

CHARACTERIZATION OF A THERMALLY IMIDIZED SOLUBLE POLYIMIDE FILM

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Synopsis

A soluble aromatic poly(amic acid) film was converted to a soluble polyimide by staging at 25° intervals to 325°C and characterized at each interval by several analytical methods. The behavior observed was consistent with an interpretation that a reduction occurred in molecular weight of the poly(amic acid) during the initial stages of cure before the ultimate molecular weight was achieved as a polyimide. This interpretation was supported by the results of solution viscosity, gel permeation chromatography, low angle laser light scattering photometry and infrared spectroscopy analyses. The results of this study serve to increase our fundamental understanding of how polyimides are thermally formed from poly(amic acids).

INTRODUCTION

Aromatic polyimides are established as key materials for coating, electronic and aerospace applications involving extreme use environments. Literally hundreds of chemical structural variations, both linear and crosslinked, have been examined since this class of polymers was first reported in the 1960s(1-3).

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Traditional polyimides are formed from the room temperature reaction of aromatic dianhydrides with aromatic diamines in aprotic solvents, to yield high molecular weight poly(amic acid) precursors which are then thermally cyclodehydrated to yield the fully imidized product (Scheme I). Many early reports were rightfully concerned with studying both initial poly(amic acid) formation^(1,3) and imidization kinetics⁽⁴⁾. The effect of temperature and residual water on poly(amic acid) solution stability was noted^(1-3,5,6) and the potential for hydrolysis of both the poly(amic acid) and polyimide by water produced during imidization was speculated^(3,6). Numerous studies have also noted the possibility of side reactions which may accompany the thermal imidization process^(3,5,7-9).

Solution property measurements have shown little or no difference in molecular weight between fully imidized polymer and the parent poly(amic acid) precursor⁽¹⁰⁻¹³⁾. However, we have noted⁽¹⁴⁾ the previously reported embrittlement^(3,15) of certain films at intermediate (150°-200°C) stages of cure. This observation, coupled with the presence of an anhydride band at 1860 cm^{-1} in the infrared spectrum of many incompletely cured films, has led us to question whether this molecular weight constancy is maintained throughout the entire interval between poly(amic acid) and polyimide.

Accordingly, we studied the conversion of soluble poly(amic acids) to soluble polyimides at intermediate stages of cure^(14,16,17). These early fragmentary studies suggested an initial reduction in molecular weight during cure of the poly(amic acid), consistent with side reactions yielding film embrittlement and anhydride formation, before the ultimate molecular weight was achieved as a polyimide. The present study reports a more comprehensive characterization of a soluble polyimide⁽¹⁸⁾ cured at 25° intervals to 325°C (Scheme II). To help eliminate previous ambiguities, a large amount of poly(amic acid) was synthesized, films cast and thermally staged and all characterizing analyses performed on the

same film samples. Further, this particular polymer system allowed all solution property measurements to be conducted in a common solvent, eliminating the traditional need for analyzing the poly(amic acid) and polyimide in different solvents. This study is intended to complement previous research on polyimide formation by providing information on the conversion between amic-acid and imide.

EXPERIMENTAL

Materials. Starting materials, solvents and other chemical supplies were obtained from commercial sources. The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F) was purified by refluxing for 2.5 hr. in 50/50 toluene/acetic anhydride, m.p. 243°C. The diamine monomer, 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (BDAF), was recrystallized from ethanol with charcoal, m.p. 156°C.

Resin Synthesis. Solid 6F dianhydride (5.9979 g, 0.01350 mole) was added over 15 min. at RT to a stoichiometric amount (7.0000 g, 0.01350 mole) of BDAF dissolved in N,N-dimethylacetamide (DMAc) in a dry dark-glass bottle equipped with a stopper and magnetic stirrer. The 15% w/w resin solution was stirred for 20 hr. ($\eta_{inh} = 1.45$ dL/g) and refrigerated until used.

Preparation of Film Specimens. Films were cast by doctoring the poly(amic acid) onto soda-lime plate glass in a dust-free chamber. A doctor blade set at 15 mil was used to spread the resin. After drying for 24 hrs. at RT under a slight dry air flow, the plates were placed in a vacuum desiccator at 40°C for 72 hrs. Approximately 1 mil tack-free films were then removed from the plates.

The poly(amic acid) films were laid in a baking dish and placed in a preheated forced air oven for 15 min. periods. Upon removal from the oven, sufficient sample (0.8-1.0 g) was retrieved for future analyses. The oven was then

taken to the next temperature and the procedure repeated. Samples staged at 25°C intervals from 75°C to 325°C as well as the 40° sample were prepared. Film from each curing stage was refrigerated in a dry container until analyzed.

Characterization. Infrared spectra were obtained on a Nicolet 60SX Fourier Transform Infrared (FTIR) system. Thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer TGS-2 instrument in 15 cm³/min flowing air. Density measurements were performed by an outside laboratory using the density gradient technique.

All solution property measurements were made in a 0.1 M anhydrous LiBr in DMAc (Fluka AG) solvent. Inherent viscosity (η_{inh}) was measured at 0.5% (w/v) concentration at 25°C using a Cannon-Ubbelohde viscometer. Intrinsic viscosity ($[\eta]$) was also measured at 25°C. Gel permeation chromatography (GPC) analyses were conducted on a Waters Associates high pressure liquid chromatograph using two DuPont Zorbax PSM Bimodal-S (6.2 mm x 25 cm) size exclusion columns and a Waters Model 401 Refractive Index Detector.

Static weight average molecular weight (\bar{M}_w) determinations were conducted on an LDC/Milton Roy CMX-100 Low Angle Laser Light Scattering (LALLS) photometer. Measurements of the Rayleigh Factor (R_θ) were made at 5 concentrations, generally ranging from 0.0008 to 0.008 g/ml. Using these solutions, specific refractive index increment (dn/dc) measurements were made at 28°C on a Chromatix Model KMX-16 Laser Differential Refractometer (LDC/Milton Roy, Rivera Beach, FL 33404) operating with a 633 nm He-Ne laser. Dynamic GPC/LALLS analyses were also conducted using previously described techniques⁽¹⁹⁻²¹⁾.

RESULTS AND DISCUSSION

A total of 12 film samples were prepared, starting with the poly(amic acid) (40°) specimen and continuing with samples staged at 25° intervals from 75° to 325°C. These 12 films were subjected to a battery of tests, primarily over an intensive one-month period, in an effort to characterize their respective molecular weights. An appreciation of several points peculiar to polyimides was necessary in order to gain understanding and confidence in our analytical measurements.

First, a particular film sample is not necessarily all polymer, it may contain residual solvent. This raises the question of how much actual polymer is being analyzed, a point which impacts every measurement conducted in this research. Further, molecular structure is continually changing as the polymer is transformed from amic-acid to imide. Water of imidization is lost during this process. No accepted method is available for determining the exact extent of imidization in any sample. Thus, we relied on a combination of FTIR and TGA to achieve a qualified estimate of how much poly(amic acid) and polyimide was actually in a film specimen.

Figure 1 gives TGA curves to 400°C for all samples. The weight loss to 350°C was assumed due to loss of solvent and water of imidization. An estimate of the percent imide in each film was based on respective infrared spectra and the intensity of the 1780, 1720, 1380 and 720 cm^{-1} imide related bands relative to amic-acid related bands. The calculated weight loss due to water of imidization was then subtracted from the total loss to determine the amount of residual solvent in a particular film. Table I summarizes this data for the 12 film samples. The percent residual solvent values were then used to make adjustments to polymer weight where appropriate during this research. While subjective, this correction is considered to be warranted and preferred to attempting no weight adjustments.

