"CONTROLLED FRACTIONATION OF POLYSTYRENE"

by

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"WORK FOR WORK'S SAKE"

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INTRODUCTION

Although polystyrene is a relatively new commercial plastic, it has been known to science for over a hundred years. Polystyrene is a polymerized product of the basic fundamental unit or monomer, styrene. In defining the scope of this work, the term polymerization should be well-defined.

The fundamental polymerization reaction was formerly conceived as the self-addition of molecules capable of such a reaction wherein primary valance forces are involved in the union. The word polymer was introduced by Berzalius (4) nearly a century ago to recognize the fact that two compounds may have the same chemical composition but different molecular weights and he classified polymerism as a special type of isomerism. But recently with the advances in the field, the above definitions do not satisfy rational minds. It is more practical and useful and also more consistent with actual usage to define polymerization as any chemical combination of a number of similar molecules to form a single molecule (4). There are numbersof different ways of polymerization.

The styrene which becomes polystyrene on polymerization falls within one of these groups of polymers. It is substitution of phenyl in the ethylene group.

Like other covalent compounds, the polymer has molecular weight and if the molecules are very large, it is a high polymer. The high polymer in a pure form is not known though the importance of the substances is increasing very rapidly.

Both the natural and synthetic high polymeric substances are mixtures (31); individual molecules may differ in size; that is, in the number of repeating monomer units which is often called the degree of polymerization. It also differs in shape and sometimes in chemical composition. The system of the high polymeric substances may, however, be homogeneous in all respects but the molecular size. But the very heterogeneity of the polymer is of utmost importance. The peculiar properties of such substances which make them, as a class different from crystalline homogeneous materials, are due to the heterogeneity of the molecular weight. Since being non-uniform, they are infinitely variable. The molecular weight distribution of a high polymer for example, may vary from sample to sample; with natural products it depends on the source of the material, with synthetics on the method of preparation, and with both on previous treatment such as purification, bleaching or milling. Therefore, in the interpretation and use of a measured value of any property, that is a function of molecular weight such as osmotic pressure or solution viscosity, it must be clearly recognized that two samples giving the same value may yet be very different in other respects because of a different molecular size distribution and that a "molecular weight" calculated from such a value will be merely an average value. As many of the industrially important properties of high polymers likewise depend on the shape of the distribution curve, it is highly important that methods be available for determining the molecular weight distribution in the heterogeneous material without necessarily separating it into homogeneous fractions and

for preparing fractions at least approaching homogeneity with respect to molecular weight, in order to make it possible to determine the true relation between a given property and molecular weight. Such fractionation methods, fortunately, have been and are being developed. One of the most widely used methods now for the fractionation, is the fractional precipitation method. It was used for purification of rubber but now it is being employed on natural as well as synthetic polymers for their separation into different fractions according to their degree of polymerization. There are several different methods of carrying out the fractional precipitation. The one that was used during this work is based on the principle that the distribution coefficient depends on molecular weight. In the method the heterogeneous polymer, polystyrene, was completely dissolved in a suitable solvent and then partially precipitated with a suitable non-solvent. The precipitated phase, which contained the high molecular weight fraction, and the supernatant solution were separated by decantation without centrifuging; more of the polymer was then precipitated, and the procedure was repeated.

HISTORICAL

The idea that high polymeric materials might be heterogeneous is not new . Early in the 19th century, natural rubber was believed to consist of two compounds, one soluble and one insoluble in organic solvent (32) It was separated into fractions by the method of extractions.

Fractional precipitation is one of the most widely used methods today for the separation of synthetic polymers into different fractions according to the different degree of polymerization in the sample. It was first used for the purification of the polymer, and became very popular in the field of cellulose. Later it was taken up by Staudinger and his coworkers and was applied to a number of different synthetic polymers. In 1929 (29) he reported a fractionation of polystyrene that is of special interest because the precipitation was effected by an excess of solvent. Later on about 1930, Whitby (30) described the fractional precipitation of polystyrene from benzene solution. He used the concentration about 1.5 per cent and used ethanol as non-solvent. By this method, he was able to get six fractions. The idea behind the work carried out by Whitby was to prove that polystyrene is rubber-like and heterogeneous. The molecular weight of the sample used by Whitby varied from 4400 to 900. After that, in 1934, a study of the fractional precipitation of polystyrene was made by Danes (7.) He tried to measure the viscosity of the fractions in order to determine the degree of polymerization. He emphasized the temperature dependence of the solubility. His solvent was benzene and

precipitant was a mixture of methanol and acetone. Schulz (24a) in 1936, obtained fractionation of polystyrene using ethyl methyl ketone as solvent and methanol as the precipitant. He was able to obtain seven fractions. In the same year, Dobry and Schwab(8) fractionated polystyrene with methanol from various solvents. The idea was to get fractions for osmometric and viscometric study. In 1943, Alfrey, Bartovics, and Mark (1) fractionated polystyrene for osmatic pressure and viscosity measurements. The temperature dependence was carefully observed during the process to get equilibrium conditions during precipitation. This gave homogeneous fractions.

THEORETICAL

Polystyrene, discovered about a hundred years ago by Simon(29c) has acquired considerable technical importance in recent years because its dielectric properties are superior to those of any other natural or synthetic resin. The initial substance, styrene (phenyl ethylene or vinyl benzene), is prepared commercially from benzene and ethylene which unite to form ethyl benzene in presence of a catalyst, aluminum chloride.(19) At a higher temperature ethyl benzene may be decomposed in the presence of suitable contact catalysts into styrene and hydrogen

$$C_6H_6 + C_2H_4 \rightarrow C_6H_5\,CH_2CH_3 \downarrow C_6H_5\,CH{:}CH_2 + H_2$$

Styrene, $C_6H_5CH = CH_2$, polymerizes in the dark, more rapidly in the light and at higher temperature, to form the chain-polymer, polystyrene. This seems to be invariably amorphous, although Katz(16) reports that stretched polystyrene shows a trace of X-ray diffraction pattern. The virtual absence of an X-ray pattern suggests that the compound has an irregular structure which may, perhaps, be represented in the following way (where R is a phenyl group)

$$-CHR-CHR-CH_2-CH_2-CHR-CH_2-CHR- \quad 1.$$

rather than by the formula

$$-CHR-CH_2-CHR-CH_2-CHR-CH_2- \quad 2.$$

Against this assumption is the fact discovered by Staudinger (28) that, during decomposition by heating ("cracking"), only fragments in which CH_2- and CHR-groups alternate are obtained, for example,

$$CHR = CH-CH_2R \quad \text{or} \quad CH_2 = CR-CH_3$$

but never fragments in which phenyl groups are attached to adjacent carbon atoms. This argument is not conclusive, however, since it is conceivable that linkages of the $CHR-CH_2$ type are more stable than those of the CHR-CHR type, so that the latter are the first to be destroyed in cracking. The irregular structure is assumed by Staudinger to be due to the irregular distribution of optical antipodes along the chain. It is impossible at the present time to decide in favor of formula 1, or 2, and the question whether or not polystyrene is a true homopolymer must be left open.

High-polymeric polystyrene (molecular weight 200,000-300,000) softens at temperatures up to 180° C. and may then be worked into shape by molding or casting under pressure. The product is particularly useful for electrical purposes owing to its great resistance toward chemical agents and its hydrophobic nature. Furthermore, the valuable dielectric properties, resulting from the absence of polar groups, the isotropic electrical character and the absence of inhomogeneities of texture render it superior to crystalline substances. It would be difficult to obtain material superior to polystyrene in this respect.

