

1975

Degradation of High Performance Polyimide Precursor Resins

Kumiko Takeuchi

College of William & Mary - Arts & Sciences

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<https://dx.doi.org/doi:10.21220/s2-1sde-7c96>

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DEGRADATION OF HIGH PERFORMANCE
POLYIMIDE PRECURSOR RESINS

A Thesis

Presented to

The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of
Master of Arts

by

Kumiko Takeuchi

1975

APPROVAL SHEET

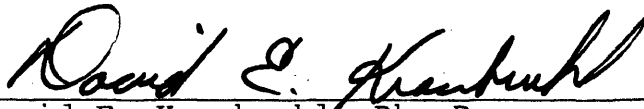
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Kumiko Takeuchi

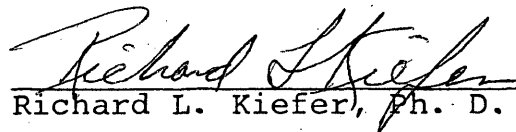
Approved, September 1975



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ACKNOWLEDGMENTS

The author wishes to express her appreciation to Professor David E. Kranbuehl, under whose guidance this investigation was conducted, for his direction, patient guidance, and criticism throughout the investigation. The author is indebted to Professors Robert A. Orwoll and David W. Thompson for their suggestions and technical assistance and to Misses M. Deborah Gibbs and Nancy C. Johnston for their technical assistance.

The author is also indebted to the Langley Research Center of the National Aeronautics and Space Administration for their preparation of the polymer samples used in this investigation.

Thanks are especially due to the author's friends in Christ for their encouragement and support with their unceasing prayers.

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ABSTRACT

The stability of a series of BTDA-DABP, BTDA-MDA, and ODPA-MDA polyimide precursor resins in DMAC was investigated by measuring their molecular weight as a function of time. The molecular weight measurements were made using a membrane osmometer. The dependence of the rate of degradation on the chemical nature of the isomeric diamine and the geometric structure about the amide linkage was examined and correlated with the basicity of the diamine. The effect of the presence of water and of the temperature in the polymer solution was also investigated and found to accelerate the rate of degradation. The degradation rate was increased three times by the addition of 1(v/v)% H₂O to the anhydrous solution and increased approximately ten times by increasing the reaction temperature from 27 to 37°C.

DEGRADATION OF HIGH PERFORMANCE
POLYIMIDE PRECURSOR RESINS

INTRODUCTION

The rapid development of modern technology has generated a need for new industrial materials of prolonged service at elevated temperatures. As a result, a distinguishing feature in the recent developments of polymer chemistry has been the considerable interest evinced in thermoresistant polymers. In the past several years synthetic polymers have found extensive use in various fields of technology, as coatings and objects intended for service at high temperature. For example, they are used in making nosepieces in rockets and artificial satellites which must withstand the enormous quantities of heat evolved as a result of friction against air at high speeds. They are also used as linings of the internal surfaces of parts which come into contact with hot exhaust gases in jet engines.

Among these polymers, polyimides are one of a growing number of aromatic and heterocyclic polymers recently developed in the search for structural stability at elevated temperature. Polyimides are distinguished by their conspicuous heat resistance and thermal stability, compared with other organic polymers used as adhesives, elastomers, structural composites, etc. Utilization of high performance polyimide polymers has not been confined to aerospace needs

only, but has been broadened by terrestrial requirements, both industrial and commercial, for electrical and thermal insulation, coatings and films, fire-resistant fibers, adhesives and elastomers, structural foams, bearing races, vacuum valve seats, and coated cookware.

It is the objective of the present study to investigate the stability or shelf life of a series of high performance polyimide polymers and their precursor resins by measuring the change in their molecular weight under a variety of storage conditions. This work will lead to an examination of the relationship of molecular weight to the fabrication characteristics and mechanical properties of these polymers in order to maximize the potential uses of these materials as structural composites, adhesives, elastomers and protection coatings.

Molecular weight is a measure of the size of a polymeric or macromolecular material. It is the single most important molecular factor governing the thermal and rheological properties of a particular polymer material. Molecular weight is used as the principle parameter in characterizing a polymer. A knowledge of the molecular weight is important in any study of the effect of varying polymerization conditions and in maintaining quality controls of materials selected for fabrication. Ultimately an understanding of the stability of a polymer and its molecular weight-property relationships is critical to the optimization of desirable fabrication characteristics with required mechanical properties.

Molecular weights of high performance polymers composed of 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) combined with isomeric diaminobenzophenone (DABP) and methylenedianiline (MDA) are determined in the amide forms of their precursors. Measurements are made on the amide form, since the imide form is often difficult to dissolve, while the amide form is soluble in many polar solvents and is much more convenient to work with. The molecular weight of the polyimides can be determined by taking into account that the amide and imide forms differ only in the absence of H₂O.

The stability of a series of BTDA-DABP and -MDA and 4,4'-oxydiphthalic anhydride (ODPA)-MDA polyimide resin precursors in dimethylacetamide (DMAC) is determined by measuring their molecular weights as a function of time. The molecular weight measurements are made using a membrane osmometer. The dependence of the rate of degradation on the chemical nature of the isomeric diamine and the geometric structure about the amide linkage is examined. The effects of the temperature and the presence of water in the polymer solution are also investigated. In addition to characterizing the relative stability of these polyimide precursor resins, the mechanism for degradation is also discussed.

HIGH PERFORMANCE POLYIMIDE POLYMERS

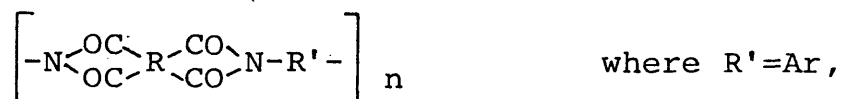
Polyimides are cyclic-chain polymers. The synthesis of polyimides can be found in the literature as early as 1908.¹ However, particular interest in the synthesis of polyimides arose only in recent years when it was found that many polymers of this class had extremely valuable properties for industrial uses in many fields.

Polyimides may be divided into two broad groups according to their structure and method of preparation:

1. Polyimides with aliphatic units in the main chain;
2. Polyimides with aromatic units in the main chain.

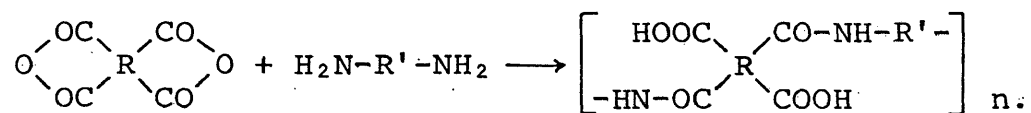
The latter polymers, characterized by their remarkable heat resistance and thermal and thermooxidative stability, are of interest in the present study (hereafter the name polyimides is used to mean the aromatic polyimides in this paper).

Polyimides, with the general formula

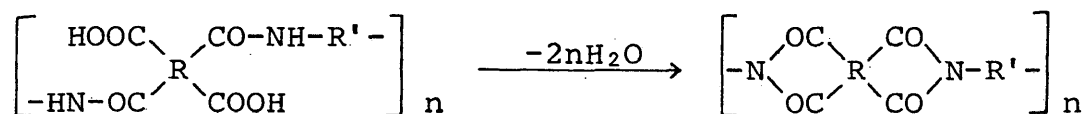


are generally synthesized by a two-stage polycondensation method which makes it possible to obtain soluble products in the first stage of the reaction. The first stage is the acylation of a diamine by a tetracarboxylic acid dianhydride in a polar solvent, such as dimethylformamide (DMF), dimethyl-

acetamide (DMAC), N-methylpyrrolidone (NMP), tetramethylurea (TMU), or dimethyl sulfoxide (DMSO), in which a polyamic acid is formed according to the equation:



Polyamic acids have been processed to give polyimide films, coatings, reinforced composites, moldings, foams, and fibers. The second stage of the reaction - the dehydrocyclization of the polyamic acid (imidization) - proceeds according to the equation:



and is carried out thermally or chemically.

Most polyimides are characterized by insolubility in organic solvents and by a very high thermal and thermooxidative stability which is of great practical significance. Polyimides are inert toward organic solvents and oils, and are also little affected by diluted acids. They dissolve in strong acids such as fuming nitric or concentrated sulfuric acid, particularly on heating. The solutions are unstable and their viscosity decreases with time due to degradation by hydrolysis. Polyimides have a relatively low stability toward alkalis and superheated steam; under the reaction of both of which they are hydrolyzed. This is due primarily to the presence of C=O groups in rings.

Thermal stability of polyimides varies with their composition. Polyimides have considerable utility in air at 200 to 300°C.² They retain usable properties at 300°C for months, at 400°C for a few hours, and withstand exposures of a few minutes to temperatures well over 500°C. This is outstanding, since most other organic polymers do not have such high thermal stability. For example, the ceiling use temperatures of naturally occurring organic polymers such as cellulose, rayon, silk, wool, and rubber are below 150°C; highly crosslinked synthetic polymers such as epoxies, urea-formaldehyde, melamine-formaldehyde, and phenol-formaldehyde resins generally start decomposing while aging in the 125 to 150°C range; aliphatic polyamides, aliphatic polyesters, and synthetic rubbers also belong in this same range of thermal stability; and silicones and perfluorinated hydrocarbons generally start decomposing after extended periods at temperatures near 250°C.²

The high reactivity of tetracarboxylic dianhydrides and diamines makes it possible to vary the chemical structure of polyimides and to investigate the corresponding changes in physical properties. High performance polyimide polymers composed of BTDA and ODPA combined with DABP and/or MDA are studied in the present paper. These polyimide polymers have been studied^{3,4} for the purpose of examining how structural variations in the diamines influence their glass transition temperatures. This is a necessary first step in developing polyimides with markedly improved processing characteristics,

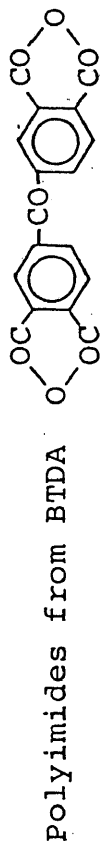
while maintaining thermal and thermooxidative stability.

Table I shows⁴ inherent viscosity (η_i) and glass transition temperature (T_g) of polyimides from BTDA combined with isomeric DABP and MDA.

In the present study, the dependence of the stability of these polyimides on the chemical nature of the diamines and geometric structure about the amide linkage is investigated under various environmental conditions in order to develop techniques for maintaining quality control and to maximize the potential uses of these materials.

Table II lists⁵ comparative properties for typical examples of the major commercial thermoplastic polymers.

TABLE I



Diamine	Polymer Structure	η_i	T_g , °C	Diamine Melting Point, °C
 m,m'-DABP		0.74	260	146 - 148
 p,p'-DABP		0.79	288	251 - 253
 m,m'-MDA		0.80	216	62 - 63.5
 p,p'-MDA		0.96	270	86 - 87.5

a) Measured for a concentration of 5mg polymer/ml DMAC at 35°C.

b) Determined by thermomechanical analysis

c) V. Guidotti and N. J. Johnston, "New Aromatic Polyamides. I. Polyamides from 4,4'-Benzophenonedicarboxylic Acid Dichloride," presented at the ACS 167th National Meeting, Los Angeles, Ca., April 6-11, 1974.

