that polymer degradation can proceed via several mechanisms, all of which involve free radicals, and can be summarized as follows. In solutions, at low temperatures, the initiating free radicals come from the added peptizer. Eventhough O_2 accelerates the reaction, it is not essential and there is appreciable degradation in the absence of O_2. Thiols are active only when O_2 is present even at high temperatures[55] . The rubber radicals produced by thermal scission should be just as active as those produced by mastication and are capable of reaction with thiols and serves to emphazise the importance of the role of O_2 in peptisation by thiols and disulfides. O_2 is also necessary for degradation by redox systems and in its absence structurizing takes place.

Tobolsky and Mercurio[56] studied the intiated



SCHEME III

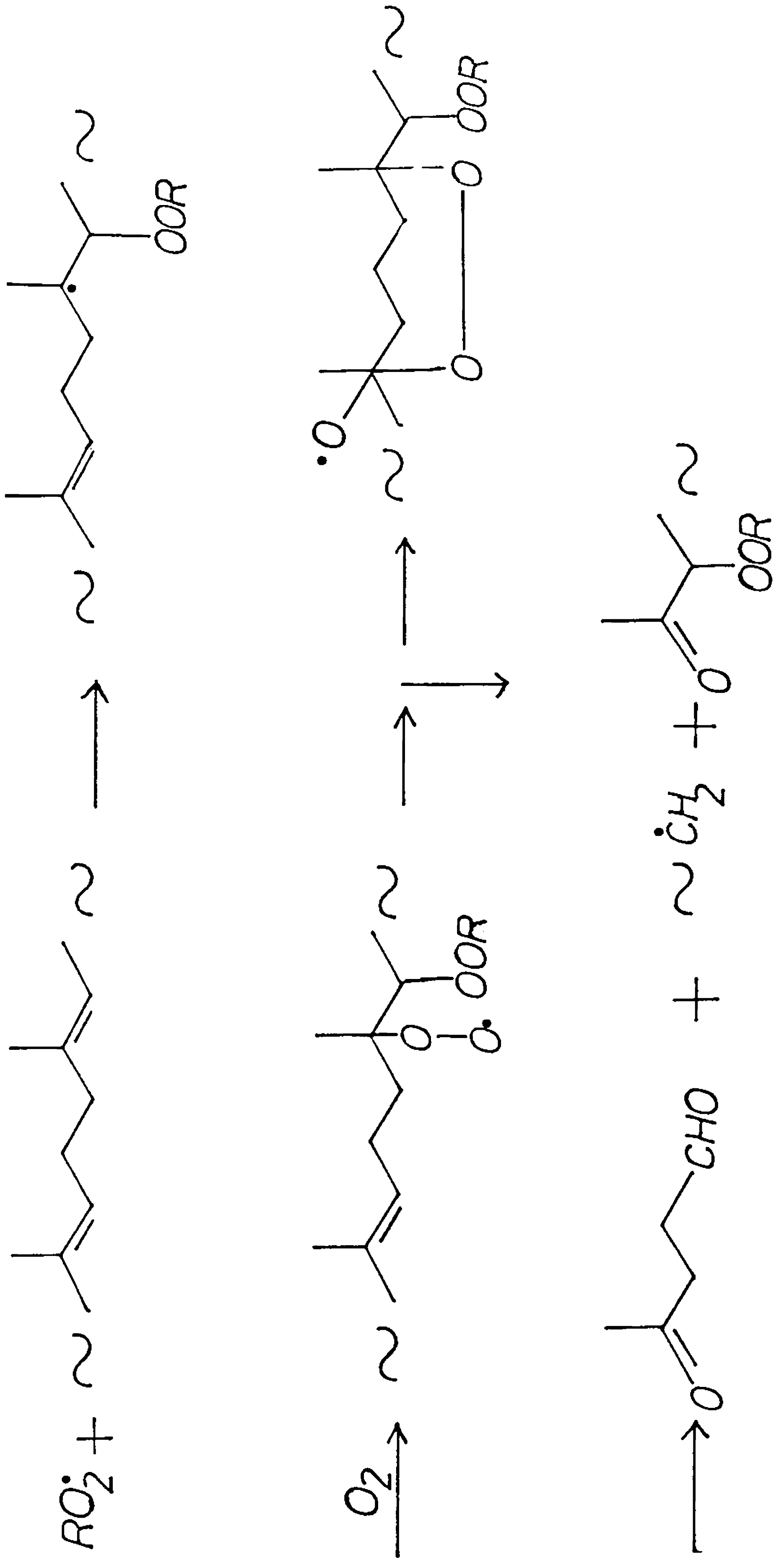
oxidation of radiation crosslinked NR and of dilute solutions of the polymer in benzene. Scission was followed by means of chemical stress relaxation of the vulcanizate and by viscometry of the raw polymer. Under their conditions, approximately one scission was produced by each initiating radical. It was proposed that peroxy radicals interact to give alkoxy radicals. These cleave, producing chain scission, and radicals formed couple to terminate the oxidation of chains.

Several possible routes to the scission in NR had been postulated by them (Scheme III) by Bevilacqua and coworkers[57] and Mayo[58] (Scheme IV).

There are two possible peroxy radicals that can be formed along the polyisoprene chain by simple hydrogen abstraction and addition of oxygen without rearrangement. One of these peroxy radicals can cyclize to form a six membered ring by attack at the mono substituted end of the double bond. The peroxy radical that cannot, may participate in the reaction shown in scheme IV.

1.4 Photochemical breakdown

In the presence of atmospheric oxygen, light brings about change in the physical properties of both vulcanized and unvulcanized natural rubber,



SCHEME IV

ordinarily with degradation of quality. The surface of such products becomes sticky, inelastic, brittle or even cracked. If ozone is present in addition to atmospheric oxygen during exposure to light, the changes are much more rapid.

Many authors have studied the active spectral range of solar radiation, mercury light and electric lamps. Kroger and Staude[59] proved that rubber shows highest absorption in the range 2000 - 2500 A°. Bateman[60] established that during exposure to ultraviolet light, the short wave ultraviolet range is most active upto about 3700 A°, although in the range from 2700 A° to 2500 A°, a perceptible decrease of effectiveness is observed. Asano[61] assumed that the radiation longer than 3100 A° had no significant influence and that changes in rubber are much more rapid at wave lengths between 2000 and 2250 A°. Experiments by Pummerer[62], who studied the formation of photogels in rubber solutions during exposure to light, show that the effective light is of shorter wave length than 3150 A°. According to other experiments made by him, direct solar radiation is just as effective as the light of a mercury quartz lamp. According to Bondy,[63] the active component of solar light which governs oxidation lies between 3000 and 4800 A°. His results lead to the conclusion that solar and ultraviolet light are equally effective, although ozone is formed only at short wave lengths which are not present in sunlight.

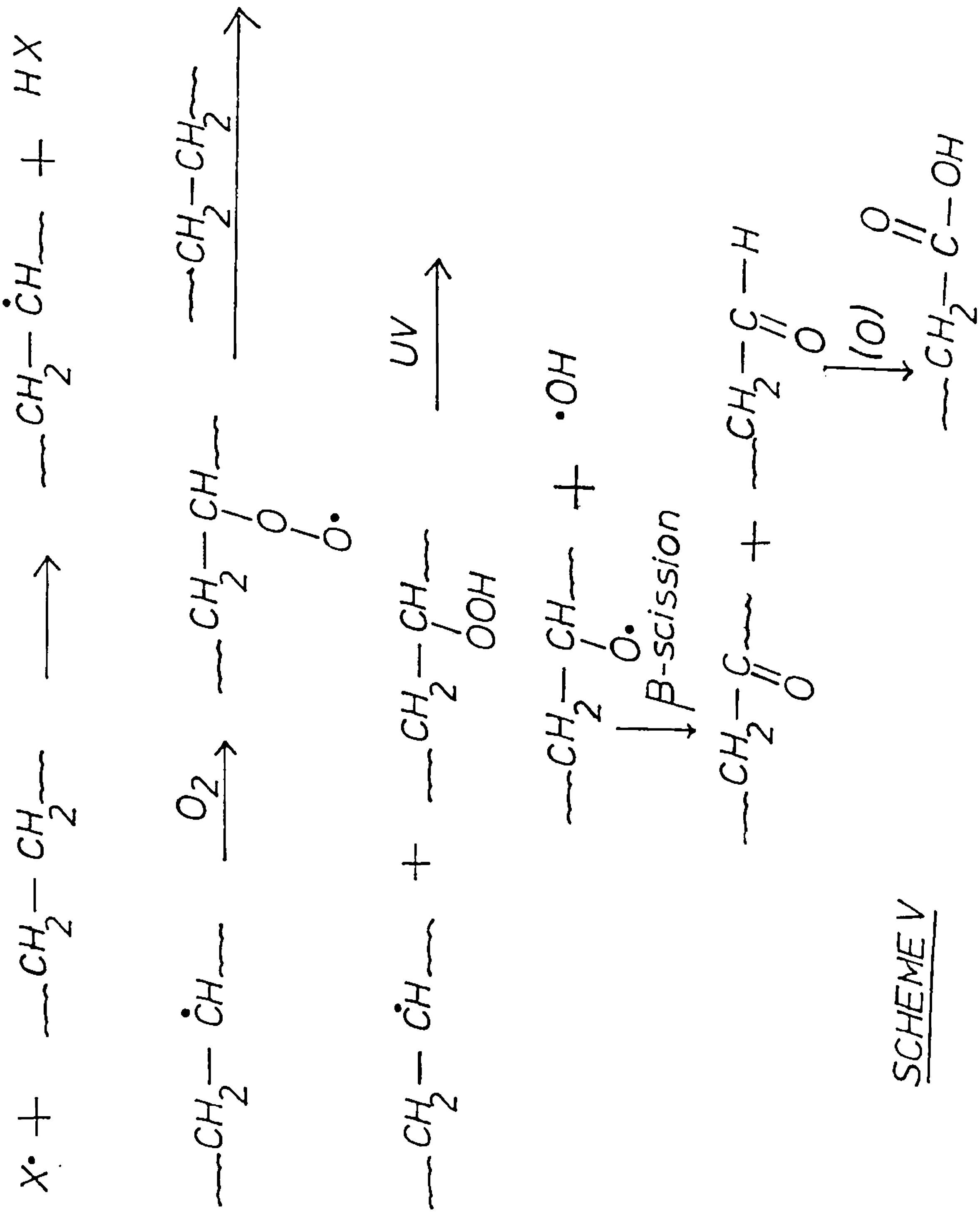
Changes caused by the action of light in the structure of rubber are very diverse. Rubber is depolymerized[64]. It has long been known that rubber exposed to light undergoes significant structural changes, due to the influence of oxygen[65]. Shortening of the chains of the polymer is reflected by the decrease of viscosity of rubber solutions[66].

Mastication of natural rubber increases considerably its susceptibility to deterioration on exposure to light.[67] As it is noted that this susceptibility increases rapidly at the beginning of mastication (about 2 minutes). It increases slowly and uniformly with the time of mastication. This high susceptibility is due, in part to the increase of double bonds, which was observed spectroscopically and in part to the decrease of viscosity as a result of which mobility of the free radicals may increase.

Liquid rubbers do have disadvantages; the most important one is its poor physical properties due to loss of regularity of polymer backbone in the final vulcanizate and the difficulty of adding reinforcing fillers, and handling the resulting sticky material. Mullins[68] and Cunneen[69] have shown that depolymerised (liquid) natural rubber made by thermal oxidation of raw rubber does not have the regular pattern of functional groups needed for chain extension and when vulcanized by conventional methods has poor physical properties.

Use of solar energy for preparation of liquid rubbers, was studied by Tillekeratne and coworkers[70]. In the absence of added sensitizers, only the UV fraction of the solar spectrum reaching the earth surface is useful in the preparation of liquid rubbers. Ions of transition metals act as sensitizers for the photo oxidation of polymers. The nature of the anion associated with the metal ion is very important in the process. As the electron affinity of the anion increases, the absorption of the metal shifts towards the shorter wave lengths than those present in sunlight at the surface of the earth. Therefore metal complexes like ferric acetyl acetonate and cobaltous acetyl acetonate can absorb the UV radiations reaching the surface of the earth, whereas ferricchloride can not.

Mechanism of initiation is that the transitional metal ions can absorb UV radiations and generate free radicals on the polymer backbone. Thereby subsequent reaction with oxygen gives rise to hydroperoxides, which are destroyed by transition metal ions with the associated scission of polymer chain (scheme V).



SCHEME V

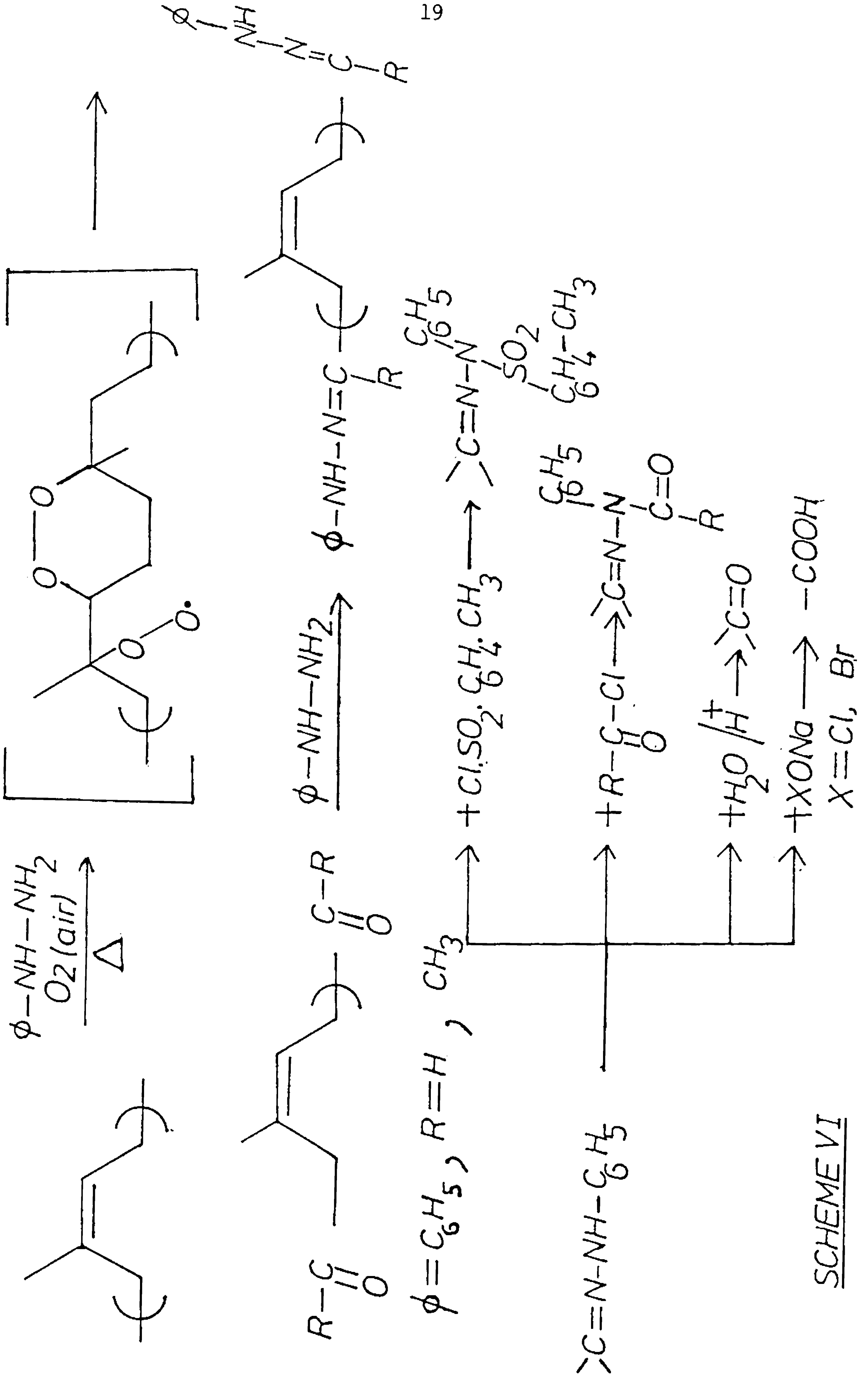
$$R{-}OOH + M^{n+} \longrightarrow RO\bullet + HO^{-} + M^{(n+1)+} \quad \text{(Oxidation)}$$

$$R{-}OOH + M^{n+} \longrightarrow ROO\bullet + H^{+} + M^{(n-1)+} \quad \text{(Reduction)}$$

These radicals then initiate a conventional oxidation chain reaction.

The activity of nitro benzene on rubber in UV light is very much greater than that of the metal complexes. The excitation of nitro benzene to a high energy electronic state is easier due to the presence of non bonding pair of electrons on the N-atom. The electronically excited nitrobenzene molecules collide with oxygen molecules generating singlet oxygen. It can also be due to the abstraction of a H-atom from the polymer backbone by the activated triplet state of the nitrobenzene.

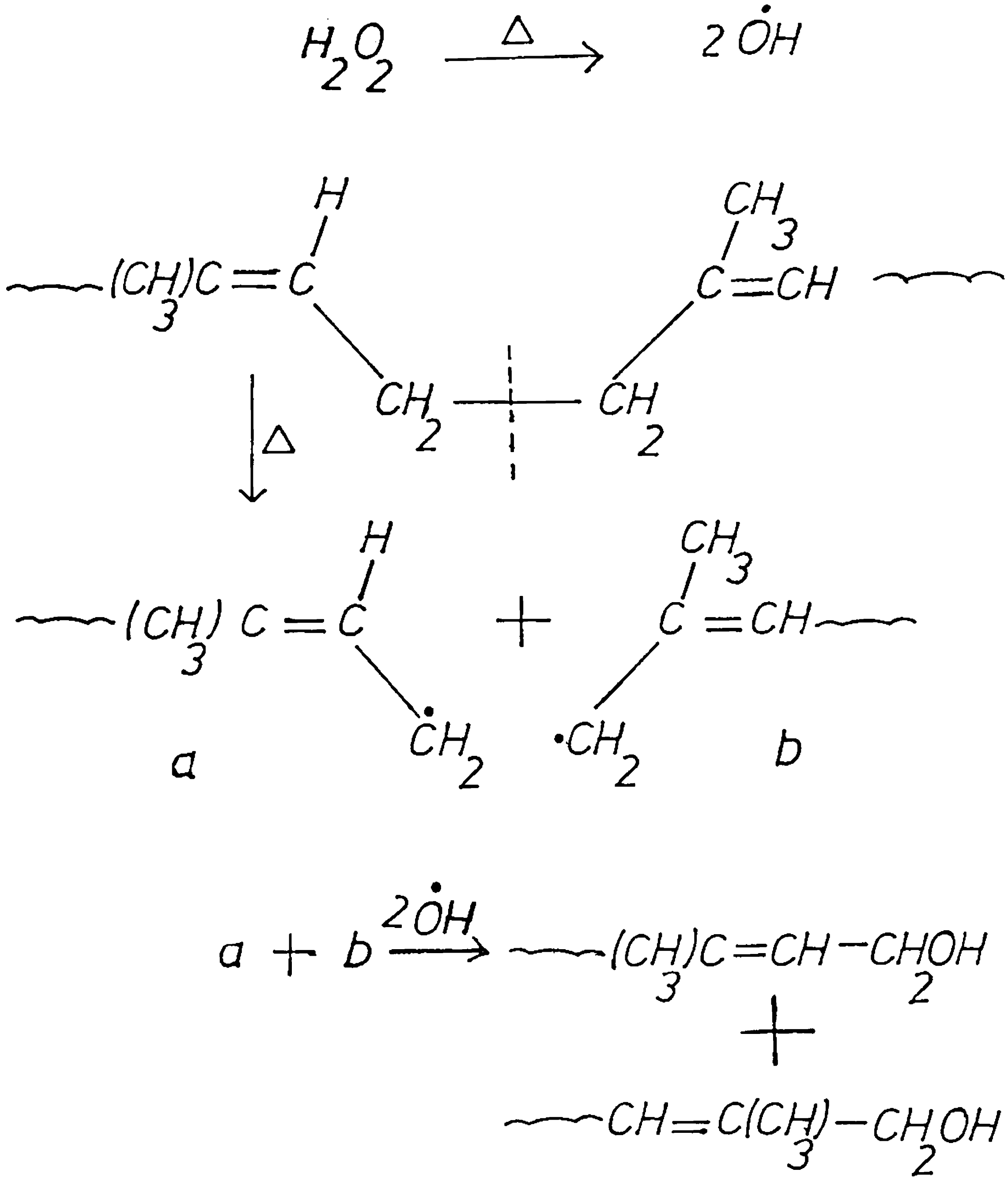
Although the foregoing description presents several methods for the depolymerisation of natural rubber, most of them involve cumbersome procedures, and in several cases the products are not suitable for further applications such as chain extension. The methods aimed at the introduction of desired functional groups in the NR oligomers are those reported by Pautrat[71], Brosse[1] et al and Gupta et al[19]. According to the first two authors NR in latex stage or in an organic solvent was degraded on a large scale, by the redox system - phenyl hydrazine/


φ—NH—NH$_2$
O2 (air)
Δ
φ—NH—NH$_2$
φ = C$_6$H$_5$, R = H , CH$_3$
+ Cl.SO$_2$.C$_6$H$_4$.CH$_3$
+ R—C(=O)—Cl
+ H$_2$O / H$^+$
+ XONa
X = Cl, Br
—COOH

SCHEME VI

atmospheric oxygen, at 50° - 70°C. The method yielded liquid NR with terminal carbonyl groups which in the presence of excess $Ph\text{-}NH\text{-}NH_2$ were transformed into phenyl hydrazones. This terminal functional groups opened several ways to modify functionality (Scheme VI).

Gupta et al obtained hydroxyl terminated liquid NR (Scheme VII) using hydrogen peroxide as the reagent, although the processing conditions viz. high temperature and pressure, may aggravate side reactions. The efficiency of functionalization reported was very low.



SCHEME VII

Part II : Segmented Polyurethanes.

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments and subsequent phase separation into separate domains. The soft segment generally used to be a polyether or polyester of molecular weight (Mn) between 1000 and 5000 possessing a glass transition temperature (Tg) well below ambient temperature. Hard segments are typically formed by the extension of an aromatic diisocyanate with a low molecular weight diol or diamine and have a Tg or melting transition above the used temperature. The hard segment domains provide physical crosslinking, act as reinforcing fillers and are responsible for the performance of these materials at higher temperatures.

The existence of phase segregation caused by the clustering of hard and soft segments into separate microdomains has been well documented for block copolymers and segmented polyurethanes[72-74]. Consequently many of the physical and mechanical properties (ie. enhanced modulus, high extensibility and resiliency) have been interpreted in terms of a two phase system. Past studies have dealt primarily with the influence of hard and soft segment chemical structure and molecular weight on the extent of phase segregation and domain formation. Schneider[75] and Rustad[76] have shown that the choice of polyether rather than polyester soft segments and the use of 2000 rather than 1000 molecular weight leads to better phase segregation. Seefried et al[77] has illustrated that MDI - based polyurethanes, in contrast to TDI urethanes, possess a more perfect domain organization due to short range order including crystallinity, and consequently, show a higher extent of segregation between hard and soft segments.

Through techniques such as differential thermal analysis, dynamic mechanical analysis and x-ray studies, models of phase segregation and domain structure have been developed which are reasonably successful in accounting qualitatively for the many features of segmented polyurethanes[72-74]. However, in most polyurethanes previously investigated, difficulties arise because the phenomena of interest are obscured by one or more of the following competing effects:

(1) specific interactions between the hard and soft segment phase via hydrogen bonding,
(2) crystallnity occuring in either or both the soft and hard segment phases and
(3) chemical crosslinking.

It is therefore of interest to examine the structure-property relations in a series of segmented polyurethanes in which these added complexities are excluded.

Segmented polyurethanes which incorporate a polybutadiene (PBD), rather than polyester or polyether soft segment, were initially of interest only as binders in solid rocket propellants. Now such materials are finding increasing usage in a variety of speciality applications which emphasize the low moisture permeability conferred by the butadiene soft segment. In particular, there have been a number of studies which have emphasized the potential of these polyurethanes as electrical potting compounds or adhesives[78-80].

The polyurethanes prepared from hydroxyl terminated polybutadiene (prepared by free radical polymerisation consisting of 60% trans, 20% vinyl and 20% cis content)[81-83] with toluene 2,4 diisocyanate (TDI) can be cured to full properties with the use of butane 1,4 diol (BDO) or other low molecular weight diols[84,85] rather than requiring MOCA or the alternative diamine curing agents which are generally used in TDI polyurethanes containing polyether or polyester soft segments. Although the physical properties which result are acceptable for many of the applications, it is significant that the tensile strength, tear strength and abrasion resistance of these HTPBD polyurethanes are far lower than the values for typical tough polyester or polyether polyurethane elastomers. Legasse[86] studied a polybutadiene containing polyurethane which was based on a commercial casting formulation containing a mixed diol as the curing agent. Results on the transition behaviour and morphology of this polymer were presented but the emphasis was on the time dependence of the hard segment transition behaviour and properties. Ono[87] and coworkers carried out a careful study of the effect of the number average molecular weight of hydroxyl terminated poly butadiene (HTPBD) on the properties of elastomers prepared both by chain extension with diphenylmethyl diisocyanate (MDI) and by a one shot reaction with MDI and a short chain diol curing agent. The results indicated the marked superiority in properties of the segmented elastomers and also showed that significant improvement in the properties of the latter materials occured below 3000 HTPBD molecular weight.

Schneider and Matton[88] conducted a detailed study of the thermal transition behaviour of a series of poly butadiene containing polyurethanes which are compositionally similar, in certain respects, to the elastomers studied by Legasse and by Ono et al. They prepared a series of polyurethanes from HTPBD (ARCO 45), bis(2-hydroxyl propyl aniline) HPA (Upjohn, Isonol C-100) Toluene 2,4 diisocyanate and Butane 1,4 diol. The soft segment glass transition temperature in the polyurethanes studied by them was in the range of -73°C to -77°C as compared to a value of -81°C for the pure HTPBD. These are the smallest differences in temperature between the polyurethane soft segment and the free soft segment ever reported[77] and indicate that phase segregation in these various polyurethanes are very nearly complete. The hard segment transitions observed are T_1 at 40°C and T_2 at 103°C (Tg of the hard segments) and a softening region by TMA at 180°C, presumed to arise from the dissociation of allophonate bonding. The dependence of T_1 on hard segment length and thermal cycling suggested that it represents domains consisting primarily of shorter hard segment units. Factors contributing to the rather low mechanical properties of HTPBD polyurethanes are also discussed.

W.J. Mac Knight and coworkers[89] studied the structural and mechanical properties of polybutadiene containing polyurethanes where a series of segmented polyurethanes based on HTPBD and their hydrogenated derivatives (HYPBD) were synthesised. Thermal, mechanical and spectroscopic studies were carried out over a wide range of temperatures to elucidate the structure - property relationships existing in these polymers. Both thermal and dynamic mechanical response showed a soft segment Tg at -74°C for the unsaturated polyurethanes and at -69°C for the hydrogenated samples. In addition two hard segment transitions are observed by differential scanning calorimetry at 40 and 75°C and a softening region by thermal mechanical analysis (TMA) at 190°C. The low Tg very close to that of HTPBD and HYPBD and independent of hard segment content, indicated that these polymers are well phase separated. Results of Infra red analysis revealed that at room temperature 90-95 percent of the urethane N-H groups formed hydrogen bonds. Since hydrogen bonding is present only within the hard segment domain in these polyurethanes, the extent of H-bonding served as additional evidence for nearly complete phase separation. From dynamic mechanical studies the plateau modulus above the soft segment Tg and stress-strain behaviour depended upon the concentration of the hard segments. The thermal and mechanical response of these polyurethanes appeared to be consistent with behaviour observed for other phase segregated systems.

Brunette et al[90] carried out extensive studies on the thermal and mechanical properties of linear segmented polyurethanes with butadiene soft segments. They synthesised a series of segmented polyurethanes based on HTPBD soft segment with varying hard segment content between 20 and 60 weight percent. These materials are linear amorphous and have no potential for hydrogen bonding between hard and soft segments. The existence of a two phase morphology was deduced from dynamic mechanical behaviour and thermal analysis. Both techniques showed Tg's of soft segment at -56°C and hard segment between 20 and 100°C, depending on the urethane content. Depending on the nature of the continuous and dispersed phase, the urethanes behaved as elastomers below 40 weight percent hard segment or as glass like materials at higher hard segment contents. The effect of thermal history on the transitions of the HTPBD - urethanes was also investigated and the results suggested that the absence of H-bonding to the soft segment must account for the extra ordinary insensitivity to thermal history in dynamic mechanical, thermal and stress-strain behaviour.

Xu et al[91] conducted studies on the separation of 3 poly butadiene based polyurethanes by means of solvent extraction. Characterisation of the fractions obtained indicated that the molecules of the original polyurethanes are quite dissimilar in chemical composition and average hard segment length. These poly urethanes are blends of two fractions of segmented copolymer with very different average hard segment content and average hard segment length. In these polyurethanes in addition to the segregation of the hard and soft segments, the segregation of macromolecules as a whole according to their composition is considered in the interpretation of their morphology and properties and has been proved to be the origin of the existence of two hard segment Tg's. This kind of compositional nonuniformity is the result of poor compatibility between the components of the system.

Chen et al[92] followed the copolymerisation of a model polyurethane system, HTPBD/2,6 (or 2,4) - TDI/1,4 - butanediol by optical microscopy. It was found that initial reactant incompatibility was the key factor in determining the final morphology of the bulk polymerized sample. Models were proposed to describe the morphology during polymerisation of this particular polyurethane system for several hard segment compositions where both macrophase separation and microphase separation of reactants occur. Globule and spherulite formation and the presence of multiple Tg's and Tm's reported by previous workers could be explained by the two levels of heterogenities present during polymerisation.

Bengston et al[93] reported the thermal and mechanical properties of solution polymerised segmented polyurethanes with butadiene soft segments. They synthesised a series of HTPBD containing polyurethanes of high molecular weight in solution. The value of the soft segment Tg was very close to that of free HTPBD and independent of hard segment content indicating complete or very nearly complete phase segregation. Since the hard segments of TDI/BDO are amorphous, the driving force for phase segregation must arise from the large degree of incompatibility between the polar hard segment and non-polar soft segment. The values of the hard segment glass transition increased with the average hard segment length following a Fox-Flory type relationship. In contrast to the Tg observed in bulk polymerised samples, only a single hard segment Tg occured in these samples. This indicated that the double Tg behaviour was a result of the heterogeneous nature of the bulk polymerisation. With increasing hard segment content the properties vary from soft to rigid elastomers and rubber toughened plastics. This variation in properties was caused by changes in the sample morphology which depended upon the relative fractions of hard and soft segments present. Unlike polyester and polyester urethanes, these materials evidence no change in the soft segment Tg following thermal treatment and no effect of thermal history on the mechanical properties.

Fu et al[94,95] studied the effect of mono disperse 2, 4 TDI/BDO hard segments in segmented polyurethanes with polybutadiene, polycaprolactone and polytetramethylene ether glycol soft segments in interpreting the structure property relationships. They synthesised monodisperse hard segments through a simple technique. High purity material was obtained in good yield. The structures of these hard segments were confirmed by I R, ^{1}H-NMR and ^{13}C-NMR. Tg and Tm are reported. The Tg's of the hard segments were inversely proportional to the reciprocal of their molecular weights. The polyurethanes were synthesised by a two step bulk polymerisation technique. The thermal and mechanical properties demonstrated that the hard segment length played an important role in the phase segregation although the degree of phase segregation was also affected by the type of soft segment. The tensile strength was determined by the degree of phase segregation and the melting temperature of the crystallisable soft segments.

Ghatge et al[96] studied the effect of low molecular weight aliphatic diols on the polyurethane elastomers prepared from HTPBD. Hydroxyl terminated polybutadienes were prepared by using azo initiators such as di(4-hydroxybutyl)-2,2' azo bis isobutyrate and di(3-hydroxyl butyl)-2,2' azo bis isobutyrate, one of which contained primary and the other secondary hydroxyl groups. Physical properties of the polyurethanes prepared from these HTPBD's are compared with those of the urethanes prepared from ARCO 45 M. It was found that the physical properties of the elastomers increase with increase in molar ratio of low molecular weight diol to HTPBD.

1.5 Scope of the present investigation.

It is revealed from the literature reviewed above that the studies made so far on depolymerisation on natural rubber so as to get a suitable product which can be used for further applications such as chain extension, are not quite successful. Only Gupta[19] and to a certain extent Pautrat[71] and Brosse[1] succeeded in preparing depolymerised natural rubber with desired functional groups. Gupta[19] reported the preparation of Hydroxyl terminated liquid natural rubber using hydrogen peroxide as the reagent but the processing conditions viz. high temperature and pressure may aggravate side reactions and also the efficiency of functionalization reported was also very low. Hydroxyl end groups are most suitable for chain extension reactions especially for polyurethane synthesis.