The above type of polymerization i.e. that of polystyrene

falls in one of the two major types of polymerizations, the first being condensation polymerization The general class of condensation polymerization is represented by the equation

X-R-Y -- X-R-Y --X-R-Y--

---------- -R-Z R-Z-R- (4)

In the formula X-R-Y is a bifunctional radical and X and Y are functional groups capable of reacting with each other to form the known functional group Z. Thus if X is -HO- and Y is -COOH-, Z will be -CO-O-. The compounds X-R-Y are called bifunctional compounds and their reactions are bifunctional reactions. Reactions of the type -R- -- Y-R'-Y- product, may be included in this class.

The other type of polymerization is addition polymerization of unsaturated compounds. Thus Cohen (5) states that "the property of undergoing polymerization is peculiar to unsaturated compounds, from a natural tendency to saturate themselves." So far as the formation of materials of high molecular weight is concerned, such reactions are much less clear-cut than bifunctional condensations, for the latter involve only the application of the known reactions of typical functional groups, and the general structural plan of the product may be inferred directly from the structure of the starting material." Polystyrene falls in the Vinyl type of polymerization. Substituted ethylenes of the type CH_2= CH-R, in which R is a negative group, polymerize more readily than does ethylene itself. The behavior of styrene may be taken as typical of this group. The polymerization is carried on as

explained in the beginning.

Polystyrene is not a definite material having a constant set of properties. By whatever method it is prepared it can be separated by fractional extraction or precipitation into fractions having the same chemical composition but different properties and molecular weights. The lower members are readily soluble in ether and the highest members are quite insoluble. The apparent molecular weights range from 1000 to 25,000 or more (perhaps as high as 200,000). All these fractions are soluble in benzene and the viscosity of the solutions increases progressively with increasing molecular weight. The average molecular weight of the crude polymer depends upon the conditions of its formation. Those formed very rapidly, e.g. by the action of heat at high temperature or by the action of stannic chloride at ordinary temperature, have relatively low molecular weights. Those formed more slowly, e.g., by spontaneous polymerization at room temperature have much higher molecular weights.

The polystyrenes having molecular weights above 10,000 show colloidal behavior; they swell before dissolving and the viscosity of their solution is very high. Nevertheless, there is considerable evidence to show that these solutions are true molecular dispersions, and that the molecule and the colloidal particle are identical. (27)

Chemically the polystyrols are completely saturated. They do not decolorize permangenate or absorb bromine. Under drastic conditions they can be completely hydrogenated without any significant change in molecular weight (27). On being heated to

about 320° C. they revert to the monomer styrene. It is doubtful if this reversion is ever quantitative.

The polymerization of vinyl compounds is enormously susceptible to catalytic and anticatalytic effects. Heat also accelerates the polymerization, and in general the more rapidly the polymer is formed, the lower is the average molecular weight of the product. Oxygen and peroxides are catalysts, and antioxidants are inhibitors. Light, especially the shorter wavelengths of the visible spectrum, accelerates the polymerization.

It seems that polymerization is not a formation of crystalline substance with uniform molecular weight, but is the repetition of the monomeric unit to form a long chain polymeric unit. Of course, such a formation cannot be uniform and as a result the polymer is a non-uniform hetergeneous product of long chain molecules not all of which have the same molecular weight. In order to separate the chains of the desired molecular weight fractions, it is necessary to devise and investigate suitable methods for fractionation of the sample into the fractions having the same molecular weight of the same degree of polymerization.

The methods used up to the present time for the fractionation of such polymeric substances are, in general, six. These divisions are very broad and some of the methods are subdivided. These methods (5a) are:

(1) Molecular distillation

(2) Ultrafiltration through graded membranes

(3) Chromatographic adsorption

(4) Ultracentrifuge

(5) Rate of solution method (diffusion into a single solvent

(6) Solubility method

Molecular Distillation

The basic principle on which the separation is carried out in this method is that the larger molecules are less volatile than the smaller ones. The method is in more popular usage for purification of high polymer, that is, the removal of low-molecular-weight material, than for the separation of high-molecular-weight fractions. In any polymerization or polycondensation reaction, however, molecules from all the way from unreacted monomer up to those in the high-molecular-weight range are formed, and, in a sense, the removal of the low-molecular-weight material is a fractionation. (5a)

Molecular distillation is essentially a distillation at very low pressure 10^{-3} or 10^{-6} mm. of mercury. The distance between the distilling pan and the collecting plate is shorter than the mean free path of the evaporating molecules, so that they suffer (on the average) no collisions while in the vapor state. Under these conditions, even very slightly volatile substances can be distilled without decomposition. Moreover, the diffusion velocity of a molecule is inversely proportional to the square root of the molecular weight, so that the lighter molecules distill off first, leaving purified residue. The method may also be used to prove the heterogeneity of substances.

ULTRAFILTRATION

It is often possible to separate particles of different sizes by ultrafiltration through carefully graded cellulose or nitrocellulose membranes. This separation is based on sieving action; the pore sizes are chosen in such a way that particles up to a certain size can pass but larger ones cannot. This is satisfactory enough with spherical particles, even though complications may occur when the membrane interacts with the solution and passage through the membrane takes place in ways other than by sieving action. The method (20) is not very satisfactory for chain polymers and it is too slow.

Chromatographic Adsorption

Chromatographic adsorption is a useful method for separating mixtures into their components; even closely related substances have often been successfully separated (5a). The method consists in filtering the solution containing the mixture to be separated through a column of an adsorbent, "developing" the chromatogram by washing with pure solvent and eluting various parts of the column separately to recover the adsorbed material. The principle on which the separation is based is preferential adsorption; the components preferentially adsorbed are found in the upper part of the column, those more poorly adsorbed are found in the lower part, those most poorly adsorbed in the filtrate. Elution reverses the process of adsorption, that is, it causes the substance to pass from the adsorbed layer into solution again; it can be carried out either by filtering the elutant through the column and collecting the filtrates in a series of containers or separating the column into bands and eluting each separately. The method is quite satisfactory in the case of the cellulose derivatives but it is not widely employed for the fractionation of chain polymers.

Ultracentrifugation

This method is based on the principle that sedimentation velocity increases with the molecular weight. (5a).

An ultracentrifuge is an instrument in which sedimentation in centrifugal fields can be measured-- quantitatively; the centrifugal fields employed are often quite strong, and the appara-

tus for producing them is rather complex.

An ultracentrifuge can be used in two different ways (a) to measure sedimentation velocity, that is, the rate of settling of particles in a given centrifugal field, under standard conditions; (b) to measure sedimentation equilibrium, that is, the concentration gradient when equilibrium between sedimentation and diffusion has been established. The second method is used for molecular weight determinations on high polymers; the first method can be used for molecular-weight determination also but its chief value is for the measurement of heterogeneity.

Singer and Gross (5a), in 1934 performed ultracentrifuge measurements on polystyrene. They encountered a difficulty due to the "matting" of the molecules, that is, chain entanglements which prevent molecules from acting independently.

Rate of Solution Methods

The method involves placing the polymer in contact with a solvent, removing the supernatant solution after a definite time interval, replacing it with fresh solvent, and repeating the procedure until the desired number of fractions has been obtained.[5a] As would be expected, the smaller molecules concentrate in the first fractions and the larger ones in the last, for the smaller molecules diffuse more rapidly and are, therefore, first extracted.

