

A Theoretical Study on Polymerisation of Styrene by Alternating Current

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Abstract: An examination of the experimental data obtained from polymerisation of styrene of in THF using alternating current through a series of plots showed that relationships of rate of Polymerisation and limiting viscosity of polystyrene with frequency of current are of Freundlich and Langmuir Adsorption Isotherm types at higher and lower frequencies respectively. The experimental data are closely reproducible from these empirical relationships. The total Chain Length of polystyrene at different frequencies have been calculated and are found to decrease with the increase in frequency of current.

Keywords: Polymerisation, Styrene, Alternating Current, Chain Length, Frequency.

I. Introduction

Several workers [1,2,3] have successfully done polymerisation using direct current but very little work has been performed on polymerisations using alternating current. Bhadani [4] has successfully polymerised styrene in THF by square wave current of 4 mA at 0°C. It was found that the polymer yield and molecular weight of the polymer decreased with the increase in frequency of current used. At frequency, 100 c/s the polymer yield was nil, i.e. at high frequencies no polymer was formed.

This communication is intended to find out some empirical relations between the frequency of alternating current with the rate of polymerisation and limiting viscosity of polystyrene. The data available in the literature [4] has been given in the Table. I. It is to be noted that a great range of frequencies (0 c/s to 100 c/s) has been covered up within a few readings which made practical difficulty in plotting graphs, hence for the sake of convenience the available data has been divided into two parts one for lower frequencies (0 c/s to 0.05 c/s) and the other for higher frequencies (0.5 to 100c/s).

It has also been attempted to find out the chain length of polystyrene at different frequencies using different values of radius of polystyrene molecules.

II. Calculations

The rate of polymerisation was calculated by dividing the polymer yield with the duration of electrolysis (i.e. time). Other parameters like reciprocal of rate of polymerisation, logarithm of reciprocal of rate of polymerisation and of frequency, reciprocal of limiting viscosity and its logarithm (Table- II) were appropriately calculated from the Table –I.

An attempt has been made to find out some empirical relations between the frequency of electric current with the rate of polymerisation and the limiting viscosity. Finally, an attempt was also made to determine the Chain Length of polystyrene molecules by calculating their radii. (Table-IV).

TABLE-I

Polymerisation of Styrene by square wave current of 4 MA at 0° C. Na (C₆H₅)₄ B, 20 ml Styrene, 0.402 Molar solution.

Frequency in c/s (v)	Duration of electrolysis in min (t)	Polymer Yeild total in gm. (m)	Limiting Viscosity (η)	Mol. wt. x10 ⁻⁵ (M)
0.0	6	2.707	2.73	10.50
0.0015	10	2.422	2.25	7.92
0.003	11	2.348	2.23	7.82
0.05	25	2.992	2.12	7.31

0.5	50	1.971	0.99	2.58
5.0	135	1.406	0.68	1.78
20.0	240	0.10	-	-
50.0	280	0.10	-	-
100.0	300	nil	-	-

TABLE-II

Frequency (v)	Rate of polymerisation.	R ⁻¹ (R) = m/t	log (v)	log R ⁻¹	I/[η]	log (I/[η])
0.0	0.4512	2.216	-	0.3045	0.3663	-0.4361
0.0015	0.2422	1.129	-2.8239	0.6158	0.4444	-0.3522
0.003	0.2134	4.585	-2.5229	0.6708	0.4484	-0.3483
0.05	0.0796	12.56	-1.3010	1.0989	0.4718	-0.3263

0.5	0.0246	40.65	-0.3010	1.6090	-	-
5.0	0.0141	70.88	0.6990	1.8505	-	-
20.0	0.0004	250.00	1.3010	2.3979	-	-
50.0	0.0003	333.40	1.6990	2.5229	-	-

Frequency And Rate Of Polymerisation

The plot of reciprocal of rate of polymerisation against frequency of electric current at both lower and higher frequencies gave a curve (Fig.-I &II) which was tested for parabola and hyperbola. On plotting the logarithm of rate of polymerisation against logarithm of frequency (v) of current gave a linear relationship only at higher frequency (fig. III). This clearly indicates that the rate of polymerisation and the frequency of current follow a Freundlich Adsorption

Isotherm type of relationship. However, a plot of $\frac{v}{t/m}$ against (v) will give a straight line which shows that they follow a Langmuir Adsorption Isotherm type relationship.

Further, a plot of limiting fluidity (1/[η]) against frequency (v) of electric current gave a hyperbolic curve, while a plot of $\frac{v}{1/[\eta]}$ against (v) will also give a smooth straight line similar to v/t/m vs v

The Linear Equations:

The relation between the rate of polymerisation and the frequency of current at higher frequencies may therefore be set down to as:-

$$(\text{Rate of Polymerisation})^{-1} = k \cdot v^{1/a}$$

or, $\frac{1}{R} = R \cdot v^{1/a}$ (1)

or, $\log (1/R) = \log k + 1/a \log (v)$ (2)

Where, **a** & **k** are constants and R= Rate of Polymerisation. The value of 1/a has been found from the slope of Fig. III to be equal to 0.304 and that of log k =2.0 from the intercept on Y-axis.

