ABSTRACT

Title of Thesis: Characterization of TDI-HEMA Homopolymer Prepared via an Immiscible Solvent System. Synthesis and Investigation of Oligodichloroketene

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Thesis directed by: Dr. William H. Snyder, Profesor of Chemistry and
Dr. David S. Kristol, Profesor of Chemistry

The objective of this thesis has been divided in two parts.

The first part is subdivided into two areas. First a "Universal" calibration curve for gel permeation chromatography (GPC) was constructed using different molecular weight standards of PMMA and MMA-HEMA copolymers. By measuring the viscosity of the different molecular weight solutions and calculating the Vr, (retention volume), from GPC data, plots of ln $[\eta]$ Mw against Vr and ln Mw against Vr are obtained. These curves can be used to obtain the molecular weight of any linear (not crosslinked) copolymer by simple measurements of viscosity and GPC data.

The second subdivision is the characterization of the forward polymer of TDI-HEMA blocked by p-cresol prepared using the heterogeneous method. The molecular weight was obtained from Light Scattering, Vapor-Pressure Osmometry and viscosity-GPC data, using the "Universal" calibration curve obtained in the first part. Comparing the molecular weights thus obtained with the molecular weights calculated using the homogeneous preparation method shows that the amount of gel formation has been dramatically reduced.

The second part of this work relates to the characterization of the oligomeric material which resulted from the reaction of dichloroacetylcholride and $(C_2H_5)_3N$. The reason for characterizing the polymeric substance was the possibility that the resulting material would have the

structure $-\!\!-(\ CCl_2-CO\ )_n-\!\!-$, which may be hydrolyzed to obtain a polycarbonyl compound. This could be acomplished if the polymerization took effect through the carbon-carbon double bond.

CHARACTERIZATION OF TDI-HEMA HOMOPOLYMER PREPARED VIA AN IMMISCIBLE SOLVENT SYSTEM. SYNTHESIS AND INVESTIGATION OF OLIGODICHLOROKETENE

by
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DEDICATION

This work is dedicated to my parents, Ileana, and all my good friends who in the course of my life have encouraged and loved me in my most difficult moments. I specially like to mention the late professor William H. Snyder whose life work was the persuit of knowledge. Without his devotion to the research this work could not have been possible. I thank him for sharing his knowledge and inspiring my life in many ways.

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I wish to acknowledg my indebtedness to the late professor William H. Snyder for his invaluable guidance during the course of my thesis. I would also like to express my sincere appreciation and thanks to professor David S. Kristol for his invaluable assistance and freindship in finishing this work and preparing the final copy.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. COPOLYMERIZATION[1,2,3,4]

Polymeric substances containing two or more structural units combined more or less in random sequence are distinguished by the term copolymer. For example, a linear copolymer composed of two bifunctional units I and M, for example, may be represented as follows:

$$I - M - M - I - I - M - I - M - M - I \; .....$$

The structural units may occur in random sequence. There may be a preponderance of long sequences of like units or the two types may tend to alternate. In the polymerization of a mixture of two or more monomers the composition and hence the properties of the resulting copolymer are determined by the rate at which different monomers add to the growing chain.

Acrylic and methacrylic monomers are readily incorporated into copolymers with monomers of almost every type. Classical studies of copolymerization were largely concerned with the problems of determining the gross composition of the copolymers and establishing the relative reactivity of monomers. The monomers reactivity ratios r_1 and r_2 are the ratios of the rate constants for a given radical adding its own monomer to that for its adding to other monomers. Thus if $r_1 > 1$ it means that the radical $M_1\cdot$ prefers to add $M_1\cdot$; when $r_1 < 1$ means that it prefers to add $M_2\cdot$. The reactivity ratios are unaffected in most cases by the presence of solvents, chain transfer agents, inhibitors or the particular polymerization process; that is, bulk, emulsion, etc.

Alfrey and Pice[5] in 1947 proposed an empirical equation to relate the reactivity ratios of monomers in binary copolymerization to two fundamental parameters for a given monomer and its corresponding radical.

These parameters are Q, representing the resonance stabilization of monomer and corresponding radical, and e, the polarity of a given monomer and its corresponding radical. The relationship between Q and e parameters and the actual reactivity ratios is:

$$r_1 = \frac{K_{11}}{K_{12}} = \frac{Q_1}{Q_2} \exp [- e_1 (e_1 - e_2)] \qquad (1)$$

$$r_2 = \frac{K_{22}}{K_{21}} = \frac{Q_2}{Q_1} \exp [- e_2 (e_2 - e_1)] \qquad (2)$$

where the subscripts correspond to monomer 1 and 2.

Young[6] reported e and Q values for methylmethacrylate (MMA) as 0.4 and 0.74 and for 2-hydroxyethylmethacrylate (HEMA) as 0.2 and 0.8, respectively. Using these e and Q values and equations (1) and (2), r_1 (HEMA) and r_2 (MMA) can be calculated as 1.12 and 0.85 respectively.

II. CHARACTERISTICS AND USE OF BLOCKED ISOCYANATE MONOMERS AND POLYMERS.[26,27]

Blocked isocyanates and their polymers are being used to develop adhesives for bonding to biomaterials such as dentin for restoration work. The characterization of these materials is of great importance since the processing of the set adhesives depends to a great extent on such factors as molecular weight distribution and branching in the initial polymers.

The crown and root are the basic parts of the human tooth. The root contains a coating called cementum, while the crown is covered by a thin coating of enamel. Beneath the enamel surface and extending to the pulp is the composite dentin which contains 60% hydroxyapatite, 20% organic matter and 20% water by weight. The organic matter is mainly collagen which is a fibrous protein that contains free hydroxyl and amino groups on the side chains of the amino acids. These two functional groups in dentin may react with isocyanate functions in these novel adhesives producing covalent chemical bonds with dentin. Presently used adhesives rely on physical bonds with the dentin and enamel rendering; them less than ideal for use as permanent restorative materials. The reactions of isocyanate with side chain groups are as follows:

$$R - NCO + HO - \text{collagen} \longrightarrow R - NH - COO - \text{collagen}$$

$$R - NCO + H_2N - \text{collagen} \longrightarrow R - NH - CO - HN - \text{collagen}$$

There are some limitations in using functional monomers to produce adhesive polymers, since water reacts with isocyanete groups. The reaction of water with NCO results in the formation of an amino group formed with the loss of CO_2. This amino group can again react with another NCO on the polymer adhesive, forming a new intrapolymeric bond as shown below:

$$R - NCO + H_2O \longrightarrow R - NH_2 + CO_2$$

$$R - NH_2 + R - NCO \longrightarrow R - NH - CO - HN - R$$

As it can be seen from the above reactions, one water molecule can destroy two NCO groups that were available for reaction with a protein amino group. Since the water concentration on the dentin surface will be fairly high compared to the surface concentration of protein amino groups, many NCO groups will probably be destroyed before they get to the protein. A procedure that will prevent the reaction of isocyanate with water and at the same time will favor the reaction of the isocyanate with the amino groups in the protein will be especially useful in obtaining a successful chemical bonding of the adhesive with dentin.

To prevent the destructive effect of water, the isocyanate monomer is reacted with a blocking agent R'- OH. This blocked monomer will be applied to the tooth and then polymerized expecting that the affinity of the NCO in the blocked monomer for the amino groups in the protein will be greater than for the blocking agent, that is, the amino groups in the collagen will displace the blocking agent, R'- OH,

$$\text{adhesive} - R - NH - COO - R' + H_2N - \text{collagen} \longrightarrow$$

$$\text{adhesive} - R - NH - CO - HN - \text{collagen} + R' - OH$$

The success of such an approach depends on the proper choice of (a) organic isocyanate and (b) blocking agent, R'- OH, in the course of the monomer synthesis, and (c) on the formulation of a suitable polymeric matrix to bond with these blocked isocyanate monomers.

III. MOLECULAR WEIGHT AND ITS DISTRIBUTION.[2,7]

The existence of a distribution of molecular weights in essentially all synthetic polymers and many naturally occurring ones, results from the presence of a statistical element in all known synthetic polymerization precesses. Since a distribution of molecular weights exists in any finite sample of polymer, the experimental measurement of molecular weight can give only an average-value.

Just as several of polymer chain dimension parameters, such as end-to-end distance, radius of gyration, etc, are of interest so are several types of average molecular weights. The most important and common of these average molecular weights are the number average $\bar{M}n$, the weight average $\bar{M}w$, and the viscosity average $\bar{M}v$, the relative values of which are indicated in figure 1.

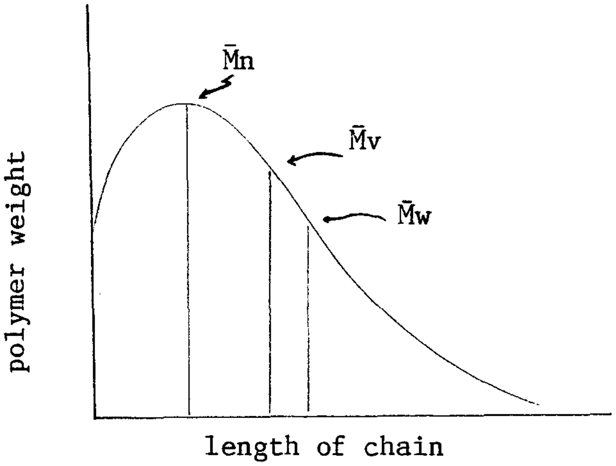


Fig. 1. The various average molecular weights located on the distribution curve for a high polymer.

1. NUMBER AVERAGE MOLECULAR WEIGHT[2,7]

The type of average molecular weight called the number average molecular weight is the simple counting average in which the mass of the sample, expressed in atomic mass units or daltons, is divided by the number of molecules it contains.

If the sample contains N_i molecules of the ith kind for a total of molecules $\sum N_i$, and each of the ith kind of molecules has a mass w_i, then the total mass of all the molecules is $\sum N_i w_i$. The average molecular mass is

$$m_n = \frac{\sum N_i w_i}{\sum N_i} \qquad (3)$$

and multiplication by Avogadro's number gives the number average molecular weight

$$\overline{M}n = \frac{\sum M_i N_i}{\sum N_i} \qquad (4)$$

Number average molecular weights of commercial polymers usually lie in the range of 10,000 - 100,000, although some materials have values of Mn as much as tenfold higher, and others tenfold lower.

Methods for determination of the number average molecular weight fall into two categories, chemical or physical methods based on end-group analysis, and those based on measurement of one of the colligative properties; vapor-pressure lowering, freezing-point depression, boiling point elevation, and osmotic pressure.

2. WEIGHT AVERAGE MOLECULAR WEIGHT[1,7]

After $\bar{M}n$, the weight average molecular weight $\bar{M}w$ is the next higher average molecular weight which can be measured by absolute methods. This quantity is defined as

$$\bar{M}w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{5}$$

since mass $w_i = N_i M_i$ and weight fraction $c_i = w_i / w$ the equation for $\bar{M}w$ can be written as

$$\bar{M}w = \frac{\sum w_i M_i}{W} = \sum c_i M_i \tag{6}$$

where

$$W = \sum w_i \tag{7}$$

Because heavier molecules contribute more to Mw than light ones, Mw is always greater than $\bar{M}n$ except for a hypothetical monodisperse polymer. The value of $\bar{M}n$ is greatly influenced by molecules at the low end of the molecular weight distribution curve, just as $\bar{M}w$ is influenced by the presence of high molecular weight species. The quantity $\bar{M}w$ / $\bar{M}n$ is a measure of the breadth of the molecular weight distribution curve.

The weight average molecular weight can be determined by light scattering, gel permeation chromatography (which also can be used to obtain $\bar{M}n$), and equilibrium ultracentrifugation experiments. The latter method is seldom used for coil synthetic polymers.

3. VICOSITY AVERAGE MOLECULAR WEIGHT.[3,7,8]

Intrinsic viscosity measurement leads to the viscosity average molecular weight, defined by the equation,

$$\bar{M}v = \left[\sum c_i M_i^a \right]^{1/a} = \left\{ \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right\}^{1/a} \qquad (8)$$

Thus $\bar{M}v$ depends on 'a' as well as on the distribution of molecular species. For many polymers, $\bar{M}v$ is 10 - 20 % below $\bar{M}w$. For a = 1 $\bar{M}v = \bar{M}w$.

IV. INTRINSIC VISCOSITIES IN RELATION TO MOLECULAR WEIGHTS OF HIGH POLYMERS.[1,2,7,11,12,13,14]

In 1930, Staudinger[9,10] called attention to the utility of viscosity measurements on dilute polymers solutions as a means of characterization. High polymers molecules possess the capacity to greatly increase the viscosity of the liquid in which they are dissolved, even when present at concentrations which are quite low. For a given series of linear polymers homologs, the higher the molecular weight the greater the increase in viscosity produced by a given weight concentration of polymer. The intrinsic viscosity may be regarded as a measure of the ratio of the effective hydrodynamic volume, Ve, of the polymer in a given solvent to its molecular weight M. In other words, the intrincsic viscosity, which represents the capacity to enhance the viscosity, increases with M; therefore, viscosity measurements afford a measure of molecular weight. However, an absolute value for the molecular weight of a polymer cannot be derived from solution viscosity measurements. The dependence of the intrinsic viscosity on molecular weight must be established more or less empirically in each individual case by comparison with molecular weights determined by one of the absolute methods; that is, vapor phase osmometry, membrane osmometry, light scattering, or G.P.C.

The viscosity of diluted polymer solutions is conveniently measured in simple capillary viscometers of the Ostwald-Fenske, or Ubbelohde types, through which the time required for a fixed volume of liquid to flow is measured. If the solution and solvent have the same density, and neglecting possible effects of shear rate, the flow times of these liquids are proportional to their viscosities. From t_o , the flow time of the solvent, t, the flow time of the polymer solution and the solute concentration, are derived several quantities whose definning equations and names are as follows,

(a) Relative viscosity (the viscosity of the solution divided by the viscosity of the solvent.)

$$\eta_r = \eta / \eta_o = t / t_o \tag{9}$$

(b) Specific viscosity (expresses the incremental viscosity attributable to the polymeric solute.)

$$\eta_{sp} = \eta_r - 1 = (\eta - \eta_o) / \eta_o = (t - t_o) / t_o \tag{10}$$

(c) Reduced viscosity (measure of the specific capacity of the polymer to increase the relative viscosity.)

$$\eta_{red} = \eta_{sp} / c \tag{11}$$

(d) Inherent viscosity

$$\eta_{inh} = (\ln \eta_r) / c \tag{12}$$

(e) Intrinsic viscosity (the limiting value of (d) and (c).)

$$[\eta] = (\eta_{sp} / c)_{c \to 0} = [(\ln \eta_r / c)]_{c \to 0} \tag{13}$$

The intrinsic viscosity $[\eta]$ is independent of concentration by virtue of extrapolation to c = 0, but is a function of the solvent used.

The advantage of using a Ubbelohde type viscometer to obtain the viscosity of dilute polymer solutions is that the measurement is independent of the amount of solution in the viscometer and thus, measurements at a series of concentrations can easily be made by successive dilution. For highest precision, the following precautions are usually observed: the viscosity measurements are made in a constant temperature bath regulated to at least $\pm$ 0.02 ^{o}C, and the efflux time is kept long enough (preferably greater than 100 sec.) to minimize the need for applying kinetic energy corrections to the observed data. For accuracy extrapolating to $c = 0$, the solution concentration is restricted to the range that gives relative viscosities between 1.1 and 1.6 .

Viscosity data, as a function of concentration, are extrapolated to infinite dilution. The procedure for doing this is relatively simple. Plots of η_{sp} versus c usually are very nearly linear for $\eta < 2$, and it has been pointed out[3] that the slopes of these plots for a given polymer-solvent system vary approximately as the square of the intrinsic viscosity. Thus the equation proposed by Huggins is:

$$\eta_{sp} / c = [\eta] + k' [\eta]^2 c \tag{14}$$

where k' is approximately constant for a series of polymers homologs in a given solvent. In a similar way plot of $\ln \eta_r / c$ against c leads to the Kraemer (1930) equation,

$$\ln \eta_r / c = [\eta] + k'' [\eta]^2 c \tag{15}$$

where $k'' = k' - 0.5$. Generally, k" is negative and smaller in magnitude than k'; hence $(\ln \eta_r) / c$ changes less rapidly with concentration than does η_{sp} / c . For this reason extrapolation of $(\ln \eta_r) / c$ is somewhat preferred over extrapolaion of η_{sp} / c . Typical values for k' in good solvent for the polymers are 0.4 ± 0.1 .

When the logarithms of the intrinsic viscosities of a series of fractionated linear polymer homologs are plotted against the logarithms of their molecular weights, relationships which are linear wihin experimental error are obtained. The indicated linear relationships may be expressed by the simple empirical Mark-Houwink equation:

$$[\ \eta\ ] = K'\ Mv^a \qquad (16)$$

where K' and a are constants determined respectively, by the intercept and the slope. For many systems, the value of a lies between 0.6 and 0.8 Typical values of K' ranges between 0.5 and 5 x 10^{-4}. Both K' and a are functions of solvent as well of polymer type. This empirical relation between viscosity and molecular weight is valid only for linear polymers

Intrinsic viscosity measurements leads to viscosity average molecular weight, defined by,

$$\bar{M}v = \left[\sum c_i M_i^a \right]^{1/a} = \left\{ \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right\}^{1/a} \qquad (17)$$

Since $\bar{M}v$ is not usually available (except for hypothetical monodisperse polymers for which all average are equal), and because $\bar{M}v$ is more nearly equal to $\bar{M}w$ than other average molecular weights, it is common to replace $\bar{M}w$ for $\bar{M}v$ in equation (16) ,

$$[\ \eta\ ] = K'\ \bar{M}w^a \qquad (18)$$

V. GEL PERMEATION CHROMATOGRAPHY[2,3,7,15,16,17]

Gel permeation chromatography (GPC) is an important technique for the rapid characterization of the molecular weight and molecular weight distribution of polymers. The term was coined by John C. Moore in 1964 to describe a separation technique similar to, but improved over, the method long known in the biological field as gel filtration.

Polymer molecules are separated by size because of their ability to penetrate part of the internal volume of gel particles, that is, the stationary phase. The pores in these gels are of the same size as the dimentions of polymer molecules. The liquid phase (mobile phase) contains solvent and dissolved polymer. The smaller molecules will penetrate the internal volumes of the gel particles more easily than the larger ones so that the motion of low molecules will be impeded more in the moving liquid phase. The net result is that the high molecular weight molecules will elute first.

It has been found empirically that smooth curves may be obtained by plotting the logarithms of molecular weight versus retention volumes and that columns packed with carefully selected pore sizes give linear plots of these quantities. This method does not yield a universal calibration curve for all the samples. Retention times for branched samples are always larger than those for the linear homologs of the same molecular weight. Exact treatment requires that the calibration be made directly in terms of hydrodynamic volume.

According to the Einstein's viscosity law one can write,

$$[\eta] = K (V / M) \tag{19}$$

where $[\eta]$ is the limiting viscosity index (intrinsic viscosity),

V, the hydrodynamic volume of the particles, M, their molecular weight, and K, a constant. This equation shows that the product [η] M is a direct measure of the hydrodynamic volume of the particles and suggests the use of log [η] M instead of log M in the calibration of the chromatograms. It is interesting to note that the universal calibration curve (log [η] M) versus Vr (retention volume) takes into account interactions of all types - those between polymer and solvent, and in the case of copolymers the heterocontact interactions - which are included in [η] . For linear polymers, interpretation in terms of molecular weight is straight forward: if the Mark-Houwink constants K' and a are known, for example, log [η] M can be written log M^{1+a} + log K' and Vr can be directly related to M . The basic molecular equation is:

$$M = \frac{\sum N_i M_i^b}{\sum N_i M_i^{b-1}} \tag{20}$$

where b = 1 for $\bar{M}n$ and b = 2 for $\bar{M}w$. If we assume N_i (number of i molecules) is proportional to the curve height above the base line in millivolts and M_i is equivalent to the value which can be obtained from the calibration curve at a given retention volume, then we estimate $\bar{M}w$ and $\bar{M}n$ by a straight forward graphical analysis. The ratio of $\bar{M}w$ / $\bar{M}n$ is a measure of the polydispersity of the system.

VI. LIGHT SCATTERING. DETERMINATION OF MOLECULAR WEIGHT AND POLYMER DIMENTIONS.[1,2,3,7,18,19,20,21,22,23]

Scattering of light occurs whenever a beam of light encounters matter. The intensity of scattered light depends on the polarizability of the particles (or molecules) compared with that of the medium in which they are suspended. It depends also on the size of the particles and on their concentration. The intensity of the scatterd light is equal to the sum of the contributions from the individual particles; each being unaffected by the other if the solution is sufficiently dilute.

In polymer solutions, light scattering can be used to measure $\bar{M}w$ since the amplitude of the scattering is proportional to the mass of the scattering particle, but it is the intensity, the squared of the amplitude, which is measured.

The working equation for determination of the weight average molecular weight, second virial coefficient, and radius of gyration by light scattering, according to Debye is:

$$Kc / R_\theta = (1 / Mw) \left[1 + (16 \pi^2 / 3 \lambda^2) S_z^2 \sin^2 (\theta / 2) \right] + 2 A_2 c \qquad (21)$$

where the constant K is given by:

$$K = 2 \pi^2 n^2 (dn / dc)^2 / No \lambda^4$$

c concentration of polymer solution (g/ml).

R_θ reduced intensity at angle θ, where $R_{\theta,u}$ is the reduced intensity of the unpolarized incident light at angle θ.

n refractive index of solvent.