TABLE II

Typical Properties of Commercial Thermoplastic Polymers

Properties	Cellulose Acetate	Polytetrafluoroethylene	66-Nylon	Linear Polyethylene	Polyimide	Epoxy ¹⁾
Burning rate	Slow to self-exting.	None	Self-exting.	Very slow	None	Slow
Effect of sunlight	Slight	None	Discolors	Requires Protection	None	None
Effect of strong acids or bases	Decomposes	Very resistant	Attacked, acids	Resistant	Attacked, alkalis	Attacked
Effect of organic solvents	Soluble	Very resistant	Resistant	Resistant below 80°C	Very resistant	Resistant
Clarity	Transparent	Opaque	Opaque	Opaque	Opaque	Transparent
Heat-deflection (distortion) temp., °F, 264psi	111-195	250 ²⁾	150-220	110-130	650	115-550
Glass transition temp., °K	312-430	160-400	330	148	>490	-
Tensile strength, psi	1900-9000	2000-5000	9000-12000	3100-5500	10500	4000-13000
Elongation, %	6-70	200-400	60-300	20-1000	5.0-7.0	3.0-6.0
Tensile modulus, 10 ⁵ psi	0.6-4.0	0.58	1.8-4.2	0.6-1.8	4.5	3.5
Impact strength, ft-lb/in of notch	0.4-5.2	3.0	1.0-2.0	0.5-2.0	1.1	0.2-1.0
Water absorption, 1/8 in bar, 24hr, %	1.7-6.5	0.00	1.5	< 0.01	0.32	0.08-0.15

TABLE II - continued

Properties	Cellulose Acetate	Polytetrafluoroethylene	66-Nylon	Linear Polyethylene	Polyimide	Epoxy ¹⁾
Specific gravity, g/cm ³	1.22-1.34	2.14-2.20	1.13-1.15	0.941-0.965	1.43	1.11-1.40
Refractive index, n _D ²⁵	1.46-1.50	1.35	1.53	1.54	-	1.55-1.61
Dielectric constant, 1000 cycles	3.4-7.0	< 2.1	3.9-4.5	2.30-2.35	3.4	3.5-4.5
Dielectric loss, 1000 cycles	0.01-0.07	< 0.0002	0.02-0.04	< 0.0005	0.002	0.002-0.02

1) Thermosetting resin

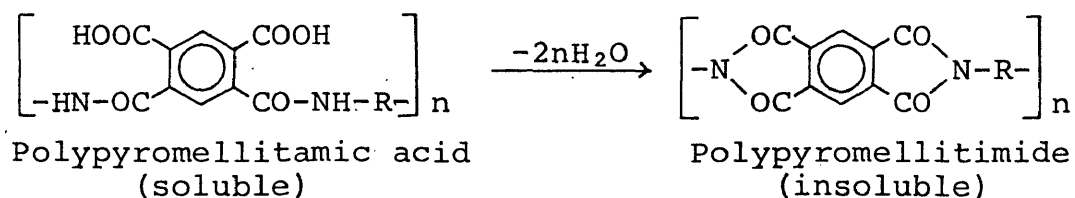
2) 66 psi

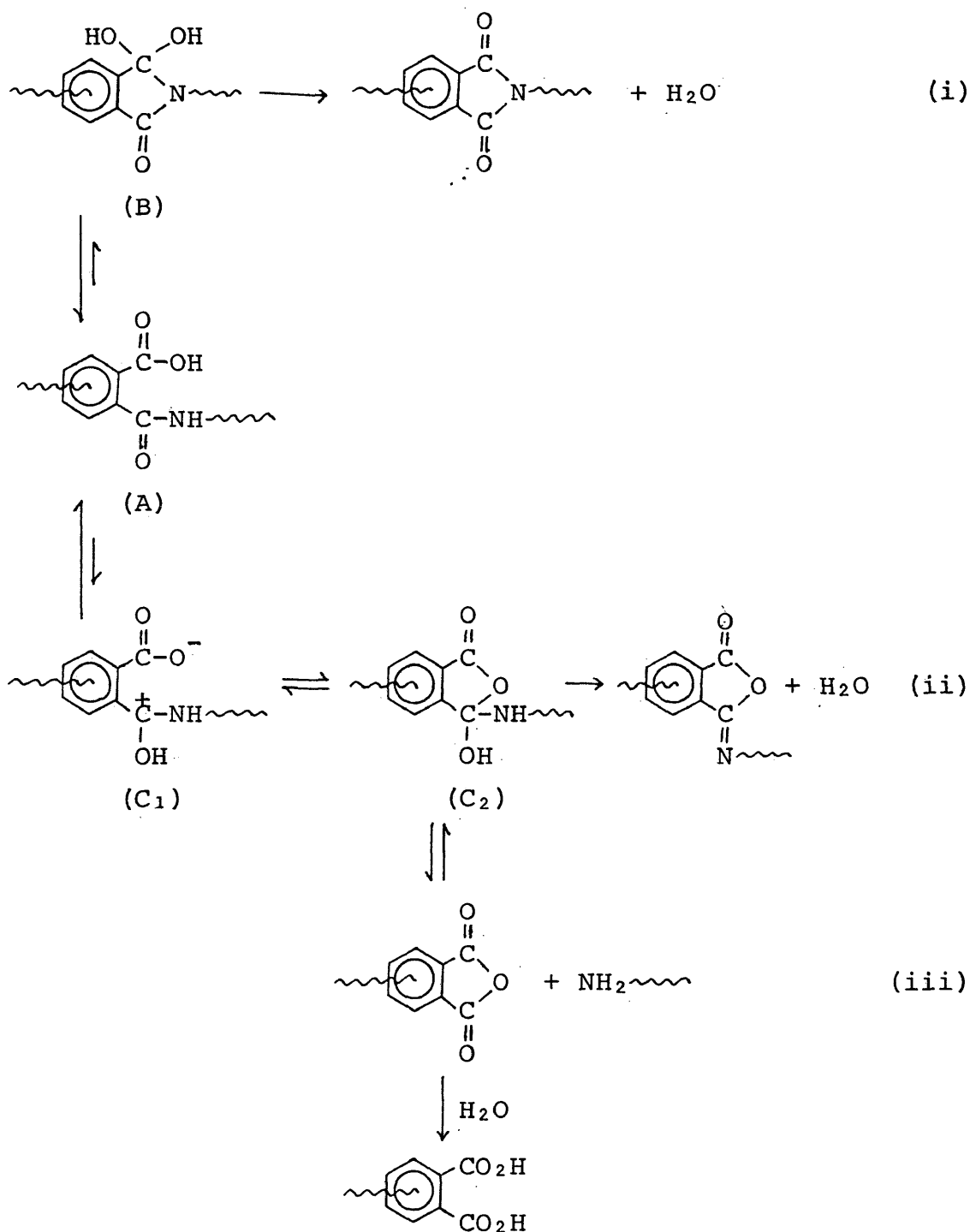
3) J. Brandrup and E. H. Immergut, eds., Polymer Handbook, Interscience, New York, 1966.

POLYIMIDE POLYMER DEGRADATION

For some time, polyimide polymers have enjoyed a significant degree of superiority over the other classes of thermooxidatively stable polymers. This superiority is, however, offset by the tremendous difficulty associated with the processing of polyimides. One of the principle problems with polyimides is degradation of their precursor resins in solution during storage and during processing to give the polyimide products.

Degradation of polyimide polymers and their precursor polyamic acids in solution has been investigated by several authors.⁶⁻¹⁰ Emphasis has been placed on higher temperatures and/or the presence of water in the polymer solutions as the main cause of polyimide degradation. Frost and Bower⁶ noted a reduction of molecular weight when polypyromellitic acid solutions were aged, and found that the rate of decline increased at higher temperatures and in the presence of water. Frost and Kesse⁷ extended these observations further and proposed a mechanism for the degradation of polypyromellitic acids in solution and during cure:





The structure B is presumed to be an intermediate in the normal curing reaction shown in equation (i). Although this reaction is slow at room temperature, it is essentially irreversible and becomes important as aging proceeds. A

second largely irreversible reaction [equation (ii)] may occur to a small extent to give the isoimide. The structure C₂ not only eliminates water to form the isoimide, but also splits out the amine group at a slow rate to give anhydride [equation (iii)]. Early in the preparation, this reversal of the condensation reaction is negligible, but in the later stages the concentration of amine group is so low that water begins to compete significantly for the anhydride so generated. If water is originally present in a considerable amount, degradation by this mechanism proceeds rapidly from the beginning. If the initial system is essentially anhydrous, however, the hydrolysis rate will be dependent upon the rate of generation of water by equations (i) and (ii), and the degradation will be less rapid.

This proposed mechanism^{7, 11} may be applicable to other polyimide polymers such as those prepared from BTDA with various diamines.

Kinetic study of polymer degradation has been reviewed by Tanford.¹² Degradation of condensation polymers by hydrolysis or by heating has been studied kinetically and found to occur by random scission. With random scission the rate at which bonds are broken is proportional to the total number of intact bonds:³¹

$$-d(N_0p)/dt = kN_0p \quad (\text{iv})$$

where N_0 is the initial number of monomer molecules, p a fraction of functional groups reacted, t time, and k the rate

constant. N_0p is the number of bonds at time t . The solution of equation (iv), with the condition that $p=p_0$ at zero time, is

$$p = p_0 e^{-kt} \quad (v)$$

At the initial stage of the degradation of a large polymer, p remains close to unity. Since p_0 is also close to unity, we can expand $e^{-kt} = 1 - kt$. Thus

$$p \cong 1 - kt \quad (vi)$$

From the well-known relationship $\bar{M}_n = M_0/(1 - p)$ (where M_0 is the contribution of each monomer unit to the polymer molecular weight) and equation (vi), a linear relation between $1/\bar{M}_n$ and t is found:

$$\frac{1}{\bar{M}_n(t)} = \frac{kt}{M_0} + \frac{1}{\bar{M}_n(0)} \quad (vii)$$

Mark and Tobolsky³² examined the degradation data obtained for the initial stages of the hydrolysis of cellulose in phosphoric acid in order to test this relationship. Their results showed a good agreement between the experiment and this theoretical treatment.

OSMOTIC PRESSURE MEASUREMENTS

1. Introduction

Osmotic pressure measurement is the most practical colligative property method used to obtain number-average molecular weights of high polymers in solution. The reason for this preference becomes evident when one compares the magnitudes of the osmotic pressure and other colligative properties such as vapor-pressure lowering, boiling-point elevation, and freezing-point depression for such a solution. The relative applicability of the colligative methods to polymer solutions is demonstrated in Table III.¹³ It is clear that direct measurement of vapor-pressure lowering in polymer solutions is not rewarding. While temperature differences of the order of $1 \times 10^{-3} \text{ } ^\circ\text{C}$ can currently be measured with considerable precision, the osmotic pressure measurement is more practical. Since the observed effect is much larger than for other methods, the measurement by osmometry is made to a higher precision. The fact that polymer solutions exhibit marked deviations from Raoult's law at quite low concentrations precludes the possibility of increasing the magnitudes of other colligative properties by using more highly concentrated solutions. Osmotic pressure measurement, however, is suitable at very high dilution because of its

TABLE III

Colligative Properties of a Solution of a
Polymer of $M=20000$ at $c=0.01\text{g/cm}^3$

Property	Value
Vapor-pressure lowering	4×10^{-3} mmHg
Boiling-point elevation	1.3×10^{-3} °C
Freezing-point depression	2.5×10^{-3} °C
Osmotic pressure	15cm solvent

large magnitude. The extrapolation to infinite dilution can be carried out with a certain degree of assurance to obtain the number-average molecular weight, \bar{M}_n .

Osmotic pressure measurement also provides the most accurate values of the second virial coefficient, B , for polymer solutions. The second virial coefficient is useful for the characterization of the thermodynamic interactions between polymer and solvent molecules. A third possible application concerns the evaluation of solvent activities over a considerable range of polymer concentration.¹⁴

2. Theoretical Considerations

Virial Expansion

The fundamental principle and the equations of equilibrium osmometry are well known.¹³⁻¹⁷ The existence of pressure when a solution is separated from the solvent by a semipermeable membrane is thermodynamically due to the difference of the "escaping tendency" or fugacity of a given component (solute or solvent) in the solution phase and in the solvent phase. Owing to the presence of solute molecules, the chemical potential of the solvent on the solution side is lower than that of the pure solvent. Solvent flows through the membrane, from the solvent to the solution side, as a result of this chemical potential difference. However, the chemical potential can be increased by the application of pressure to the solution and equilibrium is attained when the chemical potential of the solvent, μ_1 , is identical in the two phases, that is,

$$\mu_1(p, 0) = \mu_1(p', c) \quad (1)$$

where c is the concentration of solute, p and p' are the total pressures on the solvent and solution phases, respectively, and the subscript 1 refers to the solvent. The pressure difference, $p' - p$, at equilibrium is defined as the osmotic pressure π . The change in the chemical potential of the solvent is given by

$$\begin{aligned} \Delta\mu_1 &\equiv \mu_1(p', c) - \mu_1(p', 0) \\ &= \mu_1(p, 0) - \mu_1(p', 0) \\ &= \int_{p'}^p \bar{V}_1(p) dp = \int_{p'}^{p' - \pi} \bar{V}_1(p) dp \end{aligned} \quad (2)$$

The latter equality follows from the relation that the partial derivative $\partial\mu_1(p, 0)/\partial p$ is equal to the partial molar volume of the solvent $\bar{V}_1(p)$. For a dilute solution, \bar{V}_1 is nearly equal to the actual molar volume V_1 and is virtually independent of the pressure, certainly for the small pressure changes encountered in osmotic pressure. Thus, equation (2) becomes

$$\pi V_1 \cong -\Delta\mu_1 \quad (3)$$

or, in terms of the activity, a_1 , of the solvent

$$\pi V_1 \cong -RT \ln a_1 \quad (4)$$

where R is the gas constant in liter atmosphere degree⁻¹mole⁻¹ and T the absolute temperature. When the solution is sufficiently dilute, Raoult's law is obeyed and the activity a_1 is approximately equal to the mole fraction n_1 of the solvent.