A second inherent property of poly(amic acids) and polyimides also merits discussion. Dilute solutions are known to exhibit polyelectrolyte behavior^(3,11,22,23). When this occurs, the hydrodynamic volume of the polymer increases, affecting viscosity, GPC, light scattering and other dilute solution property measurements. Cotts has shown that perhaps the most effective method of suppressing polyelectrolyte effects is the use of carefully redistilled solvent⁽¹¹⁾. However, in our study we chose the older method of conducting all analyses in dilute ionic solutions^(22,23). Intrinsic viscosity measurements showed that 0.1 M LiBr in DMAc functioned fairly satisfactorily in suppressing polymer ionization in dilute solution. Our experience is that polyelectrolyte effects need only be considered at concentrations less than 0.002 g/ml.

A third potential problem, varying solubility, was circumvented by the choice of the 6F-BDAF polymer system used in this study. Traditional polyimide materials are soluble in aprotic solvents such as DMAc at the amic-acid stage but become insoluble in those solvents after receiving moderate amounts of cure. Fully imidized polymer is generally soluble in concentrated sulfuric acid. However, this solvent cannot be used on incompletely cured material because it degrades the polymer. Thus, previous molecular weight studies tended to be conducted only on poly(amic acids) and polyimides in two different solvents and intermediate stages were not investigated. This 6F-BDAF system was soluble in the 0.1 M LiBr/DMAc solvent at all stages of cure to 325°C, although overnight dissolution was required for films heated above 225°. A very slight gelation noted with the 325°C specimen cleared with two-day dissolution. Thus, we feel potentially complicating factors have been minimized through an appreciation of the role of residual solvent, by conducting all solution property measurements in 0.1 M LiBr/DMAc and by selection of the 6F-BDAF polymer system.

Solution Viscosity. Table I contains intrinsic viscosity ($[\eta]$) data for all film samples. When appropriate, sample concentrations were corrected for residual solvent as previously discussed. A plot of $[\eta]$ as a function of temperature is given in Figure 2. An initial decrease in the viscosity of dissolved films is noted with cure temperature, reaching a minimum in the 150°-200° interval. This previously observed behavior correlates with the appearance and intensification of an anhydride band in the infrared spectrum at 1860 cm^{-1} (14,16,17). The increase in viscosity for films cured above 200° correlates with the gradual disappearance of the anhydride band. Figure 3 shows spectra of the anhydride region for the 12 thermally staged films.

An obvious conclusion is that the polymer backbone experienced chain scission at low cure temperature, producing anhydride and, presumably, amine end groups and that these groups reacted at higher temperature to increase chain length. If this indeed occurred, the poly(amic acid) experienced an initial reduction in molecular weight during cure before it achieved its ultimate molecular weight as a polyimide. Gaining the experimental evidence to substantiate this conclusion was a primary goal of this research. Additional points should be made about the information in Table I and Figure 2. An inflection occurs in the curve around 250°C. This inflection was observed to occur nominally at T_g for other soluble aromatic polyimides(14). The T_g for fully-cured 6F-BDAF film is 262°C. We offer no explanation for this observation. Second, exactly the same trend is observed if no correction for residual solvent is made. Further, η_{inh} is a good estimate of $[\eta]$ for films cured above 225°C.

Specific Refractive Index Increment. The specific refractive index increment, dn/dc , is a critical parameter in calculating the optical constant, K , required for the calculation of molecular weight by LALLS(24-27). This parameter is a measure of the change in refractive index of a polymeric solution with concentration and is a

squared function in the mathematical equation yielding K . Normally, only one dn/dc value is determined for a given polymer type and this value is then assumed to be independent of molecular weight for all samples of that polymer⁽²⁸⁻³¹⁾. However, we recognized that the 6F-BDAF molecular structure was continuously changing as the films were incrementally cured. Thus, we deemed a dn/dc determination desirable on each thermally staged sample so that optimized \bar{M}_w values could be calculated from LALLS measurements. This information is summarized in Table I. The residual solvent-corrected values appear to be constant only above 225°C, when most of the imidization is complete. The differing values obtained for low temperature cured films promotes the desirability of conducting individual dn/dc measurements.

Static LALLS. Static LALLS measurements were conducted on each of the 12 film samples. Individual sample solutions used for this determination had previously been used for dn/dc measurements. Respective dn/dc values from Table I were used in data reduction. Table I gives \bar{M}_w values for each of the thermally staged films.

In obtaining this data, \bar{M}_w was determined by rearranging the standard equation:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w} + 2A_2c + 3A_3c^2 + \dots$$

to read

$$\left(\frac{Kc}{R_\theta}\right)^{1/2} = \left(\frac{1}{\bar{M}_w}\right)^{1/2} + A_2c\bar{M}_w^{1/2}$$

by assuming that $A_3 = \frac{\bar{M}_w A_2^2}{3}$, according to the argument forwarded by Cotts⁽¹¹⁾. Here, c is the concentration and A_2 and A_3 are virial coefficients. K and R_θ have been previously defined. Figure 4 gives a plot of this data for the 40°C poly(amic acid) film, the 200°C intermediate-staged film and the 325°C polyimide film. The

uncertainty in the y-axis intercept for all data was generally less than 2%. Figure 5 gives a plot of \bar{M}_w as a function of cure temperature for all samples. These data show the same trends as viscosity data and support the interpretation that the poly(amic acid) underwent an initial reduction in molecular weight during cure before the ultimate molecular weight was achieved as a polyimide. Exactly the same trends are observed when neither dn/dc or LALLS data are corrected for residual solvent.

Mark-Houwink Plot. Using the appropriate viscosity and static LALLS data in Table I, Figure 6 gives the classical plot of the Mark-Houwink Equation $[\eta] = K\bar{M}_w^a$. A surprisingly linear correlation was observed except for the 40°C specimen, whose viscosity value appeared to be out of line. Note the trend toward lower molecular weight for the sequence of 75°, 100°, 125°, 150°, 175° and 200°C films. Note also the trend toward higher molecular weight for the sequence of 200°, 225°, 250°, 275°, 300° and 325°C films. The fact that all data points tend to fall on a single line supports the general theory that little change in polymer configuration in solution is expected in going from poly(amic acid) to polyimide⁽¹¹⁾. Calculated "a" and "K" values of approximately 0.6 and 1.14×10^{-3} are consistent with values of 0.53 and 2.76×10^{-3} reported by Wallach for chemically imidized materials⁽¹⁰⁾.

GPC/LALLS. In the absence of reliable number average molecular weight data (\bar{M}_n), we relied on the combination of gel permeation chromatography (GPC) with LALLS to provide an estimate of the trend in \bar{M}_n with temperature. The GPC mobile phase was 0.1 M LiBr/DMAc. Figure 7 illustrates the importance of suppressing polyelectrolyte effects when conducting dilute solution measurements on poly(amic acid) and polyimide materials. This figure, taken from an earlier study⁽¹⁴⁾, shows GPC chromatograms for 40°, 150°, 250° and 325°C 6F-BDAF films using both neat DMAc and 0.1 M LiBr/DMAc as mobile phases. The four upper curves obtained in DMAc, appear as higher molecular weight distributions than the

four lower curves of the same specimens obtained in the dilute ionic solvent. The use of the upper set of curves to calculate molecular weights would result in erroneous values.

