On the Polymerization of Chloroprene as Revealed by the Raman Effect.

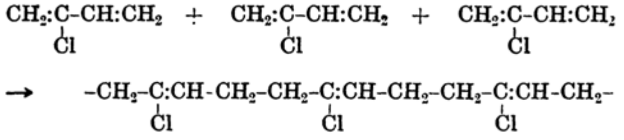
By Tutomu KUBOTA.

(Received November 26, 1938.)

Several authors⁽¹⁾⁽²⁾⁽³⁾ have applied the Raman spectra to the study of the polymerization mechanism, e.g., the polymerization of styrene⁽¹⁾⁽²⁾ and methacrylic acid esters,⁽³⁾ which is considered to proceed by the opening of the double bonds of monomers. The present paper deals with an analogous experimental research on the polymerization mechanism of chloroprene, one of dienes which have conjugate double linkages. Carothers and his co-workers⁽⁴⁾ explained the polymerization mechanism of chloroprene as follows: the first step,

---

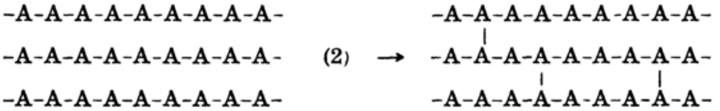
(1) Signer and Weiler, *Helv. Chim. Acta*, **15** (1932), 649.
(2) Mizushima, Morino, and Inoue, this Bulletin, **12** (1937), 136.
(3) Hibben, *J. Chem. Phys.*, **5** (1937), 706.
(4) Carothers, Williams, Collins, and Kirby, *J. Am. Chem. Soc.*, **53** (1931), 4203.



$$CH_2{:}\underset{Cl}{C}-CH{:}CH_2 + CH_2{:}\underset{Cl}{C}-CH{:}CH_2 + CH_2{:}\underset{Cl}{C}-CH{:}CH_2 \qquad (1)$$

$$\rightarrow -CH_2-\underset{Cl}{C}{:}CH-CH_2-CH_2-\underset{Cl}{C}{:}CH-CH_2-CH_2-\underset{Cl}{C}{:}CH-CH_2- \qquad (2)$$

and the second step,



$$\begin{array}{l}-A-A-A-A-A-A-A-A-A-\\-A-A-A-A-A-A-A-A-A-\\-A-A-A-A-A-A-A-A-A-\end{array}\quad (2) \rightarrow \begin{array}{l}-A-A-A-A-A-A-A-A-A-\\-A-A-A-A-A-A-A-A-A-\\-A-A-A-A-A-A-A-A-A-\end{array}\quad (3)$$

where A is a chloroprene unit. According to their theory, it is expected that the polymerized chloroprene will have a new C:C frequency which is nearly equal to that of 2-chlorobutene-(2), but is different from that of the monomer.

Raman spectra of monomeric chloroprene, polymerized chloroprene in the solid state, and 2-chlorobutene-(2) were photographed and the results are given in Table 1. When the liquid sample (monomer) solidifies,

Table 1.

Chloroprene (liquid)			Polychloroprene (solid)			2-Chlorobutene-(2)		
158	(1b)	e	158	(2b)	e	—		
249	(4b)	e	248	(4b)	e	230	(2b)	e
—			—			339	(4)	e,k
387	(3)	e	387	(3)	e	389	(0)	e,k
—			—			433	(3)	e,k
—			—			459	(3)	e,k
518	(4)	e	521	(4)	e	523	(2)	e,k
—			—			(544)	(1)	e
—			—			564	(0)	e,k
629	(6)	e	630	(6)	e	606	(8)	e,k
—			—			645	(0)	e,k
—			—			670	(4)	e,k
735	(0)	e	735	(0)	e	795	(0)	e,k
882	(2b)	e	882	(2b)	e	—		
923	(2b)	e	921	(2b)	e	—		
1020	(2)	e	1018	(2)	e	1025	(0)	e,k
—			—			(1115)	(2)	e
1214	(3)	e	1216	(4)	e	—		
—			1260	(0)	e	—		

Table 1.—(*Concluded*)

Chloroprene (liquid)			Polychloroprene (solid)			2-Chlorobutene-(2)		
1287	(7)	e	1287	(7)	e	1287	(4)	e,k
1359	(0)	e	1359	(0)	e	—		
1381	(1)	e	1381	(1)	e	1380	(5)	e,k
1417	(6)	e	1419	(6)	e	1441	(8b)	e,k
1526	(1)	e	1526	(1)	e	—		
1581	(4)	e	1581	(4)	e	—		
1628	(15)	e,k	1628	(15)	e,k	(1633)	(4)	e,k
—			1658	(3)	e	1670	(7)	e,k
—			—			2857	(2b)	e,k
—			—			2918	(10)	e,i,k,q
—			—			2942	(2b)	e,k
—			—			2981	(5)	e,k,q
3015	(6)	e	3015	(6)	e	3025	(2b)	e,k
3113	(5b)	e	3109	(5b)	e	—		

the intensity of the C:C frequency of the monomer decreases slightly but there appears another frequency (1658 cm.$^{-1}$), which should be assigned also to the C:C frequency. The latter frequency is not much different from 1670 cm.$^{-1}$, the frequency due to the C:C bond of 2-chlorobutene-(2), the molecule of which has the methyl groups instead of the heavier groups of (2). From the intensities of the Raman lines it may be concluded that the polymerization proceeds linearly but not to a large extent. In the solid state, at least at the first stage, the larger part of chloroprene does not polymerize by the primary linkages but is held together by the van der Waals forces. Similar phenomena were also observed by Mizushima and his co-workers(2) about styrene and by Hibben(3) about methyl methacrylate.

The author thanks Prof. Mizushima for his kind advices and also expresses his thanks to Mr. K. Fuwa, Mr. A. Wada and Mr. R. Kitani for their kind encouragements.

Laboratory, Tokyo Electric Co.,
Kawasaki near Tokyo.