[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Natural and Synthetic Rubber. XVII. The Separation of Sol Rubber and Gel Rubber[1]

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

The sol rubbers, on which reliable physical and chemical measurements have been made, have been prepared either by fractional precipitation[2] from a mixture of benzene and alcohol, or by slow diffusion in absolute ethyl ether.

The separation of sol from gel rubber by diffusion assumes that the components can be separated from one another like sugar from sand and disregards the possibility that sol and gel rubbers may be mutually soluble in each other. If this latter condition actually exists, then the diffusion may only be expected to produce a two-phase, three-component system in equilibrium, and the relative amounts of sol and gel rubbers in the sol phase should be determined and not assumed. The same general reasoning applies to the fractional precipitation method of separation. Thus there is no "absolute" method of determining the relative quantities of sol and gel rubbers in any sample.

However, the relative efficiencies of separation by these two methods may be evaluated by preparing samples of "sol" rubber by each method and then attempting a further separation of each of these samples by the other method. This has been done with the following results.

Samples of sol rubber were prepared by fractional precipitation from sprayed latex rubber and were allowed to diffuse in ether. They dissolved rapidly and completely. They were quantitatively recovered unchanged from the ether by evaporation at reduced pressure. Also 30 g. of sprayed latex was allowed to diffuse in absolute ether, yielding 24 g. of soluble and 6 g. of insoluble material. The insoluble portion was leathery, rich in nitrogen; it was not analyzed further. The 24 g. of soluble material was recovered from the limpid ether solution by evaporation at reduced pressure, then subjected to fractional precipitation from a mixture of alcohol and benzene, with the following results:

Fractions	A_0	A_1	A_2	A_3	A_4	A_5	B
Amount, g.	3	6	1	1.5	1	0.5	10.5

One-half gram was lost during the operation. The A_0 fraction contained the so-called "acetone soluble" portion of natural rubber, since it was recovered by the evaporation of the benzene–alcohol mixture after completion of the fractionation. The A_1 fraction was found free of nitrogen, but not free of rubber degraded by oxidation, as it had a glossy appearance and gave 0.06% oxygen by the active hydrogen method[3] instead of 0.02 or 0.03% which is normal for good samples. This is not surprising, as it has always been found that two and sometimes three successive precipitations are needed to remove all traces of such oxidized material. Fractions A_2 to A_4 were typical high grade sol samples. Fraction A_5, which was very small and obtained with considerable difficulty, was obviously a mixture of A and B. Fraction B, the insoluble part, proved to be nitrogen free. In view of this last unexpected result, B was subjected to another fractionation, which removed only a small amount of impure A, amounting to about 2 g., and left a little more than 8 g. of a substance which was called BB. The characteristics of this BB fraction were: no nitrogen; 4.65% oxygen by combustion; 1.48% oxygen by active hydrogen measurement; slow solubility in benzene; extremely slow solubility in ether; no "leathery" feeling, no "tackiness" and no resemblance whatever to rubber degraded by oxidation. The high oxygen content of this material may safely be assumed to be due to an impurity.

The viscosities of the several fractions were measured in 0.23% solutions in benzene at 20°. The viscosities expressed in C. G. S. units × 10^3 were:

Benzene	A_1	A_2	A_3	A_4	BB
6.47	12.40	17.20	17.30	17.20	21.03

The low viscosity of A_1 is due to the accumulation therein of rubber degraded by oxidation. A_2 to A_4 are good samples of sol rubber. Their viscosities compare favorably with those recorded for thrice refractioned sol rubber (17.70) or twice re-

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[1] Original manuscript received October 22, 1936.

[2] THIS JOURNAL, 53, 2733 (1931).

[3] *Ibid.*, 57, 2318 (1935).

fractioned rubber (17.40 to 17.65) prepared in this Laboratory.

These results indicate quite clearly that a single diffusion of rubber into ether is insufficient completely to separate sol from gel rubber. They also show that while there is no absolute criterion by which the fractional precipitation method may be judged, it is decidedly more efficient than the ether diffusion method.

Summary

Sol rubber prepared by a single diffusion in ether can be separated into two components by fractional precipitation, whereas sol rubber prepared by a single fractional precipitation completely diffuses in ether, thus indicating the superiority of the fractional precipitation method as a means of preparing sol rubber.