Table I summarizes \bar{M}_w and \bar{M}_n values obtained by GPC/LALLS. Data reduction was achieved using the MOLWT3 V1.003 software package supplied by the LDC/Milton Roy. As might be anticipated, \bar{M}_w values obtained by static LALLS and dynamic GPC/LALLS did not always agree in absolute value. However, the trends are consistent. \bar{M}_n values probably are a little high since GPC/LALLS has been reported to over estimate \bar{M}_n for broad distribution polymers, due largely to the lack of sensitivity of the LALLS detector to the low molecular weight portion of the polymer⁽²¹⁾. Thus, polydispersity values by GPC/LALLS tend to be somewhat low. Figure 8 gives the cumulative weight fraction plot for the 40°, 200° and 325°C films. Figure 9 gives plots of \bar{M}_n and \bar{M}_w as a function of cure temperature for the 12 specimens. The general molecular weight trends observed by GPC/LALLS were totally consistent with other data generated in this study.

Infrared Spectroscopy. The intensity of the anhydride band that appears at 1860 cm^{-1} in the infrared spectrum of many incompletely cured polyimide films can be used to determine \bar{M}_n by end-group analysis if the extinction coefficient for that band is known. Normally, this parameter is determined by measuring the absorbance of model compounds in solution. However, applying such values to unknowns in the solid phase, particularly to amorphous polymer films, may not be appropriate. The same concentration of material in the liquid and solid phases may absorb at two different intensities⁽³²⁾.

We elected to approach this problem in the following manner. The \bar{M}_n of a previously reported polyimide film, prepared from 4,4'-bis(3,4-dicarboxy-phenoxy)diphenyl sulfide dianhydride (BDSDA) and BDAF and staged at 175°C, had been measured by membrane osmometry⁽¹⁷⁾. The infrared spectrum of that

film of known thickness and density was determined and the absorbance of the anhydride band noted(33). Dividing the film density by \bar{M}_n gave the polymer concentration in moles/cm³. Then, the Lambert-Bouguer-Beer Law was applied:

$$A = \log \frac{I_0}{I} = abc$$

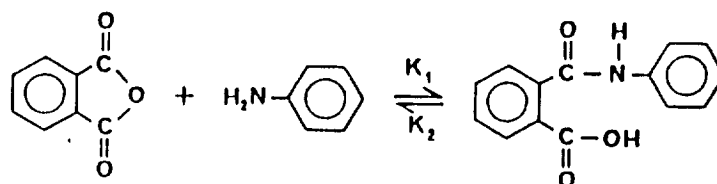
Here, the absorbance A of the 1860 cm⁻¹ anhydride band is the logarithm of the intensity of radiation entering the film, I_0 , divided by the intensity of transmitted radiation, I , "a" is the desired extinction coefficient, "b" is the thickness in cm, and "c" is the above concentration. A value of 175 cm²/mmole was calculated for the extinction coefficient of the anhydride band in the amorphous BDSDA-BDAF 175°-staged film. This value agreed surprisingly well with a value of 179 cm²/mmol independently obtained for 3,3',4,4'-benzophenone tetracarboxylic dianhydride in a diglyme solution(33) and a literature value of 181 cm²/mmole for pyromellitic dianhydride in N,N-dimethylformamide(34). This agreement gave us confidence that our initial approach was justified and suggested that the fear of different extinction coefficients for model compounds in solution and for solid polymer films may have been unfounded in this case.

The appropriate infrared absorbance measurements were made on the 12 6F-BDAF samples and film thickness was determined at the location exposed to the infrared radiation. Then, from Beer's Law and the 175 cm²/mmol extinction coefficient value, the polymer concentration was calculated. Dividing this value into the respective film density given in Table I yielded \bar{M}_n in g/mole.

Table I lists \bar{M}_n values calculated for the 150° sample, for which the anhydride band was barely detectable and subject to the greatest error, through the 300° sample, the highest temperature for which the band was detectable. The behavior of the 1860 cm⁻¹ band can be followed in Figure 3. The \bar{M}_n values in Table I show exactly the same molecular weight trends as indicated by solution property measurements and exhibit reasonable agreement with inflated \bar{M}_n values

obtained by GPC/LALLS. Thus, this solid-state approach, uncomplicated by factors which may influence dilute solution property measurements, substantiates those results and supports the thesis that poly(amic acid) films undergo an initial reduction in molecular weight during thermal cure followed by a molecular weight increase. Further, this particular infrared technique holds promise for determining \bar{M}_n values for insoluble polyimides at intermediate stages of cure.

Review of the Literature. Little quantitative information exists on molecular weight behavior during cure except in the Russian literature⁽³⁵⁻⁴¹⁾. Kamzolkina, et. al⁽³⁵⁾ studied the relationship between the equilibrium constant and temperature for the interaction between phthalic anhydride and aniline as a model reaction of chain extension.



At 40°C in acetonitrile, a K_1 value of 1970 L/mole was determined for the model amic-acid. At 200°, that value was 4. Respective values in THF were 17,600 and 11. The authors concluded that the dependence of the equilibrium constant on temperature was critical to the synthesis of high molecular weight polyimides. Further, they predicted a reversion in molecular weight of the poly(amic acid) during cure.

In studying this unimolecular decomposition, the amine concentration was experimentally shown to initially increase and then decrease during the thermal imidization of the poly(amic acid) from 9,9-bis(4-aminophenyl)fluorene and 3,3',4,4'-carboxydiphenyl-2,2-propane dianhydride at 165°C⁽³⁵⁾. In addition, \bar{M}_n for this polymer was shown to substantially decrease during solid phase imidization at 150°⁽³⁶⁾. This particular event was quantified by a UV-VIS spectral analysis of a

derivative of the newly formed amine⁽⁴¹⁾. Thus, while we found no direct evidence of free amine end-groups in our infrared study, possibly because the amine region was obscured by bands already in the poly(amic acid) spectrum, other studies have been reported on the basis of this group. Nechayev noted that, in the solid phase, synthesis does not begin until the temperature is taken above 200°C⁽³⁶⁾.

Finally, in a study similar to the present research, viscosity, molecular weight as determined by sedimentation velocity, and selected tensile properties were reported for a soluble aromatic polyimide film as a function of cure temperature⁽³⁷⁾. An initial decrease in magnitude of all measured parameters was observed with temperature, followed by an increase in values for film cured above 200°C. This was attributed directly to molecular weight behavior during cure. Our present research tends to confirm results of this previous study.

Several articles^(42,43) have disagreed with preliminary results of our research and incorrectly attempted to extend it to crosslinked systems. We recognize an inherent difference between linear and crosslinked polyimides. Further, we feel it is unwise to address the molecular weight of infinite molecules. Our intention in publishing spectra of the anhydride region of an addition polyimide was to show that, for whatever reason, anhydride formed in that system as well⁽¹⁶⁾. Beyond that, our research has been conducted on linear, soluble systems.