λ	wavelenght of the incident radiation.
No	Avogadro's number.
$\bar{S}_z^2$	mean square radius of gyration.
$\bar{M}w$	weight average molecular weight.
A_2	second virial coefficient (ml-mole / g^2)
dn / dc	specific refractive index increment which is the concentration dependence of the refractive index of the polymer solution.
$R_{\theta,u}$	Rayleigh ratio which can be calculated, for the Brice-Phonix Universal Light Scattering Photometer. Series 2000, from the observed scattering ratio G_θ / G_W, by means of the following equation:

$$R_{\theta,u} = \frac{T\,D\,a\,n^2\ (R_W / R_c)}{1.049\ h}\ (r / r')\ \left\{\frac{\sin\theta}{1+\cos^2\theta}\right\}$$

$$\left\{\frac{1}{(1-R^2)(1-4R^2)}\right\}$$

$$\Big\{ \left[(G_\theta / G_W * F)_{solution} - (G_\theta / G_W * F)_{solvent} \right]$$

$$- 2R \left[(G_{180-\theta} / G_W * F)_{solution} \right.$$

$$\left. - (G_{180-\theta} / G_W * F)_{solvent} \right] \Big\}$$

$T\ D$	the experimentally determined product of the diffuse transmittance of opal glass reference standard and correction factor which mark the reference opal glass transmitting diffusor equivalent to a perfect reflecting diffusor.
G_{θ} / G_W	scattering ratio, or average observed ratio of the galvanometer deflection for the light scattered from the solution at 90° (no neutral filters in primary beam) to that for the transmitted light at 0° position with the working standard plus neutral filter or filters.
a	constant relating the working standard to the opal glass reference standard.
h	width of the diaphragm, or the edge of the sample table, which determines the depth of scattering solution viewed.
n	refractive index of solvent.
1.049	overall correction factor for surface reflections from the scattering cell and for back reflection by the standard opal glass.
R_W / R_c	experimentally determined correction factor for incomplete compensation for reflection effects.
r / r'	is a calibration factor relating the narrow beam geometry to the standard beam geometry in order to account for the angular dissymetry measurement when using a cylindrical cell. This is done by determining the scattering ratio of $G_s / G_W F$ of the square cell to the cylindrical cell by taking readings at 90° and 0°.
F	product of transmittance of the neutral filters.

The graphical method developed by Zimm is the must common method to calculate the molecular parameters. In this method, the left hand side of equation (21) is plotted against $\sin^2(\theta / 2) + k\,c$, where k is an arbitrary constant. The intercept on the $K\,c / R_{\theta,u}$ axis in a Zimm plot is proportional to the reciprocal of the molecular weight. The second viral coefficient, A_2, is calculated from the slope of $K\,c / R_{\theta,u}$ versus c of the lines at constant angle by equation (21) and to a first approximation is independent of angle. Similarly the radius of gyration, $\bar{S}_z^2$, is derived from the slope of the zero concentration line (on the $K\,c / R_{\theta,u}$ versus $\sin^2(\theta / 2)$ plot) as a function of angle. $\bar{M}w$ is obtained from $\theta = 0$ and $c = 0$ lines as:

$$\bar{M}w = \frac{1}{K\,(c / R_{\theta,u})_{c = 0,\ \theta = 0}} \tag{23}$$

A_2 is obtained from the equation:

$$A_2 = 0.5\,K\left[(c / R_{\theta,u})_{c_2} - (c / R_{\theta,u})_{c_1}\right] / (c_1 - c_2) \tag{24}$$

where it is the slope of the $\theta = 0$ line.

$\bar{S}_z^2$ is obtained from the equation:

$$S_z^2 = \frac{3\,\lambda^2}{16\,\pi^2} * \frac{\text{slope}}{\text{intercept}} \tag{25}$$

where it is the slope of the $c = 0$ line.

The light scattering method is applicable to polymers of almost any molecular weight from a few thousand into the millions which are soluble in a solvent for which dn/dc is not too small. Several restrictions on the applicability of this method to copolymer systems should be mentioned: the measurements should be made in a solvent for the highest possible value of dn/dc if correct values of $\bar{M}w$ are to be obtained. Use of the complete theory for binary copolymers is complex, but yields parameters describing the distribution of compositions, (for example, which monomer may be concentrated in the high or low molecular weight fractions) as well as correct values of $\bar{M}w$. The major limitations of the light scattering method is that the solution should be free from all extraneous scattering materials.

VII. VAPOR - PRESSURE OSMOMETRY: Mn DETERMINATION.[2,3,18,24]

In recent years vapor-phase osmonetry (VPO) has became popular, and is now the method of choice for measuring $\bar{M}n$ of a sample too low in molecular weight to be measured by membrane osmometry. In (VPO), the property measured is the small temperature difference resulting from rates of solvent evaporation from droplets of pure solvent and polymer solution maintained in an atmosphere of solvent vapor. An important assumption of this method is that the temperature difference is proportional to the vapor-pressure lowering of the polymer solution at equilibrium and thus to the number average molecular weight. The basic equation used is:

$$\frac{\Delta V}{c} = \frac{K}{\bar{M}n} + K A_2 c \tag{26}$$

where ΔV is the volatage difference (which is of course directly related to ΔT), K is the instrument constant for a particular solvent and temperature; it is determined by measuring ΔV for a series of different solute concentrations of known solute molecular weight, A_2 is the second virial coefficient, and c the concentration of polymer in solution in g/l.

VIII. KETENES THEIR DERIVATIVES AND POLYMERS.[28,29,30,31,32]

Ketenes constitute a class of compounds with the general formula R'R"C = 0 . In 1905 Staudinger synthesized the first ketene by treatment of diphenychloroacetylchloride with zinc.

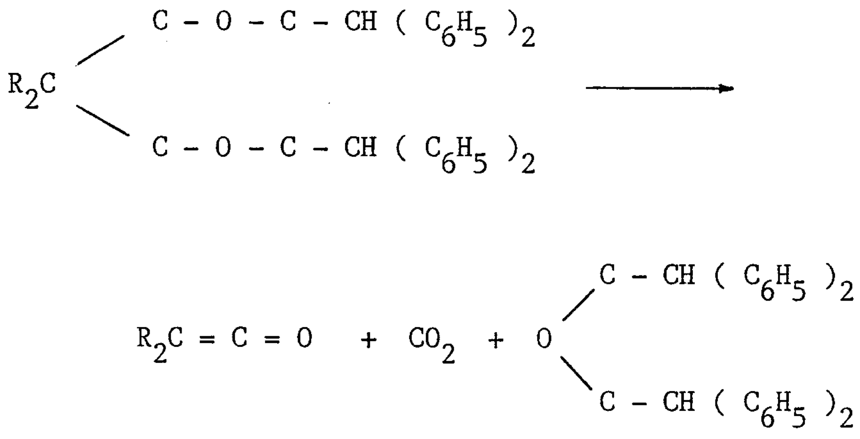
$$(C_6H_5)_2 \ CCl_2 \ C = 0 \ + \ Zn \qquad\qquad (C_6H_5)_2 \ C = C = 0 \ + \ ZnCl_2$$

At first there was some difficulty with the preparation of the pure colored orange diphenylketene, because its sensitivity to oxygen and moisture was not sufficiently known. During vaccum distillation moisture from the water aspirator pump entered the distillation apparatus; so that the diphenylketene obtained was permanently contaminated with diphenylacetic acid and/or with the anhydride of the latter, diphenylacetic anhydride. This problem was eliminated by placing a drying tube with sulfuric acid between the aspirator pump and the distillation apparatus.

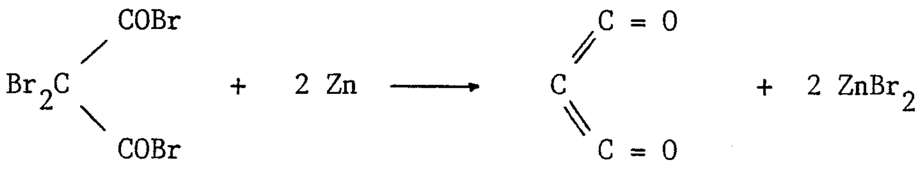
Klever[28] prepared dimethylketene from α - bromodimethylacetyl bromide in Strassburg in 1906 . In contact with air this compound instantaneously forms an explosive peroxide and undergoes fast dimerization. Ruzicka[28] in Karlsruhe worked with phenylmethylketene, which has properties intermediate between the two above mentioned ketenes.

The simplest member of the ketene class, ketene itself, $CH_2 = C = 0$ was obtained by Wilsmore in 1907 using an electrically heated platinum wire to decompose acetic anhydride.

Ott[28] found a new method for the preparation of ketenes: the thermal decomposition of disubstituted malonic anhydrides.



This method was frequently used for the synthesis of unstable ketenes. One of the most interesting ketenes, corbon soboxide, was obtained by Diels[28] soon after the discovery of ketenes, when he treated malonic acid with phosphorous pentoxide. Later Staudinger[28] and co-workers were able to prepare the same product from dibromomalonyl bromide.



Futher research on ketenes and phosphorous compounds made it possible to obtain ketene imine derivatives by a new procedure.

$$(C_6H_5)_2 C = C = O + (C_6H_5)_3 P = N - C_6H_5 \longrightarrow$$

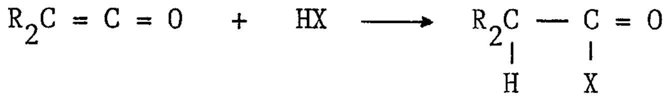
$$(C_6H_5)_2 C = C = N - C_6H_5 + (C_6H_5)_3 P = O$$

Thioketenes, on the contrary, could be obtained from phosphine sulfides only in their polymeric state.

$$x\,(C_6H_5)_2\,C=C=O \;+\; x\,(C_6H_5)_3\,P=S \longrightarrow$$

$$[\,(C_6H_5)_2\,C=C=S\,]_x \;+\; x\,(C_6H_5)_3\,P=O$$

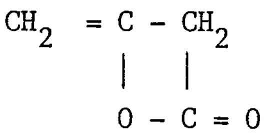
The high reactivity of the ketenes is of special interest. They all are easily converted to acids and acid derivatives by reacting them with water, alcohols, and amines.



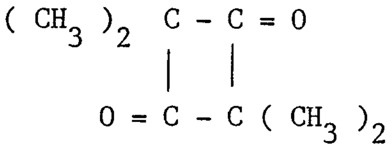
$$R_2C=C=O \;+\; HX \longrightarrow \underset{H}{R_2C}-\underset{X}{C}=O$$

As a result of the reactions of ketenes a whole group of new compounds- mainly four-member rings- such as β-lactones, β-lactams, etc. became available.

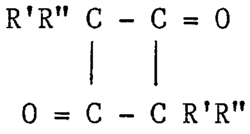
The polymerization of ketenes can proceed in different ways. In general, ketenes undergo a spontaneous dimerization at room temperature; the simple ketene yield vinylaceto- β -lactone



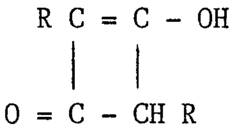
which is used in the preparation of acetic acid derivatives by splitting it to acetylketene. From dimethylketene, tetramethyldiketocyclobutane is formed:



The products of spontaneous dimerization have the structure of cyclobutanedione

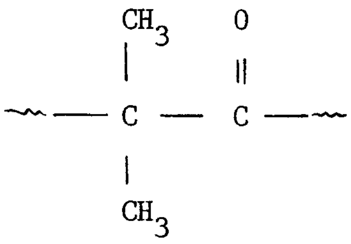


or cyclobutenolone

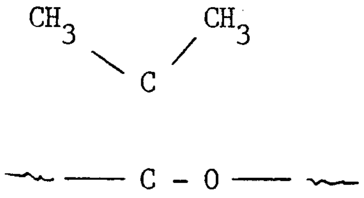


In contrast, in the presence of catalyst the reaction leads to β -lactonic dimers.

Before 1959, only one high-molecular weight polymer had been described namely amorphous polydimethylketene, obtained from the two monomeric units (I) and (II) by irregular placement. It can be obtained by opening of the C = C or C = 0 double bond, respectively.



(I)



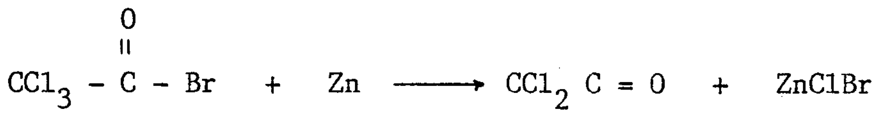
(II)

Chain growth is influenced by several factors, such as the nature of the monomer and of the catalyst system and the polarity of the reaction medium. The presence of impurities can deeply modify low-temperature polymerizations.

Due to the formation of cyclobutane derivatives and many heterocyclic four-member rings from the addition of ketenes to unsaturated componds, halogenated ketenes have been of great interest in these cycloaddition reactions.

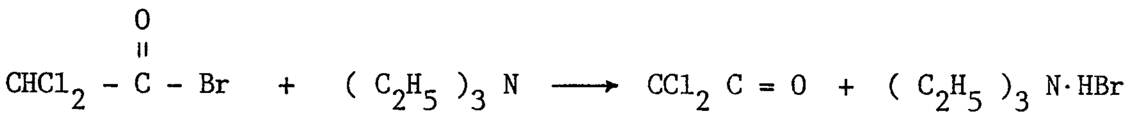
Yarovenko[28] prepared difluoroketene. It reportedly distills with ether. This material behaves like ketene and is practically impossible to separate from ether. Staudinger in 1913 attempted the synthesis of dichloroketene by thermal decomposition of the anhydride of dichloromalonic acid and diphenylketene. However, dichloroketene could not be detected and it was concluded that this material was possibly produced but quickly polymerized under the reaction conditions.

In 1965, W.T. Brady and co-workers investigated two routes to the sysnthesis of dichloroketene. The first, which involves the dehalogenation of trichloroacetylbromide with zinc activated with copper, was found to be very succesful.



$$\mathrm{CCl_3 - \overset{\overset{O}{\|}}{C} - Br \;+\; Zn \longrightarrow CCl_2\,C = O \;+\; ZnClBr}$$

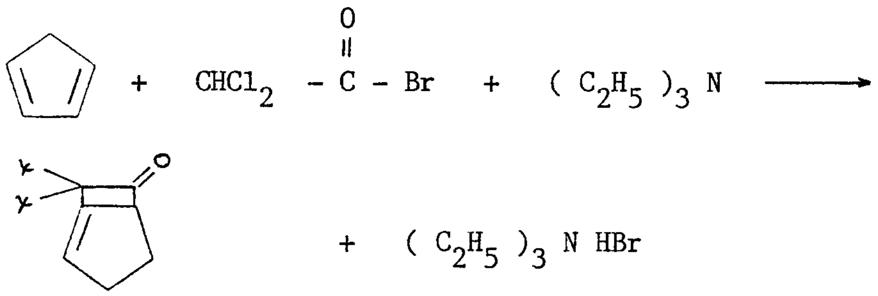
The second approach that they took was the dehydrohalogenation of acid halides with tertiary amines.



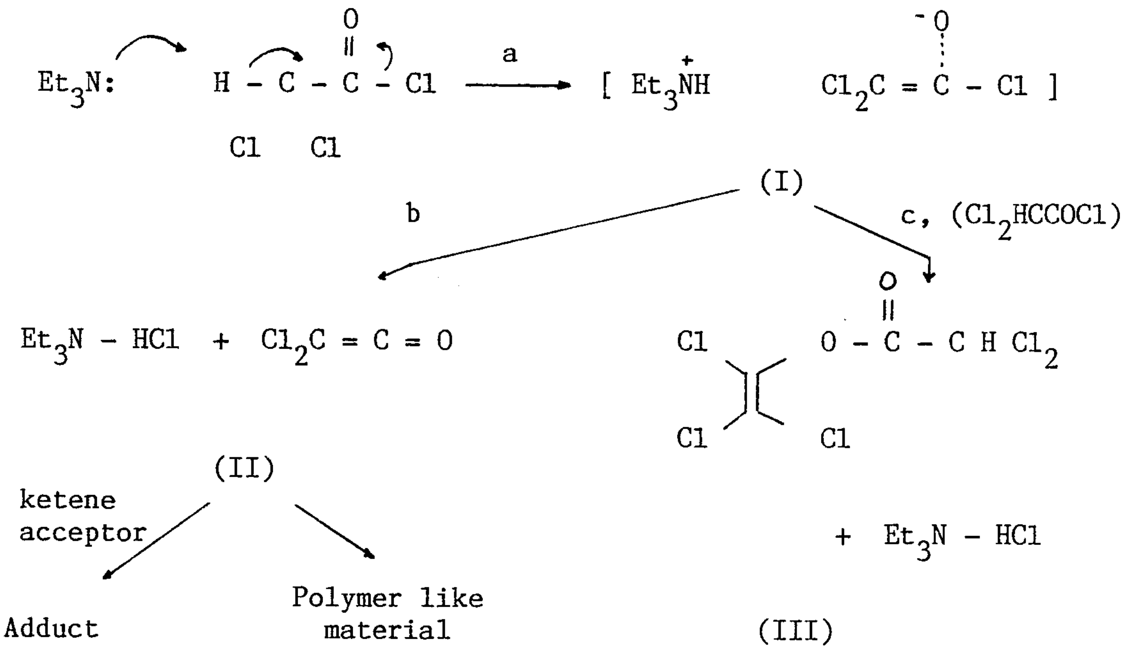
$$\mathrm{CHCl_2 - \overset{\overset{O}{\|}}{C} - Br \;+\; (\,C_2H_5\,)_3\,N \longrightarrow CCl_2\,C = O \;+\; (\,C_2H_5\,)_3\,N\cdot HBr}$$

That the dehydrobromination occured was evidenced by the consumption of the acid halide and formation of triethylammonium bromide. However, only a small amount of dichloroketene was obtained because, although it was produced most of it polymerized in the presence of the amine salt, because tertiary amine salts are known to catalyze the polymerization of some ketenes.

The formation of dichloroketene by the above process was demonstrated by conducting the dehydrohalogenation at a low temperature in the presence of a reactive olefin, cyclopentadiene. This resulted in the formation of the cycloaddition product, 7,7-dichlorobicyclo [3,2,0] hept -2 en-one.



In 1968, Lavannish conducted futher studies on the reaction of acid chlorides and triethylamine in order to identify the products and to propose a general mechanism for their formation.



He concluded that the generation of dichloroketene from dichloroacetyl chloride and triethylamine must involve proton abstraction to yield the enolate complex I (path a). Transfer of chlorine (path b), forming triethylamine hydrochloride, would give II, which in the presence of a suitable acceptor would give an adduct or in the absence of an acceptor would produce a polymeric material. However, if the concentration of dichloroacetyl chloride is sufficiently high, trapping of I prior to chlorine transfer become competitive and significant amounts of III are obtained (path c).

IX. RESULTS AND DISCUSSION.

In the characterization of TDI-HEMA polymer blocked by p-cresol (prepared by heterogeneous method), a sequence of experimental techniques was used to examine and characterize HEMA polymers in general. These techniques were tested with the TDI-HEMA polymer and the techniques were double checked by using other experimental methods.

A series of PMMA polymers and MMA-HEMA copolymers of standard (monodisperse) molecular weights were used to find a and K, constants for the Mark-Houwinck equation (16). The viscosities of these samples were measured in THF at 25 ^{o}C and from these data the intrinsic viscosities, $[\eta]$, were obtained by extrapolation of the data, (ln η /c and/or η_{inh}/c). to zero concentration. The viscosity data is shown in tables (1)-(3). Figures (1)-(9) give the family of lines obtained in these extrapolations, for the series of polymer and copolymer samples which differ only in molecular weight. The curves have slopes which are not constant, but vary in a regular pattern, increasing as $[\eta]$ increases. The values of $[\eta]$ were obtained from a statistical treatment of the data. This family of lines is described by no theory, but by several sets of purely empirical equations, such as, the Huggins equation (14) and Kraemer equation (15). The constants K' and K" are Known as the Huggins and Kreamer's constants, respectively, and table (4) gives a summary of these constants together with $[\eta]$ for their respective polymers or copolymers. The magnitude of K" reflects the change of the inherent viscosity as compared to the reduced viscosity as a function of concentration. Although many attempts have been made to relate these values of K' and K" to polymer properties because there is no theoretical basis, these attempts have proven of little value. The values of K' and K" are used to obtain concentrations of a given polymer so that its viscosity lies in the range where its solution behaves ideally.(4)

Since the molecular weights of the samples were known from the supplier and the viscosities were measured, the a and K constants could be calculated from the equation $[\eta] = K M^a$ in its linear form by a statistical analysis of the data. The values of a and K are given in table (5) for the different samples.

In order to prepare a "Universal" calibration curve for GPC, PMMA polymers and MMA-HEMA copolymers were prepared in the lab (polydisperse samples) having approximately the same average molecular weights and com positions as the one obtained for standard measurements. GPC curves were obtained for the polydisperse samples. From these curves several molecular weights, M_i , were selected on the basis of their retention volumes. The $[\eta]_i$ corresponding to these M_i were calculated using the a and K from the monodisperse standards. The data for these calculations are shown on tables (6)-(8).

The "Universal" calibration curve is obtained by plotting the hydrodynamic volume, $\ln [\eta]_i M_i$, against retention volume, Vr. This is shown graphically on figure (10). The advantage obtained from this technique is the possibility of estimating Mw and Mn from the measurements of the $[\eta]$ and the retention volumes of any non-crosslinked HEMA-copolymer at the same experimental conditions as those used in constructing the "Universal" calibration curve. In order to verify the dependence of this curve on viscosity, the $\ln M_i$ against Vr were plotted. This is seen in figure (11). The linearity obtained gives good evidence of the possibility of using this calibration curve instead of the one shown on figure (10), which is a function of $[\eta]$. This will eliminate the necessity for measuring [η] in the approximation of $\bar{M}w$ and $\bar{M}n$ from GPC data.

In order to test the validity and accuracy of the "Universal" calibration curve, a TDI-HEMA polymer, prepared using the heterogeneous method of synthesis, was analyzed for molecular weight determination and checked by means of other standard techniques.