Hence there is ample scope to develop a method for the production of HTNR with minimum amount of side products; photochemical degradation of natural rubber was studied earlier by many scientists.[59-64, 67,68-70] None of them however, has reported the formation of hydroxyl end groups during the process. So it was decided to adopt photochemical method for depolymerising natural rubber and to hydroxylate it at chain ends.

Segmented polyurethanes are a class of thermoplastic elastomers of great commercial importance. These materials derive most of their useful properties from the incompatibility of the hard and soft segments. Segmented polyurethanes incorporating a hydroxy-terminated polybutadiene (HTPBD) soft segment offer the advantage of low moisture permeability and have been the subject of several studies aimed at exploiting this property for adhesives and electrical potting compounds. In analogy HTNR based polyurethanes should also be a phase segregated system and more over the strain induced crystallisation of the soft segment is expected to give better properties than HTPBD containing polyurethanes. This class of materials is also of interest as a model system in which there is no possibility of hydrogen bonding between hard and soft segment, in comparison with the more familiar polyester or polyether polyurethanes. Since the hydrogen bonding interactions are limited to the hard segment fractions, studies of HTNR containing polyurethane could throw further light on the role of hydrogen bonding in determining the extent of phase segregation, the stability of the hard segment domain structure and other related polyurethane properties.

The thesis is divided into the following chapters:

Chapter 1 : Introduction

Chapter 2 : Production of Hydroxyl Terminated Liquid Natural Rubber.

Chapter 3 : Synthesis and Characterization of Segmented Polyurethanes based on HTNR soft segments.

Chapter 4 : Studies on Block Copolymers from Poly(ethylene oxide) and HTNR.

Chapter 5 : Summary and Conclusion.

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CHAPTER - II

PRODUCTION OF HYDROXYL-TERMINATED LIQUID NATURAL RUBBER (HTNR)

2.1 Materials

Natural crumb rubber (ISNR-5, $\overline{M}n$ = 820,000, intrinsic viscosity in benzene at $30^{\circ}C$ = 4.45 dl/g, wallace plasticity P_0 = 39.0) was supplied by the Rubber Research Institute of India, Kottayam. Hydrogen peroxide - 30% W/V solution supplied by E. Merck (India) was used. Toluene, commercial grade (Trimoorthy Traders, Bombay), Tetrahydrofuran (THF) (E.Merck, India) and Methanol (BDH, India) were distilled before use.

2.2(a) Depolymerisation procedure

A 5 wt % solution of NR in toluene was mixed with 30% W/V H_2O_2 solution and methanol in the volume ratio 20:1:3 respectively. Alternatively a 5 wt % solution of NR in toluene was mixed with a 30% W/V H_2O_2 solution and tetrahydrofuran in the volume ratio 20:1:5 respectively. Irradiation was carried out in a closed glass vessel with constant stirring using a Phillips HPK-125 W high pressure mercury vapour lamp. In each case aliquots were withdrawn at definite intervals of time for analysis.

2.2(b) Large scale production of HTNR

(i) By ultraviolet radiation (Expt.1):

Natural crumb rubber was masticated for 30 minutes at 40°C, one kilogram of it was dissolved in 10 litres of toluene, and the solution was charged into a photochemical reactor, a borosilicate glass vessel of 15 litres capacity fitted with a water condenser and a mechanical stirrer. Hydrogen peroxide solution (500ml) was added and thoroughly mixed with the rubber solution. The mixture was then homogenized to a certain extent by the addition of 1.5 litres methylalcohol or 2.5 litres tetrahydrofuran as the case may be. The 400 W medium pressure mercury vapour lamp (obtained from SAIC, Madras) in an immersion well was placed in the solution.

After about 60 hrs. of irradiation 2g of hydroquinone (about 0.02 % W/V of the reaction mixture) was dispersed in the solution and was allowed to stand for 30 minutes. A layer of water separated at the bottom along with some white deposits as byproduct. This was removed, and the liquid rubber was recovered from the top toluene layer by distilling off the solvent under low pressure. Finally, the product was washed with methanol, treated with 0.5% W/W Santowhite M.K. antioxidant and dried in vacuum. The sample for analysis was purified by repeated precipitation by methanol from a toluene solution and dried in a vacuum oven. The byproduct was washed with methyl alcohol and dried in a vacuum oven to get 10% yield of a highly viscid material.

(ii) By sunlight (Expt.2):

The reactor consisted of a flat bottomed borosilicate glass flask of 15 L capacity. It was fitted with a water condenser and a mechanical stirrer. The whole assembly with the material for irradiation having the same composition as in the above method, was placed in sunlight. After 60 hrs. exposure the liquid rubber was recovered by the procedure described above.

2.3 Measurements

The molecular weight distributions were determined using a gel permeation chromatograph (GPC) (Waters Associates, Model 6000A solvent delivery system with differential refractometer R-401). IR spectrum was recorded in a Perkin-Elmer Model 377 IR spectrometer. The ^{1}H-NMR spectrum of the samples were recorded from a solution in $CDCl_3$ using a JEOL - JNM spectrometer in the CW mode. The ^{13}C-NMR spectrum (proton decoupled) was recorded under ambient conditions from a solution in $CDCl_3$ using a JEOL-FX 90 Q FT NMR Spectrometer operating at 22-49 MHz. TMS was used as the internal standard. Solution viscosity was measured in toluene solvent using the Ubbelhode viscometer. Hydroxyl, hydroperoxide, carboxyl and carbonyl groups were estimated using standard methods[1,2].

The depolymerised rubber was compounded in a Brabender Plasticorder (PL-3S) and tensile measurements were done in a Zwick Universal Testing Machine (1445).

2.4 Results and Discussion

(i) Mechanism of depolymerisation of NR:

The molecular weight measurements at different intervals of time for the depolymerisation of NR in UV light from a high pressure mercury vapour lamp is listed in Table I, (Expt. 2.2(a) and those from 2.2(b) (i) and 2.2(b) (ii) are listed in Table II and Table III respectively. Figure 1 represents the GPC traces of the products from 2.2(b) (i) and Figure 2 those from 2.2(b) (ii). From these data it is clear that sunlight is almost as effective as UV light in bringing about degradation of NR in solution. There is a continuous decrease in molecular weight as the irradiation progresses, and liquid rubber resulted after 30 hours of irradiation in 2.2(a) and after 60 hours in 2.2(b)(i) and 2.2.(b) (ii) respectively. Production cost is very low in 2.2.(b) (ii) since sunlight is readily available in tropical countries like India. The use of masticated rubber in 2.2(b) (i) & (ii) helped to increase the concentration of the rubber solution from 5 wt % in 2.2(a) to 10 wt %. This increased the

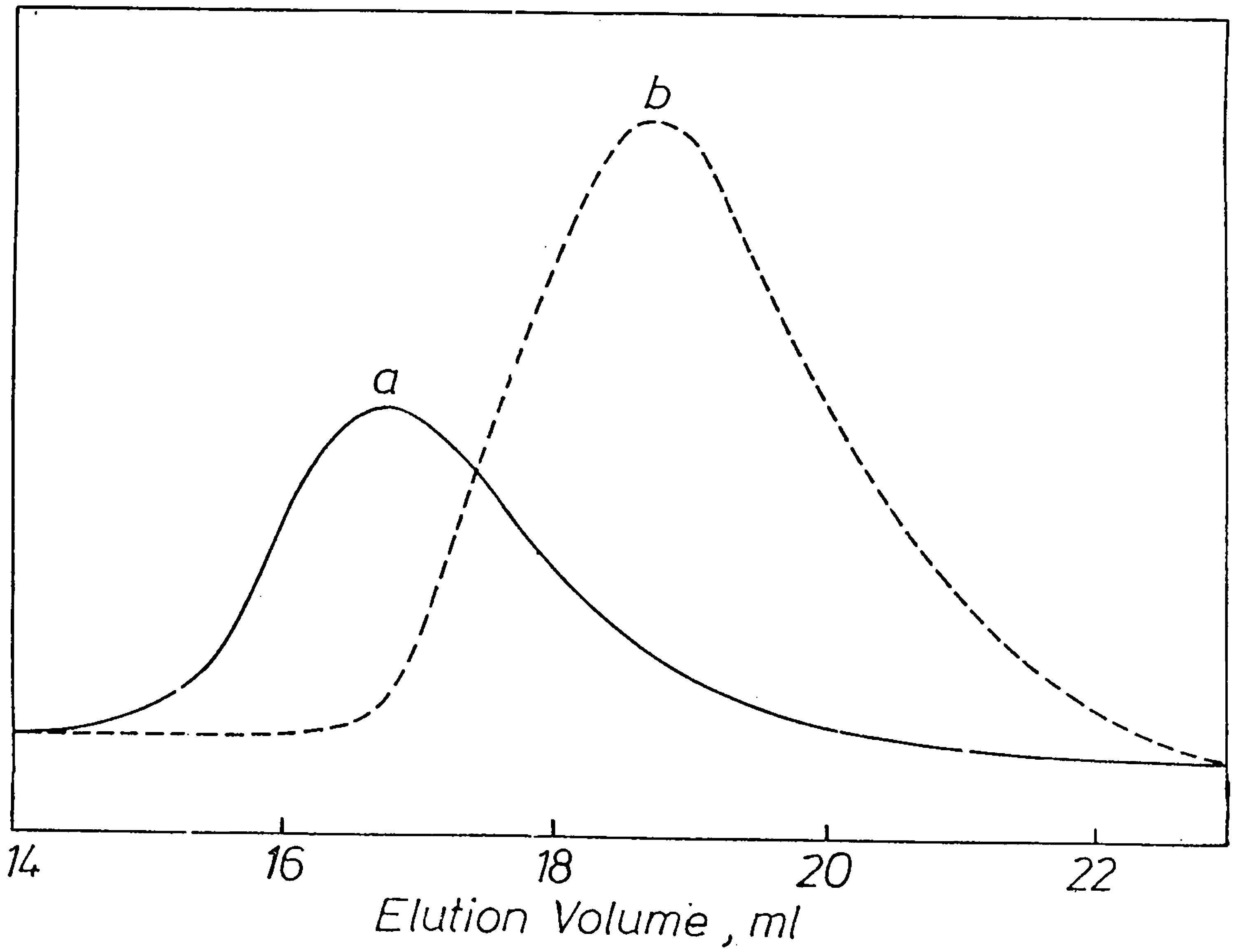


Fig.1 GPC Traces of HTNR Samples obtained by UV irradiation (a) 30 hrs (b) 60 hrs.

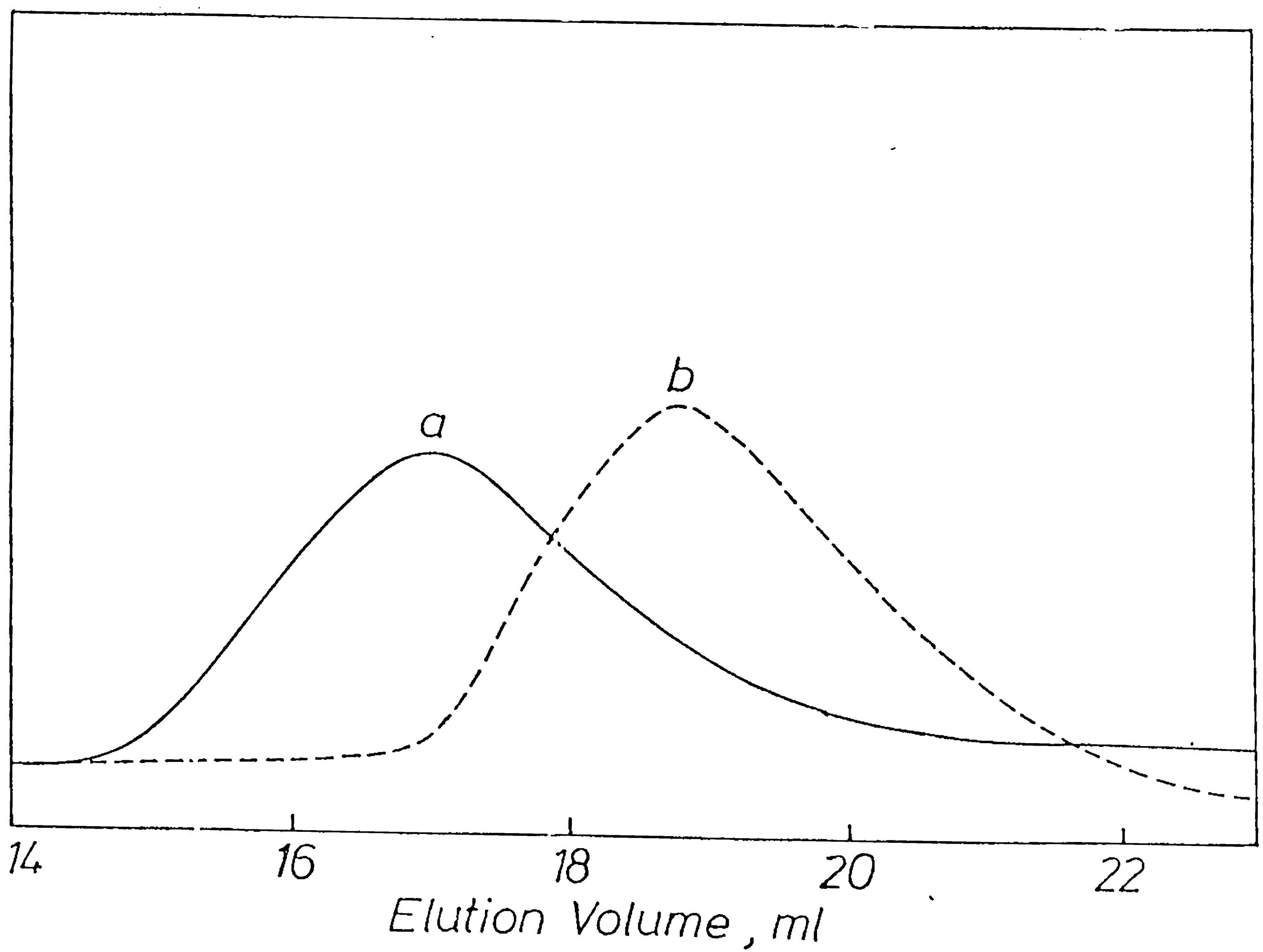


Fig.2 GPC Traces of HTNR Samples obtained by Sunlight irradiation for (a) 30 hrs. (b) 60 hrs.

TABLE - I

Dependence of molecular weight on irradiation time.

Time of irradiation	Homogenising solvent					
	Methanol			T H F		
	$\bar{M}n$	$\bar{M}w$	D**	$\bar{M}n$	$\bar{M}w$	D**
5	38000	67600	1.77	31600	51900	1.64
10	20800	41400	1.99	13200	24900	1.89
20	9600	20400	2.12	6900	14200	2.06
30	8700	15100	1.72	5000	8100	1.61

a Corrected to the nearest hundred

* Light source HPK 125W mercury vapour lamp

** Molecular Weight dispersity.

TABLE - II

Dependence of Molecular Weight[a] on the Time of Exposure to UV Radiation.

Time of irradiation (hrs)	Homogenising solvent, Tetrahydrofuran					Homogenising solvent, Methanol				
	$\bar{M}n$	$\bar{M}v$	$\bar{M}w$	$\bar{M}z$	D^b	$\bar{M}n$	$\bar{M}v$	$\bar{M}w$	$\bar{M}z$	D^b
10	244200	392800	441600	636900	1.80	301400	421000	592000	714600	1.96
20	42500	78000	89400	169800	2.10	94300	192100	252600	479900	2.67
30	21000	39100	46900	84400	2.23	44700	81200	91400	163600	2.04
40	6900	12400	14200	24300	2.06	8400	13400	15200	31900	1.80
50	4100	6900	8300	17400	2.02	5300	7900	9500	18000	1.79
60	2300	3900	6400	11600	2.78	3000	4200	7200	13100	2.40

a Corrected to nearest hundred

b Molecular weight dispersity.

TABLE - III

Dependence of Molecular Weight[a] on Time of Exposure to Sunlight

Time of irradiation (hrs)	Homogenising solvent, Tetrahydrofuran					Homogenising solvent, Methanol				
	$\overline{M}n$	$\overline{M}v$	$\overline{M}w$	$\overline{M}z$	D[b]	$\overline{M}n$	$\overline{M}v$	$\overline{M}w$	$\overline{M}z$	D[b]
10	301500	413000	521200	742400	1.72	394100	492700	601900	812700	1.52
20	49600	89100	94200	178300	1.89	114900	212500	284200	596800	2.47
30	26000	42400	48100	101000	1.84	61000	89100	131400	233500	2.15
40	8400	13200	15100	28900	1.79	10500	18300	19600	36200	1.86
50	4700	8100	9400	24100	2.00	6200	8900	10600	28900	1.70
60	2900	4700	7100	18400	2.40	3300	5100	8200	20800	2.48

a Corrected to the nearest hundred

b Molecular weight dispersity.

production rate, even though the irradiation time had to be increased from 30 hours to 50 hours to get a molecular weight (Mn) of around 5000. However, the concentration was limited to 10 wt % beyond which the solution formed was not workable.

HTNR with any range of molecular weight could be prepared by suitable choice of the composition of the reaction mixture and exposure time. The hydroxyl functionality remained slightly less than 2 (vide infra). The extent of depolymerisation was found to increase with decreasing concentration of NR, increasing amount of hydrogen peroxide and also by longer exposure time. Varying the amount of homogenizer ie. tetrahydrofuran or methylalcohol, beyond the specified amount did not have any effect on depolymerisation. The choice of tetrahydrofuran rests on the fact that it is miscible with both toluene and aqueous H_2O_2 and at the same time it can dissolve rubber also. Methyl alcohol, being a nonsolvent to NR, has the advantage that the viscosity of the reaction mixture will be slightly reduced by its addition[3]. The extent of degradation was slightly higher when THF was used. However, on the basis of production cost, methyl alcohol is preferred in the large scale production of HTNR.

The liquid NR recovered from the solution after distillation of the solvent under reduced pressure was almost clear and colourless. When this material was kept for a few days, its viscosity gradually increased. This drawback entailed processing modifications. Hence after depolymerisation, about 0.02% W/V of hydroquinone was dispersed in solution for the removal of radical species that may be present in the solution. The recovered material was further modified by adding 0.5% W/W of Santowhite M.K, a nonstaining antioxidant. These modifications render the HTNR slightly coloured, and it could be stored without any appreciable change in viscosity. The addition of phenyl β -Naphthylamine caused the material to become profusely coloured, and hence it was not used as antioxidant for the HTNR.

Hydroxyl group estimation by acetylation and phthaloylation methods gave an average value of 12.06 mg of KOH/g and 21.22 mg of KOH/g which gave functionalities of 1.87 and 1.91 respectively for samples from 2.2 (a) after 30 hours irradiation and 36.27 mg of KOH/g and 30.94 mg of KOH/g which gave functionalities of 1.94 and 1.82 respectively when methanol was used as homogenising solvent, and 47.80 mg of KOH/g and 36.56 mg of KOH/g, which gave functionalities of 1.96 and 1.89 when THF was used as the homogenizing solvent in 2.2(b) (i) & (ii). The possible presence of hydroperoxy groups (-OOH) in the depolymerised samples was ruled out by the negative results obtained when estimations of hydroperoxy groups were carried out iodometrically. Another group likely to be formed during depolymerisation process by oxidative cleavage of the rubber molecules, is the carbonyl group (C=O). Spectral data did not give any significant indication of its presence and its estimation by the hydroxylamine method[1] gave only a very low value of 1.42 mg of KOH/g, which indicated that its probable presence due to a side reaction is negligible.

The presence of primary hydroxyl groups in the depolymerised product was confirmed by the IR absorptions at
3600 - 3400 cm^{-1} (broad O-H, Str.); 3040 (m), 2980 (s), 2920(s), 2860 cm^{-1} (s) (C-H Str.); 1660 cm^{-1} (m)(C=C, cis Vinylene); 1450(s), 1375 cm^{-1} (s) (C-H, def.); 1310 cm^{-1} (m) (C-O, Str., aliph. prim. alcohol); 885 cm^{-1} (m) ($-CH_3$ def.); 830 cm^{-1} (s) (C-H, out of plane def. in $-CHR = CCR^1$).

The IR spectrum of the samples obtained by UV light and sunlight irradiation are given in figs. 3 and 4 respectively.

Fig.3 IR Spectrum of HTNR obtained by UV irradiation.

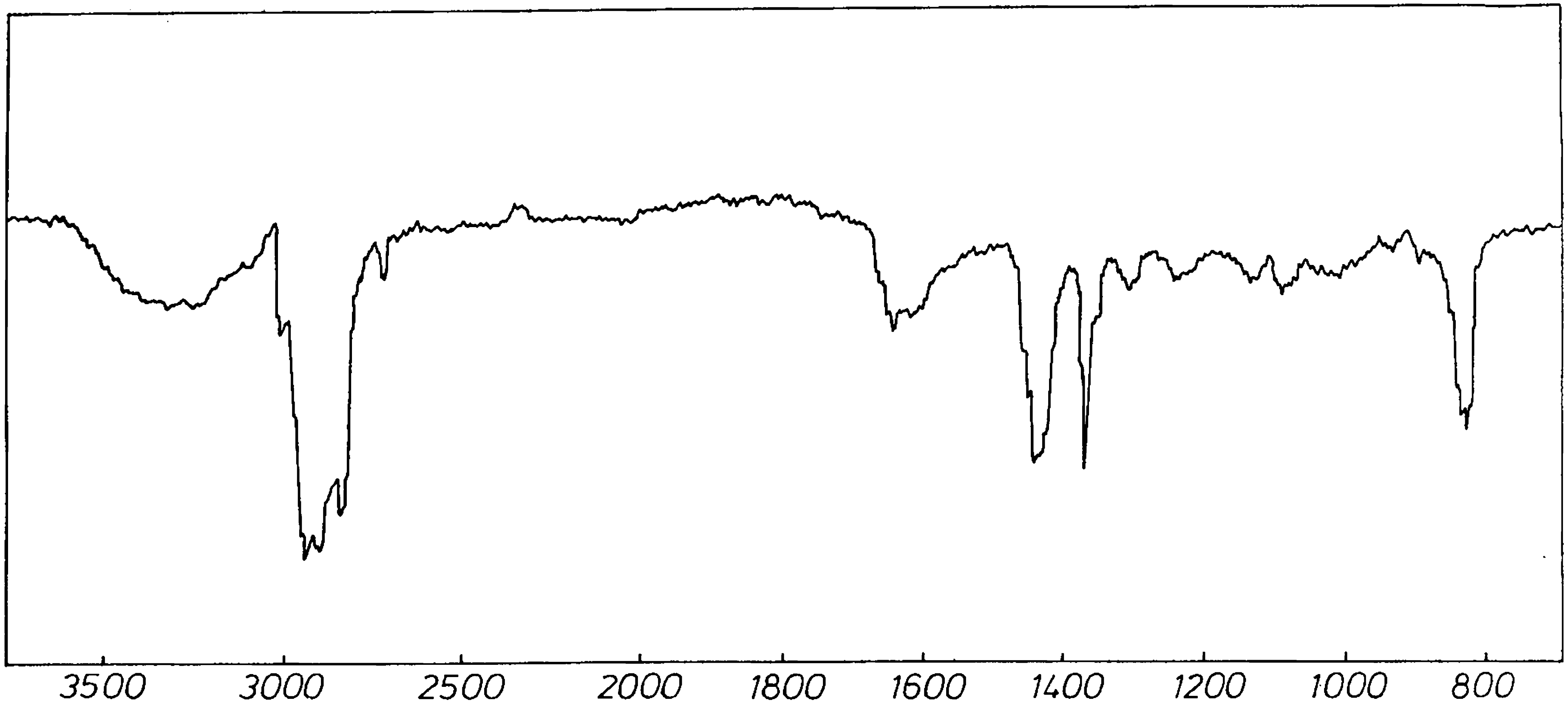


Fig.4 IR Spectrum of HTNR obtained by Sunlight Irradiation.

The ^{1}H-NMR and ^{13}C-NMR spectra in $CDCl_3$ at 25°C of the products (Figs.5, 6, 7 and 8) gave further support to the above conclusion.

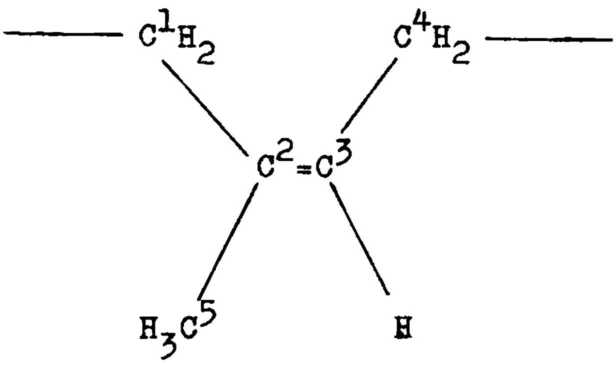
^{1}H-NMR:

δ = 1.60 (S; $-CH_3$, 3H); 2.0 (S; $-CH_2-C{=}C$, 4H);
5.1 (M; $>C = C<_{H}$, 1H)

The spectrum also contains minor peaks at δ = 1.22, 1.3 and 2.4 indicating the probable presence of side products. In both cases the signal due to allylic hydroxyl protons in the ^{1}H-NMR spectra are masked by the multiplets at δ = 5.1 of the $>C = C<_{H}$ protons.

The FT ^{13}C-NMR spectra indicates ^{13}C shieldings typical of cis 1,4-polyisoprene at the following positions.

C^1 : δ = 32.23; C^2 : δ = 135.16; C^3 : δ = 125.03;
C^4 : δ = 26.38; C^5 : δ = 23.40



Apart from these major peaks the spectra also contains minor peaks at δ = 78.39, 76.98 and 75.57 due to $CDCl_3$.

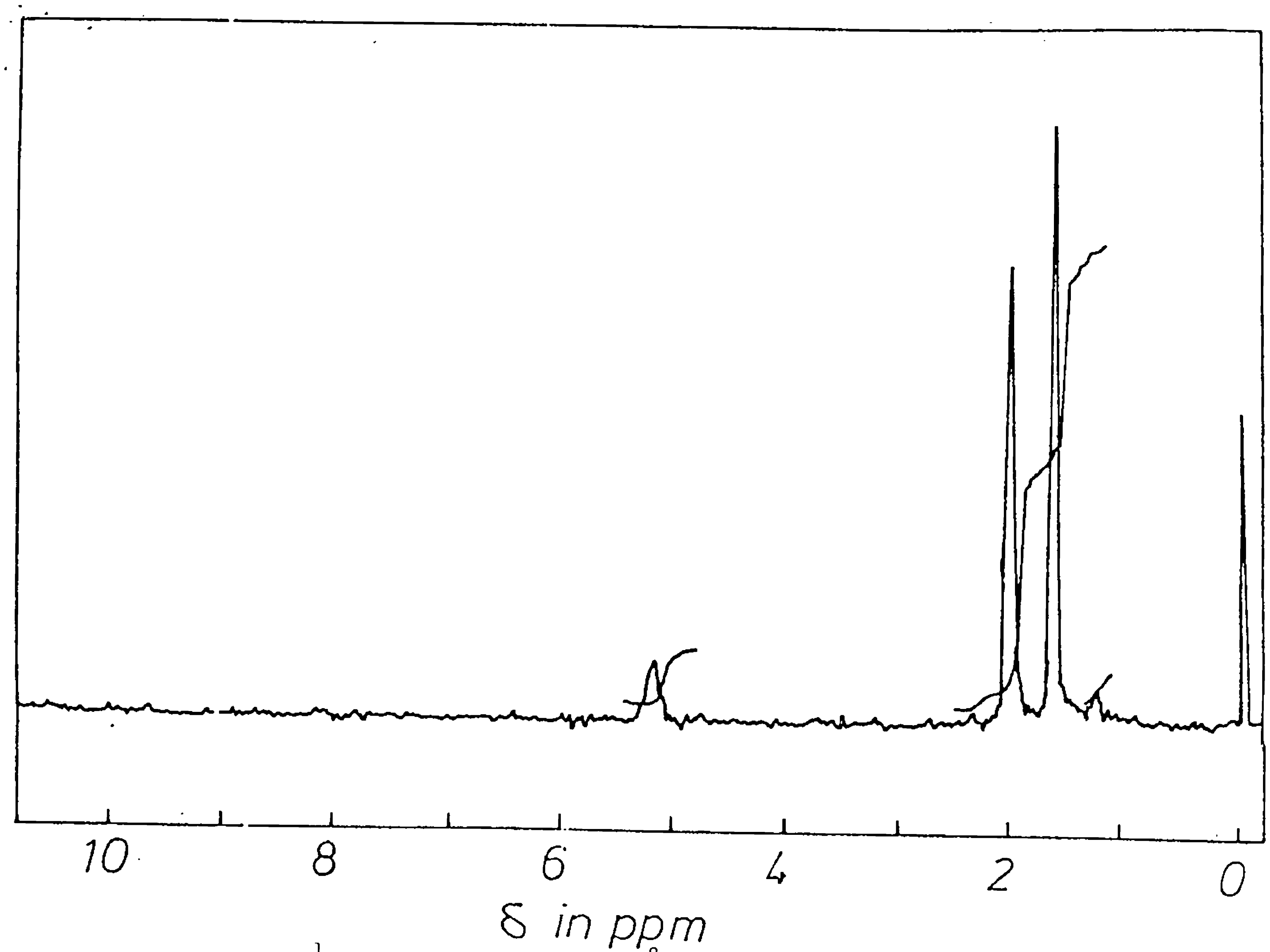


Fig.5 ^{1}H-NMR Spectrum /$CDCl_3$/25°C of HTNR by UV Irradiation.

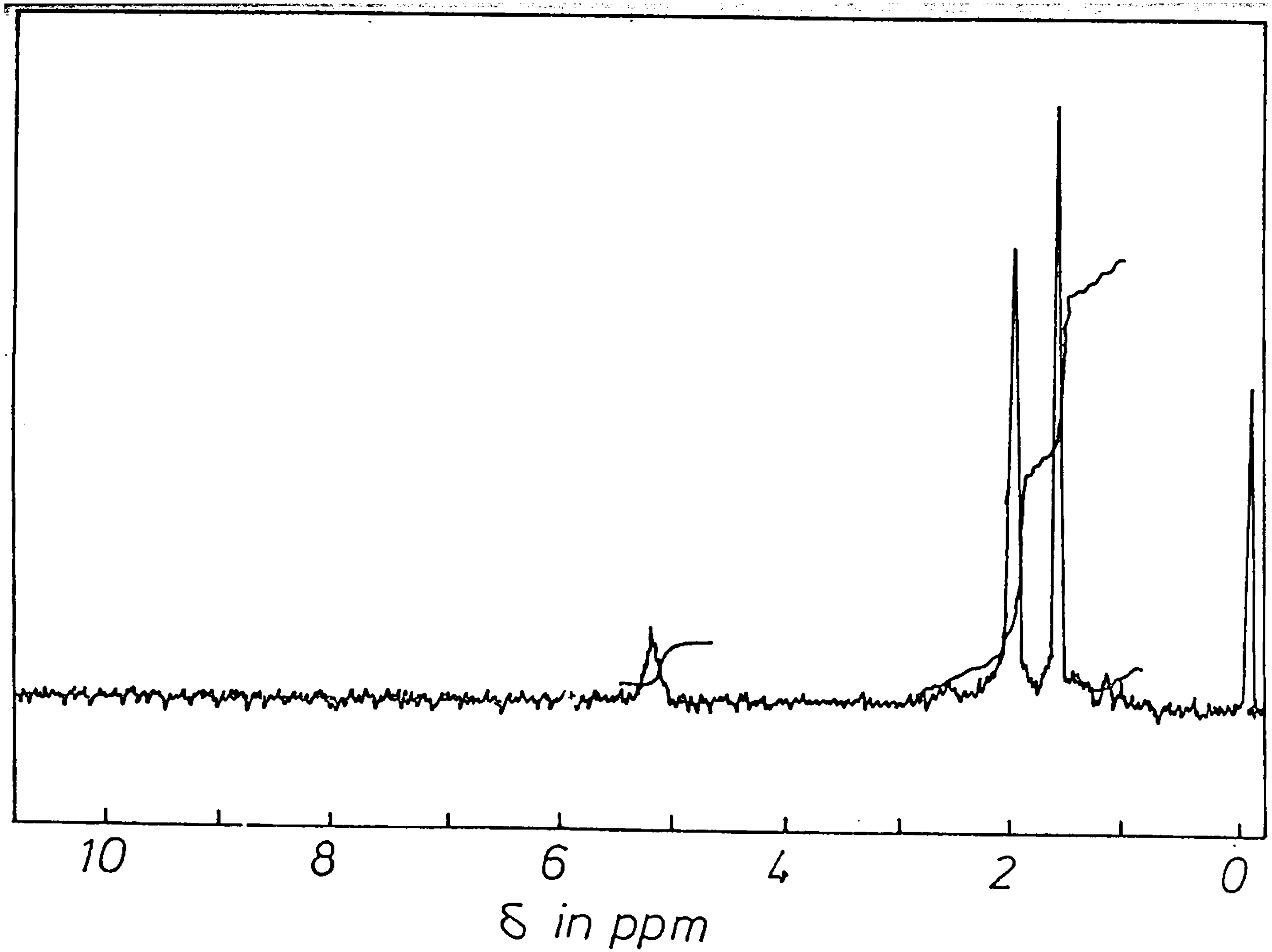


Fig.6 ^{1}H-NMR Spectrum/$CDCl_3$/25°C of HTNR by Sunlight Irradiation.