CONCLUDING REMARKS

In the absence of a viable alternate interpretation of experimental results obtained in this research, we conclude that the 6F-BDAF poly(amic acid) film exhibited an initial decrease in molecular weight during thermal cure before it achieved its ultimate molecular weight as a polyimide. The greatest effect was observed between 150-200°C. Further, this molecular weight behavior was related

to the presence of an anhydride band in the infrared spectrum which developed during cure. Since this band also occurs in the spectrum of many other incompletely cured polyimide films, a logical general conclusion would be that poly(amic acid) materials, synthesized in aprotic solvents and thermally imidized, also experience this reversion in molecular weight.

The dependence of molecular weight on the polymerization solvent and anhydride or amine acidity or basicity was not considered. Thus, other materials may exhibit this behavior to a lesser or greater extent. Our unconfirmed experience is that chemically imidized polyimides do not exhibit a reversion in molecular weight. In addition, the acid group appears necessary to initiate the unimolecular decomposition since poly(amic esters) do not develop anhydride during cure. The conclusion from this research is not intended to be considered as good nor bad. However, it is a possibly unappreciated phenomenon which is a consequence of thermal imidization and which may have application to the processing of polyimides into useful articles. This research has increased our fundamental understanding of the conversion of poly(amic acids) to polyimides.

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TABLE I. CHARACTERIZATION OF THERMALLY STAGED 6F-BDAF FILM

SAMPLE	RESIDUAL SOLVENT			VISCOSITY			LIGHT SCATTERING ⁵				FTIR		SAMPLE
	WEIGHT ¹ LOSS, %	IMIDE, ² %	SOLVENT, ³ %	$[\eta]^4$ (dL/g)	$[\eta]^5$ (dL/g)	η_{inh}^5 (dL/g)	dn/dc (mL/g)	\overline{M}_w LALLS (g/mole)	\overline{M}_w GPC/LALLS g/mole	\overline{M}_n GPC/LALLS g/mole	density (g/cm ³)	\overline{M}_n (g/mole)	
40°	19.7	0	16.0	0.679	0.810	0.841	0.118	197,000	152,000	102,000	1.378	-	40°
75°	20.3	0	16.6	0.792	0.945	0.926	0.130	109,000	108,000	69,000	1.382	-	75°
100°	20.0	0	16.3	0.590	0.710	0.717	0.128	80,000	77,000	53,000	1.370	-	100°
125°	17.4	5	13.9	0.449	0.525	0.518	0.133	52,000	49,000	32,000	1.392	-	125°
150°	18.3	20	15.3	0.444	0.522	0.513	0.147	48,000	50,000	31,000	1.417	118,000	150°
175°	11.6	50	9.7	0.456	0.504	0.475	0.139	44,000	64,000	34,000	1.433	25,600	175°
200°	5.8	75	4.9	0.454	0.472	0.471	0.138	39,000	54,000	36,000	1.436	21,340	200°
225°	3.2	80	2.5	0.490	0.516	0.510	0.132	51,000	63,000	41,000	1.437	34,900	225°
250°	0.3	95	0.1	0.689	0.692	0.604	0.131	68,000	68,000	45,000	1.437	40,350	250°
275°	0.4	98	0	0.670	0.670	0.638	0.132	81,000	80,000	53,000	1.442	37,300	275°
300°	0.4	100	0	0.670	0.670	0.648	0.133	82,000	83,000	54,000	1.440	61,900	300°
325°	0.4	100	0	0.756	0.756	0.725	0.133	106,000	115,000	60,000	1.442	-	325°

¹TGA loss to 350°C.

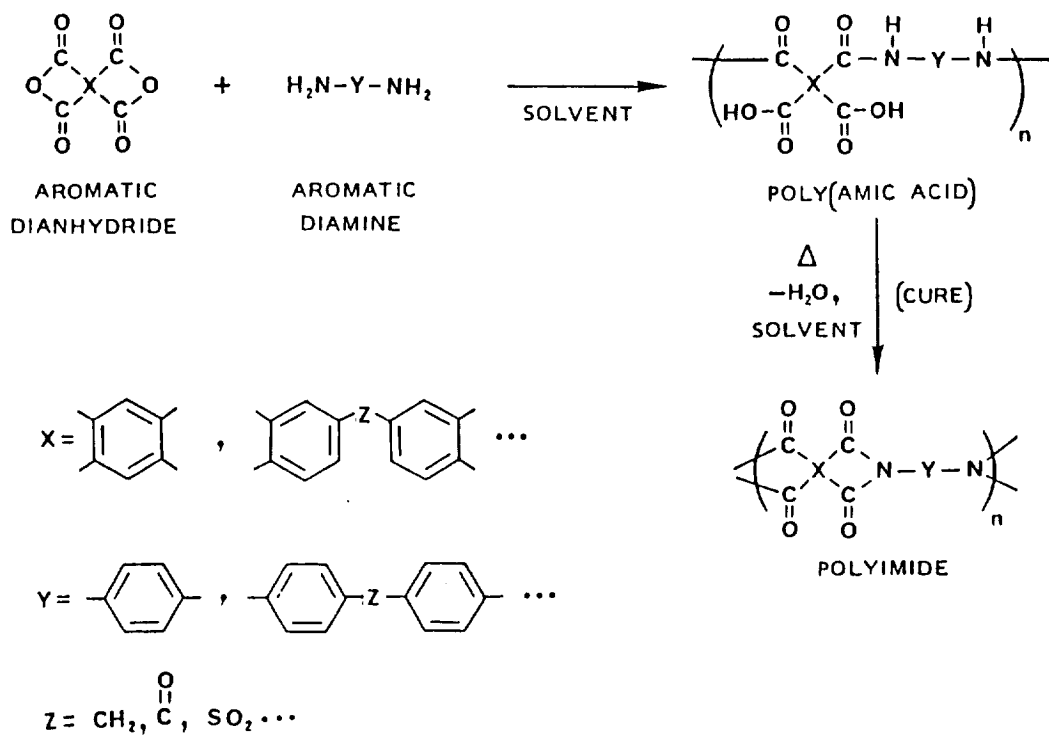
²Estimate based on infrared spectra.

³Calculated.

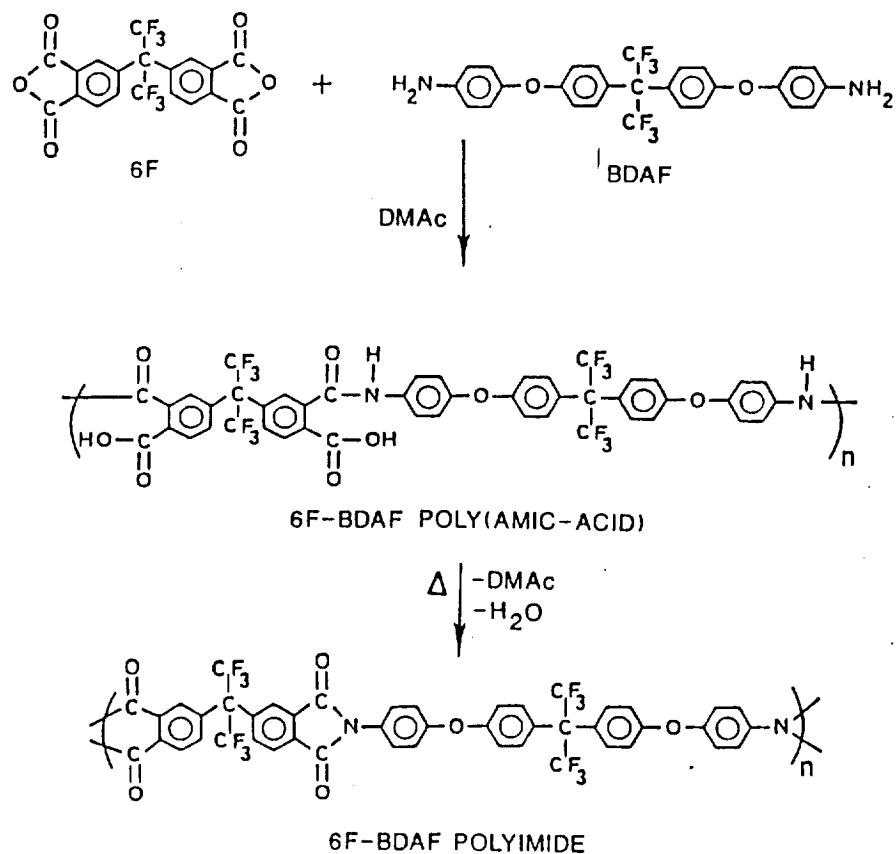
⁴As measured.

