

## Synthesis and Characterisation of *p*-Toluene Sulfenyl Chloride Modified Natural Rubber

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Cameroon *et al.*<sup>1</sup> have reported evidence of block copolymers being formed by direct addition reaction of *p*-toluene sulfenyl chloride with *cis* 1,4-polybutadiene in toluene solution. In the absence of any detail information on the reaction of *p*-toluene sulfenyl chloride with *cis* 1,4-polyisoprene, preliminary investigations were made of such similar reactions with natural rubber.

*Para*-toluene sulfenyl chloride was shown to add quantitatively to the olefinic double bonds of natural rubber in toluene solution. Characterisation of the modified rubber was made by elemental analysis, nuclear magnetic resonance spectroscopy and differential scanning calorimetry. It was demonstrated by electron microscopy that when highly purified natural rubber was used, *p*-toluene sulfenyl chloride modified natural rubber gave evidence of formation of 'block-copolymer' of modified sequence/unmodified sequence.

Within the framework of chemical modification of natural rubber (NR) it has been the aims of scientists to work towards achieving a novel modified NR possessing the dual properties of an elastomer as well as a thermoplastic. One of the first few attempts was to graft by redox initiation, polymethylmethacrylate branch chains onto the backbone of NR (commercially known as MG rubber)<sup>2</sup>. While it appeared to exhibit a certain degree of thermoplasticity when cast from solution in a suitable solvent<sup>3</sup>, the MG rubber failed to demonstrate any organised semi-microscopic structure as witnessed in phase segregations of incompatible blocks of block copolymers<sup>4</sup>, nor had it been able to exhibit long-range elasticity desired of thermoplastic elastomer (as for instance in S-B-S triblock copolymer). The advent of a wide range of thermoplastic elastomers in the commercial market has spurred scientists to create an equivalent material by chemical modification of NR. The Malaysian Rubber Producers' Research Association

(MRPRA) has recently grafted terminally reactive prepolymer of polystyrene onto NR by dry mixing<sup>5</sup>. In RRIM, attempts were made to study the possibility of synthesising block polymers of NR by a simple direct route: that of reacting a reactive agent, *para*-toluene sulfenyl chloride with the double bonds of NR. A recent study demonstrated that a block copolymer was formed by direct addition of *p*-toluene sulfenyl chloride to a polybutadiene<sup>1,6,7</sup>. From this study it seems possible to prepare block copolymers of NR by the same route. As observed by Cameroon *et al.*<sup>1</sup> the attractive features of this modification reaction are:

- It proceeds readily in solution at room temperature without catalysts or promoters.
- No crosslinking and chain scission are apparent.
- Varying proportions of modified units can be produced simply by varying the *p*-toluene sulfenyl chloride: polybutadiene ratio.

The present study aims to prepare two-block copolymers of NR using p-toluene sulfenyl chloride. It was hoped that ideas on preparing the still unattainable tri-block copolymers of NR by this route would emerge. Some interesting preliminary results obtained in reacting p-toluene sulfenyl chloride with NR are discussed in this paper.

## EXPERIMENTAL

### Materials

The purified NR used was obtained from the cream of Tjir 1 clone latex that had previously been ultra-centrifuged four times. After each ultra-centrifugation the cream obtained was re-dispersed in water for subsequent ultra-centrifugation. The final cream was filmed and dried in a vacuum oven at 60°C. Tjir 1 was chosen as it had been shown to possess unimodal molecular weight distribution<sup>8</sup>.

The rubber solution (in toluene) was further dried over molecular sieves prior to the reaction. Analar grade toluene, carbon tetrachloride and dioxane were also dried over molecular sieves before use. Para-toluene thiol (99% Eastman Kodak) was used as supplied.