In 1930 Whitby (31) extracted polystyrene with each of the solvents ether, and diethyl oxalate The method has been applied to other high polymeric substances too.

Solubility Method

The solubility method is one of the most widely used methods for the fractionation of natural and synthetic polymers. The basic principle of the method is the decrease in solubility with the increase in molecular weight.[5a] It depends on the greater solubility in a given liquid of the lower-molecular-weight species, and on the fact that the solvent power of a binary liquid mixture (of solvent and non-solvent) depends on the proportion of the two components. If a non-solvent or a precipitant is added to a polymer solvent system, as in fractional precipitation, or a polymer is added to a solvent-non-solvent mixture, as in fractional solution, two phases are obtained at equilibrium, if the proportions of the components are properly adjusted. The upper layer is a solution in which polymer is present in low concentration; the lower layer, or "precipitated" phase, is either a swollen gel or a very viscous liquid, and contains a high proportion of polymer. The material of higher molecular weight tends to concentrate in the precipitated phase, that of lower molecular weight in supernatant liquid.

The first theory about the solubility fractionation was put forward by Brønsted (5). In chemically similar materials the potential energy of the molecule is proportioned to its magnitude. On the basis of this assumption, the relation between molecular magnitudes and distribution in different equilibria is discussed.

The equation

$$\ln C^{1}/C = \chi M/RT$$

was set up; where C and C'^{1} are the concentrations of polymer in two phases at equilibrium, M is the molecular weight of the polymer and λ is a constant characteristic of the polymer-solvent system but independent of M.

Schulz (24) developed these ideas further by assuming that in the case of binary liquid mixtures λ is a linear function of the liquid composition and showed that the equation

$$Y^{*} = A + B/M$$

adequately expresses the relation between Y^{*} the critical liquid composition at the precipitation point, and the molecular weight, M, of the polymer; A and B are empirical constants.

The Brønsted-Schulz theory was remarkably successful in predicting the solubility behavior of high-polymer solutions. However, it was soon suspected that the entropy of mixing of polymer and solvent molecules was a factor of importance and should not be neglected in developing the theory of solubility.

Much work has been done on the thermodynamic properties of the solutions by Flory (12, and, 13), Meyer and Huggins (14). In case of binary solution (14) the activity of component #1 of a solution is related by thermodynamics to its partial molal heat of mixing ($\bar{L}_1$) and entropy of mixing ($\Delta\bar{S}_1$) according to the equation

$$\ln a_1 = \frac{\bar{L}_1}{RT} - \frac{\Delta\bar{S}_1}{R} \quad (a_1 \text{ is activity}) \text{ ----1}$$

for component #2

$$\ln a_2 = \frac{\bar{L}_2}{RT} - \frac{\Delta\bar{S}_2}{R} \quad (a_2 \text{ is activity}) \text{-----2}$$

The heat of mixing depends on the relative attraction energies of like molecules and of unlike molecules in the solution

With the aid of certain reasonable approximations, one can deduce the equations

$$\bar{L}_1 = K \bar{V}_1 \bar{V}_2 \quad \text{---------- 3}$$
$$\bar{L}_2 = K \bar{V}_2 \bar{V}_1 \quad \text{---------- 4} \qquad (23)$$

where $\bar{V}_1$ and $\bar{V}_2$ are the volume fractions of the components and K is a constant whose magnitude depends on the nature of both compounds.

Entropy is a measure of randomness. The simple case of a solution composed of two kinds of molecules, both spherical of the same size and alike as regards their attractions and repulsions for other molecules, can be treated by the methods of statistical mechanics. The number N of possible distributions of the two molecular species among the available sites can be computed as a function of the composition. Assuming all these alternatives to be equally probable, the entropies of mixing are computed to be

$$\Delta \bar{S}_1 = -R \ln N_1 \quad \text{----------5}$$
$$\Delta \bar{S}_2 = -R \ln N_2 \quad \text{----------6}$$

The substitution of (1) and (2) gives for L_1 and L_2 equal to zero

$$a_1 = N_1 \text{ - - - - - - } 7$$

$$a_2 = N_2 \text{ - - - - - - } 8$$

This represents Raoult's Law. Empirically, this law is found to hold true (approximately) for many binary solutions for

there is little or no heat of mixing. But for the solutions of long chain compounds these equations do not hold at all well.

The quantitative calculations of the entropy of mixing for such solutions has been carried out independently by Flory (13) and by Huggins (15).

$$\ln a_1 = \ln v_1 + \left(1 - \frac{V_1}{V_2}\right) v_2 + \mu_1 v_2$$

and relation between μ_1 & μ_2

$$\mu_1 \bar{V}_2 = \mu_2 \bar{V}_1$$

μ_1 & μ_2 are approximately constant, independent of the solution, and V_1 and V_2 are partial molar volumes of solvent and polymer.

In practice μ if found to vary with temperature according to the equation

$$\mu = \alpha + \beta/T \qquad (5a)$$

where α & β are constant

The solubility methods can be further divided:

1. Fractional precipitation
   (i) By addition of precipitant
   (ii) By cooling

2. Fractional solution
   (iii) Solvent of varying composition
   (iv) Varying temperature

3. Distribution between two immiscible solvents

Fractional Precipitation (General)

Fractional precipitation procedures are those in which the heterogeneous polymer is completely dissolved in a suitable liquid and then partially precipitated. The precipitated phase, which contains the high molecular weight fraction, and the supernatant solution are separated by decantation with or without centrifuge; more of the polymer is then precipitated and the procedure is carried on until the maximum amount of solute is taken out.

There are two ways in which precipitation can be effected, and these will be dealt separately

(i) By adding a precipitant

(ii) By lowering the temperature

and a combination of both the methods could be as well used. In this work, a combination of both the methods has been used which will be explained later.

In the actual fractionation the choice of solvent and precipitant is very important as has been recently confirmed by Morey and Tamblyn (21). They have carried out the fractionation of cellulose acetate in different solvent-non-solvent systems. The conclusions they have drawn are:

(a) The effect of initial concentration on the efficiency of the fractionation by precipitation is minor.

(b) The choice of the solvent and precipitant is important and can lead to very marked differences in separability.

The relative solvent and precipitating powers can be deter-

mined by titrating a solution of the polymer in the solvent with the precipitant, the end-point being indicated by the sudden appearance of opalescence or turbidity (2,)(10). The larger the amount of precipitant needed to reach the end-point, the greater is the solvent power of the solvent or the smaller is the precipitating power of the precipitant. Ebring (9) compared the precipitating power of the saturated alcohols from methyl to octyl, on polystyrene dissolved in ethyl acetate, beetyl acetone, carbon tetrachlorid, chloroform, methyl ethyl ketone, benzene, xylene, tolvene and monomeric styrene.

(i) Fractional precipitation by the addition of the precipitant.

In this method fractionation is effected by adding to the solution of the polymer a suitable amount of precipitant, enough to cause separation into two phases, but not enough to cause precipitation of all the polymer present; the phases are then separated, and the supernatant liquid again treated in the same fashion until all the polymer (monomer may remain in the solution) has been precipitated. Various modifications of these fundamental principles are possible. The work done on the polystyrene by this method has already been discussed in the historical outline.

(ii) Fractional precipitation by cooling.

