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GELATION OF NATURAL RUBBER CAUSED BY TRIALKYL ALUMINIUM COMPOUNDS

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SUMMARY

A gelation reaction of natural rubber (NR) brought about by trialkyl aluminium compounds is described. It is shown that trialkyl aluminium compounds modified with a suitable cocatalyst could gel a toluene solution of NR ; at the same time the original NR chains could undergo scission. A reaction mechanism is proposed and the significance of this gelation in the formation of interpenetrating networks is discussed.

INTRODUCTION

Gelation *i.e.* three dimension network formation has attracted much study in the polymer industry, NR also receiving its share. Much of the research on NR has been concentrated on micro-gelation (Allen & Bristow, 1963). Some reports of gelled material formed during isoprene polymerization are available (Saltman *et al.*, 1958 ; Schoenberg *et al.*, 1964 ; Farrar, 1966). In this paper the action of modified trialkyl aluminium compounds *i.e.* Ziegler catalyst components in bringing about gelation of NR on a macro scale is described.

EXPERIMENTAL*

Materials : Crepe, gel-free, prepared from triple centrifuged NR latex (RRI, Sri Lanka) ; toluene A.R. dried over calcium hydride ; triisobutyl aluminium (Koch-Light) 95% pure ; zinc acetylacetonate pure (Koch-Light) ; sodium metal A.R. (BDH) ; benzoyl peroxide lab. reagent (Fisons) ; methanol, chloroform, carbon tetrachloride — all A.R. grade.

Gelation of crepe solutions : Portions of lightly milled crepe (15g) were placed in dry reaction vessels of approximately 700 ml capacity (wide neck reaction flask FR 700 F, multi-socket lid MAF 2/2 — Jobling), Suba seal rubber stoppers (SU 850 — Gallenkamp) and glass stoppers used to close the sockets. Dry toluene (300 ml) was added to each flask with a little antioxidant (Flectol H — Monsanto) and kept in the dark over a period of three days to dissolve the crepe. To the crepe solutions thus prepared it was proposed to add the modified triisobutyl aluminium compound, the amount of alkyl compound corresponding to 1%, 2·5%, 4% and 6% of the amount of NR (on a molar basis). The modifiers consisted of zinc acetylacetonate and water in the ratio (on a molar basis) triisobutyl aluminium/water/zinc acetylacetonate 10 : 5 : 2. The calculated quantities of water and zinc acetylacetonate (suspension in dry toluene) were added to each of the reaction vessels, stirred magnetically to ensure homogenization and contents heated to 70°C under dry nitrogen. Corresponding quantities of triisobutyl aluminium (10% in dry toluene) were injected into the reaction vessels under nitrogen flow, using a Hamilton syringe.

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In all cases gelation of the crepe solutions occurred soon after the addition of the alkyl aluminium solution. The gelled material was stripped of toluene without any heat treatment, by evaporation in a fume cupboard followed by vacuum drying at room temperature. A blank was conducted for the crepe used, that is addition of water and zinc acetylacetonate to a toluene solution of the crepe without the addition of alkyl aluminium and toluene removed at room temperature.

Determination of viscosity : Preliminary experiments showed that although the original crepe (blank) was completely soluble in toluene at room temperature, the gelled samples were only partially soluble even under Soxhlet extraction. For separation of insoluble (*i.e.* macro-gel) from soluble material (*i.e.* micro-gel if any and rubber, not crosslinked) the following method was adopted (Purdon & Mate, 1963) : 500 mg quantities of gelled material, dried thoroughly, were placed with about 50 ml toluene in 100 ml volumetric flasks and agitated in a flask shaker overnight. The flasks were kept in the dark for two days (exposure to daylight could cause a rapid reduction of viscosity of NR solutions), contents were topped up to the 100 ml mark and after transferring to plastic buckets were centrifuged at 2500 rpm for one hour. Two 20 ml portions were pipetted out of the top layer of liquid in the buckets; one portion was dried in Petri dishes and amount of solid material determined while the other portion was used to determine viscosity. Suppose original material weighed W_1 g and the 20 ml portion yielded W_2 g on drying then macro-gel content