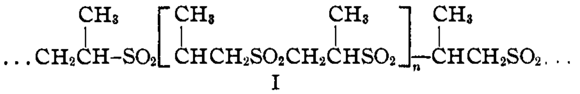
COLUMBUS, OHIO RECEIVED FEBRUARY 23, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reaction between Sulfur Dioxide and Olefins. V.[1] The Structure of the Polysulfones from Olefins of the Type $RCH{=}CH_2$

BY F. J. GLAVIS, L. L. RYDEN AND C. S. MARVEL

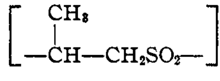
It has been demonstrated[2] that propylene and sulfur dioxide combine to form a polysulfone (I)



$$\cdots CH_2\overset{CH_3}{\overset{|}{C}}H{-}SO_2\left[\overset{CH_3}{\overset{|}{C}}HCH_2SO_2CH_2\overset{CH_3}{\overset{|}{C}}HSO_2\right]_n\overset{CH_3}{\overset{|}{C}}HCH_2SO_2\cdots$$

I

in which the propylene units are oriented so that like parts of the hydrocarbon residues are linked through the sulfone groups. The hydrolysis of the polysulfone with alkali gave products which could not be reconciled with the structure II,

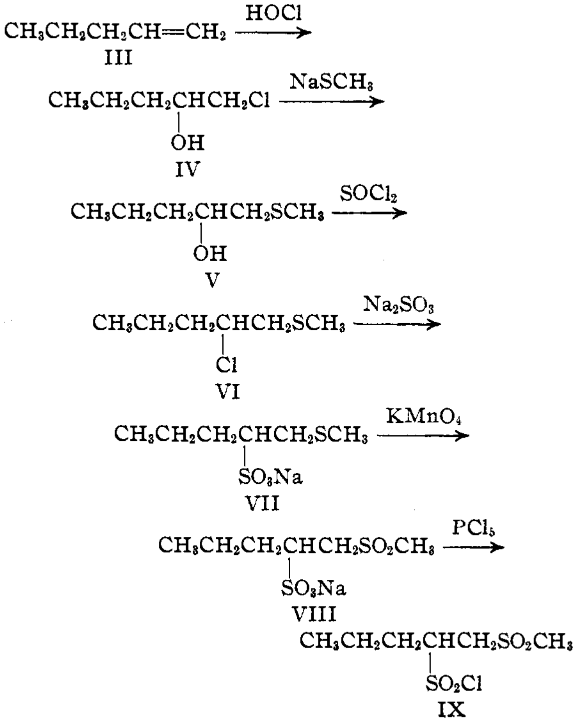


$$\left[-\overset{CH_3}{\overset{|}{C}}H-CH_2SO_2-\right]_n$$

II

which had previously been assigned to the addition product.[3] The experiments described in this communication were undertaken to determine whether the polysulfones from other olefins of the type $RCH{=}CH_2$ would be structurally comparable to propylenepolysulfone (I), or would have a simple symmetrical unit similar to that indicated in formula II.

1-Pentenepolysulfone, prepared as described previously,[4] can be hydrolyzed by warming it with 20% sodium hydroxide solution to yield *n*-butyraldehyde and a sodium salt of composition $C_6H_{13}S_2O_4Na$. This salt can be oxidized readily by hydrogen peroxide to give a compound $C_6H_{13}S_2O_5Na$, which, with phosphorus pentachloride, yields a sulfonyl chloride melting at 64–65°. The same sulfonyl chloride (IX) has been synthesized from 1-pentene by the following series of reactions



$$CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{HOCl}$$

III

$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_2Cl \xrightarrow{NaSCH_3}$$

IV

$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH_2SCH_3 \xrightarrow{SOCl_2}$$

V

$$CH_3CH_2CH_2\underset{\underset{Cl}{|}}{C}HCH_2SCH_3 \xrightarrow{Na_2SO_3}$$

VI

$$CH_3CH_2CH_2\underset{\underset{SO_3Na}{|}}{C}HCH_2SCH_3 \xrightarrow{KMnO_4}$$

VII

$$CH_3CH_2CH_2\underset{\underset{SO_3Na}{|}}{C}HCH_2SO_2CH_3 \xrightarrow{PCl_5}$$

VIII

$$CH_3CH_2CH_2\underset{\underset{SO_2Cl}{|}}{C}HCH_2SO_2CH_3$$

IX

This synthesis of the sulfonyl chloride (IX) establishes the structure of the sulfonic acid salt $C_6H_{13}S_2O_5Na$ (VIII). Likewise, it shows that the salt $C_6H_{13}S_2O_4Na$ must have the structure shown in formula XII. 1-Pentenepolysulfone must, accordingly, have the structure shown in formula X, and thus be strictly comparable to propylenepolysulfone (I) in the arrangement of the hydrocarbon residues.

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[1] For the fourth paper in this series, see Ryden and Marvel, THIS JOURNAL, **58**, 2047 (1936).

[2] Hunt and Marvel, *ibid.*, **57**, 1691 (1935).

[3] Staudinger and Ritzenthaler, *Ber.*, **68**, 458 (1935).

[4] Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).