The efficiency of the fractional precipitation very markedly depends on the temperature as has been pointed out by Alfrey and Mark (1), Dane's (6), and Flory (11). It seems that

careful control of temperature during the process is very necessary. In this method, after the polymer is dissolved in a proper solvent, the temperature of the solution is lowered and allowed to remain for a fixed time and the precipitate is removed in the same way as above and process repeated with the supernatant liquid.

2. Fractional solution.

In the fractional solution procedure, the polymer is placed in contact with solvent-non-solvent mixture, and the system is allowed to come to equilibrium; after the supernatant solution is decanted, the residue is treated with a fresh mixture, richer in solvent than the first, and this process is repeated until the polymer has all dissolved, or until no more will dissolve. In this way the lower molecular fractions are extracted first, the high molecular ones the last.

3. Distribution between two immiscible solvents.

This method depends upon the fact that the distribution coefficient is a function of the molecular weight.

In precipitation and solution methods, the solvent and non-solvent are completely miscible; only the presence of polymer causes a separation into two phases. It is also possible, however, to use a solvent system which is heterogeneous even in the absence of polymer; and the distribution of polymer molecules in such a system depends on molecular weight. A fractionation can, therefore, be accomplished by varying the composition of one of the phases. This method has not been in much use with the polymer.

Comparison of fractional precipitation and fractional solution methods.

Rogovin and Glazmann [32] have pointed out that in the process (1) the overlapping of fractions occurs because the longer molecules pull the shorter ones down into the precipitate while the shorter keep the longer ones in the solution by entanglement and other forms of interaction. (2) that the reproductivity of the results is not good. (3) that a limited number of fractions only can be obtained in one run, so that refractionation is necessary and (4) that fractionation is effected only with respect to the degree of chemical substitution.

But most of the objections to the fractional precipitation method disappear when the solution is made sufficiently diluted. Precipitation "en bloc" occurs only when the solution is concentrated enough to allow interaction between the molecules; moreover, there is no reason why chain entanglements in the solid sample should not cause a similar difficulty in the solution process. It is true,however, due to the slowness of the solution methods the equilibrium conditions are better maintained than in precipitation methods.

Spurlin [26] rejected the fractional solution method in favor of the precipitation because the former method does not so readily permit refractionation.

Kemp and Peters [17] have made a comparison of several procedures applied to rubber.

Very recently Madorsey and Straus [18] have done high-

vacuum pyrolytic fractionation of polystyrene. Samples of polystyrene of an average molecular weight of about 230,000 and weighing 25 to 50 mg. were pyrolyzed in a vacuum of 10^{-6} mm. of mercury at 350° - 420° C. The time of pyrolysis varied from .5 to 4.0 hours. The following results were obtained:

(1) A solid residue having an average molecular weight of 2182.

(2) A waxlike fraction consisting of a mixture of a dimer, trimer and tetramer of styrene, with an average molecular weight of 264.

(3) A liquid fraction consisting of 94.5 mole % styrene, 5.6 mole % toluene, and traces of ethyl benzene and methyl styrene.

(4) A gaseous fraction consisting mainly of carbon monoxide.

VISCOSITY DETERMINATION

One of the most striking properties of solution of high molecular weight substances is their high viscosity. For many years viscosity has been applied as an empirical but useful guide to the quality of many materials, so that a whole series of standard technical methods for its measurement have been devised, (18a).

In 1930, Staudinger (29a) who as early as 1926 had drawn attention to the relationship between molecular weight and viscosity of homologous polymer is proportional to the molecular weight. According to empirical equation

$$Nsp/c = Km\ M$$

in solution of low concentration. From this, knowing Km, the molecular weight $M = 2\ Nsp/Kmc$ may be calculated. For this purpose the relative viscosity Nrel that is the ratio of the solution to that of the pure solvent, is determined. Subtracting unity, the specific viscosity Nsp is obtained

$$Nsp = Nrl - 1$$

The viscosity is measured in dilute solution, in which case, according to Staudinger, Nsp is proportional to the concentration, so that Nsp/c is constant.

Staudinger gives values of Nsp for so-called basal molar solutions, that is, for solutions containing one molecule of the

of the polymerized structural unit in one liter of solution for example, the weight of a styrene residue in the case of polystyrene and refers to the constant mentioned above to this concentration. The constant K_m for a given homologous polymeric series may change with the solvent and temperature. Value of the constant used during the investigation of work is

$$K_m = 1.8 \times 10^{-4} \quad (29\ b)\ (17a)$$

EXPERIMENTAL

The literature search shows that there has not been much work done on the actual fractional precipitation of the polystyrene except some work for the measurement of the viscosity of the polystyrene fractions. But the literature search gave an idea of the factors influencing the process. These factors are:-

1 Temperature.

2 Concentration.

3 Choice of solvent-non-solvent system.

4 The cycle of time.

As far as the temperature was concerned, it was brought within control during the entire work by working at 25°C. and allowing the precipitate to settle at 15 - 16° C.

The concentration is not very important within certain limits and for the convenience of the work, was chosen to be 2.5%.

As to the choice of solvent-non-solvent system, quite a few systems were studied, basing the experiments on data from the works of various authors and finally two of the systems seemed to offer promise. These systems were chosen from the standpoint of the recovery of the solvent and non-solvent so as to avoid economic waste. There are many systems but the question of recovery of the solvent and non-solvent makes the list relatively small. The presence of poisonous fumes from certain

organic solvents and non-solvents eliminate some of the systems. The only method left was to work by trial and error and working in this way, it was found that in case of the polystyrene (commercial), the system of ethyl-acetate as solvent and acetone as non-solvent works satisfactorily.

The cycle of time all throughout the work was kept between 20 hours and 24 hours.

ACTUAL EXPERIMENTAL PROCEDURE NO. 1

CHEMICAL USED:- (1) Polystyrene -- (solute)
(commercial grade " Lustron"
by Monsanto Chemical Corporation)
(2) Ethyl acetate -- (Solvent)
Commercial Solvents Corporation (Technical)
(3) Acetone (C.P.) -- (Non-solvent)
Commercial Solvents Corporation

APPARATUS:- No special apparatus was used. The general ordinary apparatus like beakers, flasks, were used.

PROCEDURE:- An accurately weighed (dried) quantity of polystyrene, (crystalline pieces) was dissolved in a weighed quantity of ethyl-acetate to obtain the desired concentration. It was allowed to dissolve at 25° C. and after complete dissolution and equilibrium, the sample was kept at 15° C. for about 20 -24 hours. Then for the separation of the fraction; (i.e. precipitate); the supernatant liquid was decanted and weighed. The precipitate was dried on water-bath and removed with the help of distill water. The fraction was dried (to remove the water) until constant weight. From this weight, the percentage weight of the fraction was calculated.

To the weighed supernatant liquid a weighed amount of non-solvent, acetone, was added to get the second fraction. The procedure as above was repeated.

In the same way other fractions were obtained.

RESULT :- The results were tabulated and a curve of percentage fractions versus the ratio of the non-solvent/ solution was drawn. In the ratio the solution was taken to be 100 so the ratio was on percentage basis.

EXPERIMENT NO. 2

TITLE: DETERMINATION OF VISCOSITIES

CHEMICALS USED:- (1) Fractions of polystyrene obtained by the procedure described.

(2) Benzene (solvent)

Commercial Solvent Corporation (Technical)

APPARATUS:- Ostwald's viscometers were used in thermostatically controlled constant temperature water-bath.

PROCEDURE:- An accurately weighed quantity of each fraction was dissolved in definite volume of benzene.