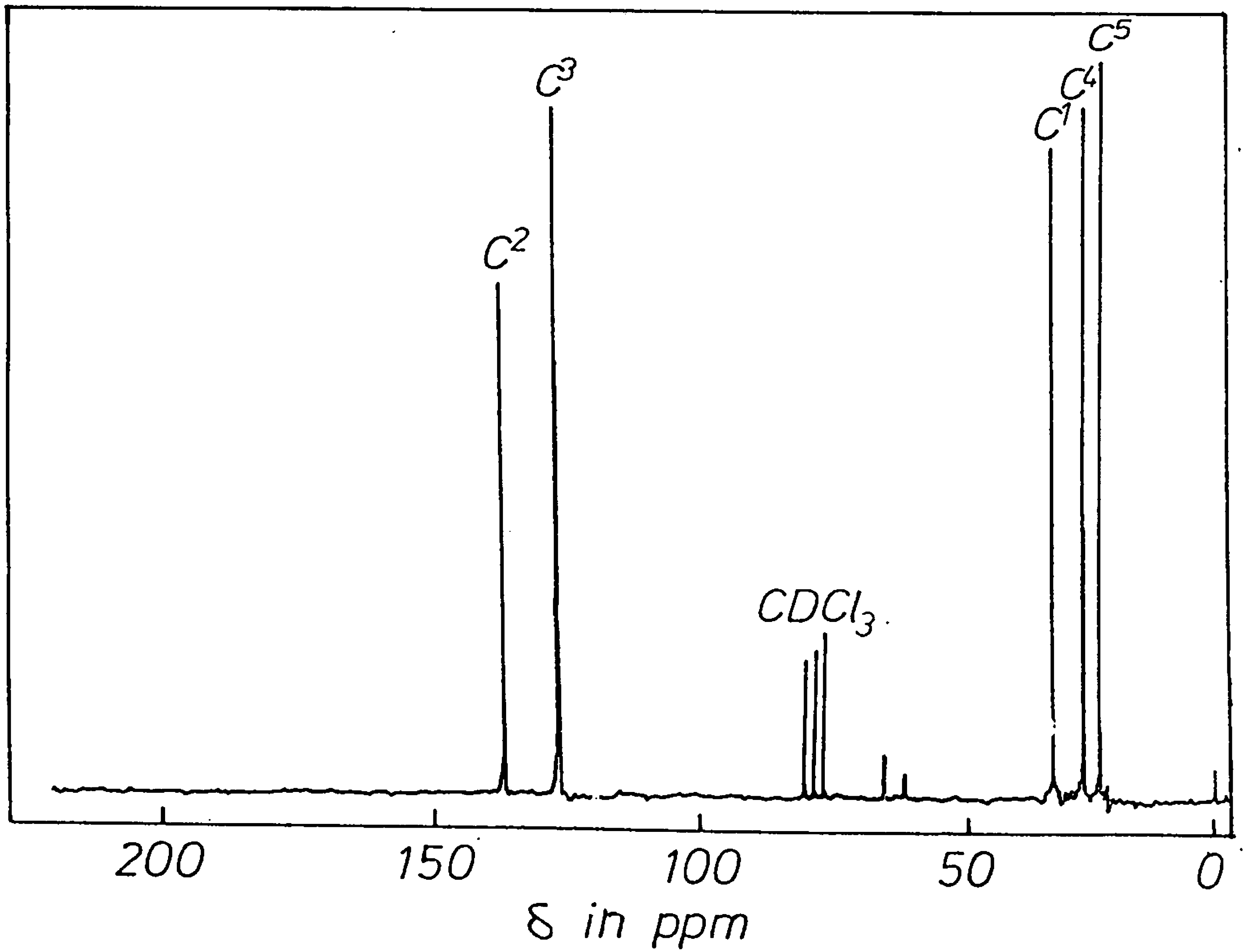


Fig.7 ^{13}C-NMR[H] Spectrum/CDCl$_3$/25°C of HTNR by UV Irradiation

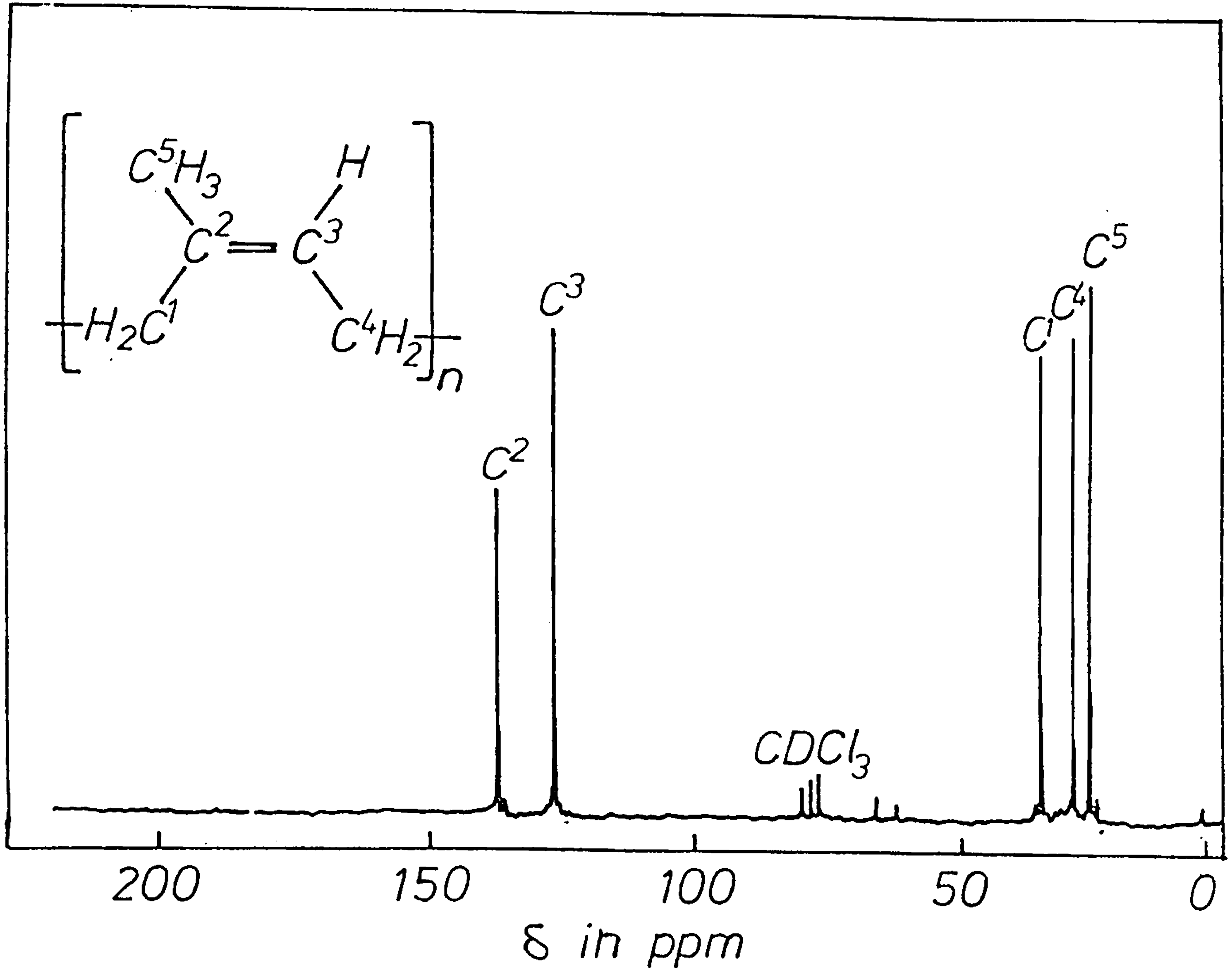
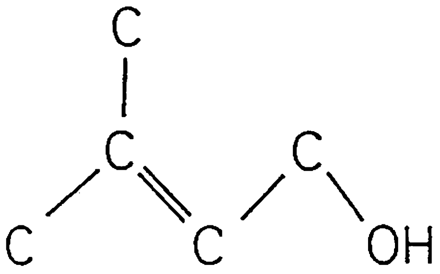
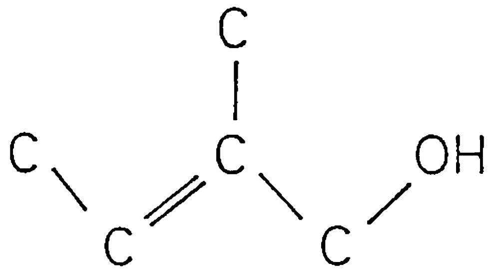


Fig.8 ^{13}C-NMR [H] Spectrum/$CDCl_3$/25°C of HTNR by Sunlight Irradiation.

The minor peaks at $\delta = 60.72$ and 63.51 are in close agreement with the reported values for the β - carbons attached to the hydroxyl groups in structures like A and B respectively.[4]



A



B

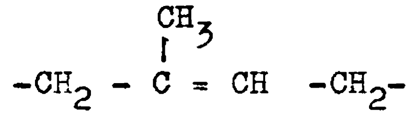
The slight shift of the peak position of structure B is attributed to the presence of an additional methyl group at the β -carbon. These observations and a functionality of approximately two obtained for the products lead to the conclusion that the depolymerised NR has hydroxyl end groups. The depolymerisation process does not affect the stereoregularity of NR which is confirmed from the simplicity of the ^{13}C-NMR spectra (with respect to C^1 and C^5 shieldings). Moreover the products obtained after depolymerisation readily reacted with diisocyanates such as toluene 2,4 diisocyanate, leading to chain extension. Rapid reaction with isocyanate is characteristic of primary hydroxyl groups. The reactivity of the hydroxyl group towards diisocyanate decreases in the order primary secondary tertiary. This observation along with the aforementioned findings corroborates the presence of primary hydroxyl groups at the chain ends of the liquid rubber.

The identical nature of the products obtained from all the three experiments suggested that course of degradation process follows the same path. In the light of analytical data obtained in the present studies and the theories of earlier investigators, a mechanism of chain scission and hydroxylation is discussed below:

The most probable point of attack on the NR molecule is the α-methylene carbon atom. This is supported by the fact that, in oxidation processes, the initial product is a hydroperoxide and that there is no change in the degree of saturation[5]. The presence of a $-CH_3$ group attached to the ethylenic carbon atom in polyisoprene tends to reduce the C–H dissociation energy by hyperconjugation, facilitating substitution at the 2-methylenic carbon atom[6]. The studies on light ageing of NR has established that the double bonds in the chains are not affected in the initial stages and they disappeared slowly only after prolonged exposure to light[7-9].

Based on the foregoing discussion it is inferred that whether it is degradation by chemical species or by radiation, the point of attack is not the double bond in the chain but the C^{α} – H bond.

It is further evidenced by the fact that there is no change observed in the IR absorption band of the isoprene unit,

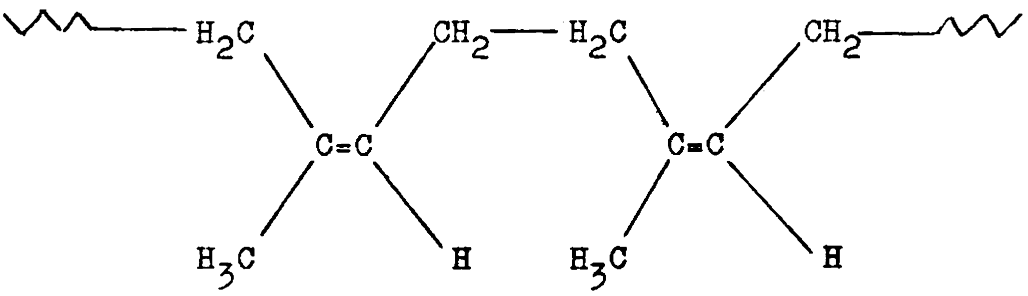


$$-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$$

viz. 830 cm^{-1} in IR spectra. (Figs. 3 & 4)

In all the earlier proposals free radical mechanism has been suggested for the degradation of NR. The chemical reagents used in the process are free radical generators such as thiols, peroxides etc[10-13]. These free radicals interact with the labile C^{α} - H proton, giving rise to macroradicals[6,14,15] In a similar manner in the photochemical degradation, the photons remove the C^{α} - H proton, giving rise to macroradicals[7]. The peroxide formed by the interaction of these radicals with oxygen decompose to yield the various degradation products containing the carbonyl, carboxyl and hydroxyl groups at the chain ends[7,14,16]. The estimation of hydroperoxide group and the identification of carbonyl and carboxyl groups were given as proof of participation of oxygen in the degradation process.

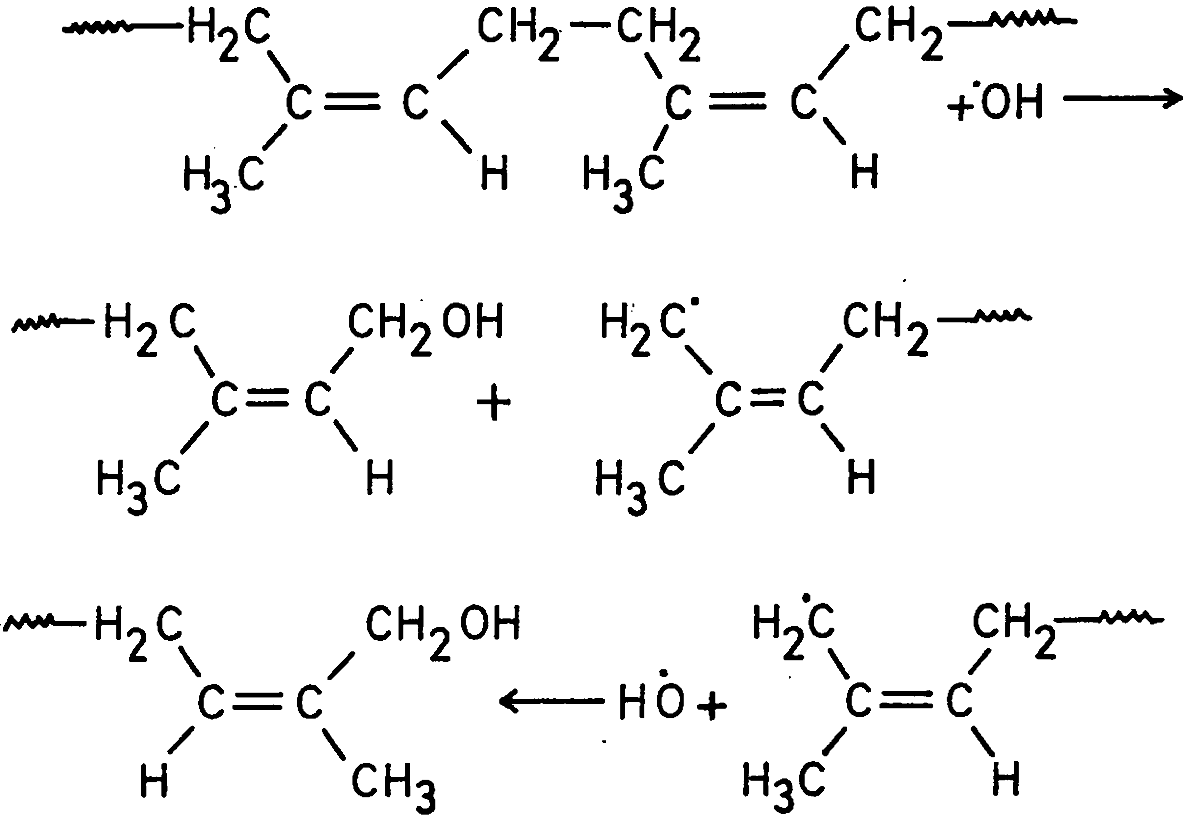
However, analysis of the main product obtained in the present studies did not show any indication of the presence of peroxide, carbonyl and carboxyl groups. The hydroxyl functionality of very nearly two and the absence of the other oxygen bearing groups suggest that a mechanism other than the conventional one is to be sought in the present processes. In our studies we could clearly establish, with the aid of spectral data, the existence of structures A & B (page 52) in the depolymerised products. The generation of such structural entities entails the cleavage of the original rubber molecule in between the α-carbon atoms. In the case of NR the σ- bond between α -methylenic groups which connect the isoprene units are not in the same plane with the double bonds. This is because there is a tendency of coiling up of the rubber segments due to its cis configuration.



The steric hindrance caused by such an unbalanced structure with pendent methyl groups weakens the CH_2-CH_2 bond, leading to its rupture under favourable conditions which are provided by thermal energy[17,18] or the chain modifications caused by radical species[14,19] or by radiation[7,20,21]. The radical reagent used in the degradation process, namely hydrogen peroxide, is

$$H_2O_2 \xrightleftharpoons{h\nu} H_2O_2^{*}$$

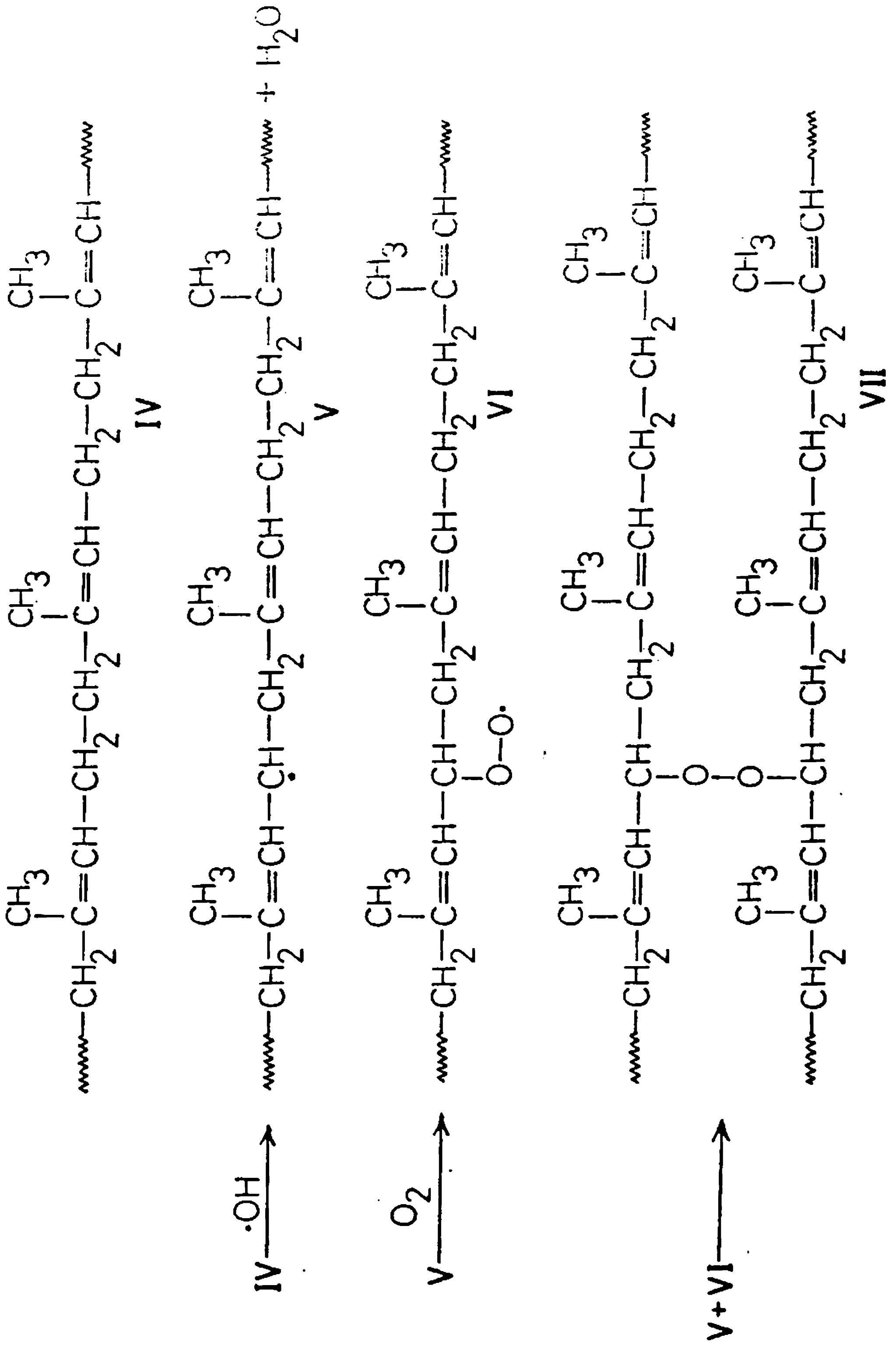
$$H_2O_2^{*} \longrightarrow 2\,{}^{\bullet}OH$$

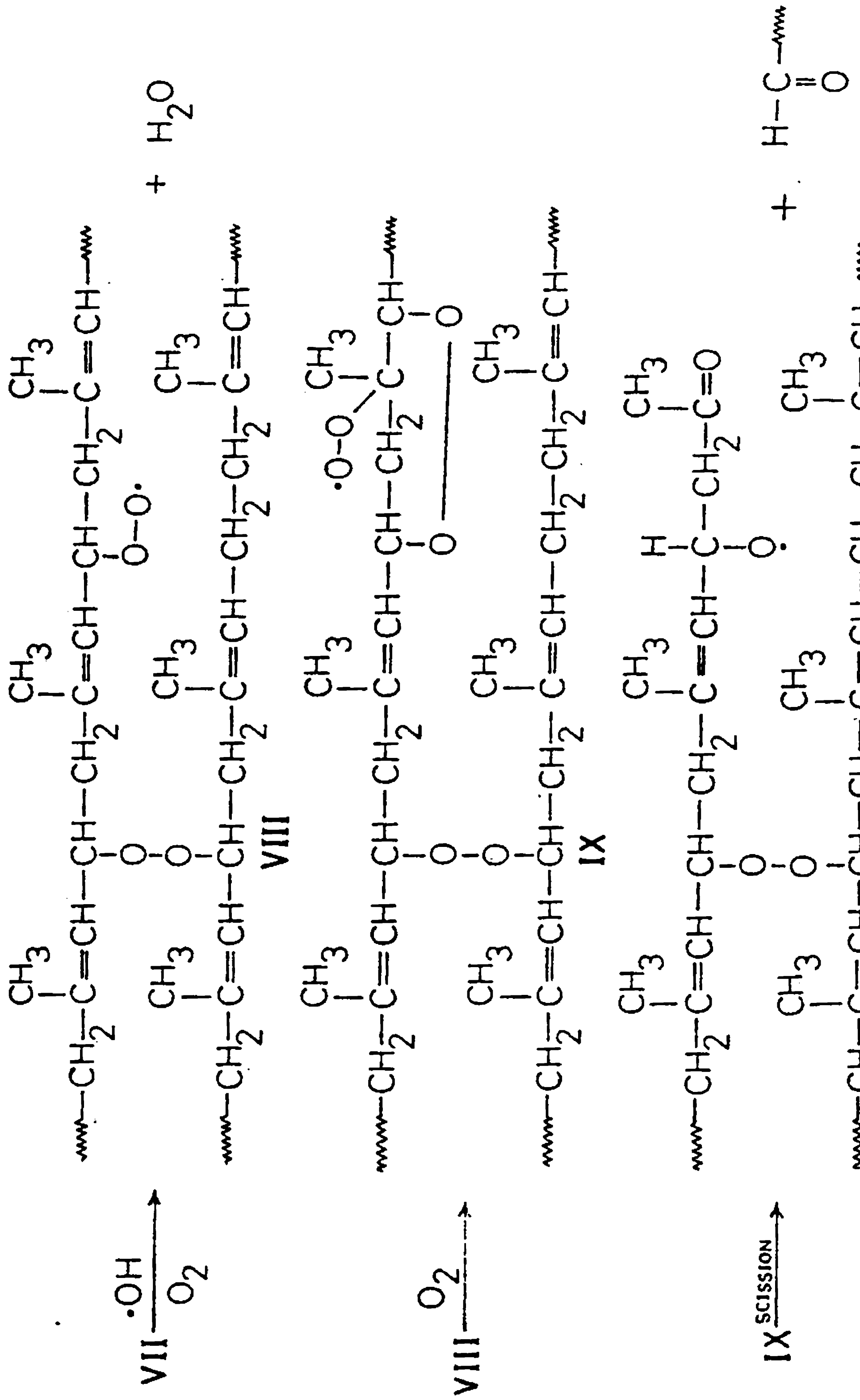


susceptible to decomposition under the influence of radiation up to 370 nm, yielding hydroxyl radicals[22].

Based on the above discussion, the following mechanism is suggested for the depolymerisation and hydroxylation of NR (see page 56).

The byproduct isolated from the reaction mixture was found to contain carbonyl group (IR peak 1710 cm^{-1}) in Fig. 9. Chemical analysis of the material gave hydroxyl value of 18.46 mg of KOH/g, carboxyl value of 5.94 mg of KOH/g and carbonyl value of 12.29 mg of KOH/g. The formation of these groups may be through side reaction with free oxygen, giving peroxide radicals and subsequent decomposition. The low solubility of the byproduct and the observation that its yield increased with increase in rubber concentration, hydrogen peroxide and irradiation time, show that crosslinking plays an important role in its formation. Based on these factors, the following mechanism in which the macroperoxide crosslink and also decompose to yield carbonyl and carboxyl groups is proposed.


IV
IV
·OH
V
+ H_2O
V
O₂
VI
V+VI
VII


VII
•OH
O2
+ H2O
VIII
O2
IX
SCISSION
+

(ii) Mechanical properties of HTNR vulcanizate:

With a view to study the change in mechanical properties caused by the depolymerisation process, the liquid NR was compounded as per a conventional recipe . The properties of the vulcanized material are listed in Table IV. On comparison with properties of a standard vulcanizate, considerable loss in properties was observed, which is due to the reduction in chain length of the rubber molecule caused by depolymerisation.

TABLE - IV

Compounding and Mechanical properties of HTNR

	Depolymerised Rubber $\bar{M}n$-10,500	Control sample (Crumb rubber)
Formulation		
Rubber	100	100
ISAF black	50	50
ZnO	5	5
Stearic acid	2	2
Sulfur	2.5	2.5
CBS	0.8	0.8
PBN	1.0	1.0
Properties		
Tensile strength (MPa)	10.2	28.7
Stress at 200% (MPa)	6.8	6.7
Stress at 300% (MPa)	9.1	8.8
Elongation at break (%)	324	580
Hardness, Shore A	47	62

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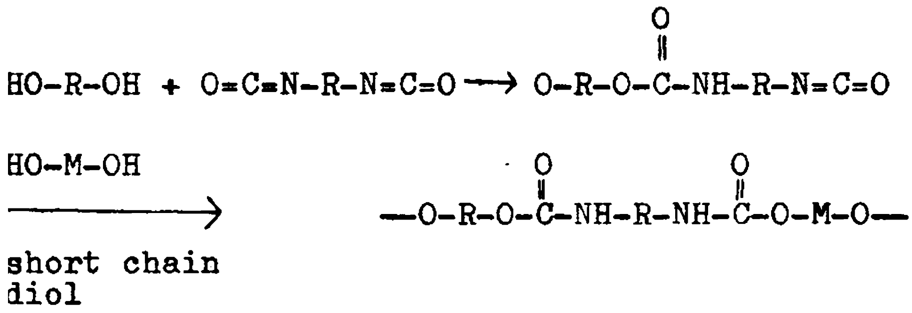
CHAPTER - III

SYNTHESIS AND CHARACTERISATION OF SEGMENTED POLYURETHANES BASED ON HTNR SOFT SEGMENTS.

3.1 Introduction

The most widely used method for the preparation of polyurethanes, in general, is the reaction of di or poly functional hydroxyl compounds such as hydroxyl terminated polyethers or polyesters and hydroxyl terminated polybutadienes with di or poly isocyanates in presence of a chain extender viz. a short chain diol or diamine.



$$HO{-}R{-}OH + O{=}C{=}N{-}R{-}N{=}C{=}O \longrightarrow O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}N{=}C{=}O$$

$$\xrightarrow[\text{short chain diol}]{HO{-}M{-}OH} {-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}M{-}O{-}$$

If difunctional reactants are used, linear polyurethanes will result. When the functionality of the hydroxyl or isocyanate compound is increased, branched or crosslinked polymers will be obtained. The properties of the polymers depend upon the molecular weight, degree of crosslinking, effective intermolecular forces, stiffness of the chain segments and crystallinity. Because of the many structural variations possible in their formation, the urethanes may be considered as the most versatile polymer. The different grades of polyurethanes which are of commercial significance are flexible foams, rigid foams,

elastomers, surface coatings and adhesives.
Solid urethane elastomers were developed in the early 1940's in Germany and England. The introduction of liquid casting techniques by Muller made possible the manufacture of urethane elastomers based on either polyesters or polyethers. Solid urethane elastomers are now widely used and are well known for their general toughness, excellent wear and tear properties and good oil resistance. Elastomeric polyurethane block copolymers consist of alternating blocks of flexible chains of low Tg (soft segments) and highly polar and relatively rigid blocks (hard blocks). The micro phase separation of these two dissimilar blocks produces regions of hard block concentration which act as crosslink points for the soft blocks. This microphase separation and the hydrogen bonded domain structure which results from it, is now recognised as the principal feature controlling the properties of these elastomers.

3.2 Materials

Hydroxyl terminated liquid natural rubber (HTNR) with $\overline{M}n$ = 3000 and having a functionality of 1.94 (prepared in our lab by a method described earlier in Chapter 2) is used. Toluene diisocyanate (80/20 mixture of 2,4 and 2,6 isomers) and Dibutyl tin dilaurate (DBTDL) obtained from Fluka,Switzerland were used. Butane 1,4 diol was obtained from BDH, England. Tetrahydrofuran (THF) was of reagent grade, dried and distilled before use.

3.3 Preparation of polyurethanes

The overall composition of the polyurethanes prepared are given in Table V. The two techniques generally used for the synthesis of polyurethane elastomers are (a) one step process and (b) two step process.

3.3(a) One step process

The required stoichiometric amount of HTNR, butane 1,4 diol and DBTDL (0.03% by wt. of HTNR) were taken in a resin kettle which was maintained at 70°C in a nitrogen atmosphere. The materials were stirred vigorously and TDI added dropwise and stirring continued till the temperature had risen to 85°C. The product was then cast into a preheated tray treated with silicone release agent, degassed in a vacuum oven and cured at 110°C for 10 hrs followed by room temperature ageing for one week in a moisture free atmosphere.

3.3(b) Two step process-bulk polymerisation

The required quantity of HTNR along with (0.03% by wt. HTNR) DBTDL were taken in a resin kettle, provided with a dropping funnel, mechanical stirrer and an inlet and outlet for nitrogen. The

TABLE - V

Overall Composition of the Polyurethanes

Sample	Molar ratio HTNR/TDI/BDO	Percent hard segment
HTNR 10	1/2/1	12.4
HTNR 20	1/3.15/2	19.5
HTNR 30	1/5.2/4	29.7
HTNR 40	1/8.6/7.2	41.7
HTNR 50	1/12.4/10.7	51.0
HTNR 60	1/17.4/15.8	59.7
HTNR 70	1/27.6/25.3	70.2

R value (NCO/OH) = 0.96 (for all polymerisations)

2% excess isocyanate added for all bulk polymerisations.

kettle was maintained at 70°C and TDI was added dropwise with constant stirring. The reaction was allowed to continue for 1 hour. This was followed by the addition of desired stoichiometric amount of butane 1,4 diol as a lot with vigorous stirring for 3 seconds and the contents were degassed in a vacuum oven and cast into a preheated tray coated with silicone release agent and cured at 110°C for 10 hours followed by ageing at room temperature for one week in a moisture free atmosphere.

3.3(c) Two step process - Solution polymerisation

Weighed quantity of HTNR dissolved in tetrahydrofuran so as to get 10% solution, was taken in a flat bottomed flask equipped with a magnetic stirrer, nitrogen inlet, a dropping funnel and a reflux condenser. DBTDL (0.03% by wt. of HTNR) was added as catalyst and the solution was brought to reflux. The final desired stoichiometric amount of TDI was added followed by 1 hour reaction to endcap HTNR. This was followed by the addition of the desired amount of butane 1,4 diol in THF (50% soln.) dropwise over a period of three hours followed by one and a half hours of reaction. The excess THF was distilled off and the viscous polymer was cast into trays treated with silicone release agent and kept for curing at 80°C for 24 hours followed by one week room temperature ageing in a moisture free atmosphere.