The GPC data for TDI-HEMA is shown on table (10) and the GPC chromatogram can be seen on figure (13). From the retention volumes obtained from the chromatogram and the "Universal" calibration curve, figures (10)-(11), and having obtained the [η] from viscosity measurements, the Mw and Mn were calculated resulting in the values of 15,700 and 12,900, respectively. (The sample calculations for $\bar{M}w$ and $\bar{M}n$ are given on page (77)).

To check the value of $\bar{M}n$ vapor-pressure osmometry on the TDI-HEMA polymer was performed. The instrument's constant for THF and 25 ^{o}C was obtained using a standard sample of sucrose octaacetate. This data is shown on table (11). Figure (14) shows the graphical method to calculate K, the instrument's constant. The calculations are shown in page (78). Using this constant the value of $\bar{M}n$ (11,355) for TDI-HEMA sample is obtained from the vapor-pressure osmometry measurements which are given in table (12) and figure (15), shows the graphical representation of calculating $\bar{M}n$. Also the second virial coefficient, A_2 , (polymer-solvent interaction), is calculated. (Sample calculations are given on page (79)).

In the same manner, the value obtained for $\bar{M}w$ from the GPC calculations using the "Universal" calibration curve was checked by means of light scattering which was performed on a sample of TDI-HEMA polymer.

Light scattering measurements for pure solvent (THF) and polymer solutions are given in tables (14)-(18). The conversion of the data into workable information to use in the Zimm plot (in order to evaluate $\bar{M}w$) is given in tables (19)-(22) and an explanation of these tables is given on page (90).

The Zimm plot representing the above data is seen in figure (16). In this figure the Rayleigh number is plotted against the scattered angle. From the plot the molecular weight is obtained from the intercepts of the c = 0 and $\theta = 0$ lines on the y-axis, given a value of $\bar{M}w = 12500$. A_2 has a value of 5.60×10^{-5} ml mole g^{-2} which is calculated from the slope of the $\theta = 0$ line. In a similar manner, the radius of gyration is given to be 10.96 nm and calculated from the slope of the c = 0 line. The sample calculations for $\bar{M}w$, A_2 and radius of gyration are given on page (91).

The shape of the Zimm plot (curvature) depends on the size of the molecule and its interaction with the solvent. As the size of the molecule increases the curvature on the Zimm plot increases. Also, as the solvent power increases it will be reflected in an increase in curvature on the plot.

The second virial coefficient is a measure of the deviation of the solution from Van't Hoff's Law for osmotic pressure and it is therefore a measure of solvent power. A large value of A_2 occurs with good solvents and a small (or negative) values of A_2 with "poor" solvents (in the thermodynamic sense). From the shape of the Zimm plot on page (67), it can be seen that the molecule in question is not of a large size and the calculated value of A_2 shows that THF falls in the middle range of solvent power. This suggests that a better solvent for TDI-HEMA should be used during its analysis. Since M is constant for the same material in different solvents, A_2 M also serves as a relative measure of solvent power. The value of A_2 M for the homopolymer under investigation is 0.7.

In a similar manner the radius of gyration is a measure of the extension of the molecule in a given solvent, expressing the power of the solvent to solvate the sample. The value calculated on page (91) shows that in THF the extension of the molecule is moderate. A change in the radius of gyration is accompanied by a change in intrinsic viscosity. The $[\eta]$ varies as the cube of the radius of gyration.

To conclude, table (26) gives a summary of the molecular weights of TDI-HEMA polymers as they were obtained by different experimental methods. This shows the validity of the "Universal" calibration curve cunstructed from the GPC data. Table (27) shows the comparison of molecular weights for homo-hetero method of synthesis which gives strong evidence for the reduction in the gel formation (diadduct, triadduct, etc) during preparation.

Table 26. Summary of molecular weights of TDI-HEMA homopolymer.

Experimental Technique	$\bar{M}n$	$\bar{M}w$
GPC	12900	15700
V.P.O.	11400	-
L.S.	-	12500

Table 27. Comparison of molecular weights for homo-hetero methods of synthesis.

Method of synthesis	$\bar{M}n$	$\bar{M}w$
Homogeneous	870*	944035
Heterogeneous	11400	12500

*from GPC data.

In an attempt to synthesize a polycarbonyl structure compound, dichloroketene was considered as useful starting material. If its polymerization should proceed through the carbon-carbon double bond, the structure of the resulting material would be the appropriate one to qualify for an intermediate for polycarbonyl synthesis.

The two synthetic approaches taken, in order to make dichloroketene, were: (1) the dehalogenation of trichloroacetylbromide using activated zinc(32) and (2) the dehydrohalogenation of dichloroacetylchloride using triethylamine(34) . In the first reaction sequence the amount of dichloroketene obtained was in good yield, but in the vacuum distillation step performed in order to concentrate the ketene derivative in the hydrocarbon solvent, some of the material was lost through dimerization (ring formation). Due to the lost of material the second, amine, reaction was prefered over the zinc one.

In 1967 Lavanish et.al, reacted dichloroacetylchloride with triethylamine in order to study the effects of varying experimental conditions on the generation of dichloroketene and to propose a general mechanism for this reaction. They observed that in the absence of a trapping agent (an olefin) able to react with dichloroketene, a viscous material was obtained having a polymeric apparance; it is well known that amines have the ability to initiate some ketenes polymerizations. If the viscous material was formed by polymerization through the carbon-carbon double bond instead of through the carbon-oxygen double bond, then the intermediate step that we were interested in was easily produced.

In order to determine the structure of this "polymeric" material the dehydrogenation was repeated with triethylamine and dichloroacetylchloride. Since the assumption that polymerization will take place was made, two reaction temperatures were used, (room and zero degree temperature), to detect, if any, an effect in the degree of polymerization. The techniques used to determine the structure were: elemental analysis, nuclear magnetic resonance (nmr), infrared spectroscopy (ir) and vapor-phase osmometry. The reactions run at 0^{o} and 25 ^{o}C gave essentially identical results. The elemental analysis gave C, 21.2; Cl, 63.9; (C_2Cl_2O) requires C, 21.6; Cl, 64.0. The nmr was obtained in deuterochloroform, since it appears to be an adequate solvent for this oily material and the nmr is shown on page (99). The values at 9.66 δ and 6.00 δ are for an aldehyde hydrogen and a hydrogen attached to a carbon bearing two chlorines, respectively. Similarly the ir which is shown on page (103) gives the expected absorptions for carbonyl aldehyde (1749 cm^{-1}) and carbon hydrgen (2880 and 2980 cm^{-1}). As can be seen these three techniques are in agreement with the proposal, that if polymerization was to take place it will do so through the carbon-carbon double bond. The proposal structure is:

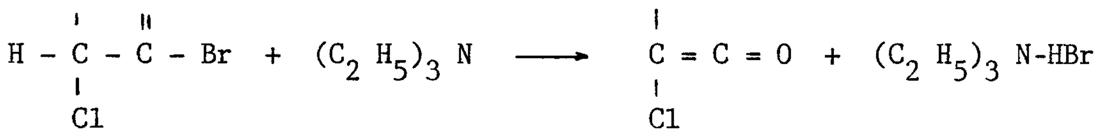
$$H ---[\ C_2 - CL_2 - O\ ]_x --- H$$

The next question to be answered is: if it is a polymeric material, then more than one repeating units must be present. In order to determine the numerical value of x, degree of polymerization, vapor-pressure osmometry was performed on the sample. Table (24) gives the data for the calibration constant, K, for acetone at 28 °C, using a standard sample of sucrose octaacetate. After obtaining the instrument's constant the same technique was used to calculate the molecular weight of the oily material. This data is represented graphically in figure (19), and table (25) gives the data. A sample calculation is given on page (98). From this technique the value of the molecular weight was determined to be 667.1 and the degree of polymerization was therefore no more than 5. The following oligomer is the proposed structure.

$$H ---[\ C_2 - Cl_2 - O\ ]_5 --- H$$

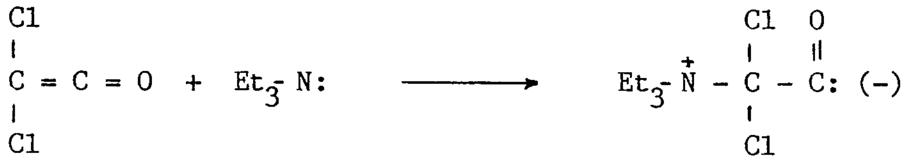
From the conclusive data on the structure and degree of polymerization of oligodichloroketene a mechanism was postulated in order to enlighten its formation:

1.



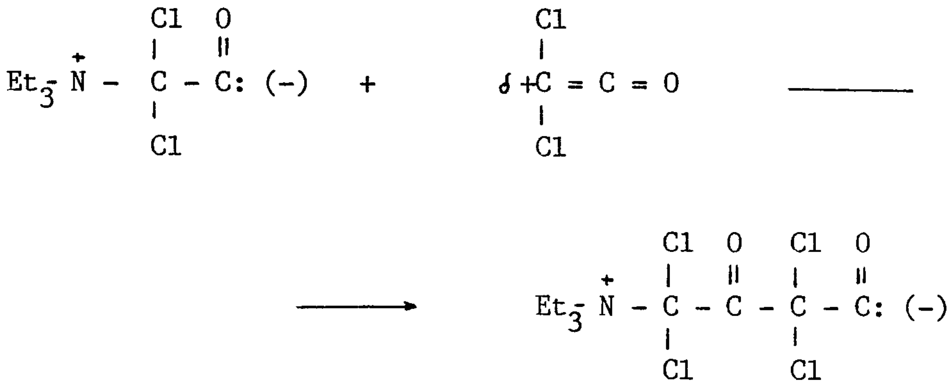
$$H - \underset{Cl}{\overset{Cl}{C}} - \overset{O}{\overset{\|}{C}} - Br + (C_2H_5)_3N \longrightarrow \underset{Cl}{\overset{Cl}{C}} = C = O + (C_2H_5)_3N\text{-}HBr$$

2.



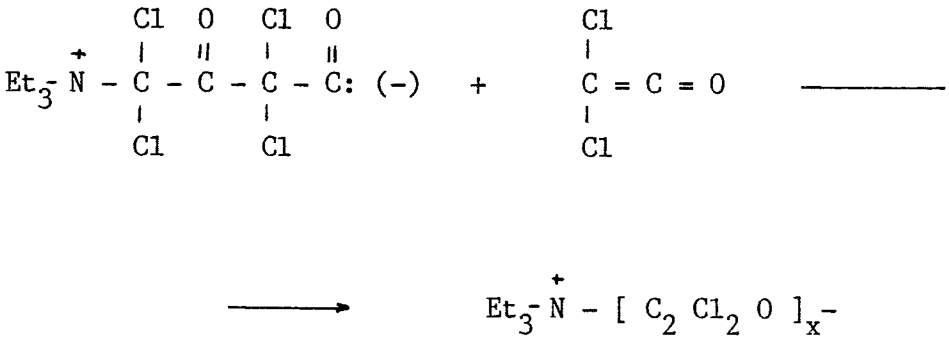
$$\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}=\mathrm{C}=\mathrm{O} + \mathrm{Et_3\text{-}N:} \longrightarrow \mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{:}\ (-)$$

3.



$$\mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{:}\ (-) + \delta{+}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}=\mathrm{C}=\mathrm{O} \longrightarrow \mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{:}\ (-)$$

4.



$$\mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{:}\ (-) + \underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{C}}}=\mathrm{C}=\mathrm{O} \longrightarrow \mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-[\mathrm{C_2\,Cl_2\,O}]_x-$$

5.

$$\mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}-[\mathrm{C_2\,Cl_2\,O}]- \quad + \quad \mathrm{Et_3\text{-}}\overset{+}{\mathrm{N}}\cdot\mathrm{HBr} \longrightarrow \mathrm{Et_3}\,\overset{+}{\mathrm{N}}-[\mathrm{C_2\,Cl_2\,O}]-\mathrm{H} \quad + \quad \mathrm{Et_3\text{-}N:}$$

After step (5), the reaction product is distilled under reduced pressure to remove any side reaction products. It is observed that due to the heat applied for distillation, the triethylamine-oligodichloroketene material (product of step 5) splits apart giving oligodichloroketene as the main product from the reaction.

The evidence for the above statement can be seen from the nmr spectra of the product before and after distillation (pages (99)-(100)) and having for comparison the nmr spectrum of triethylamine. The nmr spectrum of the triethylamine-oligodichloroketene adduct indicates strong triethylamine absorption, whereas the nmr spectrum of the oligodichloroketene displays only absorption from the aldehyde hydrogen and the hydrogen attached to the dichlorocarbon.

Since the purpose of identifying the oily substance from Lavanish's report in 1968 was to have a good candidate for polycarbonyl preparation the hydrolysis of this material was carried out using aqueous sodium hydroxide at room temperature. TLC analysis of the reaction mixture gave no indication of reaction taking place. This suggests that more vigorous conditions from the one used in this work must be used in order to bring about the hydrolysis of oligodichloroketene.

APPENDIX 1

INTRINSIC VISCOSITY MEASUREMENTS.

Dilute solution viscosity was measured in a capillary viscometer of the Ubbelohde type (Cannon: E-968, 50 ml. capacity) in a constant temperature bath regulated to ± 0.01 °C.

First, the solvent flow time is determied with a pipette or syringe a suitable amount of solvent (about 10.0 ml.) is filtered into the viscometer which is then placed in the bath for at least 10 minutes in order to allow for temperature equilibration. If a "millipore" filter holder attached to a syringe is available, it may be used conveniently for the filtration. After temperature equilibration has been achieved the solvent is forced up through the capillary into the bulb above the top mark by means of a rubber bulb. The bulb is removed; the timer is started when the center of the meniscus exactly coincides with the top mark. The timer is stopped when the center of the meniscus coincides with the bottom mark. The efflux time is thus determined at least three times. The readings should agree to within 0.1 sec. of the mean value.

The appropiate amount of solution is filtered into a clean, dry container and the correct amount of filtered solution is pippeted into the viscometer, which has been cleaned and dried. The solution is allowed to eqilibrate and the flow time is determined as before. The value of η_r is calculated; it should fall in the range 1.1 to 1.6, preferably closer to the higher value.

A set of four relative viscosities, η_r, in the above range should be obtained by continuous dilution. Intrinsic viscosity measurements for poly (MMA) - (MMA)-HEMA copolymers and TDI-HEMA, blocked p-cresol forward polymer were done in tetrahydrofuran (THF) at 25 °C; for polydichloroketene the measurements were made in acetone at 28 °C.

GEL PERMEATION CHROMATOGRAPHY MEASUREMENTS.

Initially the GPC columns were calibrated using fine standard polystyrene samples (supplied by Pressure Chemical Co.) with molecular weights of 2 K, 9 K, 17.5 K, 50 K and 100 K.[18]

The gel permeation chomatography set up consists of: chart recorder (linear), pump (Altex-model 110 A), refractomonitor control unit (LDC), refractormonitor optical unit (LDC), and two columns, Zorbax PSM-60-S (P.N. 8509578 and P.N. 850957808 Dupont Co.).

The column is flushed for about one hour with distilled solvent at 1.5 ml/min. and system pressure of about 1000 psi. The differential refractometer and recorder are turned on. The recorder baseline is checked for about 20 minutes at a sensitivity of 8 . The baseline should be flat with no noise. A solution of TDI-HEMA, p-cresol blocked forward polymer (2 g/l in THF) was prepared, filtered and an aliquot injected by means of a syringe. The point on the chart paper when injection occurred was marked.

VAPOR PRESSURE OSMOMETRY MEASUREMENTS.

The measurements were made using Wescan Vapor Pressure Osmometer - model: 233-200. The instrument was calibrated with a standard solute of known molecular weight (sucrose octaacetate, molecular weight 678.6).

To determine $\bar{M}n$ and A_2 of an unknown sample, at least three different concentrations were prepared in the specific solvent (20 g/l, 40 g/l, 60 g/l). The solvent zero reading was determined initially with pure solvent on both thermistors, then the samples were run in the osmometer starting with the more dilute solution first. In each determination a series of several drops were read and averaged. For all readings, exactly five minutes were allowed for equilibration after dropping the solution on to the thermistor.

For the TDI-HEMA, p-cresol blocked forward polymer the solvent used was THF and the instrument settings were: temperature controls, course = 1, fine = 892.3, approximate T = 25 °C, range switch = 2, current switch = 20 microamperes. For polydichloroketene the solvent used was acetone and the instrument settings were: temperature controls, course = 1, fine = 930, approximate T = 28 °C, range switch = 2, current switch = 20 microamperes.

LIGHT SCATTERING MEASUREMENTS.

A Brice Phonix light scattering photometer, series 2000, was used for the determination of the molecular parameters of the unknown polymer. Necessary electrical connections and photometer calibrations were made as per the instrument manual.

The samples were weighted accurately and dissolved in distilled solvent. Accuracy in light scattering measurements is favored by the proper choice of the solvent. The solution was directly filtered into the cylindrical cell # c-101, using 25 mm diameter millipore filter holder, through Scheicher and Schuell's pH 7.9 - 0.1 nm nitrocellulose filter. The light scattering measurement was performed on a minimum of four different solution concentrations (2, 4, 8, 12 g/l).

The scattering measurement was done for the pure solvent first and then for the polymer solution starting with the highest concentration. Light from the mercury arc (green light , 546 nm) is incident on the cylindrical cell containing the polymer solution. A photomultiplier mounted on a rotating table views the scattered light at any selected angle. The photo current is amplified by a voltmeter. A series of neutral filters (F_1 , F_2 , F_3 , and F_4) makes it possible to use the system for a wide range of intensities. The disc is rotated and the voltmeter readings are taken at angles of 0^o, 45^o, 60^o, 75^o, 90^o, 105^o, 110^o, 120^o, and 135^o, with respect to the incident beam. In each case different filters are used in front of the incident beam in various combinations to keep the voltmeter readings at a sensitive position on the scale and an average of at least six voltmeter readings are taken.

In order to account for the angular dissymetry measurement when using a cylindrical cell, a calibration factor r / r' relating the narrow beam geometry to the standard beam geometry is determined. This is done by taking the scattering measurement of the polymer solution in a square cell (40 x 40 mm, cat. No. D-101) at angles 0^o and 90^o.

After taking the readings, about 2 ml of polymer sample is used for determining the specific refractive index increment. The value of dn/dc of the polymer sample is determined by using a Brice-Phonix differential refractometer, model BP-2000-V. The differential refractometer was calibrated initially using, as reference, a solution having a known refractive index difference between solution and solvent (solution of KCl in distilled water). The value of the instrument constant K can be obtained from the following relationship.

$$\Delta n = K \Delta d$$

where Δn - refractive index difference between KCl and distilled water.

Δd - total slit image displacement in instruments units.

An average value of K calculated was 9.0576×10^{-3} using green light, 546 nm.

In the determination of dn/dc of the polymer solutions, the exact concentration measurements was done by taking a specified volume of the polymer solution, after all the scattering, in a previously weighted aluminum cup. The correct concentration was calculated from the final weight of the cup after all the solvent was evaporated and the cup was dried in an oven for 10 minutes.

The transmittance of filters and the working standard constant a, of the cell were determined experimentally as for the instrument manual. After determining all the necessary parameters, the values of weight average molecular weight, second virial coefficient and radius of gyration were calculated using the Zimm plot.

PREPARATION OF DICHLOROKETENE AND POLYDICHLOROKETENE.

1. Preparation of dichloroketene by dehalogenation.

A 34.15778 g (0.52245 moles) portion of zinc activated with copper and 100 ml of absolute ether were added to a 250 ml flask equipped with a stirrer, reflux condenser, and dropping funnel under a nitrogen atmosphere. A 23.64600 g (0.10449 moles) of freshly distilled trichloroacetylbromide was added dropwise over a period of 2 hours to the stirred mixture. At the conclusion of the exothermic reaction the ether solution was separated from the unreacted zinc. The unreacted zinc was washed with ether, and this ether combined with the ether solution. The amount of zinc consumed in the reaction was 6.8070 g (0.1041 moles).

2. Isolation of dichloroketen in hydrocarbon solvent.

A 100 ml portion of the dark-green ether solution obtained by dehalogenation as described above containing 10.453 g of dichloroketene was vigorously stirred while 100 ml of dry octane was added dropwise under a nitrogen atmosphere. This resulted in the precipitation of the zinc halide. After the addition, the octane solution was separated from the precipitated zinc halide with a pipet. The ether was removed by distillation to yield 100 ml of an octane solution containing dichloroketene.

The dichloroketene was concentrated by distillation of the octane under reduced pressure.

3. Assay procedure for hydrocarbon solution containing dichloroketene.

An aliquot of a hydrocarbon solution (10 ml) containing dichloroketene was treated with a large excess of water (50 - 70 ml) and vigorously shaken in a separatory funnel. The aqueous layer containing dichloroacetic acid (all water was excluded to prevent hydrolysis of trichloroacetylbromide) was titrated with a standard solution of sodium hydroxide (0.100 N).

4. Preparation of dichloroketene polymer by dehydrohalogenation.

Into a 1000 ml flask equipped with a stirrer, reflux condenser, and dropping funnel under a nitrogen atmosphere were placed 200 ml of dry ether and 73.69500 g (0.5000 moles) of dichloroacetylchloride. A solution of 50.59500 g (0.5000 moles) of triethylamine in 50 ml of dry ether was placed in the dropping funnel. The dichloroacetylchloride solution was cooled to 0 °C by means of an ice-water bath. The amine solution was then added dropwise to the vigorously stirred acid chloride solution over a period of 2 hours.

Stirring was continued for three hours. The tan slurry was filtered and the filtrate was concentrated by distillation to remove the ether. Vaccum distillation of the filtrate (to remove unreacted acidchloride and any volatile side products) gave 31.13500 g of a dark highly viscous residue which was dissolved in acetone and filtered through Scheicher and Schuell's pH 7.9 - 0.1 nm nitrocellulose filter. The acetone was evaporated in a vaccum oven leaving the dark highly residue for characterization.