An equal volume of each solution was allowed to run through the viscometer and the time for each run was noted by an electric timer. Great care was taken to keep the temperature of the bath constant.

In the same way the procedure was repeated to get the time for the benzene (solvent) to run through the same viscometer.

CALCULATIONS:- The concentration of the solution was very low and there was very little difference between the densities of the solution and the solvent.

The viscometers were calibrated for the solvent first. The ratio of the time required

CALCULATIONS: (contd) - in seconds for the flow of solution to the flow of the solvent through the same capillary of the viscometer gave the relative viscosity of the solution. The specific viscosity was obtained from these by subtracting unity.

$$\frac{t_2 d_2}{t_1 t_2} = Nrel$$

where: (t_2 = time in seconds for the flow of solution

t_1 = time in seconds for the flow of solvent

d 1 and d 2 are corresponding densities.)

But the densities are nearly equal, therefore unity

$$\frac{t_2}{t_1} = N \text{ relative}$$

$Nr - 1 = Nsp$

Substituting in Staudinger's equation

$$\frac{Nsp}{Cgm} = Km \times M$$

where: Nsp = specific viscosity

Cgm = concentration in basal mols per liter

K_m = constant 1.8×10^{-4}

M = Molecular Weight

CONDITIONS OF THE EXPERIMENT:-

The temperature was kept constant = 34.9 -- 35.05° C. The results obtained are tabulated for each sample in the Tables 2; 3; 4; and 5.

FRACTIONATION OF POLYSTYRENE

Table No. 1 --- Curve No.1

Weight of the polystyrene taken	5.0 g.
Weight of the solvent (ethyl acetate)	195.0 g.
Concentration of the solution	2.5 per cent
Non-solvent used	Acetone
Temperature of working	35° C.
Temperature of precipitation	15° C.
Time allowed for precipitate to settle	20 - 24 hours

Number of the fractions	Sample 1 Wt of fractions in per cent	Sample 2 Wt of fractions in per cent	Sample 3 Wt of fractions in per cent	Sample 4 Wt of fractions in per cent	Ratio of g. Non-solvent / 100 g. of solution
1	22.02	20.042	20.046	22.286	0
2	7.14	6.404	10.47	9.254	.03
3	15.504	17.62	15.344	14.82	.06
4	11.664	11.86	11.338	12.76	0.2 2
5	16.5	14.964	12.62	15.042	0.55
6	7.28	10.03	8.803	10.18	1.0
7	1.99	2.95	1.84	2.9	1.6
8	11.925	11.2	14.05	--	Recovered by evaporation

FRACTIONATION OF POLYSTYRENE

Sample No. 1 Table No. 2

Weight of the polystyrene taken	5.08 g.
Weight of the solvent (ethyl acetate)	195.0 g.
Concentration of the solution	2.5 per cent
Non-solvent used	acetone
Temperature of working	25° C.
Temperature of precipitation	15° C.
Time allowed for precipitate to settle	20 - 24 hours
D. P. determined by $\frac{\eta sp}{Cgm} = Km \times \frac{M}{104}$	$Km = 1.8 \times 10^{-4}$ at 35° C.

Number of the fractions	Wt. of fractions in per cent	Ratio of g. of acetone / 100 g. of solvent	Cm, for viscosity determination	Relative viscosity t2/t1	Degree of polymerization
1	22.02	0	3.13	94.5/54.63	1896.
2	7.14	.03	1.636	70.48/54.63	994.9
3	15.504	.06	1.582	66.65/54.63	772.3
4	11.668	.2	1.142	61.35/54.63	528.4
5	16.5	.55	1.04	59.23/54.63	449.9
6	7.28	1.0			
7	1.99	1.6	1.216 (Both the fractions combined)	57.8/54.63	265.7
8 Recovered by evaporation	12.1	infinity	1.384	56.38/54.63	128.8

FRACTIONATION OF POLYSTYRENE

Sample No. 2 Table No. 3

Weight of the polystyrene taken	5.08
Weight of the solvent (ethyl acetate)	195.0 g.
Concentration of the solution	2.5 per cent
Non-solvent used	acetone
Temperature of working	25° C.
Temperature of precipitation	15° C.
Time allowed for precipitate to settle	20-24 hours
D.P. determined by $\frac{\eta sp}{Cgm} = Km \times \frac{M}{104}$	Km = 1.8×10^{-4} at 35° C.

Number of the fractions	Wt. of fractions in per cent	Ratio of g. of acetone / 100 g. of solvent	Cm, for viscosity determination	Relative viscosity t2/t1	Degree of polymerization
1	20.042	0	2.128	35.35/24.2	1202
2	6.404	.03	1.196	29.15/24.2	950
3	17.620	.06	1.308	70.05/59.34	766.4
4	11.86	.22	0.670	63.3/59.34	552.5
5	14.964	.55	1.258	66.25/59.34	538.
6	10.03	1.0			
7	2.95	1.6	1.82 (Both the fractions combined)	65.25/59.34	304
8 Recovered by evaporation	11.20	Infinity	1.10	61.2/59.34	158.3

FRACTIONATION OF POLYSTYRENE

Sample No. 3 Table No. 4

Weight of the polystyrene taken 5.08

Weight of the solvent (ethyl acetate) 195.0 g.

Concentration of the solution 2.5 per cent

Non-solvent used acetone

Temperature of working 25.° C.

Temperature of precipitation 15.° C.

Time allowed for precipitate to settle 20-24 hours

D.P. determined by $\frac{Msp}{Cgm} = Km \times M$ $Km = 1.8 \times 10^{-4}$ at 35° C.

Number of the fractions	Wt. of fractions in per cent	Ratio of $\frac{\text{g. of acetone}}{100 \text{ g. of solvent}}$	Cm, for viscosity determination	Relative viscosity t_2/t_1	Degree of polymerization
1	20.046	0	.992	$71.25/58.98$	1164
2	10.47	.03	1.364	$72.70/58.98$	932
3	15.344	.06	.956	$66.43/58.98$	733
4	11.338	.22	1.44	$68.54/58.98$	626
5	13.62	.55	1.31	$65.18/58.98$	445
6	8.805	1.0	0.74	$61.0/58.98$ (Both the fractions combined)	338.2
7	1.84	1.6			
8	14.05	Infinity	0.622	$59.24/58.98$	39.37
Recovered by evaporation					

FRACTIONATION OF POLYSTYRENE

Sample No. 4 Table No.5

Weight of the polystyrene taken	5.08
Weight of the solvent (ethyl acetate)	195.0 g.
Concentration of the solution	2.5 per cent
Non-solvent used	acetone
Temperature of working	25.° C.
Temperature of precipitation	15.° C.
Time allowed for precipitate to settle	20 -24 hours
D.P. determined by $\frac{Nsp}{Cgm} = Km \times M$	Km $=1.8 \times 10^{-4}$ at 35° C.