3.4 Measurements

Infra red spectrum of the samples were recorded on a Perkin Elmer 377 IR spectrometer. Tensile measurements were conducted on a Zwick 1445 Universal Testing Machine. Differential Scanning Calorimetry (dsc) was carried out using a Dupont 9000 Thermal Analyser System. A heating rate of 10^{o}C min.$^{-1}$ and a sensitivity of 5 m cal S^{-1} was used. Cyclohexane (crystal-crystal transformation at 186 K) and Indium (melting point at 429.8 K) were used as thermal standards for temperature calibration. Thermal stability of the polyurethanes synthesised were determined using a Dupont 1090 Thermogravimetric Analyser (TGA) at a heating rate of 20^{o}C min.$^{-1}$. Dynamic mechanical analysis (DMA) conducted on a Rheovibron Viscoelastometer DDV II. The temperature range of -80^{o}C to 210^{o}C was scanned at 5^{o}C min.$^{-1}$ at 3.5 Hz.

3.5 Results and Discussion

3.5(a) IR Spectra

The infra red spectra of the NCO endcapped prepolymer and the final product are given in figures 9 and 10. The very strong band characteristic for the hard segment are 3310 - 3440 cm^{-1} (N-H stretching), 1710 - 1730 cm^{-1} (C=O stretching), 1535 cm^{-1}(N-H bend-

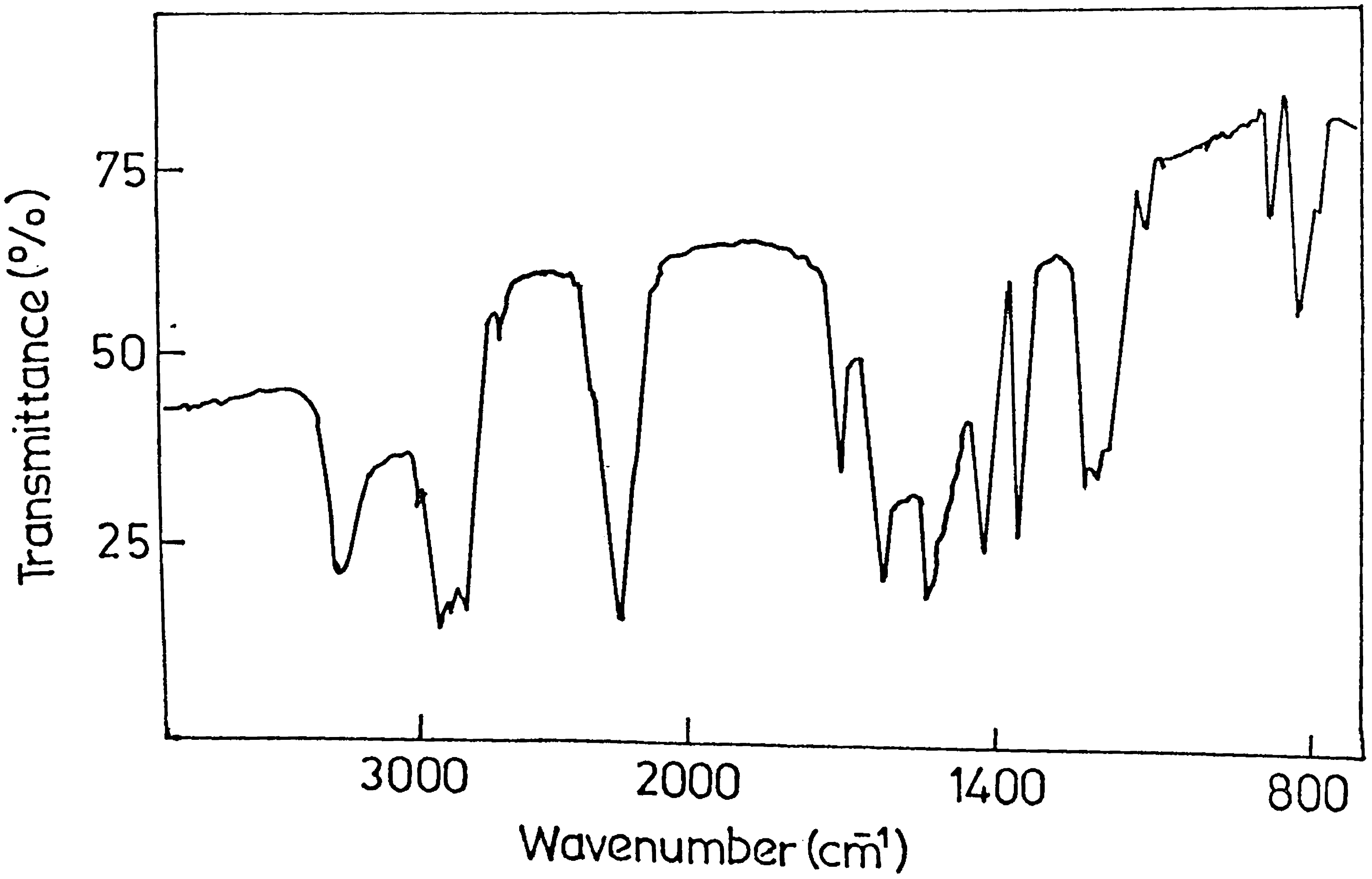


Fig.9 IR Spectrum of -NCO endcapped Natural Rubber.

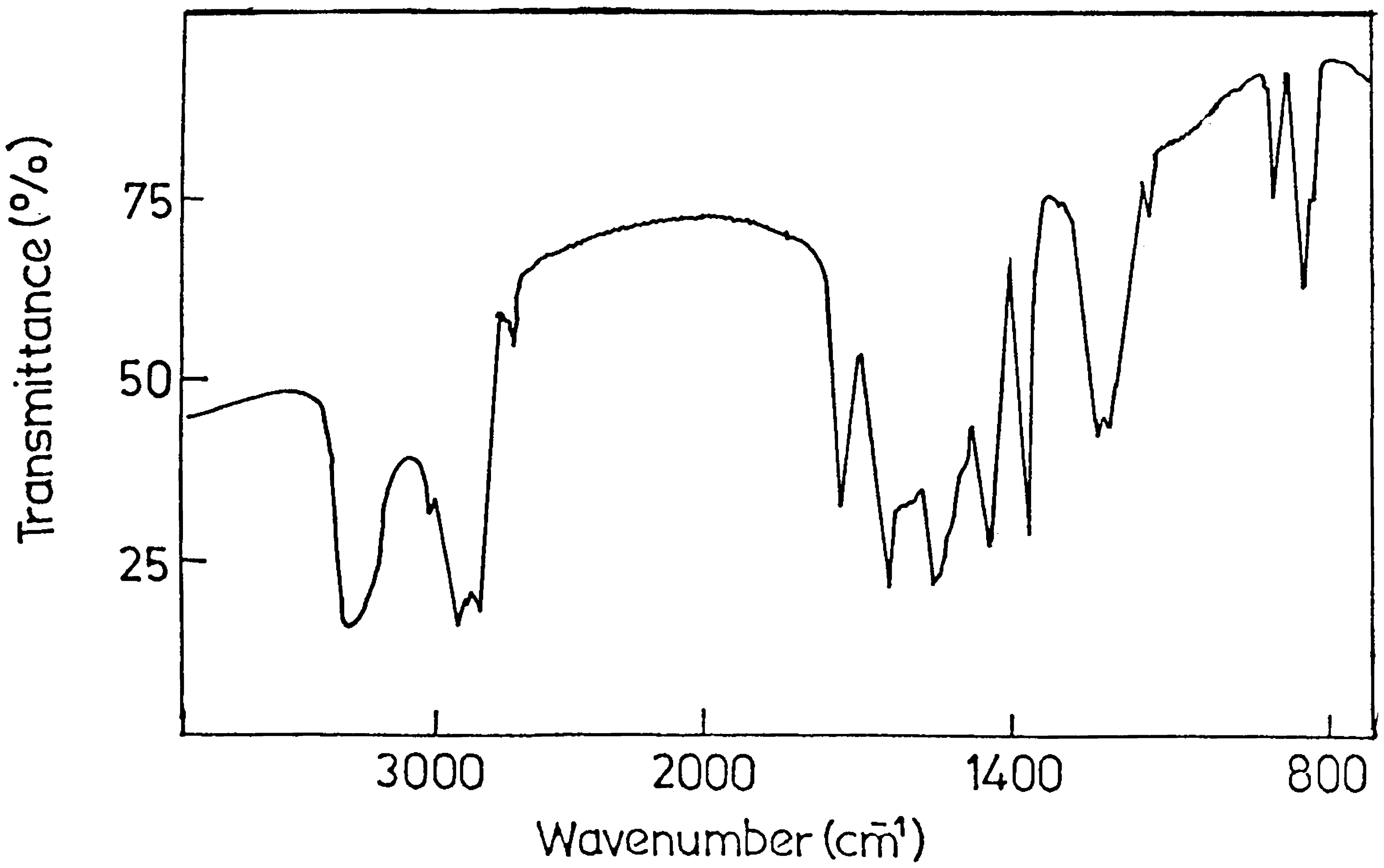


Fig.10 IR Spectrum of HTNR based polyurethane.

ing and CN stretching). The characteristic band related to the soft segment are those related to the double bond at 830 cm^{-1} (cis 1,4). The band due to the primary hydroxyl groups in the IR Spectrum of HTNR at 3400-3600 cm^{-1} (figs 3 & 4) vanishes and we get peak for NCO 2200-2400 cm^{-1} (fig 9) which on further chain extension with a low molecular weight diol (butane 1,4 diol) disappears. Hence complete conversion of endcapped material to polyurethane is envisaged.

3.5(b) Stress-strain behaviour

The effect of hard segment content on the stress-strain behaviour of the polyurethanes synthesised by all the 3 methods were studied. The results obtained are summarized in Tables VI, VII and VIII for one step, two step (bulk) and two step (solution) polymerisation respectively. Stress-strain curves are presented in figures 11, 12 and 13. In the one step process there is no general trend in the mechanical properties of polyurethanes. Above 30% hard segment content the samples are brittle. This may be attributed to the heterogenity of the reaction mixture and also due to the incompatibility of the reactants. The final product may be a blend of homopolymers of the hard and soft segments and also some copolymers with $(AB)_n$ type structure where A is the hard segment

TABLE - VI

Mechanical properties of bulk polymerised samples (One step)

Sample	Tensile strength MPa	Elongation at break (%)	Modulus at 100% elongation MPa
HTNR 10	1.08	420	0.36
HTNR 20	3.08	343	1.02
HTNR 30	2.00	140	1.40
HTNR 40	0.98	20	--

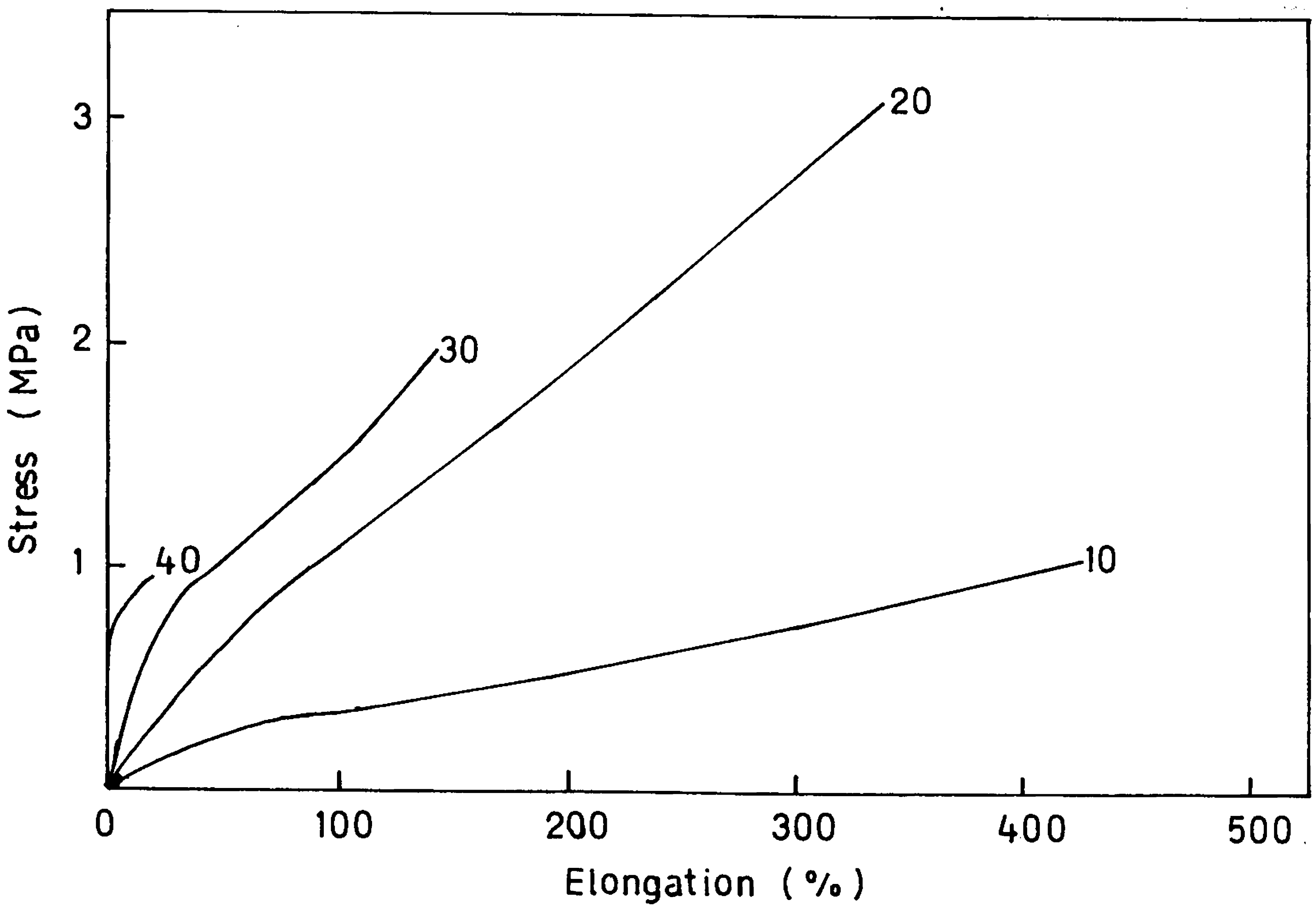


Fig.11 Tensile Curves of one step bulk polymerised polyurethanes.

TABLE - VII

Mechanical properties of bulk polymerised samples.
(Two step)

Sample	Tensile strength MPa	Elongation at break (%)	Modulus at 100% elongation MPa
HTNR 10	1.04	640	0.24
HTNR 20	2.21	720	0.30
HTNR 30	3.62	700	0.80
HTNR 40	4.50	420	1.90
HTNR 50	3.42	200	2.40
HTNR 60	1.15	47	--

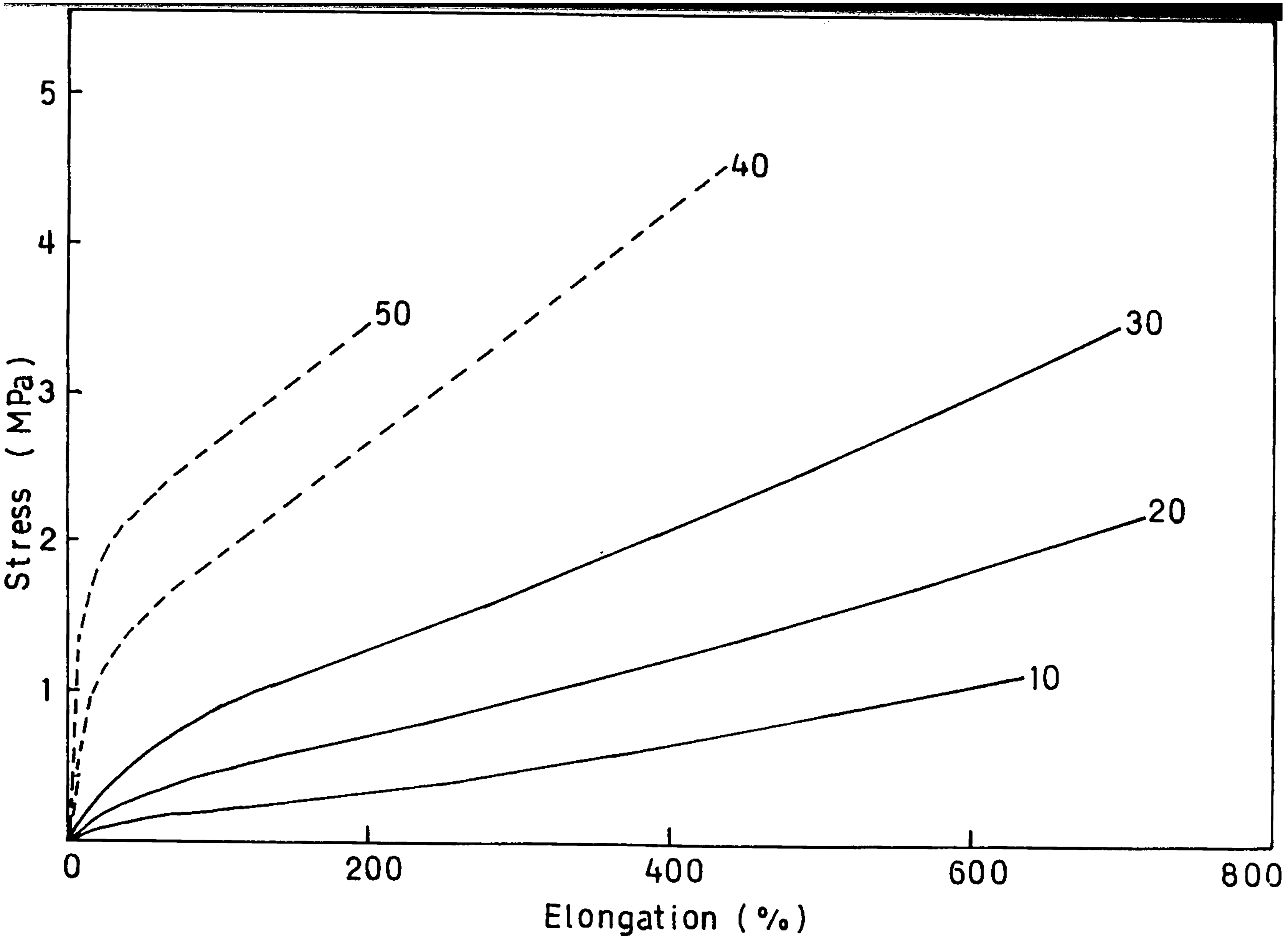


Fig.12 Tensile Curves of two step bulk polymerised polyurethanes.

TABLE - VIII

Mechanical properties of solution polymerised samples.
(Two step)

Sample	Tensile strength MPa	Elongation at break (%)	Modulus at 100% elongation MPa
HTNR 10	2.92	900	0.98
HTNR 20	4.45	760	1.21
HTNR 30	6.49	745	1.94
HTNR 40	7.94	500	3.10
HTNR 50	10.60	260	5.40
HTNR 60	14.40	190	9.62
HTNR 70	22.00	174	20.9

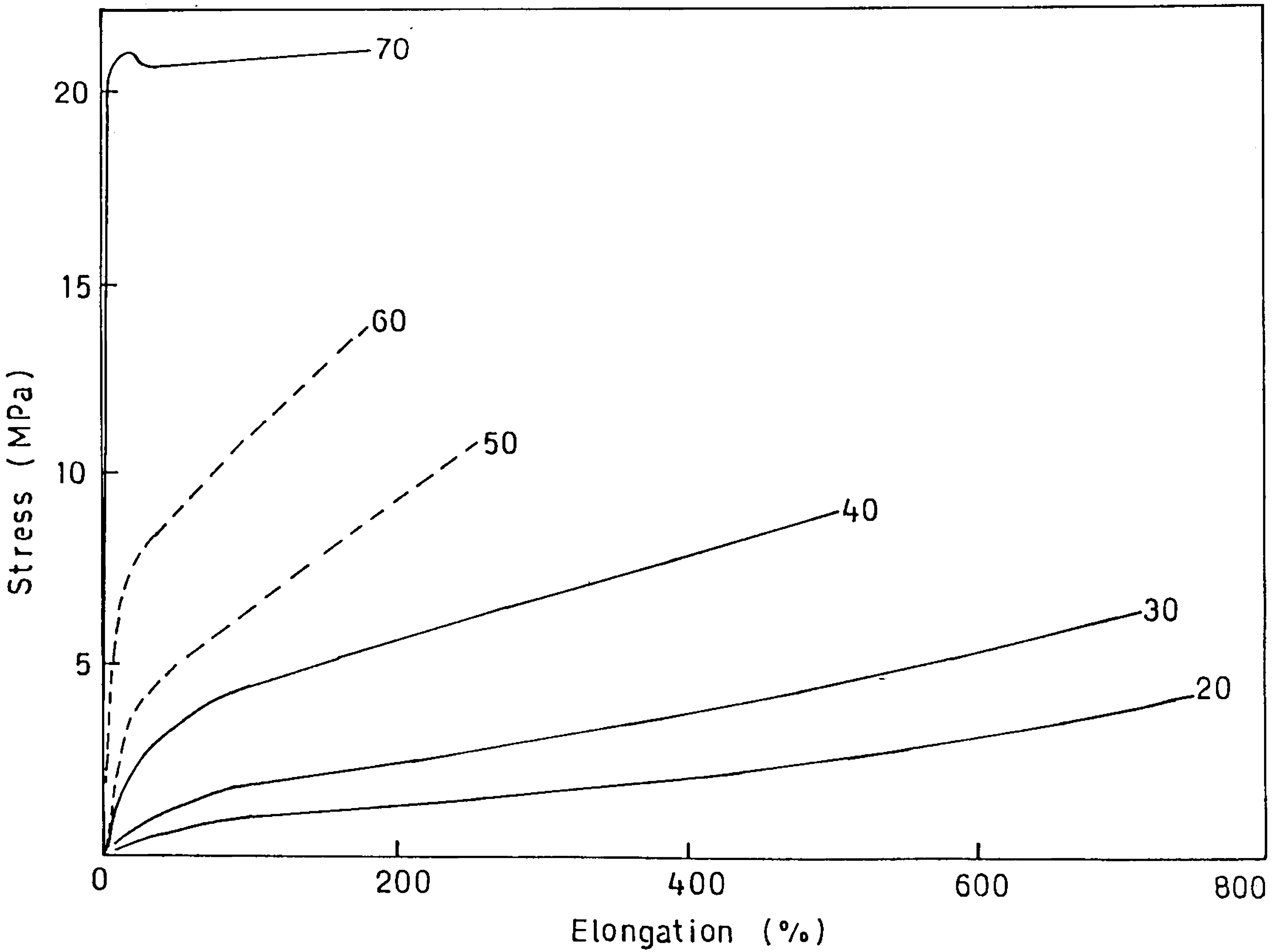


Fig.13 Tensile curves of two step solution polymerised polyurethanes.

from BDO and TDI and B is the soft segment from HTNR.

In two step (bulk and solution) processes, three general types of mechanical behaviour are observed depending on hard segment contents:
In the solution polymerised samples materials with hard segment content below 40% are soft elastomers. At 70% hard segment content they behave as a rubber toughened plastic displaying necking and strain whitening. Intermediate compositions behave as rigid elastomers. This variation of mechanical properties is very likely caused by the changes in sample morphology. When volume fractions of the 2 phases are similar, both phases may be continuous. The stress strain data suggest that below 40% hard segment content the natural rubber soft segment is the continuous phase with hard segment domains acting as physical crosslinks and reinforcing filler. At 70% hard segment content, the hard segment is expected to comprise the continuous phase with domain of elastomer toughening the material. Intermediate materials appear to be bicontinuous in nature. The deformation of these samples proceeds in two steps: first the relatively high modulus hard segment deforms followed by the low modulus deformation of the elastomer.

The changes in the bulk polymerised sample morphology occured at lower hard segment contents and over a narrower range of composition than for the solution polymerised samples. Brittle low modulus plastics were obtained at hard segment contents above 50% and soft rubbers resulted below 30% hard segment content.

It is to be noted that the same strain rate and sample cross section were used to study all the 3 series of samples. The tables show a marked difference between bulk and solution polymerised materials. The solution polymerised materials exhibit tensile strength which are 2 to 11 times higher than those of corresponding bulk polymerised samples and maintain high elongations at high hard segment content. These differences are due to the differences in products obtained by different synthetic routes.

3.5(c) Thermal analysis

The dsc curves of the bulk polymerised samples (one step and two step) are given in Figures 14 and 15 and those of solution polymerised samples in figure 16. The transition temperatures observed are tabulated in tables IX, X and XI respectively. The soft segment glass transition is found to be about -59°C for all the samples prepared by bulk polymerisation and around -64°C for solution polymerised samples. One step polymerised samples exhibited more than one hard segment glass transition. But for two step bulk polymerised samples a maximum of two hard segment Tg's are observed in some cases. Measurements for HTNR and HTNR extended by 2,4 TDI indicate that they have the same glass transition temperature at -68°C which is 9°C lower than that of the soft segment transition of the polyurethanes. No other transitions have been observed for HTNR/2,4 TDI.

The Tg of the soft segment region is found to be independent of the hard segment content. These results are consistent with those reported by the previous workers[1-4] who worked on polyurethanes based on polybutadiene soft segments. Our results indicate that the natural rubber soft segments are so incompatible with the urethane hard segments that they are completely phase segregated no matter what may be the sample preparation technique (ie. compression moulding or solvent casting). Segmented polyurethanes are usually considered to be random copolymerised products of diisocyanates, macromolecular diisocyanates and extenders. If this was the case the macromolecules will all have the same average chemical composition and average hard segment length and therefore would be statistically identical. The microphase separation of hard and soft segments is postulated to explain their morphological features and properties.

TABLE - IX

dsc results of bulk polymerised polyurethanes
(One step)

	Sample	Tg of the soft segment °C	Tg of the hard segment (°C) T_1	T_2	T_3
A	HTNR	-68	--	--	--
B	HTNR 0	-68	--	--	--
C	HTNR 10	-59	8	--	--
D	HTNR 20	-56	15	31	--
E	HTNR 30	-56	26	47	--
F	HTNR 40	-55	15	53	72

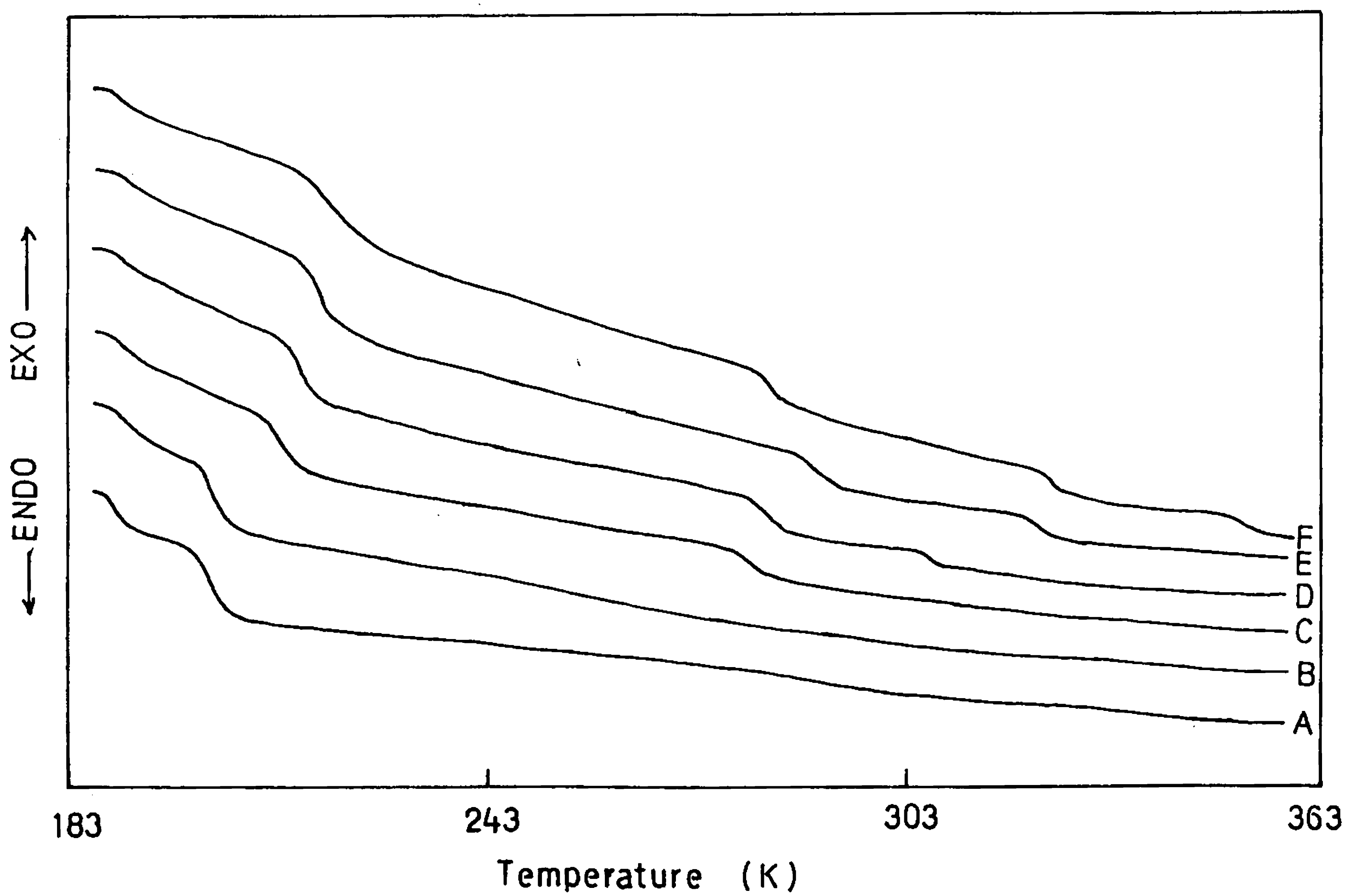


Fig.14 dsc curves of bulk polymerised (one step) polyurethanes.

TABLE - X

dsc results of bulk polymerised polyurethanes (Two step)

	Sample	Tg of the soft segment °C	Tg of the hard segment (°C)	
			T_1	T_2
	HTNR	-68	--	--
	HTNR 0	-68	--	--
A	HTNR 10	-59	--	--
B	HTNR 20	-59	7	--
C	HTNR 30	-58	20	43
D	HTNR 40	-58	31	55
E	HTNR 50	-58	49	70
F	HTNR 60	-56	56	91

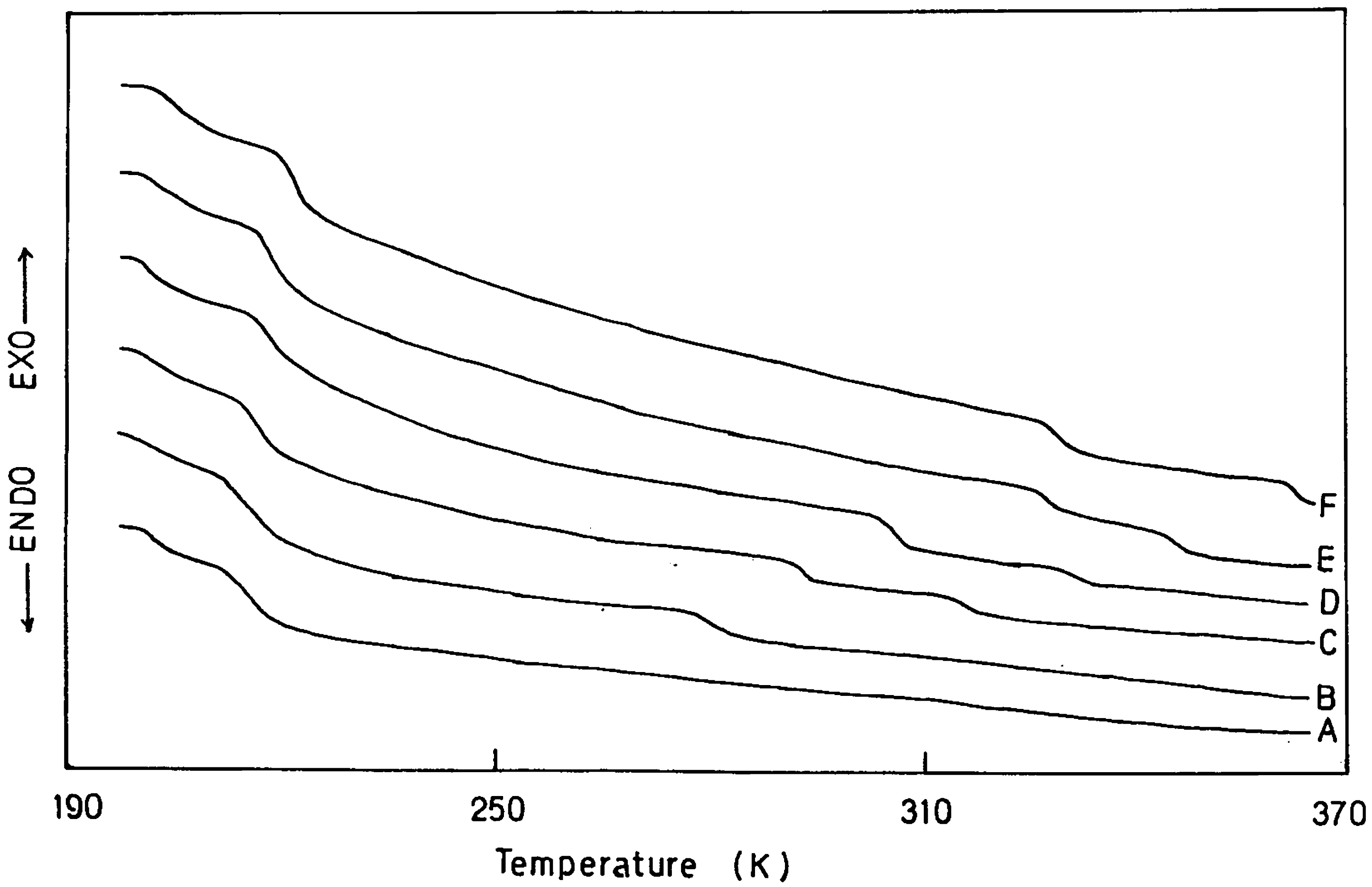


Fig.15 dsc curves of bulk polymerised (two step) polyurethanes.