5. Reaction of dichloroketene oligomer with sodium hydroxide.

Into a test tube were placed 50 mg of dichloroketene oligomer in 5 ml of THF. One ml of 0.10 M sodium hydroxide solution was added to the THF solution over a period of one hour. The solution was warmed to 65 °C by means of a water bath. The above procedure was repeated using this time a 1.00 M sodium hydroxide solution TLC was performed on the reaction mixture three times a day for three days.

APPENDIX 2

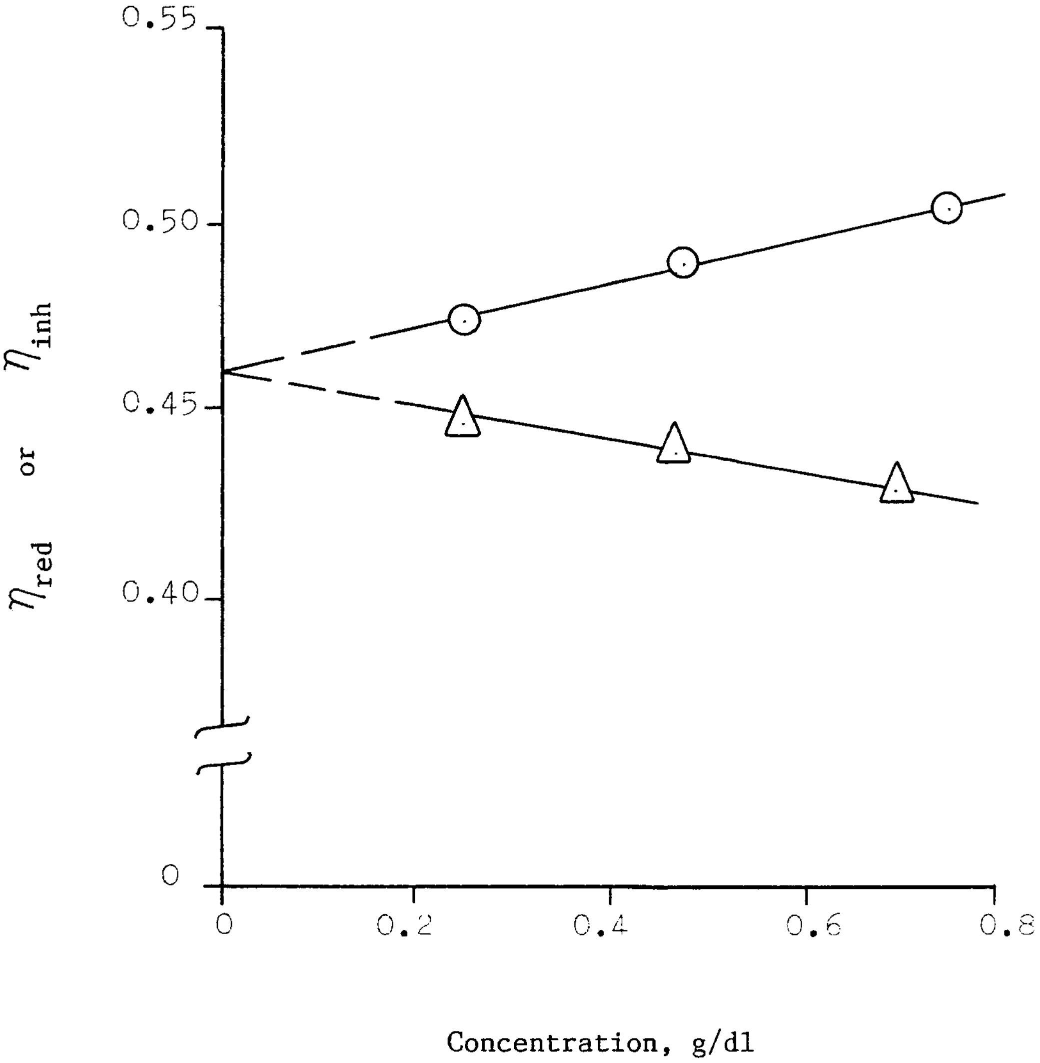


Fig. 1. Reduced (o) and inherent (Δ) viscosity-concentration curves for PMMA (Mw = 5 K) in THF at 25 °C.

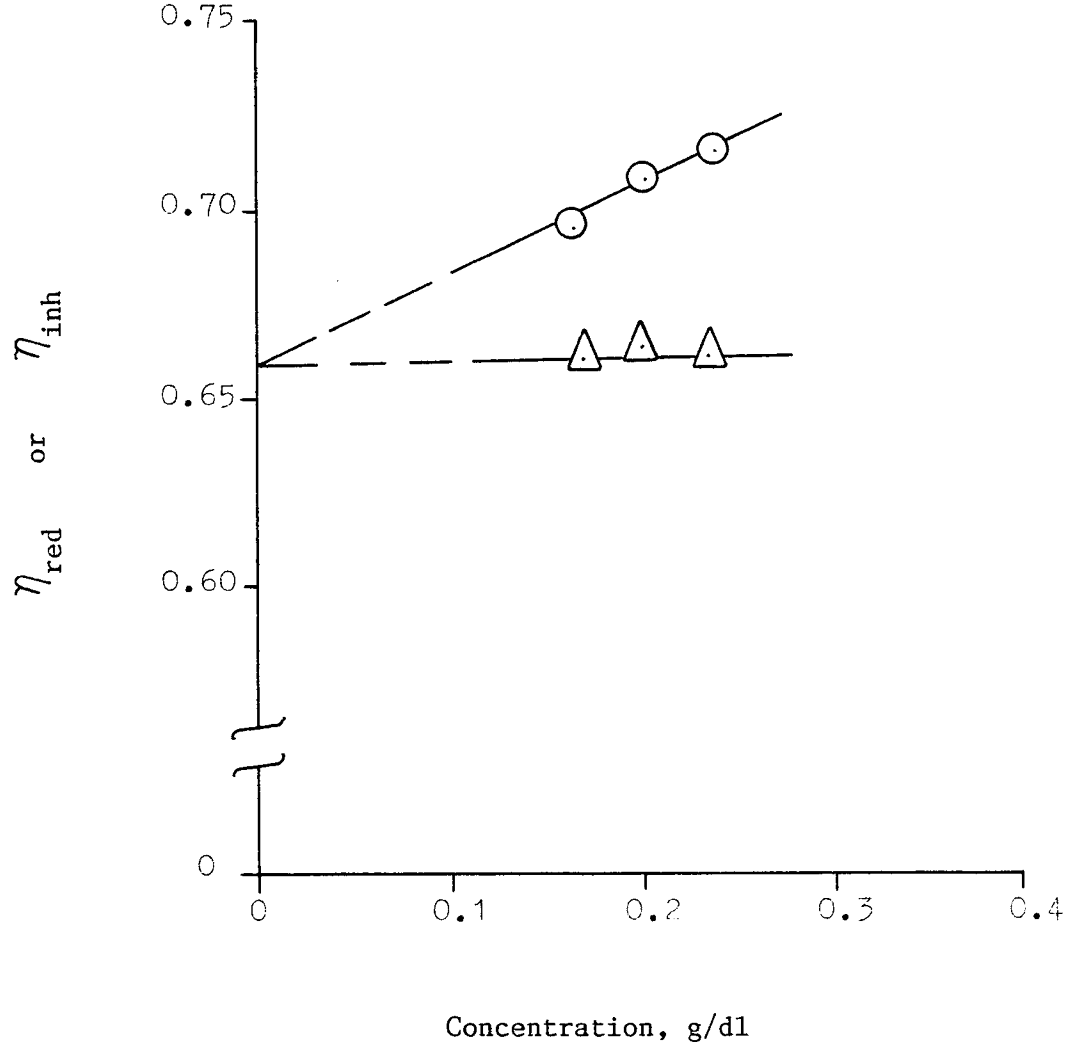


Fig. 2. Reduced (o) and inherent (Δ) viscosity-concentration curves for PMMA (Mw = 10 K) in THF at 25 °C.

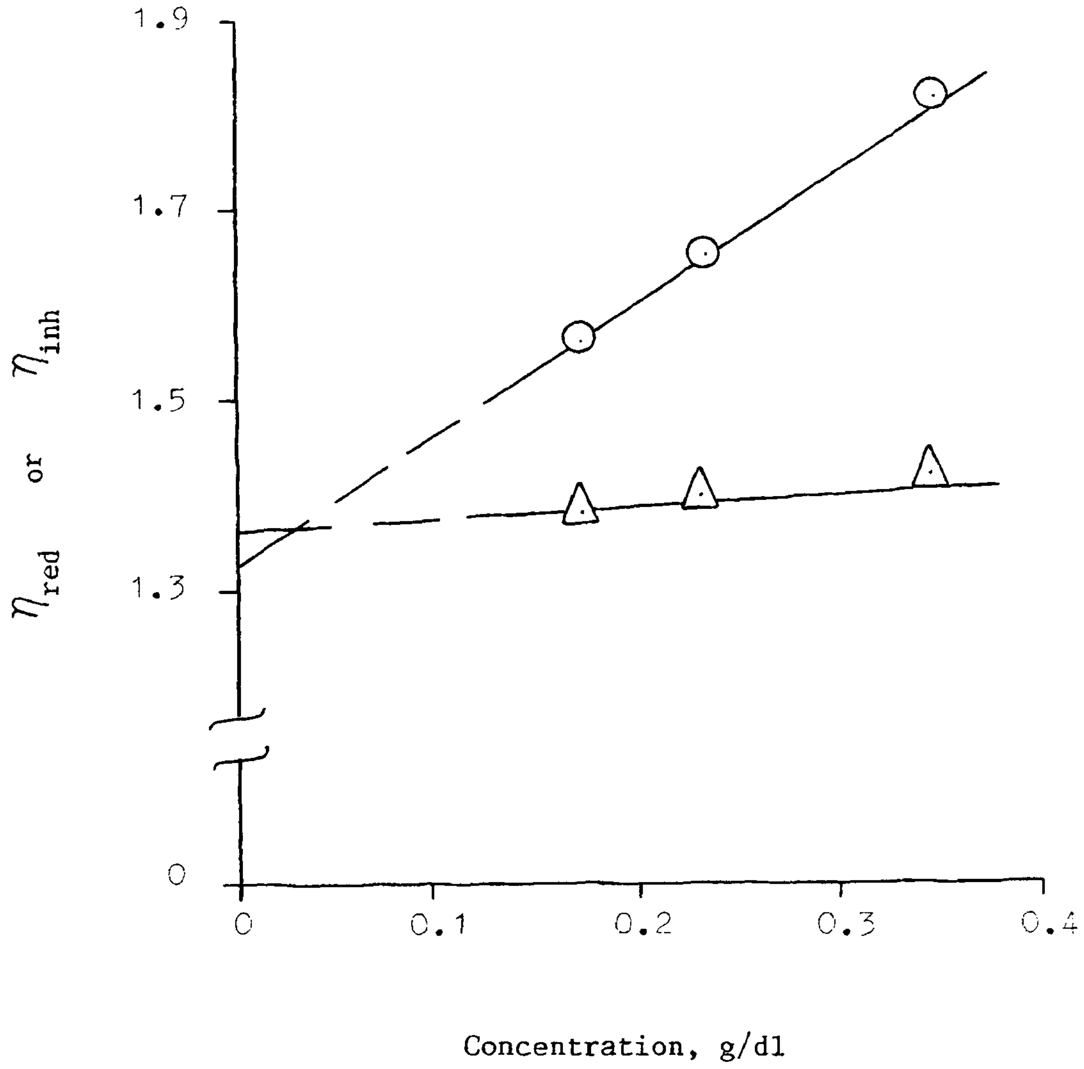
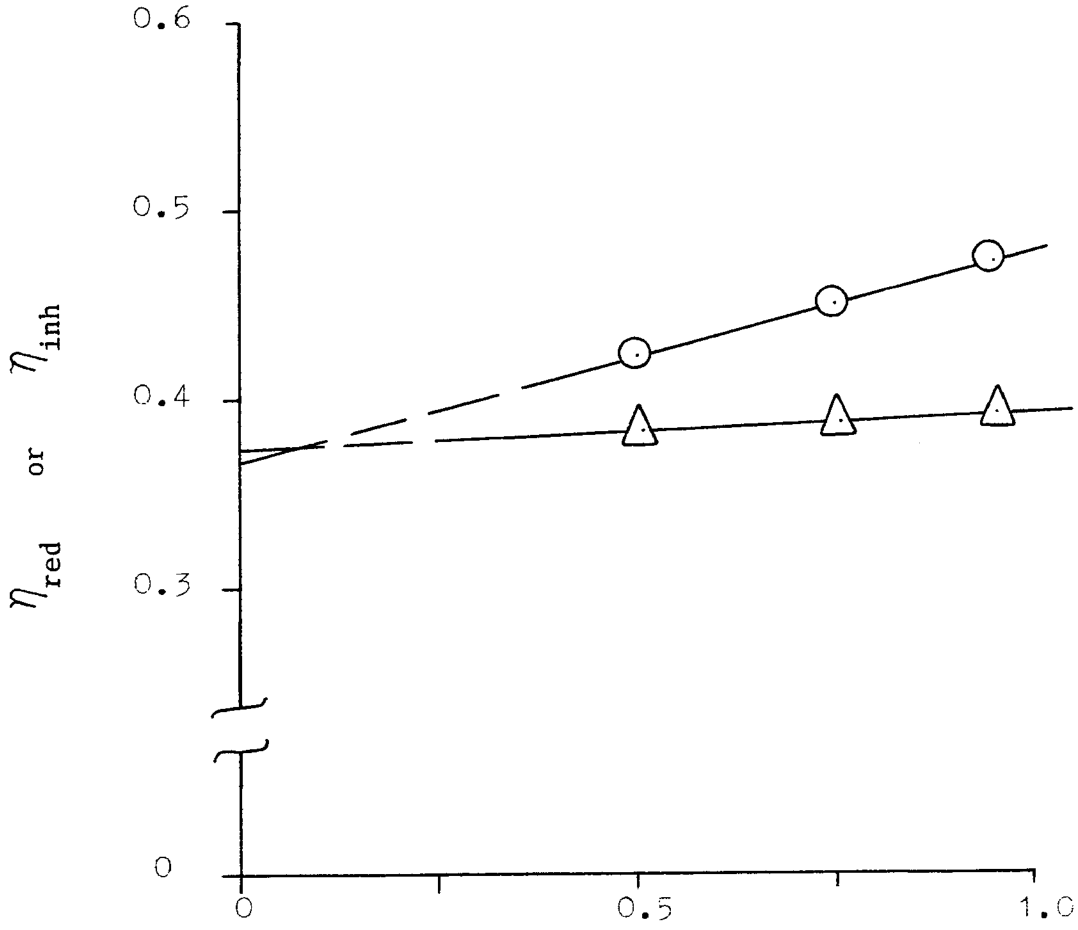


Fig. 3. Reduced (o) and inherent (Δ) viscosity-concentration curves for PMMA (Mw = 20 K) in THF at 25 °C.



Concentration, g/dl

Fig. 4. Reduced (o) and inherent (Δ) viscosity-concentration curves for 10% MMA-HEMA copolymer (Mw = 5 K) in THF at 25 °C.

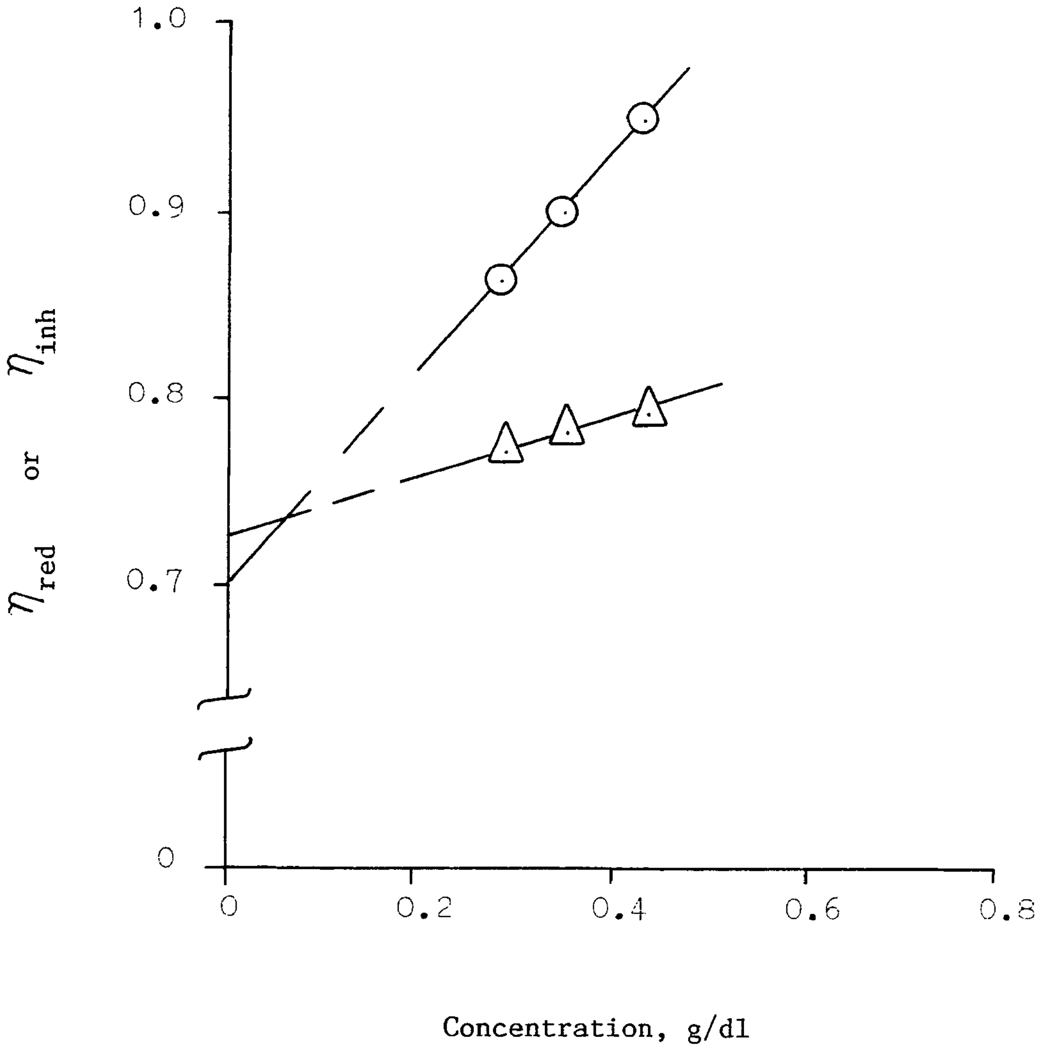


Fig. 5. Reduced (o) and inherent (Δ) viscosity-concentration curves for 10% MMA-HEMA copolymer (Mw = 10 K) in THF at 25 °C.

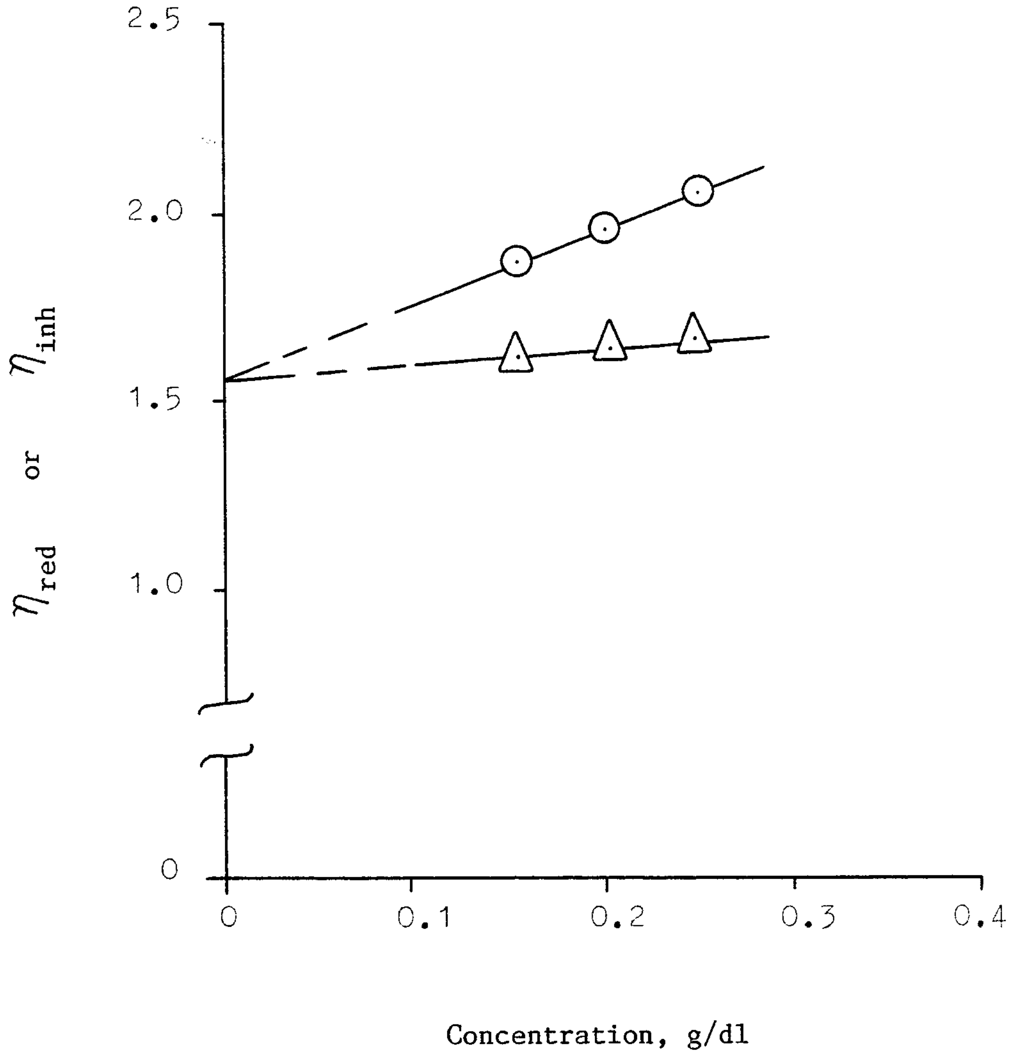


Fig. 6. Reduced (o) and inherent (Δ) viscosity-concentration curves for 10% MMA-HEMA copolymer (Mw = 20 K) in THF at 25 °C.