At lower frequencies the relationship may be put as:

$$\frac{1}{R} = \frac{k_1 k_2 v}{1 + k_1 v}$$

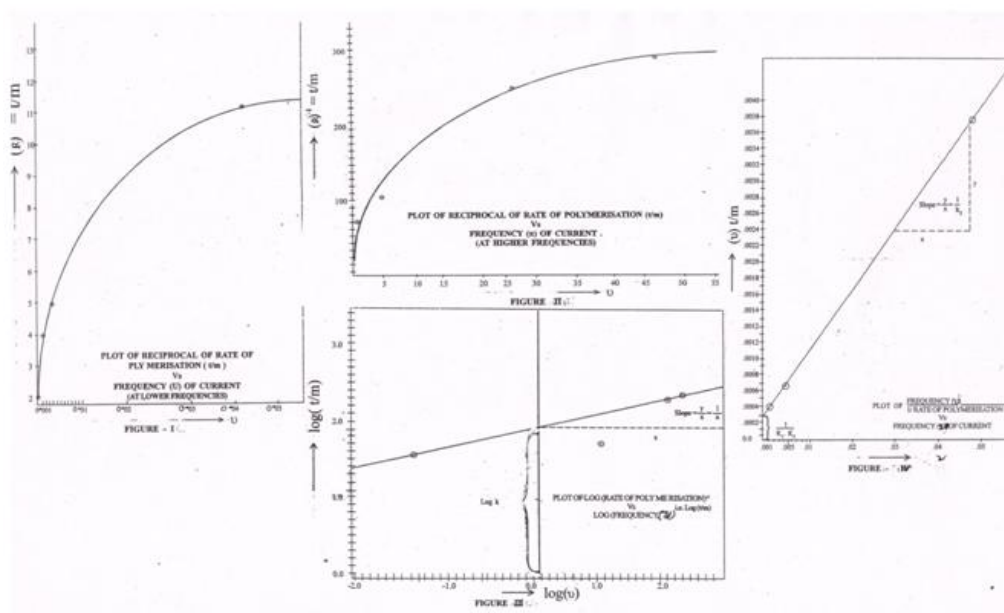
Which may be rewritten as:

$$\frac{v}{1/R} = \frac{1}{k_1 k_2} + \frac{v}{k_2}$$
 (3)

Similarly, the relationship between limiting viscosity and frequency of alternating current may also be set down to:

$$\frac{v}{1/[\eta]} = \frac{1}{k_1 k_2} + \frac{v}{k_2}$$
 (4)

Similar to equation (3)



These equations (3) &(4) like equation (2) are equations of straight line $y=mx+c$. Values of ‘m’ in each case have been calculated from the slope of graphs-III &IV respectively to be:

$$\text{Slope } =, \frac{1}{k_2} = 0.07 \text{ and } \frac{1}{k_1 k_2} = 2.4$$

These values of ‘m’ and ‘c’ enable us to reproduce the experimental values quite case closely within a maximum error limit of 0.9% in case of equation (2) 5% in equation (3) and 2.25% in equation (4)

TABLE-III

(v)	$(1/[\eta])$	$(R)^{-1} = (\frac{t}{m})$	$\frac{v}{t/m}$	$\frac{v}{1/[\eta]}$
0.0015	0.4444	4.129	0.0003632	0.003375
0.003	0.4484	1.686	0.0006401	0.006690
0.05	0.4718	12.56	0.003982	0.1059

Radius and Chain Length of Polystyrene At Different Frequencies:

The radius of polystyrene molecules formed at different frequencies of alternating current may be calculated if its density (d) is known.

Since, $V = \frac{M}{d}$ (Where, V = Volume, M = Mol. wt.,
and d = Density of polystyrene)

But $V = \frac{4}{3} \pi r^3$ assuming the polystyrene molecules to be spherical ; (r = radius)

$$\text{or, } \frac{3V}{4\pi} = r^3 \quad \text{or} \quad r = \left(\frac{3V}{4\pi}\right)^{1/3} \quad \dots\dots\dots (5)$$

The molecular weight changes with the change of frequency of electric current and hence different values of radius (r) are given below in Table- IV. The density⁵ of polystyrene may be taken as 0.903 g/cm³ at 0° C.

Again the Chain Length of polystyrene may be calculated according to the equation:

$$\text{Total Chain Length} = 2\pi r. (\text{length of monomer unit}) \quad \dots\dots\dots (6)$$

The length of monomer unit may be taken to be 2.5 A.

Using these values of radius (Table-IV), the Chain Length of polystyrene molecules formed at different frequencies have been calculated.

It is important to note that the length of polystyrene molecules decreases with the increase in frequency of alternating current used for polymerisation.

Table-IV

Frequency (ν)	Mol. Wt. (M)	Volume ($V=M/d$)	Radius (r)	Chain Length (in A)
0.0	10.30	11.4064	1.396	22.9172
0.0015	7.92	8.7244	1.279	20.0803
0.003	7.82	8.6600	1.275	20.0175
0.5	7.31	8.0952	1.246	19.5622

It is expected that the empirical formulae so derived, might be of general application for all polymerisation reactions using alternating current. These relations and the values of 'm' and 'c' also enable us to determine the parameters like rate of polymerisation, and limiting viscosity at the various intermediate frequencies.

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