TABLE - XI

dsc results of solution polymerised polyurethanes.
(Two step)

	Sample	Tg of the soft segment ^oC	Tg of the hard segment ^oC
	HTNR	-68	--
	HTNR 0	-68	--
A	HTNR 10	-66	--
B	HTNR 20	-65	20
C	HTNR 30	-65	38
D	HTNR 40	-64	54
E	HTNR 50	-64	70
F	HTNR 60	-62	95
G	HTNR 70	-62	124

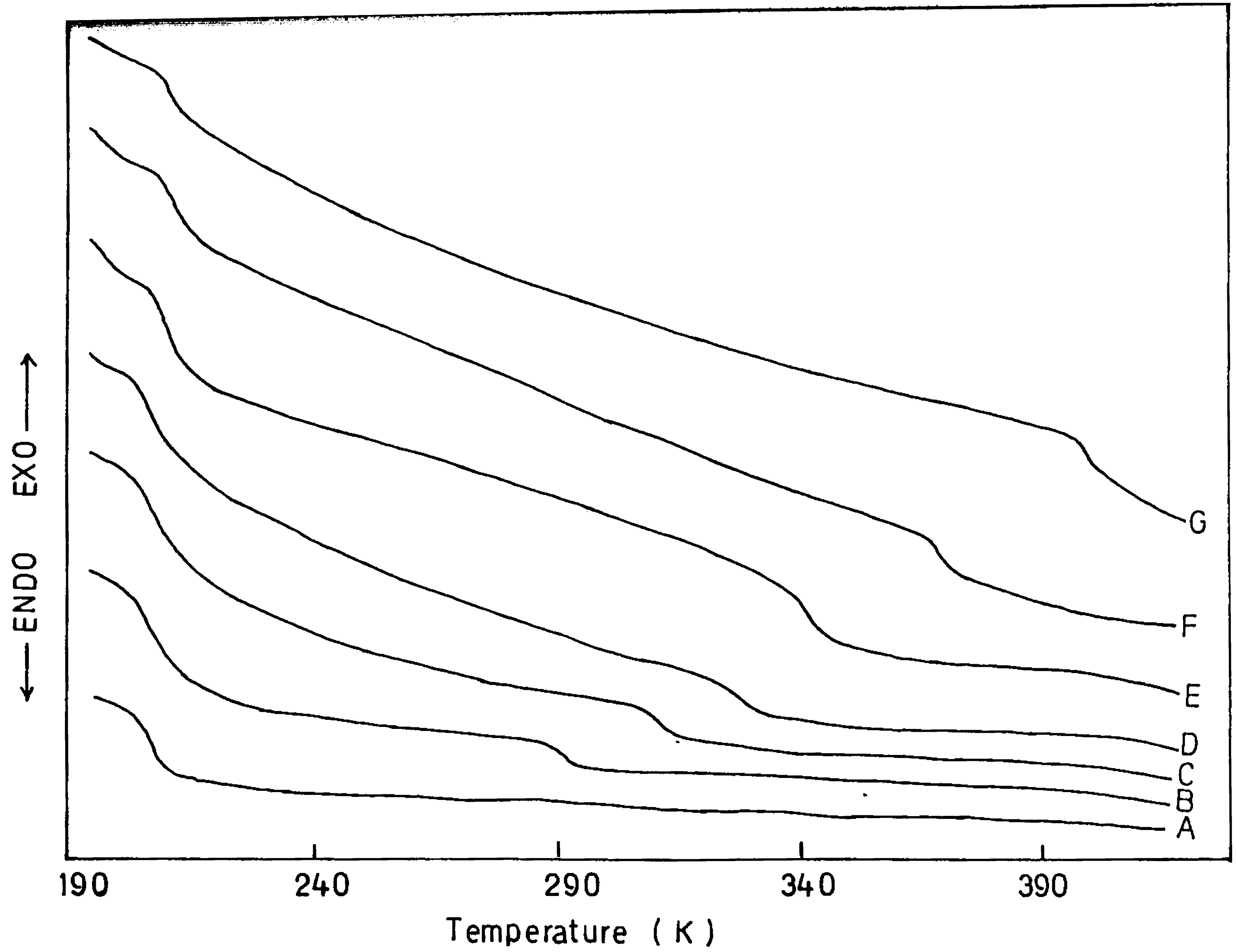


Fig.16 dsc curves of solution polymerised (two step) polyurethanes.

3.6 Fractionation of bulk polymerised samples (two step)

For this study we have used HTNR 30 and HTNR 60 samples. Since the macromolecules are expected to have different hard and soft segment compositions as evidenced from the dsc measurements, they should also differ in their solubility behaviour. Fractionation was carried out by the solvent extraction method using DMF. It was found that after several days at 85°C both the samples seperated into a sol fraction and gel fraction. The fractions were cast on a watch glass coated with silicone release agent and dried in vacuum oven. The relative amounts of the fractions are listed in Table XII. The transition behaviour of these fractions were determined by dsc measurements.

The infra red spectra of the fractions were taken and it was found that the spectra of two fractions of each polyurethanes show that their compositions are quite different (Fig.17). For fractions from HTNR 30 (sol fraction and gel fraction) band at 830 cm^{-1} have relatively much higher absorbance for gel fraction than for the sol fraction. It implies that the sol fraction is relatively hard segment rich and the gel fraction is soft segment rich A similar situation is found for HTNR 60 fractions

TABLE - XII

Fractionation results of polyurethanes

Sample	Percentage of sol fraction (Wt.%)	Percentage of gel fraction (Wt.%)	Hard segment content of original sample (Wt.%)
HTNR 30	52	48	29.7
HTNR 60	83	17	59.7

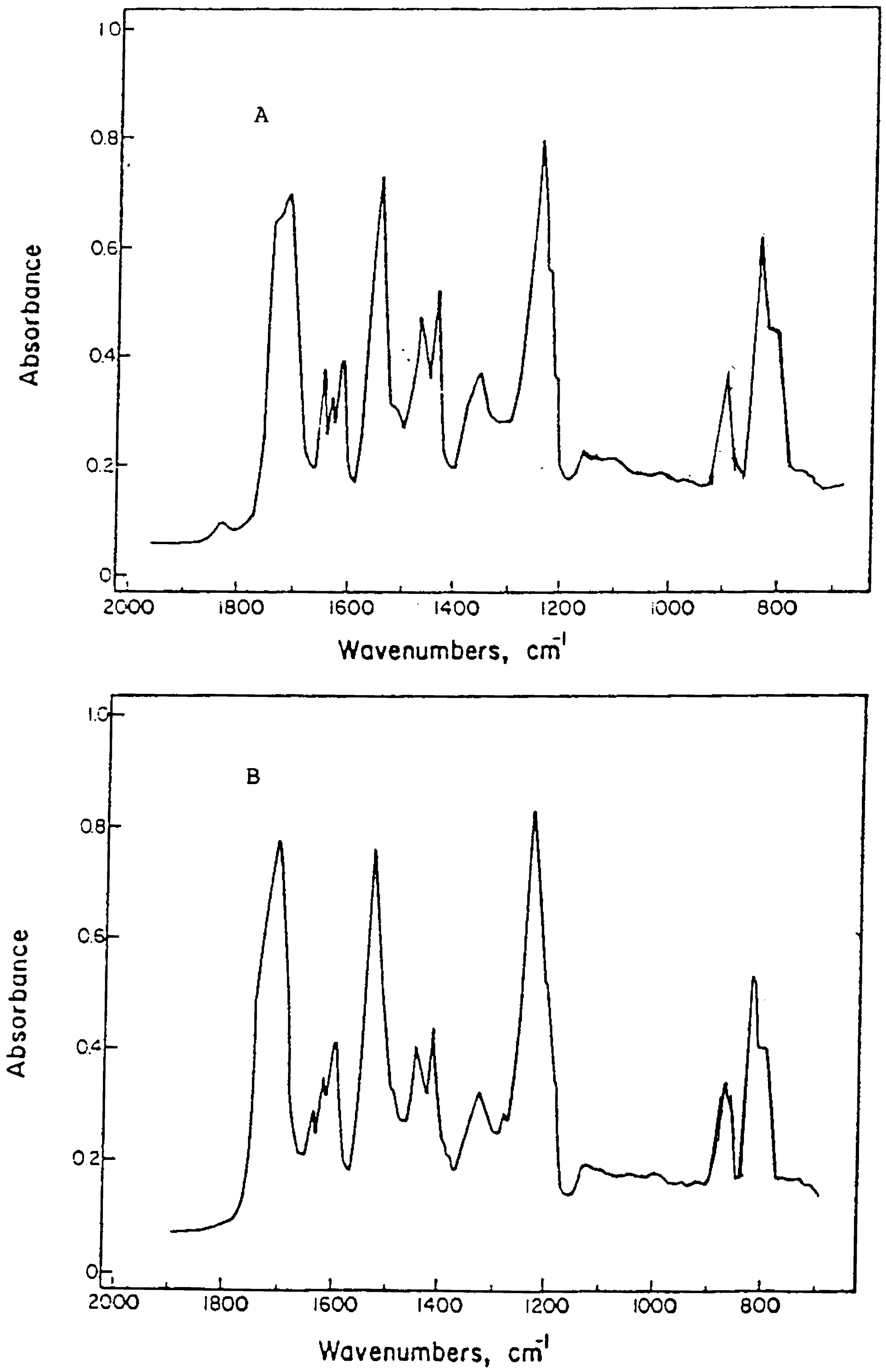


Fig.17 IR Spectra: (A) HTNR 30 gel fraction and (B) HTNR 30 sol fraction.

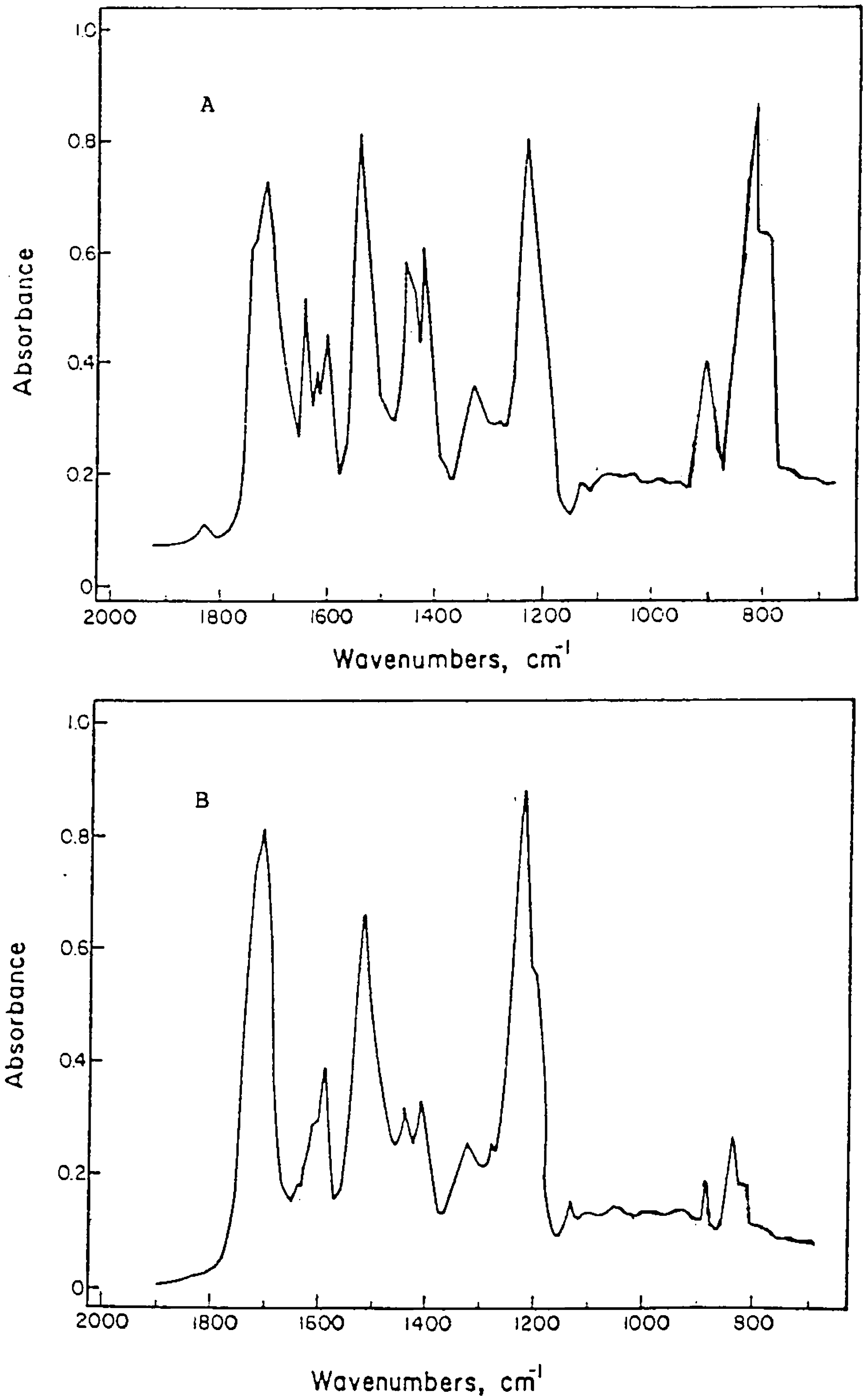


Fig.18 IR Spectra: (A) HTNR 60 gel fraction and (B) HTNR 60 sol fraction.

but with much greater compositional differences (Fig. 18).

The dsc curves of the original samples and their fractions obtained by Solvent extraction are given in figures 19 and 20 and their glass transition temperatures are summarized in Table XIII. The soft segment glass transition Tg was found to be at about -59°C for all samples. Two hard segment Tg's T_1 and T_2 are observed for HTNR 30 and HTNR 60. The sol fractions of these two samples also show two hard segment TG's located at almost the same temperatures as the T_1's and T_2's of the original samples, but their gel fraction show only T_1 transitions.

Our results indicate that as in the case of polyester, polyether and also polybutadiene[5] containing segmented copolymers, macromolecules of the segmented polyurethanes can be quite non-uniform in chemical composition and average segment length and they can be separated according to their differences in solubility. Since there is no change in the hard segment glass transitions (T_1 and T_2) even after solvent extraction, we can approximately consider these samples as mixtures of two fractions (1 & 2) of segmented copolymers which have distinctly different average chemical composition and average

TABLE - XIII

dsc results of bulk polymerised (two step) polyurethanes

Sample	Tg of the soft segment °C	Tg of the hard segment °C	
		T_1	T_2
HTNR 30	-59	20	43
HTNR 30S	-57	19	48
HTNR 30G	-58	19	--
HTNR 60	-56	56	91
HTNR 60S	-57	36	114
HTNR 60G	-59	30	--

S - Sol fraction

G - Gel fraction

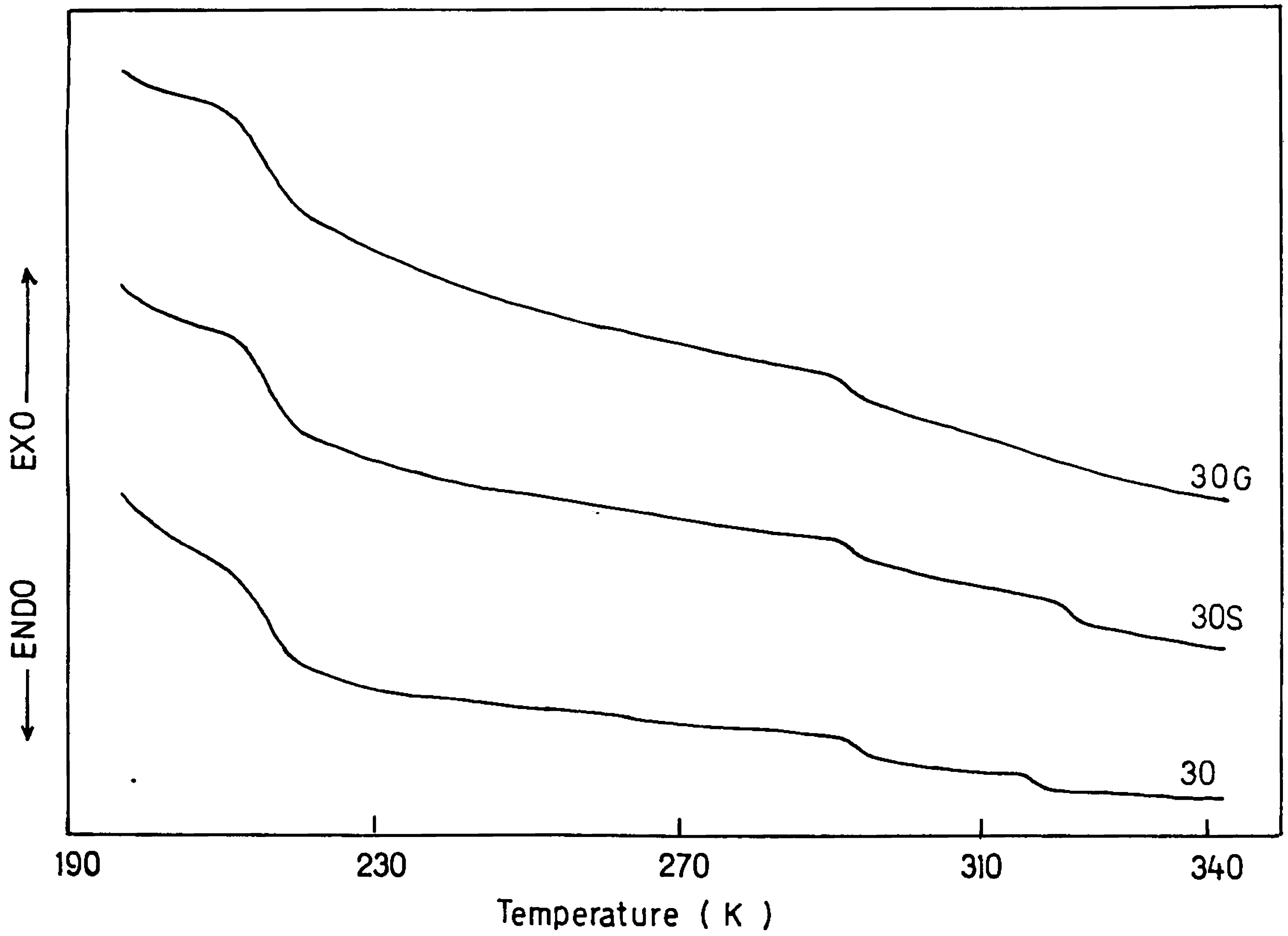


Fig.19 dsc curves of HTNR 30,HTNR 30S and HTNR 30G.

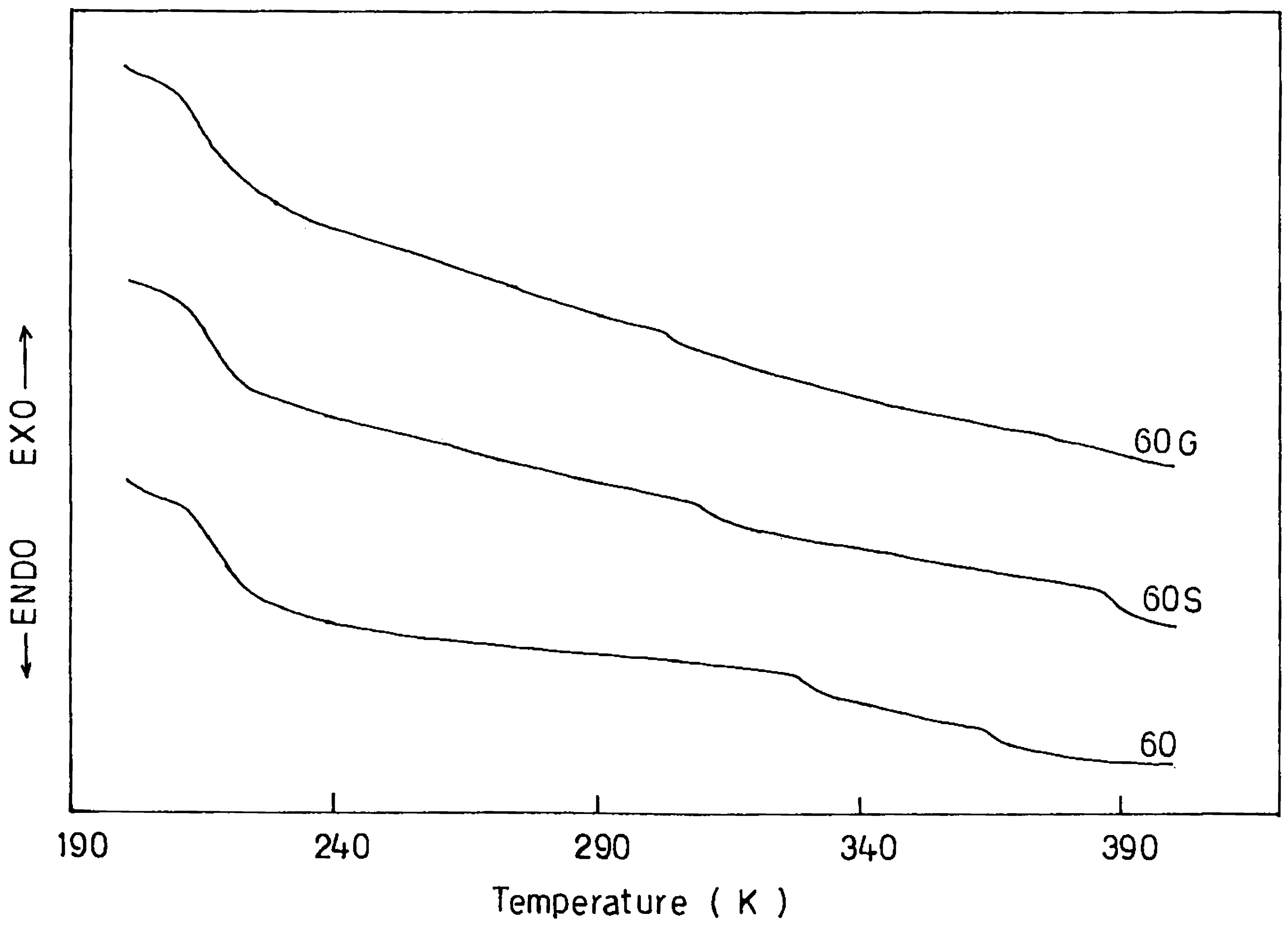


Fig.20 dsc curves of HTNR 60, HTNR 60S and HTNR 60G.

hard segment length. In addition to the segregation of hard and soft segments, the poor compatibility and great differences in solubility cause the segregation of macromolecules as a whole according to their composition during moulding or solution casting of the dissolved material and hence the separation of hard segments of different lengths. The existence of 2 hard segment Tg's for HTNR 30S and HTNR 60S means that the separation by solvent extraction under the experimental conditions is not complete, and only the gel fractions are relatively uniform, as a single hard segment transition is observed in their case.

It has been proposed[6] that a bimodel distribution of molecules in chemical composition and hard segment sequence length can result from the heterogenity of the reactants themselves. This means in the present system that both isocyanate groups of the endcapped HTNR and those of the free TDI are not distributed uniformly throughout the reaction mixture. Reactions in the free TDI rich regions will result in hard segments of longer length, and in the endcapped natural rubber rich regions will result in hard segments of shorter length. A schematic model of the heterogeneous reaction mixture and its influence on subsequent sequence distribution of polyurethane hard segments is discussed in detail in case of polyurethanes with polybutadiene soft segments[7]. Since our system is somewhat analogous to the system studied by Macknight and co-workers we can correlate our results to the model proposed by them.

3.7 Model

Three schematic models (Fig.21a, 21b and 21c) are proposed to describe the heterogeneous nature of HTNR/TDI/BDO system. Figure 21a describes the high hard segment content samples. In the matrix the TDI endcapped HTNR molecules segregate to form spherical domains with TDI end groups outside. The free TDI molecules form a continuous phase surrounding these microdomains. After BDO is added, the reaction between free TDI and BDO molecules within the BDO droplet will result in majority of hard segment rich molecules which contribute to the higher temperature hard segment Tg in HTNR/TDI/BDO samples. The limitation in solubility of Butane 1,4 diol molecules in the NR/TDI matrix causes only short hard segment sequences which gives rise to the lower Tg in these samples. These types of multiple glass transitions have been often seen in polyurethane systems and the explanation given to this was based on the segregation of hard segment sequence into groups of discrete lengths. It is to be noted that no reasonable explanation could be given as to how this can take place from systems with a most probable sequence length distribution. Figure 21b describes the low hard segment content samples. Depending on the averall compositions, NR occupies about 80 to 90% of the volume in the HTNR/TDI phase. Free TDI molecules segregate to form micro domains and the TDI endcapped NR molecules form a continuous phase surrounding these domains. After 1,4 butane diol is added, the reaction between free diisocyanate groups at the ends of the NR molecules and the butane diol molecules within the droplets will result in relatively short hard segment sequences in the matrix. The free TDI molecules will interdiffuse with the BDO droplets and react forming region of pure hard segment polymer. Between these high hard segment content samples and low hard segment content samples, a phase inversion must occur in the matrix phase. Scriven[8] proposed that materials tend to form bicontinuous phases to minimize surface free energy at certain compositions of mixtures. Figure 21c takes into consideration the intermediate hard segment content samples. A bicontinuous structure is predicted. Endcapped NR and free TDI, both have opportunities to react with BDO in the butane diol droplets and with butane diol dissolved in the NR/TDI phase. In such a case, approximately equal amounts of final polymers of long hard segment lengths and of short hard segment lengths will be found.

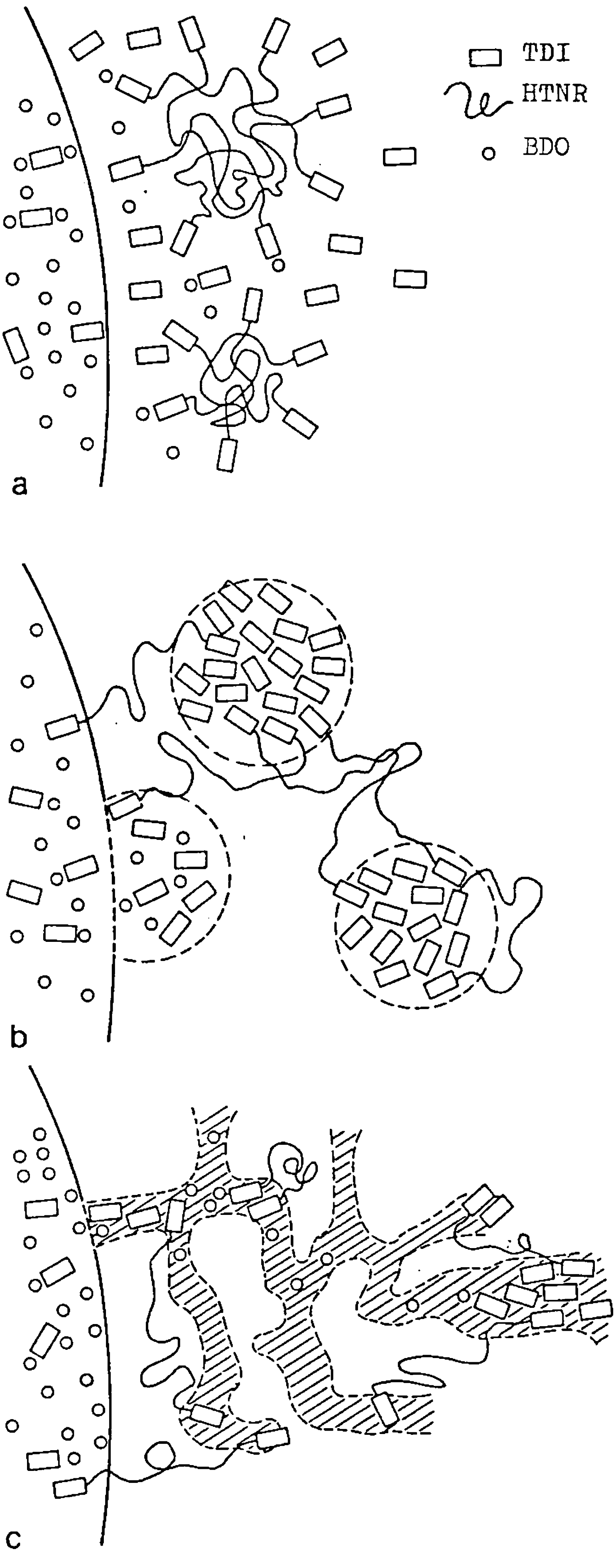


Fig. 2.1 Schematic models depicting the microstructure during polymerisation of HTNR/TDI/BDO polyurethane system.

3.8 Thermogravimetry

The thermal stability of the polyurethanes were studied using thermogravimetric analysis (TGA). Most of the polyurethanes prepared by one step and two step processes decompose in two stages. Typical thermograms of HTNR 60 prepared by two step (bulk & solution) as well as HTNR 40 prepared by one step are given in figs.22, 23 and 24 respectively. The onset of weight loss (T_0) occurs between 240° - 260°C for bulk polymerised samples (two step) and 280° - 300°C for solution polymerised samples (two step). The one step polymerised samples showed the onset of weight loss between 210° - 230°C. The first stage weight loss is complete at 340°C for bulk polymerised samples (two step),at 380°C for solution polymerised samples (two step) and at 300°C for one step polymerised samples. The second stage decomposition is rapid with a maximum rate in the vicinity of 390°C for bulk (two step), 420°C for solution (two step) and 330°C for one step polyurethanes. A plateau seperating the two stages of decomposition also suggests that the two domains decompose at two different temperatures. Results are summarized in Tables XIV, XV and XVI for bulk polymerised (two step), solution polymerised (two step) and bulk polymerised (one step) respectively. The higher thermal stability of the solution polymerised samples is obviously due to the higher degree of structural regularity of the polymer chains.

TABLE - XIV

TGA results of bulk polymerised
(two step) polyurethanes.