$$= \frac{W_1 - 5W_2}{W_1} \times 100\%$$

For determination of solution viscosity, a laboratory made suspended-level dilution viscometer conforming to type I specifications of BS 188 (1957) was used. Efflux times for pure solvent were high so that no allowance for kinetic energy of flow was considered necessary. Measurements were made in a thermostatic water bath maintained at 25 ± 0.2°C. The efflux time for the first 10 ml portion of toluene solution was recorded and then progressively diluted with 5 ml portions of toluene. All solutions and solvent were filtered with lens tissue to remove any dirt. If efflux time for pure solvent is t_0, for solution of concentration c (g/100 ml) is t, then by definition

$$\eta_{sp} = \frac{t - t_0}{t_0} \quad \text{(specific viscosity)}$$

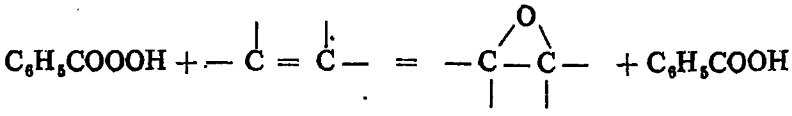
The data obtained were treated by the method of Huggins (1942) *i.e.* plotting viscosity number $\frac{\eta_{sp}}{C}$ as a function of C according to the relation :—

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 c$$

$[\eta]$ = intrinsic viscosity

k' = Huggins' constant

Determination of unsaturation : The soluble part of the gelled material was investigated for unsaturation using the perbenzoic acid method (Lee *et al.*, 1963). An approximately 10% solution of perbenzoic acid in benzene was prepared according to the method of Kolthoff *et al.* (1947). The determination of unsaturation depends on the fact that perbenzoic acid in an inert solvent reacts rapidly and quantitatively with isoprenic double bonds :—



Aliquots (20 ml) of the toluene soluble portion of gelled crepe were pipetted into 250 ml conical flasks. Freshly prepared perbenzoic acid solution (4 ml) was added to each flask and kept tightly stoppered at room temperature in the dark for 2 hours. At the end of this period 2 ml glacial acetic acid and 100 ml of 2% aqueous potassium iodide were added to each flask to liberate the iodine and titrated with 0·1N thiosulphate using starch as internal indicator. Addition of a few drops of surfactant *e.g.* Atexal WAHS (ICI Organics Division) helped in homogenizing the immiscible phases. Any iodine adsorbed on the rubber was squeezed out with a glass rod. The unsaturation of the blank crepe was also determined and calculations of the unsaturation of the soluble part of the gelled material made relative to the blank.

IR Spectra and thermal analysis

IR spectra of thin films of the well dried gelled material and films cast from the toluene soluble portions of gelled material were run on a Unicam SP 1200 spectrophotometer. Thermal transitions of these materials were also determined on a Du-Pont 900 Thermal Analyzer fitted with a DSC cell or Thermomechanical Analyser.

RESULTS

Solution viscosity : Table I gives macro-gel content, intrinsic viscosity and Huggins' constant of the soluble portion of the gelled crepe compared with the original crepe (blank). It is seen that the macro-gel content is around 40% in all cases *i.e.* addition of increasing amounts of alkyl compound appears to produce no change. Intrinsic viscosities are reduced in all cases. Reduction of [η] could be due to scission of original macromolecular chains as for example mastication of NR in air (Pike & Watson, 1952 ; Angier *et al.*, 1957) or formation of colloidal sized micro-gel (Baker, 1949; Bloomfield, 1951; Medalia, 1951) in which crosslinking causes a more compact structure. However, micro-gel formation is usually accompanied by an increase of Huggins' constant k′ (Simha, 1949 ; Soper *et al.*, 1972) whereas mastication of NR in air, has been shown not to affect the value of k′ to any marked degree if at all a slight reduction (Angier *et al.*, 1957). The values of [η] and k′ thus appear to show that the soluble portion of the gelled crepe is reduced in molecular weight compared with the original rubber without formation of micro-gel.

TABLE I

INTRINSIC VISCOSITY AND HUGGINS' CONSTANT OF SOLUBLE PORTION FOR GELLED CREPE

Amount of alkyl added (%)	1·0	2·5	4·0	6·0	None (blank)
Macro-gel content (%)	39·2	34·8	47·1	44·2	5·1
Intrinsic viscosity of soluble portion of gelled crepe $[\eta]\,g^{-1}ml$, toluene, 25°C	196	154	158	144	318
Huggins' constant k′ corresponding to [η]	0·41	0·44	0·29	0·30	0·43

Unsaturation : Average results of unsaturation of the soluble portion of the gelled material given in Table 2 show no change compared with the blank crepe.