### Preparation of Para-toluene Sulfenyl Chloride

Para-toluene sulfenyl chloride was prepared by the reaction of p-toluene thiol with dried chlorine and then purified as described in Kurzer<sup>9</sup>. This was confirmed by the disappearance of the absorption band at 2600 cm<sup>-1</sup> (due to S-H stretching vibration) in the infra-red spectrum of the product and from its reaction with a model compound, 2-methyl but-2-ene

$\text{CH}_3$   
( $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_3$ ). The latter reaction was accompanied by the rapid discharge of the red colour of p-toluene sulfenyl chloride on addition to an aliquot of the

model compound in dioxane and a temperature rise of about 5°C. This reaction was also used to determine the active concentration of p-toluene sulfenyl chloride.

### Reaction of Para-toluene Sulfenyl Chloride with Natural Rubber

Addition reactions of p-toluene sulfenyl chloride with NR were carried out in 2% solutions of NR in toluene and under nitrogen atmosphere. Varying amounts of p-toluene sulfenyl chloride were added to the rubber to give polymers modified to varying extents from 0% – 100% as shown in Table 1.

The correct amount of p-toluene sulfenyl chloride in dioxane (18% weight/volume) was added dropwise to the NR solution at room temperature. The red colour of p-toluene sulfenyl chloride disappeared rapidly and the temperature of the reaction solution rose by about 4°C.

On addition of all the p-toluene sulfenyl chloride (1 h), the solution was stirred for a further 2 h before precipitating the product from methanol. The modified polymer was purified by a further precipitation from toluene solution in methanol and dried in vacuum at room temperature.

### Characterisation

*Elemental analysis.* Both the sulphur and chlorine contents of the modified rubbers were determined by the standard procedure of oxygen combustion using the Schoniger Micro Combustion Flask followed by titration with standard barium chloride and silver nitrate solution respectively.

*Nuclear magnetic resonance.* Nuclear magnetic resonance spectra of the samples were recorded on a Hitachi 60 MHz

TABLE 1. QUANTITIES OF MATERIALS USED IN THE REACTION OF NATURAL RUBBER AND PARA-TOLUENE SULFENYL CHLORIDE

Sample	Natural rubber		p-Toluene sulphenyl chloride		Mole ratio p-toluene sulphenyl chloride Isoprene units	Extent of reaction (from stoichiometry) (%)
	Weight (g)	Amount of isoprene units (mmole)	Weight (g)	Amount (mmole)		
1	5	73	2.9	18	0.25	25
2	5	73	4.1	26	0.35	35
3	5	73	5.9	37	0.50	50
4	5	73	9.3	59	0.80	80
5	5	73	15.3	96	1.31	100

instrument from  $\text{CDCl}_3$  solution using tetramethylsilane as internal standard.

**Thermal analysis.** Thermal studies of the adducts were attempted using a Perkin Elmer Differential Scanning Calorimeter Model I B. The samples were scanned in a stream of  $\text{N}_2$  from  $-100^\circ\text{C}$  to  $150^\circ\text{C}$  at a heating rate of  $8^\circ\text{C}$  per minute.

**Electron microscopy.** Electron micrographs of the samples were obtained using a Phillips 300 electron microscope operating at an accelerating voltage of 80 kilovolts. For this study, the samples were first compressed to disks (about 1 mm thick) in a hydraulic press at  $90^\circ\text{C}$  under  $0.125 \text{ tons/in}^2$ . The disks were then held at  $50^\circ\text{C}$  for two days before being cut into blocks of approximately  $0.5 \times 0.5 \times 1 \text{ mm}$  and fixed in 2% osmium tetroxide for two days. They were again osmium-fixed for three days before dehydration and later embedded in styrene/methacrylate for sectioning and electron microscope examination.

## RESULTS AND DISCUSSION

### Physical Appearance

Freshly prepared modified rubbers were light yellow in colour which became

progressively less elastomeric and tougher as the level of modification was increased until at total saturation a hard thermoplastic resin was obtained. The products darkened in colour on prolonged storage (weeks) and appeared to degrade rapidly with a pungent odour not unlike  $\text{HCl}$ . Samples 1 and 2 appeared most unstable compared with the higher saturated adducts.

### Elemental Analysis

The sulphur contents of the Samples 1 – 5 and hence their levels of saturation (from Figure 1) are shown in Table 2. As can be seen from Table 3, the extent of reaction (or saturation) of the various samples obtained by stoichiometry, sulphur content and nuclear magnetic resonance (NMR) were in close agreement.