Since n_1 is also very near unity

$$- \ln a_1 = - \ln n_1 = - \ln(1 - n_2) \cong n_2 \cong cV_1/M \quad (5)$$

where n_2 and M are the mole fraction and molecular weight, respectively, of the solute, c is the solute concentration in mass per unit volume of the solution, and V_1 is the molar volume of the solvent. At infinite dilution the approximations involved in equations (3) and (5) vanish and we obtain as a precise limiting law

$$\left(\frac{\pi}{c}\right)_0 = \frac{RT}{M} \quad (6)$$

which is well known as the van't Hoff's limiting law for osmotic pressure.

For a mixture of macromolecules with molecular weights M_2, M_3, \dots, M_i , present at concentrations c_2, c_3, \dots, c_i ,

$$\pi_i = RT \frac{c_i}{M_i} \quad (7)$$

Summing over i , we may replace $\sum_i \pi_i$ by π since each solute molecule contributes independently to the osmotic pressure.

Then

$$\pi = RT \sum_i \frac{c_i}{M_i} \quad (8)$$

and equation (6) becomes

$$\left(\frac{\pi}{c}\right)_0 = RT \frac{\sum_i c_i/M_i}{\sum_i c_i} \quad (9)$$

where $c = \sum_i c_i$ is the total macromolecular concentration.

Since c_i is proportional to $N_i M_i$, where N_i is the number of moles of the i th solute, equation (9) becomes

$$\left(\frac{\pi}{c}\right)_0 = RT \frac{\sum_i N_i}{\sum_i N_i M_i} = \frac{RT}{\bar{M}_n} \quad (10)$$

Thus, osmotic pressure is a measure of the number-average molecular weight, \bar{M}_n .

For an ideal solution obeying Raoult's law at all concentrations, using equation (4)

$$\begin{aligned} \frac{\pi}{RT} &= -\frac{1}{V_1} \ln(1 - n_2) \\ &= \frac{1}{V_1} \left(n_2 + \frac{n_2^2}{2} + \frac{n_2^3}{3} + \dots \right) \\ &\cong \frac{1}{M} c + \frac{V_1}{2M^2} c^2 + \frac{V_1^2}{3M^3} c^3 + \dots \end{aligned} \quad (11)$$

The last approximate equality of equation (11) holds because $n_2 \cong cV_1/M$ for dilute solutions. The exact equation¹⁷ is

$$\frac{\pi}{RT} = \frac{c}{M} + (V_2 - \frac{V_1}{2}) \frac{c^2}{M^2} + (V_2^2 - V_1 V_2 + \frac{V_1^2}{3}) \frac{c^3}{M^3} + \dots \quad (12)$$

Since the molecules of the two components in an ideal solution are alike in size, $V_1 = V_2$ and, therefore, equation (11) again follows.

It is obvious that osmometry is not only a suitable method for molecular weight determination, but also for the study of nonideality and the determination of the virial coefficient. McMillan and Mayer¹⁸ have shown from statistical-

mechanical considerations that the osmotic pressure for real solutions can, in general, be written as a power series in terms of c , known as a virial expansion:

$$\frac{\pi}{RT} = \frac{1}{M} c + Bc^2 + Cc^3 + \dots \quad (13)$$

The second virial coefficient B depends upon the interaction between a pair of solute molecules, the third virial coefficient C involves the interaction of three solute molecules, etc. Since the interactions between solute molecules are influenced by the presence of solvent molecules, the virial coefficients depend upon the nature of the solvent as well as that of the solute.

Equation (13) is also expressed in the alternate form

$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_0 [1 + \Gamma_2 c + \Gamma_3 c^2 + \dots] \quad (14)$$

where $(\pi/c)_0 = RT/M$ (van't Hoff's limiting law) and $\Gamma_2 = BM$, $\Gamma_3 = CM$, etc.

Theory of B and C

McMillan and Mayer¹⁸ studied a pair of solute molecules in the solution that are separated by a distance R , where the reversible work is necessary to bring the two molecules from an infinite separation to a separation R . They showed the dependence of the second virial coefficient on R is

$$B = - \frac{N_a}{2M^2} \int_0^{\infty} \left[\exp\left(-\frac{\omega(R)}{kT}\right) - 1 \right] 4\pi R^2 dR \quad (15)$$

where N_a is the Avogadro's number, $\omega(R)$ the average potential energy of a pair of solute molecules in the solution, and k Boltzmann's constant. Using this relation for model solute molecules having simple geometrical shapes such as hard spheres of diameter D where

$$\begin{aligned}\omega(R) &= \infty & R < D \\ \omega(R) &= 0 & R \geq D\end{aligned}\tag{16}$$

They obtained equation (17) upon substitution of equation (16) into (15)

$$B = 2\pi N_a D^3 / 3M^2 = 4v/M\tag{17}$$

where $v = (\pi/6)D^3 N_a / M$ is the specific volume of the solute.

Zimm¹⁹ has derived the following relation for long rigid rods of length L and diameter D ($L/D > 10$):

$$B = \pi N_a DL^2 / 4M^2 = Lv/DM\tag{18}$$

It is interesting to note that B is inversely proportional to M for hard spheres, but independent of M for rigid rods, since L/M is constant for rods of a fixed diameter.

Flory and Huggins independently treated a more general case of coiling polymer molecules in dilute solution and performed statistical calculations based upon a lattice model for the solution.¹⁴ Their expression for the second virial coefficient given by the lattice-model treatment is

$$B = (\bar{v}^2/V_1)\psi_1(1 - \frac{\theta}{T})\tag{19}$$

where \bar{v} is the partial specific volume of the polymer, ψ_1 an entropy parameter, and θ the Flory theta temperature. This relation predicts that B for a coiling molecule will be independent of molecular weight, but will be temperature dependent.

Later treatments by a number of workers^{20,22} have made corrections to the assumption of all lattice-model treatments in which small segments of the polymer molecules would be uniformly distributed throughout the solution. This has led to an expression of the form

$$B = (\bar{v}^2/V_1)\psi_1(1 - \frac{\theta}{T})F(z) \quad (20)$$

where the average potential energy $\omega(R)$ was considered as a function of the distance R between the centers of gravity of the two molecules, suitably averaged over all the possible conformations of the two molecules. z is given by

$$z = 2(3/2\pi)^{3/2}(\bar{v}^2/N_a V_1)(M/\bar{L}_0^2)^{3/2}\psi_1(1 - \frac{\theta}{T})M^{1/2} \quad (21)$$

\bar{L}_0^2 being the mean-square distance between the ends of the polymer molecule in the unperturbed state.

The difference between equations (19) and (20) is the factor $F(z)$. Nevertheless, both agree that B vanishes when $T=\theta$, thus providing an experimental method for the evaluation of the theta temperature. Furthermore, all of the dilute-solution treatments have indicated that the factor $F(z)$ is unity at the theta temperature and decreases monotonously with increasing z which causes B to decrease slowly with

molecular weight. ψ_1 may also be evaluated from data for several temperatures in the vicinity of the theta temperature by extrapolating the function $B/(1 - \theta/T)$ to $T=\theta$.

The third virial coefficient C can be expressed according to a formula similar to equation (15), but involving the coordinates and mutual potential energy of three molecules.¹⁴ For large, hard spheres of diameter D

$$C = 5\pi^2 N_a^2 D^6 / 18M^3 \quad (22)$$

so that if we set

$$\Gamma_3 = g\Gamma_2^2 \quad (23)$$

g is equal to $5/8$. In good solvents g is approximately $1/4$ for coiling polymer molecules^{2,3} and the first three terms appearing in equation (14) may be represented in the compact form

$$\pi/c = (\pi/c)_0 [1 + (\Gamma_2/2)c]^2 \quad (24)$$

Use of the Second Virial Coefficient

As indicated in the previous section, the osmotic pressure may be expressed in virial form

$$\pi/c = RT[A + Bc + Cc^2 + \dots]$$

where
$$B = \frac{\bar{V}^2}{V_1} \psi_1 \left(1 - \frac{\theta}{T}\right) F(z).$$

It is evident that the second virial coefficient B must vanish at the theta temperature. Furthermore, both theory and experiment indicate that the third coefficient C also vanishes when $T=\theta$.¹⁴ Hence, π/c is invariant at the theta temperature;

that is, at this temperature the solution exhibits "ideal" behavior over a considerable concentration range. The theta temperature represents the critical miscibility temperature for a polymer of infinite molecular weight. It is a limiting value of the critical temperature for samples of finite molecular weight. At this unique temperature the average dimensions of the macromolecules are unperturbed by the presence of the solvent.

The second thermodynamic parameter, ψ_1 , may be evaluated by interpolating values of $B/[(\bar{v}^2/V_1)(1 - \theta/T)] \equiv \psi_1 F(z)$ to $T=\theta$, at which temperature $F(z)=1$. The parameter ψ_1 is characteristic of the polymer-solvent system and indicates how rapidly the solvent-power (in other words, entropy of mixing) will change with temperature.

Membranes

The difficulties inherent in the measurement of osmotic pressure in the past and at the present can be ascribed largely to the problem of choosing the "suitable" membrane. The success of the osmotic experiment depends on the availability of a membrane through which solvent molecules pass freely, but through which solute molecules cannot pass.

A wide variety of materials has been used as the semi-permeable barrier in membrane osmometry. They fall into two classes:^{13,17} (a) nonswellable inorganic substances represented by the classical copper ferrocyanide precipitation membrane, porous glass, porous metal foils, etc.; and (b) swellable materials such as cellulose, gelatin, rubber, etc.

From the standpoint of general utility, the swellable materials are most important.

Common organic membrane materials²⁴ include: collodion, regenerated cellulose made by denitration of collodion, gel cellophane, bacterial cellulose made by the action of certain strains of bacteria, rubber, poly(vinyl alcohol), polyurethanes, poly(vinyl butyral), and polychlorotrifluoroethylene. Of these, gel cellophane is probably most widely used at present.

Armstrong,²⁵ Coll and Stross¹⁵ have described and evaluated commercially available membranes from the practical view point of their performances in various solvents and with different temperature ranges, their response time, and their permeation limit. Coll and Stross have concluded in their paper that full adequate cellulose-based membranes may be available for most applications at room temperature, while for work above 100°C these membranes must be considered as only "potentially adequate." Tables IV and V show the solvent performance, response time, and molecular-weight-range limitations of commercially available membranes for hi-speed osmometers by Armstrong.²⁵

3. Experimental

Apparatus

Osmotic pressure measurements were made with a Hewlett-Packard Mechrolab Membrane Osmometer, Model 502. The design of the instrument is shown in Figure 1 and can be described briefly as follows.^{13, 15, 26} The membrane, which separates

TABLE IV

Solvent Performance of Commercially Available Membranes in Hi-Speed Osmometers¹⁾

Solvent and Temperature	Membrane Type						
	07	08	B-19	B-20	600-D ²)	450-D ²)	300-D ²) 600-W 450-W
H ₂ O and buffered systems, 5-25°C	1	1	3	3	1	1	1
Toluene, 30-40°C	3	3	1	1	3	3	3
Benzene, 20-25°C	2	3	1	1	2	2	3
Dimethylformamide, 55-80°C	1	2	1	1	3	3	3
Dimethylsulfoxide	None of these membranes will perform in this solvent						
Tetrahydrofuran, 20-25°C	2	3	1	1	3	3	3
Cyclohexane, 25-40°C	2	2	1	1	1	1	2
Dimethylacetamide, 55-65°C	2	2	1	1	3	3	3
Acetone, 20-25°C	2	3	1	1	3	3	3
Methyl ethyl ketone, 20-25°C	2	3	1	1	3	3	3
Fluoro alcohols, 25-40°C	2	3	1	1	2	2	3
Alcohols through C ₄ , 20-35°C	2	2	2	2	2	2	2
Decalin, 110-130°C	1	2	1	1	2	2	2
o-Dichlorobenzene, 100-130°C	2	2	1	1	2	2	2
o-Chlorophenol, 90-120°C	1	1	1	1	2	2	2
m-Cresol, 90-110°C	1	1	1	1	2	2	2

1) 1, Not recommended; 2, satisfactory; 3, excellent.