TABLE 2

DETERMINATION OF UNSATURATION (PERBENZOIC ACID METHOD)

Sample description	Amount of polymer (soluble portion) mg	Equivalent 0.1N sodium thiosulphate ml	Unsaturation %
Soluble portion gelled by following amounts of alkyl			
1·0%	52	14·1	97
2·5%	42	12·8	105
4·0%	42	12·2	103
6·0%	36	10·5	104
Blank crepe	88	24·7	100

IR spectra and thermal analysis : both showed that the gelled material and soluble portions were similar to the blank crepe used.

DISCUSSION

A literature survey has failed to reveal any reports of gelation of NR caused by trialkyl compounds. However sesquialkyl aluminium compounds, ethyl aluminium dichloride (EADC) and diethyl aluminium chloride (DEAC) have been reported to react with NR. These compounds with small amounts of water as cocatalyst effected isomerization of NR at low concentration of alkyl compound (Golub, 1968) while at high concentration cyclization occurred. (Yermakova *et al.*, 1969).

In the present study, IR spectra rule out the possibility of any NR isomerization. Had isomerization occurred, bands at 1305, 1125, 1085, 1032 and 837 cm^{-1} would have shifted as shown by Cunneen & Higgins (1963) and Golub (1968). Comparison of IR spectra of cyclized NR of low cyclicity prepared by the action of p-toluene sulphonic acid on crepe (NRPRA, Technical Information Sheet No. 17) and high cyclicity prepared by the action of titanium tetrachloride on crepe (Golub & Heller, 1963) also failed to show any evidence of cyclization. Viscosity and unsaturation results covincingly show that the action of the trialkyl compound used in the present study is to form a three-dimensional network in the NR, at the same time there results a low molecular weight fraction. This low molecular weight fraction could be formed either by scission of the original chains or by a process of elimination whereby only the longer chains undergo gelation. If the former hypothesis is assumed the following mechanism could explain simultaneous gelation and chain scission (Amass, 1974; Colclough, 1974) :—