From chlorine contents of the samples, on the other hand, extent of reaction was much lower than in the above methods. Extent of reaction obtained for the samples varied from 15% to 50%. This is because some chlorine was lost as the adducts degraded on storage. Hence, this method is unreliable for estimating the extent of reaction.

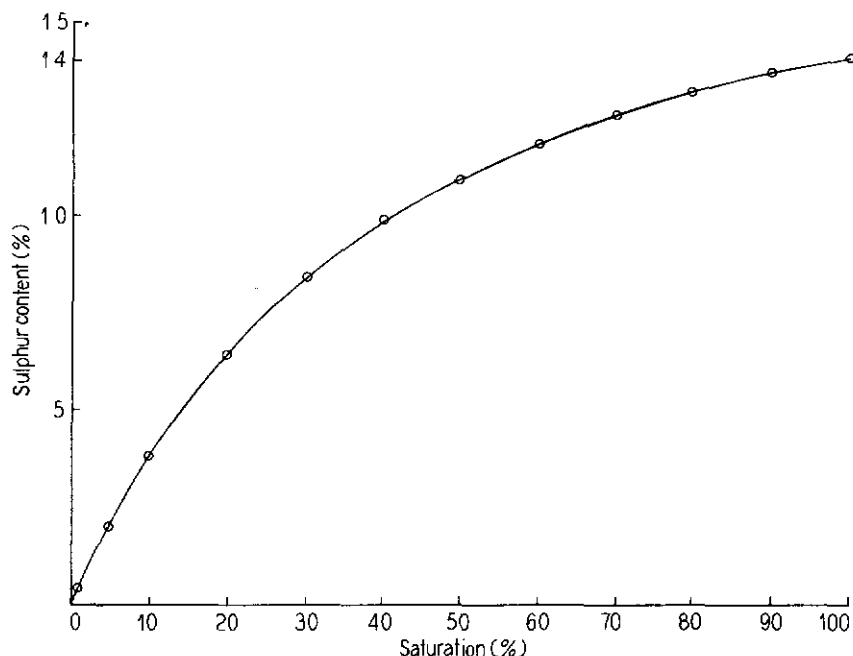


Figure 1. Theoretical relationship between sulphur content and saturation of *p*-toluene sulfenyl chloride modified natural rubber.

TABLE 2. SULPHUR CONTENT AND EXTENT OF REACTION OF PARATOLUENE SULFENYL CHLORIDE

Sample	Sulphur content (%)	Extent of reaction (%)
1	6.82	22
2	9.13	36
3	11.27	53
4	12.91	76
5	13.99	98

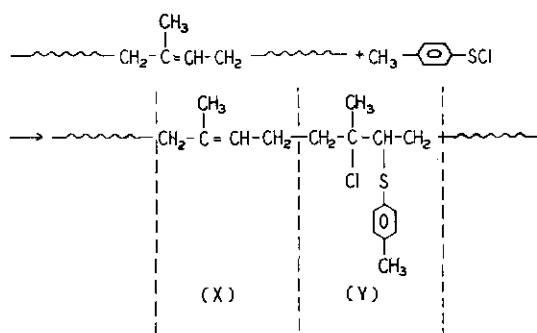
TABLE 3. EXTENT OF REACTION DETERMINED BY VARIOUS METHODS

Sample	Extent of reaction (%)		
	Stoichiometry	Sulphur content	NMR
1	25	22	22
2	35	36	34
3	50	53	50
4	80	76	85
5	100	98	96

### Nuclear Magnetic Resonance

The NMR spectra obtained for the various adducts are shown in Figure 2. Evidence showing addition reactions occurring was provided by the gradual disappearance of the peaks at 5.05 p.p.m. ( $=CH-$ ) and the increase in intensity of

the extra peak at 2.3 p.p.m. ( $CH_3 - Ar$ ) as the conversion was increased. The aromatic protons appeared as a quartet centred at 7.2 parts per million. Paratoluene sulfenyl chloride probably adds to NR in the following manner following Markownikov's rule as this is the favoured steric arrangement:



At first glance the peak for  $\text{---CH---S}$  appeared to be absent but closer inspection of the integrated areas of peaks in the spectrum for the totally saturated adduct (*Sample 5*) showed that at between 1.65 p.p.m. and 2.3 p.p.m. an extra proton was present. Thus the peak for  $\text{---CH---S}$  appeared to be superimposed in this region

Since individual peaks can be assigned to protons in different groups and peak areas are proportional to the number of protons giving rise to them, it is possible to determine the extent of modification by this method. *Table 4* shows the assignment of protons in NMR of p-toluene sulfenyl chloride modified NR.

Let  $A$  = total area of peaks < 6.0 p.p.m.

$B$  = total area of peaks > 6.0 p.p.m.

$N$  = total number of  $X$  units in chains

$M$  = total number of  $Y$  units in chains

$$\therefore A = 8N + 11M \quad (\text{each } X \text{ unit contributes 8 protons and each } Y \text{ unit contributes 11 protons})$$

$$B = 4M \quad (\text{each } Y \text{ unit contributes 4 protons})$$

$$\frac{A}{B} = \frac{2N}{M} + \frac{11}{4}$$

$$\therefore \frac{N}{M} = \left( \frac{A}{2B} - \frac{11}{8} \right)$$

Weight fraction of modified segments in a typical sample ( $y$ ) =  $\frac{My}{Mx + My}$  where  $Mx$  and  $My$  are molecular weights of unmodified and modified segments respectively,

$$y = \frac{226.5M}{68N + 226.5M}$$

Substituting for  $\frac{N}{M}$ ,

$$\frac{1}{y} = 0.15 \frac{A}{B} + 0.59$$

TABLE 4. ASSIGNMENT OF PROTONS IN NUCLEAR MAGNETIC RESONANCE SPECTRA OF PARA-TOLUENE SULFENYL CHLORIDE MODIFIED NATURAL RUBBER

Proton group	$\delta$ (p.p.m., $\text{CDCl}_3$ )
Due to unreacted isoprene units (X)	
$\text{---CH}_3$	1.65
$=\text{CH---}$	5.05
$\text{---CH}_2\text{---CH}_2\text{---}$	2.00
Due to reacted isoprene units (Y)	
$\text{---CH}_3$	1.65
$\text{---CH}_2\text{---CH}_2\text{---}$	2.00
$\text{---CHS---}$	Between 1.65 and 2.3
$\text{CH}_3\text{---Ar}$	2.3
$\text{---C}_6\text{H}_4\text{---}$	7.2