2) Recommended for Mechrolab osmometers only.

TABLE V

Response Time and Molecular-Weight-Range Limitations of
Commercially Available Membranes for Hi-Speed Osmometers

Type of Membrane	Response Time (min)	Molecular- Weight Range
Gel cellophane 600-W	10-20	15000 and up
Gel cellophane 450-W	7-10	30000 and up
Gel cellophane 600-D	15-45	10000 and up
Gel cellophane 450-D	10-20	15000 and up
Gel cellophane 300-D	5-12	100000 and up
S & S 08	7-10	20000 and up
S & S 07	7-10	80000 and up
S & S B-19	7-15	20000 and up
S & S B-20	10-20	7000 and up

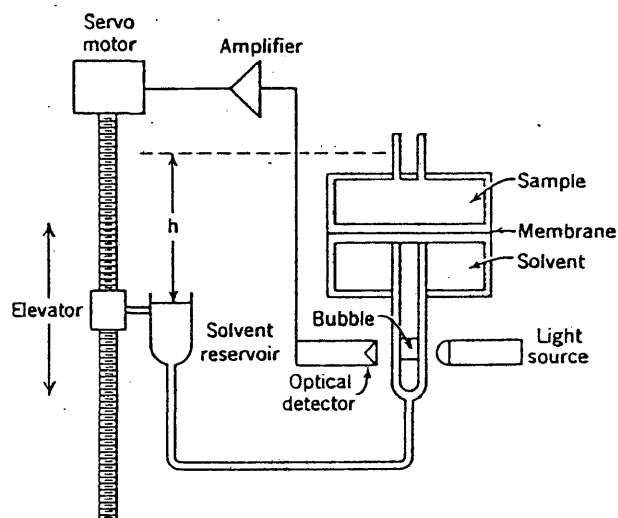


Figure 1. Sketch of the essential components of the Mechrolab membrane osmometer. In a glass capillary in the solvent chamber, below the horizontal membrane, a bubble of air is trapped. Motion of this bubble as solvent flows through the membrane is detected photoelectrically and provides a signal to a servomechanism. The height of the reservoir of solvent is adjusted to provide the hydrostatic pressure required to maintain the bubble at its original position. This is just the osmotic pressure.

the solvent (below) and solution compartments, is clamped horizontally between two well-thermostated, grooved, stainless-steel plates. Both compartments are open to the atmosphere, eliminating all valves except that draining the solution compartment. Attached to the solvent compartment is a fine capillary tube extending downward, which is connected through a flexible tube to a solvent reservoir in an elevator-tower at the left. A small air bubble is introduced into this capillary, before the osmometer is assembled, and placed so that its meniscus is between a light source and an optical detector. In operation, any minute movement of the meniscus of the bubble in response to solvent flow through the membrane is monitored by the optical detector. The detector generates a signal which operates a servo system moving the solvent reservoir to the point where the meniscus is restored to its original position. The difference in reservoir levels of solution and pure solvent in the upper compartment is the osmotic pressure of the solution. According to the manufacturer, the optimal repeat accuracy of the read pressure is of the order of 0.02 cm and the total temperature range extends from 5 to 130°C. Any thin and flexible membrane can be used.

Membranes

ArRo Laboratories, Inc. Gel Cellophane Type 450-D and 600-D were used for osmotic pressure measurements. The membranes were conditioned according to the instruction by ArRo Laboratories, Inc. (see Table VI),²⁷ that is, membranes were kept in the prescribed solution for conditioning for, at least,

TABLE VI

Membrane Conditioning Procedures:
Time in Hours - For Temperatures 10 to 120°C

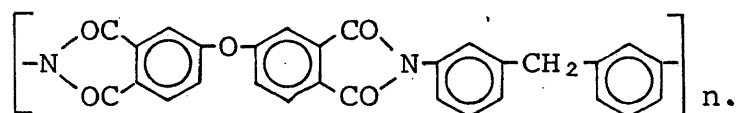
Membrane Type	50%EtOH 50%H ₂ O	100% EtOH	75%EtOH 25%Solv.	50%EtOH 50%Solv.	75%Solv. 25%EtOH	100% Solvent
300-D	2	6	4	2	4	4
450-D	2	6	4	2	4	4
600-D	2	6	4	2	4	4
450-W	2	6	4	2	4	4
600-W	2	6	4	2	4	4
08 S&S	2	2	2	2	2	2
07 S&S	2	2	2	2	2	2

the conditioning time specified. Degassing was carried out by heating the membranes in the degassed solvent at 70-80°C for three hours just before installation.

Materials

Polyimides, BTDA-p,p'-DABP, BTDA-m,m'-DABP, BTDA-p,p'-MDA, BTDA-m,m'-MDA, and ODPA-m,m'-MDA, were prepared at NASA Langley Research Center, Hampton, Va., and received as films, powder, or 15-20% DMAC solutions. The structure and physical properties of polyimides from BTDA are shown in Table I.

The structure of ODPA-m,m'-MDA is:



Solvents and Sample Solutions

Toluene (Fischer Scientific Co., Certified ACS) and Dimethylacetamide (DMAC) (Burdick and Jackson Laboratories Inc.) were used as solvents, as received, without any further purification. These solvents were degassed by boiling for about 10 minutes,²⁷ just before the installation of a new membrane. Anhydrous DMAC was obtained by distillation, under nitrogen, after being dried with calcium hydride (b.p. 164-166°C). When dried DMAC was used, the sample stack of the osmometer was connected to a glass tube of a drierite during stand-by until next measurement.

Standard polystyrene (Pressure Chemical Co.) solutions were made up by weight in toluene and DMAC, in concentrations ranging from 1.0 to 8.0g/l.

Polyimide solutions were made up, under nitrogen, by weight in DMAC, in a concentration range from 1.0 to 8.0g/l. They were kept in a thermostated water-bath during the course of the experiments.

Procedure

Osmotic pressure measurements were made by first placing pure solvent in both sides of the osmometer compartments and recording the counter-reading of the solvent, then flushing out and filling the sample side with one of the solutions and recording the counter-reading of the solution. The reference solvent height was checked between solutions by flushing and refilling the sample side with pure solvent.²⁸ The reference value is the average of the counter-readings of solvent before and after the measurement of each solution. The osmotic pressure for each solution is then given directly as the hydrostatic pressure difference between solvent and solution. All measurements were made at a temperature of 28°C.

Operational Test

The selection and pretreatment of the membrane is the most important step in obtaining meaningful osmotic data. Ideally, a semipermeable membrane should be absolutely impermeable to the solute molecules, while allowing fairly rapid permeation and transfer of the solvent. However, existing membranes only approximate ideal semipermeability and the chief limitation of the osmotic method is the diffusion of low-molecular-weight species through the membrane.¹³ Theoretical treatments of the diffusion of low-molecular-weight

species through the osmotic membrane have been reviewed by Elias.²⁹ Theory and experiment show that the apparent osmotic pressure is always less than the true osmotic pressure and falls with time. Staverman and coworkers³⁰ have shown that the osmotic pressure measured with a leaking membrane is always less than the theoretical equilibrium pressure and, hence, molecular weights based on such measurements come out too high.

The same tendency reported by Elias²⁹ was observed in the present experiments using Gel cellophanes 450-D and 600-D. Upon using approximately ideal semipermeable membranes, it was observed that the osmotic pressure first reached the maximum, in starting with measurement from "below" which depends upon the starting condition, and then decreased with time. Sometimes the maximum was not observed, especially with polyamic acid solutions. It should be noted that the rate of equilibration has varied with the performance of each membrane, the starting condition, and any other conditions inherent to the osmometer and the membrane used.

The correct osmotic pressure was sought by measuring the apparent osmotic pressure at 20, 30, 40 minutes and/or longer time-intervals using standard polystyrene solutions, since, in addition to the factors mentioned above, equilibrium was not reached within the time-interval stated in the osmometer operation manual nor in Table III (that is, 10-20 minutes). The equilibrium was reached within 30 to 40 minutes after the sample compartment was filled with each new sample solution and the difference in counter-readings between the 30 and 40

minute-intervals was, in most cases, less than ± 0.05 cm. Using the average value for solvent, before and after the measurement of each solution, seemed to minimize the drift of the osmotic pressure reading with time. Using both standard polystyrenes and polyimide precursor resins, measurements after 40 minutes were found to vary little.

Figure 2 and Table VII show a part of the results obtained from the test. The experimental value of the polystyrene with $\bar{M}_n=4800$ was somewhat lower than the calculated \bar{M}_n from \bar{M}_w/\bar{M}_n ratio. This, however, was not an unexpected result, since the molecular weight is below the molecular-weight-range limitation of the membrane (see Table V). The experiments No. 4 and 5 in Table VII showed that the membrane is relatively stable during the course of experiments for at least a month. After analyzing a considerable amount of data, the author determined that the measurement at the 40 minute-equilibration gave the most accurate reading of the osmotic pressure.

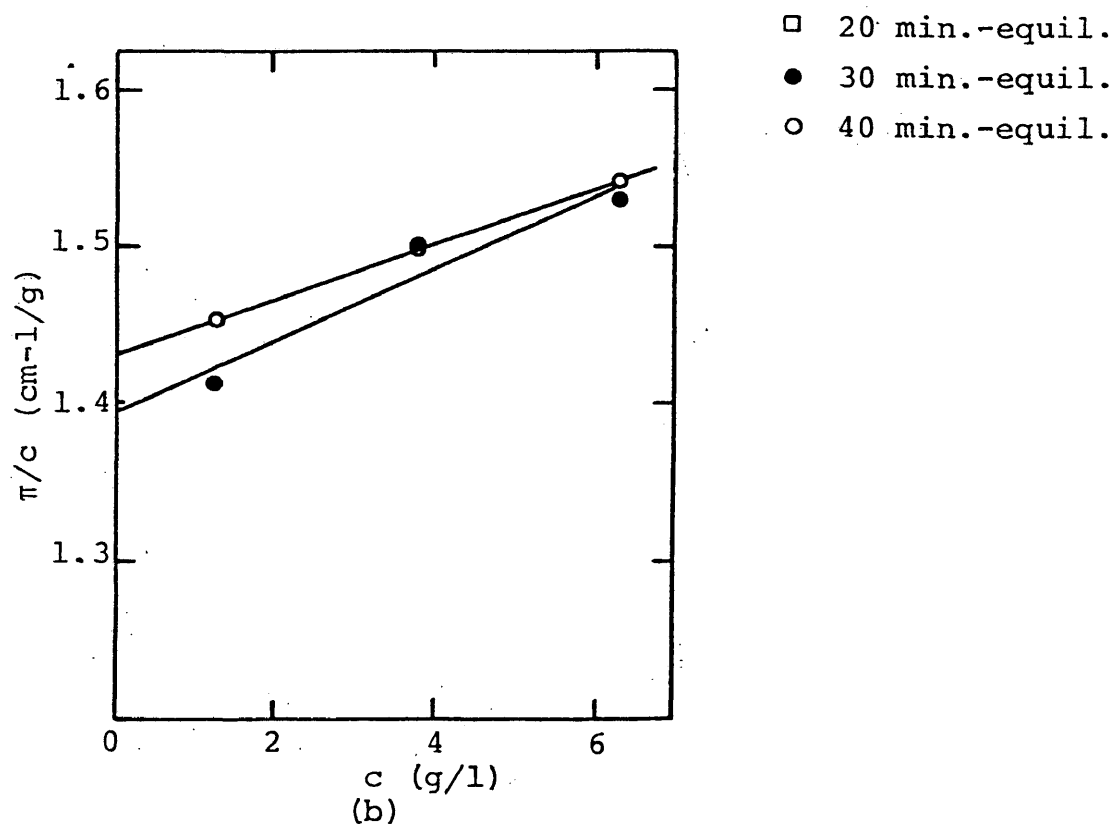
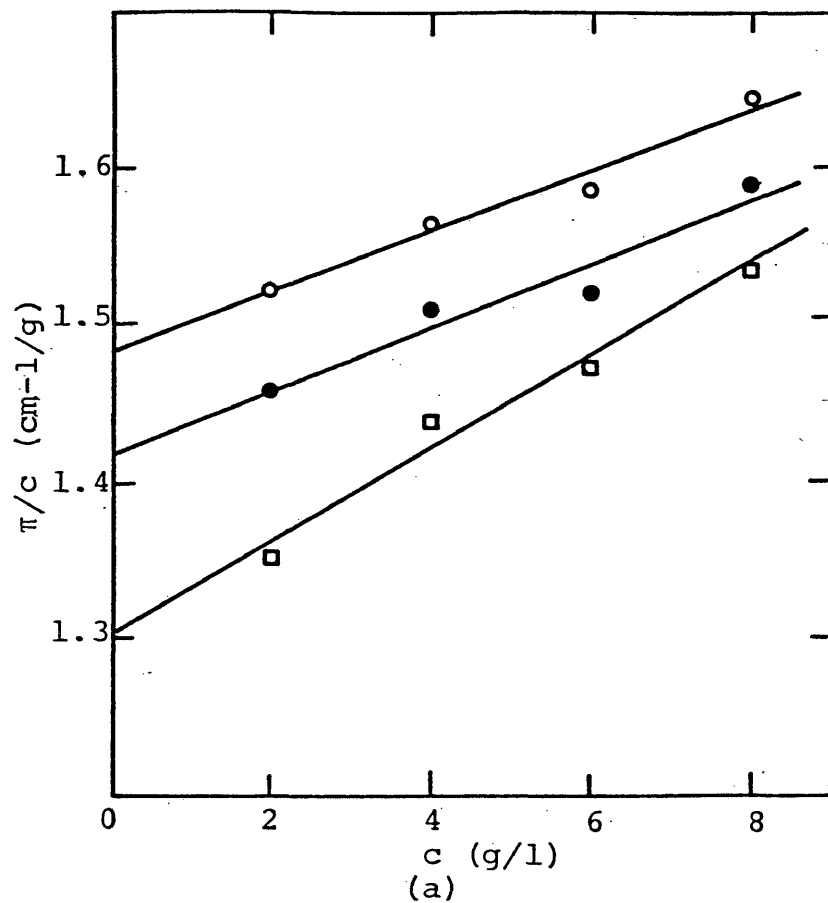