⁵Corrected for residual solvent.

SCHEME I



SCHEME II



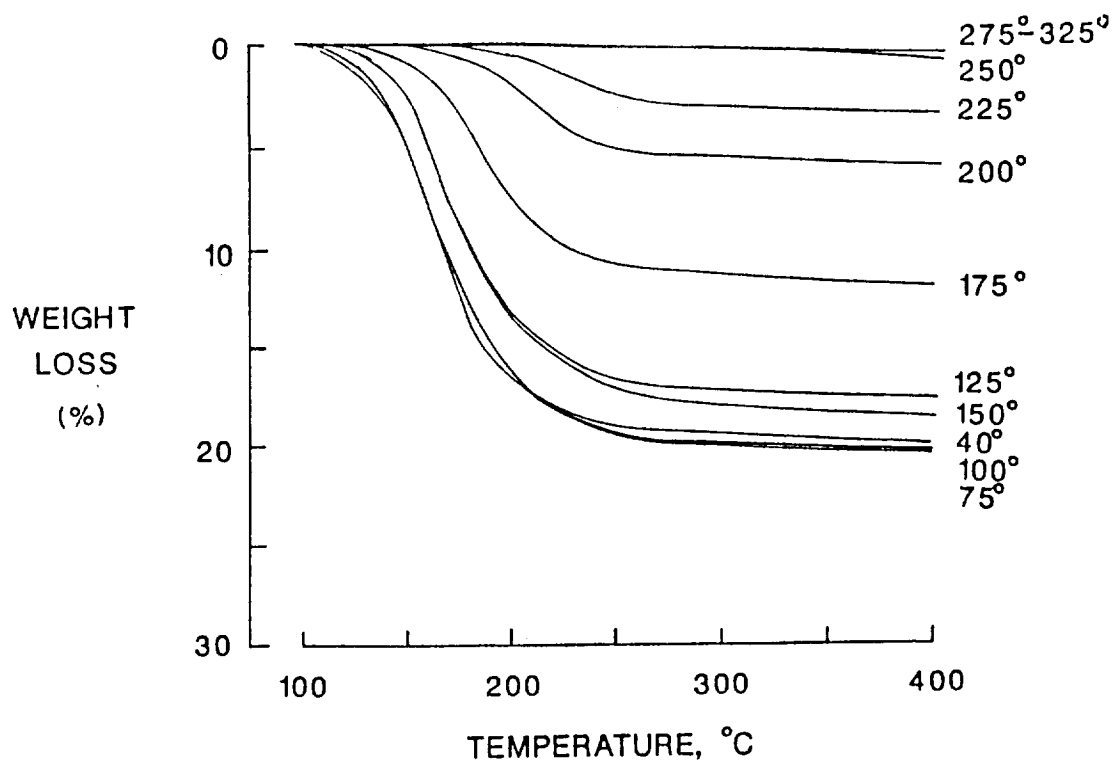


Figure 1. TGA weight loss curves for thermally staged films.

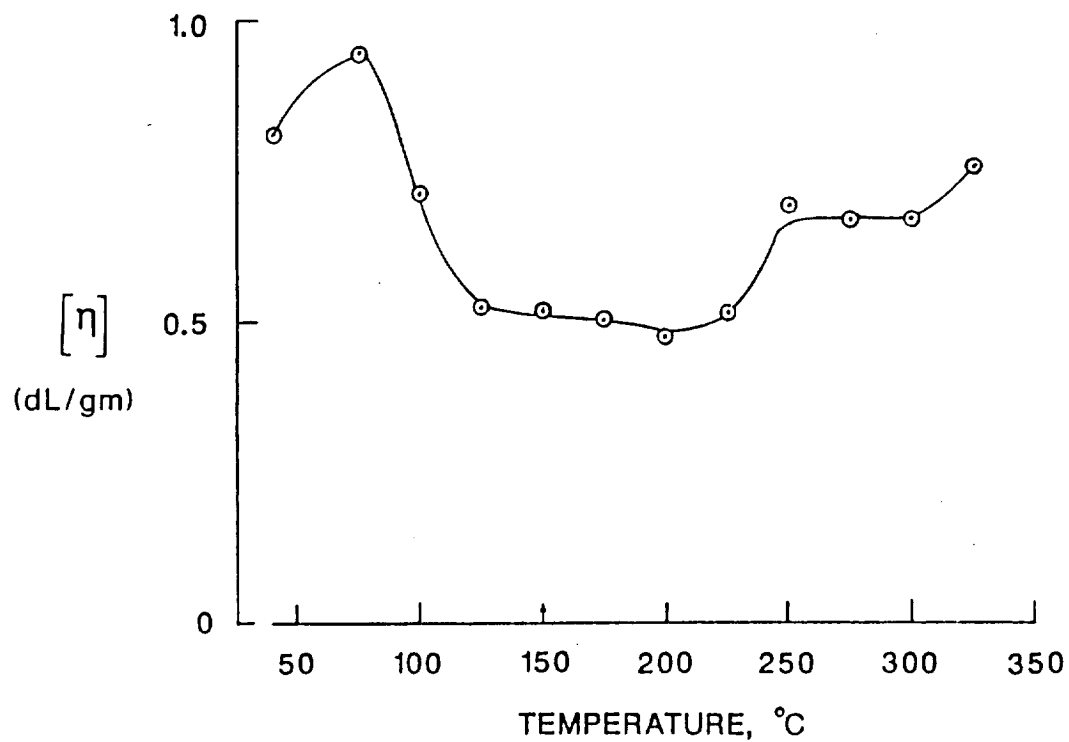


Figure 2. Intrinsic viscosity as a function of cure temperature for thermally staged films.