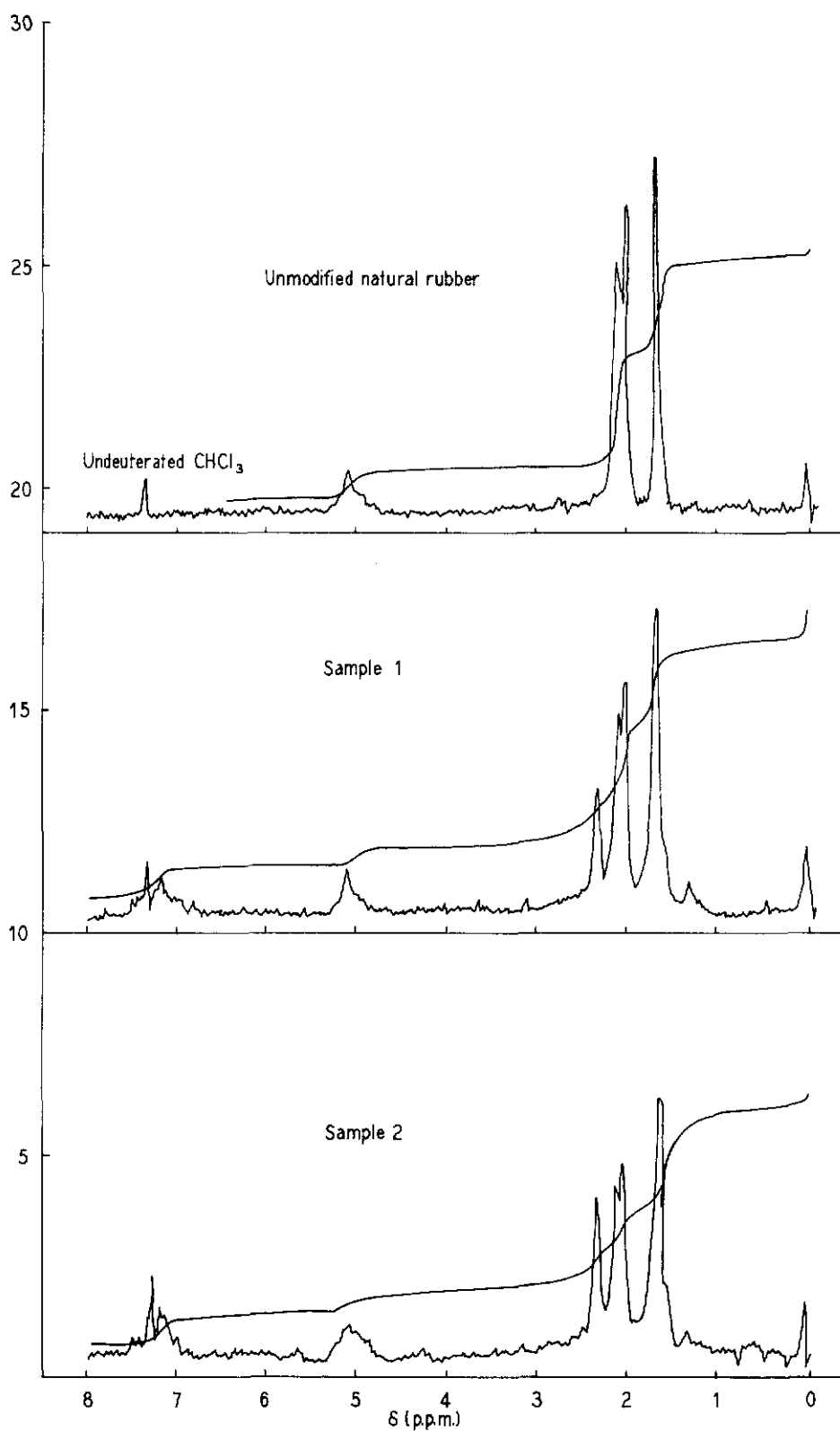


Figure 2. Nuclear magnetic resonance spectra of *p*-toluene sulfonyl chloride modified natural rubber.