Figure 2. Time dependence of osmotic pressure for standard polystyrene ($M_w=19800$; $M_w/M_n \leq 1.06$) using Gel cellophanes 450-D in toluene (a) and 600-D in DMAC (b) at 28°C .

TABLE VII

Molecular Weights of Standard Polystyrenes¹⁾ Obtained at Different Time-Intervals of Equilibration by Membrane Osmometry, Using Gel Cellophanes 450-D and 600-D at 28°C

No	Membrane	Solvent	Polystyrene		\bar{M}_n obtained at different time-intervals of equilibration				
			$\bar{M}_w^1)$ (\bar{M}_w/\bar{M}_n)	$\bar{M}_n^2)$	20	30	40	50	60 min.
1	450-D	Toluene	160000 (≤ 1.06)	151000	192000	169000	161000		
2	450-D	Toluene	19800 (≤ 1.06)	18700	22600	20800	19800		
3	600-D	DMAC	19800 (≤ 1.06)	18700		19400	18900		
4 ³⁾	600-D	DMAC	10300 (≤ 1.06)	9720		9400	9530	9660	9580
5 ³⁾	600-D	DMAC	10300 (≤ 1.06)	9720		9340	9250	9250	9200
6	600-D	DMAC	4800 (≤ 1.10)	4360		3750	3970		
7	600-D	DMAC	4800 (≤ 1.10)	4360		3410	3520	3530	3610

1) Pressure Chemicals Co., 3419-25 Smallman St., Pittsburgh, Pa. 15201.

2) Calculated from the \bar{M}_w/\bar{M}_n ratio.

3) No. 4 was measured one day after installing the membrane.

No. 5 was measured one month after installing the membrane.

RESULTS AND DISCUSSION

1. Degradation of ODPA-m,m'-MDA

The result of molecular weight measurements made on a new polyimide polymer ODPA-m,m'-MDA is shown in Table VIII. The purpose of the measurements was to determine the size of the polymer and the extent to which chemically end-capping the polymer with phthalic anhydride or simply adding phthalic anhydride to the polymer solution retards degradation. The molecular weight of the polyimide polymer which was chemically end-capped was 17600 when measured on the same day the solution was prepared. The molecular weight of the non-end-capped polymer was 13300 when measured on the same day of the preparation. The change in molecular weight due to degradation of the polymer was observed as a function of time.

The experimental results show that the polyimide polymer is unstable in DMAC. Chemically end-capping the polymer (E-1) appears to have little effect on the initial rate of degradation (see Figure 3). The rate constant for the initial stage of degradation was $5.8 \times 10^{-9} \text{ day}^{-1}$. However, adding phthalic anhydride (1% of the weight of the polymer) to the DMAC solution (U-2) is a simple and effective step which appears to almost completely stop the degradation process. This may be attributed to the fact that the phthalic anhydride reacts with

TABLE VIII

Change in Molecular Weight Due to Polymer Degradation of
ODPA-m,m'-MDA at Room Temperature

Time Elapsed in Days, t	Molecular Weight of ODPA-m,m'-MDA*, \bar{M}_n		
	E-1	U-1	U-2
0	17600	12800	13300
1	17100	-	-
2	-	11700	-
7	14600	10800	-
14	-	11200	-
15	13800	-	-
20	-	10000	-
21	-	10200	-
47	-	-	12400
50	14200	-	-
68	-	-	12900
80	12900	-	-

- * E-1: the end-capped polyimide polymer
 U-1: the non-end-capped polyimide polymer
 U-2: the non-end-capped polyimide polymer plus 1(w/w)%
 phthalic anhydride

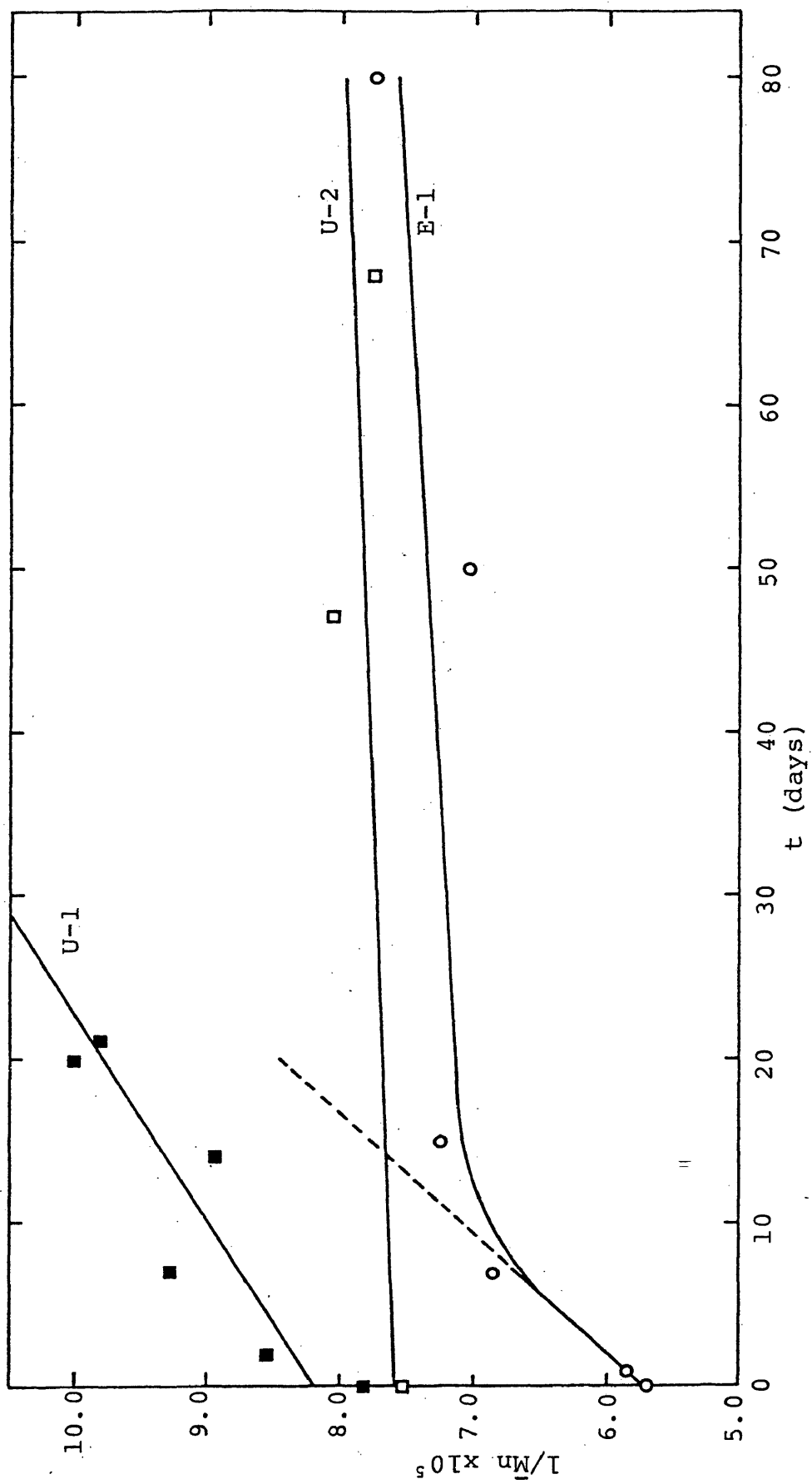


Figure 3. Change in molecular weight due to polymer degradation of ODPA-m,m'-MDA at room temperature

the water present in the solvent DMAC, assuming that the presence of water accelerates degradation of the polymer. The degradation rate of the non-end-capped polymer without phthalic anhydride (U-1) was $3.5 \times 10^{-9} \text{ day}^{-1}$. Assuming that sample E-1 consisted of only end-capped polymers, the fact that the end-capped polymer degrades suggests that the C-N bonds along the chain backbone are susceptible to degradation and that degradation need not be initiated at the end groups of the polymer.

2. Degradation of a Series of BTDA polyimide Precursor Resins

Degradation rate as a function of the chemical nature and structure of diamines. The change in molecular weight due to degradation of polyimide precursor resins composed of BTDA combined with DABP and MDA was observed as a function of time (Table IX). It was found that the degradation rate k (day^{-1}) depended upon the nature of the isomeric diamines and the geometric structure about the amide linkage. The degradation rates calculated from the slope of the plot of $1/\bar{M}_n$ vs. t in Figure 4 were 19.8×10^{-9} for BTDA-*m,m'*-MDA, 12.8×10^{-9} for BTDA-*m,m'*-DABP, 9.9×10^{-9} for BTDA-*p,p'*-MDA, and 4.4×10^{-9} for BTDA-*p,p'*-DABP. The ratio of the k 's is 4.5 : 2.9 : 2.2 : 1 in the same order. Comparing the basicity of the diamines, the strongest is *m,m'*-MDA due to the effect of its electron-donating CH_2 group at the meta position and the weakest is *p,p'*-DABP due to its electron-withdrawing C=O group at the para position. The degradation rate was greatest with BTDA-*m,m'*-MDA and smallest with BTDA-*p,p'*-DABP. If the degradation

TABLE IX

Change in Molecular Weight Due to Degradation of Polyimide Precursor Resins at 27°C

Time Elapsed in Days, t	Batch I					
	BTDA-p,p'-DABP Mn $\times 10^4$	BTDA-m,m'-DABP Mn $\times 10^4$	BTDA-p,p'-MDA Mn $\times 10^4$	BTDA-m,m'-MDA Mn $\times 10^4$		
0	9290	8420	13470	14470	0.691	
1	10040	0.996	-	-	-	
2	-	8470	12750	11890	0.841	
3	10300	0.971	-	-	-	
7	9250	1.08	10910	9280	1.08	
14	8920	1.12	9560	7260	1.38	
21	8210	1.22	8390	5800	1.72	
28	7490	1.34	6820	-	-	
slope ($k/M_0 \times 10^4$)	0.011	0.032	0.024	0.048		
intercept ($1/Mn(0) \times 10^4$)	0.998	1.19	0.730	0.722		
rate constant ($k \times 10^9$) (day $^{-1}$)	4.4	12.8	9.9	19.8		