Number of the fractions	Wt. of Fractions in per cent	Ratio of g. of acetone / 100 g. of solvent	Cm, for viscosity determination	Relative viscosity t_2/t_1	Degree of polymerization
1	22.286	0	1.12	$60.38/_{49.1}$	1142
2	9.254	.03	1.03	$57.84/_{49.1}$	960
3	14.82	.06	1.086	$56.34/_{49.1}$	754
4	12.76	.22	1.32	$56.58/_{49.1}$	631.5
5	15.042	.57	1.14	$53.68/_{49.1}$	453.5
6	10.18	1.0			
7	2.90	1.6	1.11	$51.9/_{49.1}$ (Both fractions combined)	288
8 Recovered by evaporation	7.189	Infinity	--	--	--

FRACTIONATION OF POLYSTYRENE

Table No. 6 **Curve No. 2**

Weight of fraction in percentage vs. corresponding D.P. for all the four samples

No. of the fractions	Sample 1		Sample 2		Sample 3		Sample 4	
	Wt. of fr. in per cent	D.P. of the fractions	Wt. of fr. in per cent	D.P. of the fractions	Wt. of fr. in per cent	D.P. of the fractions	Wt. of fr. in per cent	D.P. of the fractions
1	22.02	1296	20.042	1202	20.046	1164	22.886	1142
2	7.14	994.9	6.404	950	10.47	932	9.254	960
3	15.504	772	17.62	766	15.344	753	14.82	754
4	11.664	528	11.86	552.5	11.378	626	12.76	631.8
5	16.5	449.9	14.964	450	13.62	538	15.042	445
6	7.28		10.03		8.803		10.18	
Combined		265.7		304		338		288
7	1.99		2.95		1.84		2.9	
		128.8		158		39.9		
8	11.925		11.2		14.05		--	

FRACTIONATION OF POLYSTYRENE

Table No. 7 Curve No.3

Average degree of polymerization with corresponding average accumulative weight per cent of fraction.

Fraction Number	1	2	3	4	5	6& 7	8
Average weight of fractions in per cent	21.0%	29.0%	44.7%	57%	72%	82%	95%
Average D.P.	1226	959	756	584	471	298	128