Sample	Decomposition temperature °C		
	T_0	T^a_{10}	T^b_{50}
HTNR 10	234	318	381
HTNR 20	244	320	384
HTNR 30	253	324	383
HTNR 40	254	319	392
HTNR 50	259	336	390
HTNR 60	266	340	396

a - Temperature corresponding to 10% wt. loss

b - Temperature corresponding to 50% wt. loss

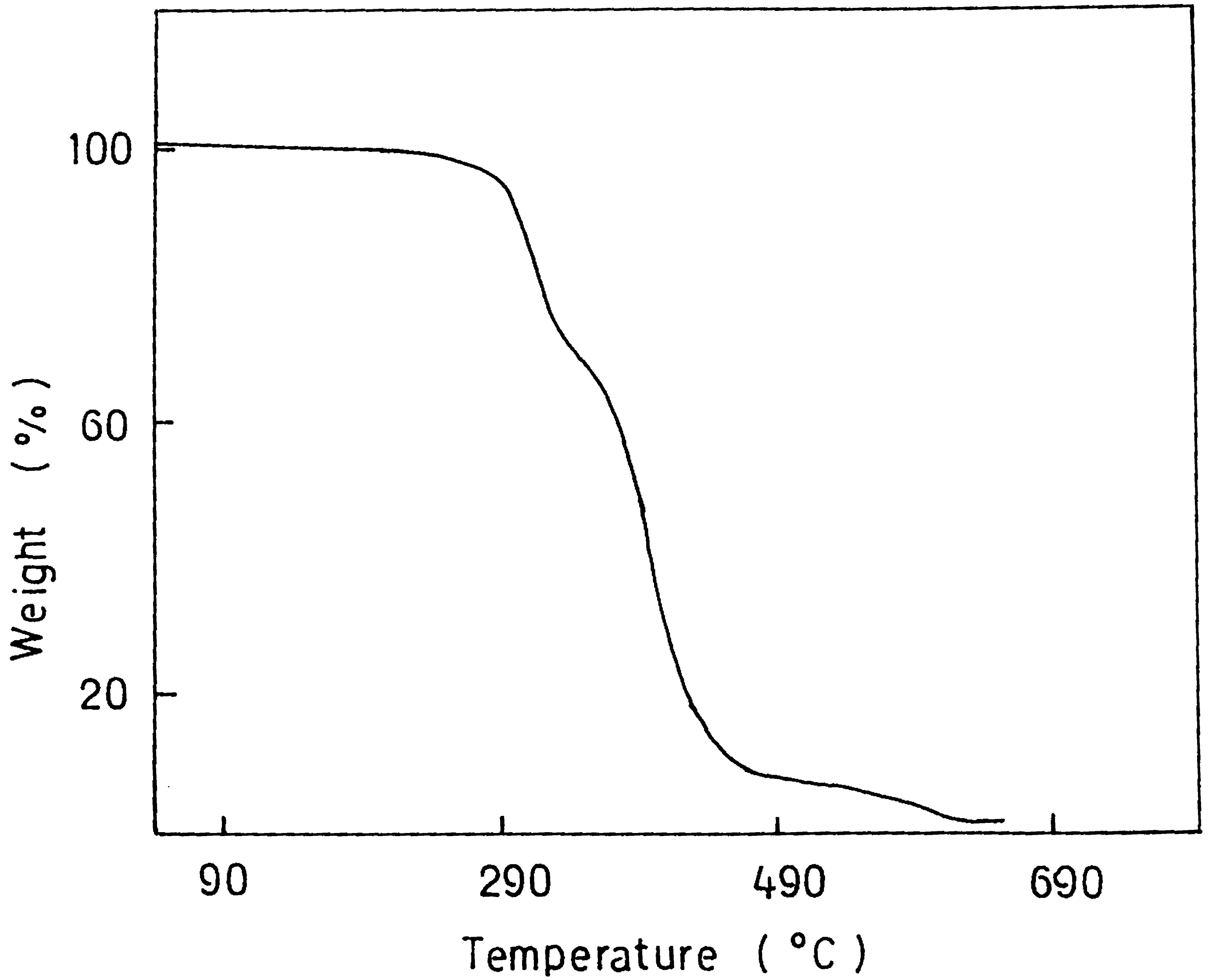


Fig. 22 TGA curve of HTNR 60 (two step) bulk polymerised.

TABLE - XV

TGA results of solution polymerised (two step) polyurethanes.

Sample	Decomposition temperature °C		
	T_0	T_{10}^{a}	T_{50}^{b}
HTNR 10	278	359	412
HTNR 20	282	372	410
HTNR 30	286	370	404
HTNR 40	280	375	408
HTNR 50	288	378	410
HTNR 60	294	380	420
HTNR 70	308	386	424

a - Temperature corresponding to 10% wt. loss

b - Temperature corresponding to 50% wt. loss.

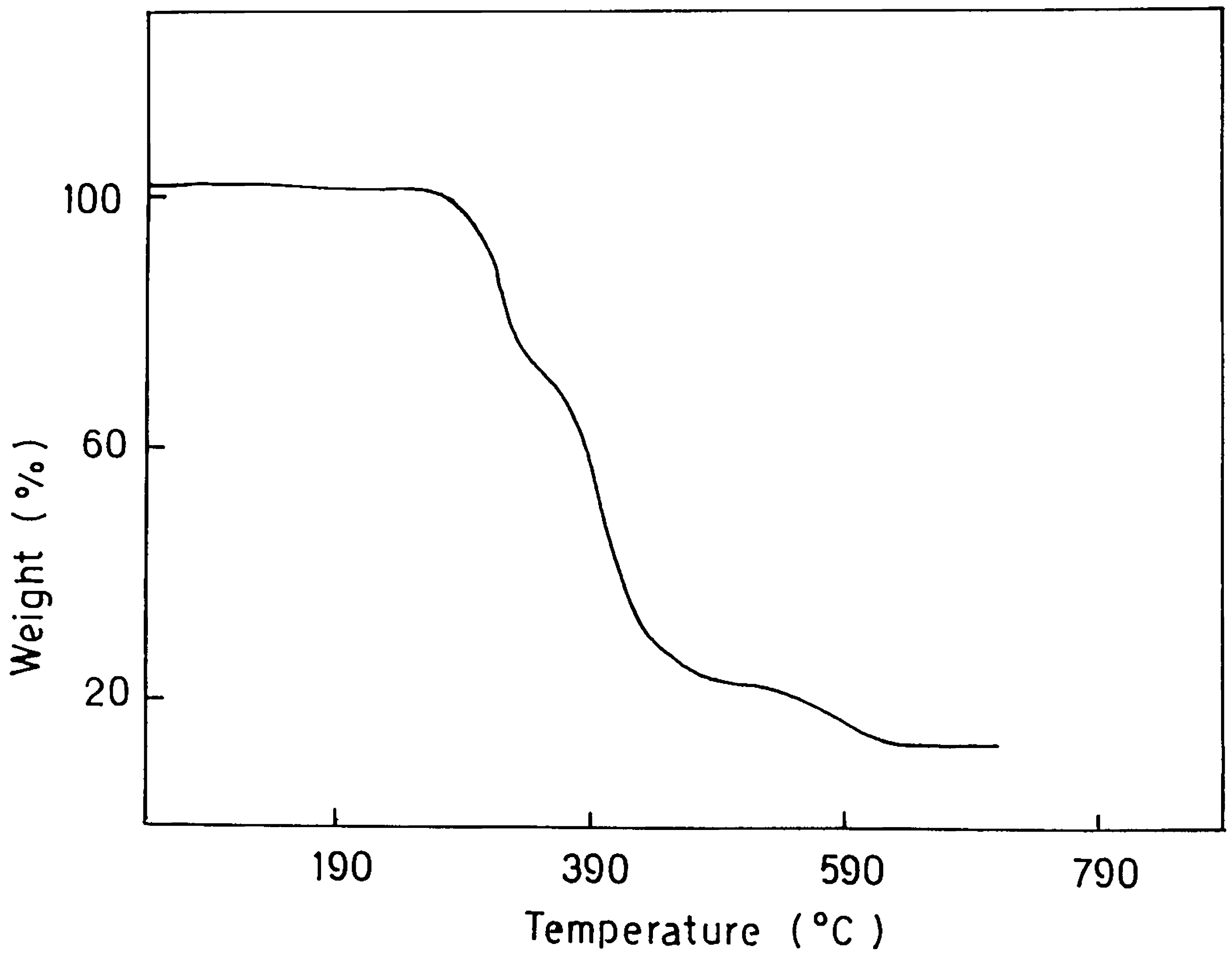


Fig.23 TGA curve of HTNR 60 (two step) solution polymerised.

TABLE - XVI

TGA results of bulk polymerised (one step) polyurethanes

Sample	Decomposition temperature ^{o}C		
	T_0	T_{10}^{a}	T_{50}^{b}
HTNR 10	210	283	324
HTNR 20	216	290	328
HTNR 30	222	296	329
HTNR 40	228	296	330

a - Temperature corresponding to 10% wt. loss

b - Temperature corresponding to 50% wt. loss.

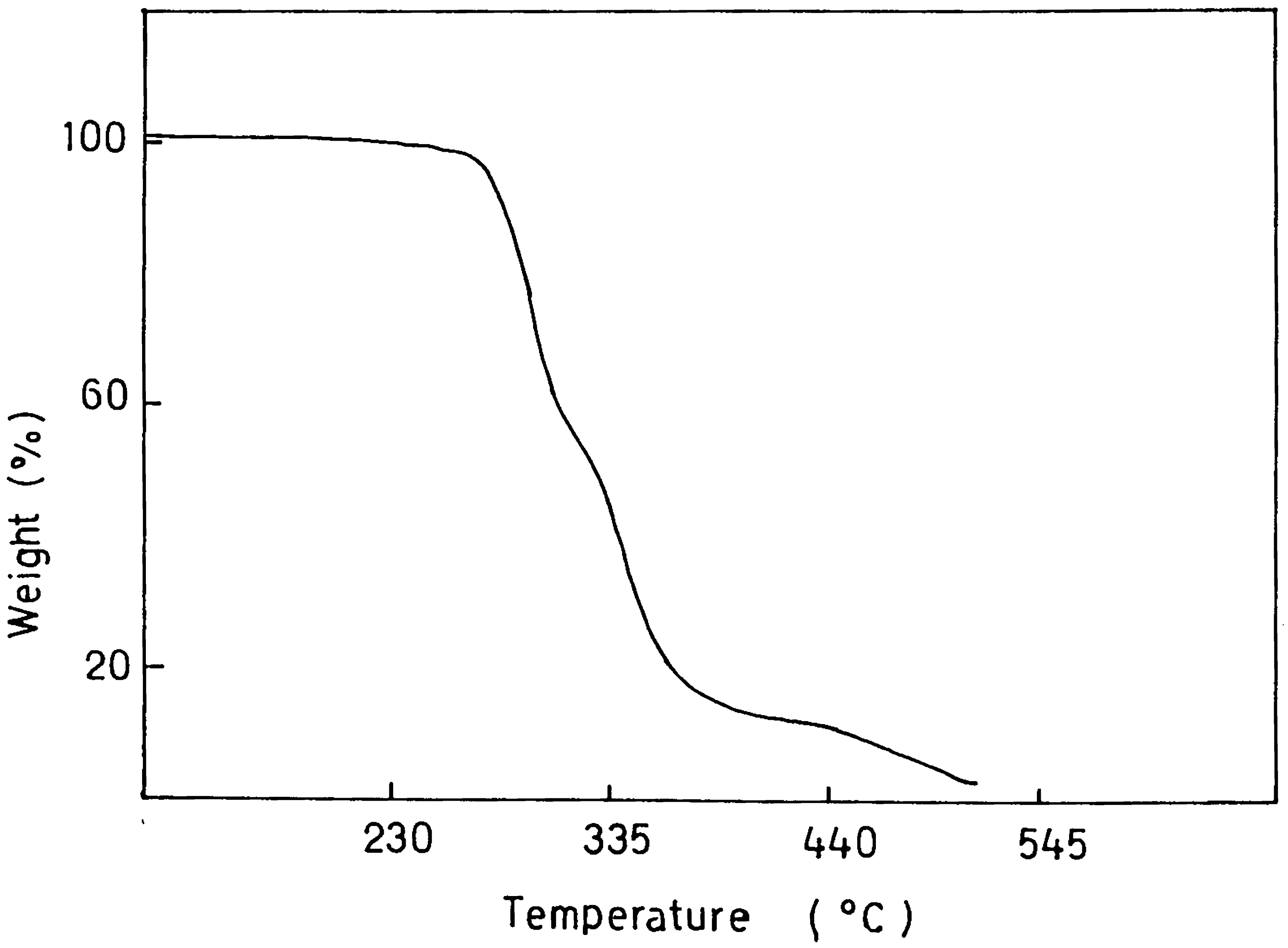


Fig.24 TGA curve of HTNR 40 (one step) bulk polymerised.

3.9 Sample characterization (solution polymerised samples)

The appearance of samples obtained from the solution polymerisation differs from that of the bulk polymerised samples. The latter are generally yellow to brown coloured brittle materials whereas the solution polymerised samples are tough elastomers and rubber toughened plastics having a pale yellow colour. Solution polymerised samples are completely soluble in THF at room temperature in contrast to the low temperature insolubility of the bulk polymerised samples. The complete solubility is taken as evidence for the expected absence of allophonate crosslinks due to the low reaction temperature (68°C) and the use of exact stoichiometric amounts of reactants as well as the homogeneous reaction conditions. Molecular weights of the solution polymerised samples were determined from gel permeation chromatography data using a calibration curve for polystyrene. The $\overline{Mn}$ of the solution polymerised samples are generally in the order of magnitude greater than the $\overline{Mn}$ of the corresponding bulk polymerised samples. The poly dispersity index($\overline{Mw}/\overline{Mn}$) of the solution polymerised samples is about 2, which is the expected value for step growth polymerisations. The molecular weight data is presented in Table XVII.

TABLE - XVII

Molecular weight data of solution polymerised (two step) polyurethanes.

Sample	Percent hard segment	$\overline{M}n$	$\overline{M}w$	D[*]
HTNR 10	12.4	12100	23700	1.96
HTNR 20	19.5	24300	55200	2.27
HTNR 30	29.7	27400	56700	2.07
HTNR 40	41.7	61500	109800	1.78
HTNR 50	51.0	48000	120000	2.50
HTNR 60	59.7	35000	67200	1.92
HTNR 70	70.2	19600	35200	1.79

Molecular weight dispersity.

3.10 Dynamic mechanical analysis

The relaxation behaviour of several of the samples synthesised by solution as well as bulk polymerisation techniques (two step) are given in figs. 25, 26, 27,28, 29 and 30 respectively. As can be seen, the plots illustrate two principal relaxations corresponding to the two phases present in the material. The Tg values, determined at 3.5 Hz from the Tan δ peaks are listed in Table XVIII. Consistent with the dsc results, the soft segment Tg, -39°C ± 2° in case of bulk polymerised samples and -43°C ± 2° in case of solution polymerised samples, is independent of the hard segment content. The value for Tg obtained by DMA is approximately 20° higher than the value obtained from dsc. The soft segment Tg is also characterised by a step decrease in the value of storage modulus of 1 to 2 orders of magnitude.

The hard segment Tg varies systematically with increasing hard segment content. Samples of lowest hard segment content display only an increase in Tan δ with increasing temperature. Increasing the hard segment leads first to a shoulder and finally for HTNR 70, a sharp peak. This increase of hard segment Tg is a result of increasing hard segment length.

Consistent with the findings for other phase segregated systems[8], the level plateau storage modulus

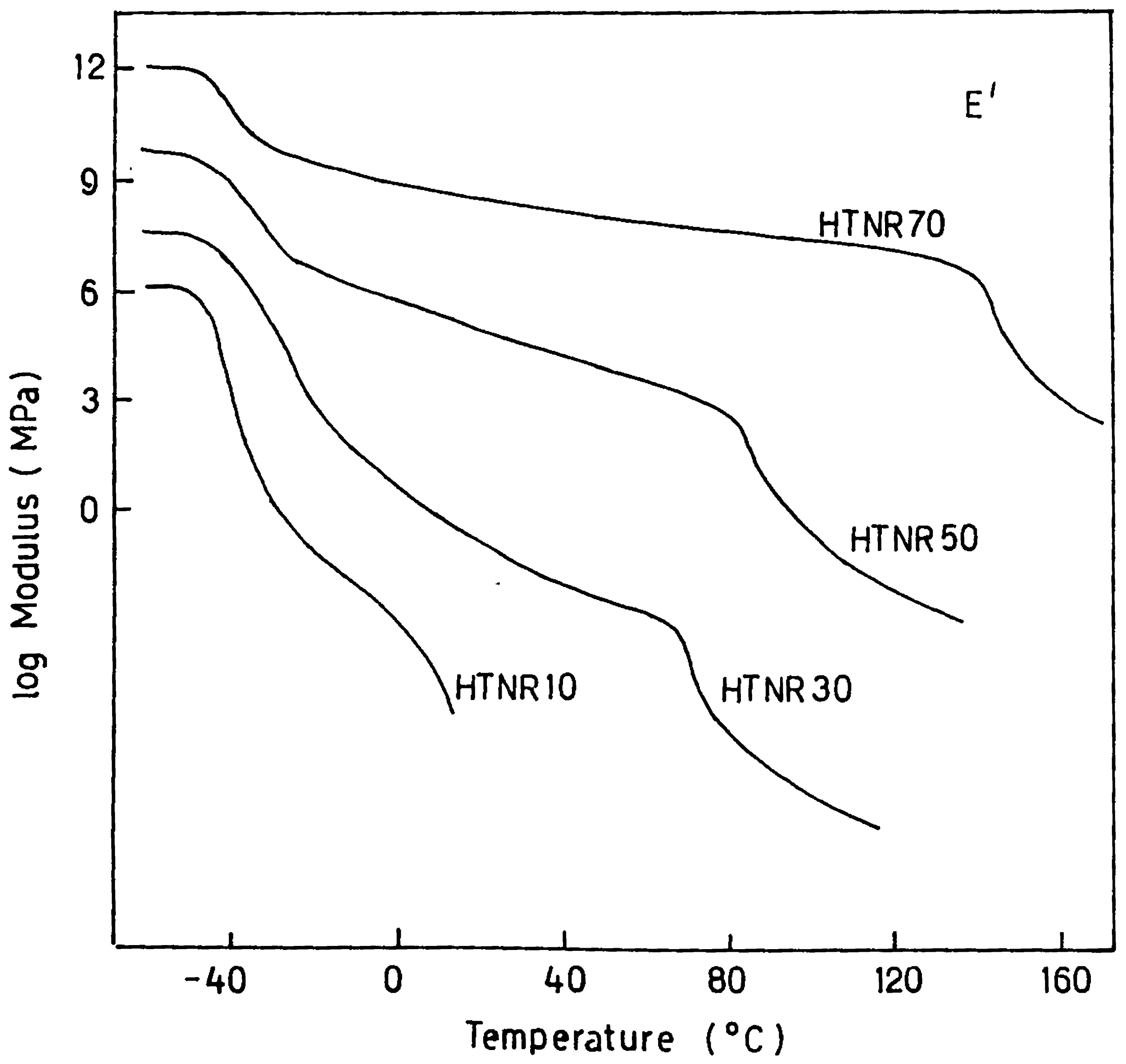


Fig.25 Rheovibron results: plot of log. storage modulus vs temperature of solution polymerised polyurethanes.

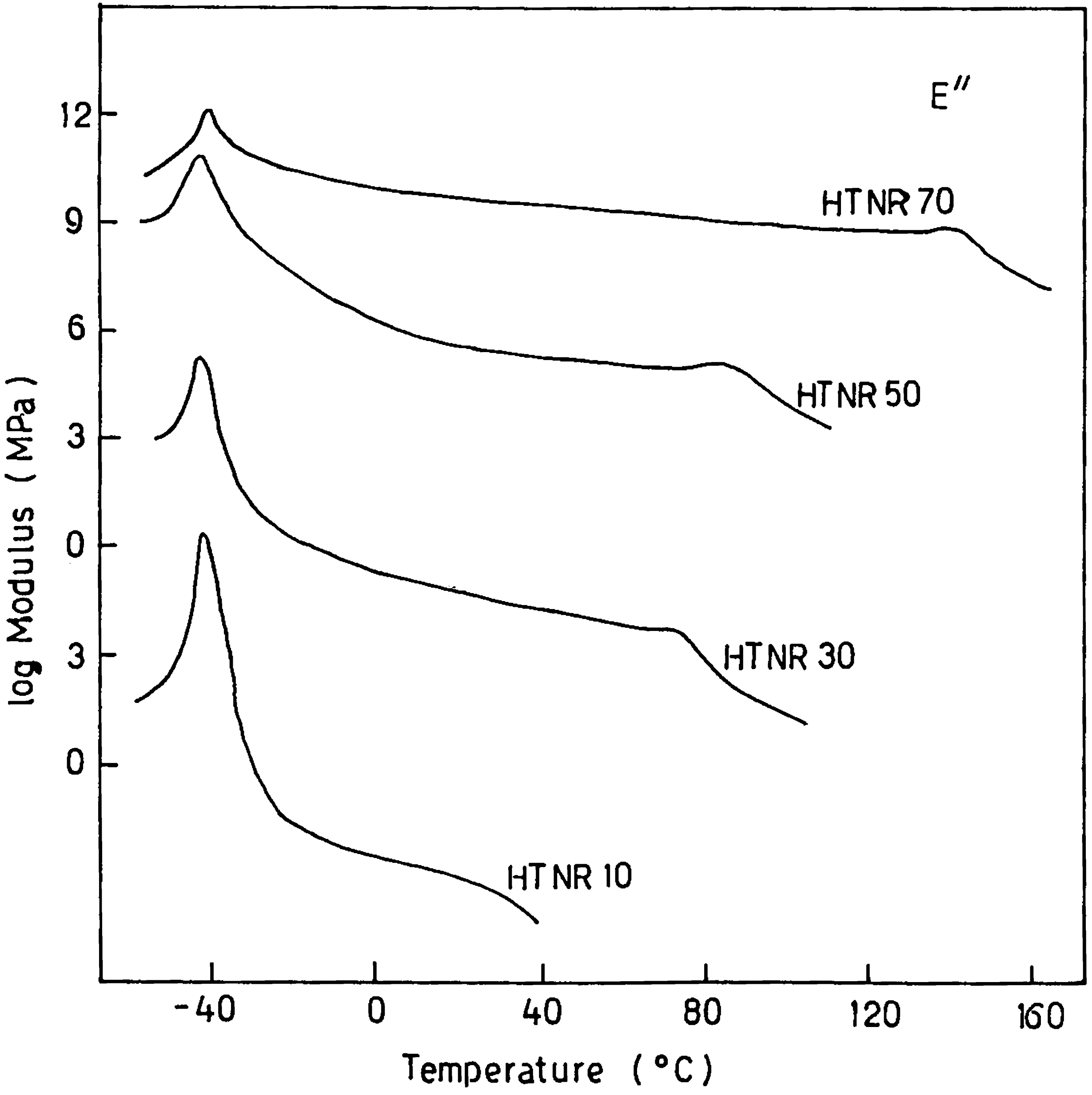


Fig.26 Rheovibron results: plot of log. loss modulus vs temperature of solution polymerised polyurethanes.

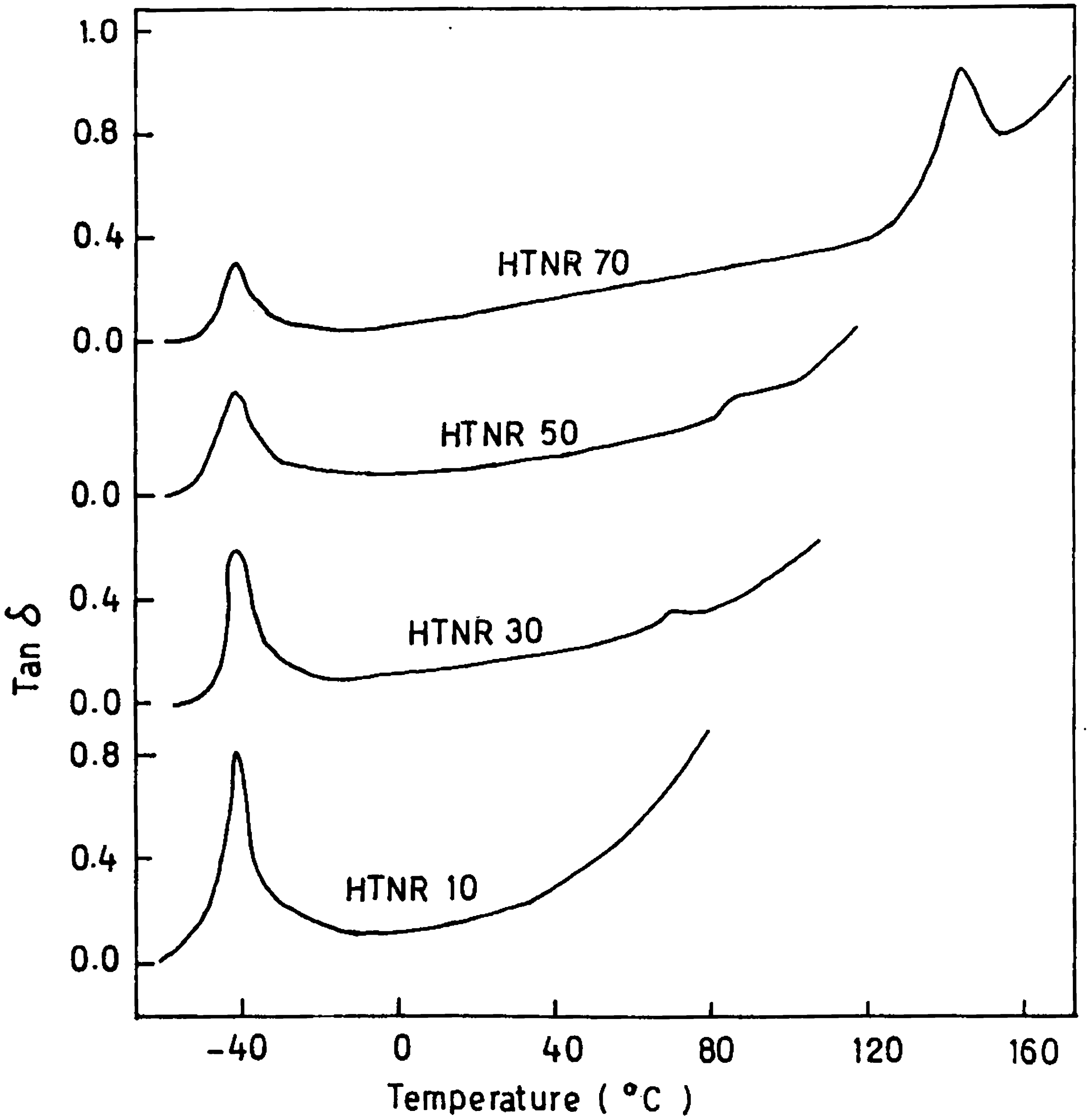


Fig.27 Rheovibron results: plot of Tan δ vs. temperature of solution polymerised polyurethanes.

TABLE - XVIII

Rheovibron results of bulk and solution polymerised samples (two step)

Sample	Bulk polymerised			Solution polymerised	
	Tg of the soft segment °C	Tg of the hard segment °C		Tg of the soft segment °C	Tg of the hard segment °C
HTNR 10	-39	--	--	-43	--
HTNR 20	-38	27	--	-43	--
HTNR 30	-38	40	61	-42	69
HTNR 40	-37	53	73	-41	71
HTNR 50	-37	74	87	-41	86
HTNR 60	-36	76	106	-40	115
HTNR 70	--	--	--	-40	143

Tg values determined from Tan δ peaks.

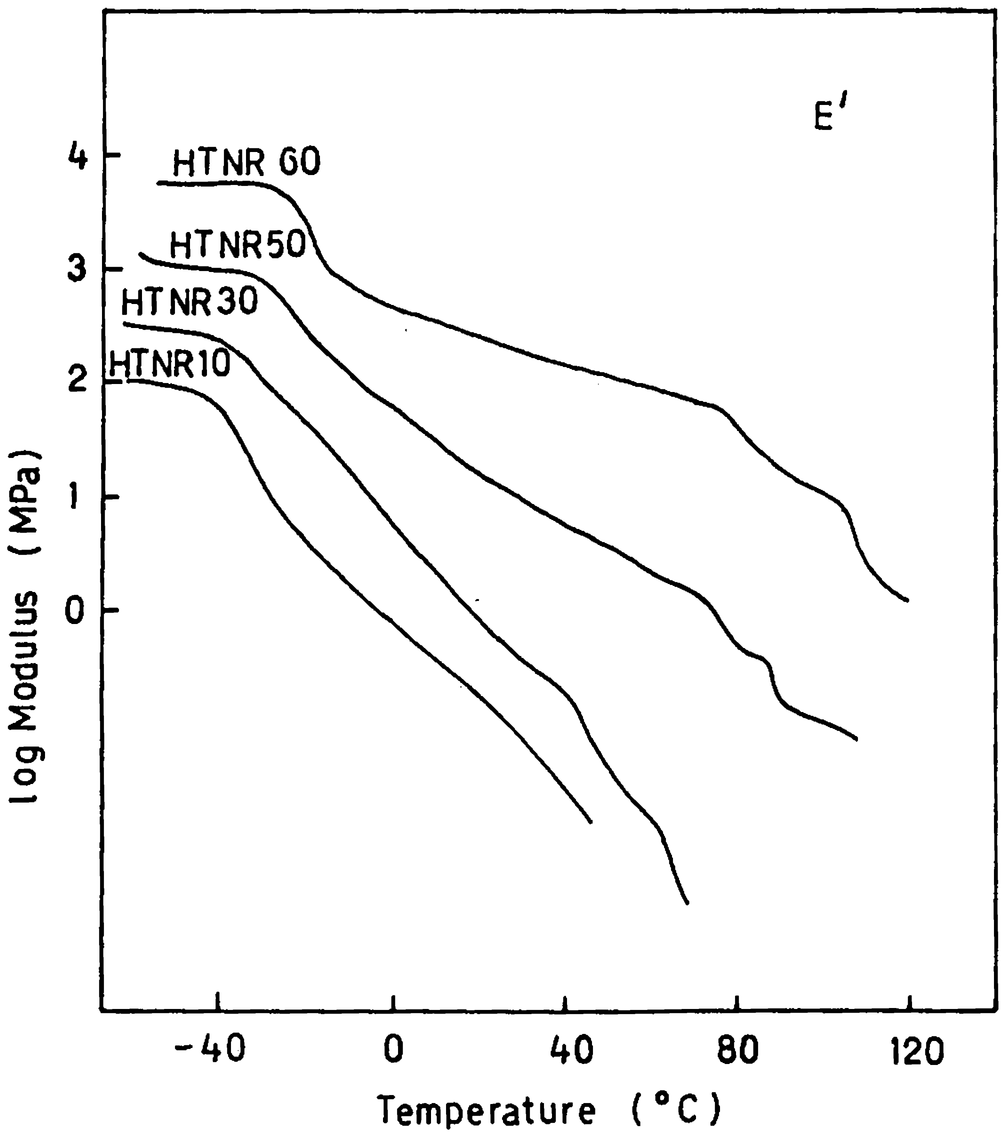


Fig. 28 Rheovibron results: plot of log. storage modulus vs. temperature of bulk polymerised (two step) polyurethanes.

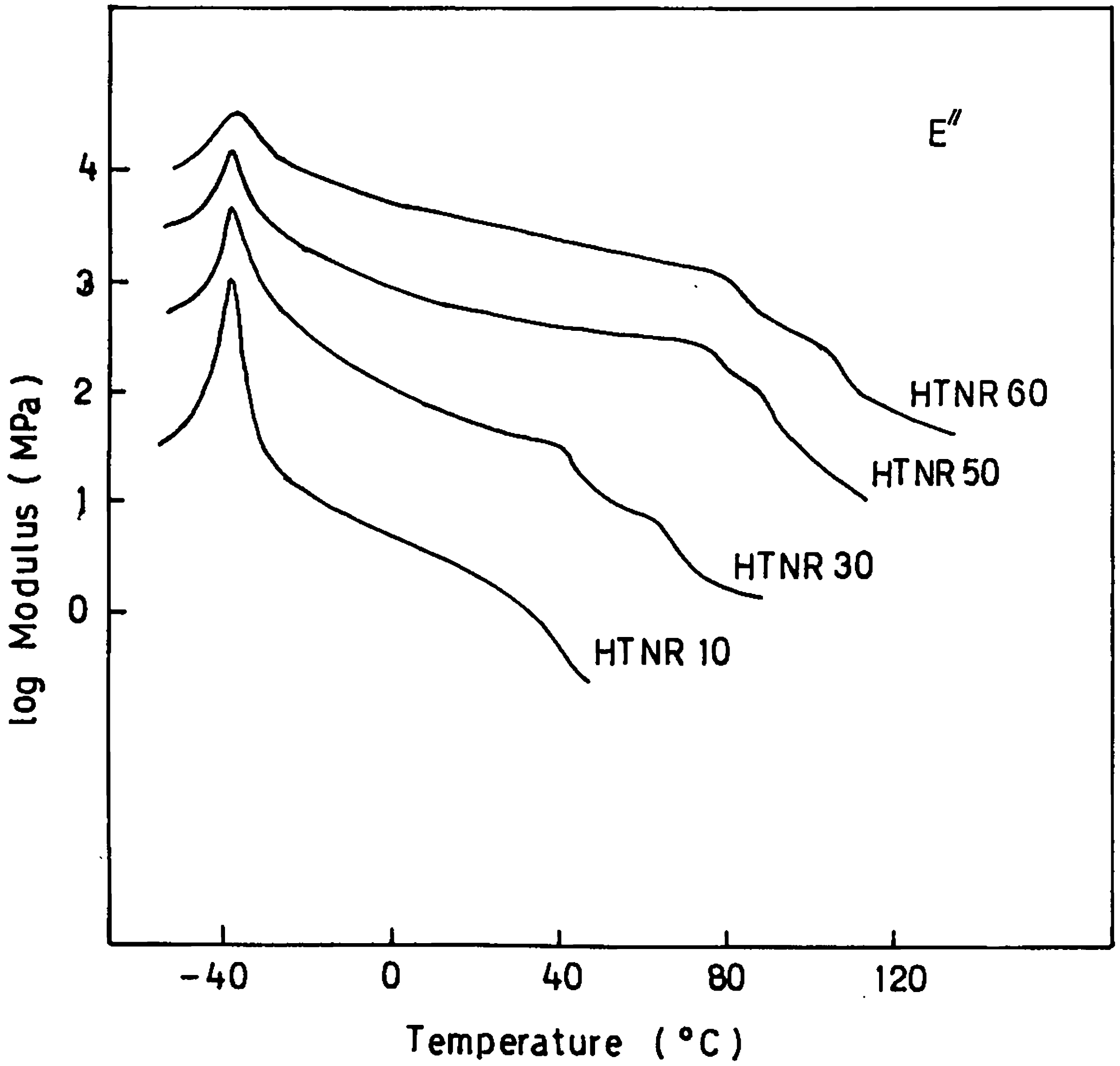


Fig.29 Rheovibron results: plot of log. loss modulus vs. temperature of bulk polymerised (two step) polyurethanes.