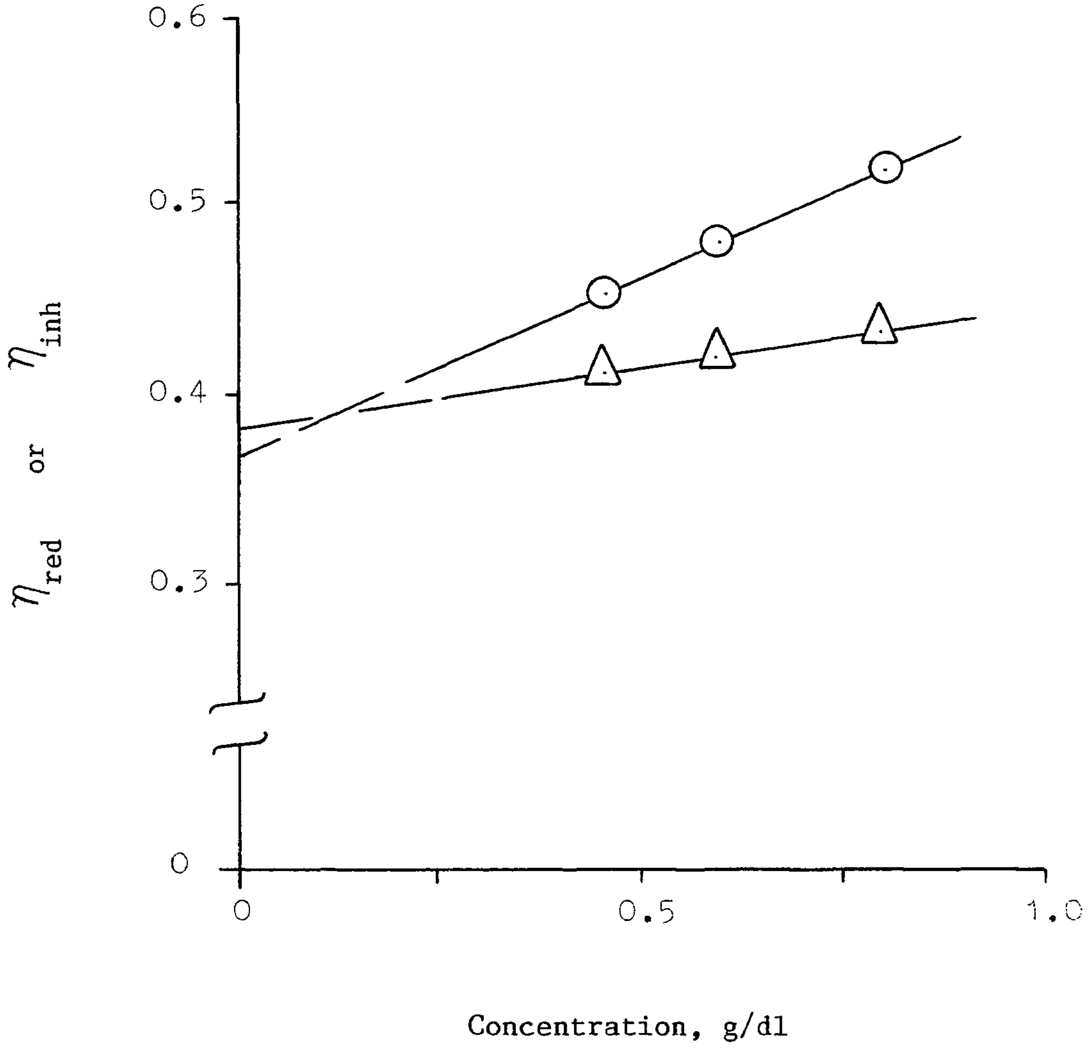


Fig. 7. Reduced (o) and inherent (Δ) viscosity-concentration curves for 30% MMA-HEMA copolymer (Mw = 5 K) in THF at 25 °C.

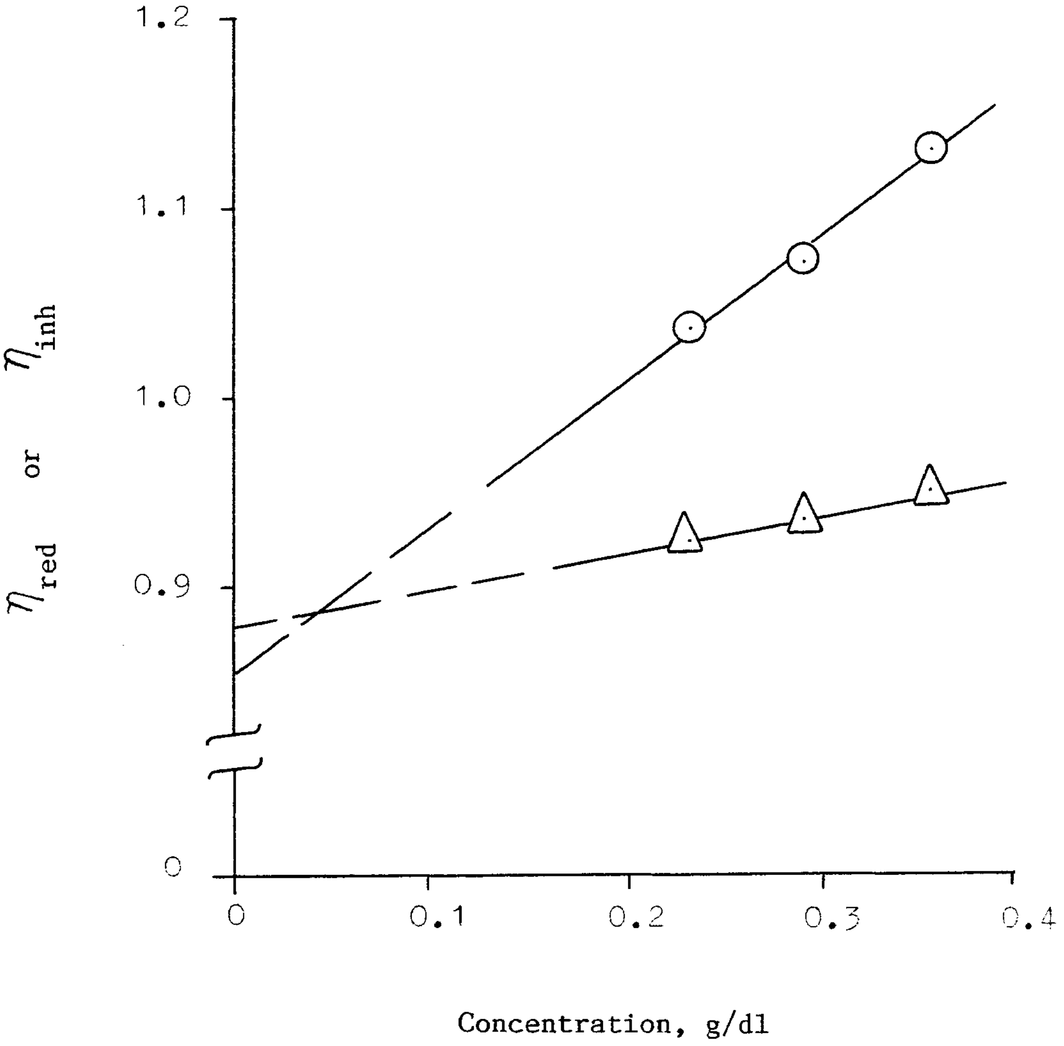
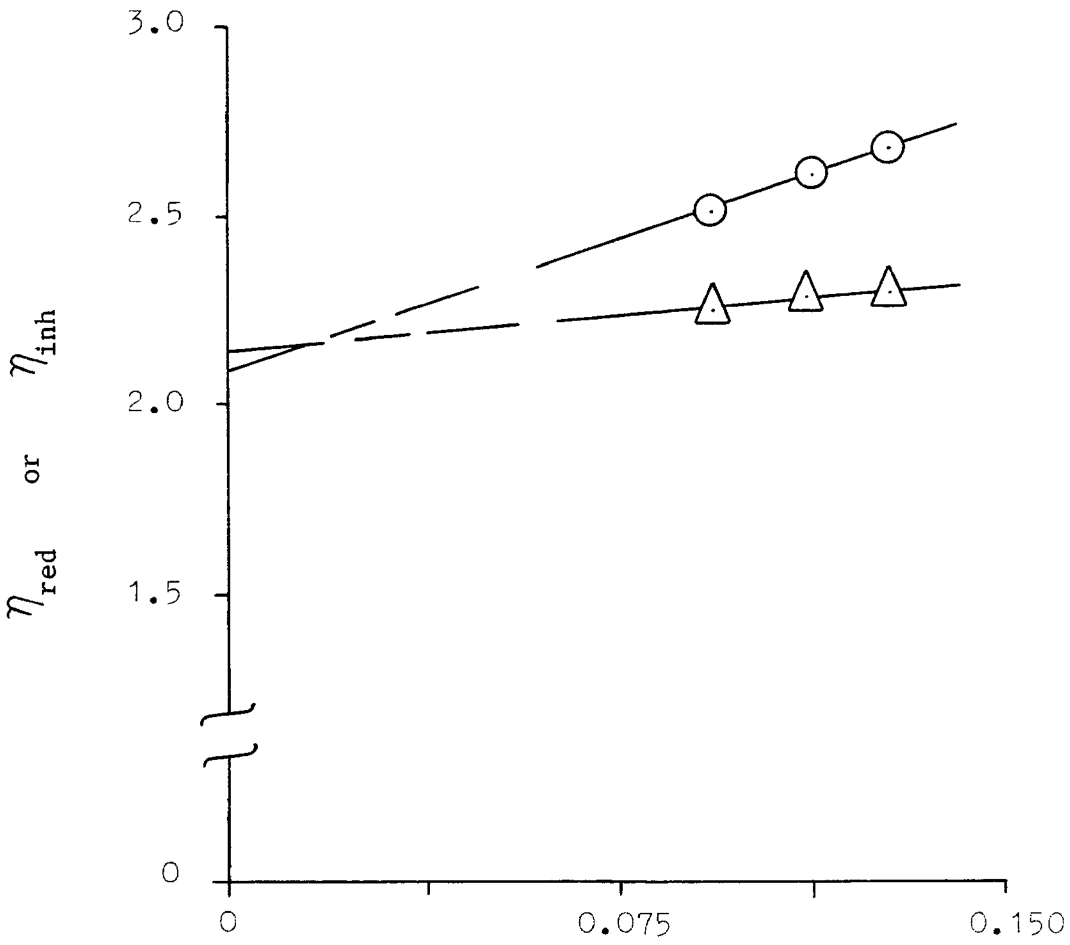
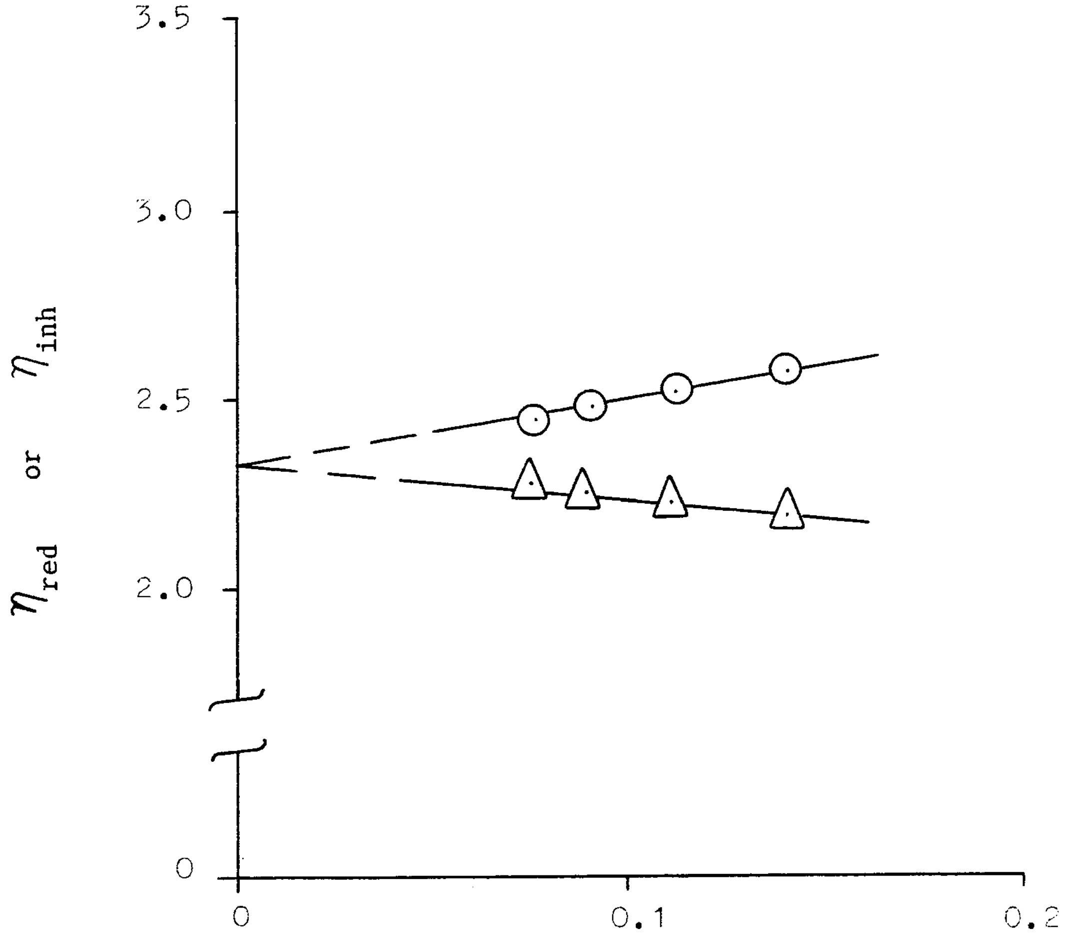


Fig. 8. Reduced (o) and inherent (Δ) viscosity-concentration curves for 30% MMA-HEMA copolymer (Mw = 10 K) in THF at 25 °C.



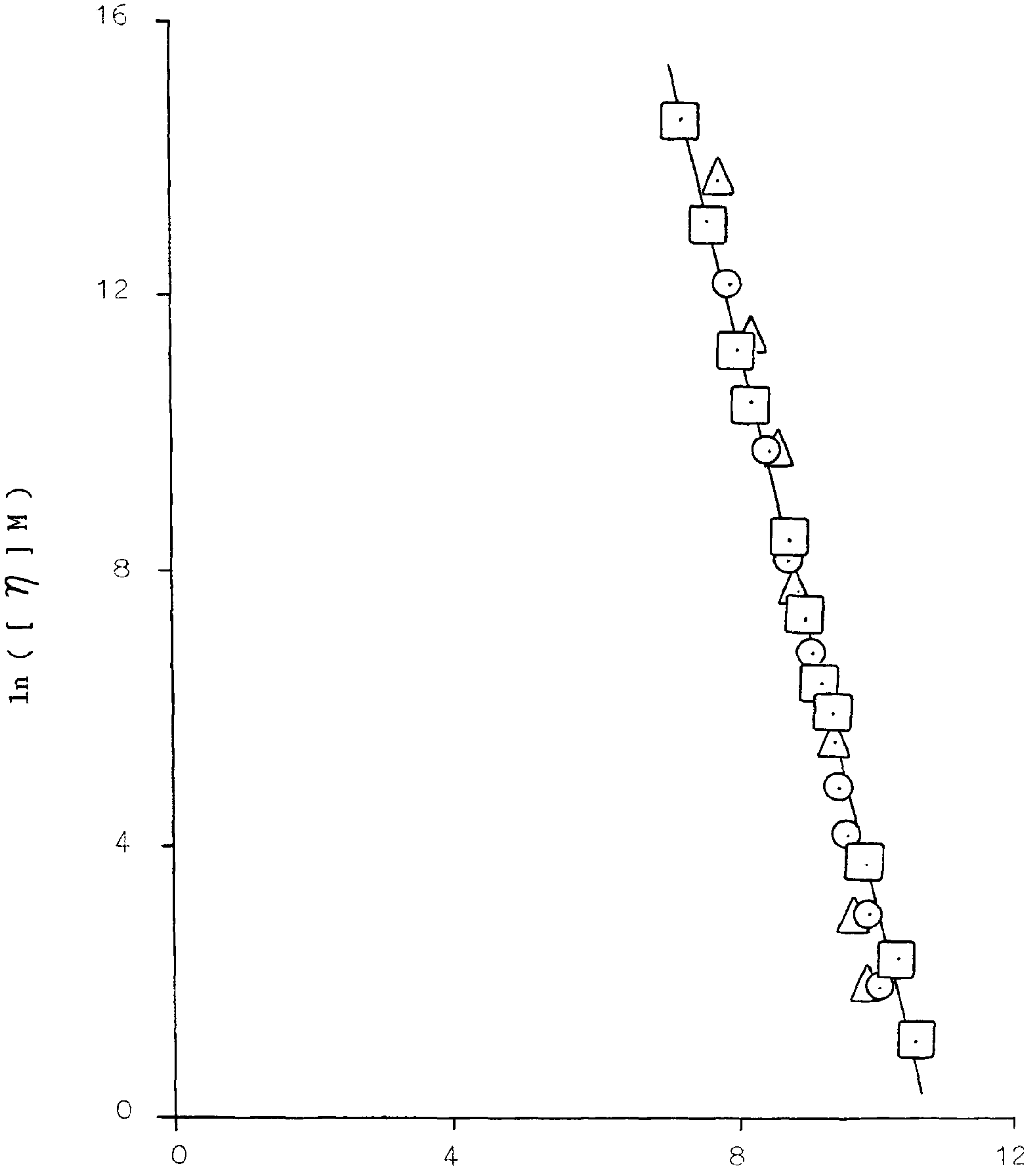
Concentration, g/dl

Fig. 9. Reduced (o) and inherent (Δ) viscosity-concentration curves for 30% MMA-HEMA copolymer (Mw = 20 K) in THF at 25 °C.



Concentration, g/dl

Fig. 12. Reduced (o) and inherent (Δ) viscosity-concentration curves for TDI-HEMA, blocked p-cresol polymer in THF at 25 °C.



Retention volume, ml

Fig. 10. "Universal" calibration curve for GPC, based on hydrodynamic volume. PMMA (▯), 10% MMA-HEMA (o) and 30% MMA-HEMA (Δ) in THF at 25 °C.

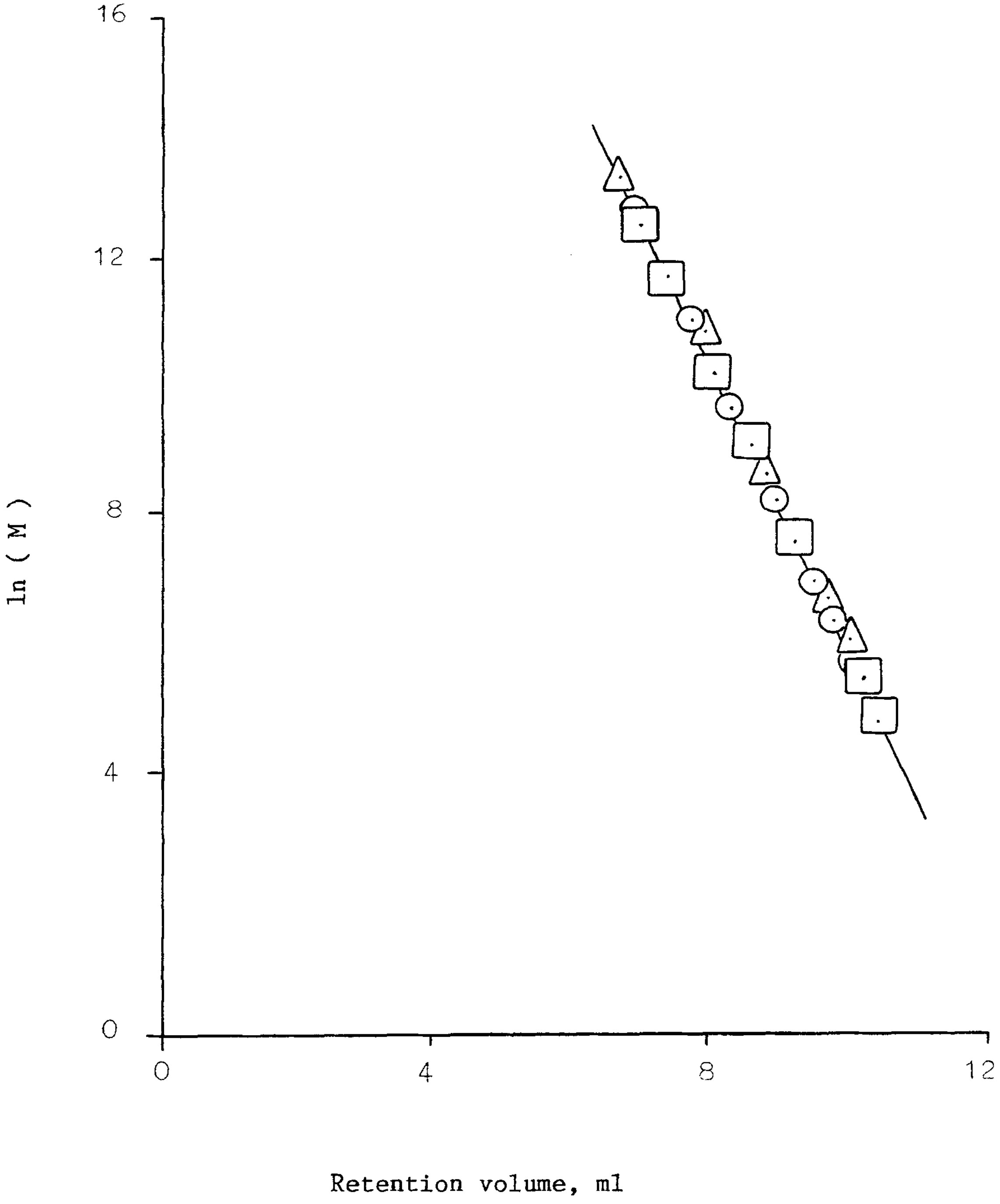


Fig. 11. "Universal" calibration curve for GPC, based on molecular weight. PMMA (▯), 10% MMA-HEMA (o) and 30% MMA-HEMA (Δ) in THF at 25 °C.