TABLE IX - continued

Batch II

Time Elapsed in Days, t	BTDA-p,p'-DABP		BTDA-m,m'-MDA	
	\bar{M}_n	$1/\bar{M}_n \times 10^4$	\bar{M}_n	$1/\bar{M}_n \times 10^4$
0	9860	1.01	11200	0.893
3	10300	0.971	10100	0.990
6	-	-	9250	1.08
7	9430	1.06	-	-
11	-	-	8130	1.23
14	9280	1.08	7390	1.35
21	-	-	6330	1.58
22	8270	1.21	-	-
28	8360	1.20	5550	1.80
slope ($k/M_0 \times 10^4$)		0.0082		0.033
intercept ($1/\bar{M}_n(0) \times 10^4$)		0.987		0.876
rate constant ($k \times 10^9$) (day^{-1})		3.3		13.6

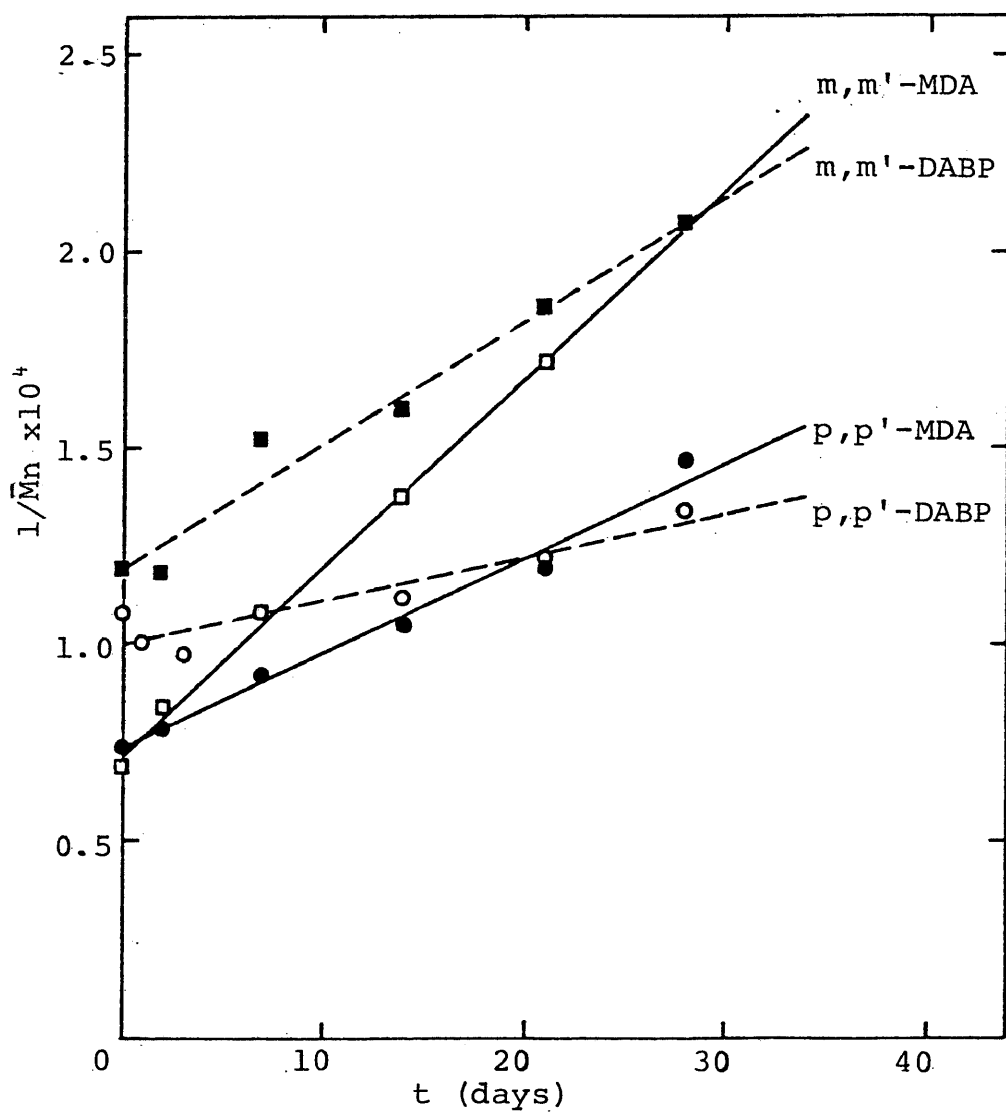


Figure 4. Change in molecular weight due to degradation of polyimide precursor resins as a function of time at 27°C

rate is correlated with the basicity of the diamine in such a manner that the more basic the diamine, the faster degradation occurs, then the following would be observed:

$k_{\text{MDA}} > k_{\text{DABP}}$ and $k_{\text{m,m'-compound}} > k_{\text{p,p'-compound}}$. From the data obtained, it can be seen that k is greater for the MDA polymers than for the DABP polymers: $k_{\text{p,p'-MDA}}/k_{\text{p,p'-DABP}}$ is 2.2 and $k_{\text{m,m'-MDA}}/k_{\text{m,m'-DABP}}$ is 1.5. It is also seen that the p,p'-compounds degrade less rapidly than the m,m'-compounds: $k_{\text{m,m'-DABP}}/k_{\text{p,p'-DABP}}$ is 2.9 and $k_{\text{m,m'-MDA}}/k_{\text{p,p'-MDA}}$ is 2.0. Thus, the degradation rate is correlated with the basicity of the diamines for polyimide precursor resins studied.

It has been reported^{3,33} that, in the preparation of polyimide polymers from isomeric diamines, the more basic the amine group, as a general rule, the more reactive it is toward other monomers, for example, aromatic dianhydrides. The result of the present study suggests that diamines which favor the polymerization reaction also favor degradation of the products.

Figures 5a and b and Table IX show the results of degradation studies on polymers from two different batches. The degradation rate of BTDA-p,p'-DABP (batch II) was 3.3×10^{-9} and that of BTDA-m,m'-MDA was 13.6×10^{-9} . Both of these values are somewhat lower than those for batch I. The uncertainty in k was estimated graphically from the error bars.³⁴ The results of the analysis are

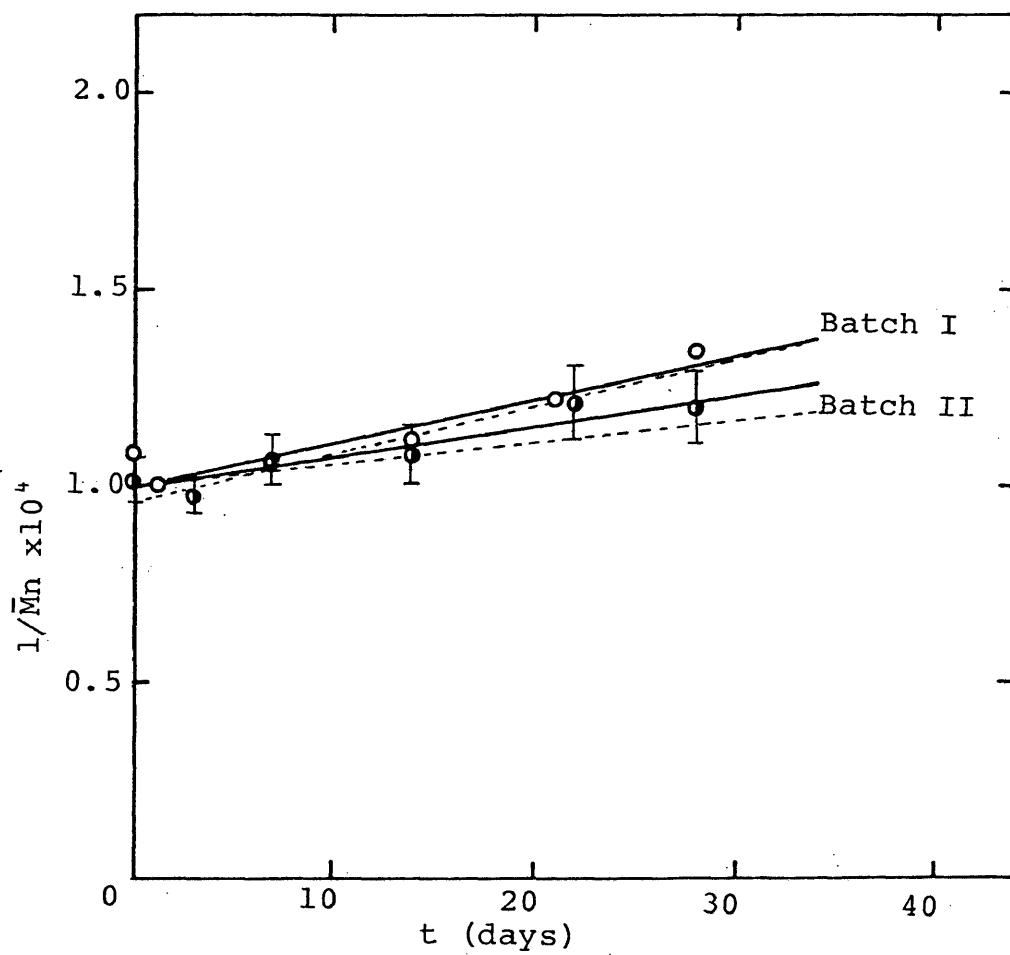


Figure 5a. The change in molecular weight due to degradation of BTDA-p,p'-DABP at 27°C

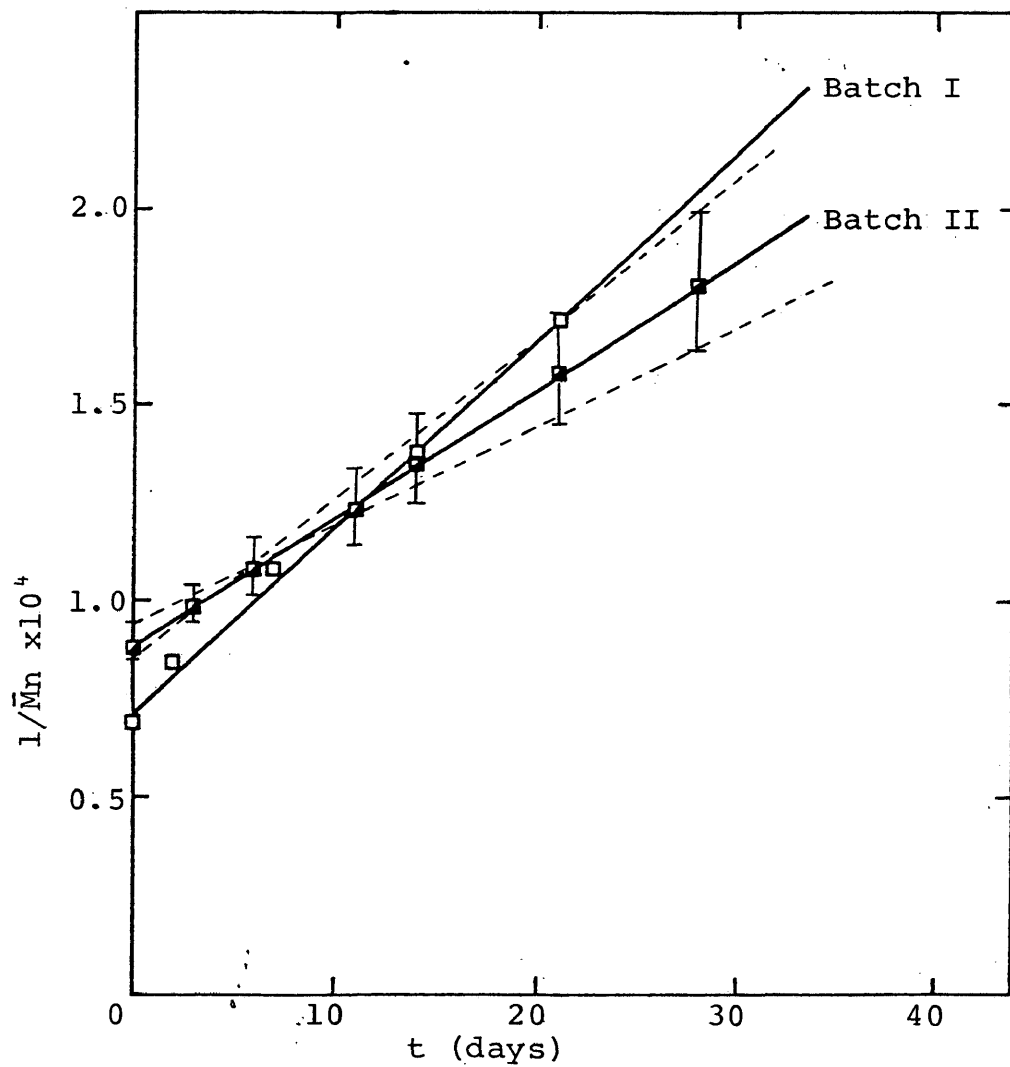


Figure 5b. The change in molecular weight due to degradation of BTDA-*m,m'*-MDA at 27°C

	$k \times 10^9$
BTDA-p,p'-DABP (batch I)	4.4 ± 1.0
BTDA-p,p'-DABP (batch II)	3.3 ± 1.0
BTDA-m,m'-MDA (batch I)	19.8 ± 4.0
BTDA-m,m'-MDA (batch II)	13.6 ± 3.0

The results suggest that there is a small effect of the polymerization conditions on the rate constant k . Variation in the amount of exposure to moisture during synthesis is a possible cause.