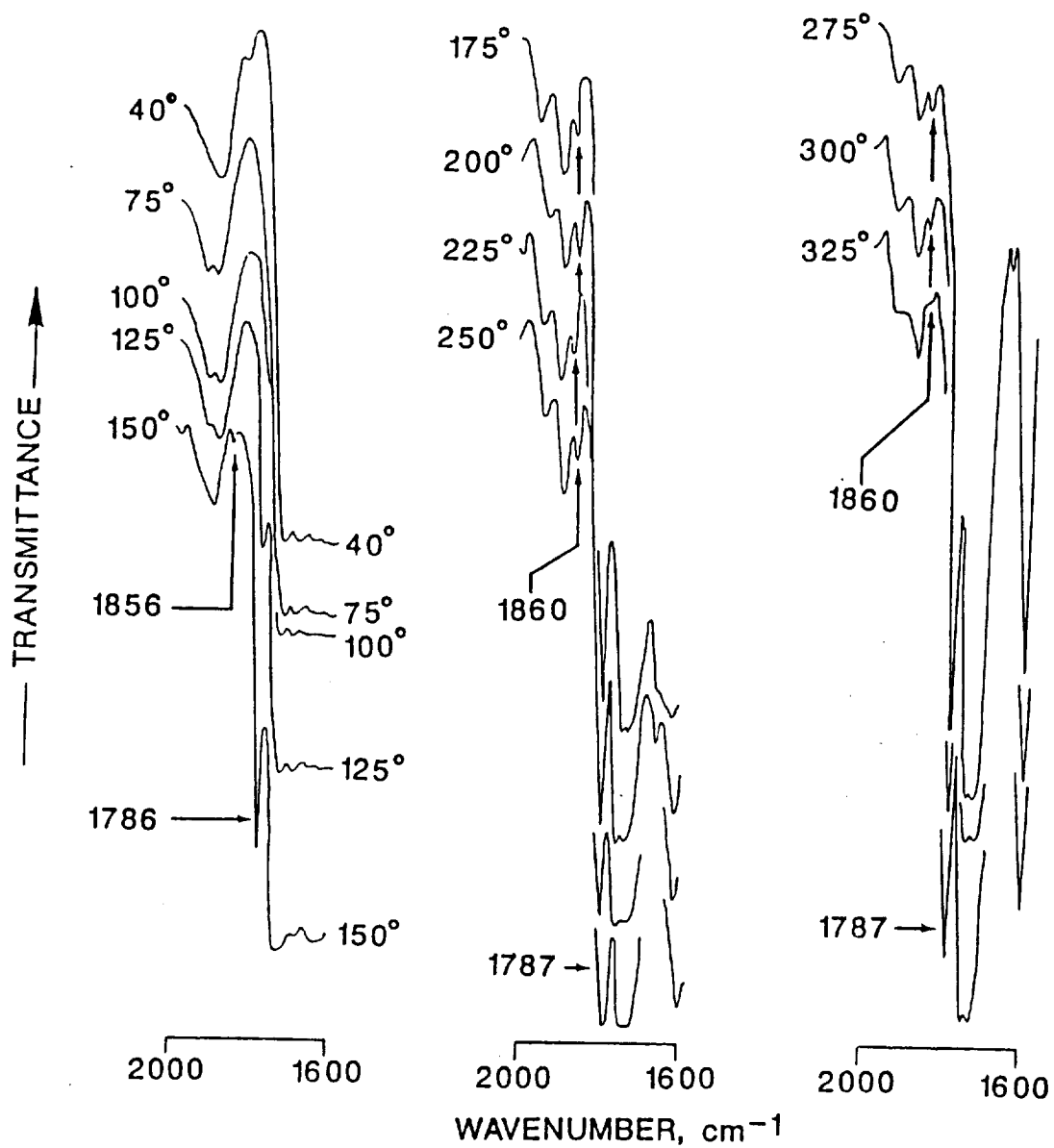


Figure 3. FTIR spectra of anhydride region of thermally staged films.

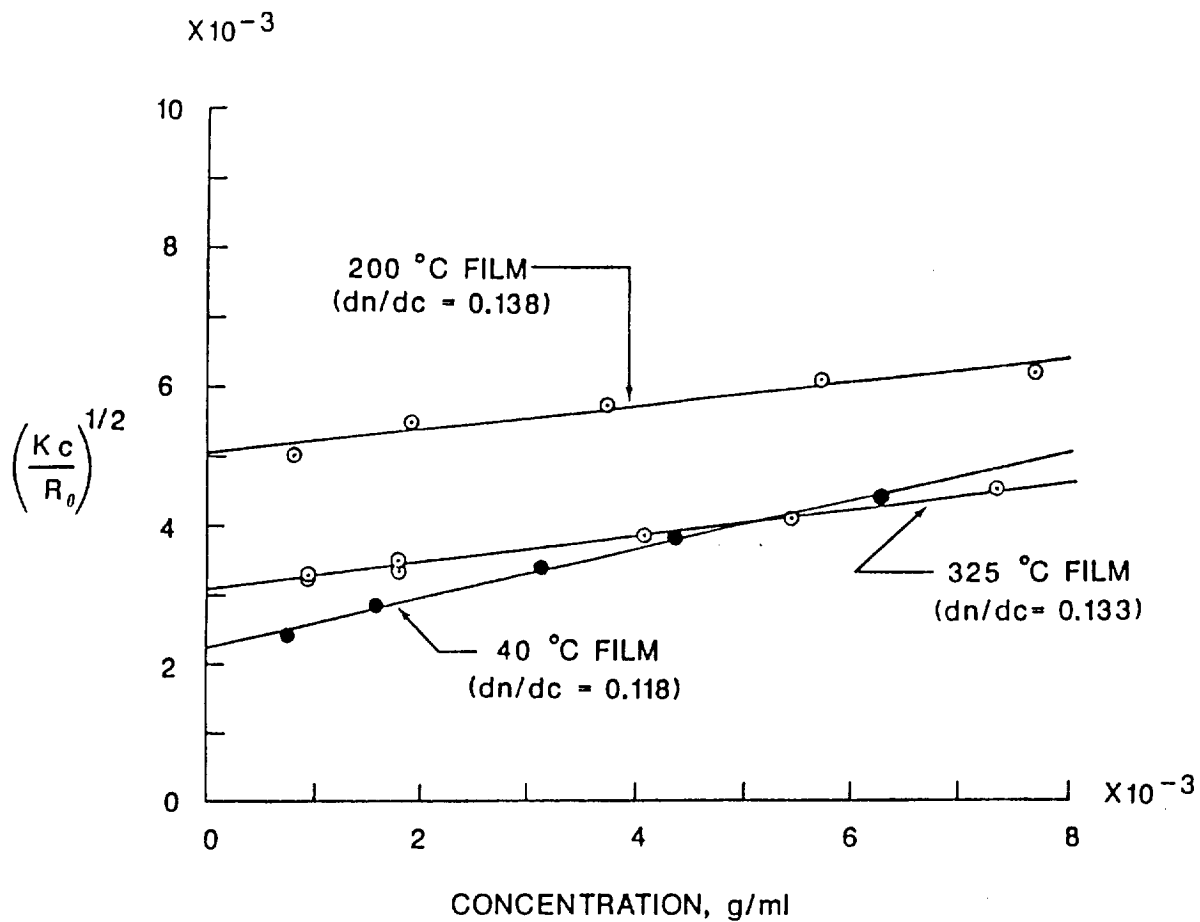


Figure 4. LALLS experimental data for three films.