Conditions:

Chart speed = 2 cm/min.

Flow rate = 1.5 ml/min.

Pressure = 800 psi

Sensitivity = 8

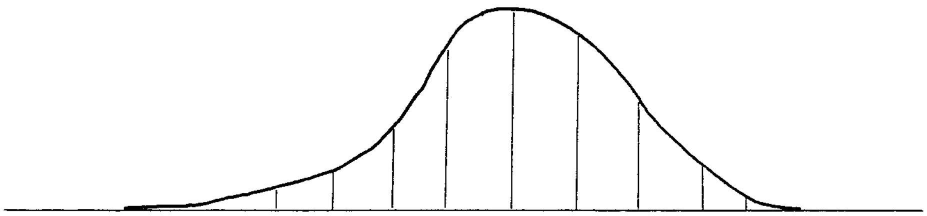


Fig. 13. GPC chromatogram for TDI-HEMA, blocked p-cresol in THF at 25 °C.

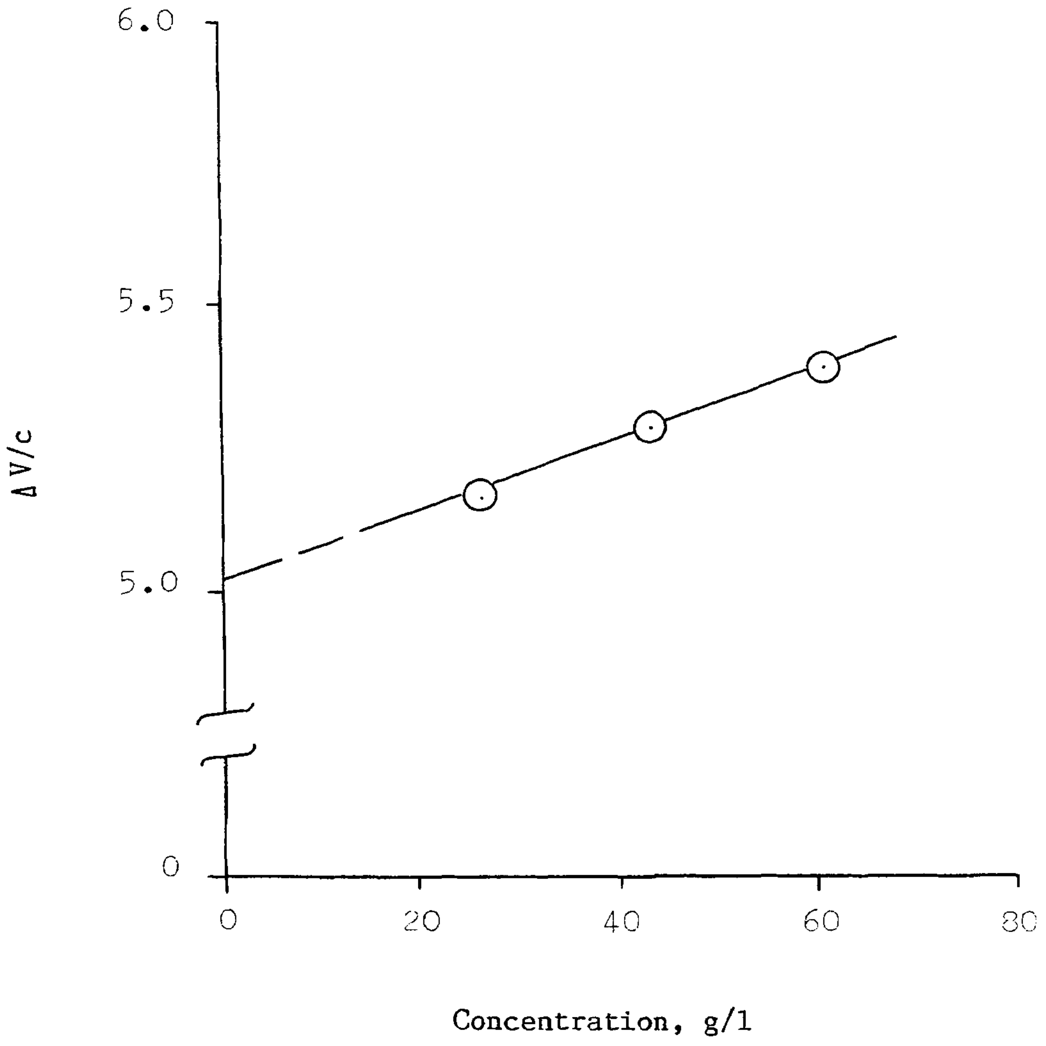


Fig. 14. Plot of ΔV/c against c for sucrose octaacetate (Mw = 678.6) in THF at 25 °C. Used in obtaining the instrument's constant.

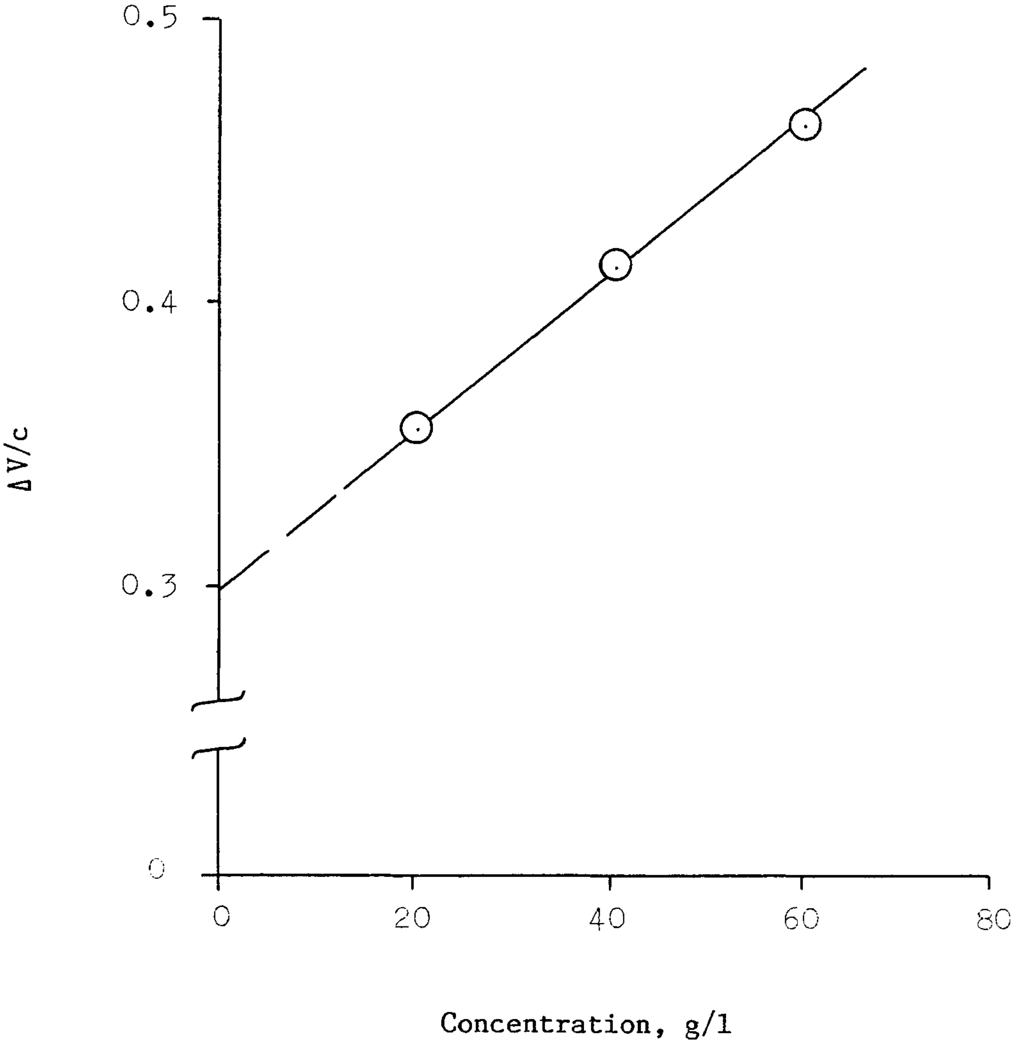


Fig. 15. Plot of ΔV/c against c for TDI-HEMA , blocked p-cresol in THF at 25 °C.

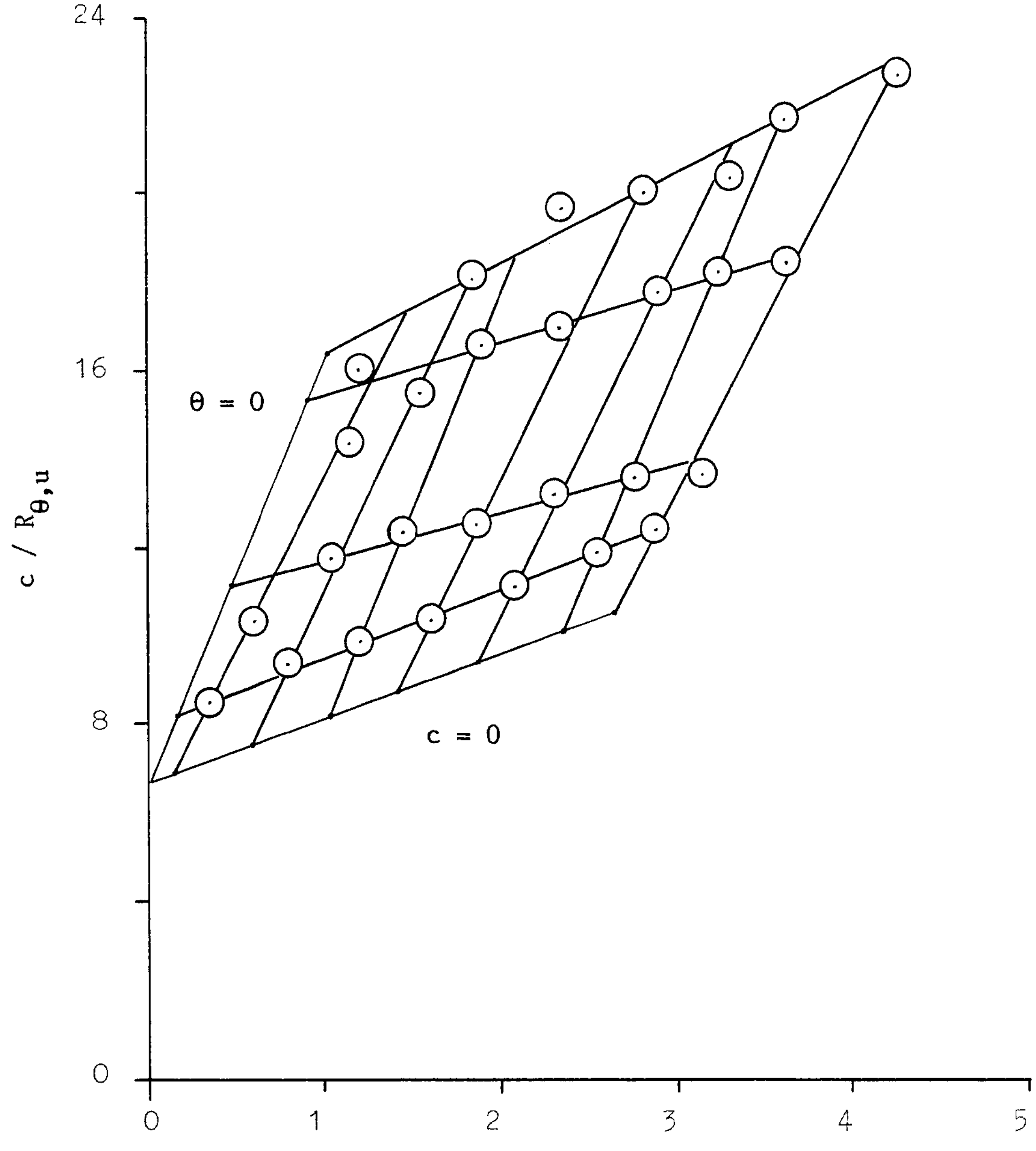


Fig. 16. Zimm plot showing the light scattering from a TDI-HEMA, blocked p-cresol sample. Molecular parameters are Mw = 12,500; $A_2 = 5.60 \times 10^{-5}$ ml mole g^{-2} ; $(S_z^2)^{.5} = 10.96$ nm.

Table 1. Data from measurements of dilute-solution viscosity: poly (methyl methacrylate) polymers in THF at 25 °C.

Mw = 5 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.246	111.0	1.116	0.116	0.471	0.109	0.445
0.464	122.4	1.230	0.230	0.496	0.207	0.446
0.737	136.2	1.369	0.369	0.500	0.314	0.426

Mw = 10 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.166	111.0	1.116	0.116	0.696	0.109	0.658
0.202	113.8	1.144	0.144	0.713	0.134	0.666
0.235	116.2	1.168	0.168	0.713	0.155	0.659

Mw = 20 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.172	126.1	1.267	0.267	1.557	0.237	1.380
0.229	136.9	1.375	0.375	1.640	0.319	1.393
0.343	161.0	1.618	0.618	1.801	0.481	1.402

Table 2. Data from measurements of dilute-solution viscosity: methyl methacrylate-HEMA copolymers in THF at 25 °C.

10 % copolymer, Mw = 5 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.509	120.9	1.215	0.215	0.422	0.195	0.383
0.764	133.7	1.344	0.344	0.450	0.295	0.387
0.955	144.6	1.453	0.453	0.475	0.374	0.391

10 % copolymer, Mw = 10 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.280	123.4	1.240	0.240	0.858	0.215	0.769
0.350	130.8	1.315	0.315	0.899	0.274	0.782
0.431	140.0	1.407	0.407	0.945	0.342	0.793

10 % copolymer, Mw = 20 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.153	127.6	1.282	0.282	1.851	0.249	1.629
0.200	138.2	1.389	0.389	1.942	0.329	1.640
0.247	149.4	1.502	0.502	2.035	0.407	1.649

Table 3. Data from measurements of dilute-solution viscosity: methyl methacrylate-HEMA copolymers in THF at 25 °C.

30 % copolymer, Mw = 5 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.460	120.2	1.208	0.208	0.452	0.189	0.411
0.586	127.4	1.280	0.280	0.479	0.247	0.422
0.805	141.0	1.417	0.417	0.518	0.349	0.433

30 % copolymer, Mw = 10 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.230	123.2	1.238	0.238	1.036	0.214	0.929
0.288	130.0	1.309	0.309	1.073	0.269	0.935
0.351	139.0	1.397	0.397	1.132	0.334	0.953

30 % copolymer, Mw = 20 K

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.093	122.5	1.231	0.231	2.489	0.208	2.239
0.111	128.2	1.288	0.288	2.589	0.253	2.275
0.126	132.6	1.333	0.333	2.632	0.287	2.272

Table 4. Intrinsic viscosity and Huggins' and Kraemer's constants for PMMA polymers and MMA-HEMA copolymers.

Polymer type	$[\eta]$, (dl/g)	k'	k"	k' - k"
Standard PMMA 5 K	0.46	0.26	- 0.22	0.48
Standard PMMA 10 K	0.66	0.52	- 0.01	0.53
Standard PMMA 20 K	1.34	0.70	0.13	0.57
10 % MMA-HEMA 5 K	0.37	0.80	0.16	0.64
10 % MMA-HEMA 10 K	0.71	1.08	0.38	0.69
10 % MMA-HEMA 20 K	1.58	0.72	0.12	0.59
30 % MMA-HEMA 5 K	0.37	1.30	0.30	1.00
30 % MMA-HEMA 10 K	0.87	0.93	0.30	0.63
30 % MMA-HEMA 20 K	2.12	0.94	0.31	0.63

Table 5. Calculation of a and k via the Mark-Houwink equation based upon viscosity data of a series of PMMA polymers and MMA-HEMA copolymers.

PMMA

Mw	$[\eta]$	$\ln[\eta]$	ln Mw
5 K	0.460	- 0.777	8.517
10 K	0.657	- 0.420	9.210
20 K	1.338	0.291	9.904

$a = 0.770$ $k = 6.0 \times 10^{-4}$

10 % MMA-HEMA

Mw	$[\eta]$	$\ln[\eta]$	ln Mw
5 K	0.367	- 1.002	8.517
10 K	0.711	- 0.341	9.210
20 K	1.575	0.454	9.904

$a = 1.051$ $k = 4.7 \times 10^{-5}$

30 % MMA-HEMA

Mw	$[\eta]$	$\ln[\eta]$	ln Mw
5 K	0.375	- 0.982	8.517
10 K	0.865	- 0.145	9.210
20 K	2.121	0.752	9.904

$a = 1.250$ $k = 8.8 \times 10^{-6}$

Table 6. Data for GPC "Universal" calibration curve. Poly (methyl methacrylate) polymers of various molecular weights.*

Mw = 5 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
8.25	19930	1.227	10.104	9.900
8.70	7332	0.568	8.334	8.900
9.83	545	0.077	3.734	6.301
10.50	122	0.024	1.085	4.804

Mw = 10 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.95	38177	2.024	11.255	10.550
8.63	8103	0.614	8.511	8.999
9.30	1901	0.210	2.319	7.550
10.20	245	0.042	2.319	5.501

Mw = 20 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.50	109098	4.542	13.113	11.600
8.17	24343	1.431	10.458	10.100
8.93	4230	0.372	7.361	8.350
9.15	2266	0.230	6.256	7.726

*M_i was obtained from reference (18).

Table 7. Data for GPC "Universal" calibration curve. MMA-HEMA copolymers of various molecular weights.*

10 % copolymer, Mw = 5 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
8.25	19930	1.549	10.338	9.900
9.60	982	0.066	4.164	6.890
9.83	545	0.035	2.956	6.301
10.05	330	0.021	1.927	5.799

10 % copolymer, Mw = 10 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.87	46630	3.784	12.081	10.750
8.55	9897	0.742	8.902	9.200
9.00	3498	0.249	6.769	8.160
9.45	1339	0.091	4.799	7.199

10 % copolymer, Mw = 20 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.65	76880	6.399	13.106	11.250
8.33	16318	1.255	9.927	9.700
9.09	3463	0.246	6.748	8.150
9.23	2208	0.154	5.826	7.700

*M_i was obtained from reference (18).

Table 8. Data for GPC "Universal" calibration curve. MMA-HEMA copolymers of various molecular weights.*

30 % copolymer, Mw = 5 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
8.85	5167	0.387	7.600	8.550
9.30	1998	0.118	5.462	7.599
9.75	665	0.029	2.986	6.499
9.97	403	0.016	1.859	5.998

30 % copolymer, Mw = 10 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.87	47099	6.132	12.574	10.760
8.33	16984	1.713	10.278	9.740
8.77	6248	0.491	8.028	8.740
9.23	2208	0.134	5.687	7.699

30 % copolymer, Mw = 20 K

Vr, ml	M_i	$[\eta]_i$	$\ln([\eta]_i M_i)$	$\ln M_i$
7.29	219696	42.063	16.039	12.300
7.65	76880	11.316	13.676	11.250
8.10	28283	3.241	11.426	10.250
9.00	3641	0.249	6.813	8.200

*M_i was obtained from reference (18).

Table 9. Data from measurements of dilute-solution viscosity: forward homopolymer of TDI-HEMA, blocked p-cresol in THF at 25 ^{o}C.

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	99.5	-	-	-	-	-
0.075	117.3	1.185	0.185	2.458	0.169	2.255
0.089	121.3	1.222	0.222	2.493	0.201	2.251
0.109	126.4	1.277	0.277	2.529	0.244	2.233
0.142	135.0	1.364	0.364	2.568	0.310	2.191

$[\eta] = 2.340$

Table 10. Data from gel permeation chromatography: forward homopolymer of TDI-HEMA, blocked p-cresol in THF at 25 °C. Calibration with narrow-distribution MMA-HEMA samples, same conditions.

Vr, ml	Recorder Divisions ($N_i M_i$)	Molecular weight (M_i)	$N_i \times 10^4$	$N_i M_i^2$
7.83	1.0	51534	0.2	53115
7.95	2.9	38177	0.8	116601
8.07	7.0	28282	2.5	199975
8.19	9.9	22026	4.5	218328
8.34	10.0	18033	5.5	178868
8.46	10.0	12088	8.3	121287
8.58	7.0	9228	7.6	64718
8.70	4.9	7331	6.7	36017
8.82	3.0	5884	5.1	17657
8.94	1.0	3714	2.7	3725
	$\sum$ 56.7		$\sum$ 44.0	$\sum$ 889129

$$\bar{M}w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{889129}{56.7} = 15700$$

$$\bar{M}n = \frac{\sum N_i M_i}{\sum N_i} = \frac{56.7}{4.4 \times 10^{-3}} = 12900$$

Polydispersity = $\bar{M}w$ / $\bar{M}n$ = 1.2

Table 11. Data from vapor-phase osmometry calibration: sucrose octaacetate in THF at 25 °C.

c, (g/1)	$\bar{V}$, (mv)	ΔV, (mv)	$\Delta V/c$, (mv-1/g)
0	9.73	0	-
20.60	115.80	106.07	5.15
40.27	222.00	212.27	5.27
60.05	333.37	323.64	5.39

Instrument constant = K = intercept * Mw

= 5.02 * 678.6

K = 3406.6

Table 12. Data from vapor-phase osmometry: forward homopolymer of TDI-HEMA, blocked p-cresol in THF at 25 °C. Calibration with sucrose octaacetate.

c, (g/l)	$\bar{V}$, (mv)	ΔV, (mv)	$\Delta V/c$, (mv-l/g)
0	4.60	0	-
19.96	11.63	7.03	0.35
40.68	21.28	16.68	0.41
59.81	32.11	27.51	0.46

$\bar{M}n$ = K / intercept = 3406.6 / 0.30 =

$\bar{M}n$ = 11355

A_2 = slope / K = 2.70×10^{-3} / 3406.6 =

A_2 = 7.93×10^{-7} l-mole/g^2

Table 13. Filter constants for Brice-Phoenix No. 2000, Instrument (transmittance of neutral filters at 546 mu).