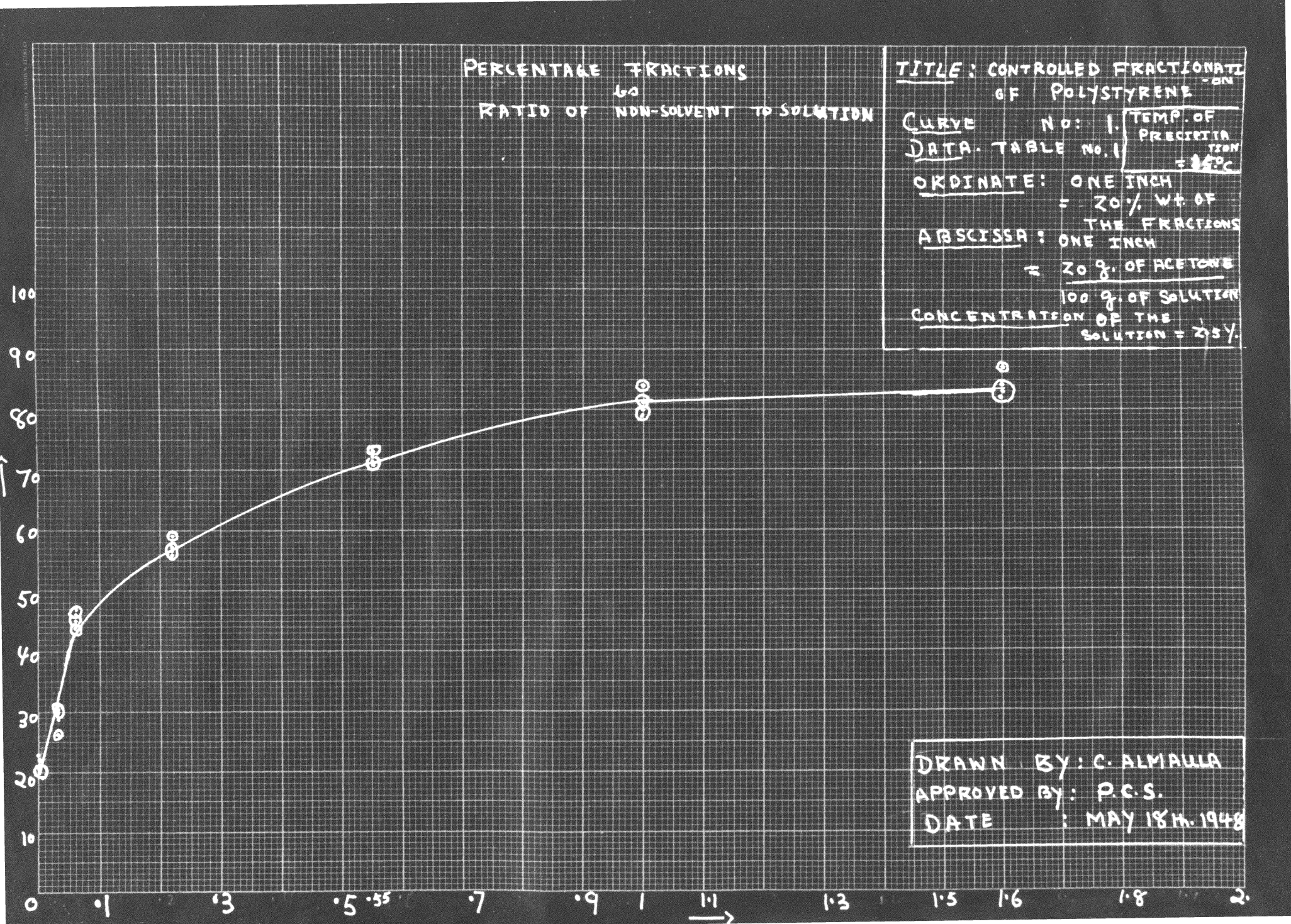
FRACTIONATION OF POLYSTYRENE

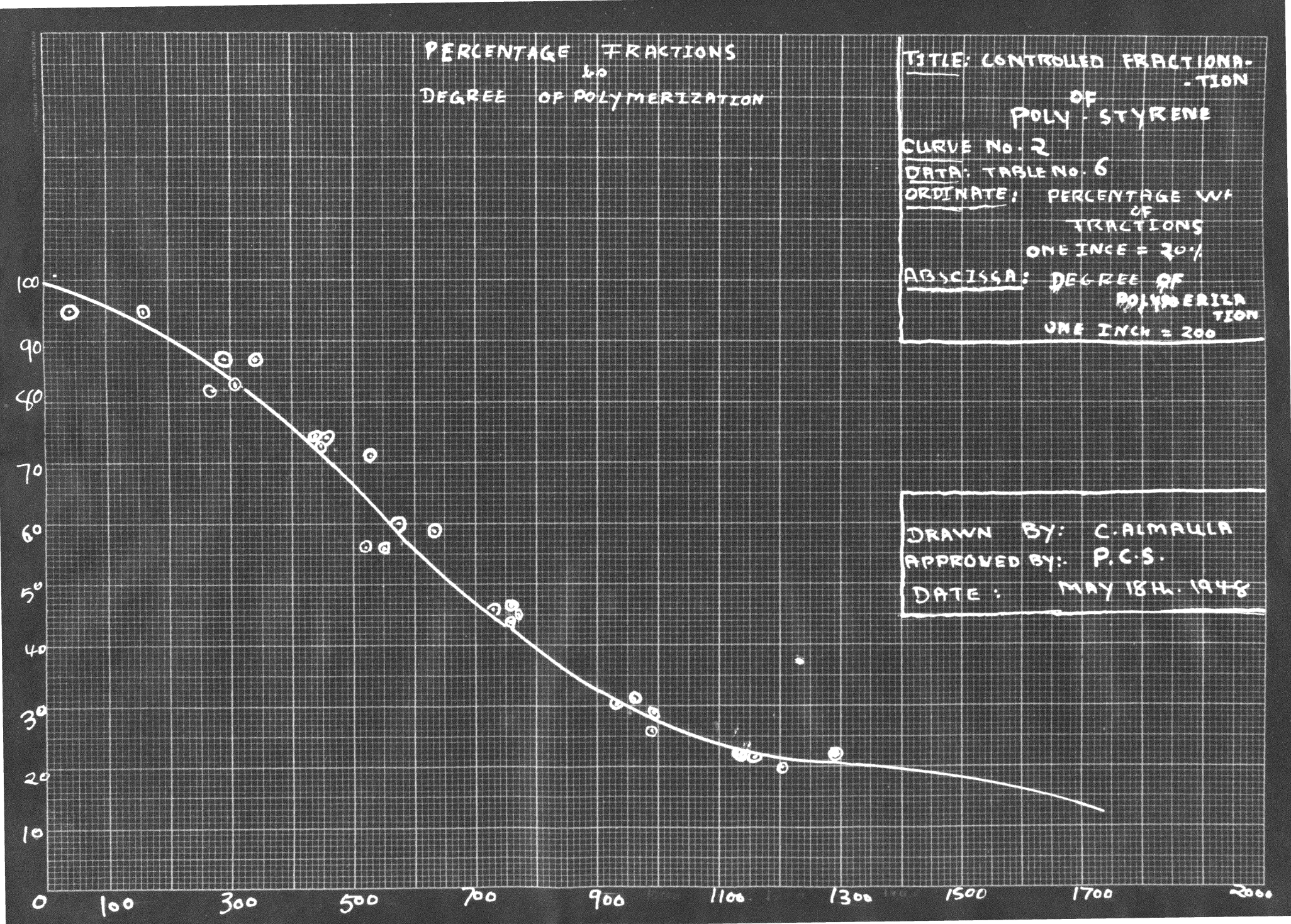
Table No. 8 Curve No.4

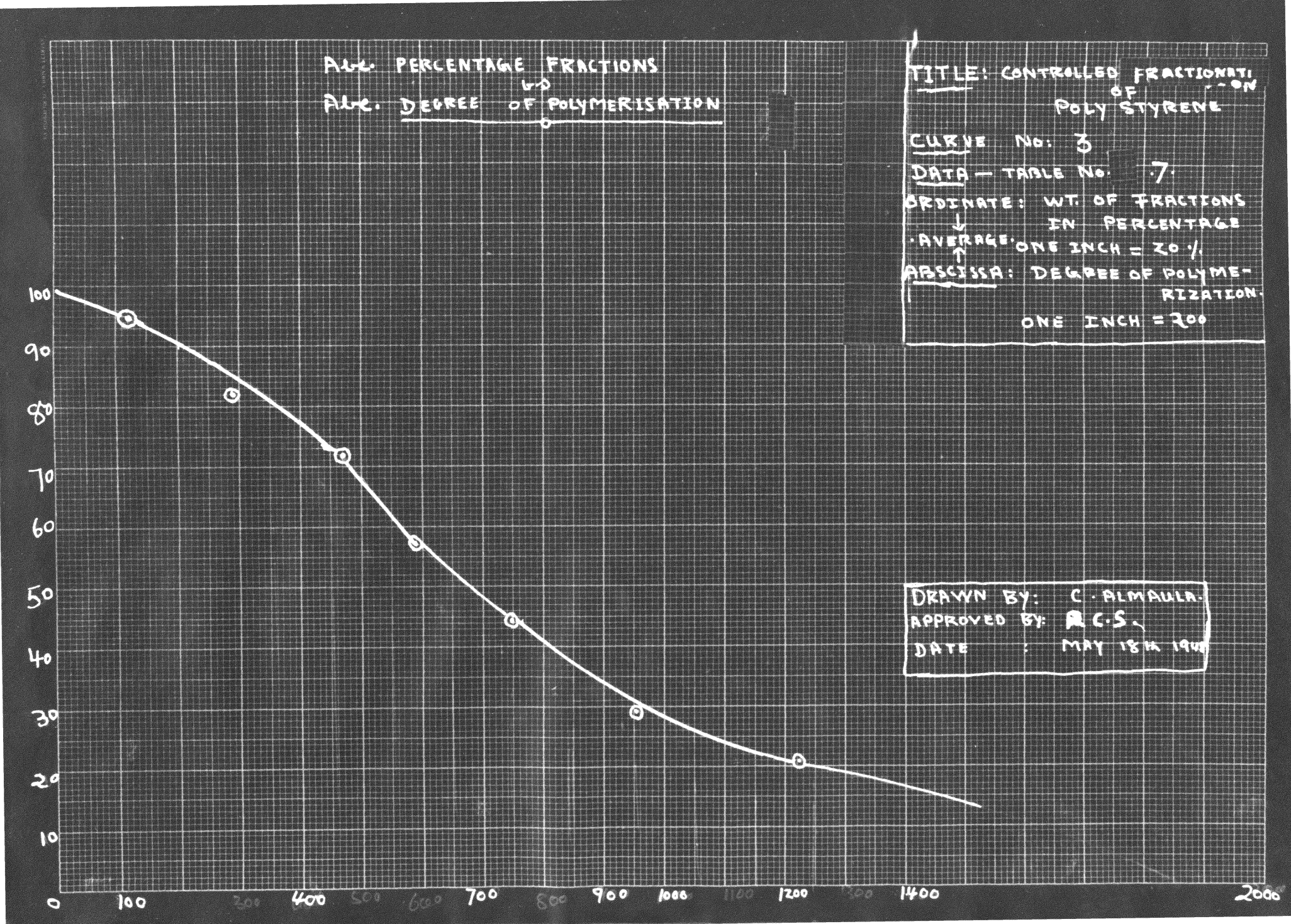
Distribution Curve

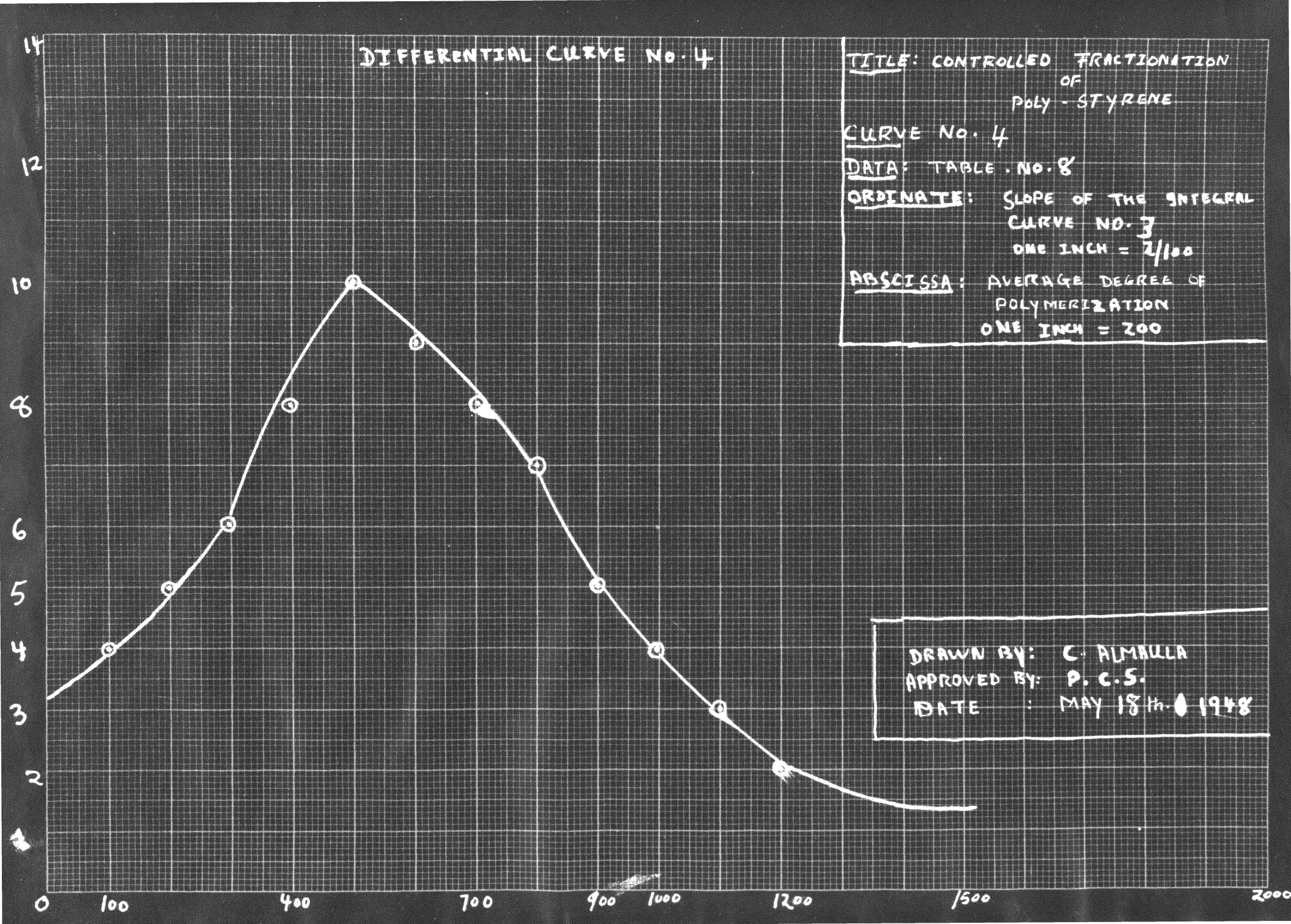
(Differentiation of the Curve 5.)

Degree of polymerization	Slope of the curve
100	4/100
200	5/100
300	6/100
400	6/100
500	7/100
600	8/100
700	10/100
800	9/100
900	8/100
1000	7/100
1100	5/100
1200	3/100
1300	2/100


PERCENTAGE FRACTIONS
to
RATIO OF NON-SOLVENT TO SOLUTION
TITLE: CONTROLLED FRACTIONATION OF POLYSTYRENE
CURVE NO: 1.
DATA. TABLE NO. 1
TEMP. OF PRECIPITATION = 25°C
ORDINATE: ONE INCH = 20% Wt. OF THE FRACTIONS
ABSCISSA: ONE INCH = 20 g. OF ACETONE / 100 g. OF SOLUTION
CONCENTRATION OF THE SOLUTION = 2.5%
100
90
80
70
60
50
40
30
20
10
0
·1
·3
·5
·55
·7
·9
1
1·1
1·3
1·5
1·6
1·8
2.
DRAWN BY: C. ALMAULA
APPROVED BY: P.C.S.
DATE: MAY 18th. 1948


PERCENTAGE FRACTIONS
vs
DEGREE OF POLYMERIZATION
TITLE: CONTROLLED FRACTIONA-
-TION
OF
POLY-STYRENE
CURVE No. 2
DATA: TABLE No. 6
ORDINATE: PERCENTAGE WT
OF
FRACTIONS
ONE INCH = 20%
ABSCISSA: DEGREE OF
POLYMERIZA
TION
ONE INCH = 200
DRAWN BY: C. ALMALLA
APPROVED BY: P.C.S.
DATE: MAY 18th. 1948
100
90
80
70
60
50
40
30
20
10
0
100
300
500
700
900
1100
1300
1500
1700
2000


Alt. PERCENTAGE FRACTIONS
to
Abs. DEGREE OF POLYMERISATION
TITLE: CONTROLLED FRACTIONATION OF POLY STYRENE
CURVE No: 3
DATA — TABLE No. 7.
ORDINATE: WT. OF FRACTIONS IN PERCENTAGE
AVERAGE
ONE INCH = 20 %
ABSCISSA: DEGREE OF POLYMERIZATION.
ONE INCH = 200
DRAWN BY: C. ALMAULA.
APPROVED BY: C.S.
DATE : MAY 18TH 1948
100
90
80
70
60
50
40
30
20
10
0
100
400
700
900
1000
1200
1400
2000


DIFFERENTIAL CURVE No. 4
TITLE: CONTROLLED FRACTIONATION OF Poly - STYRENE
CURVE No. 4
DATA: TABLE. No. 8
ORDINATE: SLOPE OF THE INTEGRAL CURVE NO. 3
ONE INCH = 1/100
ABSCISSA: AVERAGE DEGREE OF POLYMERIZATION
ONE INCH = 200
DRAWN BY: C. ALMALLA
APPROVED BY: P. C. S.
DATE: MAY 18th. 1948
14
12
10
8
6
5
4
3
2
0
100
400
700
900
1000
1200
1500
2000

DISCUSSION OF THE RESULTS

The quantitative results of the fraction are satisfactory taking into the account that the investigation was done on a synthetic heterogeneous polymer.