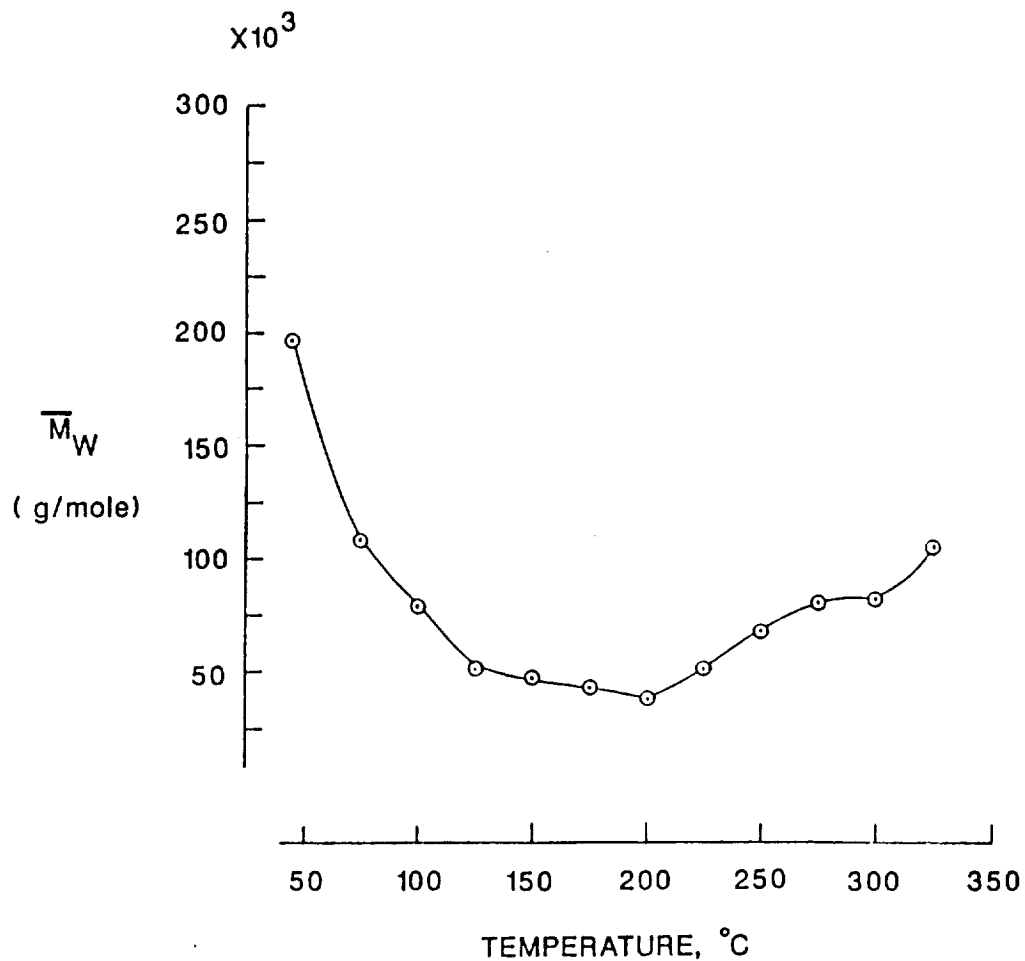


Figure 5. \bar{M}_w as a function of cure temperature for thermally staged film.

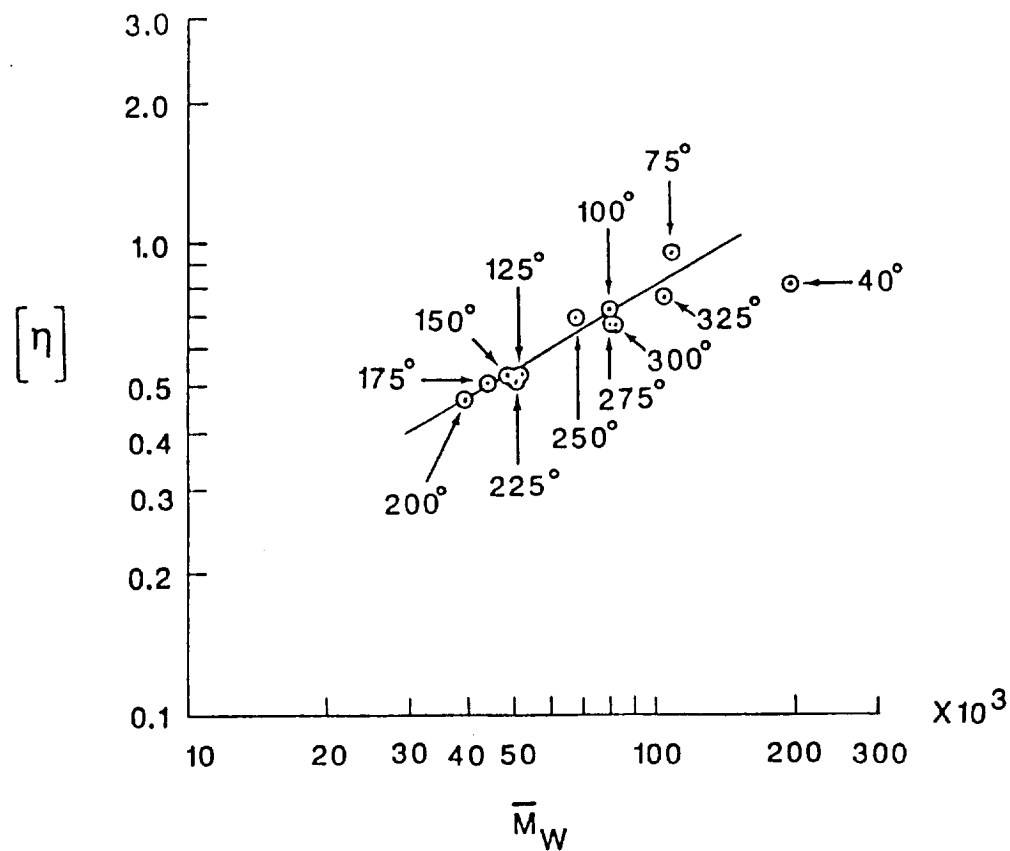


Figure 6. Mark-Houwink plot of $[\eta]$ vs. \bar{M}_w for thermally staged films.