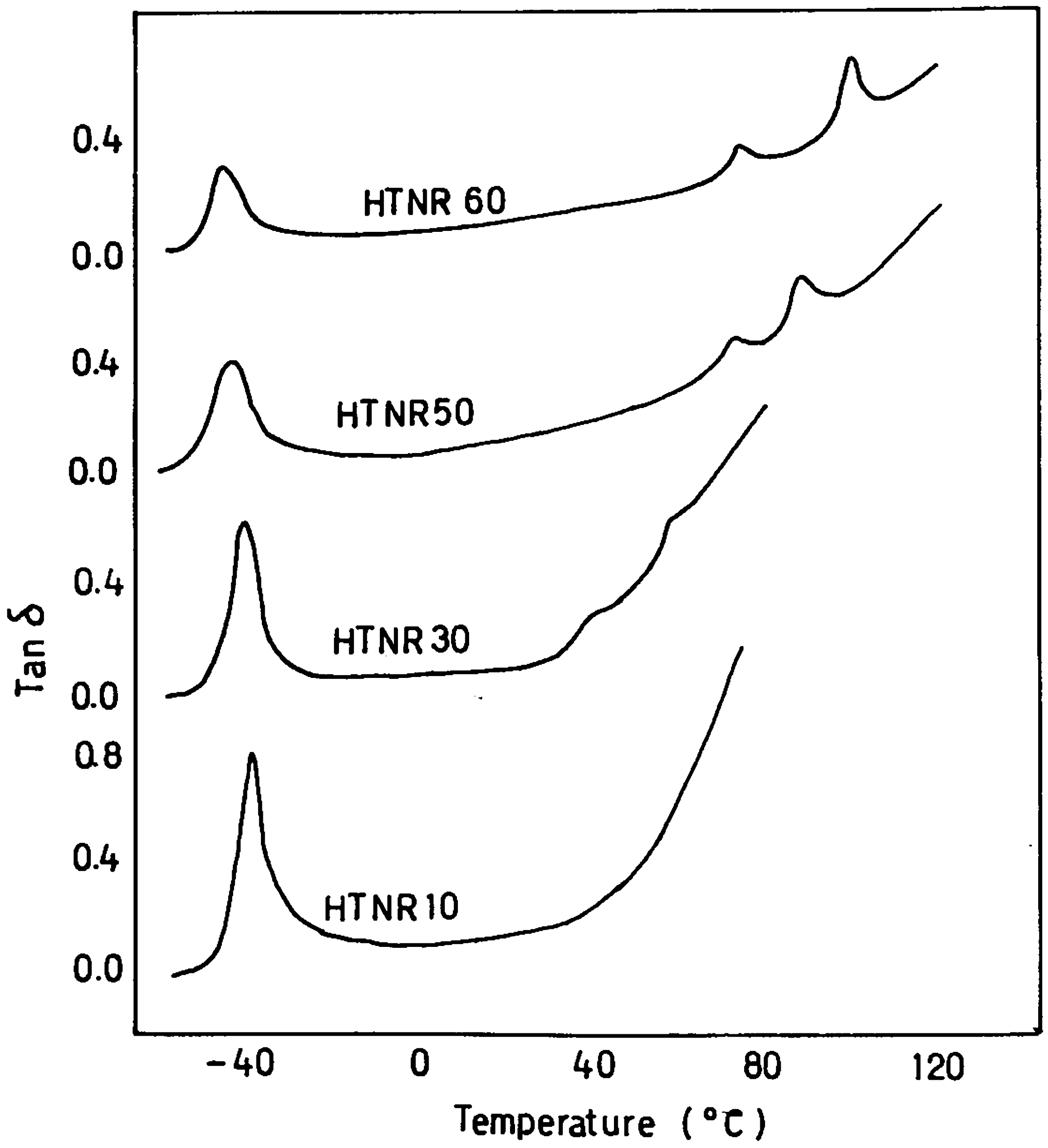


Fig.30 Rheovibron results: plot of Tan δ vs. temperature of bulk polymerised (two step) polyurethanes.

above the soft segment Tg increase with increasing hard segment content. This can be attributed to an increase in the volume fraction of the hard segment. The reinforcing nature of the hard segment domains is responsible for the increase in modulus.

It is interesting to note the temperature dependence of Tan δ as illustrated in figs. 27 and 30. As the hard segment content increases, the magnitude of the soft segment damping peak decreases while the magnitude of the hard segment peak or shoulder increases. Such changes in damping behaviour of these materials clearly reflect the changes in the relative amounts of the constituent phases. The change in hard segment sampling behaviour between samples HTNR 50 and HTNR 70 (in case of solution polymerised samples) suggests a change in sample morphology. The HTNR 70 displays a pronounced Tan δ peak of magnitude close to that of soft segment damping peak of the lowest hard segment content sample while HTNR 50 displays only a shoulder. The plateau modulus of HTNR 70 is also higher than that of HTNR 50. Unlike the behaviour of other polyurethanes[9] and consistent with the results of other HTPBD polyurethanes[1,3,4,10], the dynamic mechanical properties of HTNR based polyurethanes are unaffected by thermal history. Samples were quenched from 160°C to -80°C and immediately retested and were also stored in room temperature for one week prior to retesting. The values for the various viscoelastic functions are essentially unchanged. This invariance in properties suggests that no thermally activated phase mixing, altering sample morphology, occurs. The absence of thermal history effects can be attributed to the lack of urethane hydrogen bonding to the HTNR soft segment[4] by the hard segment NH groups.

3.11 Effect of catalysts

Effect of catalysts on the properties of the polyurethanes synthesised from HTNR, BDO and TDI by solution polymerisation technique is studied. As a typical case we have studied the system of HTNR 40. The catalysts used are triethylamine and dibutyl tin dilaurate, also we synthesised HTNR 40 in the absence of a catalyst. The degree of condensation (DC) was calculated which corresponds to the average number of structural unit per chain if the polymerisation had proceeded according to theory. Thus for HTNR 40 (ie 1:8:7), the degree of condensation value is $\overline{Mn} \left\{1 \times 3000 \text{ (MW of HTNR)} + 8.6 \times 174.16 \text{ (MW of TDI)} + 7.2 \times 90 \text{ (MW of BDO)}\right\}^{-1}$. Uncatalysed polymerisation is slow. Of the two catalysts compared, dibutyl tin dilaurate is superior to triethylamine. Data in Table XIX show that HTNR 40 polyurethanes formed without and with catalysts amine and tin have **Mn** values in the ratio 10:15:17. Also from the study of tensile strengths

TABLE - XIX

Effect of catalysts on the properties of segmented polyurethanes (two step(s)

Sample	Catalyst	DC[a]	$\bar{M}n$	Tensile strength MPa	Elongation at break(%)
HTNR 40	DBTDL[b]	12.1	61500	7.94	500
HTNR 40	TEA[c]	10.5	53500	5.93	410
HTNR 40	--	6.9	35200	3.29	360

a - Degree of condensation

b - Dibutyl tin dilaurate

c - Triethyl amine.

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it is clear that DBTDL is more efficient catalyst for the polyurethane synthesis. A similar study on the effects of catalysts in case of polyester RIM urethanes and castable urethanes have been reported[11].

3.12 Effect of polyol molecular weight.

Polyurethanes have been synthesised with HTNR having two different molecular weights other than HTNR 3000. Tensile properties were measured and reported in Table XX. It was found that as the polyol molecular weight goes up the tensile strength decreases for all the compositions under consideration, but the elongation at break is increased. It is to be noted that as the molecular weight of the polyol is decreased to 2300 then also there is a slight decrease in tensile strength. This may be due to the inability of the soft segment to crystallise when stress is applied. A similar study was reported by Ono et al[12]. They demonstrated that the tensile strength and related mechanical properties increased significantly below 3000 HTPBD molecular weight, may be here the strain induced crystallisation of the soft segment does not play an important role on the strength exhibited by these materials.

TABLE - XX

Tensile properties of segmented polyurethanes (solution polymerised, two step) - Effect of HTNR molecular weight

Sample	$\bar{M}n$ of soft segment	Tensile strength MPa	Elongation at break (%)
HTNR 30	5000	3.91	940
HTNR 40	5000	5.20	810
HTNR 50	5000	7.98	453
HTNR 30	2300	5.41	615
HTNR 40	2300	8.10	384
HTNR 50	2300	9.2	190

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CHAPTER - IV

STUDIES ON BLOCK COPOLYMERS FROM POLY(ETHYLENE OXIDE) AND HTNR

4.1 Introduction

Segmented block copolymers have been well characterised by the incompatibility of the segments present and the subsequent phase segregation of the hard and soft segments into separate micro domains[1,2]. However the conventional polyurethane elastomers which are based on polyesters and polyethers, possessing high strength and toughness are not completely phase separated systems[3-5]. A certain degree of phase mixing is present in these materials which is attributed to the interaction of the hard and soft segments, both containing polar groups, through secondary bond forces[1,2,6-10]. Moreover block polymers containing nonpolar hydrocarbon soft segments were found to possess inferior properties despite increased degree of phase separation. Materials based on polybutadiene[6-8], polyisobutylene[9] and polymyrcene[10] soft segments are reported examples. Hence it was argued that the useful properties of block copolymers are not entirely due to the high degree of phase separation[11]. Factors such as the soft segment functionality, molecular weights of the segments, glass transition temperature of soft segment, compositional heterogenity, degree of phase mixing, morphology etc. also accounted for the characteristic properties of the block copolymers.

Block copolymers consisting of non polar soft segments which possess high degree of phase separation can be considered as ideal systems on the basis of which structure-property relation can be well followed. The synthesis and studies of such materials, in which the non polar soft segment is derived from natural rubber and the hard segment is poly(ethylene oxide), are described in this chapter.

4.2 Materials

Hydroxyl terminated natural rubber (HTNR) having $\overline{M}n$ of 3000 prepared in our lab as per an earlier procedure (Chapter 2). Toluene diisocyanate (TDI) (80/20 mixture of 2,4 and 2,6 isomers) obtained from Fluka, Switzerland was used after distilling in an inert atmosphere. Poly(ethylene oxide) (PEO) obtained from Fluka, was used as received. Tetrahydrofuran (THF) (BDH) was dried and distilled before use. Dibutyl tin dilaurate (DBTDL) (Fluka) was used as catalyst without further purification.

4.3 Synthesis of Block Copolymers.

The materials were synthesised by the bulk and solution polymerisation techniques. The overall composition of the reactants are given in Table XXI.

TABLE - XXI

Overall composition of the block copolymers

Sample	Molar composition HTNR/TDI/PEO	PEO content %
NR:PEO - 1000	1/2.01/0.98	22.6
NR:PEO - 2000	1/2.01/1.02	37.8
NR:PEO - 3000	1/2.01/1.01	47.4
NR:PEO - 4000	1/2.01/1.02	54.6
NR:PEO - 6000	1/2.01/0.96	63.2

R value (NCO/OH) = 1.02

4.3(a) Single Stage Bulk Copolymerisation

HTNR along with DBTDL (0.03% by wt. of HTNR) were taken in a resin kettle provided with a mechanical stirrer and an inlet and outlet for nitrogen. PEO was melted and added into the HTNR /DBTDL mixture and stirred vigorously for 10 minutes. The entire system was kept at 80°C. TDI was added in a lot, stirred vigorously for 3 seconds and entire content were cast into a preheated tray coated with silicone release agent. Degassed in a vacuum oven at 70°C for two minutes and kept for curing at 100°C for 8 hours followed by ageing at room temperature for one week in a moisture free atmosphere.

4.3(b) Two stage Bulk Copolymerisation.

HTNR along with DBTL (0.03% by wt. of HTNR) was taken in a resin kettle provided with a dropping funnel, mechanical stirrer, and an inlet and outlet for nitrogen. TDI was added dropwise with constant stirring to the system kept at 60°C. When the addition was completed the temperature of the system was raised to 80°C and reaction continued for 1 hour. This was followed by the addition of molten PEO as a lot with vigorous stirring for 3 seconds and the contents were cast into a preheated tray coated with silicone release agent, degassed in a vacuum oven at 70°C and cured at 100°C for 8 hours followed by ageing at room temperature for one week in a dry atmosphere.

4.3(c) Two stage Solution Polymerisation.

HTNR was dissolved in THF so as to get a 10% solution and then taken in a flat bottomed flask equipped with a magnetic stirrer, nitrogen inlet and a reflux condensor. DBTDL catalyst (0.03% by wt.of HTNR) was added and the solution was brought to reflux. The final desired stoichiometric amount of TDI was added in drops followed by two hours of reaction to endcap HTNR. This was followed by the addition of the required amount of PEO as a solution in 50ml of THF dropwise during 2 to 3 hours followed by 2 hours of reaction. The excess THF was distilled off and the viscous polymer was cast into trays treated with silicone release agent, kept in a vacuum oven at 50°C to remove the traces of solvent present and then cured at 70°C for 24 hours followed by one week ageing at room temperature in a moisture free atmosphere.

4.4 Measurements

Infra red (IR) spectrum of the samples was recorded on a Perkin-Elmer model 377 IR spectrometer. Differential scanning calorimetry (dsc) was performed with a Dupont 9000 thermal analyser systems. A heating rate of 20°C min.^{-1} and a sensitivity of 5m.cal.s^{-1} was used. Cyclohexane (crystal-crystal transformation at 186K) and indium (melting point at 429.8K) were used as thermal stability of these materials were studied using Dupont 1090 Thermogravimetric analyser (TGA) at a heating rated 20°C.min.$^{-1}$ Stress-strain data were obtained on a Zwick 1445 Universal Testing Machine as per ASTM D 412-80 test method at 20°C using dumb bell shaped test pieces. Optical micrographs of the samples were taken on a "Leitz" Orthoplan microscope.

4.5 Polymer Designation

The samples are designated as follows. As an example NR:PEO-4000 (B2) indicates the sample where NR represents the hydroxyl terminated liquid natural rubber soft segment, PEO represents the poly(ethylene oxide) hard segment and (B) shows that the samples was bulk polymerised (2) indicates two stage. (1) in place of (2) indicates one stage. The letter 'S' in place of 'B' indicates the sample prepared by solution polymerisation.

4.6 Results and Discussion.

The infra red spectra of the soft segment in its endcapped form and the final sample prepared by solution polymerisation are given in figures 31 and 32 respectively. The presence of NH and CO bands at 3440 - 3150 cm^{-1} and 1690 cm^{-1} respectively in figure 31 indicates the endcapping reaction. This is further evidenced by the presence of strong absorption band of the -NCO group at 2260 cm^{-1}. The final product formed by chain extension does not contain the -NCO band which indicates that the chain extension reaction

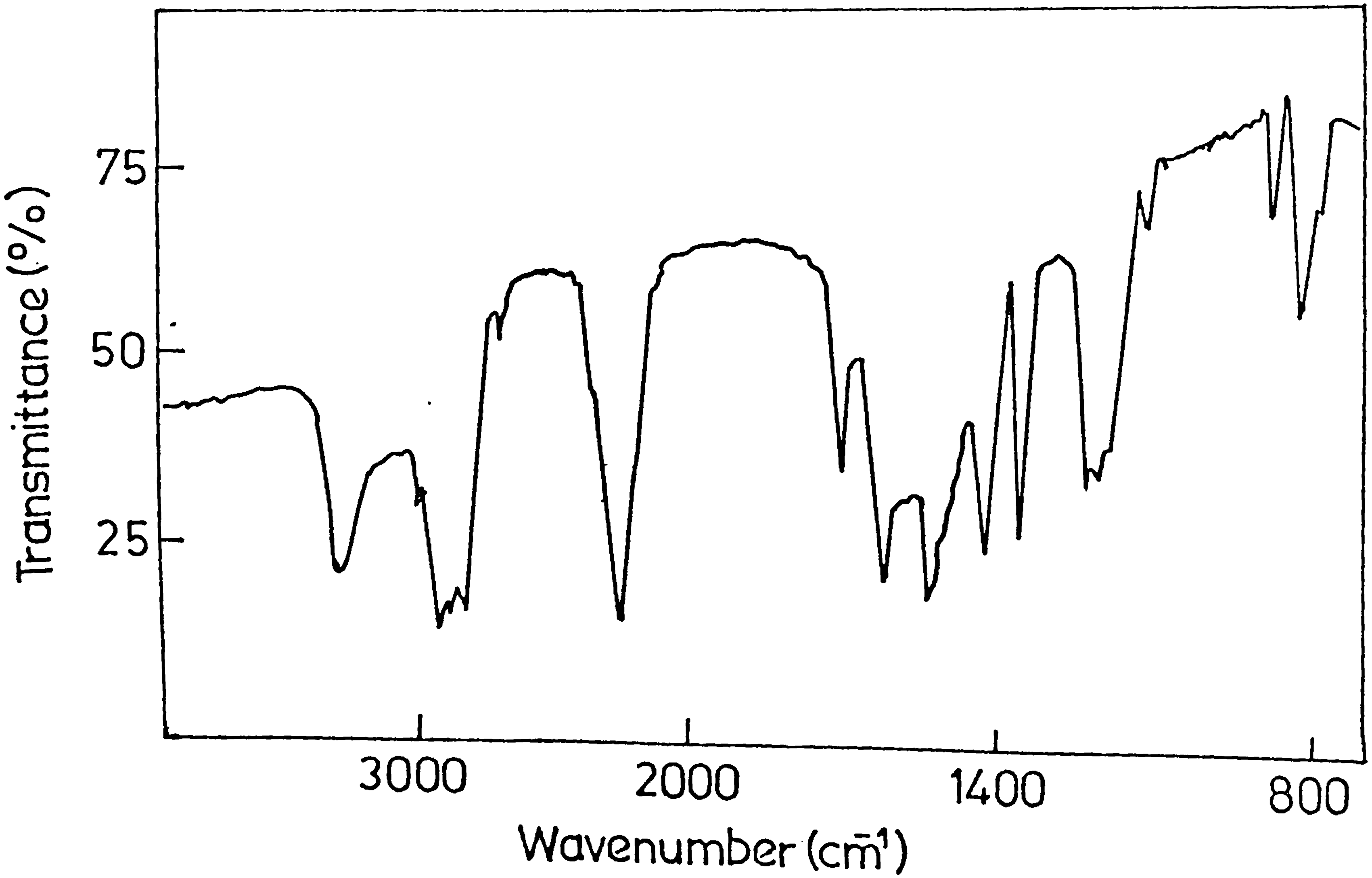


Fig.31 IR Spectrum of -NCO endcapped natural rubber.

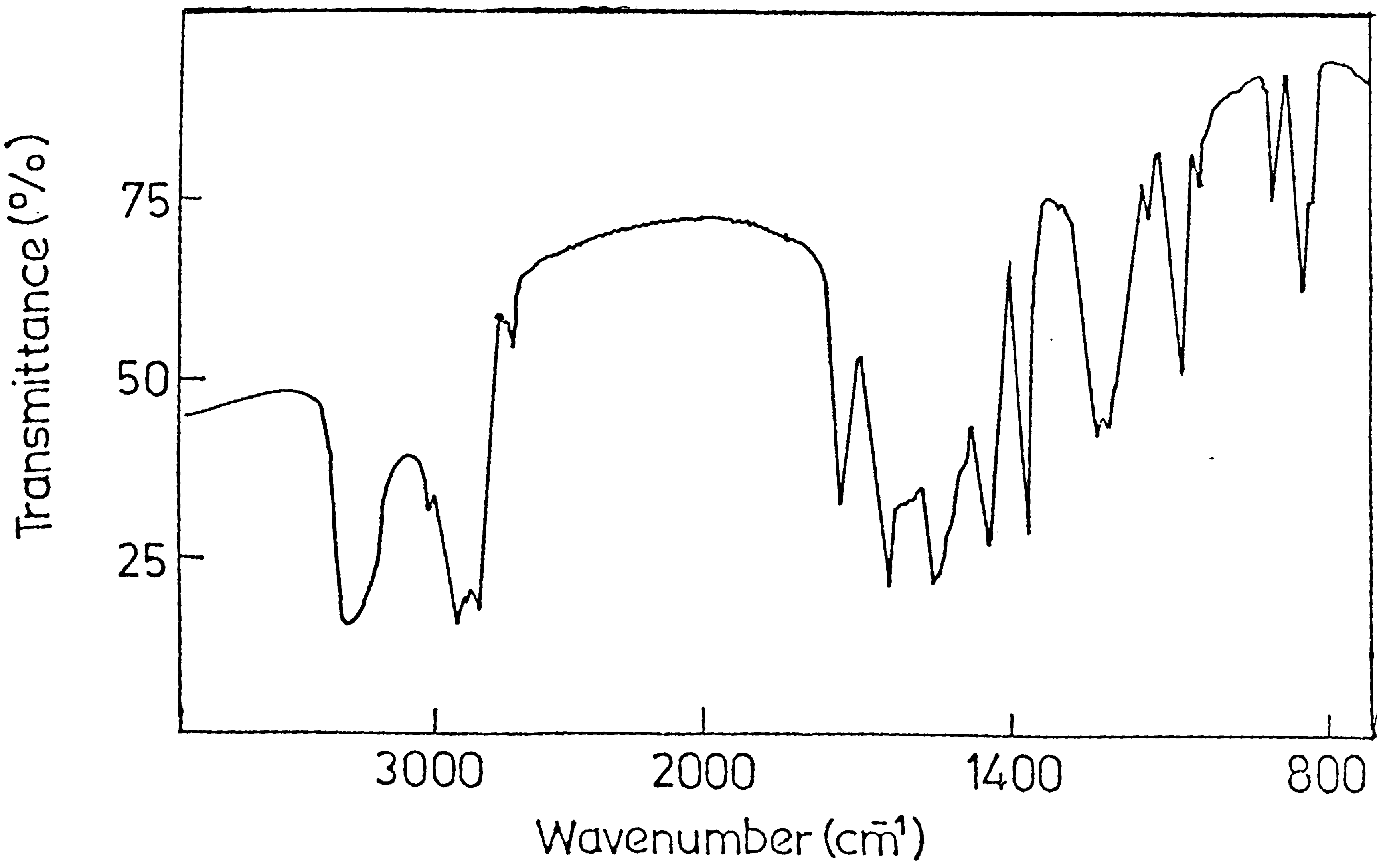
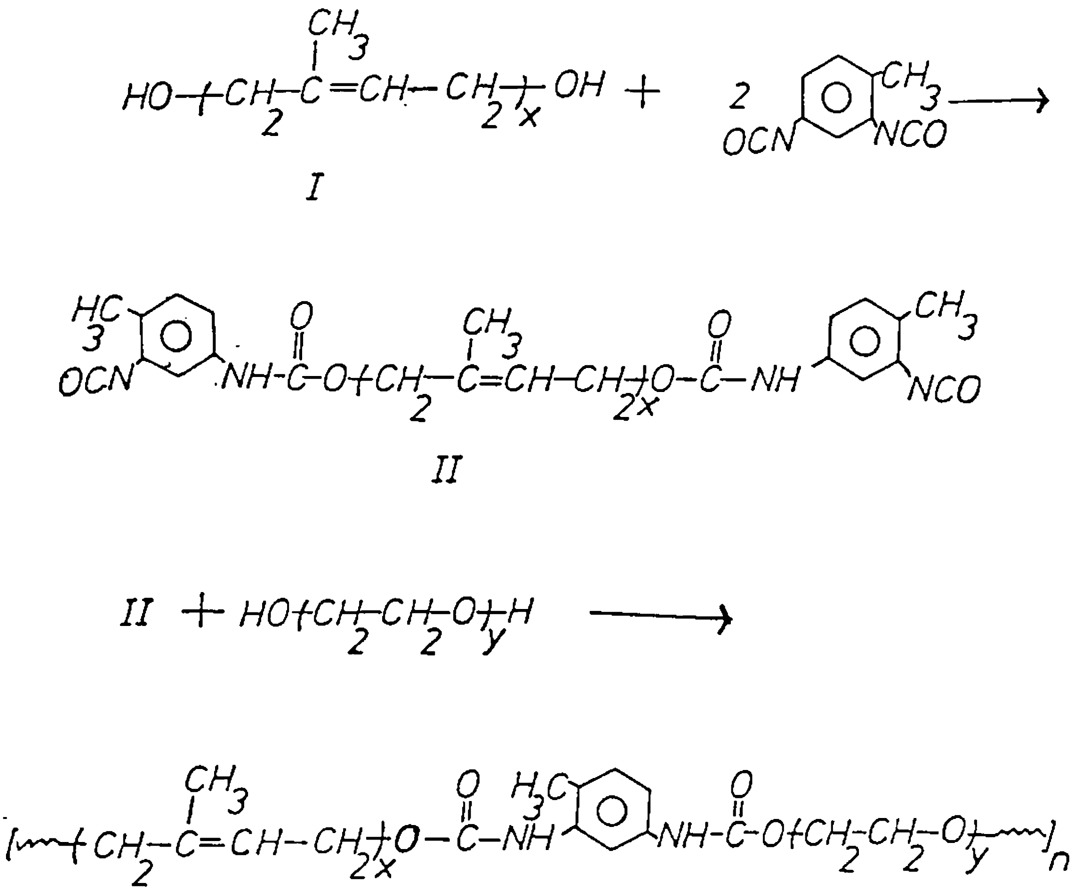


Fig.32 IR Spectrum of HTNR based block copolymer.

goes to completion. Thus the two stage reaction proceeded in a regular manner yielding the block copolymers. The courses of the reactions and the structure of the final product can be represented as shown below:



The coupling agent toluene diisocyanate reacts well with both the components yielding the final product.

4.5(a) Thermal Analysis

The dsc curves of the two stage bulk and solution polymerised samples are given in figures 33 and 34. The transition temperatures observed are tabulated in Table XXII along with that of bulk (one stage) polymerised samples. It shows that there are only 2 transitions associated with each of the samples examined. The glass transitions (Tg) and the melting transitions (Tm) corresponding to the natural rubber and poly(ethylene oxide) segments respectively. The Tg values of all the materials are found to be very close to each other irrespective of the method of preparation and the hard segment length. They differ only by a maximum of 5° with the Tg value of hydroxyl terminated liquid natural rubber viz. -68°C. Pascault and Camberlin[12] have shown that an increase in Tg of 4°C of the soft segment above the corresponding Tg of the homopolymers suggests complete phase separation. This observation can be very well applied to the present materials so that they can be considered as system in which the phase segregation is complete or very nearly so.

The crystallinity of the hard segments is evidenced by the nature of the melting transition. The melting temperature increases with molecular weight of the PEO and the values correspond well with the melting temperatures of the homopolymers,

TABLE - XXII

dsc results of block copolymers

	Sample	Bulk polymerised				Solution polymerised	
		One stage		Two stage			
		Tg of soft segment °C	Tm of hard segment °C	Tg of soft segment °C	Tm of hard segment °C	Tg of the soft segment °C	Tm of the hard segment °C
	HTNR	-68	--	-68	--	-68	--
A	NR:PEO - 1000	-62	40	-66	39	-65	42
B	NR:PEO - 2000	-61	48	-64	42	-65	44
C	NR:PEO - 3000	-61	50	-64	56	-65	58
D	NR:PEO - 4000	-60	63	-64	59	-65	63
E	NR:PEO - 6000	-59	60	-63	62	-64	69

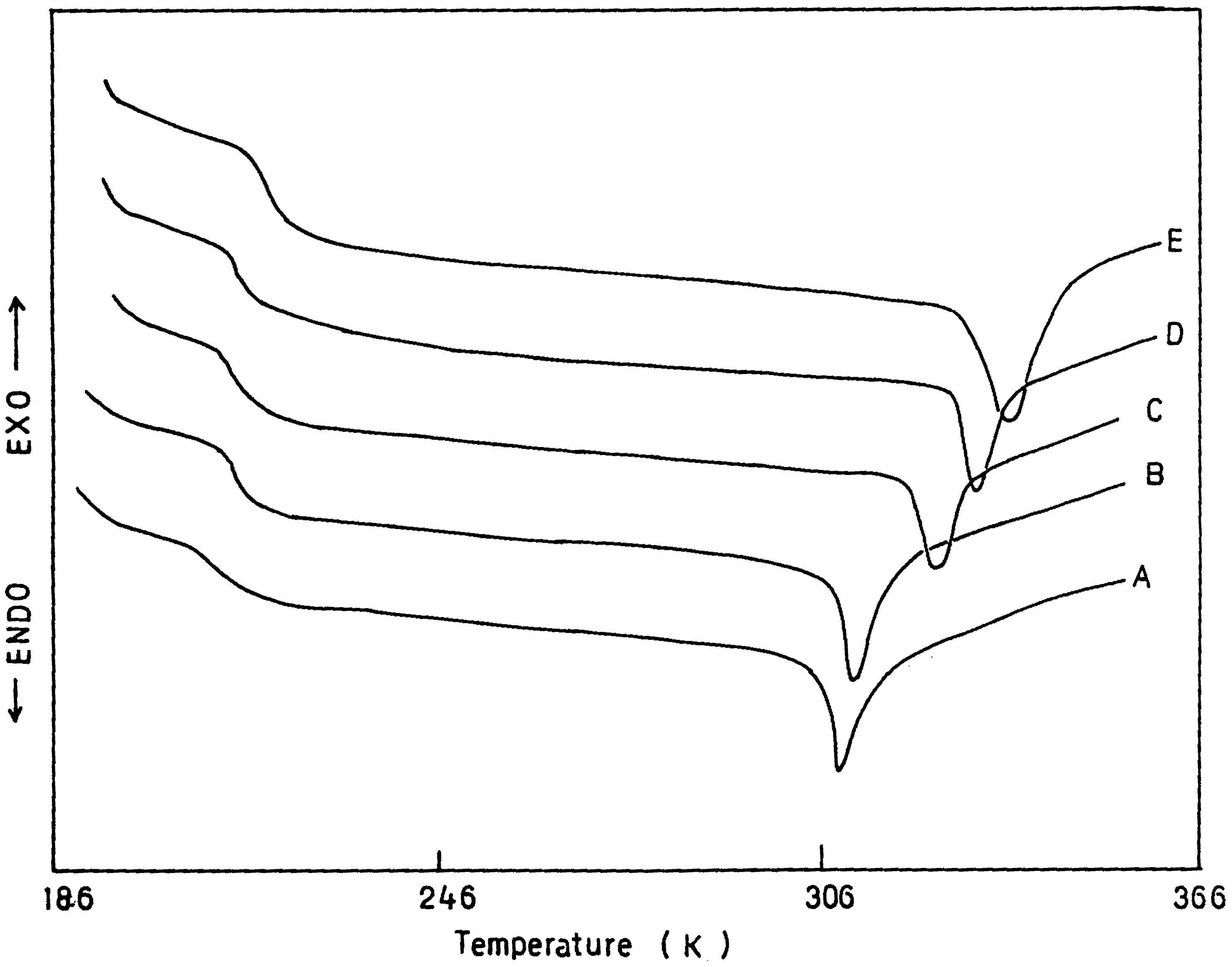


Fig.33 dsc curves of bulk polymerised (two step) block copolymers from HTNR and PEO.