Filter	Constant
F_1	0.5005
F_2	0.2557
F_3	0.1205
F_4	0.0612

Table 14. Data for pure THF using cylindrical cell.

Angle	Filter out	Voltmeter reading (average)
0	F_4 out	198.27
45	All out	11.45
60	"	5.75
70	"	4.47
75	"	4.11
90	"	4.01
105	"	4.41
110	"	4.76
120	"	5.48
135	"	9.07

Table 15. Data for pure THF using square cell.

Angle	Filter out	Voltmeter reading (average)
0	F_3 out	141.70
90	All out	12.01

The Rayleigh ratio for pure solvent using square cell is calculated as:

$$R_{\theta,u} = \frac{\mathrm{TD}\ a\ n^2\ (R_W / R_c)}{1.049\ h} (r / r') \left\{ \frac{1}{(1 - R^2)\ (1 - 4R^2)} \right\}$$

TD = 0.330 a = 0.040 n = 1.4070 R = 0.0367 h = 1.200

$$n^2 R_W / R_c = 2.14826$$

$$r / r' = \frac{12.01 * F_1 F_2 F_4 / 141.70}{4.01 * F_1 F_4 / 198.27} = 1.07156$$

$$R_{\theta,u} = 2.615 \times 10^{-2}$$

Table 16. Data for forward homopolymer (TDI-HEMA, blocked p-cresol) using cylindrical cell.

Angle	c, (g/l)	Filter out	Voltmeter reading (average)
0	2.35	F_1 F_2	197.57
45	"	F_2 F_3 F_4	175.85
60	"	F_2 F_3 F_4	107.70
70	"	All out	167.17
75	"	"	151.56
90	"	"	129.04
105	"	"	134.13
110	"	"	141.44
120	"	"	168.10
135	"	F_2 F_3 F_4	121.99

Angle	c, (g/l)	Filter out	Voltmeter reading (average)
0	4.92	F_1 F_4	171.59
45	"	F_1 F_3 F_4	131.29
60	"	F_2 F_3 F_4	157.33
70	"	"	125.47
75	"	"	114.28
90	"	All out	197.84
105	"	F_2 F_3 F_4	106.56
110	"	"	113.44
120	"	"	135.62
135	"	"	195.21

Angle	c, (g/1)	Filter out	Voltmeter reading (average)
0	9.46	F_1 F_4	122.82
45	"	F_1 F_3 F_4	131.59
60	"	F_2 F_3 F_4	160.63
70	"	"	125.34
75	"	"	114.69
90	"	All out	198.20
105	"	F_2 F_3 F_4	107.99
110	"	"	115.52
120	"	"	138.40
135	"	F_1 F_3 F_4	102.81

Angle	c, (g/1)	Filter out	Voltmeter reading (average)
0	14.41	F_1 F_2 F_3	189.23
45	"	F_1 F_3 F_4	138.23
60	"	F_2 F_3 F_4	162.81
70	"	"	126.17
75	"	"	115.25
90	"	All out	198.68
105	"	F_2 F_3 F_4	106.19
110	"	"	113.55
120	"	"	135.84
~~135~~	~~"~~	~~"~~	~~195.27~~

Table 17. Data for forward homopolymer (TDI-HEMA, blocked p-cresol) using square cell. Determination of (r / r').

Angle	c, (g/1)	Filter out	Voltmeter Reading (average)	r / r'	r / r' (average)
0	2.35	F_3	126.95	1.5025	1.5119
90		F_1 F_3 F_4	125.32		
0	4.92	F_1 F_4		1.4899	
90		All out	197.39		
0	9.46	F_4	167.61	1.5839	
90		F_1 F_2 F_4	103.15		
0	14.41	F_1 F_3	139.28	1.4712	
90		F_3 F_4	107.68		

$$r / r' = \frac{G_s / G_W * F \quad \text{square cell}}{G_s / G_W * F \quad \text{cylindrical cell}}$$

Table 18. Refractive index calculateions.

c, (g/1)	d_1	d_2	d'_1	d'_2	d	n $x10^3$
2.35	4.481	4.860	4.681	4.690	0.370	3.351
4.92	4.290	5.076	"	"	0.777	7.038
9.46	3.998	5.433	"	"	1.426	12.916
14.41	3.625	5.729	"	"	2.095	18.976

$$\Delta d = (d_2 - d_1) - (d'_2 - d'_1)$$

$$K = 9.0576 \times 10^{-3}$$

$$\Delta n = K \, \Delta d$$

$$dn / dc = 1.291 \times 10^{-3}$$

Table 19. Light scattering data for the Zimm plot.

1	2	3	4	5	6	7	8	9	10	11
θ	Solvt	Solvt	c	Soln	Soln	(6)-(3)	Soln-Solvt	$R_{\theta,u}$	$\frac{c}{R_{\theta,u}}$	$\sin^2 \theta/2$
	G_θ	$\frac{G_\theta}{G_W} F$	g/ml	G_θ	$\frac{G_\theta}{G_W} F$		$\frac{G_{180-\theta}}{G_W} - \frac{G_{180-\theta}}{G_W}$			+ 100 c
		(10^3)	(10^3)		(10^3)	(10^3)	(10^3)	(10^6)		
0	198.27	-	2.35	197.57	-	-	-	-	-	-
45	11.45	1.7794	"	175.85	54.794	53.015	36.603	278.65	8.416	0.3810
60	5.75	0.8935	"	107.70	33.559	32.666	25.364	250.66	9.355	0.4850
70	4.47	0.6947	"	167.17	26.071	25.376	21.318	235.38	9.967	0.5635
75	4.11	0.6387	"	151.56	23.636	22.997	20.233	228.73	10.25	0.6051
90	4.01	0.6232	"	129.04	20.124	19.501	19.501	212.23	11.05	0.7345
105	4.41	0.6853	"	134.13	20.918	20.233	22.997	197.18	11.89	0.8639
110	4.76	0.7397	"	141.44	22.058	21.318	25.376	192.24	12.20	0.9055
120	5.48	0.8516	"	168.10	26.216	25.364	32.666	186.88	12.55	0.9845
135	9.07	1.4095	"	121.99	38.012	36.603	53.015	181.11	12.95	1.0881

Table 20. Light scattering data fo the Zimm plot.

1	2	3	4	5	6	7	8	9	10	11
θ	Solvt	Solvt	c	Soln	Soln	(6)-(3)	Soln-Solvt	$R_{\theta,u}$	$\frac{c}{R_{\theta,u}}$	$\sin^2 \theta/2$
	G_θ	$\frac{G_\theta}{G_W} F$	g/ml	G_θ	$\frac{G_\theta}{G_W} F$		$\frac{G_{180-\theta}}{G_W} - \frac{G_{180-\theta}}{G_W}$			+ 100 c
		(10^3)	(10^3)		(10^3)	(10^3)	(10^3)	(10^6)		
0	198.27	-	4.92	-	-	-	-	-	-	-
45	11.45	1.7794	"	131.29	92.199	90.420	68.627	472.73	10.408	0.6385
60	5.75	0.8935	"	157.33	56.446	55.553	47.805	423.49	11.618	0.7420
70	4.47	0.6947	"	125.47	45.016	44.321	39.960	408.95	12.308	0.8210
75	4.11	0.6387	"	114.28	41.001	40.362	37.546	399.85	12.305	0.8626
90	4.01	0.6232	"	197.84	35.526	34.902	34.902	379.84	12.953	0.9920
105	4.41	0.6853	"	106.56	38.230	37.546	40.362	397.71	13.380	1.1214
110	4.76	0.7397	"	113.44	40.699	39.960	44.321	362.69	13.565	1.1630
120	5.48	0.8516	"	135.62	48.657	47.805	55.553	355.82	13.827	1.2420
135	9.07	1.4095	"	195.21	70.036	68.627	90.420	343.22	14.335	1.3456

Table 21. Light scattering data for the Zimm plot.

1	2	3	4	5	6	7	8	9	10	11
θ	Solvt	Solvt	c	Soln	Soln	(6)-(3)	Soln-Solvt	$R_{\theta,u}$	$\frac{c}{R_{\theta,u}}$	$\sin^2 \theta/2$
	G_θ	$\frac{G_\theta}{G_W} F$	g/ml	G_θ	$\frac{G_\theta}{G_W} F$		$\frac{G_{180-\theta}}{G_W} - \frac{G_{180-\theta}}{G_W}$			+ 100 c
		(10^3)	(10^3)		(10^3)	(10^3)	(10^3)	(10^6)		
0	198.27	-	9.46	122.82	-	-	-	-	-	-
45	11.45	1.7794	"	131.59	129.10	127.33	99.459	664.54	14.235	1.0925
60	5.75	0.8935	"	160.63	80.514	79.621	68.520	606.96	15.586	1.1960
70	4.47	0.6947	"	125.34	62.825	62.131	57.163	572.45	16.526	1.2750
75	4.11	0.6387	"	114.69	57.487	56.848	53.444	562.74	16.811	1.3166
90	4.01	0.6232	"	198.20	49.722	49.099	49.099	534.34	17.704	1.4460
105	4.41	0.6853	"	107.99	54.129	53.444	56.848	523.88	18.058	1.5754
110	4.76	0.7397	"	115.52	57.903	57.163	62.131	519.76	18.549	1.6170
120	5.48	0.8516	"	138.40	69.371	68.520	79.621	510.00	18.549	1.6960
135	9.07	1.4095	"	102.81	100.868	99.459	127.325	498.92	18.961	1.7996

Table 22. Light scattering data for the Zimm plot.

1 θ	2 Solvt G_θ	3 Solvt $\frac{G_\theta}{G_W}$ F (10^3)	4 c g/ml (10^3)	5 Soln G_θ	6 Soln $\frac{G_\theta}{G_W}$ F (10^3)	7 (6)-(3) (10^3)	8 Soln-Solvt $\frac{G_{180-\theta}}{G_W} - \frac{G_{180-\theta}}{G_W}$ (10^3)	9 $R_{\theta,u}$ (10^6)	10 $\frac{c}{R_{\theta,u}}$	11 $\sin^2 \theta/2$ + 100 c
0	198.27	-	14.41	189.23	-	-	-	-	-	-
45	11.45	1.7794	"	138.50	175.18	173.40	124.77	909.35	15.841	1.5870
60	5.75	0.8935	"	162.81	105.21	104.31	86.926	796.89	18.077	1.6905
70	4.47	0.6947	"	126.17	81.529	80.835	72.635	746.04	19.309	1.7695
75	4.11	0.6387	"	115.25	74.473	73.834	67.933	732.03	19.678	1.8111
90	4.01	0.6232	"	198.68	64.256	63.633	63.633	692.52	20.801	2.0699
105	4.41	0.6853	"	106.19	68.619	67.933	73.834	664.68	21.672	2.0699
110	4.76	0.7397	"	113.55	73.374	72.635	80.835	659.07	21.857	2.1115
120	5.48	0.8516	"	135.84	87.778	86.926	104.31	645.03	22.332	2.1905
135	9.07	1.4095	"	195.27	126.18	124.77	173.40	620.35	23.221	2.2941

ZIMM PLOT

The row scattering data (tables 14- 19) must be converted into terms suitable for calculation of molecular parameters. This is illustrated in table (19)-(22).

In column (2), the voltmeter readings (G_θ) are recorded as a function of angle for pure solvent. These readings are proportional to the intensity of scattered light. The reading at 0° measures the intensity of the direct beam. In column (3), the ratio of voltmeter readings at the indicated angles to that at 0° is given; having been first corrected for the presence of the nutral filters.

In column (4),the concentration of the polymer solutions are shown in g/ml. In columns (5) and (6) the data are tabulated for the polymer solution corresponding exactly to the measurements given for the pure solvent in columns (2) and (3). In column (7), the excess scattering arising from the polymer alone, column (6)-(3), is given. The correction for the dissymetry measurements and the values of the Rayleigh ratio for the unpolarized light are given in columns (8) and (9) respectively. In column (10), the values of $c/R_{\theta,u}$ are tabulated and column (11), shows the values of $\sin^2 \theta/2 + kc$.

Calculation of K constant.

$$K = 2\pi^2 n^2 (dn/dc)^2 / No. \lambda^4$$

$$(dn/dc) = 1.291$$

$$\lambda = 5.46 \times 10^{-5}$$

$No. = 6.023 \times 10^{23}$

$n = 1.407$

$K = 1.216 \times 10^{-5}$

Zimm Plot.

Wieght average molecular weight, Mw.

intercept at $\theta = 0$ and $c = 0$ lines = 6.6

$$\bar{M}w = \frac{1}{K * \text{intercept}}$$

$\bar{M}w = 12500$

Second virial coefficient, A_2 .

slope from $\theta = 0$ line = 9.209

$A_2 = 0.5 * \text{slope} * K$

$A_2 = 5.599 \times 10^{-5}$ ml-mole/g^2

Rdius of gyration, $(\bar{S}_z^2)^{1/2}$.

slope from $c = 0$ line = 0.9296

$S_z^2 = [(3 \lambda^4) / (16 \pi^2 n^2)] * (\text{slope} / \text{intercept})$

$(S_z^2)^{1/2} = 10.96$ nm

APPENDIX 3

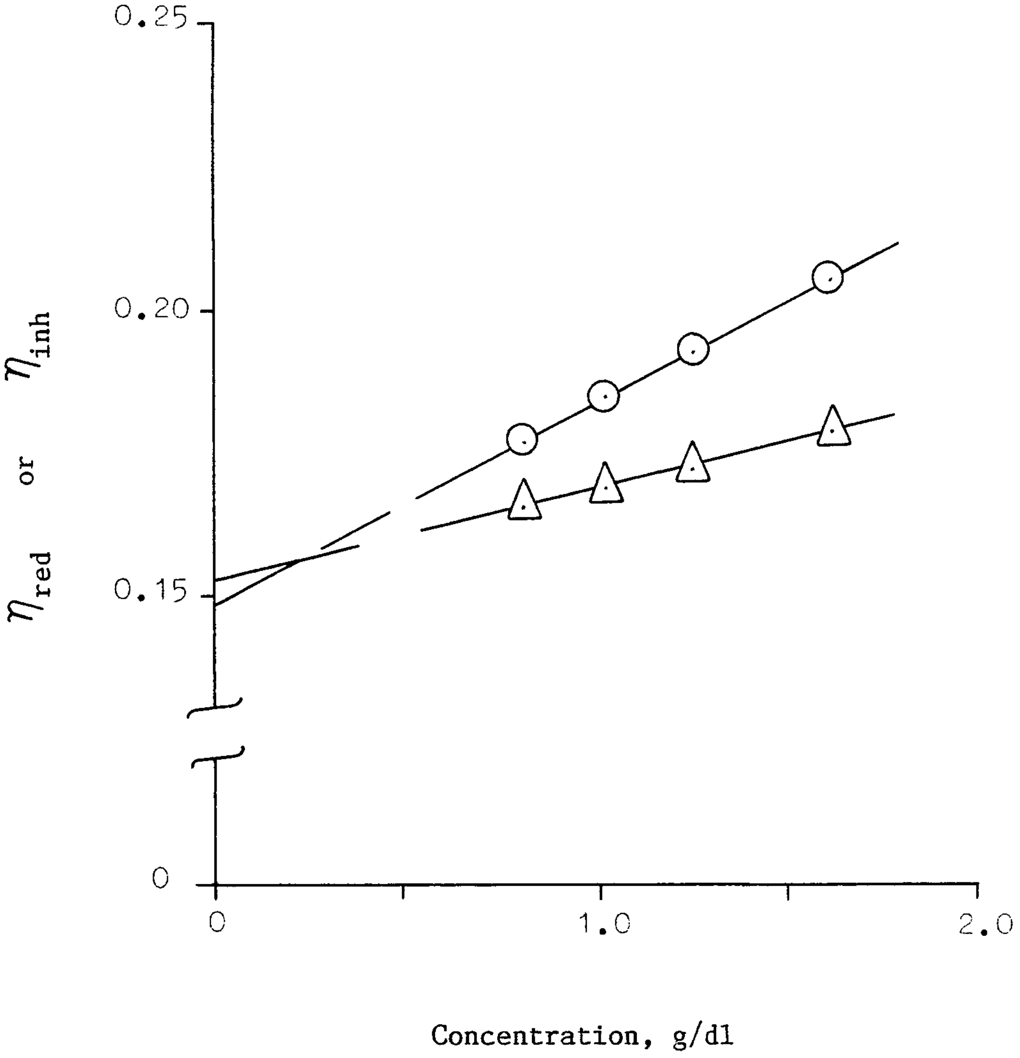
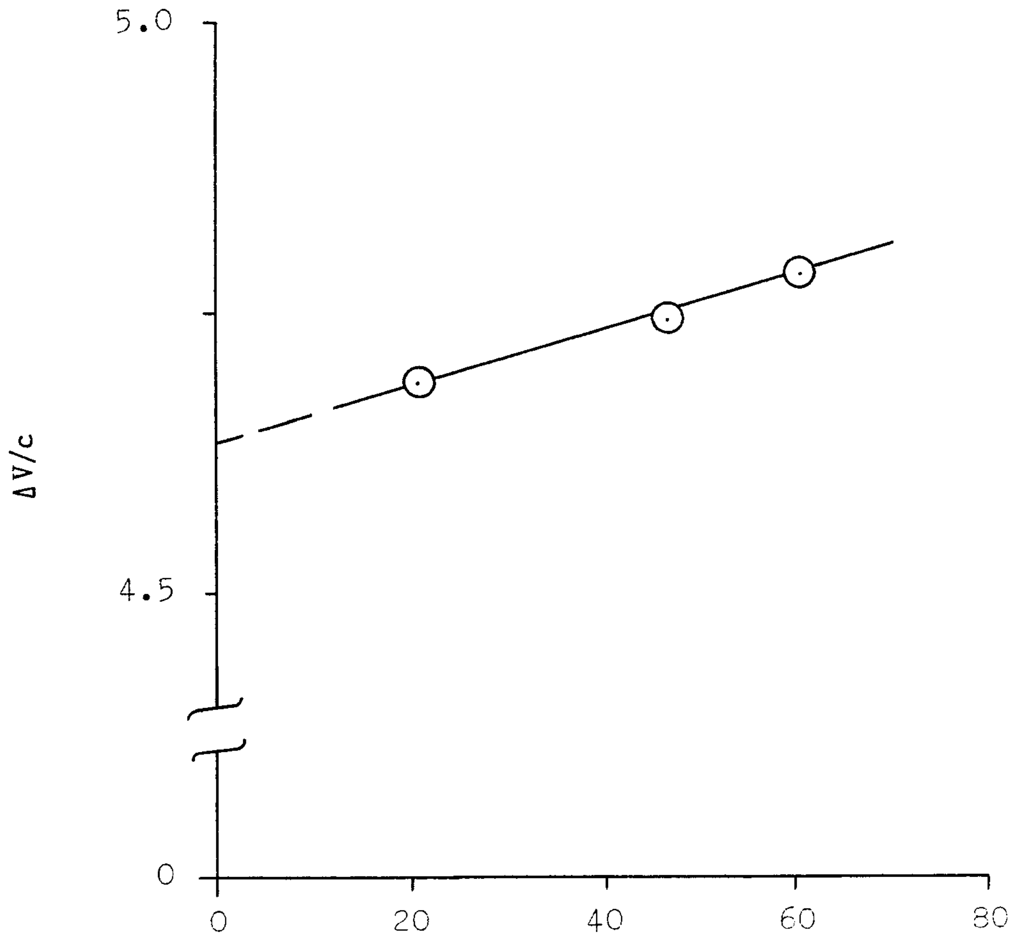
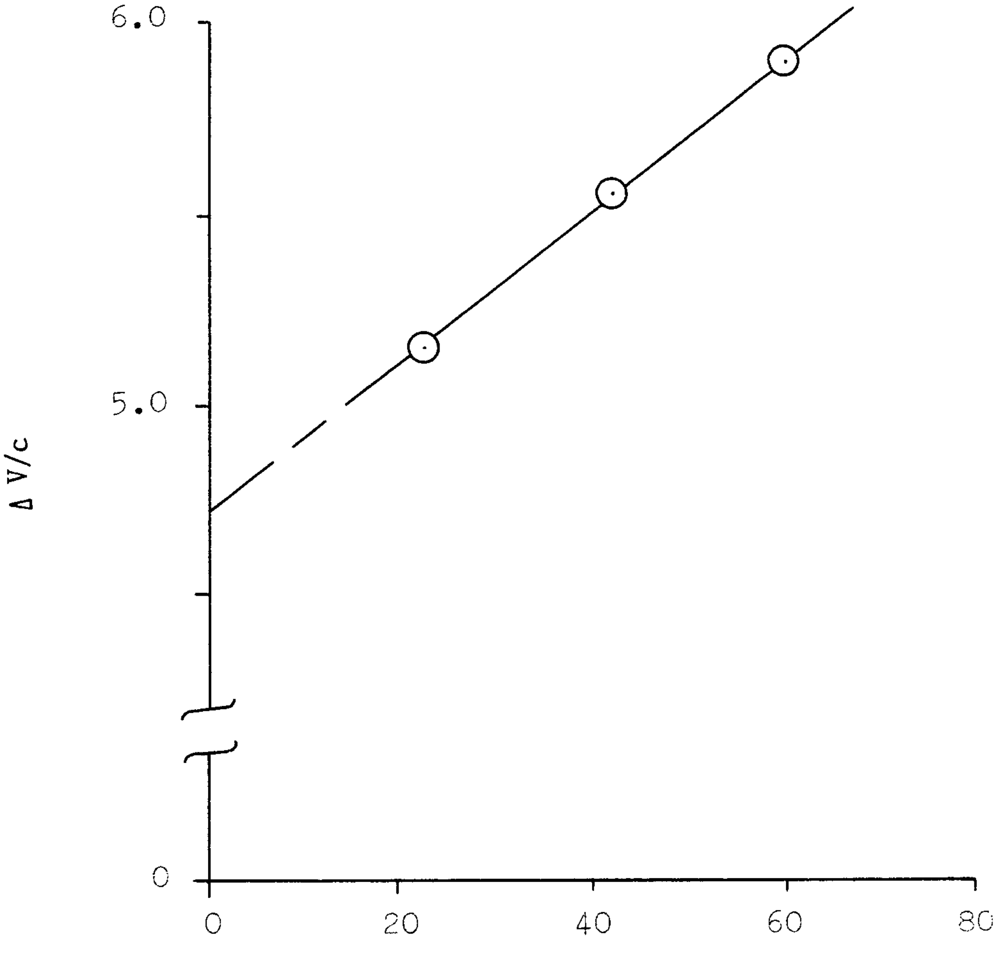


Fig. 17. Reduced (o) and inherent (Δ) viscosity-concentration curves for oligodichloroketene in acetone at 28 °C.