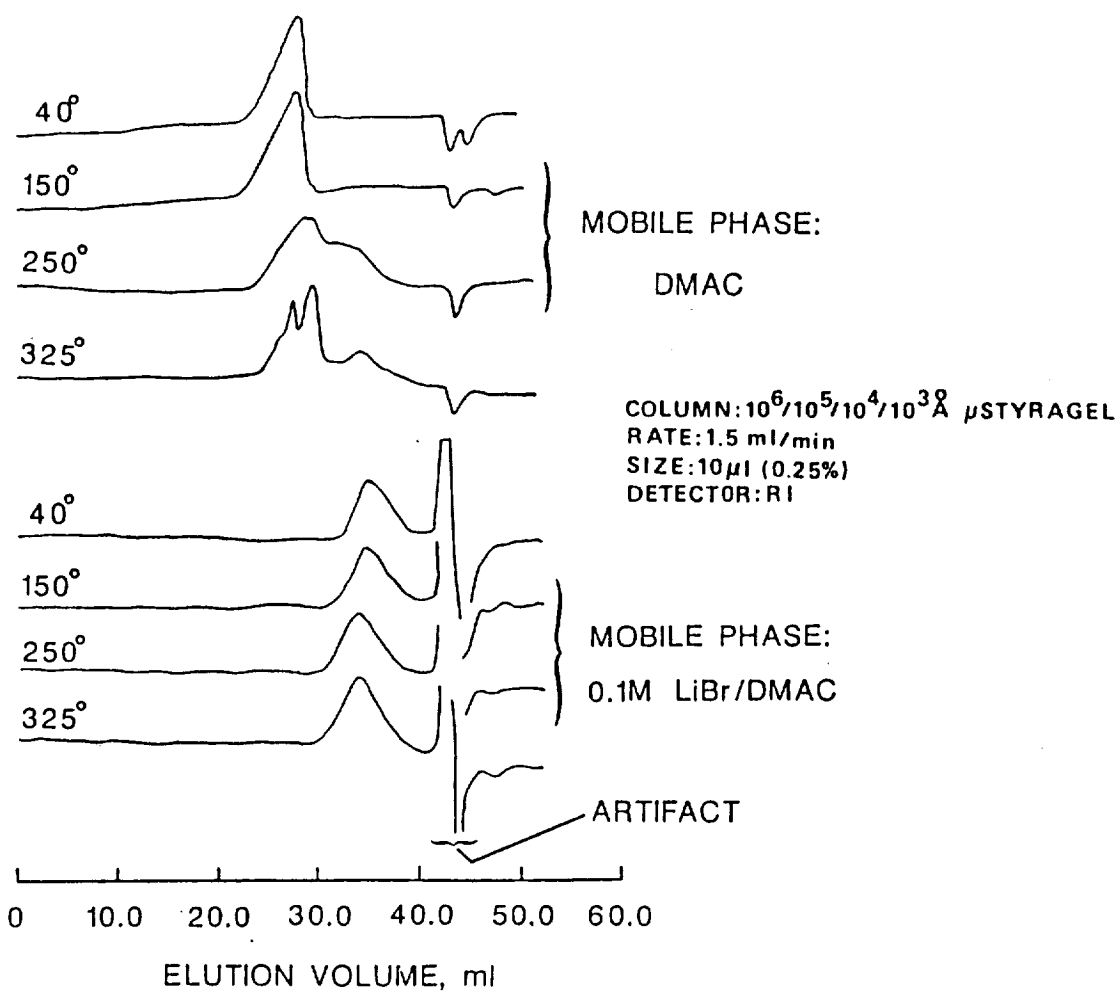


Figure 7. GPC curves for thermally staged films in two mobile phases.

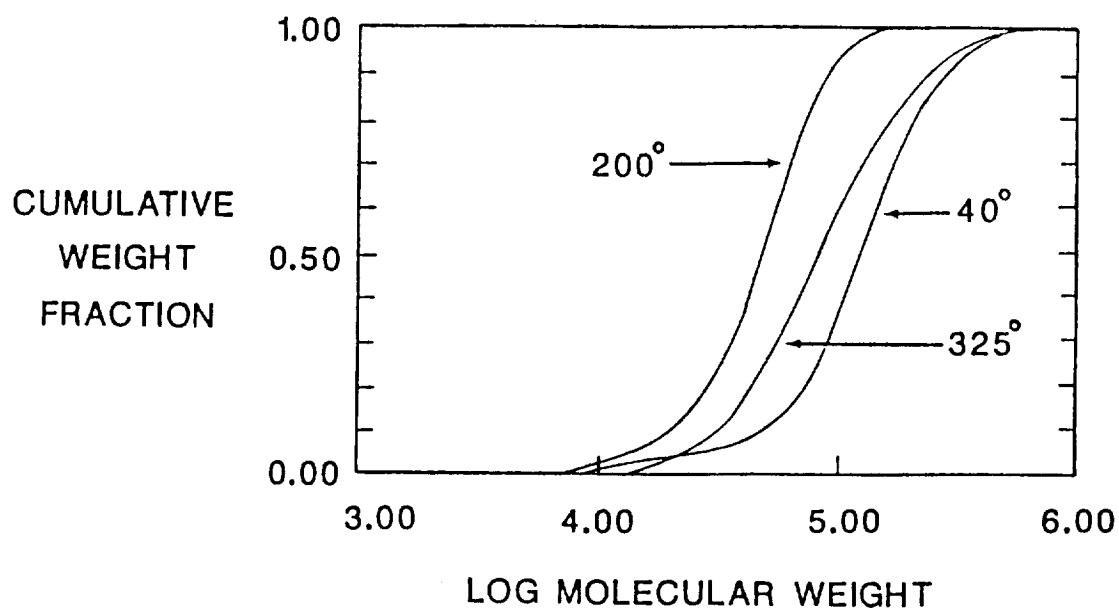


Figure 8. Cumulative weight fraction plot as determined by GPC-LALLS.

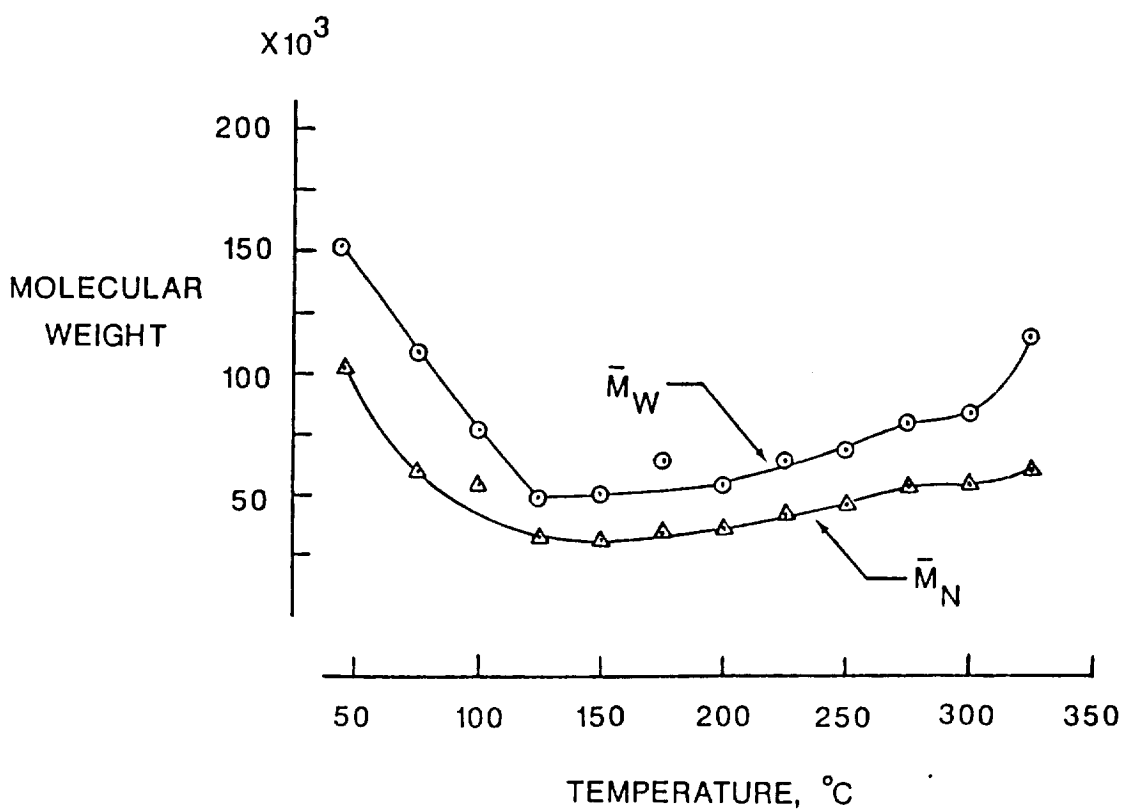


Figure 9. Molecular weight of thermally staged films as determined by GPC-LALLS.