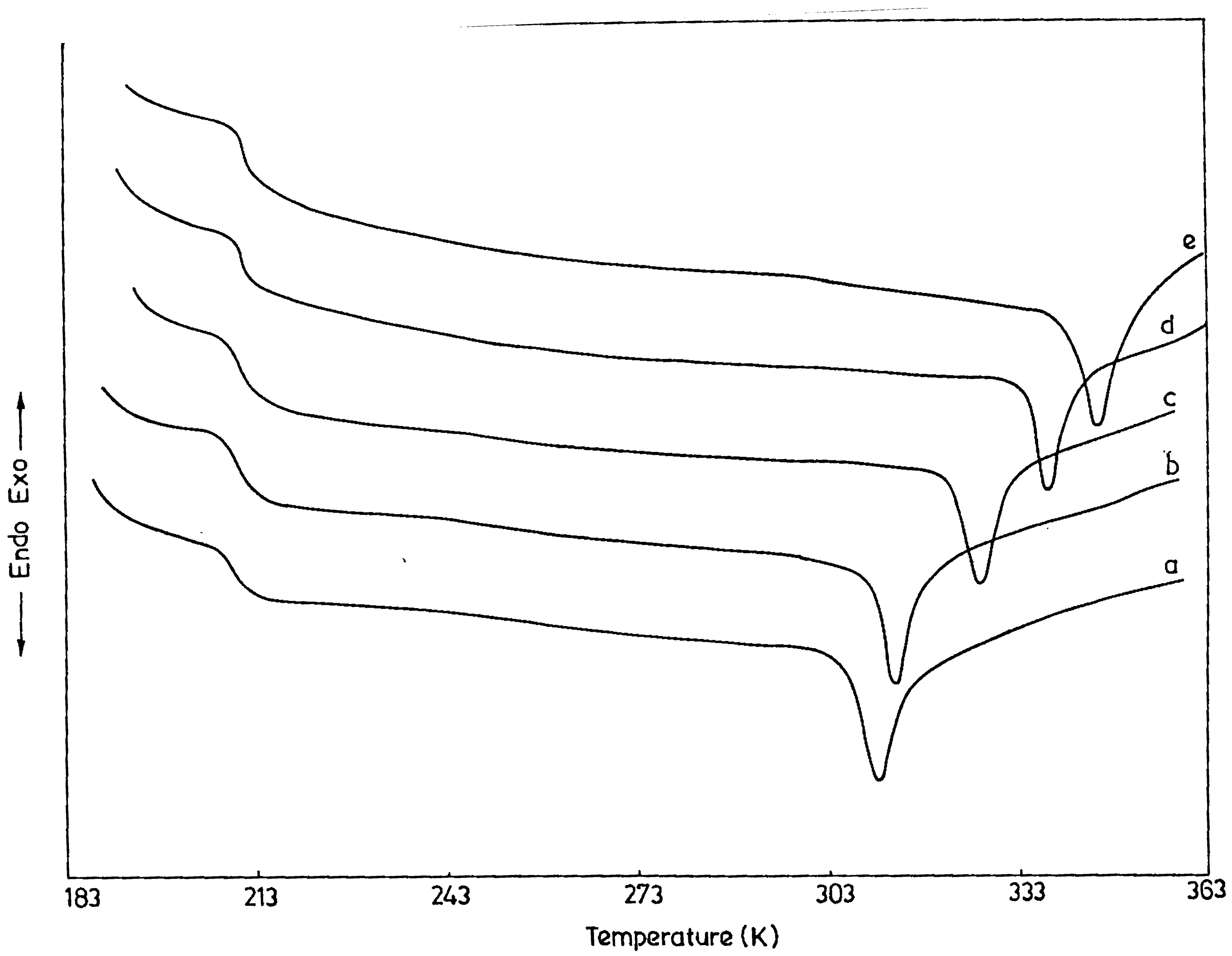


Fig.34 dsc curves of solution polymerised (two step) block copolymers based on HTNR and PEO.

once again indicating that almost complete phase separation occurs in the polymers. Only a single hard segment transition was observed in all cases irrespective of the method of their preparation. There are reported cases where the bulk polymerisation leads to more than one hard segment transition[2]. This was attributed to the poly dispersity of the hard segment length when they were formed in situ during chain extension reactions. Our observation of a single hard segment transition for all the samples is consistent with the fact that performed hard segments with very narrow molecular weight distributions were employed in their preparation.

Thermal stability of the materials were studied using thermogravimetric analysis (TGA) and typical thermograms of a bulk polymerised sample and a solution polymerised sample are shown in figures 35 and 36. The results were tabulated in Tables XXIII and XXIV respectively. Most of the copolymers decompose in two stages corresponding to the phases present. The onset of weight loss (To) occurs between 180 - 210°C for bulk polymerised samples (one stage), 280°- 300°C for bulk polymerised samples (two stage)and 300° - 320°C for solution polymerised samples respectively. The first stage weight loss is complete at 280°C for bulk polymerised samples (one stage) at 360°C for bulk polymerised (two stage) and at 380°C for solution

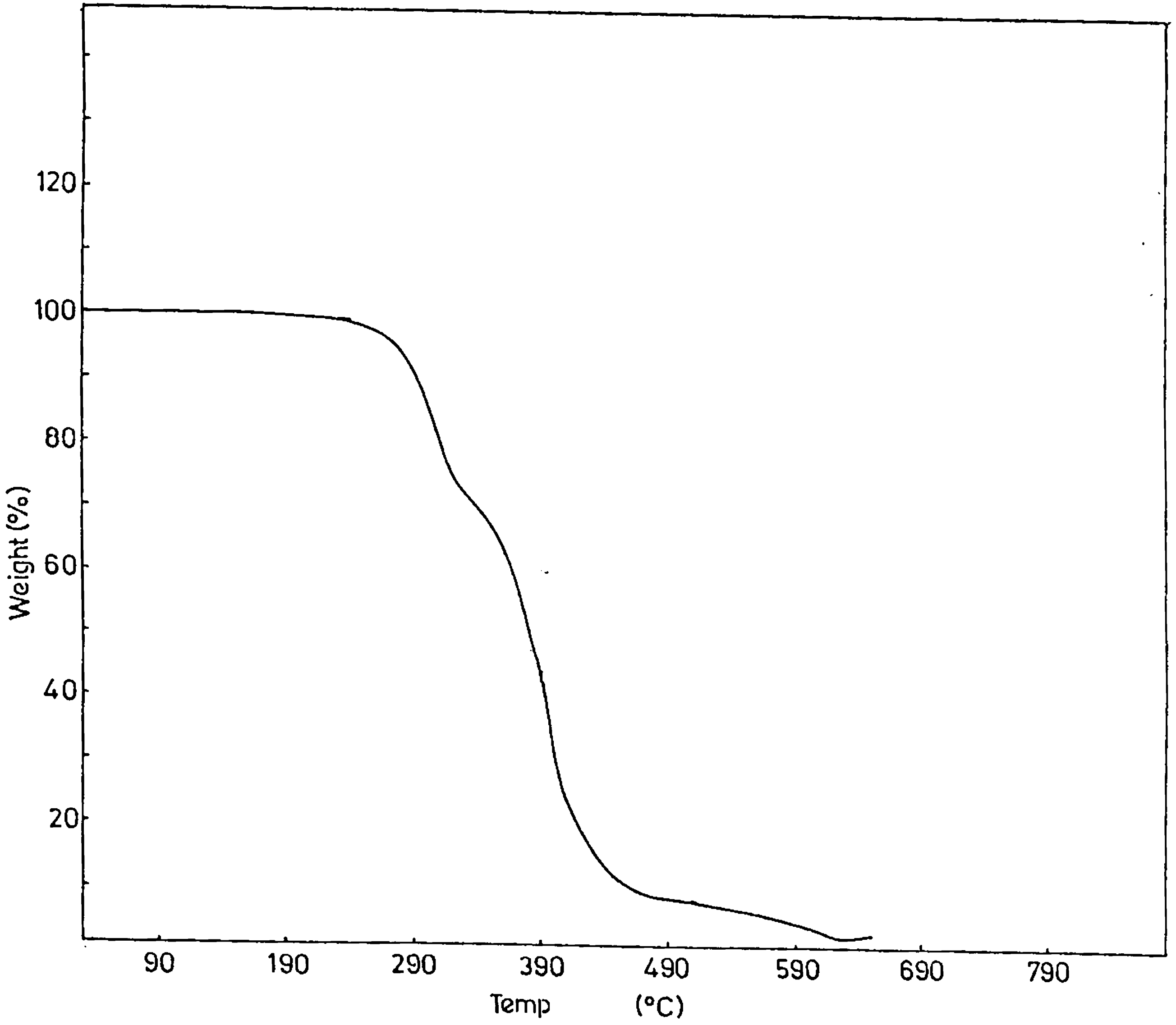


Fig.35 Typical TGA curve of a bulk polymerised (two step) block copolymer based on HTNR and PEO.

NR:PEO-3000

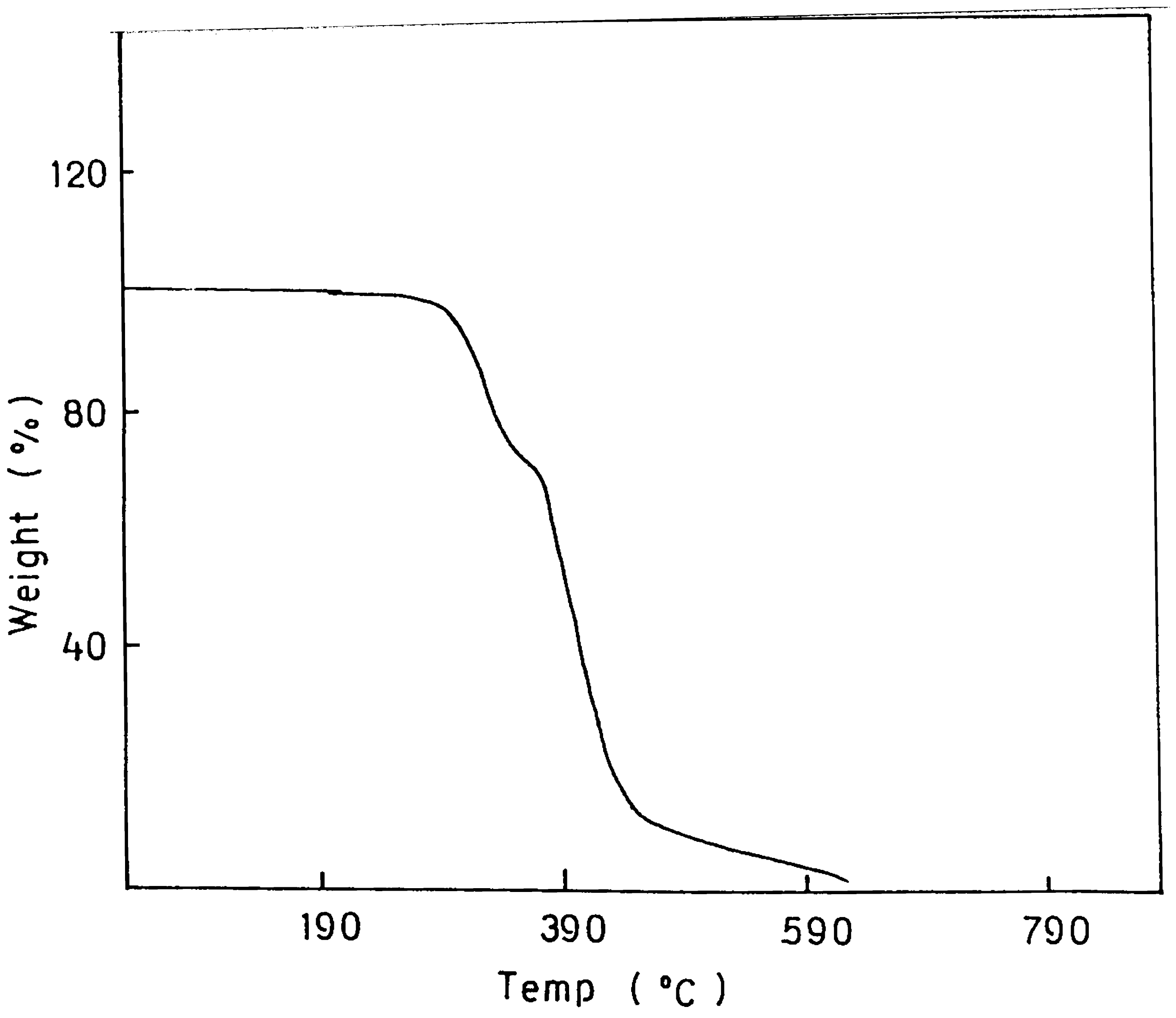


Fig.36 Typical TGA curve of a solution polymerised (two step) block copolymer based on HTNR & PEO.

NR:PEO-3000

TABLE - XXIII

TGA results of bulk polymerised block copolymers

Sample	One stage Decomposition temperature °C			Two stage Decomposition temperature °C		
	T_0	T_{10}^{a}	T_{50}^{b}	T_0	T_{10}^{a}	T_{50}^{b}
NR:PEO - 1000	180	218	330	380	348	410
NR:PEO - 2000	189	220	334	283	354	410
NR:PEO - 3000	194	228	336	287	357	420
NR:PEO - 4000	200	241	340	290	360	423
NR:PEO - 6000	208	282	346	296	365	430

a - Temperature corresponding to 10% wt. loss

b - Temperature corresponding to 50% wt. loss.

TABLE - XXIV

TGA results of solution polymerised block copolymers

Sample	Decomposition temperature °C		
	T_0	T_{10}^{a}	T_{50}^{b}
NR : PEO - 1000	304	383	408
NR : PEO - 2000	308	387	414
NR : PEO - 3000	310	394	418
NR : PEO - 4000	315	397	424
NR : PEO - 6000	319	410	436

a - Temperature corresponding to 10% wt. loss

b - Temperature corresponding to 50% wt. loss.

polymerised samples. The second stage dcomposition is rapid with a maximum rate in the vicinity of 340°C for bulk (one stage) samples and in the vicinity of 430°C for both bulk (two stage) and solution polymerised samples. A plateau seperating the two stages of decomposition also suggests that the two domains decompose at different temperatures. The higher thermal stability of the solution polymerised samples is obviously due to the higher degree of structural regularity of the polymer chain.

4.6(b) Optical Microscopy

The optical micrographs of a microtomed thin section of NR:PCO-2000(s) and NR:PEO-6000(s) are given in fig. 37 and 38 respectively. They were taken in plane polarized light. The hard phase is visible as white regions and the rubber phase as the black regions. Both the samples are phase separated systems but large difference in their morphology is observed in the micrographs. NR:PEO-2000(s) is phase separated into parallel regions of hard and soft phases. The rubber phase is the continuous phase and poly(ethylene oxide) appears as a dispersed phase. This is consistent with the low hard segment content of the sample. Crystallite formation is hardly noted in the micrograph. The low molecular weight of the hard segment whose melting temperature remains close to the ambient temperature

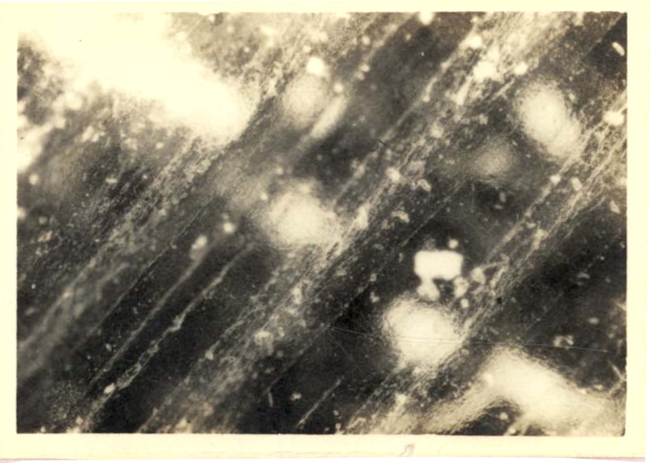


Fig.37 Optical micrograph of NR:PEO-2000(s).

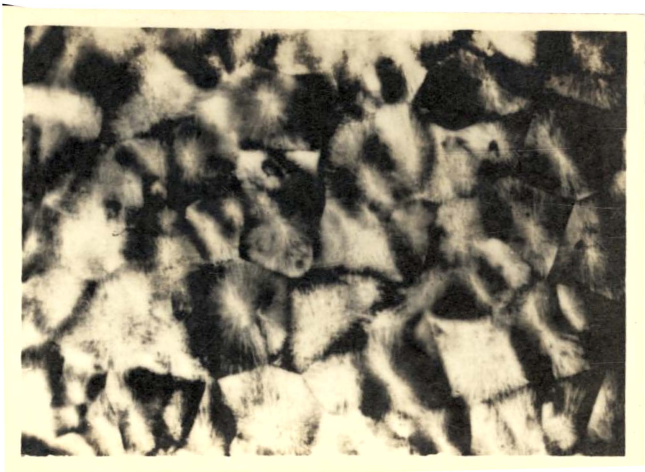


Fig.38 Optical micrograph of NR:PEO-6000(s)
X - 25.

may not aid crystallite formation. The NR:PEO-6000(s) is characterized by the spherulites of hard segments as seen in the micrograph in figure 38. Bicontinuous phase and other intermediate compositions could be observed in between these two extreme samples.

4.6(c) Stress-strain Behaviour

The stress-strain properties of the block polymers are summarized in Table XXV. Figure 39 represent the tensile curves of the solution polymerised samples. The tensile strength of all the materials studied are much lower than the conventional block copolymers, which was not expected from materials with high degree of phase separation. The variation in properties observed is attributed to the various factors which are discussed below.

One of the contributing factors of the high mechanical properties of polyurethane elastomers was found to be the existence of a certain extent of phase mixing in the materials consisting of polar soft and hard segments. The present materials are deprived of this phenomenon since the soft segments do not possess polar groups for mutual interaction with hard segments. Similar materials were reported in literature which possess comparitively low mechanical properties[11,13,14].

The nature of the hard domains which act as physical crosslinks between soft segments, plays an important role in the mechanical properties of block copolymers. Unlike in the case of polyurethane hard domains,where strong intermolecular attractive forces bring about firm segmental cohesion, the poly(ethylene oxide) hard segment cohesion is only due to crystallisation. The low strength and the nature of the tensile curves show that crystallisation of the soft segments does not occur under strain in the present materials.

The tensile strength of the materials increases with the poly(ethylene oxide) content. NR:PEO-1000(s) in which the hard segment content is 22% gives a tensile strength equal to 2.46 MPa. The value increases to 5.46 MPa for NR:PEO-6000(s) having a hard segment content equal to 63%. Similar increase in tensile strength was observed for the bulk samples also. In all the cases the elongation at break decreases with increase in hard segment content.

On the basis of the stress-strain curves shown in figure 39,the solution polymerised materials can be classified into three general types. Materials with hard segment content below 40% give the tensile curve similar to soft elastomers. The strain progressively increases with applied stress until the material break.

This behaviour along with the low initial modulus is consistent with the sample morphology and the low hard segment contents in NR:PEO-1000(s), (B1) and (B2) and in NR:PEO-2000(s) (B1) and (B2). In these samples the soft segments are the continuous phase with the hard domains not fully developed into crystallites (figure 37). The lack of well defined crystalline phase of poly(ethylene oxide) causes reduction in tensile strength and modulus.

Secondly samples with hard segment content above 40% behave like rigid elastomers. They possess higher modulus and tensile strength. There is a decrease in the initial strain and the tendency of showing yield point develops. These results suggest that the sample morphology changes with increased molecular weight of the poly(ethylene oxide) segments in such a way that crystalline hard domains are developed in the rubber matrix.

The third type of samples are those with high hard segment content of 60% and above. NR:PEO-6000(s), (B1) and (B2) show high initial modulus and tensile strength. The tensile curve exhibit distinct yield behaviour and the elongation at break drops to about 200% in the solution polymerised sample. The samples behave as rubber toughened plastic materials showing necking and strain whitening. According to the tensile curves initial deformation occurs to the hard domains

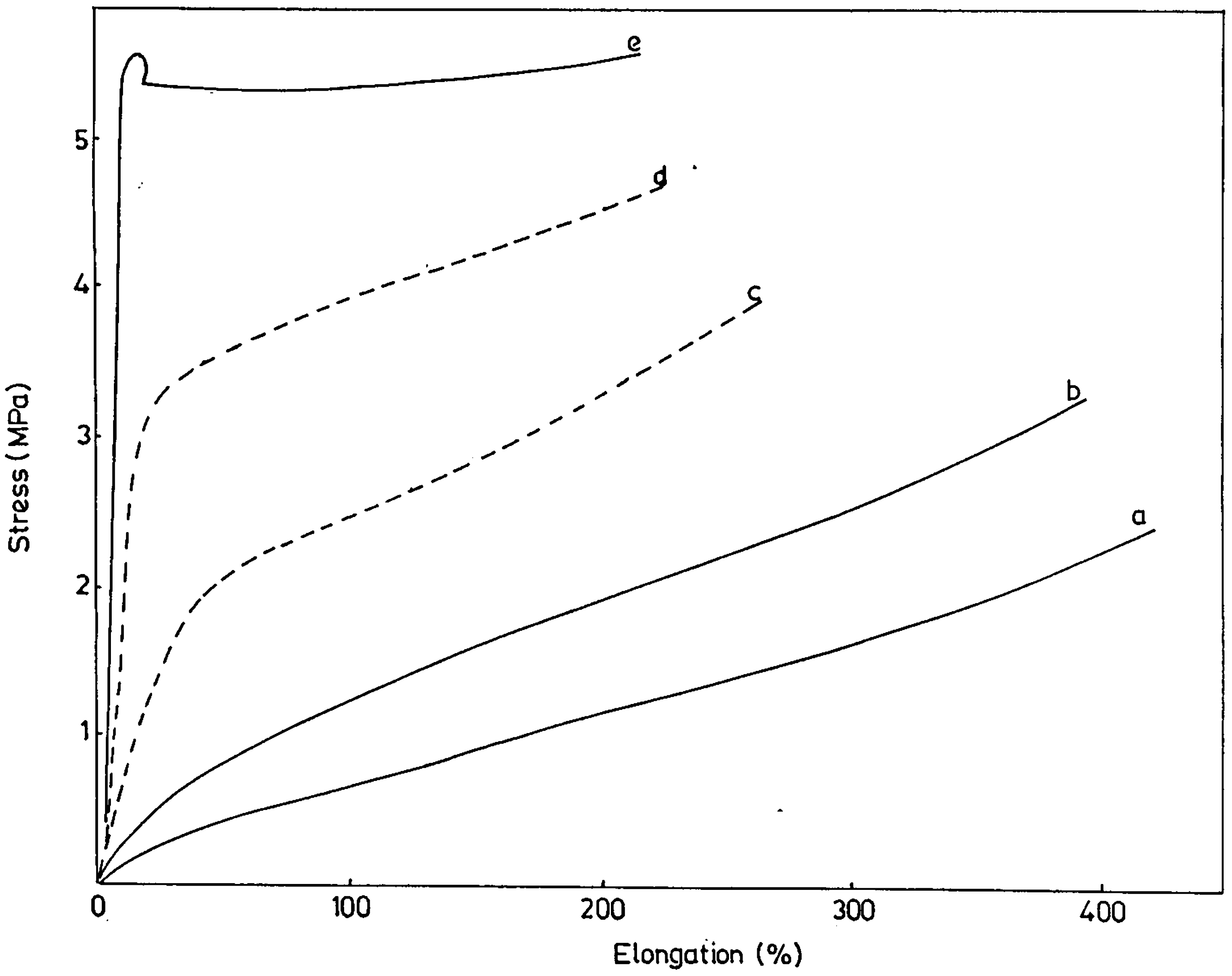


Fig.39 Tensile curves of solution polymerised (two step) block copolymers based on HTNR and PEO.

followed by the soft segment elongation. This result combined with the observations of the optical micrograph in figure 38 corroberate the phase inversion that occurs at high hard segment content.

Although the bulk and solution polymerised samples show the same trend in the stress-strain behaviour, a comparison of the test results given in Table XXV show marked differences in properties between two series of materials. The solution polymerised samples possess **more** improved properties than bulk polymerised samples. Also the variation in properties with composition of bulk samples occurs over a narrower range. As the hard segment content increases beyond 50% the material becomes brittle and does not show any further improvement in tensile properties. The deterioration in properties of the bulk samples is mainly attributed to the compositional heterogenity. The incompatibility of the two reacting components leads to nonuniform mixing during bulk polymerisation stage. Consequently macrophase separation occurs leading to uneven reaction and thus the final product may be a multicomponent mixture containing homopolymers of soft and hard segments and copolymers with a wide distribution of molecular weights.

TABLE - XXV

Mechanical properties of block copolymers

Sample	Bulk polymerised				Solution polymerised	
	One stage		Two stage		Two stage	
	Tensile strength MPa	Elongation at break (%)	Tensile strength MPa	Elongation at break (%)	Tensile strength MPa	Elongation at break (%)
NR:PEO - 1000	2.40	247.4	1.92	310.6	2.46	421.0
NR:PEO - 2000	3.92	300.4	2.18	307.9	3.24	396.0
NR:PEO - 3000	1.08	146.0	2.85	235.6	3.97	267.4
NR:PEO - 4000	4.02	193.4	3.06	174.4	4.72	230.3
NR:PEO - 6000	1.06	114.0	2.94	132.0	5.64	214.2

4.6(d) Hydrogels

The block copolymers are capable of forming hydrogels due to the highly hydrophilic nature of poly(ethylene oxide). Swelling behaviour is also observed in non polar solvents such as toluene due to the interaction of the rubber segments with the solvent. In both water and toluene, sol fraction was not observed in the case of the solution polymerised samples indicating complete reaction of the components. The swelling data is presented in Table XXVI. Samples with higher soft segment content swell highly in toluene whereas those with higher hard segment content swell highly in water. The water uptake increases with increase in hard segment content. More than 500% water absorption was recorded by the hard segment for sample with 63% PEO content.

TABLE - XXVI

Swelling of block copolymers in water and toluene

Sample	PEO content (%)	Water absorption		Water absorption by PEO in block copolymers. (%)	Toluene absorption		Toluene absorption by NR in block copolymers. (%)
		Weight increase (%)	Water content (%)		Weight increase (%)	Toluene content (%)	
NR:PEO-1000(S)	22.6	7.5	6.9	33	201.3	66.8	298
NR:PEO-2000(S)	37.8	22.3	18.2	60	141.4	58.5	256
NR:PEO-3000(S)	47.4	51.6	34.0	110	90.6	47.5	194
NR:PEO-4000(S)	54.6	165.8	62.3	306	72.3	41.9	179
NR:PEO-6000(S)	63.2	360.5	78.2	565	41.7	29.4	132

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CHAPTER - V

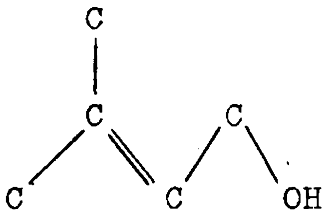
SUMMARY AND CONCLUSION

In the present study, the photochemical depolymerisation of NR in toluene, in presence of H_2O_2 and a homogenizing solvent (Methanol/Tetrahydrofuran) so as to get hydroxyl terminated liquid natural rubber (HTNR) has been carried out. The copolymerisation of this product with butane 1,4 diol and toluene 2,4 diisocyanate in presence of a catalyst, dibutyl tin dilaurate, to produce polyurethanes with HTNR soft segments is also reported. The preparation of block copolymers based on poly(ethylene oxide) with varying molecular weights and HTNR are also discussed along with a detailed study on their thermal and mechanical properties.

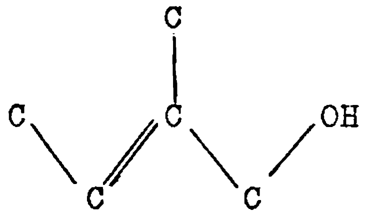
5.1 Production of hydroxyl terminated liquid natural rubber (HTNR)

The photochemical depolymerisation of NR using UV light from a medium pressure mercury vapour lamp, and sun light were conducted and the products obtained were analysed. The molecular weights (Mn) after 60 hrs of irradiation when methanol was used as the homogenising agent was 3000 and 3300 respectively. The products gave hydroxyl values of 36.27 mg of KOH/g and 30.92 mg of KOH/g respectively. The corresponding functionalities were 1.94 and 1.82. Hence it was concluded that the UV light and sun light were almost equally effective in bringing about degradation of NR.

The IR and NMR data presented in Chapter 2 clearly establishes the presence of primary hydroxyl groups in the depolymerised products. The minor peaks at $\delta = 60.72$ and $\delta = 63.51$ in the ^{13}C-NMR of the product are in close agreement with the reported values for the β-carbons attached to the hydroxyl groups in allylic structures like A and B respectively.



A



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These observations and a functionality of approximately two obtained for the product lead to the conclusion that the depolymerised NR has hydroxyl end groups. Based on the analytical data a mechanism is proposed for the depolymerisation process. The by-product obtained was found to contain carbonyl groups from IR spectra. Chemical analysis of the material gave a carboxyl value of 5.94 mg of KOH/g and a carbonyl value of 12.29 mg of KOH/g. The formation of these groups may be through side reactions with free oxygen present in air giving peroxide radicals and its subsequent decomposition to the side products. Considering these facts, a mechanism for the formation of side products is also proposed.

The photochemical degradation of NR in solution reported, is an efficient and economical method for the preparation of HTNR, since the labour and machinery requirements are low and also that it utilizes solar energy. The high clarity and processability are added advantages of the material.

5.2 Synthesis and characterization of segmented-urethanes based on HTNR soft segments.

Polyurethanes based on HTNR soft segments were synthesised with varying hard segment content (TDI/BDO) Two processes were used in the preparation of polyurethanes (1) one step process (2) two step process. Two step process was again split into two. (a) Two step bulk and (b) two step solution polymerisation processes.

The infra red analysis of the products obtained showed that complete conversion to PU's have taken place. The stress-strain behaviour of these materials were determined and it is found that the one step material does not show any general trend in contrast to the two step materials, which show three general types of mechanical behaviour. Below 40% HS content they are soft elastomers. At 70% HS, they behave as rubber toughened plastic displaying necking and strain whitening. Intermediate compositions behave as rigid elastomers. This variation of mechanical properties is likely to be caused by the changes in sample morphology.

Thermal analysis of the materials by differential scanning calorimetry shows that they are phase segregated materials. The soft segment glass transition is found to be about -59°C for bulk polymerised samples and at -64°C for solution polymerised samples. A maximum of two hard segment Tg's are observed in bulk polymerised samples in contrast to the single hard segment Tg exhibited by solution polymerised samples. Fractionation according to the difference in solubility of the bulk polymerised samples has been conducted and it was concluded that the twin Tg behaviour can be explained by considering, in addition to the segregation of hard and soft segments, the poor compatibility and greater differences in solubility, cause the segregation of macromolecules as a whole according to their composition during moulding or solution casting and hence separation of hard segments of different lengths. This can arise from the heterogenity of the reactants themselves. A schematic model has been proposed to explain the heterogenous reaction which takes place in the two step bulk polymerisation process.

Thermal stability of the materials was determined by thermogravimetry. Generally a two stage decomposition curve was observed indicating that the two phases present decompose at two different temperatures.

Dynamic mechanical analysis of the materials was also done. As expected the samples showed two principal relaxations corresponding to the two phases present in the material. The Tg values were determined from the Tan δ peaks, at 3.5 Hz. Consistent with the dsc results, the soft segment Tg of the samples were found to be independent of the hard segment content.

Effect of catalysts on the polyurethane synthesised by solution polymerisation technique is also investigated. It is concluded that DBTDL is a better catalyst than TEA from the results obtained from tensile measurement and also from the calculations of the degree of condensation.

Effect of the HTNR molecular weight on mechanical properties of polyurethanes synthesised was investigated. It was found that a molecular weight of about 3000 gave maximum tensile strength and as the molecular weight of polyol increases, tensile strength decreases but elongation at break increases.

5.3 Studies on block copolymers from poly(ethylene oxide) and HTNR.

Block copolymers were prepared from HTNR and poly(ethylene oxide) with varying molecular weights. Toluene 2,4 diisocyanate was used as the coupling agent for combining the two components. The materials were synthesised by the bulk and solution polymerisation techniques (ie. one step and two step). The products were characterized by IR analysis, differential scanning calorimetry, thermogravimetry and optical microscopy. Their mechanical properties were also evaluated. With increasing PEO content, the properties vary from soft to rigid elastomers and rubber toughened plastics. This variation in properties is caused by the changes in sample morphology which depends on the relative fractions of PEO and HTNR segments. Water absorption capability of these block copolymers was determined. Hydrogels with water content apprximately upto 80% were obtained.

It is concluded that the bulk and solution polymerisation processes for the preparation of block copolymers from HTNR and PEO led to highly phase separated materials. The solution polymerised samples exhibited higher breaking stresses than bulk polymerised samples at the same nominal hard segment molecular weight. These materials are high water absorbing substances and can form hydrogels. Hydrogels having upto 80% water content were obtained. Non porous gels are useful as carriers of fragrances or as warm/cold compresses. Foam-hydrogels from this material can be used as humidity absorbers and also as enzyme carriers.

The polyurethanes prepared from HTNR having TDI/BDO hard segments can be used for shoe soles with adequate loading of fillers like carbon black or silica. The hydrolytic stability of these polyurethanes over conventional polyester or polyether polyurethanes is an added advantage since these have a hydrocarbon backbone.

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List of Publications from the Present Work.

1. A novel method for the preparation of hydroxyl terminated liquid natural rubber, Makromol. Chem. Rapid Commun., 7, 159 (1986).
2. Production of hydroxyl terminated liquid natural rubber - mechanism of photochemical depolymerisation & hydroxylation., J. Appl. Polym. Sci., 35, 1227 (1988).
3. Segmented block copolymers from hydroxyl terminated natural rubber and poly(ethylene oxide) (Communicated).
4. Studies on polyurethane elastomers based on hydroxyl terminated natural rubber (HTNR) soft segments. (Communicated)

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