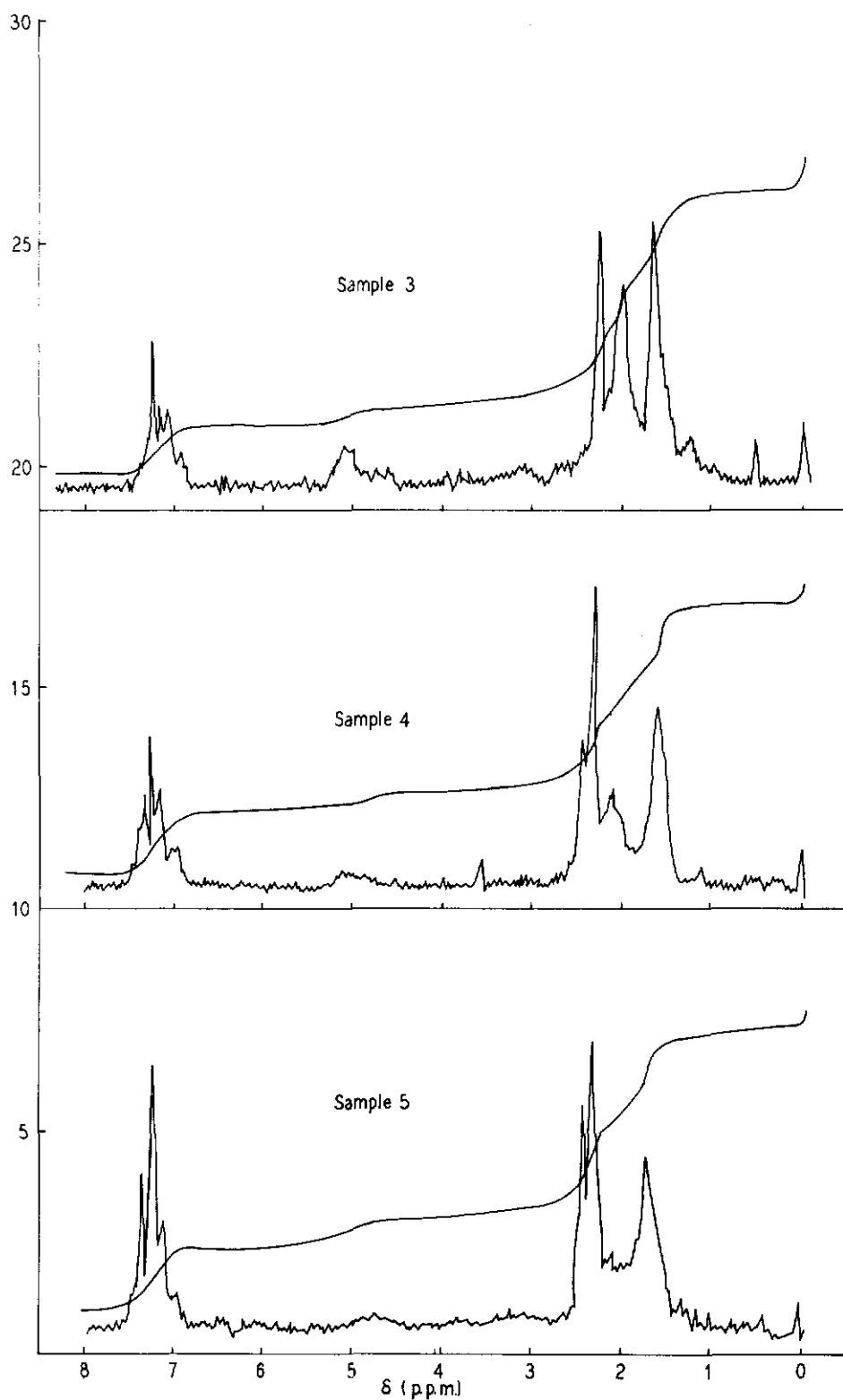


Figure 2. Nuclear magnetic resonance spectra of *p*-toluene sulfonyl chloride modified natural rubber (continued).

The weight fraction,  $y$ , can be calculated for different levels of modification (*Figure 3*) so that by measuring peak area ratio  $A : B$ ,  $y$  and in turn level of modification for any *p*-toluene sulfenyl chloride modified NR can be determined.

The results obtained for *Samples 1 – 5* showed excellent agreement with those obtained by other means (*Table 3*).

#### Thermal Analysis

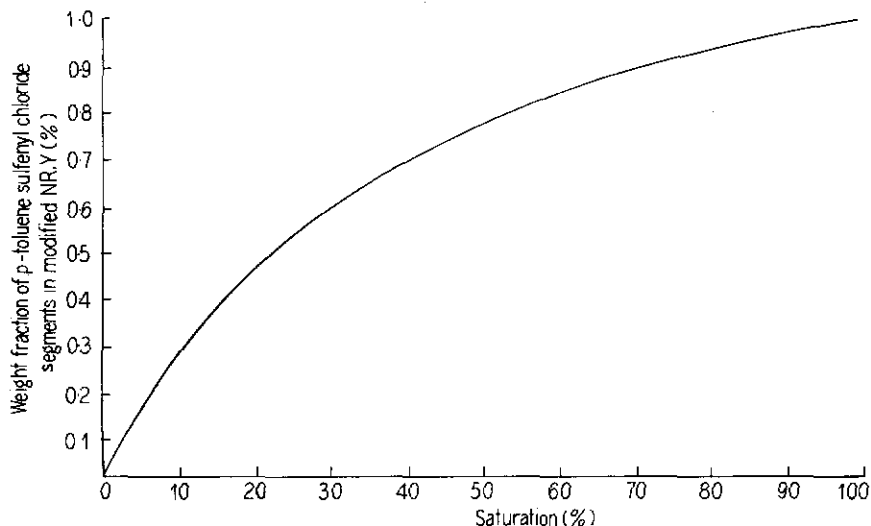
Attempts to obtain well-defined differential scanning calorimeter traces for *Samples 1 – 4* were unsuccessful. However, the totally saturated product (*Sample 5*) showed a sharp glass transition temperature of  $104^{\circ}\text{C}$ .

