A Note on the Polymerisation of Styrene as revealed by the Raman Effect.

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The polymerisation of styrene is considered to proceed by the opening of the double bonds of monomeric molecules $C_6H_5CH = CH_2$ to form macromolecules.(1) Signer and Weiler applied the Raman effect to prove this polymerisation mechanism,(2) showing that the Raman line due to the presence of a double bond disappeared in the polymerisation product. If we assume, as Staudinger and Steinhofer(3) considered, that the terminal valency of the long thread molecule acquires a double bond, we cannot expect the complete disappearance of the said line for polystyrene. It would, however, be very difficult in the case of Signer's experiment to prove the existence of this line, the intensity of which must be very small owing to the high molecular weight (40000) of the sample used. For this reason we have carried out an intensity measurement on the Raman lines of polystyrene having a lower polymerisation degree according to the method described in our previous communication.(4) For a polymer,(5) for which the cryoscopic measurement (in benzene solution) gave a molecular weight of 1150, the intensity of the line 1602 was found to be five times as large as that of the line 1634, while for the monomer the latter was twice as strong as the former; so that the line 1634 decreased in intensity by 1/10 relatively to the line 1602, when about 11 molecules in the mean polymerised to form one long molecule. If we assume quite simply that the intensities of the lines of 1634 and 1602 are proportional to the number of ethylene bonds and benzene nuclei respectively, the observed intensity change can conform with the view that polystyrene does not consist of ring molecules but of thread molecules which have ethylene bonds as the terminal valency.(3)

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(1) Staudinger, "Die hochmolekularen organischen Verbindungen", Berlin, (1932).

(2) Signer and Weiler, *Helv. Chim. Acta*, **15** (1932), 649.

(3) Staudinger and Steinhofer, *Ann.*, **517** (1935), 35.

(4) Mizushima, Morino and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; see also *Physik. Z.*, **35** (1934), 905.

(5) The sample was prepared by heating the monomer at 130°C for ten hours.

We have also followed the polymerisation process at room temperature by means of such an intensity measurement and found that the viscosity of the sample changed considerably, before the intensity change was appreciable. Hence we must consider that the viscosity change is in some cases caused by the formation of micelle built up from small single molecules held together by the van der Waals force, but not by the formation of macromolecule in which all the atoms are linked together by electron pair bonds.

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Raman Lines of Styrene and Polystyrene.

Monomer	Polymer(6)	Monomer	Polymer
212 (1)	224 (2)	1204 (6)	
241 (3)		1240 (0)	
445 (1b)		1301 (1)	
510 (0)		1321 (3)	
558 (1)	558 (2)	1414 (6)	
621 (3)	622 (4)	1450 (0)	1450 (1)
	763 (1)	1496 (2)	
774 (4)		1555 (0)	
796 (0)	795 (1)	1575 (1)	1580 (1)
835 (0)	835 (0)	1601 (10)	1602 (10)
909 (2)	904 (0)	1632 (20)	1634 (2)
999 (9)	999 (12)	2909 (0)	
1035 (2)	1031 (3)		2930 (2)
1156 (2)	1156 (3b)	3009 (3)	
1183 (3)		3059 (7)	3050 (8)
	1197 (4b)		

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(6) For the polymer some of the weak lines might escape our observation owing to the inevitable background.