$$R_3Al + H_2O \rightleftharpoons H^+ + (HOR_3Al)^-$$

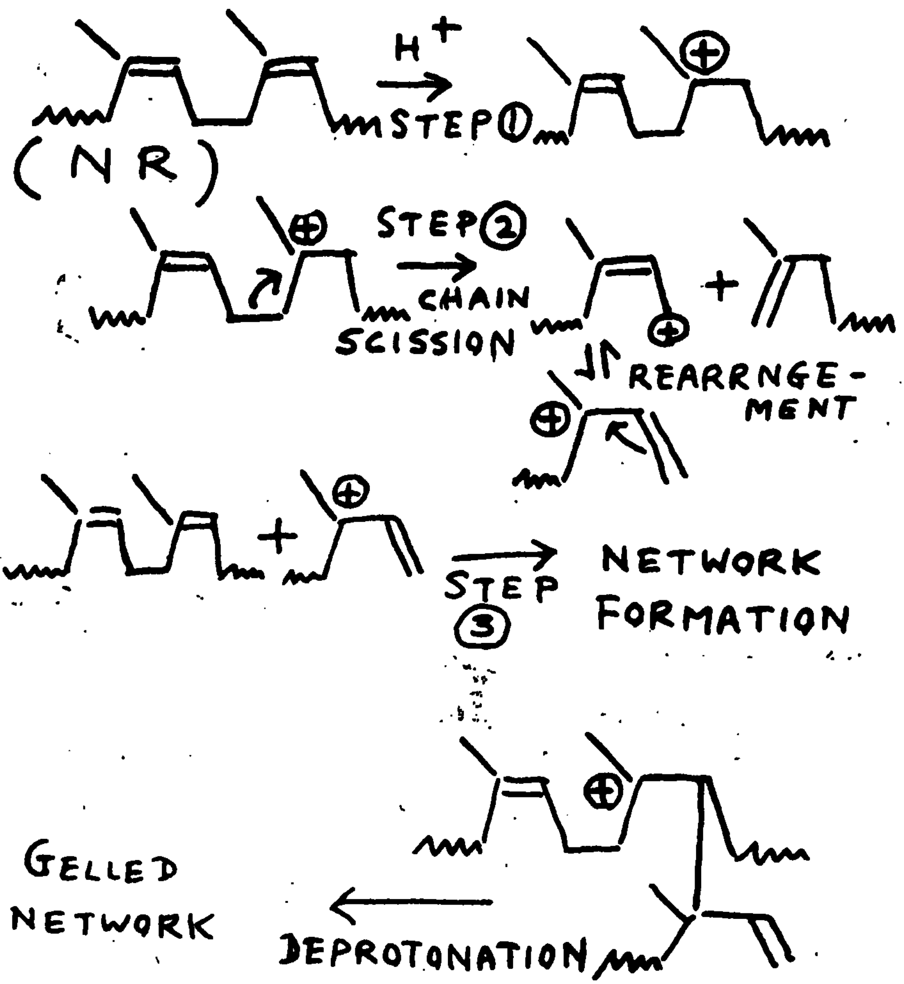


Fig. 1 — Scheme for chain scission (reduction of mol. wt.) and network formation (gelation) caused by action of trialkyl aluminium initiator on NR.

It is well known that alkyl aluminium compounds possess Lewis acidity, the strength decreasing in the order AlX_3, $AlRX_2$, AlR_2X, AlR_3 (X = Halogen, R = Alkyl)

(Kennedy, 1968 ; Saegusa *et al.*, 1968). The acidity developed in the trialkyl case is presumably not strong enough, even after modification with water and the zinc compound, to effect any cyclization of NR. However protonation of NR chains could occur with formation of tertiary carbonium ions as postulated in some other cases (Lee *et al.*, 1963) — Step 1. The tertiary carbonium ion so formed could undergo scission into two smaller fragments, the scission occurring at the weak C — C bonds midway between the 1, 5 double bonds (Watson, 1964) — step 2. The fragment containing the primary carbonium ion could stabilize to a tertiary carbonium ion, favouring step 2. The tertiary carbonium ion fraction thus formed could add on to poly (isoprene) chains similar to a propagation step in a cationic polymerization — step 3. Deprotonation would result in a three-dimension network. The reduced viscosity is accounted for by the chain scission in step 2.

Zinc acetylacetonate appears to play no part in the gelation. The reason why the zinc compound was used was that it formed part of the initiator system used in another aspect of the present study (Mendis, 1975). Indeed in a few other experiments gelation was observed using alkyl aluminium/water only. Triethyl aluminium appeared to behave in the same manner as triisobutyl aluminium. Tests with cis - 1, 4 poly (butadiene) (Shell BR 1220, without extraction) also produced gelation. However, when a synthetic cis - 1, 4 poly(isoprene) (Natsyn 2200 of 96% cis content, without extraction) was used, gelation was not observed. This anomalous behavior needs explanation. It is not certain whether non-rubber constituents play a part in the gelation. Generally non-rubber constituents in NR prevent double bond movement (Cunneen *et al.*, 1965). It could be that the crepe (triple centrifuged) used in this study lacks non-rubber constituents, favouring movements of double bonds as shown in the rearrangement of step 2, Fig. 1. Added basic antioxidants could hinder double bond movement in the cis-1, 4 poly(isoprene) case, gelation not being favoured.

CONCLUSIONS

The gelation effects described are of significance when a monomer is polymerized, using the alkyl aluminium/water/zinc acetylacetonate initiator system, in the presence of NR (*in situ* polymerization). The gelation could result in an interpenetrating type of network (IPN). Thus scanning electron micrographs clearly showed changes in surface texture when gross products formed by polymerization of epichlorohydrin in the presence of NR were compared with blends of the homopolymers (Mendis, 1975). In this case, both substances being elastomers, any differences due to interpenetrating network formation may not be significant. However when monomers yielding plastic substances *e.g.* tetrahydrofuran (THF) and 3, 3 — bischloromethyl oxacylobutane (BCMO) are used it may be possible that NR could improve mechanical properties such as impact strength by network formation during polymerization.

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