#### Electron Microscopy

The electron micrographs of *Samples 1 – 4* were obtained at magnifications of 4158 and 27 000 times. The micrographs of *Samples 1* and *2* are shown in *Figure 4*. The staining agent osmium

tetroxide used only stained any unreacted isoprenic units of NR and provided a distinct contrast between modified and unmodified segments in an electron micrograph.

In all the micrographs lighted regions of *p*-toluene sulfenyl chloride modified segments (from  $0.1\mu$  to  $5\mu$ ) showed up clearly from dark regions of unmodified segments. This seems to demonstrate that phase separations of *p*-toluene sulfenyl chloride modified segments from the unmodified segments have occurred as a result of their incompatibility, which could only be possible if fairly long chains of modified segments were present *i.e.* sequential addition of *p*-toluene sulfenyl chloride to NR. In *Sample 1*, the modified phases appeared spherical and were of rather uniform sizes. As the level of modification was increased, the modified phases became more irregular in size with a corresponding increase in the size of the largest modified phase visible. The irre-



*Figure 3. Weight fraction of p-toluene sulfenyl chloride segments versus extent of modification.*



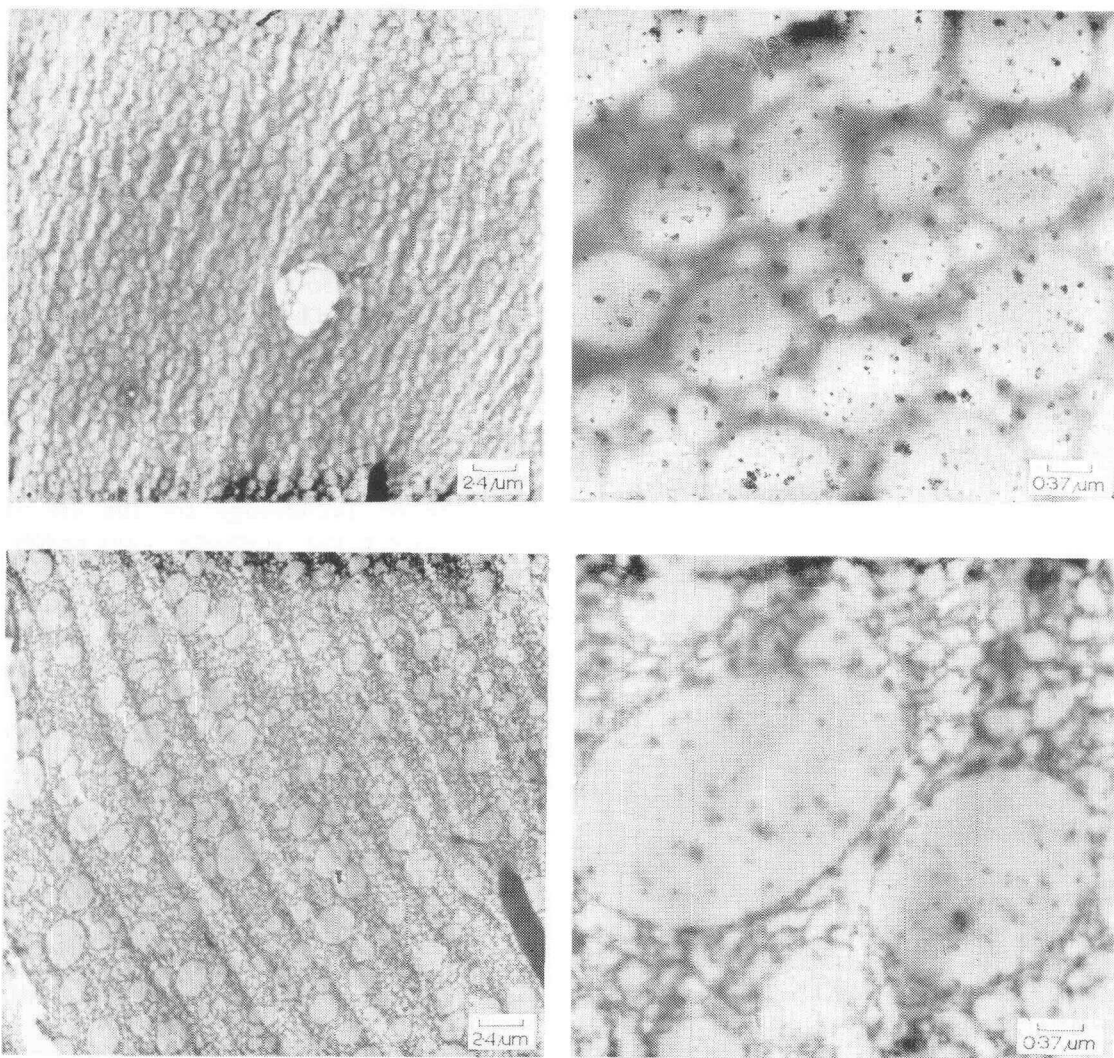


Figure 4. Electron micrographs of Samples 1 and 2.

gular size of modified regions was to be expected from the polydispersity of the NR itself.

#### Degradation

As discussed earlier, p-toluene sulfenyl chloride modified NR degraded on prolonged storage as observed by its physical appearance and chlorine analyses. The glass transition temperatures of these samples, although not very clearly