The distribution curve as well as the curve for the weights of the fractions in percentage vs. the ratio of the non-solvent to solution, (which is theoretically non-solvent to solvent ratio) reveals that there is a sharp break at about 57 - 60 %. This clearly shows that sixty per cent of the material consists of very high degree of polymerization and forty per cent of the material consists of low degree polymerization compared to the highest degree of polymerization of the first fraction. The slope of the curve on both sides is very constant and reveals that the rate of polymerization of the material increases constantly up to sixty per cent and then decreases constantly.

The fractionation of the material is very efficient under the proper conditions of the non-solvent - solvent system and thermal conditions. The ratio of the non-solvent to solvent is quite proportional to the molecular weight distribution of the material. It confirms that longer the chains of the repeating unit the binding power is very weak and polymer breaks down easily on the addition of proper non-polar groups. Of course, it is not empirical but perfectly within scientific control. The thermal condition as well as the ratio of polar to non-polar groups if carefully regulated breaks down the chains of the desired lengths.

Comparison of the results of the samples 1; 2; 3; and 4, in Table No. 1, show that fraction weights for a given amount of non-solvent agree within less than 2% range.

Conclusion:- The above renge of variation in the results is within limit of error since only one satisfactory integral or differential curve can be drawn through the points. Therefore, the author concludes that a controlled fractionation of polystyrene has been carried out which was the objective of the research.

CONCLUSIONS

1 Four samples of polystyrene dissolved in ethyl acetate (concentration 2.5 per cent) were fractioned by (i) Cooling (lowering temperature)
(ii) By addition of non-solvent (acetone)

2 Seven fractions were obtained; each one of it around ten per cent with the exception of the first one.

3 The temperature at addition of non-solvent was 25° C. and the temperature during precipitation was 15° C.

4 The results were checked by the viscosity measurements and relative degree of polymerization was obtained from Staudinger's equation.

(5) Agreement between four independent sets of fractionations was closed that it must be concluded that control of the fractionation within reasonable limits has been attained.

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