Water effect. The effect of the presence of water in the solvent DMAC on degradation of polyimide precursor resins was investigated and the results are shown in Table X and Figures 6a and b. The water content of anhydrous DMAC was checked by Hewlett-Packard 5750 Research Gas Chromatograph⁽¹⁾ and was found to be less than 0.05%. In order to examine the water effect, 1(v/v)% of H₂O was added to the solvent when the polymer solutions were prepared. The degradation rates obtained were 12.8×10^{-9} for BTDA-p,p'-DABP (batch I) and 31.8×10^{-9} for BTDA-p,p'-MDA (batch I). These results show that the presence of water increased the degradation rates of BTDA-p,p'-DABP and BTDA-p,p'-MDA about three times (2.9 for BTDA-p,p'-DABP and 3.2 for BTDA-p,p'-MDA).

Table XI and Figure 7 show the results of a detailed investigation of the degradation of BTDA-m,m'-DABP (batch II)

(1) A 6' x 1/4" column packed with Porapak Q (80/100 mesh) was used for the separation of water from DMAC at 250°C. Porapak Q is prepared especially for good water-separation. A linear calibration curve for water content was obtained from the peak heights of water added to the solvent in the amounts of 0.1 and 1.0(v/v)% of the solvent.

TABLE X

Effect of Water on Degradation of Polyimide Precursor Resins
(Batch I) in DMAC Containing 1(v/v)% H₂O at 27°C

Time Elapsed in Days, t	BTDA-p,p'-DABP		BTDA-p,p'-MDA	
	\bar{M}_n	$1/\bar{M}_n \times 10^4$	\bar{M}_n	$1/\bar{M}_n \times 10^4$
0	8330	1.20	10800	0.926
3	8660	1.15	8020	1.25
7	7290	1.37	6020	1.66
14	6780	1.47	4970	2.01
22	5310	1.88	-	-
slope ($k/M_0 \times 10^4$)		0.032		0.077
intercept ($1/\bar{M}_n(0) \times 10^4$)		1.12		1.00
rate constant ($k \times 10^9$) (day ⁻¹)		12.8		31.8

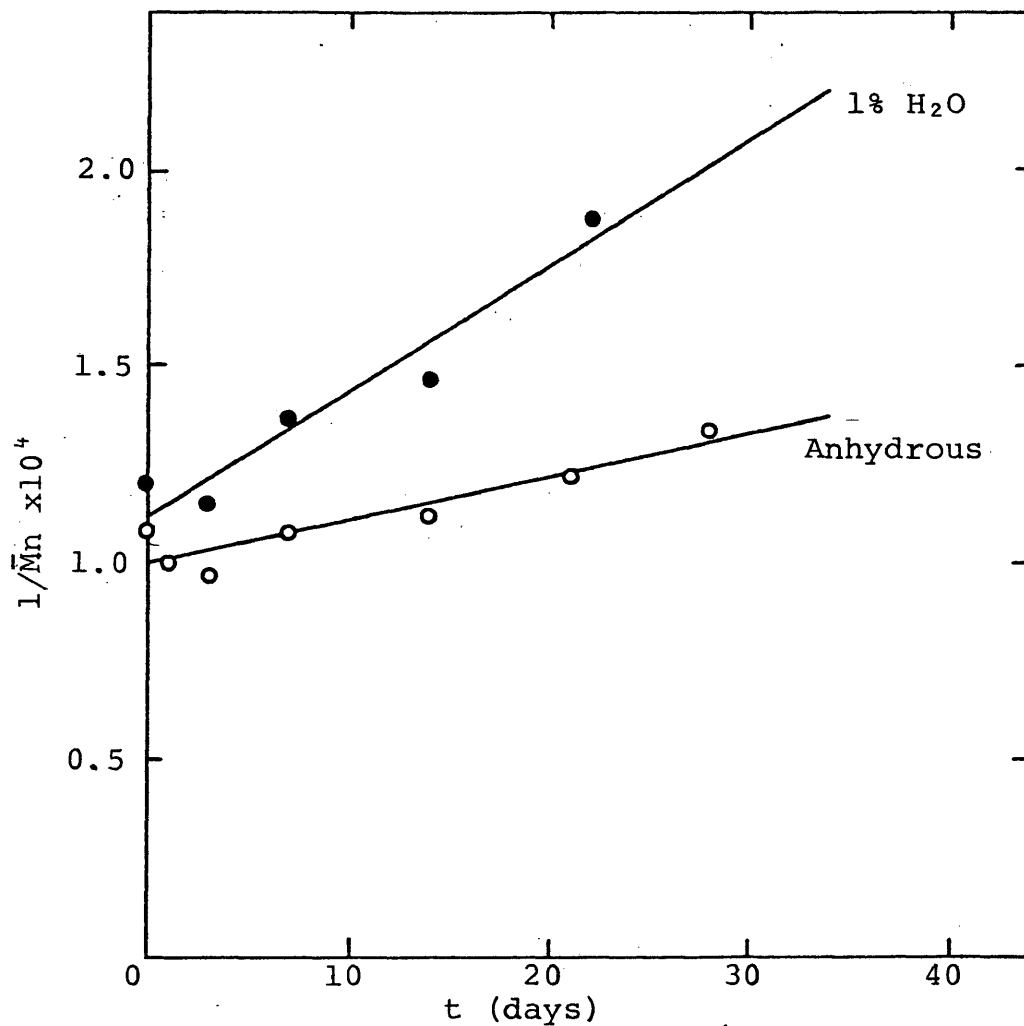


Figure 6a. Effect of water on degradation of BTDA-p,p'-DABP in DMAC containing 1(v/v)% H₂O at 27°C



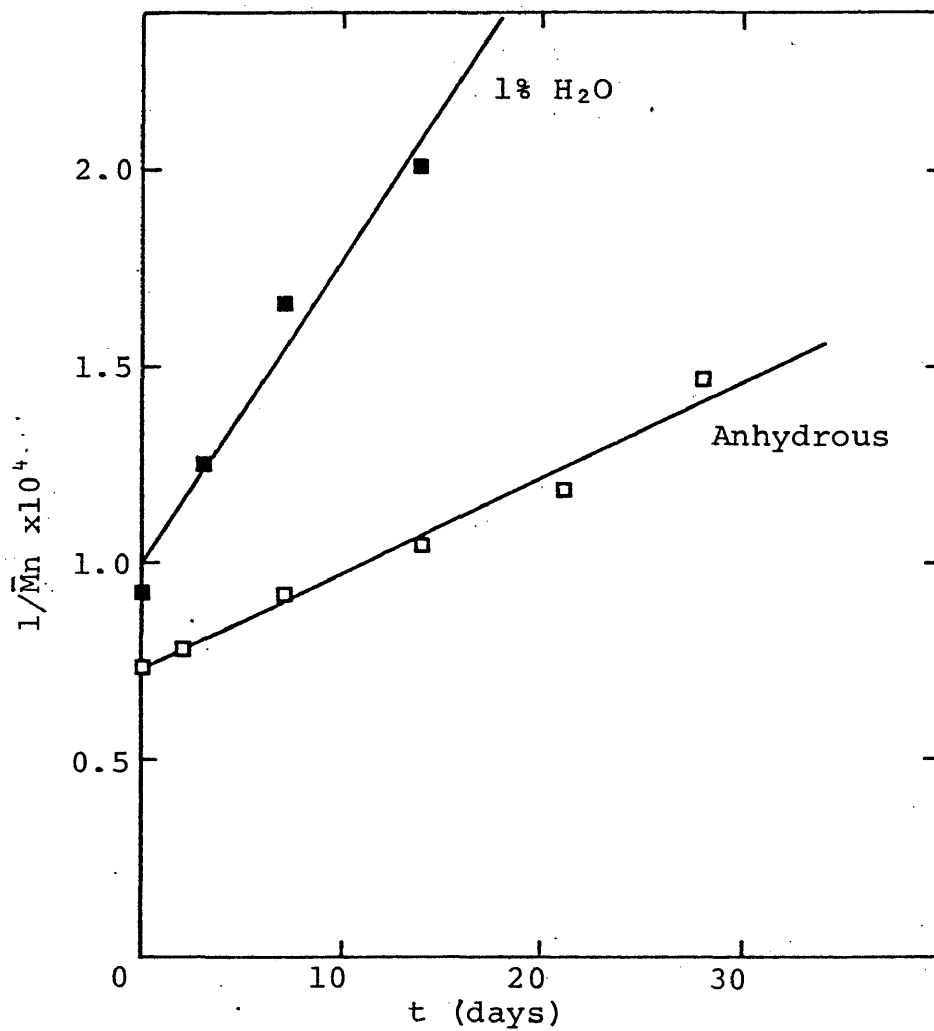


Figure 6b. Effect of water on degradation of BTDA-p,p'-MDA in DMAC containing 1(v/v)% H₂O at 27°C

TABLE XI

Effect of Water on Degradation of BTDA-m,m'-DABP (Batch II) at 27°C

Time Elapsed in Days, t	H ₂ O Content \bar{M}_n	0.5% $1/\bar{M}_n \times 10^4$	\bar{M}_n	0.3% $1/\bar{M}_n \times 10^4$	\bar{M}_n	0.1% $1/\bar{M}_n \times 10^4$	<0.05% ¹⁾ Anhydrous ²⁾
0	9010	1.11	8590	1.16	10900	0.917	
2	8600	1.16	-	-	-	-	
3	-	-	8160	1.22	9550	1.05	
7	7140	1.40	6450	1.55	8270	1.21	
14	4870	2.05	5350	1.87	6860	1.46	
slope ($k/M_0 \times 10^4$)		0.068		0.053		0.038	0.032
intercept ($1/\bar{M}_n(0) \times 10^4$)		1.04		1.13		0.927	1.19
rate constant ($k \times 10^9$) (day ⁻¹)		27.3		21.3		15.2	12.8
							12.2