Concentration, g/l

Fig. 18. Plot of ΔV/c against c for sucrose octaacetate (Mw = 678.6) in acetone at 28 °C. Used in obtaining the instrument's constant.



Concentration, g/l

Fig. 19. Plot of Δ V/c against c for oligodichloroketene in acetone at 28 °C.

Table 23. Data from the measurements of dilute-solution viscosity: dichloroketene oligomer in acetone at 28 °C.

c, g/dl	t, sec	η_r	η_{sp}	η_{red}	ln η_r	η_{inh}
0	97.0	-	-	-	-	-
0.808	110.9	1.143	0.143	0.177	0.134	0.166
1.010	115.0	1.186	0.186	0.184	0.171	0.169
1.243	120.2	1.239	0.239	0.192	0.214	0.172
1.616	129.2	1.332	0.332	0.205	0.287	0.178

$[\eta] = 0.152$

Table 24. Data from vapor-phase osmometry calibration: sucrose octaacetate in acetone at 28 ^{o}C.

c, (g/1)	$\bar{V}$, (mv)	ΔV, (mv)	ΔV/c, (mv-1/g)
0	5.06	0	-
20.00	98.58	93.52	4.68
40.66	197.58	192.60	4.74
60.01	292.00	286.94	4.78

Instrument constant = K = intercept * Mw

= 4.63 * 678.6

K = 3141.9

Table 25. Data from vapor-phase osmometry: dichloroketene oligomer in acetone at 28 °C. Calibration with sucrose octaacetate.

c, (g/l)	$\bar{V}$, (mv)	ΔV, (mv)	ΔV/c, (mv-l/g)
0	5.70	0	-
21.82	117.90	112.20	5.14
41.64	236.00	230.30	5.53
59.59	356.00	350.30	5.88

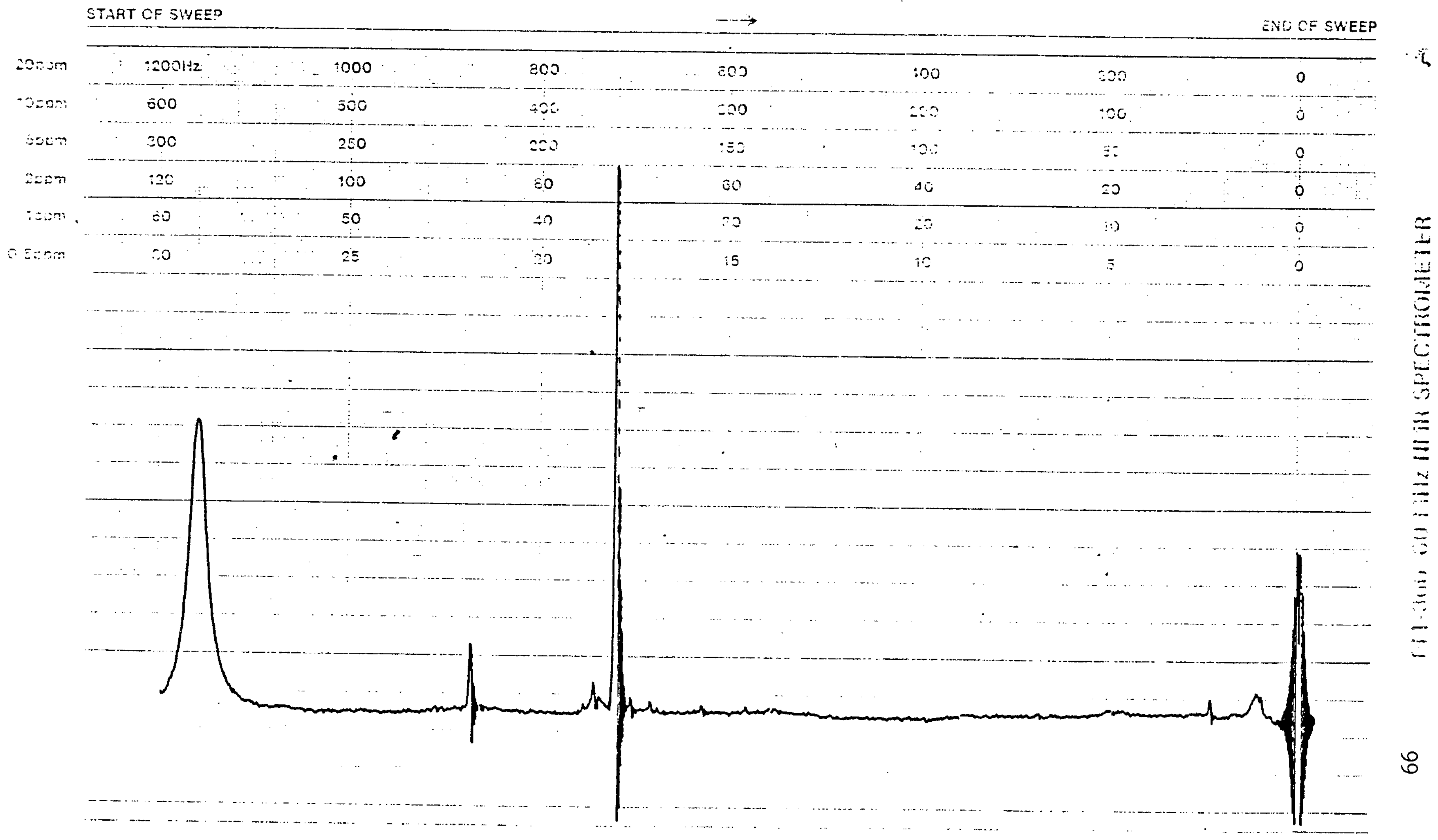
Mn = K / intercept = 3141.9 / 4.71 =

Mn = 667.1

A_2 = slope / K = 0.0196 / 3141.9 =

$A_2 = 6.2 \times 10^{-6}$ l-mole/g^2

Fig. 20. NMR spectrum of oligodigloroketene



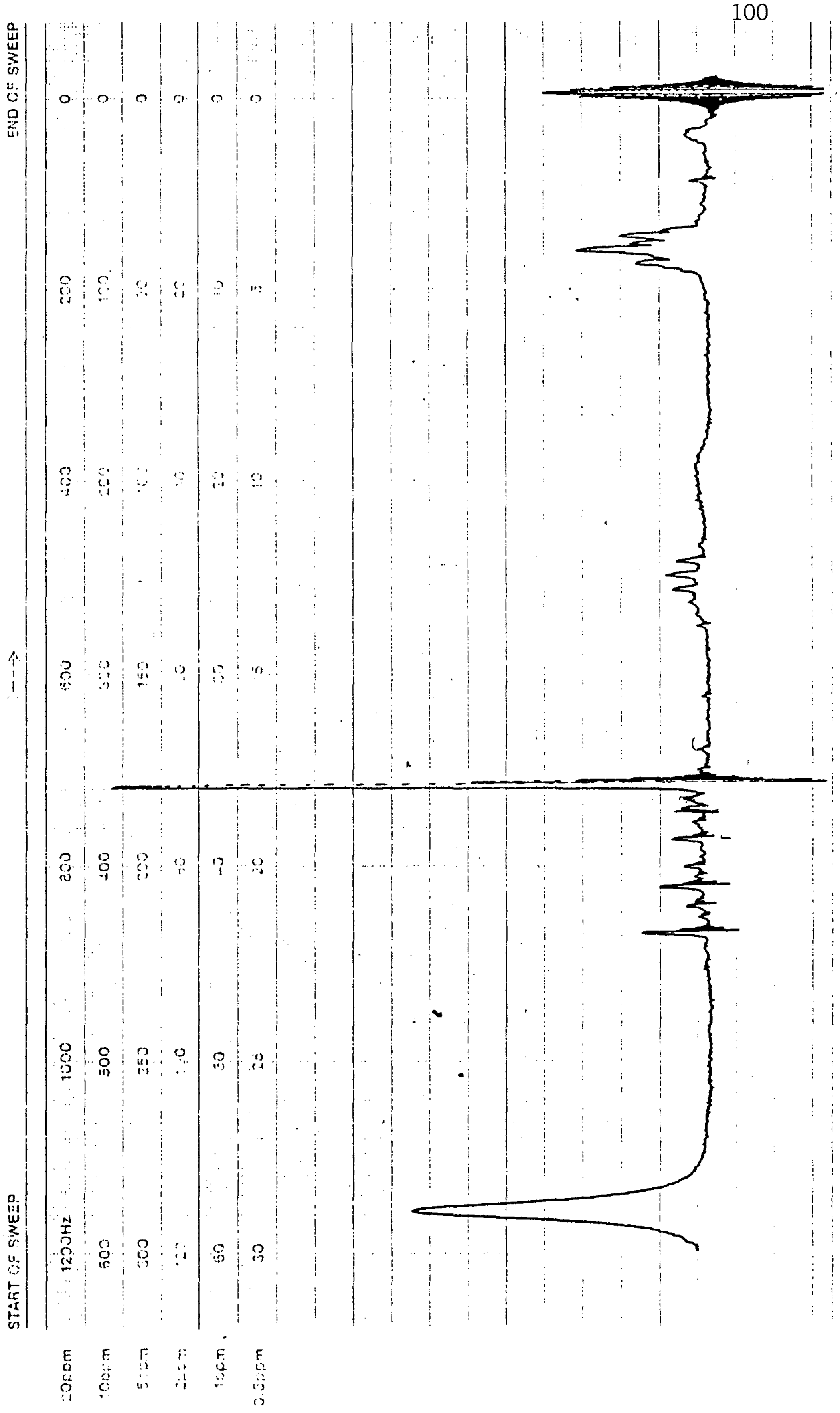
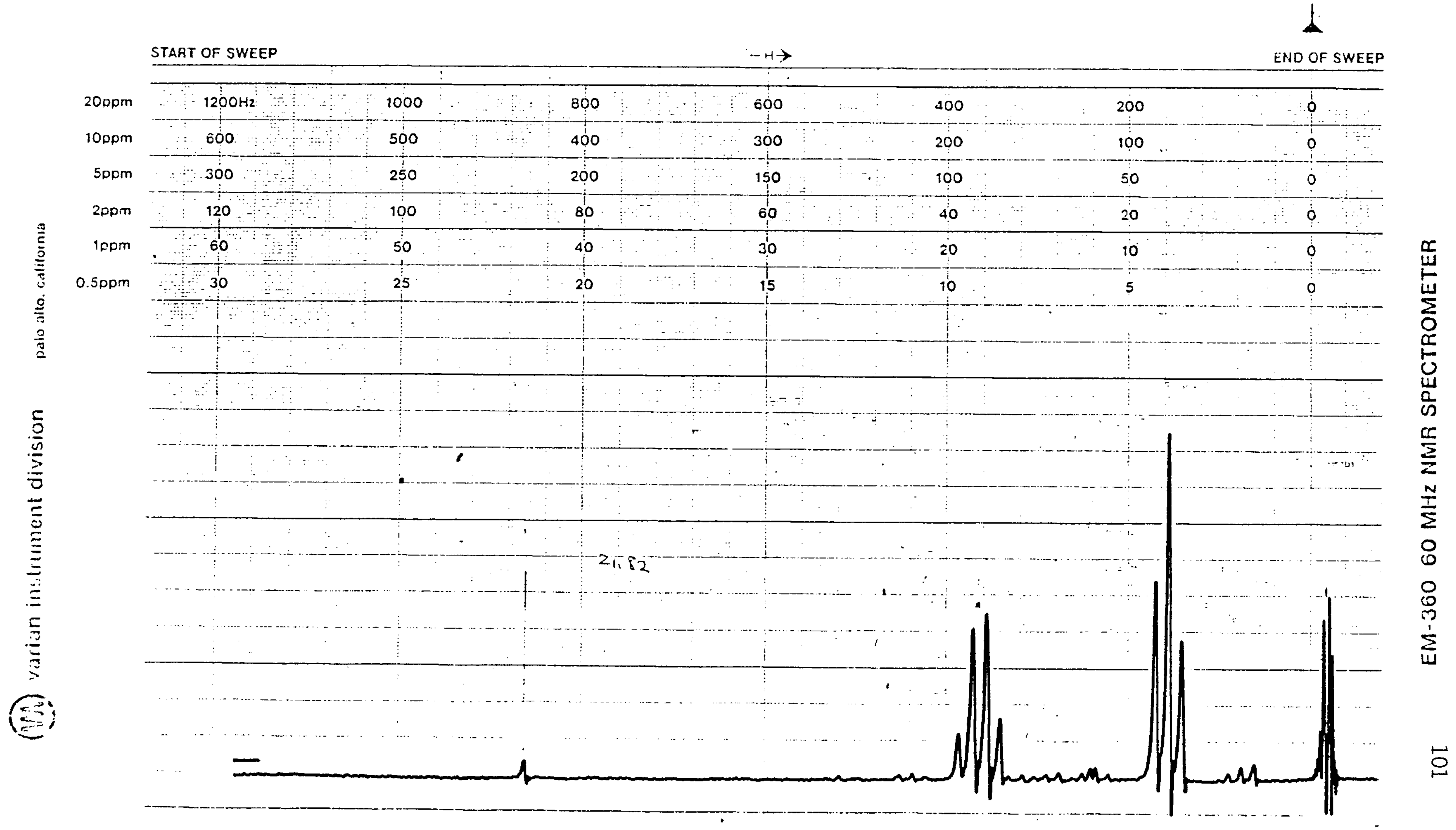


Fig. 21. NMR spectrum of triethylamine-dichloroketene

Fig. 22. NMR spectrum of triethylamoniumhydrobromide in deuterochloroform.



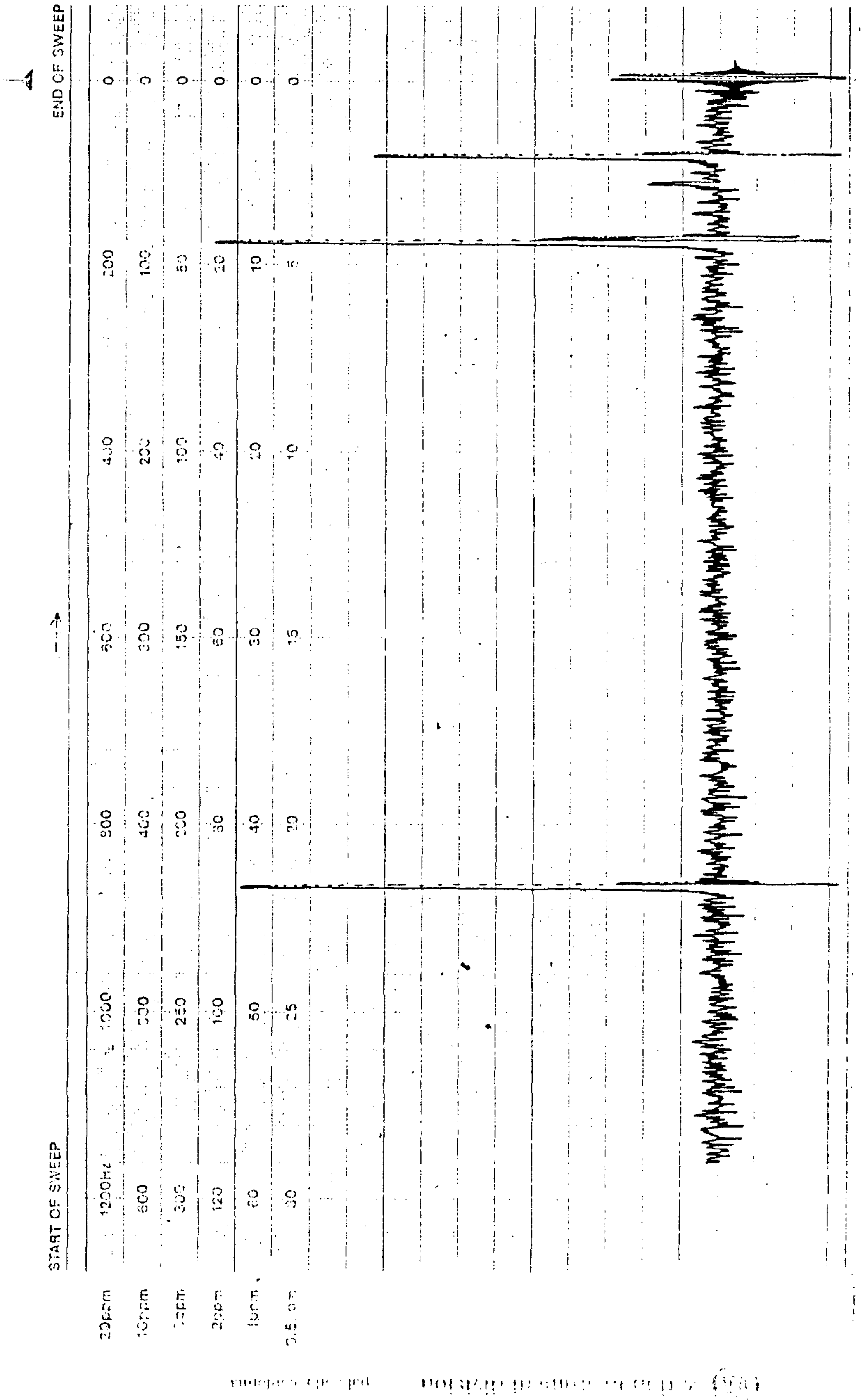
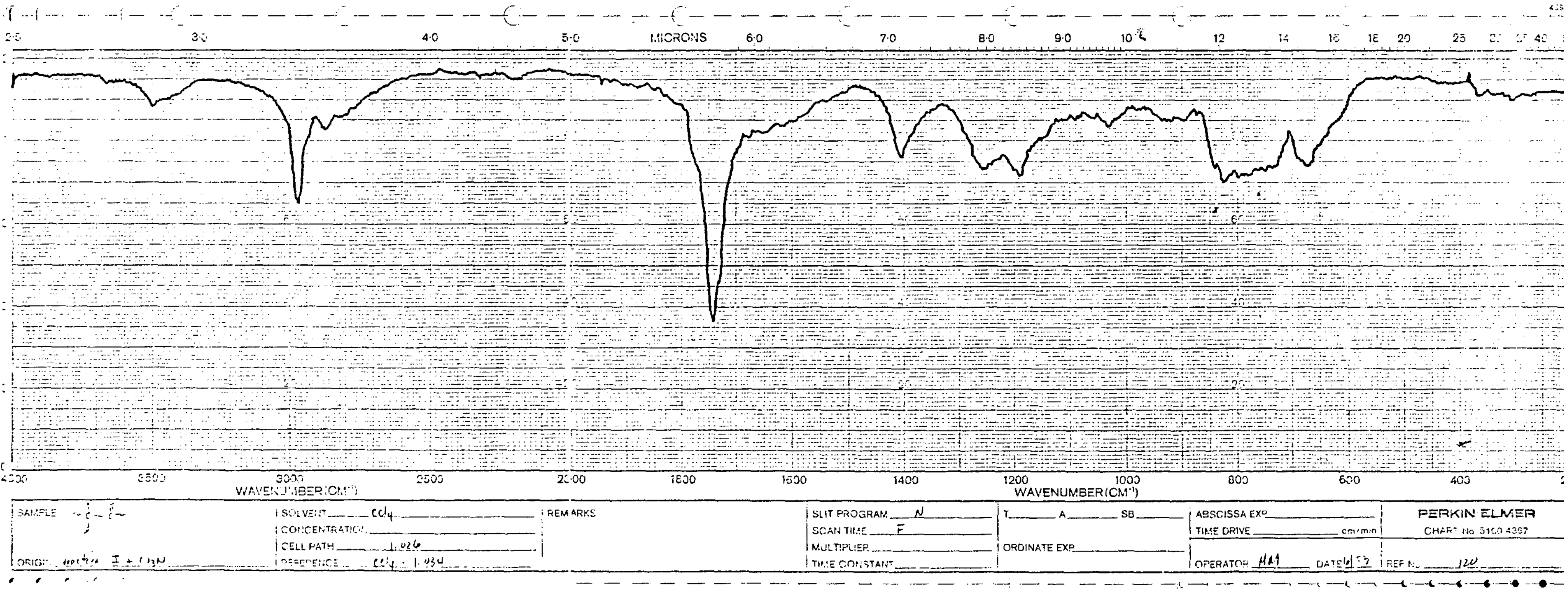


Fig. 23. NMR spectrum of deuterochloroform.

Fig. 24. IR spectrum of oligodichloroketene in carbontetrachloride.



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