defined, were also observed to decrease somewhat.

It was reported recently that similar decompositions of the adducts of p-toluene sulfenyl chloride with synthetic *cis*-1,4 polyisoprene (I) and methanesulfenyl chloride with *cis* 1,4-polybutadiene (II) respectively occurred by the following mechanism<sup>10</sup>:

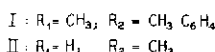
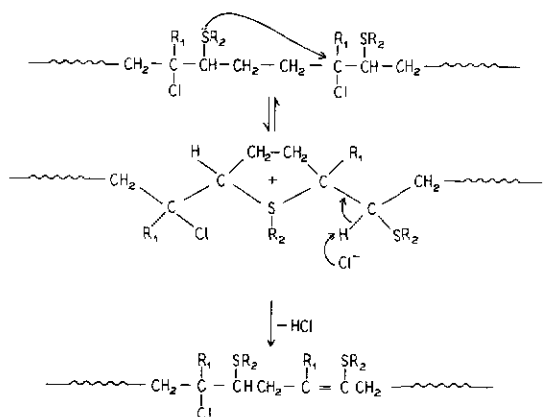
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Para-toluene sulfonyl chloride modified NR samples prepared for this work probably decomposed by a similar mechanism on prolonged storage.

Thus p-toluene sulfonyl chloride reacted quantitatively with NR in solution at room temperature. Different levels of modification can be obtained by simply varying the mole ratio of p-toluene sulfonyl chloride to NR. The extent of modification obtained by NMR agreed closely with those obtained by stoichiometry and elemental analysis. These modified rubbers became progressively less elastomeric and thus more thermoplastic as the levels of conversion were increased. The fully saturated product was a hard thermoplastic resin with a glass transition temperature of about  $104^\circ\text{C}$ .

Evidence of phase segregation in the partially modified rubber was provided by electron microscopy. This in turn showed that p-toluene sulfonyl chloride added in sequence to NR double bonds. These adducts especially those with modification less than 50% had poor stability on prolonged storage at room temperature.