1) result of Batch I

2) calculated from the graph of Figure 8

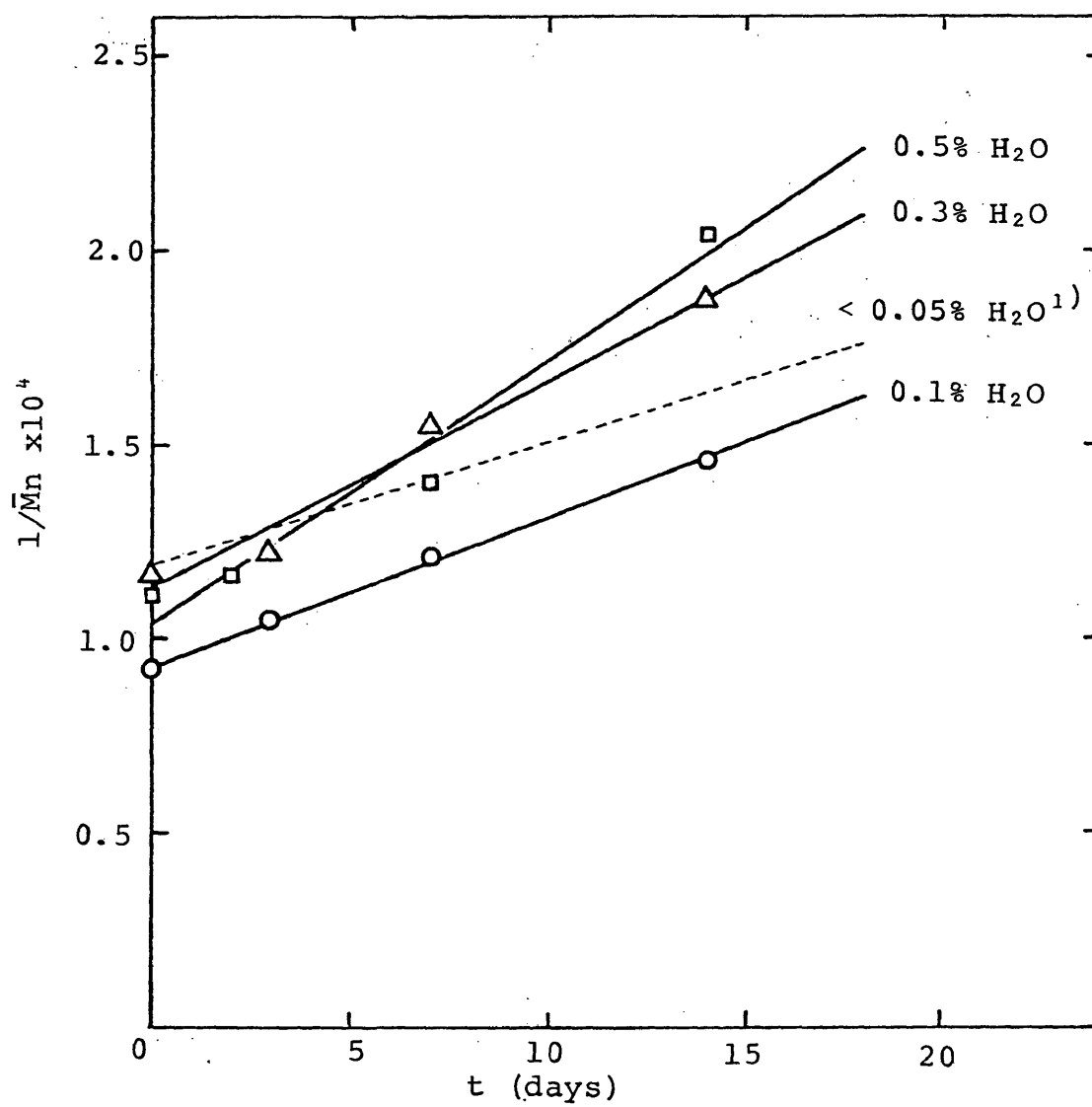


Figure 7. Effect of water on degradation of BTDA-*m,m'*-DABP (Batch II) at 27°C

1) result of Batch I

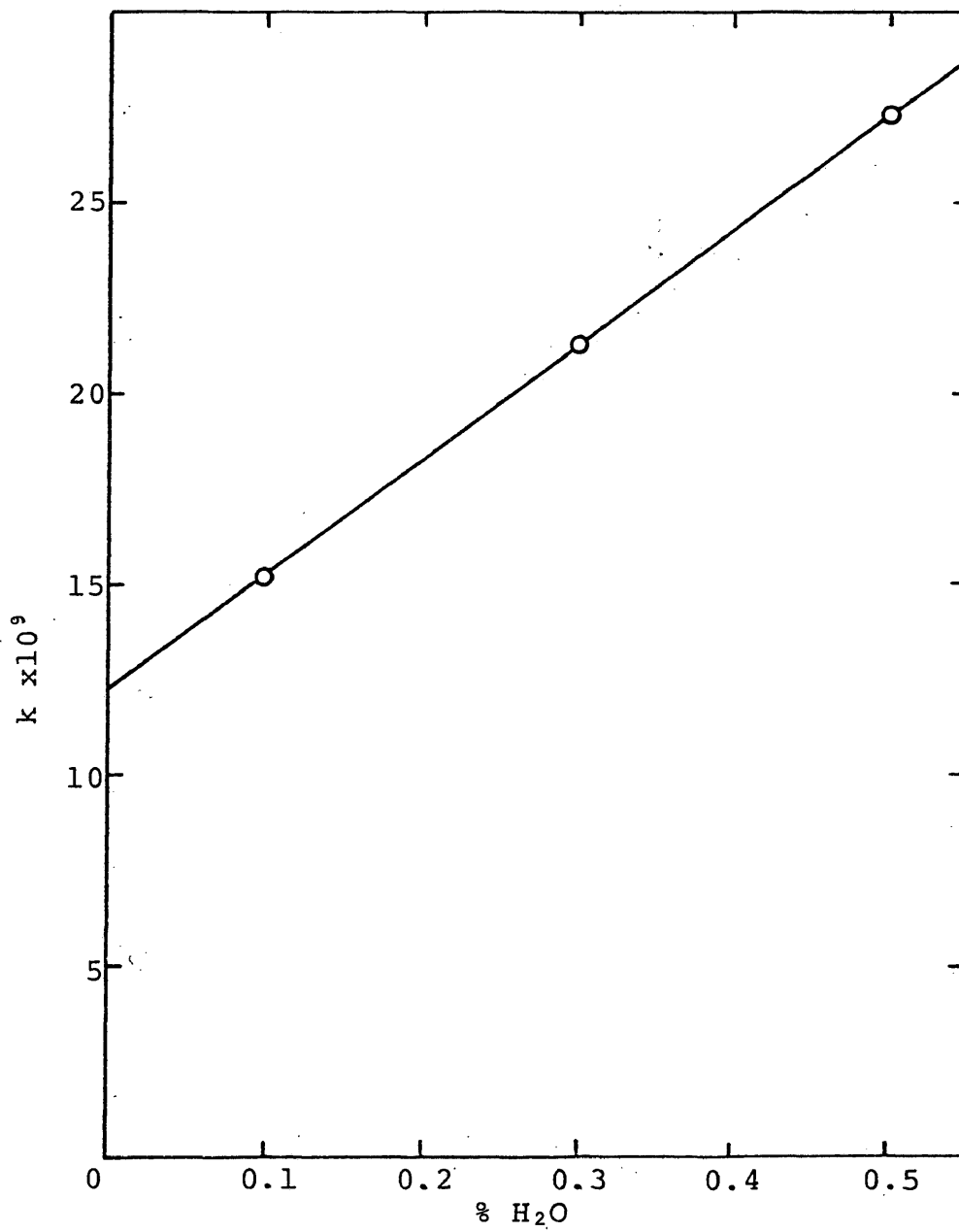


Figure 8. Plot of the degradation rate constant of BTDA-*m,m'*-DABP vs. the amount of water added to the solvent DMAC

in DMAC containing different amounts of water. Polymer solutions containing 0.1, 0.3, and 0.5(v/v)% H₂O were prepared by adding water to the solvent. The degradation rate increased with the larger amounts of water: $k_{0.1\%H_2O}$ was 15.2×10^{-9} ; $k_{0.3\%H_2O}$, 21.3×10^{-9} ; and $k_{0.5\%H_2O}$, 27.3×10^{-9} . In Figure 8 the degradation rate for each solution is plotted against the amount of water added. The observed linear relationship suggests that the degradation rate is proportional to the water content in the concentration range studied. From Figure 8 it can also be seen that the results are consistent with the rate constant, 12.8×10^{-9} , obtained for BTDA-m,m'-DABP of batch I in anhydrous DMAC containing less than 0.05% of water.

Temperature effect. The effect of temperature on the degradation of the most stable polymer BTDA-p,p'-DABP was investigated and the result is shown in Table XII and Figure 9. The degradation rate at 37°C⁽²⁾, 34.1×10^{-9} , is approximately ten times greater than that at 27°C.

(2) H₂O content may be 0.10-0.15(v/v)%, by gas chromatography analysis, in the 37°C solutions.

TABLE XII

Effect of Temperature on Degradation of BTDA-p,p'-DABP (Batch II)

Time Elapsed in Days, t	Temp.	27°C*		37°C	
		\bar{M}_n	$1/\bar{M}_n \times 10^4$	\bar{M}_n	$1/\bar{M}_n \times 10^4$
0		9860	1.01	9730	1.03
1		-	-	9180	1.09
3		10300	0.971	7920	1.26
5		-	-	7620	1.31
7		9430	1.06	-	-
11		-	-	5080	1.97
14		9280	1.08	-	-
22		8270	1.21	-	-
28		8360	1.20	-	-
slope					
(k/M ₀ × 10 ⁴)		0.0082		0.0849	
intercept					
(1/M _n (0) × 10 ⁴)		0.987		0.993	
rate constant					
(k × 10 ⁹) (day ⁻¹)		3.3		34.1	

* the same result in Table IX

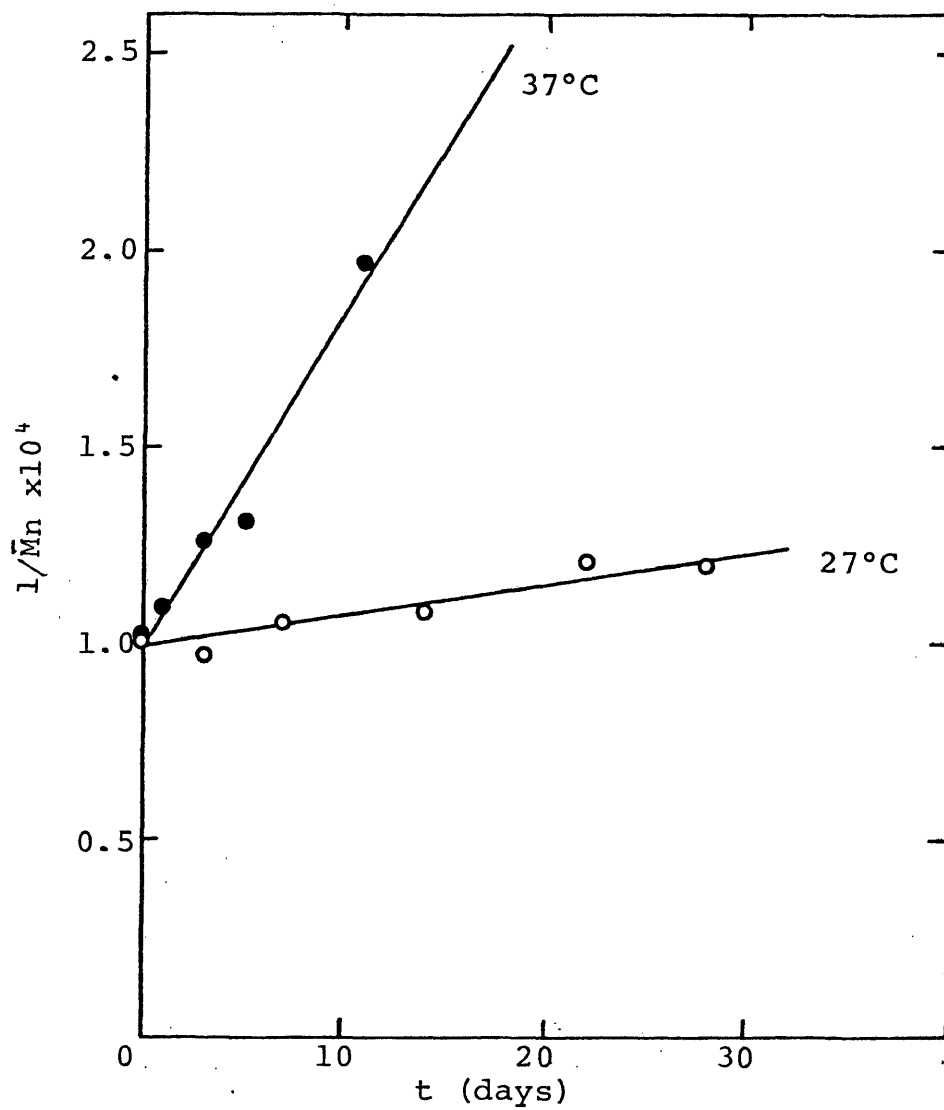


Figure 9. Effect of temperature on degradation of BTDA-p,p'-DABP (Batch II)

CONCLUSION

Degradation of high performance polyimide precursor resins was investigated by measuring the molecular weight of the polymers in solution, using a membrane osmometer. It was found that polyimide precursor resins composed of BTDA and ODPA combined with DABP and MDA were unstable in DMAC.

The degradation rate was found to depend upon the chemical nature of the isomeric diamine and the geometric structure about the amide linkage. The polymers of DABP were less susceptible to degradation than those of MDA and p,p'-compounds were more stable than m,m'-compounds. These results suggest that degradation is correlated with the basicity of the diamine. That is, the rate of the degradation reaction increases with the basicity of the diamine group in the polyimide precursor resin.

The presence of water and a higher temperature increased the degradation rate of the polymers. A linear relationship between the degradation rate constant and water content was obtained in the concentration range studied. When the solution contained 1(v/v)% H₂O, the rate was three times greater than that of the anhydrous solution. When the reaction temperature was raised ten

degrees from 27 to 37°C, the degradation rate of BTDA-p,p'-DABP was increased approximately ten times.

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